Microencapsulation of Imidazole Curing Agents by Spray-Drying Method Using W/O Emulsion

Min Jae Shin,[1] Jin Gon Kim,[2] Jae Sup Shin[2]

[1]*Department of Chemical and Biomolecular Engineering, KAIST, Daejeon 305-701, Korea*
[2]*Department of Chemistry, Chungbuk National University, Cheongju, Chungbuk 361-763, Korea*

Received 15 April 2011; accepted 20 August 2011
DOI 10.1002/app.35490
Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Imidazoles were microencapsulated for the latent curing of the epoxy resin— imidazole system. Using polycaprolactone as the wall material, the microcapsules were formed by spray-drying method using water/oil (W/O) emulsion. Poly(vinyl alcohol) was used as the emulsion stabilizer. The imidazoles used in this study were imidazole and 2-methylimidazole. The amount of imidazoles in the microcapsule was measured using elemental analysis. The permeability of the microcapsules was measured in ethanol, and the shelf life of the microcapsules was also studied for the epoxy resin. The curing behavior of these microcapsules to epoxy resin was examined using a differential scanning calorimeter. In the curing reaction, the microcapsule of imidazoles exhibited delayed kinetic behaviors compared to pure imidazoles. And the curing times were estimated at 150 and 180°C using an indentation method. These microcapsules of imidazoles exhibited a long shelf life. When comparing the previous method in which simple dichloromethane solution was used for spray-drying, finer microcapsules were formed using the W/O emulsion. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: microencapsulation; curing of polymers; differential scanning calorimetry

INTRODUCTION

Epoxy resins are widely utilized in a number of industrial applications, including adhesives, coatings, and electronics because of their excellent mechanical and chemical properties, such as their high tensile and compressive strengths, good solvent and chemical resistance, and high heat distortion temperatures. The superior mechanical and chemical properties of epoxy polymers result from the curing processes, where a low molecular weight resin is transformed into an infinite molecular weight polymer with a three-dimensional network structure. This curing process can be carried out using a wide range of curing agents, such as amines, anhydrides, polyamides, phenol formaldehyde resins, and polysulfides.[1–4] Although epoxy resins with primary and secondary amines are cured through a step growth polymerization, tertiary amines undergo a chain growth polymerization. Imidazoles are tertiary amines that are often used as hardeners in a variety of epoxy resin systems to initiate the homopolymerization of the epoxy compounds.[5–12]

Recently, an epoxy-imidazole resin system was used to form an anisotropic conducting film (ACF) for use in electronic equipment, such as LCDs.[13,14] LCDs are mainly used in the production of television and computer monitors. The production speed of these LCDs is dependent on the curing rate of the ACF. Therefore, the development of ACFs with fast reactivities and manageable properties is very important. The epoxy system must be a one-pot system for electronic equipment applications, such as LCDs. Therefore, the storage stability is very significant at room temperature. In the one-pot system, the epoxy resin and the curing agent do not have to react with each other at the storage temperature and the preparation temperature for setting the equipment. The ACF system which was used in the LCD production was cured at 180°C. So, it is very important to find the ACF systems which get both the fast reaction rate at 180°C and the latent curing property at room temperature. Especially, decreasing this temperature is very helpful economically. Therefore we tried the experiments both at 180 and at 150°C.

Unfortunately, imidazole is not a latent curing agent for epoxy resin systems. In the epoxy-imidazole system, imidazoles react with the epoxy resin at room temperature, and the epoxy resin changes into a hard polymer after it has been mixed with the imidazole curing agent at room temperature for a period of time ranging from 1 h to 1 day. Imidazoles must be converted to an unreactable form to create a

Correspondence to: J. S. Shin (jsshin@chungbuk.ac.kr).
Contract grant sponsor: Ministry of Knowledge Economy, Republic of Korea; contract grant number: 10031690.

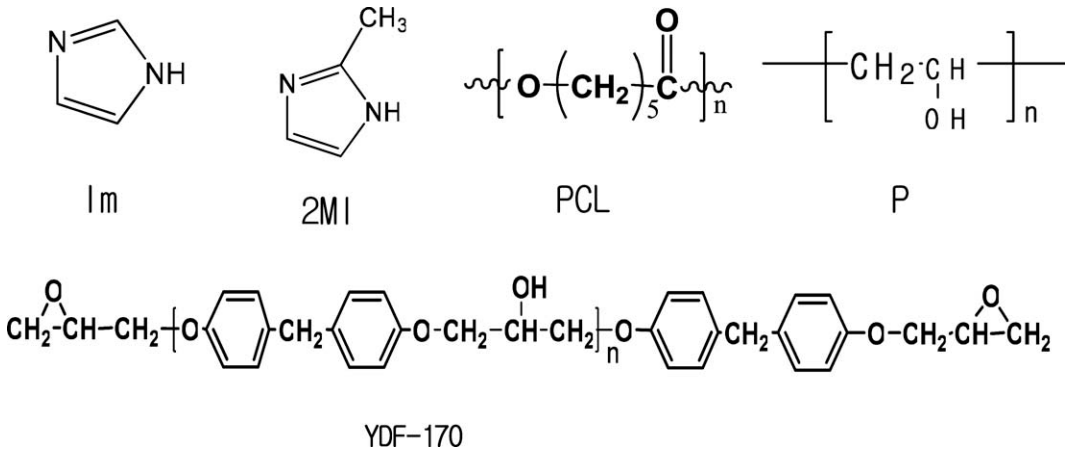

Figure 1 The structures of the materials that were used in this study.

one-pot system for the epoxy-imidazole system. Among the methods of forming unreactable imidazoles, the encapsulation of the imidazole is an easy and economic method.[15–17]

Spray drying method has been widely used in large-scale production of drug-loaded microspheres.[18–21] This one-step method has good control on process parameters with excellent scale-up possibility. The mixture to be sprayed can be solvent, emulsion, suspension, or dispersion. The feed is atomized into millions of individual droplets by a nozzle giving an increased surface area of the sprayed solution, and the solvent is vaporized immediately. The product obtained can be powdered to similar sized particles in just few minutes. An advantage of this method is that it requires only about 50–100 mL of solvent or suspension to produce particles.

We previously reported on the encapsulation of imidazole curing agents with polycaprolactone (PCL) using a spray-drying method to create a one-pot system for an epoxy-imidazole system.[22] But, the previous results showed that the microencapsules had a battered round shape. This resulted in shorter self life and a faster initial release rate. So in this study, we tried to use a water/oil (W/O) emulsion for spray-drying to find a solution to this problem.

EXPERIMENTAL

Materials

Figure 1 shows the structures of the materials that were used in this present study. Diglycidyl ether of bisphenol F (YDF-170) was obtained from Kukdo Chemical. Imidazole (Im), 2-methylimidazole (2MI), PCL (Molecular weight, M_w: 80,000, 65,000, 14,000, 2000), poly(vinyl alcohol) (PVA) (88% hydrolyzed, M_w: 22,000), and dichloromethane (DCM) were obtained from Aldrich. PCL was selected as the polymer for the encapsulation of the curing agent because the melting point (59°C) of this polymer is very low, and it can easily be opened by heating the encapsulated materials. PCL has attracted scientific attention and is applied in many fields because of its biodegradability properties.[23–26]

Instruments

The differential scanning calorimeter (DSC) studies of the curing behavior were performed using a Scinco DSC N-650 under a nitrogen atmosphere. High purity indium was used to calibrate the calorimeter. All of the samples (~ 10 mg) were stored within sealed aluminum DSC pans. The DSC studies of the YDF-170 cure were performed from 15 to 200°C at a heating rate of 10°C/min.

The homo mixer (T. K. homo mixer mark 2, model 2.5) was used to control the stirring speed. HPLC was performed using an alliance dissolution system (Waters). Elemental analysis was performed using an elemental analyzer (EA) (EA 1110, CE Instruments). Scanning electron microscopy was performed using both a Hitachi S-2500C and Hitachi S-5200V scanning electron microscopes (SEMs).

Encapsulation of imidazoles by spray-drying method

The most representative method of encapsulation is shown below:

A PCL solution was made by dissolving 10.0 g of PCL (M_w: 65,000) into 200 mL of DCM. And an imidazole solution was prepared by dissolving 5.0 g of imidazole into 30 mL of 1.0 wt % PVA aqueous solution. And then the imidazole solution was added dropwise into the PCL solution which was stirred 5000 rpm.

Using a spray gun and compressed nitrogen gas (3 atm), this W/O emulsion solution was sprayed

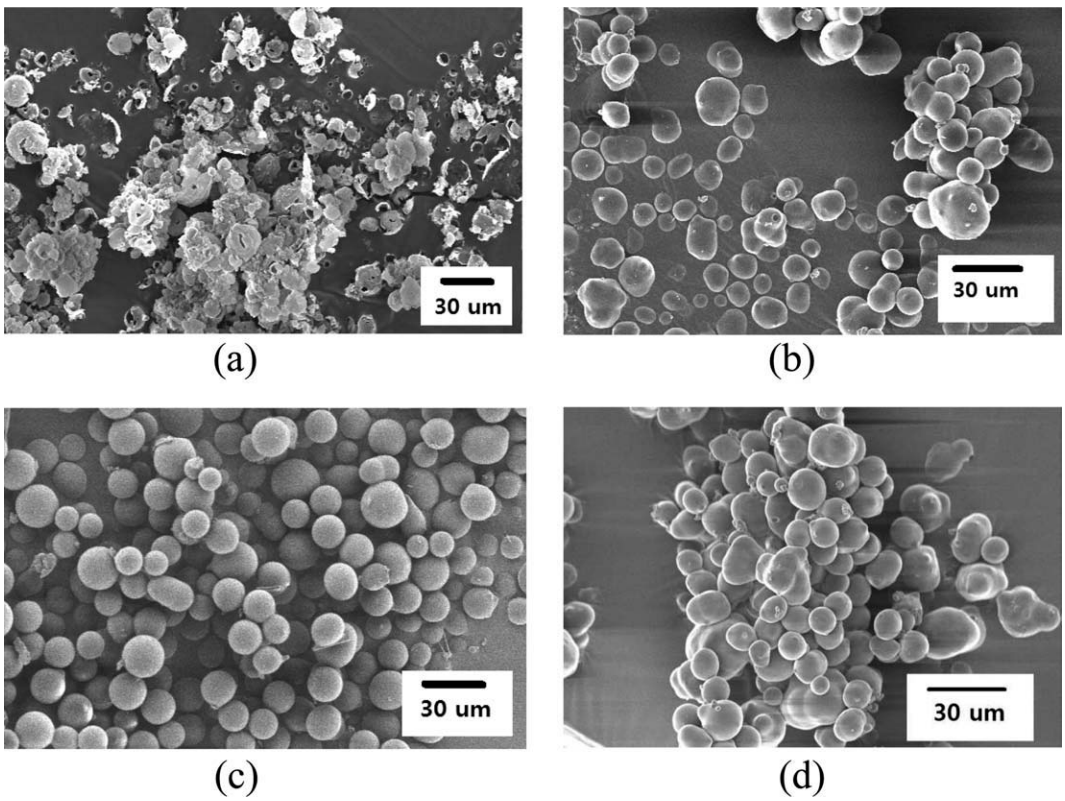

Figure 2 SEM photographs of the microcapsules that were prepared at different temperature of N_2 gas. (a) 20°C, (b) 40°C, (c) 60°C, and (d) 80°C.

into a small chamber ($60 \times 60 \times 60$ cm^3) missing one sidewall. The distance to the opposite side of the wall from the spray gun was 100 cm. The W/O emulsion solution was kept under 5000 rpm stirring during the entire spraying process. The temperature of the nitrogen gas was controlled at 60 ± 3°C. The microcapsules were collected from the wall of the chamber and their size and appearance were observed with a SEM. The imidazole content in the microcapsules was calculated based on the data of EA.

The determination of the curing time

The curing time was measured using an indentation method. The reaction vessel was heated to a desired temperature, and the mixture of the epoxy resin and the microcapsules were added to the vessel. Then the surface of the resin mixture was pierced every second, and the time was recorded when the pin did not pierce the surface.

The measurement of the permeability of the microcapsules

A 100-mL round-bottomed flask was filled with ethanol and 0.10 g of the microcapsules containing imidazole was added at 35°C. The solution was stirred with a magnetic stir bar at a very slow speed (one rounding every 2 s). Then 1 mL of the sample solution was removed from the upper part of the solution at determined intervals, and the amount of the permeated imidazoles was measured using HPLC.

RESULTS AND DISCUSSION

Encapsulation of imidazoles

In this study, the microencapsulation was conducted by the spray-drying method using W/O emulsion. The polymer to encapsulate the curing agent must encapsulate the material very well, and at the same time, easily open if necessary. Therefore, PCL was

TABLE I
The Content of Imidazole in the Microcpasule Estimated by EA

Imidazole	Formulation (PCL/imidazole, g/g)[a]	EA (%)
Im	5/5	47.1
	7.5/5	37.8
	10/5	30.9
2MI	5/5	47.5
	7.5/5	38.2
	10/5	31.1

[a] Imidazole/30 mL of 1.0 wt % PVA aqueous solution, PCL/200 mL of DCM.

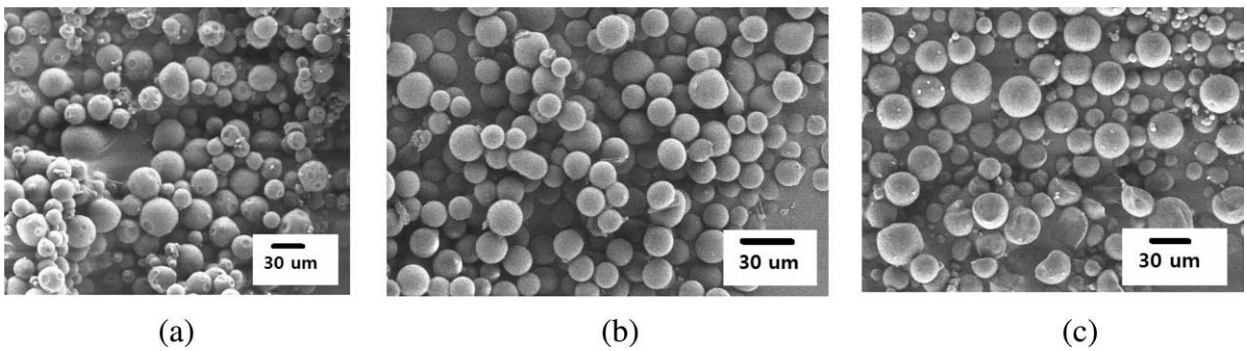

Figure 3 SEM photographs of the microcapsules that were prepared with different ratio of PCL/Im (a) 5/5, (b) 7.5/5, (c) 10/5; M_w of PCL: 65,000.

selected as the polymer for the encapsulation of the curing agent. Because the melting point of the PCL is very low, PCL will be melted very easily at high temperature.

Among the possible encapsulation methods, spray drying was selected for this study, and the W/O emulsion was used for spray drying. The previous results showed that the microcapsules which had the battered round shape were obtained from spray drying with a simple solution.[22] Therefore, in this study, we tried to use the W/O emulsion instead of using the simple solution.

The curing agents were dissolved in water and the polymeric wall material was dissolved in DCM. After PVA was used as an emulsion stabilizer, the W/O emulsion was formed from these two solutions. This W/O emulsion solution was sprayed into a small chamber, and the sprayed particles were dried during spraying. The encapsulated particles were collected from the counter sidewall and the bottom surface of the chamber. Using Im and 2MI as the core materials, and PCL as the polymeric wall material, spray drying was conducted.

The effect of the temperature of N_2 gas

The temperature of the N_2 gas used for spraying is one of the main factors when forming fine microcapsules. We conducted spray drying at several temperatures between 20 and 80°C. Figure 2 shows the SEM photographs of the microcapsules that were prepared at different N_2 gas temperatures. The PCL/Im ratio was 7.5/5 and the molecular weight of PCL was 65,000. At 20°C, microcapsules were not formed, as shown in Figure 2. At 40 and 80°C, microcapsules were formed, but the shape for all of the microcapsules was not regular. The microcapsules which were formed at 60°C had a more regular shape. So, all of the remaining experiments were performed using 60°C N_2 gas.

The effect of the ratio of PCL to imidazole

The effect of the ratio of PCL to imidazole on the formation of the microcapsules was examined. The amounts of imidazole were fixed at 5.0 g and the amount of PCL was varied from 5 to 10 g. The molecular weight of PCL was 65,000. After the microcapsules were formed, EA were conducted to measure the amount of imidazole in the microcapsules. In this experiment, the amount of imidazole was estimated from the ratio of nitrogen to carbon. In order to estimate the imidazole content precisely, three standard samples were prepared by mixing PCL, PVA, and the imidazole, and the weight ratios of PCL : imidazole : PVA in the samples were set at 5/5/0.3, 7.5/5/0.3, and 10/5/0.3, respectively. The EA data of the microcapsules were compared with those of the standard samples, and then the imidazole content in the microcapsule was determined. The EA experiments were conducted using the microcapsules from different imidazole and other PCL/imidazole ratios and the results are shown in Table I. In Table I, the estimated amount of imidazole in the microcapsule is somewhat smaller than the theoretical amount calculated from the feed amount.

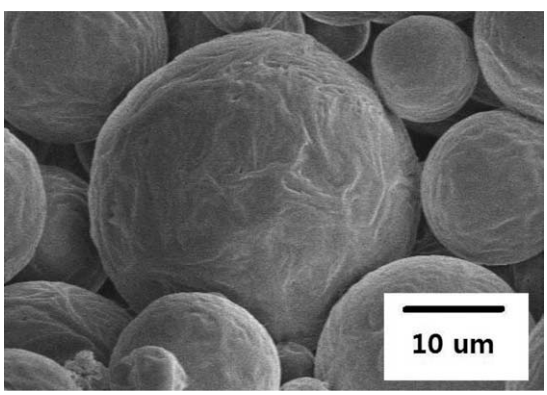

Figure 4 SEM photograph of the microcapsule. PCL/Im = 7.5/5; M_w of PCL: 65,000.

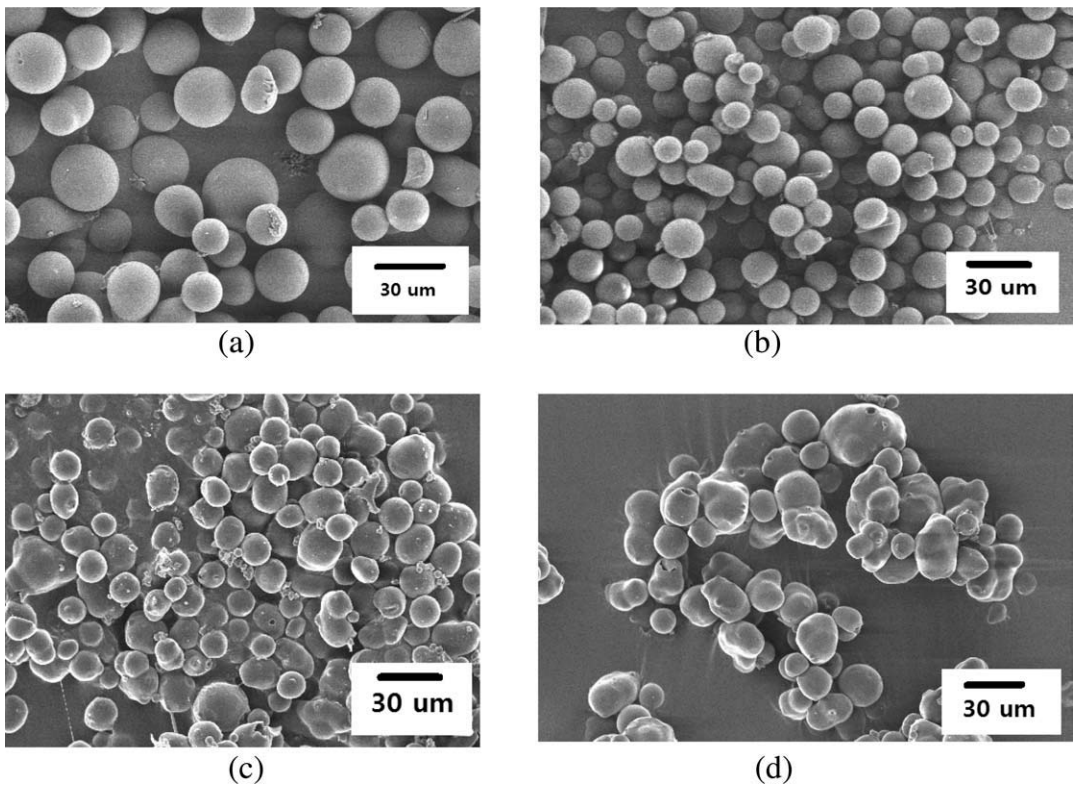

Figure 5 SEM photographs of the microcapsules that were prepared with different molecular weights of PCL (a) 80,000, (b) 65,000, (c) 14,000, and (d) 2000. PCL/2PhI = 7.5/5.

The SEM micrographs of the microcapsules that were prepared with different ratios of PCL/Im are shown in Figure 3. In this experiment, PCL 65,000 and Im were used. The PCL/Im ratios that were used to form the microcapsules were 5/5, 7.5/5, and 10/5. Almost all of the microcapsules were similar in shape. The microcapsules had sizes of 18.1 ± 4.0 μm, 17.2 ± 3.5 μm, and 18.9 ± 4.0 μm for the 5/5, 7.5/5, and 10/5 ratios, respectively. In order to investigate the surface of the microcapsules, a high magnification SEM image was obtained, as shown in Figure 4. In the figure, the microcapsules had a lot of wrinkles on the surface. These wrinkles were formed when the solvent was evaporated during microcapsule formation.

The effect of PCL molecular weight

The encapsulations were conducted using PCL with different molecular weights of 2000, 14,000, 65,000, and 80,000 to examine the effects of the PCL molecular weight on the microcapsule formation. In the formation of the microcapsules, the PCL/Im ratio was

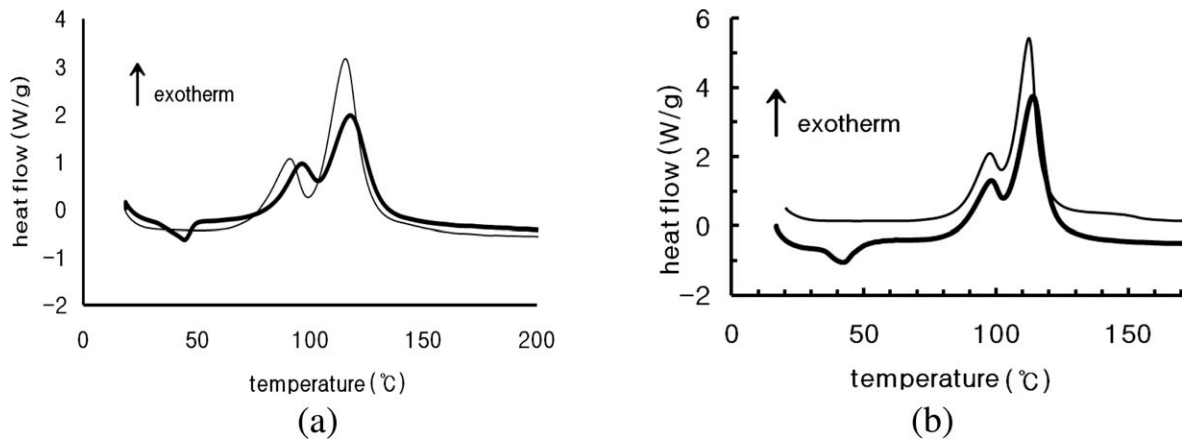

Figure 6 Scanning DSC curves for the curing of the epoxy resin. (a) (—) PCL/Im = 7.5/5, microcapsule/YDF-170 = 15/100, (—) Im/YDF-170 = 6/100, (b) (—) PCL/2MI = 7.5/5, microcapsule/YDF-170 = 15/100, (—) 2MI/YDF-170 = 6/100.

TABLE II
The Kick Off and Peak Temperatures of the Microcapsules

Imidazole	Formulation (PCL/imidazole)	Feed ratio (microcapsule/epoxy resin)	Kick off temp. (°C)	Peak temp. (°C)
Im	0/5	6/100 (Im/epoxy resin)	68	116.6
	5/5	12/100	85	121.5
	7.5/5	15/100	88	123.9
	10/5	18/100	95	126.3
2MI	0/5	6/100 (2MI/epoxy resin)	82	112.7
	5/5	12/100	86	115.4
	7.5/5	15/100	88	117.5
	10/5	18/100	93	120.5

7.5/5. The SEM photographs of the microcapsules using PCL 80,000, PCL 65,000, PCL 14,000, and PCL 2000 are shown in Figure 5. The microcapsules were sized 19.3 ± 4.0 μm, 17.2 ± 3.5 μm, 16.1 ± 3.5 μm, and 20.9 ± 7.0 μm for M_w 80,000, 65,000, 14,000, and 2000 PCL, respectively. For M_w 80,000, 65,000, and 14,000 PCL, the microcapsules were almost uniform shapes, and the microcapsule size increased with increasing PCL molecular weight. However, for M_w 2000 PCL, the size and the shape of the microcapsules were not uniform, indicating that M_w 2000 was too small to form uniformly shaped and sized microcapsules.

Curing behavior of the microcapsules for epoxy resin

DSC was used to investigate the curing behavior of the microcapsules for epoxy resin. In this experiment, the molecular weight of PCL was 65,000, the PCL/Im ratio was 7.5/5, and the microcapsule/YDF-170 ratio was 15/100. DSC was conducted from 15 to 200°C at a heating rate of 10°C/min. This result was compared with the result from the sample in which pure Im was used instead of the microcapsules. The Im/YDF-170 ratio was 6/100. These two samples had different feed ratios because the two samples had the same amount of Im for epoxy resin. The results are shown in Figure 6. In case of 2MI, DSC was also conducted at the same condition as for Im. The results are also shown in Figure 6. In this figure, the exothermic pattern was monitored using DSC because the curing reaction of the epoxy resin with imidazoles was exothermic. Similar patterns were observed for the two samples, but a delay of 2.7–9.7°C in the maximum peak temperature for the microcapsules was shown because the polymeric wall material interfered in the curing reaction between epoxy compound and imidazole curing agent. Two peaks were shown in the DSC data for both Im and 2MI: the first due to the adduct formation of epoxy resin and imidazoles, and the second due to the polymerization of epoxy resin.[12]

In the case of the microcapsules, the endothermic peak at about 50°C was due to the melting of PCL. Using the different PCL/imidazoles ratios, DSC studies were conducted and the results are shown in Table II. The starting temperature of curing (kick-off temperature) and the temperature of maximum peak (peak temperature) were described. These results were compared with the data using pure imidazoles. In Table II, the kick-off temperature and peak temperature were increased with increasing PCL amount in the microcapsules. The peak temperatures of 2MI were lower than those of Im.

The curing times were estimated at 150 and 180°C using an indentation method, and the results are shown in Table III. The curing times at 150°C were increased with increasing PCL amount in the microcapsules, and the curing times at 180°C showed a

TABLE III
The Curing Rates and the Shelf Lives of the Microcapsules

Imidazole	Formulation (PCL/imidazole)	Feed ratio (microcapsule/epoxy resin)	Curing time at 150 °C (s)	Curing time at 180 °C (s)	Shelf life at 20 °C (day)
Im	0/5	6/100 (Im/epoxy resin)	13	8	1
	5/5	12/100	15	8	4
	7.5/5	15/100	16	9	10
	10/5	18/100	17	11	13
2MI	0/5	6/100 (2MI/epoxy resin)	9	6	0.5
	5/5	12/100	10	7	2
	7.5/5	15/100	10	8	7
	10/5	18/100	12	9	10

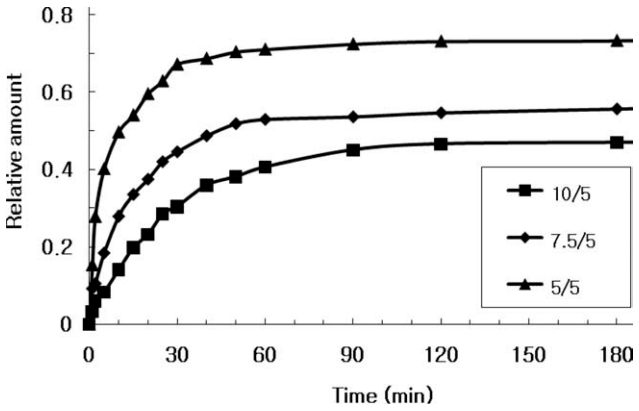

Figure 7 Release behaviors of the Im/PCL microcapsules that were prepared with different ratio of PCL/Im (M_w of PCL: 65,000).

similar trend. The curing time of 2MI was lower than that of Im at both 150 and 180°C.

After the epoxy resin and imidazoles were mixed at 20°C, this mixture was stored at the same temperature. The shelf life of the microcapsules was examined at 20°C by measuring the time before the curing started. This shelf life of the microcapsules was compared to that of the pure imidazoles, and the results are also shown in Table III. The curing reaction started at 20°C after 1 day had passed for pure Im. On the other hand, no curing occurred after storage for 13 days at 20°C for 10/5 (PCL/Im). The curing reaction started at 20°C after 0.5 days had passed for pure 2MI, but no curing occurred after storage for 10 days at 20°C for 10/5 (PCL/2MI).

Permeability of the microcapsules

The permeability of the microcapsules was examined by measuring the amount of Im permeating from the microcapsules in ethanol at various time intervals. In this experiment, the microcapsules were formed using different ratios of PCL/Im (10/5, 7.5/5, 5/5). The results are shown in Figure 7. The fast initial release rate of the 5/5 (PCL/Im) case was due to the location of a lot of Im at the surface of the microcapsules. But in the case of 10/5, the initial rate was slower than that of the 5/5 case.

The permeability of the microcapsules was also examined by changing the molecular weight of PCL. In this experiment, the microcapsules were formed using PCL molecular weights of 80,000, 65,000, 14,000, and 2000, and the PCL/Im ratio used for these experiments was 5/5. The results are shown in Figure 8. In Figure 8, the initial release rates of all the samples were very fast and all of the samples showed similar results. This means that the 5/5 PCL/Im ratio does not have enough PCL to encapsulate the Im, and more PCL is needed to encapsulate Im wholly. The permeability of the microcapsules was also examined with the PCL/Im ratio of 10/5. The results are shown in Figure 9. In Figure 9, the initial release rates of the case of PCL 2000 were very fast, however the release rate became slower as the molecular weight of PCL increased. Conclusively, PCL 2000 does not have sufficient molecular weight to encapsulate the Im.

Comparison of results with those of the previous method using simple solution

We compared these present results (SDWOE method) with the results of our previous report on the encapsulation of the imidazole curing agent with PCL by the spray-drying method using a simple solution (SDSS method).[22]

The microcapsules from the SDWOE method had sizes of 16.1–19.3 μm, which was 50% larger than the size of 9.4–12.3 μm that resulted from the SDSS

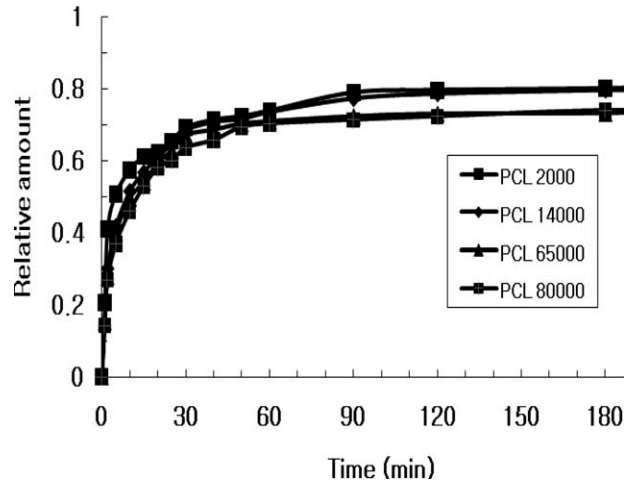

Figure 8 Release behaviors of the Im/PCL microcapsules that were prepared with different molecular weights of PCL (PCL/Im = 5/5).

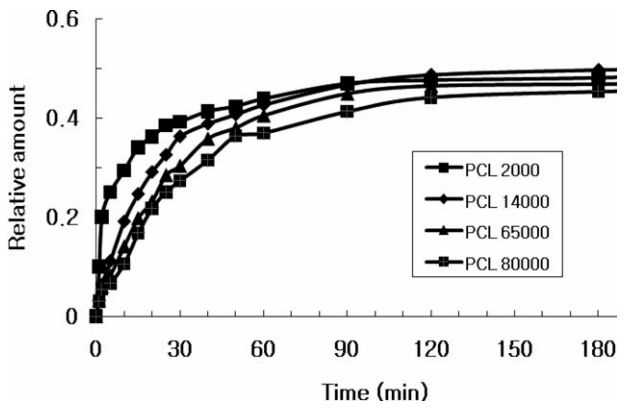

Figure 9 Release behaviors of the Im/PCL microcapsules that were prepared with different molecular weights of PCL (PCL/Im = 10/5).

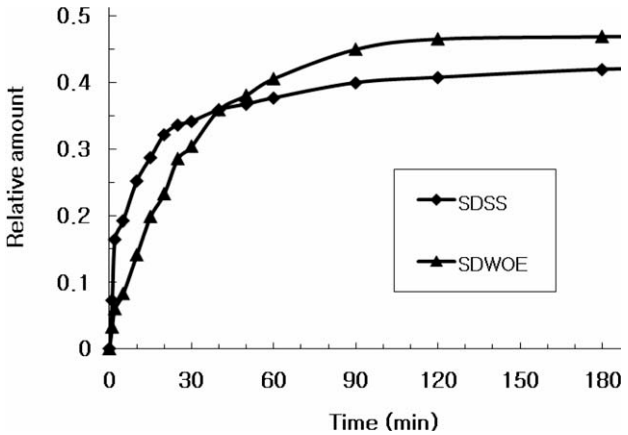

Figure 10 Release behaviors of the Im/PCL microcapsules that were prepared by different methods (SDSS method: PCL/Im = 7/3; SDWOE method: PCL/Im = 10/5).

method. This means that the W/O emulsion helps to make a larger microcapsule.

When the microcapsules with similar imidazole contents were used, both methods produced microcapsules with almost similar curing behaviors to that of DSC. So the kick off temperature and peak temperature were almost the same. However, the shelf life of the microcapsules from the SDWOE method was longer than those from the SDSS method: 13 days for a formulation (PCL/Im) of 10/5 and a feed ratio (microcapsule/epoxy resin) of 18/100 when using the SDWOE method, when compared with 7 days using the SDSS method with a formulation (PCL/Im) of 7/3 and a feed ratio (microcapsule/epoxy resin) of 20/100. We attributed this difference to the improved microencaspsulation from the SDWOE method. And similar results were obtained in the case of 2MI. A 10-day shelf life was observed for a formulation (PCL/2MI) of 10/5 and a feed ratio (microcapsule/epoxy resin) of 18/100 using the SDWOE method, as compared to 3 days using the SDSS method with a formulation (PCL/2MI) of 7/3 and a feed ratio (microcapsule/epoxy resin) of 20/100.

Figure 10 shows the permeability of the microcapsule for a formulation (PCL/Im) of 10/5 using the SDWOE method as well as the permeability of the microcapsule for a formulation (PCL/Im) of 7/3 using the SDSS method. Figure 10 shows that the permeability of the microcapsules from the SDWOE method was lower than that from the SDSS method. This also means that the microcapsule by the SDWOE method is better encapsulated than that by the SDSS method. Notably, the initial release rate of the microcapsules from the SDWOE method was slower than that from the SDSS method. We also attributed the slower initial release rate to the well-encapsulated microcapsules.

CONCLUSION

In this study, imidazole curing agents were encapsulated with PCL by a spray-drying method using W/O emulsion to create a one-pot system for an epoxy-imidazole system. The amount of imidazole in the microcapsule was measured using EA. The permeability of the microcapsules was measured in ethanol. The release rate was slower at higher molecular weights of PCL. In the curing reaction with the epoxy resin, the microcapsules of imidazoles exhibited a delayed kinetic behavior compared to pure imidazoles. And the curing times were estimated at 150 and 180°C using an indentation method. These microcapsules exhibited a long shelf life. When comparing the previous method in which simple dichloromethane solution was used for spray drying, finer microcapsules were formed using the W/O emulsion.

References

1. Ellis, B. Chemistry and Technology of Epoxy Resins; Chapman & Hall: Glasgow, 1993.
2. May, C. A. Epoxy Resins; Marcol Dekker: New York, 1988.
3. Ratna, D. Handbook of Thermoset Resins; iSmithers: Shawbury, 2009.
4. Kaszyk, J.; Abrams, E.; Horams, J. P.; Spurr, O. K. The Epoxy Resin Formulators Traning Manual; The Society of the Plastics Industry: New York, 1984.
5. Farkas, A.; Strohm, P. F. J Appl Polym Sci 1968, 12, 159.
6. Barton, J. M.; Shepherd, P. M. Makromol Chem 1975, 176, 919.
7. Ricciardi, F.; Romanchick, W. A.; Joullie, M. M. J Polym Sci Polym Chem Ed 1983, 21, 1475.
8. Jisova, V. J Appl Polym Sci 1987, 34, 2547.
9. Heise, M. S.; Martin, G. C. J Appl Polym Sci 1990, 39, 721.
10. Ooi, S. K.; Cook, W. D.; Simon, G. P.; Such, C. H. Polymer 2000, 41, 3639.
11. Ghaemy, M.; Sadjady, S. J Appl Polym Sci 2006, 100, 2634.
12. Ham, Y. R.; Kim, S. H.; Shin, Y. J.; Lee, D. H.; Yang, M.; Min, J. H.; Shin, J. S. J Ind Eng Chem 2010, 16, 556.
13. Yim, M. J.; Paik, K. W. Int J Adhes Adhes 2006, 26, 304.
14. Jang, K. W.; Paik, K. W. IEEE Trans Electron Packag Manuf 2009, 32, 74.
15. Cao, M.; Xie, P.; Jin, Z.; Zhang, Y.; Zhang, R.; Chung, T. S.; He, C. J Appl Polym Sci 2002, 85, 873.
16. Xu, H.; Fang, Z.; Tong, L. J Appl Polym Sci 2008, 107, 1661.
17. Ham, Y. R.; Lee, D. H.; Kim, S. H.; Shin, Y. J.; Yang, M.; Shin, J. S. J Ind Eng Chem 2010, 16, 728.
18. Patel, P.; Mundargi, R. C.; Babu, V. R.; Jain, D.; Rangaswamy, V.; Aminabhavi, T. M. J Appl Polym Sci 2008, 108, 4038.
19. Fu, Y. J.; Shyu, S. S.; Su, F. H.; Yu, P. C. Colloids Surf B Biointerfaces 2002, 25, 269.
20. Gavini, E.; Chetoni, P.; Cossu, M.; Alvarez, M. G.; Saettone, M. F.; Giunchedi, P. Eur J Pharm Biopharm 2004, 57, 207.
21. Sastre, R. L.; Blanco, M. D.; Teijon, C.; Olmo, R.; Teijon, J. M. Drug Dev Res 2004, 63, 41.
22. Lee, D. H.; Yang, M.; Kim, S. H.; Shin, M. J.; Shin, J. S. J Appl Polym Sci 2011, 122, 782.
23. Dubois, P.; Jacobs, C.; Jerome, R.; Teyssie, P. Macromolecules 1991, 24, 2266.
24. Jeun, J. P.; Lim, Y. M.; Nho, Y. C. J Ind Eng Chem 2005, 11, 573.
25. Kesel, C. D.; Wauven, C. V.; David, C. Polym Degrad Stabil 1997, 55, 107.
26. Kim, S. R.; Shin, Y. J.; Lee, C. I.; Pyo, H. B.; Shin, J. S. J Adhesion Interface 2008, 9, 2.