Microencapsulation of Imidazole Curing Agents by Spray-Drying Method

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ABSTRACT: An epoxy resin–imidazole system was used to form the adhesives for the anisotropic conducting film (ACF), and a latent curing system was necessary for the ACF. In this study, imidazoles were microencapsulated for the latent curing system. Polycaprolactone (PCL) was used as the wall material, and the spray-drying method was used to form the microcapsule. The imidazoles used in this study were imidazole, 2-methylimidazole, and 2-phenylimidazole. The effect of the ratio of PCL to imidazoles, and the effect of PCL molecular weight were investigated during the microcapsule formation. The amount of imidazoles in the microcapsule was measured using thermogravimetric analyzer and elemental analysis. The permeability of the microcapsules was measured in ethanol, and the shelf life of the microcapsules was studied for the epoxy resin. The curing behavior of these microcapsules to epoxy resin was examined using 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, and the curing did not occur in some of the microcapsule–epoxy resin systems at 20°C for 15 days. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 782–788, 2011

Key words: microencapsulation; imidazole; latent curing; spray-drying; epoxy resin

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.[5–11]

Recently, an epoxy-imidazole resin system was used to form an anisotropic conducting film (ACF) for use in electronic equipment, such as LCDs.[12,13] 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. Latent curing agents, such as dicyandiamide, are usually used in one-pot systems. The shelf life of dicyandiamide is almost 6 months at room temperature, but unfortunately, dicyandiamide cannot be used in the fast reacting ACF system, because the reaction rate of dicyandiamide is too slow.

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 time-

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period ranging from 1 h to 1 day. Imidazoles must be converted to an unreactable form to create a 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.[14,15]

Spray-drying method has been widely used in large-scale production of drug-loaded microspheres.[16–19] 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.

Following our previous report on the encapsulation of the imidazole curing agent with polycaprolactone (PCL) using the solvent evaporation (SE) method,[20] we now use the spray-drying (SD) method for this encapsulation to create a one-pot system for the epoxy-imidazole system. The encapsulated curing agents were characterized for epoxy resin.

EXPERIMENTAL

Materials

Figure 1 shows the structures of the materials that were used in this study. Diglycidyl ether of bisphenol F (YDF-170) was obtained from Kukdo Chemical. Imidazole (Im), 2-methylimidazole (2MI), 2-phenylimidazole (2PhI), PCL (M_w 80,000, M_w 65,000, M_w 14,000, and M_n 2,000), 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.[21–24]

Instruments

The differential scanning calorimeter (DSC) studies of the curing behavior were performed using 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. Elemental analysis was performed using an elemental analyzer (EA) (EA 1110, CE Instruments). Thermogravimetric analysis

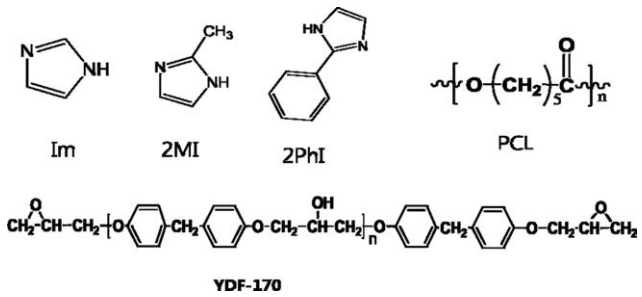

Figure 1 The structures of the materials that were used in this study.

was performed using a thermogravimetric analyzer (TGA) (SDT 2960, TA Instruments). Scanning electron microscopy was performed using both a Hitachi S-2500C and Hitachi S-5200V scanning electron microscope (SEM).

Encapsulation of imidazoles by SD method

For this most representative method, 1.2 g of imidazole and 2.8 g of PCL were dissolved in 15 mL of DCM. Using a spray gun and compressed nitrogen gas (3 atm), this solution was sprayed 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 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 and TGA.

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 2PhI 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 UV absorption was estimated at 270 nm after the sample was diluted 20 times (PCL/2PhI = 5/5), 16 times (6/4), 12 times (7/3), and 8 times (8/2) to measure the amount of the permeated 2PhI.

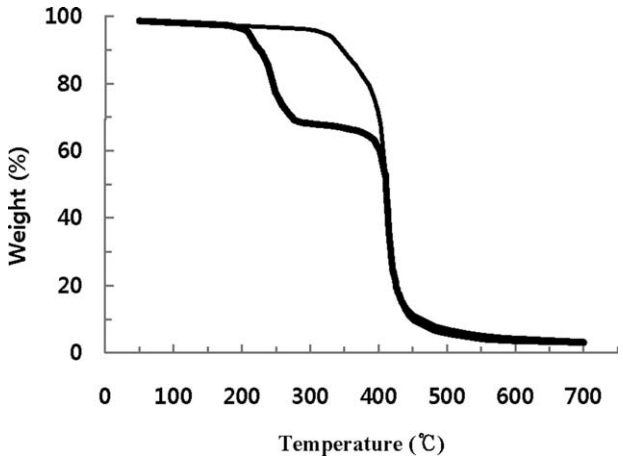

Figure 2 TGA curves of the microcapsules at 10°C/min under an N2 flow. PCL/2PhI = 7/3, Mw of PCL: 65,000.

TABLE I
The Content of Imidazoles in the Microcpasules Estimated by TGA and EA

Imidazoles	Formulation[a] (PCL/imidazoles)	TGA (%)	EA (%)
Im	5/5	47.4	48.5
	6/4	37.9	39.0
	7/3	28.6	29.1
	8/2	18.1	18.5
2MI	5/5	47.8	48.8
	6/4	38.2	37.9
	7/3	28.9	29.3
	8/2	18.5	18.4
2PhI	5/5	48.8	49.1
	6/4	39.1	39.2
	7/3	29.0	28.5
	8/2	19.2	18.9

[a] PCL + imidazoles = 4 g, DCM 15 mL

RESULTS AND DISCUSSION

Encapsulation of imidazoles

In this study, the polymer must be able to encapsulate the curing agent very well and, at the same time, easily open if necessary. Therefore, PCL was selected as the polymer for the encapsulation of the curing agent.

Among the possible encapsulation methods, the SD method was selected for this study. In this method, the encapsulated material and the polymeric wall material were dissolved in DCM; the resulting solution was spayed 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, 2MI, and 2PhI as the core materials and PCL as the polymeric wall material, the spray drying were conducted.

The effect of the ratio of PCL to imidazoles

The effects of varying ratios of PCL to imidazoles on the formation of the microcapsules were examined. The total amounts of PCL and imidazoles were fixed at 4.0 g, and the PCL/imidazoles ratio was changed from 5/5 to 8/2. The molecular weight of PCL was 65,000. TGA and EA were conducted to measure the amount of imidazoles in the microcapsules. The representative result of the TGA experiment is shown in Figure 2. In this experiment, the PCL/2PhI ratio was 7/3. This result was compared with the microcapsules that were formed using only PCL. The weight of the microcapsule sample that contained no 2PhI was abruptly reduced at around 400°C, whereas that of the sample containing 2PhI started to reduce at around 200°C. This reduced weight at around 200°C was caused by the presence of 2PhI in the PCL microcapsules. Therefore, the amount of 2PhI in the microcapsules was estimated from the weight reduction of the TGA study, and the amount of 2PhI in this microcapsules was 29.0 wt %. The TGA experiments were conducted using the microcapsules from different imidazoles and other PCL/imidazoles ratios, and the results are shown in Table I.

The amount of imidazoles in the microcapsules was also measured using the EA data. In this experiment, the amount of imidazoles was estimated from the ratio of nitrogen to carbon. To estimate the

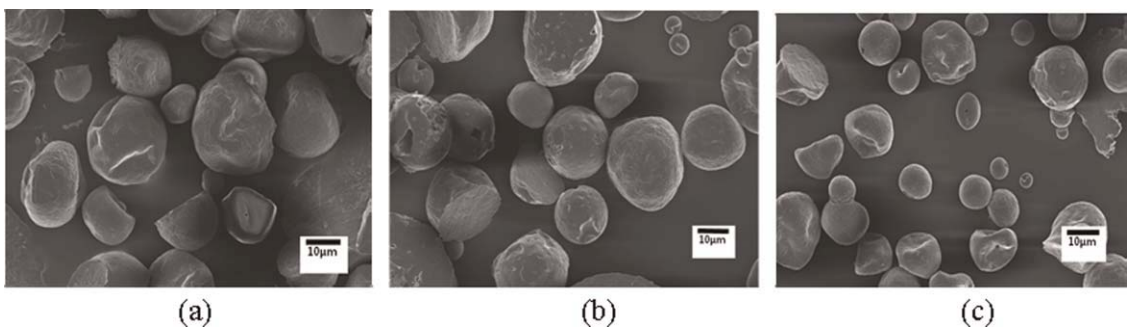

Figure 3 SEM photographs of the microcapsules that were prepared with different ratio of PCL/2PhI (a) 10/0, (b) 7/3, (c) 5/5, Mw of PCL: 65,000.

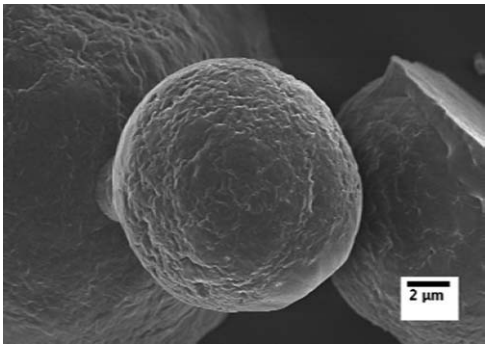

Figure 4 SEM photographs of the microcapsule. PCL/2PhI = 7/3, Mw of PCL: 65,000.

imidazole content precisely, the standard samples were prepared by mixing PCL and the imidazoles, and the weight ratios of PCL to imidazoles in the samples were set at 5/5, 6/4, 7/3, and 8/2. Using the nitrogen to carbon ratio, the standard EA graph was plotted, the EA data of the microcapsules were compared with that of the standard graph, and then the imidazole content in the microcapsules was determined. The results are shown in Table I.

The SEM micrographs of the microcapsules are shown in Figure 3. In this experiment, the PCL 65,000 and 2PhI were used. The PCL/2PhI ratios used to form the microcapsules were 10/0, 7/3, and 5/5. Almost all of the microcapsules were similar in shape. The microcapsules were sized 12.3 ± 2.5 μm, 11.5 ± 2.5 μm, and 9.4 ± 2.3 μm for 10/0, 7/3, and 5/5 ratios, respectively. Therefore, the microcapsule size decreased with increasing amount of 2PhI in the microcapsules. 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 2,000, 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/2PhI ratio was 7/3. The SEM photographs of the microcapsules using PCL 65,000, PCL 14,000, and PCL 2,000 are shown in Figure 5. The microcapsules were sized 11.9 ± 2.5 μm, 11.5 ± 2.5 μm, 9.5 ± 2.4 μm, and 13.9 ± 4.2 μm for M_w 80,000, 65,000, 14,000, and 2,000 PCL, respectively. For M_w 80,000, M_w 65,000, and M_w 14,000 PCL, the microcapsules were almost uniform shapes, and the microcapsule size increased with increasing PCL molecular weight. However, for M_w 2,000 PCL, the size and the shape of the microcapsules were not uniform, indicating that M_w 2,000 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/2PhI ratio was 7/3, and the microcapsule/YDF-170 ratio was 20/100. 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 2PhI was used instead of the microcapsules. The 2PhI/YDF-170 ratio was 6/100. These two samples had different feed ratios, because the two samples had the same amount of 2PhI for epoxy resin. The results are shown in Figure 6. In case of Im and 2MI, DSC was also conducted at the same condition as for 2PhI. In this figure, the exothermic pattern was monitored using DSC, because the curing reaction of the epoxy resin with 2PhI was exothermic. Similar patterns were observed for the two samples, but a delay of 11.5–15.8°C in the maximum peak temperature for the microcapsules, because the polymeric wall material needed to melt. Two peaks were shown in the DSC data for 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. The first peak for 2PhI was shown as a shoulder form.

The curing reaction of the epoxy resin occurred with imidazoles. Despite being reported by many

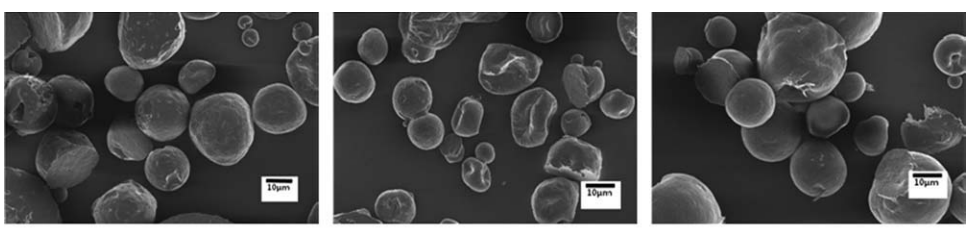

Figure 5 SEM photographs of the microcapsules that were prepared with different molecular weights of PCL, (a) 65,000, (b) 14,000, (c) 2,000. PCL/2PhI = 7/3.

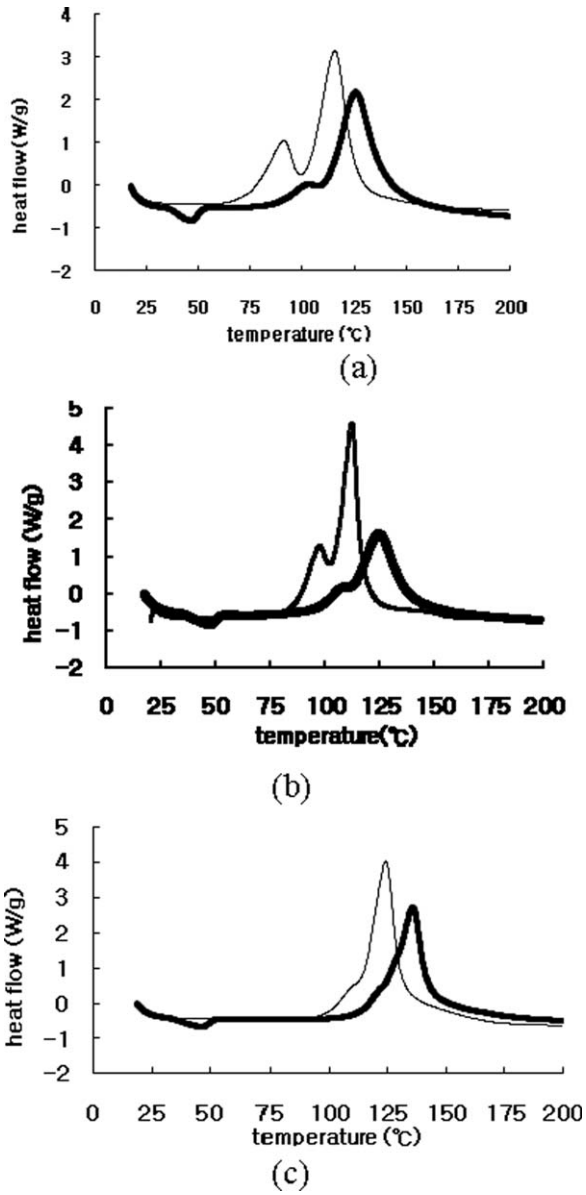

Figure 6 Scanning DSC curves for the curing of the epoxy resin.

(a). (—) PCL/Im = 7/3, microcapsule/YDF-170 = 20/100,
(—) Im/YDF-170 = 6/100,
(b). (—) PCL/2MI = 7/3, microcapsule/YDF-170 = 20/100,
(—) 2MI/YDF-170 = 6/100,
(c). (—) PCL: 2PhI = 7/3, microcapsule/YDF-170 = 20/100,
(—) 2PhI/YDF-170 = 6/100

researchers,[10,25,26] the reaction mechanism of the epoxy resin–imidazole is not yet fully understood.[23] Recently, the mechanism was examined closely. The 1:1 adduct was formed from the reaction of the epoxy resin with imidazoles, and the 1:2 adduct from the reaction of the other epoxy resin with the 1:1 adduct. The 1:2 adduct contained both a cation and an anion. The anionic polymerization of the epoxy functional groups was conducted from the anionic functional groups in the 1:2 adduct. This anionic polymerization only occurred for 5–10 times of propagation.[27]

In the case of the microcapsules, the endothermic peak at about 50°C was due to the melting of PCL. Using the different PCL/imidazole 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 order of both peak and kick-off temperatures was 2MI<Im<2PhI.

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 similar trend. The order of the curing time was 2MI<Im<2PhI 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 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 8 days at 20°C for 8/2 (PCL/Im). The curing reaction started at 20°C after 4 days had passed for pure 2PhI, but no curing occurred after storage for 15 days at 20°C for 8/2 (PCL/2PhI).

The shelf life of the microcapsule at 30°C was shorter than that at 20°C. For example, the shelf life was 4 days at 20°C for a formulation (PCL/Im) of 5/5 and feed ratio (Im/epoxy resin) of 12/100, but the shelf life at 30°C was 2 days.

Permeability of the microcapsules

The permeability of the microcapsules was examined by measuring the amount of 2PhI permeating from the microcapsules in ethanol at various time intervals. In this experiment, the microcapsules were formed using different ratios of PCL/2PhI and PCL 65,000. The results are shown in Figure 7. The fast initial release rate was due to the location of a lot of 2PhI at the surface of the microcapsules, and these phenomena were notable in case of using PCL/2PhI (5/5) or low molecular weight PCL. The permeability of the microcapsules was also examined by changing the molecular weight of PCL. In this

TABLE II
The Kick-Off Temperature and the Peak Temperature of the Microcapsules

Imidazoles	Formulation (PCL/imidazoles)	Feed ratio (microcapsule/epoxy resin)	Kick off temp. (°C)	Peak temperature (°C)
Im	0/10	6/100 (Im/epoxy resin)	68	116.6
	5/5	12/100	92	126.1
	6/4	15/100	97	129.4
	7/3	20/100	101	132.4
	8/2	30/100	105	136.2
2MI	0/10	6/100 (2MI/epoxy resin)	68	112.7
	5/5	12/100	88	123.1
	6/4	15/100	91	126.0
	7/3	20/100	96	128.5
	8/2	30/100	101	131.7
2PhI	0/10	6/100 (2PhI/epoxy resin)	94	124.8
	5/5	12/100	102	132.0
	6/4	15/100	108	134.1
	7/3	20/100	110	136.3
	8/2	30/100	113	138.6

experiment, the microcapsules were formed using PCL molecular weight of 80,000, 65,000, 14,000, and 2,000, and the PCL/2PhI ratio was 5/5. The results are shown in Figure 8. The release behaviors were similar for PCL 65,000 and 80,000, but the release behavior of PCL 2,000 was very fast. The release rate was slower at higher molecular weights.

Comparison of results with those of the SE method

We compared the results of our previous report on the encapsulation of the imidazole curing agent with PCL using the SE method[20] with those of the present study using the SD method.

The microcapsules from the SD method were not as roundly shaped as those from the SE method. Many microcapsules from the SD method had a battered round shape. The microcapsules from the SD method were sized 9.5–13.9 μm, which was fourfold larger than the size of 1.8–3.0 μm for those from the SE method.

A large amount of imidazole curing agent could not be incorporated into the microcapsules using the SE method, whereas the content of the imidazole curing agent could be increased up to 50% using the SD method. For example, although the formulation using the SE method was 5/5 (PCL/2PhI), the content of 2PhI in the microcapsules was a maximum of 25–30%. Using the SD method, when the formulation was 5/5 (PCL/2PhI), the content of 2PhI in the microcapsules was almost 50%.

When the microcapsules with similar 2PhI content were used, both methods produced microcapsules with almost similar curing behaviors to that of DSC.

TABLE III
The Curing Rate and the Shelf Life of the Microcapsules

Imidazoles	Formulation (PCL/imidazoles)	Feed ratio (microcapsule/epoxy resin)	Curing time at 150°C (sec)	Curing time at 180°C (sec)	Shelf life at 20°C (day)
Im	0/10	6/100 (Im/epoxy resin)	13	8	1
	5/5	12/100	14	9	4
	6/4	15/100	16	9	5
	7/3	20/100	16	10	7
	8/2	30/100	17	11	8
2MI	0/10	6/100 (2MI/epoxy resin)	9	6	0.5
	5/5	12/100	10	7	2
	6/4	15/100	11	7	3
	7/3	20/100	11	8	3
	8/2	30/100	12	9	4
2PhI	0/10	6/100 (2PhI/epoxy resin)	25	15	4
	5/5	12/100	27	17	8
	6/4	15/100	28	18	11
	7/3	20/100	32	20	14
	8/2	30/100	33	21	15

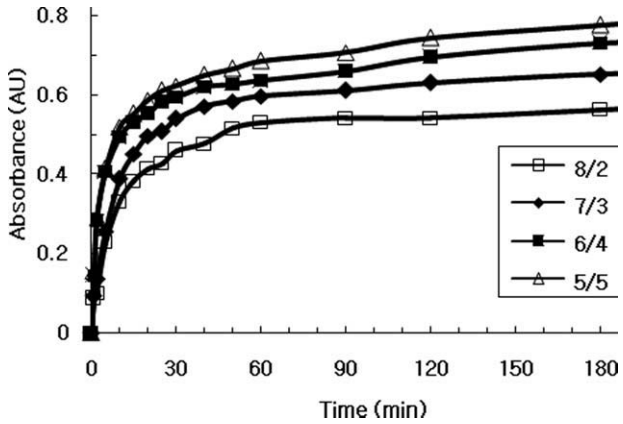

Figure 7 Release behaviors of the 2PhI/PCL microcapsules that were prepared with different ratio of PCL/2PhI. (PCL: Mw 65,000).

So, the kick-off temperature and peak temperature were almost the same.

However, the shelf life of the microcapsules from the SD method was shorter than that from the SE method: 14 days for a formulation (PCL/2PhI) of 7/3 and a feed ratio (microcapsule/epoxy resin) of 20/100 using the SD method, compared to more than 30 days using the SE method with a similar 2PhI content. We attributed this difference to the battered round shape of the microcapsules from the SD method.

The permeability of the microcapsules from the SD method was a little larger than that from the SE method. Especially, the initial release rate of the microcapsules from the SD method was faster than that from the SE method. We also attributed the fast initial release rate to the battered round shape of the microcapsules.

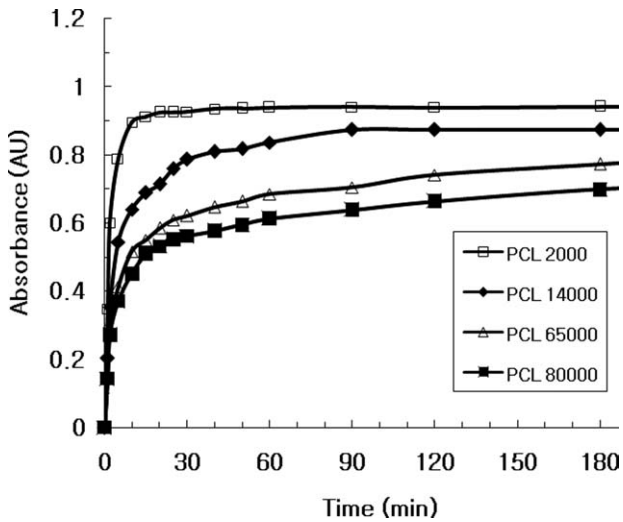

Figure 8 Release behaviors of the 2PhI/PCL microcapsules that were prepared with different molecular weights of PCL (PCL/2PhI = 5/5).

CONCLUSIONS

In this study, imidazole curing agents were encapsulated with PCL using the SD method to create a one-pot system for the epoxy-imidazole system. The amount of imidazoles in the microcapsule was measured using TGA and 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, and the curing did not occur in some of the microcapsule–epoxy resin system at 20°C for 15 days.

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