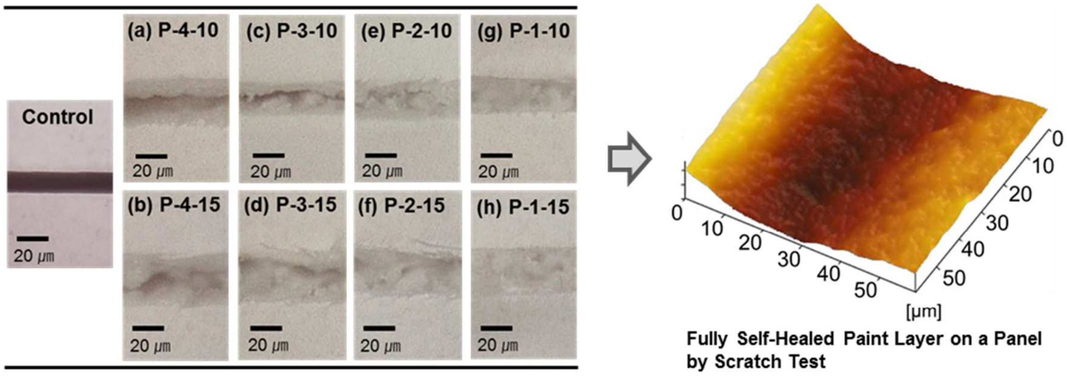
Polyurethane Microcapsules for Self-Healing Paint Coatings

Journal:	*RSC Advances*
Manuscript ID:	RA-ART-01-2014-000213.R2
Article Type:	Paper
Date Submitted by the Author:	10-Mar-2014
Complete List of Authors:	Koh, Eunjoo; Korea Research Institute of Chemical Technology, Research Center for Biobased Chemistry Kim, Nam-Kyun; Korea Research Institute of Chemical Technology, Research Center for Biobased Chemistry Shin, Jihoon; Korea Research Institute of Chemical Technology, Research Center for Biobased Chemistry Kim, Young-Wun; Korea Research Institute of Chemical Technology, Research Center for Biobased Chemistry

TOC Graphic

Polyurethane Microcapsules for Self-Healing Paint Coatings

Eunjoo Koh, Nam-Kyun Kim, Jihoon Shin,* and Young-Wun Kim*



Fully Self-Healed Paint Layer on a Panel by Scratch Test

Polyurethane Microcapsules for Self-Healing Paint Coatings

Eunjoo Koh, Nam-Kyun Kim, Jihoon Shin, and Young-Wun Kim**

Research Center for Biobased Chemistry, Korea Research Institute of Chemical Technology,
141 Gajeong-ro, Yuseong-gu, Daejeon, 305-600, Republic of Korea.

* Corresponding authors e-mail: jshin@krict.re.kr; ywkim@krict.re.kr

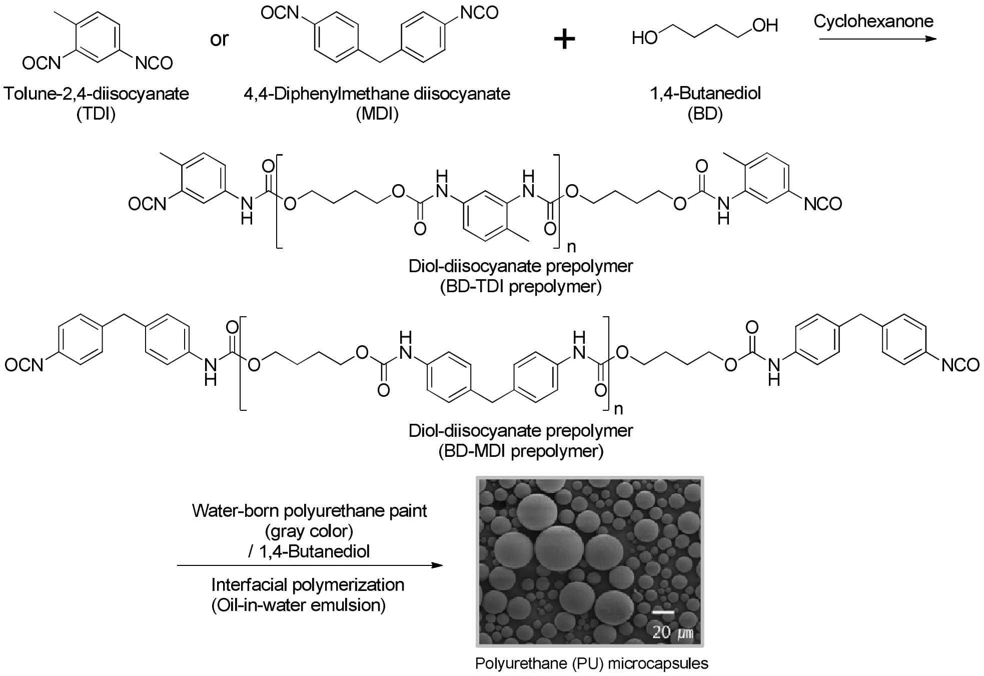
ABSTRACT

Polyurethane microcapsules containing water-borne polyurethane (PU) paint as a core material for self-repairing protection coating were successfully manufactured via interfacial polymerization of diol-diisocyanate prepolymer and 1,4-butanediol as a chain extender in an emulsion solution. The chemical structure of the resultant microcapsules was characterized by Fourier Transform Infrared Spectroscopy. Spherical capsules with regular shape were observed with 39–72 and 3.8–5.5 μm of average diameter and thickness of the shell, respectively, while controlling agitation rates (2000–8000 rpm). The PU shell wall thickness was linearly proportional to the measured capsule diameter, showing that the ratio of capsules wall thickness to diameter was constant (~0.08). The typical core content and synthetic yield of the filled capsules were approximately 44–59 wt % and 31–67%, respectively. Thermal gravimetric analysis and scanning electron microscopy results supported the determined thermal stability and morphology of the samples. Scratch tests used to evaluate self-healing protection coating systems showed that these materials had significant ability to recover from damage on the substrate, depending on the diameter and the concentration of the PU capsules in the paint layer, which could control the efficiency.

INTRODUCTION

Corrosion on metal substrate as a main destructive process can lead to significant economic loss through the failure of their potential functionalities.[1] Changes in the physical properties of coating film can generate micro cracks or scratches, which subsequently propagate and then are exposed to atmospheric moisture and oxygen, inducing disbonding of the coating film and flake formation at the coated metal substrate interface.[2–4] Corrosion tendency and rate are mainly influenced by the ionic and electronic transport properties in thin corrosion product growth.[5] Self-healing polymers have been considerably focused as a new paradigm of smart materials that have the capability to repair themselves without need for detection and by manual intervention when they are damaged, resulting in great benefits including diminished degradation, extension of the service lifespan, and reduction of the maintenance cost.[6–8] Microencapsulation has been one of the most efficient techniques widely used in self-healing systems in different fields such as surface coatings, corrosion protection, adhesive in construction, automobiles, and medical supplies.[9–13] Encapsulation of dicyclopentadiene (DCPD)[13–16] as a liquid healing agent and Grubb's catalyst particles, based on ring opening metathesis polymerization (ROMP), was reported as a first generation self-healing system.[17] A microcapsule for a self-repairing anticorrosion coating based on a polydimethylsiloxane (PDMS) healing chemistry was proposed.[18,19] Huang et al. demonstrated that polyurethane (PU) microcapsules containing hexamethylene diisocyanate (HDI) as a core material embedded in polymeric composites could achieve self-healing properties and improve the corrosion resistance of coatings.[20,21] Linseed oil,[3] epoxy resins,[8,22–24] amine,[25] and inorganic particles[1] have been used as the core healant of capsules for self-healing polymeric coatings. Paint coating composed of binders and pigments has been widely used for modification of metal surfaces due to its aesthetic appearance and corrosion protection. Hence, the concept of self-healing of cracks or scratches can be adopted for paint coatings to afford longer durability.[26] An effort to apply polymers with temperature dependent properties for healing of scratches on automotive coatings has been reported[3]. Nissan Motor Co. introduced self-healing polymer materials, such as hydrophobic paints that could repair scratches, to the market.[10]

In previous work, we reported renewable polyurethane microcapsules derived from waste vegetable oil containing isosorbide derivatives for self-healing anticorrosion coatings, which were facilely manufactured by interfacial polymerization.[23,27–28] We report herein the following: (a) synthesis of diol-diisocyanate prepolymers based on 1,4-butanediol (BD) that was reacted with toluene-1,4-diisocyanate (TDI) or 4,4-diphenylmethane diisocyanate (MDI) to prepare a PU microcapsule shell;[29] (b) interfacial polymerization[30] performed by controlling the agitation rate to form self-healing paint protection microcapsules containing water-borne PU gray paint; and (c) protection coating evaluation from scratch tests of PU capsules on a paint surface; these capsules displayed excellent protection performance with a repairing efficiency in the range of 47–100 % with various levels of core healant loading.



Scheme 1. Synthesis of PU microcapsules using a prepolymer (BD-TDI or BD-MDI) and a chain extender (BD).

RESULTS AND DISCUSSION

Synthesis of Microcapsules Diol-diisocyanate prepolymers (DB-TDI and DB-MDI) for polyurethane (PU) microcapsules were synthesized with 1,4-butanediol (DB) and toluene-1,4-diisocyanate (TDI) or 4,4-diphenylmethane diisocyanate (MDI) (Scheme 1). The microcapsules containing water-borne polyurethane (PU) paint or the PU paint/isophorone diisocyanate (IPDI) for self-healing coating were prepared by interfacial polymerization in an organic solvent-in-water emulsion. The prepolymers having approximately 20 wt % NCO content were dissolved in chlorobenzene. Water-soluble 1,4-butanediol (BD) was used to serve as a chain extender for the PU capsule shell. Thirteen PU microencapsulations for paint self-repairing PU capsule were performed with 8, 14, 25, 33, 37, and 44 wt % of core material to the prepolymer contents in emulsion at 2000, 4000, 6000, and 8000 rpm of agitation speeds (Table 1). The chemical structures of the resultant microcapsules and prepolymers were characterized by Fourier Transform Infrared Spectroscopy (FT-IR) (Fig. 1). There were bands of the prepolymer located at around 3315, 2277, and 1705 cm^{-1}; these were attributed to a secondary amine group of urethane, an isocyanate (N=C=O), and an amide carbonyl group, respectively (Fig. 1b). Reduction of the intensity of the vibration band at around 2277 cm^{-1}, corresponding to an NCO stretch, was detected, which indicated the synthesis completion of the BD-TDI prepolymer. IR peaks of the PU microcapsule wall appeared at around 3480 and 1699 cm^{-1} for the secondary amine and amide carbonyl; the single peak of the isocyanate group at 2277 cm^{-1} disappeared, proving that a chain extender (1,4-butanediol) was used to form a urethane linkage in the microcapsule shell-wall (Fig. 1c). After small amounts of PU capsules frozen in liquid nitrogen were crushed and washed with toluene to collect the core material, encapsulated water-borne PU paint and a pure core material were characterized using FT-IR (Figs. 1d and e). There was a carbonyl absorption band of the amide group at 1735 cm^{-1} and C–H stretching/bending vibrations of a long alkyl chain’s methylene groups at 2950 and 1470 cm^{-1} in the

PU urethane paint, demonstrating that the core material had been encapsulated and released.

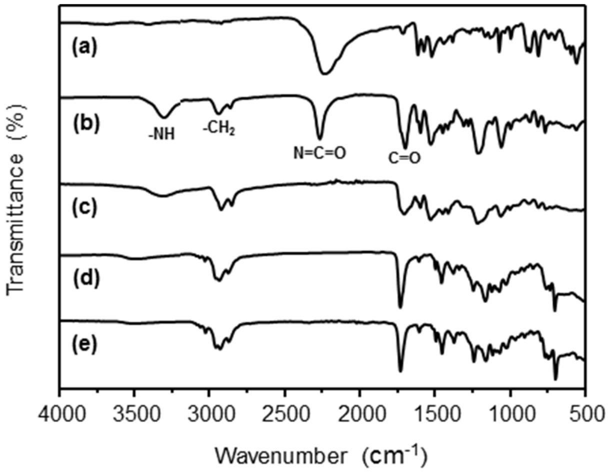


Fig. 1. FTIR Spectra of (a) toluene-1,4-diisocyanate (TDI), (b) BD-TDI prepolymer, (c) PU microcapsule wall, (d) capsule core compound released from the ruptured microcapsule (SHMC 4), and (e) pure water-borne PU paint.

Microcapsule Size Distribution The size of the microcapsules can be determined by several causes such as the geometry of the mixing device, blade hydrodynamics, viscosity, interfacial tension of the media,[10] shear/agitation rate,[11,31–33] temperature,[24] and surfactant effect.[34] The PU microcapsule size distributions were controlled by adjusting the amounts of water-borne PU paint (8–40 wt %) as a core material in total capsule amounts while holding all other factors constant, especially at 4000 rpm of agitation speed (Fig. 2a and Table 1). It was observed that the capsule size slightly increased and the PU wall thickness was significantly reduced with increasing the content of the core material. The PU microcapsules generally had 62–76 μm of average diameter and 17–4 μm of wall thickness. However, in the case of using more than 37 wt % of water-borne PU paint in the total capsule amounts (MC 5 and 6 in Table 1), it was found that the microcapsule shell wall was damaged and of poor quality, affording no characterization.

The microcapsule size distributions were also controlled with different agitation rates while all the other factors were kept constant. The temperature of the emulsion solution was kept at 50 °C, since there can be no chemical reaction between the hydroxyl group and isocyanate below 40 °C. From the result presented in Fig. 2b and Table 1, it was observed that, as the stirring speed increased, the average diameter of the TDI-derived PU shelled microcapsules significantly decreased, the thickness of the PU shell wall was slightly reduced, and the size distribution somewhat narrowed. Spherical microcapsules with average diameter in the range of 43–72 μm and wall thickness of 4–5 μm were manufactured by adjusting the agitation rate in the range of 2000–8000 rpm.

Fig. 2c and Table 1 show that the capsule size distributions were influenced by the different core/shell chemical components of the microcapsule under a selected agitation speed (8000 rpm). The average diameter of the TDI-based PU capsules (38–43 μm) was slightly larger than that of the MDI-derived capsules (23–39 μm). It should also be noted that the capsule size (39–43 μm) of the capsules with pure PU paint as a core material was larger than the size (23–38 μm) of the capsules containing PU paint/isophorone diisocyanate (IPDI). However, further study would be needed to demonstrate a correlation between the diameter and the chemical components of the capsules.

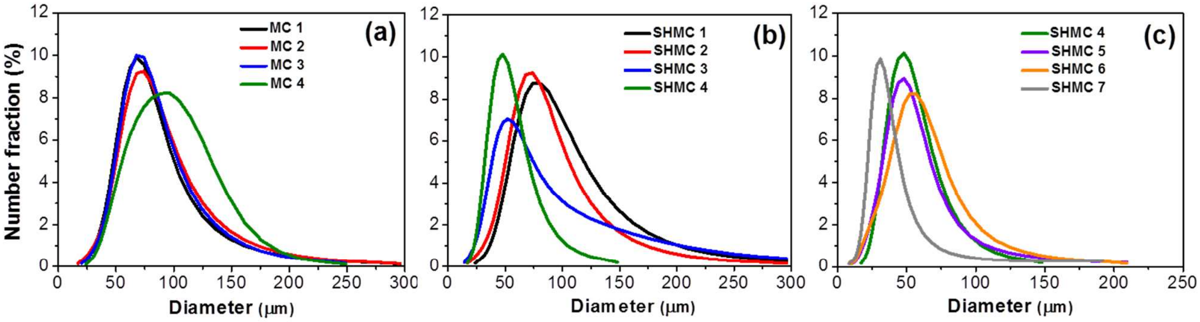


Fig. 2. Size distributions of microcapsules (a) according to different contents of core material in fixed prepolymer content (b) at different agitation rates, and (c) with different chemicals for the shell and core components in the PU capsules.

Table 1. Characterization data for self-healing paint protection PU microcapsules[a].

Sample	Type of diisocyanate for pre-polymer (amount of prepolymer (g))	Core material (g)	Agitation rate (rpm)	Yield (%)	Diameter (μm)	Wall thickness (μm)	Measured core content[b] (theoretical core content) (%)
MC 1[d]	TDI (6.0)	PU-Paint (0.5)	4000	43	62±25	17.0	8 (9.5)
MC 2[d]	TDI (6.0)	PU-Paint (1.0)	4000	48	63±26	15.0	12 (15)
MC 3[d]	TDI (6.0)	PU-Paint (2.0)	4000	57	64±21	6.0	53 (54)
MC 4[d]	TDI (6.0)	PU-Paint (3.0)	4000	34	76±36	4.0	34 (72)
MC 5[d]	TDI (6.0)	PU-Paint (3.5)	4000	–[c]	–[c]	–[c]	–[c]
MC 6[d]	TDI (6.0)	PU-Paint (4.0)	4000	–[c]	–[c]	–[c]	–[c]
SHMC 1[e]	TDI (6.0)	PU-Paint (2.0)	2000	67	72±41	5.5	59 (62)
SHMC 2[e]	TDI (6.0)	PU-Paint (2.0)	4000	56	63±44	5.0	53 (60)
SHMC 3[e]	TDI (6.0)	PU-Paint (2.0)	6000	41	51±36	4.3	49 (58)
SHMC 4[e]	TDI (6.0)	PU-Paint (2.0)	8000	31	43±23	4.0	44 (55)
SHMC 5[e]	MDI (6.0)	PU-Paint (2.0)	8000	33	39±18	3.8	45 (53)
SHMC 6[e]	TDI (6.0)	PU-paint (2.0)+ IPDI (0.5)	8000	32	38±32	3.5	46 (55)
SHMC 7[e]	MDI (6.0)	PU-paint (2.0)+ IPDI (0.5)	8000	36	23±19	1.5	47 (67)

[a] See the Experimental Section for details. [b] Measured weight of the released cores after solvent treatments. [c] Because the thickness of the PU capsule shell wall was too thin, the shape of the microcapsule was already squashed during the interfacial polymerization. So, it is not possible to measure the characterization data of the microcapsule. [d] MC means microcapsules prepared to investigate optimized synthetic conditions for PU capsules except agitation rate. [e] SHMC means microcapsule coated for self-healing tests on metal substrate.

Morphology of Microcapsules As seen in Fig. 3, the surface and shell morphology of microcapsules prepared by adjusting the amount of added core material in the emulsion solution and by applying different agitation rates were investigated using scanning electron microscopy (SEM). Spherical microcapsules were easily obtained at in the range of added core material amounts (8–40 wt %) and at all agitation rates in the range of 2000–8000 rpm. It was possible to control the shell thickness by adjusting the amounts of added PU paint in the emulsion process. Higher fill content and thinner shell walls were obtained when more core material was added, while keeping the capsule diameter at 4000 rpm. However, problems such as collapsed shape of some capsules (MC 6), or holes on the surface (MC 4 and 5) due to thinner shell walls appeared at over 37 wt % of initial core amount (Fig. 3 and Table 1). Since the measured core content and theoretical content of MC 3 was seen to be very similar in Table 1, leading to a high core content and relatively perfect shape, this synthetic condition was decided for further experiments (SHMC 1–7).

Average diameters and standard deviations of PU capsules (SHMC 1 and 2) were 72 ± 41 and 63 ± 44 μm at stirring speeds of 2000 and 4000 rpm; the sizes of the capsules (SHMC 3 and 4) at 6000 and 8000 rpm agitation rates (51 ± 36 and 43 ± 23 μm) were relatively smaller and more uniform. When 2000, 4000, 6000, and 8000 rpm agitation rates were applied for PU microcapsule synthesis 59, 53, 49, and 44% of core contents in the capsules were found respectively (Table 1). As increasing agitation speed in the interfacial polymerization process, the size of the prepared capsules steadily decreased and the amounts and volumes of the core material also dropped. Fluid shear force according to agitation rate controlled the size and the core content/volume of the capsules. It was also observed that larger microcapsules synthesized with a relatively lower agitation rate had thicker shell wall.[35] However, the ratio of shell wall thickness to capsule diameter was kept constant at approximately 0.08. There were micromoire patterns on the outer surface of all the prepared PU microcapsules (Fig. 3). The storage capacity of the core inhibitor of the filled PU capsules was measured based on the weight loss of the PU paint by solvent washing method after rupturing the capsules, which approached 44–59 wt % at room temperature (SHMC 1–7 in Table 1).

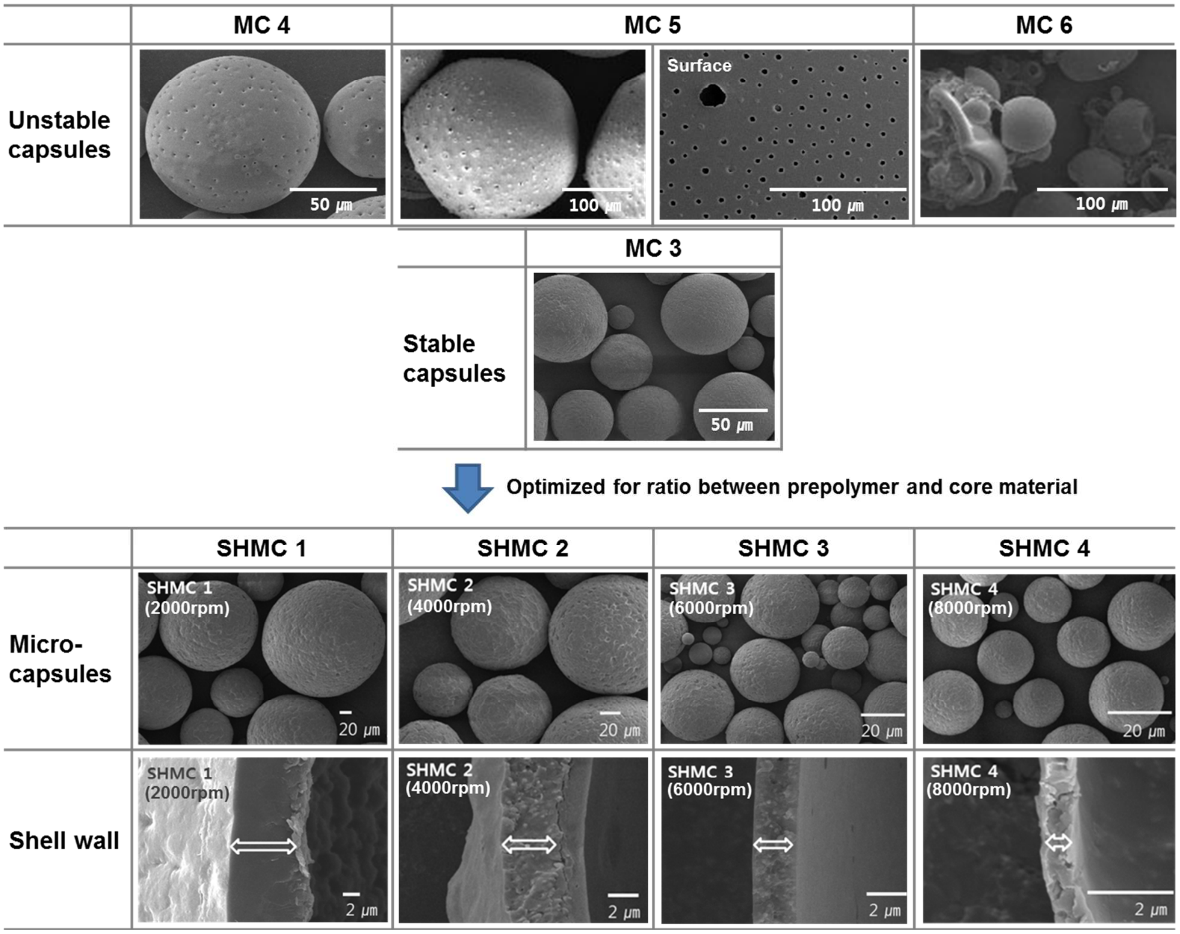


Fig. 3. Surface and shell morphology of PU microcapsules obtained according to initially added core amount and at various agitation rates.

Thermal Stability The thermal properties of the water-borne PU paint as a core material, as well as those of the BD-TDI prepolymer, the microcapsule shell wall, and the filled microcapsules (SHMC 4) were determined by thermogravimetric analysis (TGA). The resultant curves of weight loss for each material are given in Fig. 4. The decomposition of the PU paint as a core material began at 150 °C and was almost completed at 460 °C, even though there were still small thermo-degradation traces at temperatures over 500 °C. The TGA curve of the BD-TDI prepolymer was composed of two weight loss stages corresponding to the polyol soft segments at 240–300 °C and the isocyanate hard parts at 300–350 °C. About 3% weight loss for the synthesized microcapsule (SHMC 4) was found at around 100 °C; this weight loss was due to water remaining in the capsules after interfacial polymerization. The first weight loss due to the decomposition of polyol (BD) soft segments for the capsule was observed at around 260–350 °C; this temperature range significantly overlapped with the degradation temperature of the PU paint as a core material. The second weight loss was found at around 360–490 °C and was due to the breakup of isocyanate hard domains of the microcapsules composed of prepolymers. The decomposition curve of the capsule was slightly shifted to the right, compared to the above results of the breakdown temperature of the prepolymers; this shift is due to close connection of hard segments after PU microcapsule synthesis.

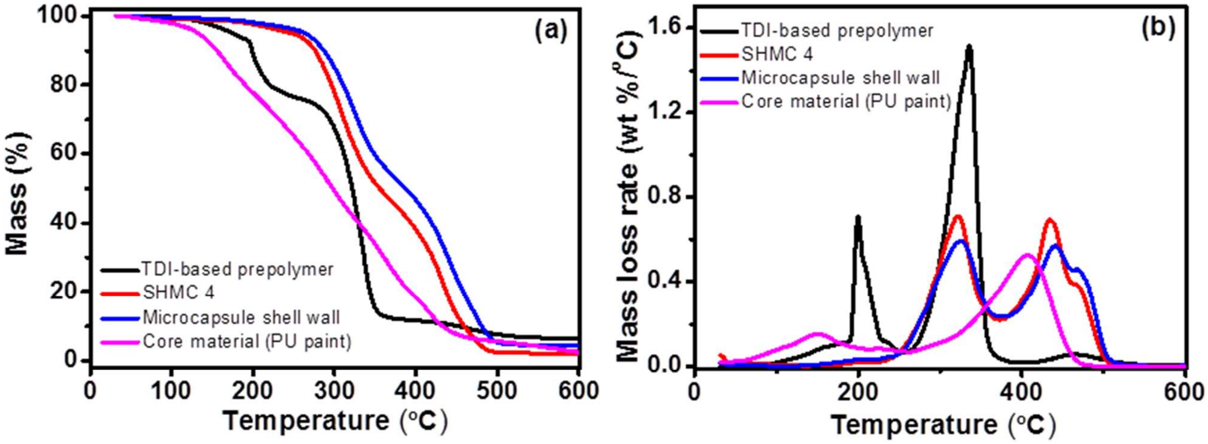


Fig. 4. (a) TGA weight loss curves of synthesized microcapsules (SHMC 4) along with authentic traces for TDI-based prepolymer, capsule shell wall, and core material. (b) Derivatives of TGA data of the prepolymer, the filled capsule, the capsule shell wall, and the core material. All experiments were conducted at a heating rate of 20 °C/min in an N_2 environment.

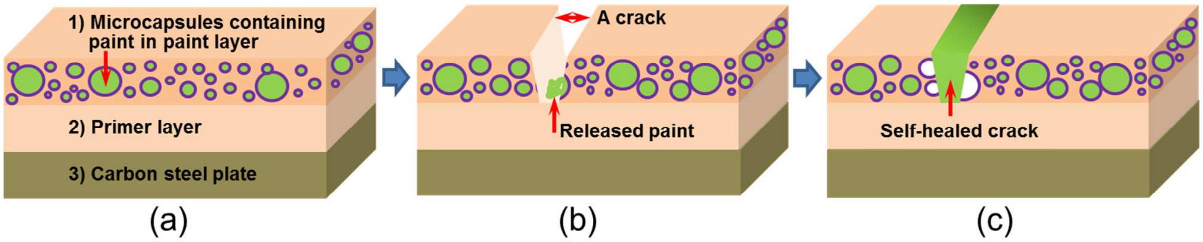
Paint Protection Study The self-healing paint coating property can be illustrated using the idea of microcapsules having water-borne PU paint (gray color) as a coating repairing material; we show inner cross section images in which the capsules were evenly phase-separated in the paint layer in Scheme 2. When a paint layer (top surface, with thickness of 25–150 μm) having self-repairing PU capsules and a primer layer (bottom layer, with thickness of about 20 μm) on a carbon steel plate (Scheme 2a) was damaged by a deep scratch of 20–40 μm in width (Scheme 2b), the paint protecting capsules burst and the core material was subsequently released around the ruptured microcapsules. After a certain period of time for hardening, a protection barrier on the scratched area of the steel panel was formed by the released PU paint (Scheme 2c). Atomic force microscopy (AFM) images were used to reveal the morphology of the repaired surface for the self-healing protection coating system with three-dimensional shape. Figs. 5b and c showed the partially recovered paint layer, which has a rough surface that has an efficiency of 47% (P-4-10 in Table 2), and the perfectly healed paint coating surface, which has a smooth covering that shows 100% efficiency (P-4-35 in Table 2), which proved the effect of capsule concentration; on the other hand, there was also an unscratched paint area having self-healing PU paint capsules, as seen in Fig. 5a. As a result, the roughness and the efficiency for the repaired surface depend on the amounts of microcapsules in the paint layer. A scanning electron microscopy (SEM) image of the repaired scratch area (SHMC 4) reveals the morphology of the self-healing paint coating (Fig. 6). The releasing behaviour of the paint could be easily detected on the metal plate in the SEM image. In addition, self-healing paint protection on the substrate is readily apparent in the microscopy images (Figs. 7, 8, and 9). There was hardly any uncovered trace in the PU paint coated cross-sectioned sample (P-4-35), whereas a distinct scratch trace was observed in the control sample. Microcapsules filled with PU paint were integrated into the paint layer and subsequently outer-coated to make a self-healing coating. The degree (%) of healing efficiency was evaluated using a scratch test with an IMT iSolution quick-scan^{TM}. The software provides quantitative image analysis of the healing efficiency after comparing the surfaces of the self-coated panels and of a blank specimen (Table 2). The healing efficiency (%) and the hardening time were measured. It was found that the degree was influenced by (a) PU capsule size controlled by agitation rates (Table 1), including 10 and 15 wt % the capsule concentration in the paint layer; (b) the concentration of the PU capsules in the paint layer, which has values of 10, 15, 25, and 35 wt %, and the capsules were made by TDI or MDI (P-4 or P-5); and (c) an additive, such as isophorone diisocyanate (IPDI), for the two different kinds of PU capsules made from the two diisocyanates and two types of capsule concentrations with values of 25 and 35 wt % in the paint layer (P-6 and P-7).

A test was carried out to evaluate the paint protection performance; we used PU paint as a self-healing agent according to the sizes of the PU microcapsules affected by agitation (2000, 4000, 6000, and 8000 rpm) with 10 or 15 wt % capsule concentrations in the paint layer. The self-coating efficiencies were determined after 3–4 h of hardening time. The results from the scratch test clearly turned out that all the steel plates displayed significant self-repairing protection performance (47–97% in efficiency), compared with the blank specimen, which had an almost identical scratch (Figs. 7a–h and Table 2). Healing efficiency increased with the enlarging of the diameter of the capsules and we assumed that larger capsules would contain more core material. However, in the cases of both samples P-1-10 and P-2-15, even though P-2-15 (8 wt % and ca. 63 μm of diameter) has a greater total content of core material, P-1-10 (5.9 wt % and ca. 72 μm of diameter) with larger diameter showed the higher protection efficiency (82% > 73%). So, when the capsules have the same diameter, microcapsules containing 15 wt % capsule concentrations in the paint layer generally exhibited 10–15 % of higher efficiency, compared those of the capsules having 10 wt % concentrations. The first self-healing protection analysis revealed that the diameter of the capsule is the more important factor to determine the efficiency, compared to the total contents of the core material.[26]

Another factor for an effect on the healing efficiency, according to the concentration of PU capsules in the paint layer, such as 10, 15, 25, and 35 wt % concentrations, consisting of two capsule types made by two diisocyanates, was investigated. The self-protecting efficiencies were determined after 3–4 h of hardening time. The scratch test clearly showed that all protection efficiency (47–97% for the TDI based capsules and 47–95% for the MDI based capsules) was directly proportional to the concentration of the microcapsules from 10 to 35 wt %, namely, the total content of the core material compared with that of the control sample (Fig. 8 and Table 2). Even though the efficiencies of the TDI based capsules are slightly higher than those of the MDI based capsules (2–5%) as shown at Fig. 8, this could be caused by the larger diameter of the TDI based capsule shells (43 > 39 μm). The second analysis of the self-repairing protection disclosed that the total content of core material is also an important factor to determine the efficiency.

In order to study the efficiency influenced by isophorone diisocyanate (IPDI) as an additive for hardening and the two different kinds of PU capsules prepared with diisocyanates (TDI or MDI) and two types concentration of capsules such as 25 and 35 wt % in the paint layer, a final scratch test was carried out (Fig. 9 and Table 2). The self-protecting efficiencies were determined after 5 h of hardening time. The test clearly showed that all the panels haves self-repairing protection functions (74–100% in efficiency). However, it was observed that samples P-6-25 and P-7-25 (74 and 75%) with an additive to accelerate the hardenability had slightly little lower efficiencies than those of samples P-4-25 and P-5-25 (85 and 80%). It was believed that the addition of IPDI (20 wt % of the total core material) caused the self-healing agent dilute, resulting in smaller diameters and longer hardening time of the capsule shell, compared to those values of the counterparts.

In this work, the self-healing paint protection property was generally developed with larger diameters of the capsule shells and with larger contents of the core reagent. Therefore, we concluded that polyurethane microcapsules containing water-borne PU paint afforded outstanding coating repair properties on steel plates through a scratch test, even when these capsules had short diameters (< ca. 30 μm) and less overall contents (< 4–5 wt %) of core material.



Scheme 2. Schematic of the self-protection process: (a) Paint coating having microcapsules with self-healing protecting paint on carbon steel plate, (b) Paint released by damage to the paint coating layer, and (c) a crack covered by a paint protection barrier.

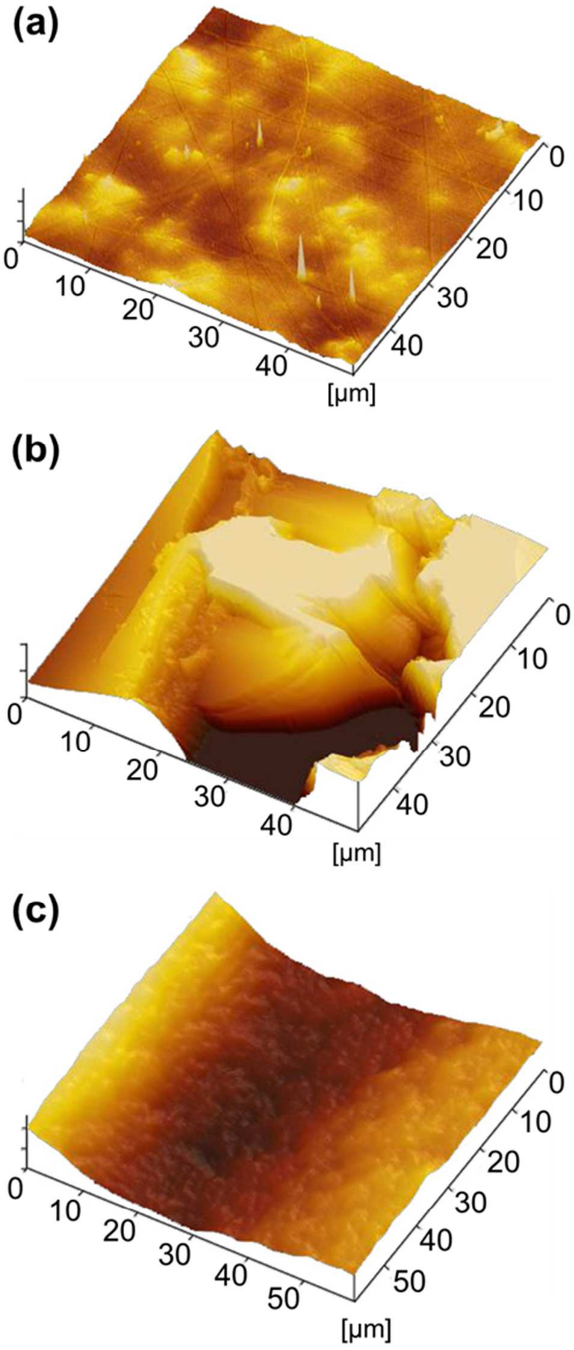


Fig. 5. AFM images of (a) unscratched paint layer containing capsules on a carbon steel plate (P-4-35), (b) partially recovered paint layer on a plate (P-4-10), and (c) fully self-healed paint layer on a panel (P-4-35).

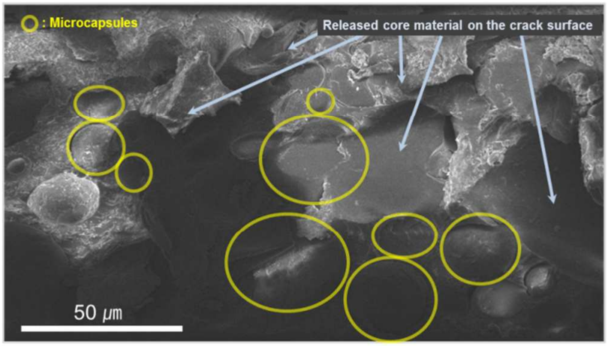


Fig. 6. A cross-section SEM image of a paint self-coated layer using 35 wt % microcapsule concentration (P-4-35).

Table 2. Self-healing efficiencies evaluated by the scratch test[a]

Paint having PU capsule	Diameter of capsules (μm)	Conc. of capsule in paint layer (wt %)	Total conc. of a core material (wt %)[b]	Healing efficiency (%)	Hardening time (h)
control sample[c]	0	0	0	0	3
P-1-10[d]	72±41	10	5.9	82	3
P-1-15[d]	72±41	15	8.9	97	3
P-2-10[d]	63±44	10	5.3	63	3
P-2-15[d]	63±44	15	8.0	73	3
P-3-10[d]	51±36	10	4.9	54	3
P-3-15[d]	51±36	15	7.4	66	3
P-4-10[d]	43±23	10	4.4	47	3
P-4-15[d]	43±23	15	6.6	59	3
P-4-25[d]	43±23	25	11.0	85	3
P-4-35[d]	43±23	35	15.4	97	3
P-5-10[d]	39±18	10	4.5	47	3
P-5-15[d]	39±18	15	6.8	57	3
P-5-25[d]	39±18	25	11.3	80	3
P-5-35[d]	39±18	35	15.8	95	3
P-6-25[d]	38±32	25	11.5	74	5
P-6-35[d]	38±32	35	16.1	100	5
P-7-25[d]	23±19	25	11.8	75	5

P-7-35 [d]	23±19	35	16.5	99	5

[a] See the Experimental Section for details (based on ASTM D 610-2008). [b]Calculated using the core content in a PU microcapsule [c]The control sample is one in which the paint layer has no PU microcapsules for self-healing protection. [d]For the naming of the paint, the middle number and the last number of the paint name display the utilized PU capsule number, such as SHMC 1–7 in Table 1, and the concentration of PU capsules in the paint layer such as 10–35 wt %, respectively.

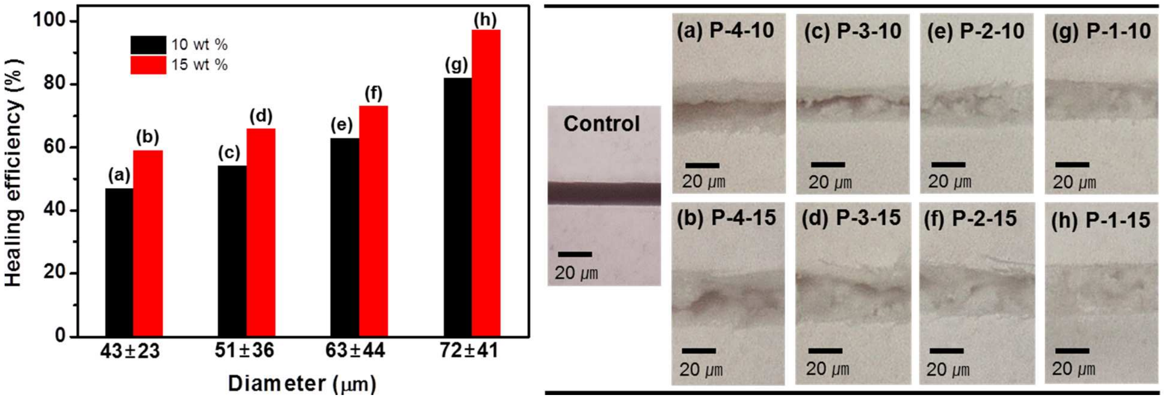


Fig. 7. Paint protection test results determined via scratch test considering the effect of capsule diameter of PU microcapsules.

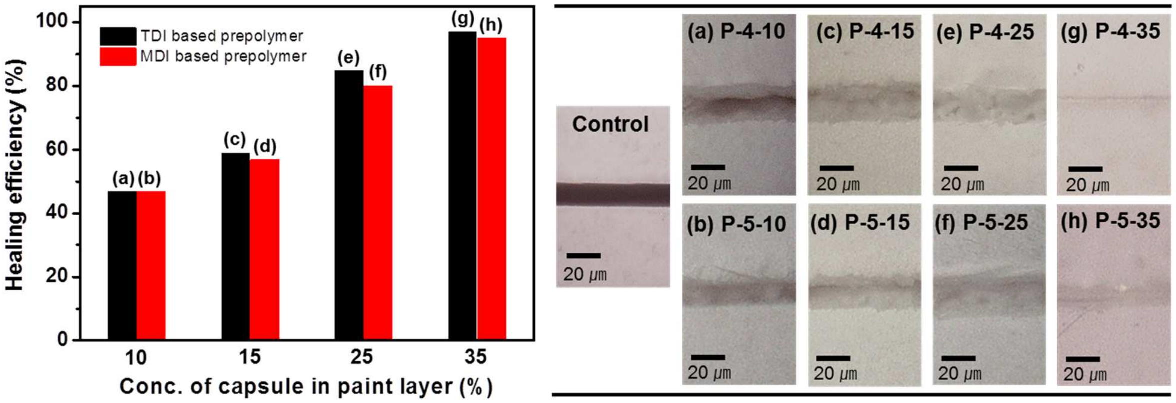


Fig. 8. Paint protection test results determined via scratch test considering the influence of capsule concentration in the paint layer.

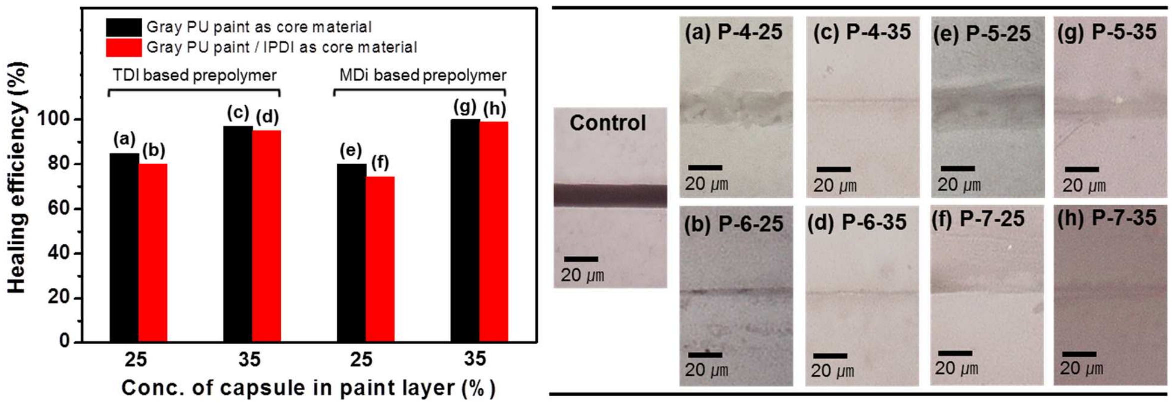


Fig. 9. Paint protection test results determined via scratch test according to the effect of addition of additives and capsule concentration in the paint layer.

CONCLUSIONS

Water-borne PU paint-filled polyurethane microcapsules for self-healing protection coatings were synthesized by an interfacial polymerization of diol-diisocyanate prepolymer and 1,4-butanediol (BD) a chain extender. The prepolymers (BD-TDI and BD-MDI) were prepared with BD and toluene diisocyanate (TDI) or diphenylmethane diisocyanate (MDI). Encapsulation of the coating agent within a PU shell wall was confirmed with FT-IR. Spherical microcapsules with diameter in the range of 39–72 μm and shell wall thickness in the range 4–6 μm were prepared under controlled agitation. The PU paint content of the resultant capsules was approximately 44–59 wt %. The microcapsules also exhibited good storage capacity and chemical stability below 250 °C. The efficiency of the PU microcapsules containing the self-healing protection agent was investigated in a paint coating system. The results by scratch testing indicated that the capsules provided remarkable protection efficiency (in the range of 0–53 %) as evaluated by the scribe degree with varied levels of self-repairing agent loading. These findings showed that water-borne PU filled microcapsules can provide a new self-healing protection coating for industrial paint applications.

EXPERIMENTAL SECTION

Materials. Toluene-2,4-diisocyanate (TDI), 4,4-diphenylmethane diisocyanate (MDI), isophorone diisocyanate (IPDI), 1,4-butanediol, cyclohexanone, chlorobenzene, and gum arabic surfactant for the synthesis of prepolymer and microcapsules were of commercial grade and used without further purification unless otherwise specified. Water-borne polyurethane (PU) paint (DHDC-2740) was used as a core material. The car paint (DHDC-2740) and diluent (DR-700) were purchased from NOROO Paint & Coatings Co., Ltd., and the primer (XKB014) and diluent (KSM-6060) were obtained from Chokwang Paint Co., Ltd., for top coatings and the primer, respectively.

Measurements Qualitative analyses of FT-IR (Bio-RAD FTS165) for the products were carried out. The molar mass (M_n and M_w) was determined by SEC in tetrahydrofuran (1.0 mL/min) at 40 °C versus polystyrene standards using a Waters high-pressure liquid chromatography system equipped with a UV Waters 2690 using three Columns (PL, Mixed-B×2 and 500Å×1 pore size) and a Waters 2414 differential refractometer. The hydroxyl value (OH) was determined using the ASTM D1957 Method (Metrohm, 888 Titrando). The NCO content in the prepolymers was calculated via titration. The synthesized prepolymer (1 g) was completely dissolved in toluene (50 mL). Di-*n*-butyl amine solution (15 mL, 0.1 N) was added using a pipette. After swirling for 15 min, isopropyl alcohol (50 mL) and a bromophenol blue indicator solution (4–6 drops) were added. Two titrations were performed with hydrochloric acid (0.1 N) to a yellow end point. The NCO content was calculated as follows: NCO, % = [(B-V) x N x 0.0420]/W x 100, where B and V (both in mL) are the volumes of HCl for titration of the blank and the prepolymer, respectively, with N normality of HCl, and W grams of prepolymer. The microcapsule size and distribution were measured using a Mastersizer particle size analyser (Microtrac S3000) in the range of 0.2–1500 μm. The microcapsules were measured at least 10 times before recording their size. Thermogravimetric analysis (TA Instruments Inc. TA3 11/SD T2960) was used to study the thermal stability and core content of the prepared capsules. Small amounts of microcapsule (10–20 mg) were heated from 25 to 800 °C at a rate of 20 °C/min in a nitrogen atmosphere. The surface morphology and capsule shell thickness were observed with a scanning electron microscopy (SEM) system (XL-30S FEG, Philips). Atomic force microscopy (AFM) measurements were carried out in the dry state under ambient conditions using a SPI3800N probe station (SII Seiko instruments Inc.) operating with amplitude feedback in tapping mode. Commercially available SI3N4 cantilevers were used for imaging. Images are mainly raw data except in some cases in which minor flatness and tilt corrections have been made.

Evaluation of Self-Healing Paint Protection Properties. Scheme 2 shows a schematic of a cross-section image in which the primer (bottom layer) and the paint layer (surface) were laminated on a carbon steel plate as a scribe supplier for protection coatings. Microcapsules were added into the paint substance at 10, 15, 25, and 35 wt %. Water-based paint and hydrophilic primer were diluted with water at ratios of 6 to 4 and 4 to 1, respectively. The coatings were applied using control bar coaters (Sheen Instruments). After curing, crossing scratches were applied manually on the coating using a razor blade and were left for a certain period of time for the release and hardening of the core material. Tests were performed according to ASTM-C1624 for the scratch test and ASTM-D610 for the evaluation of the self-healing efficiency. Observation by an optical microscope (Olympus, BX51) equipped with a device camera (IMT i-Solution TM Inc.) could evaluate the percentage of coating for scratched surface on the painted steel surface according with ASTM D 610−08. This test was useful for quantifying the amount and distribution of visible scribe surface (Figs. 6, 7, and 8).

Synthesis of Prepolymer (BD-TDI or BD-MDI). Diol-diisocyanate prepolymer was prepared as a constituent for the PU shell of the microcapsules, as shown in Scheme 1. The mixture of toluene 2,4-diisocyanate (12.65 g) (or 4,4-diphenylmethane diisocyanate (15.64 g)) and cyclohexanone (25 mL) was agitated using a magnetic stirrer at 80 °C. 1,4-Butanediol (4.5 g) was slowly added to the diisocyanate solution and the mixture was allowed to react for 24 h. The resulting mixture was then distilled at 100 °C under 15 torr for 5 h to remove cyclohexanone, water, and excess isocyanate, leaving a yellowish and viscous prepolymer in the flask. The molecular masses were determined by

SEC and were found to have an M_n value of 725 g mol^{-1} and an M_w value of 1,924 g mol^{-1} ($Đ = 2.65$) for the TDI-based prepolymer and an M_n value of 436 g mol^{-1} and an M_w value of 1,439 g mol^{-1} ($Đ = 3.30$) for the MDI-based prepolymer (14.9 and 18.5 g recovered; 84 and 86% of isolated yield for the TDI or MDI-based prepolymers, respectively).

Synthesis of Microcapsules Containing Protection Coating Material. After BD-TDI or BD-MDI (6 g) was completely dissolved into chlorobenzene (3 g) at 30 °C, the solution was slowly poured into the gum arabic solution (60 g of a deionized water containing 10 wt % gum arabic surfactant). Water-borne PU paint as core material (0.5–4.0 g) was also added to the mixed solution. After pre-agitation for 30 min at 2000 rpm using a homogenizer, the emulsion solution was encapsulated using agitation rates ranging from 2000 to 8000 rpm at 50 °C. BD (6 g) as a chain extender was slowly added to the emulsion to initiate interfacial polymerization at the solvent-in-water interface. The reaction was stopped after 2 h, and the resulting microcapsules were washed with deionized water several times and filtered in a vacuum. The isolated microcapsules were air-dried for 24 h. The yield of microcapsules was about 31–67 %.

ACKNOWLEDGEMENTS: This study was supported by the R & D Centre for Valuable Recycling (Global-Top Environmental Technology Development Program) through a grant from Ministry of Environment of Republic Korea (Project No.: GT-11-C-01-270-0).

REFERENCES

[1] D. G. Shchukin, M. Zheludkevich, K. Yasakau, S. Lamaka, M. G. S. Ferreira and H. Möhwald, *Adv. Mater.*, 2006, **18**, 1672–1678.

[2] S. J. García, H. R. Fischer and S. van der Zwaag, *Prog. Org. Coat.*, 2011, **72**, 211–221.

[3] C. Suryanarayana, K. C. Rao and D. Kumar, *Prog. Org. Coat.*, 2008, **63**, 72–78.

[4] H. S. Wong, Y. X. Zhao, A. R. Karimi, N. R. Buenfeld and W. L. Jin, *Corros. Sci.* 2010, **52**,

2469–2480.

[5] J. H. Payer, G. Ball, B. I. Rickett and H. S. Kim, *Mater. Sci. Eng., A*, 1995, **198**, 91–102.

[6] R. Porter and J. B. Miale, *Appl. Biochem. Biotechnol.*, 1984, **9**, 439–445.

[7] N. Elsner, F. Dubreuil and A. Fery, *Phys. Rev. E*, 2004, **69**, 031802-1–6.

[8] Y. C. Yuan, M. Z. Rong, M. Q. Zhang, J. Chen, G. C. Yang and X. M. Li, *Macromolecules*, 2008, **41**, 5197–5202.

[9] C. P. Chang and T. Dobashi, *Colloids Surf., B*, 2003, **32**, 257–262.

[10] D. Sondari, A. A. Septevani, A. Randy and E. Triwulandari, *Int. J. Eng. Technol.*, 2010, **2**, 466–471.

[11] P. D. Tatiya, R. K. Hedaoo, P. P. Mahulikar and V. V. Gite, *Ind. Eng. Chem. Res.*, 2013, **52**, 1562–1570.

[12] M. Nosonovsky and B. Bhushan, *Appl. Surf. Sci.*, 2010, **256**, 3982–3987.

[13] T. Szabó, L. Molnár-Nagy, J. Bognár, L. Nyikos and J. Telegdi, *Prog. Org. Coat.*, 2011, **72**, 52–57.

[14] E. N. Brown, S. R. White and N. R. Sottos, *J. Mater. Sci.*, 2004, **39**, 1703–1710.

[15] J. M. Kamphaus, J. D. Rule, J. S. Moore, N. R. Sottos and S. R. White, *J. R. Soc. Interface*, 2008, **5**, 95–103.

[16] M. R. Kessler, N. R. Sottos and S. R. White, *Composites Part A*, 2003, **34**, 743–753.

[17] S. R. White, N. R. Sottos, P. H. Geubelle, J. S. Moore, M. R. Kessler, S. R. Sriram, E. N. Brown and S. Viswanathan, *Nature*, 2001, **409**, 794–797.

[18] S. H. Cho, S. R. White and P. V. Braun, *Adv. Mater.*, 2009, **21**, 645–649.

[19] S. H. Cho, H. M. Andersson, S. R. White, N. R. Sottos and P. V. Braun, *Adv. Mater.*, 2006, **18**, 997–1000.

[20] M. Huang and J. Yang, *J. Mater. Chem.*, 2011, **21**, 11123–11130.

[21] M. Huang, H. Zhang and J. Yang, *Corros. Sci.*, 2012, **65**, 561–566.

[22] D. S. Xiao, Y. C. Yuan, M. Z. Rong and M. Q. Zhang, *Polymer*, 2009, **50**, 560–568.

[23] D. S. Xiao, M. Z. Rong and M. Q. Zhang, *Polymer*, 2007, **48**, 4765–4776.

[24] L. Yuan, G. Liang, J. Q. Xie, L. Li and J. Guo, *Polymer*, 2006, **47**, 5338–5349.

[25] D. A, McIlroy, B. J. Blaiszik, M. M. Caruso, S. R. White, J. S. Moore and N. R. Sottos, *Macromolecules*, 2010, **43**, 1855–1859.

[26] A. Kumar, L. D. Stephenson and J. N. Murray, *Prog. Org. Coat.*, 2006, **55**, 244–253.

[27] J. Yang, M. W. Keller, J. S. Moore, S. R. White and N. R. Sottos, *Macromolecules*, 2008, **41**, 9650–9655.

[28] E. Koh, S. Lee, J. Shin and Y.-W. Kim, *Ind. Eng. Chem. Res.*, 2013, **52**, 15541–15548.

[29] A. P. Esser-Kahn, N. R. Sottos, S. R. White and J. S. Moore, *J. Am. Chem. Soc.*, 2010, **132**, 10266–10268.

[30] C. Scott, D. Wu, C-C. Ho and C.-C. Co, *J. Am. Chem. Soc.*, 2005, **127**, 4160–4161.

[31] G. Li, Y. Q. Feng, X. G. Li, P. Gao, J. Wang and J. Y. Xie, *J. Mater. Sci.*, 2007, **42**, 4838–4844.

[32] V. Kantsler, E. Segre and V. Steinberg, *Phys. Rev. Lett*. 2007, **99**, 178102-1–4.

[33] B. G. Zanetti-Ramos, E. Lemos-Senna, V. Soldi, R. Borsali, E. Cloutet and H. Cramail, *Polymer*, 2006, **47**, 8080–8087.

[34] A. Bhattacharyya and J.-F. Argillier, *J. Surface Sci. Technol.*, 2005, **21**, 161–168.

[35] J.-F. Su, L.-X. Wang, L. Ren, Z. Huang and X.-W. Meng, *J. Appl. Polym. Sci.*, 2006, **102**, 4996–5006.