

# THE SYNTHESIS OF POLYURETHANE MICROCAPSULES AND EVALUATION OF SELF-HEALING PAINT PROTECTION PROPERTIES

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## ABSTRACT

Polyurethane microcapsules containing water-borne polyurethane (PU) paint as a core material for self-repairing protection coatings 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. The PU shell wall thickness was linearly proportional to the measured capsule diameter, thus, showing that the ratio of capsule wall thickness to diameter was constant. The typical core content and synthetic yield of the filled capsules were approximately 44–59 wt% and 31–67%, respectively. 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.

## 1 INTRODUCTION

Self-healing polymers have been considerably focused upon as a new paradigm of smart materials that have the capability to repair themselves without the need for detection or manual intervention when they are damaged, thus, resulting in great benefits including diminished degradation, extension of the service lifespan, and reduction of the maintenance cost. Microencapsulation has been one of the most efficient techniques which has been widely used in self-healing systems in different fields such as surface coatings, corrosion protection, adhesive in construction, automobiles, and medical supplies. Polyurethane (PU) microcapsules containing hexamethylene diisocyanate (HDI) as a core material embedded in polymeric composites could achieve self-healing properties. Linseed oil, epoxy resins, amine, and inorganic particles 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. An effort to apply polymers with temperature dependent properties for healing of scratches on automotive coatings has been reported. Nissan Motor Co. introduced self-healing polymer materials, such as hydrophobic paints that could repair scratches, to the market. We report 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; (b) interfacial polymerization<sup>30</sup> 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 47–100%, with various levels of core healant loading.

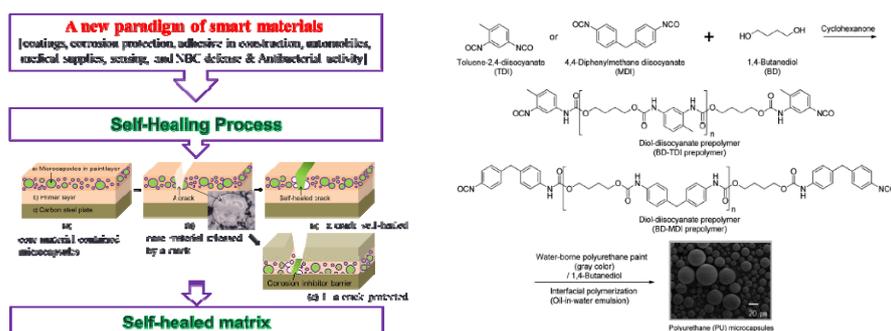


Figure. 1: The self-protection process: (a) paint coating having microcapsules with self-healing protecting paint on carbon steel plate, (b) paint released by damage to the paint coating layer, and (c) a crack covered by a paint protection barrier. Scheme 1: Synthesis of PU microcapsules using a prepolymer (BD–TDI or BD–MDI) and a chain extender (BD)

## 2 EXPERIMENT

**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 ( $1.0 \text{ mL min}^{-1}$ ) at  $40^\circ\text{C}$  versus polystyrene standards using a Waters high-pressure liquid chromatography system equipped with a UV Waters 2690 using three Columns (PL, Mixed-Bx2 and  $500^\circ\text{A} \times 1$  pore size) and a Waters 2414 differential refractometer. The hydroxyl value (OH) was determined using the ASTM D1957 Method (Metrohm, 888 Titrand). 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:  $\text{NCO, \%} = \frac{1}{4} [(B - V) \times N \times 0.0420] / W \times 100$ , 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 0.2–1500  $\mu\text{m}$ . 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  $800^\circ\text{C}$  at a rate of  $20^\circ\text{C min}^{-1}$  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.

**Synthesis of prepolymer (BD–TDI or BD–MDI);** Diol–diisocyanate prepolymer was prepared as a constituent for the PU shell of the microcapsules. The mixture of toluene 2,4-diisocyanate or 4,4-diphenylmethane diisocyanate and cyclohexanone (25 mL) was agitated using a magnetic stirrer at

80°C. 1,4-Butanediol 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.

*The Synthesis of microcapsules containing protection coating material;* the BD-TDI or BD-MDI was dissolved into chlorobenzene at 30 °C, the solution was slowly poured into a gum arabic solution of a deionized water containing 10 wt% gum arabic surfactant. Water-borne PU paint as core material 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 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%.

### 3 RESULT AND DISCUSSION

*The microcapsule size distribution;* The chemical structures of the resultant microcapsules and prepolymers were characterized by Fourier Transform Infrared Spectroscopy (FT-IR) (Fig. 2). There were bands of the prepolymer located at around 3315, 2277, and 1705  $\text{cm}^{-1}$ ; these were attributed to a secondary amine group of urethane, an isocyanate ( $\text{N}=\text{C}=\text{O}$ ), and an amide carbonyl group, respectively (Fig. 2b). Reduction of the intensity of the vibration band at around 2277- $\text{cm}^{-1}$ , 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  $\text{cm}^{-1}$  for the secondary amine and amide carbonyl; the single peak of the isocyanate group at 2277- $\text{cm}^{-1}$  disappeared, thus, proving that a chain extender (1,4-butanediol) was used to form a urethane linkage in the microcapsule shell-wall (Fig. 2c). 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 (Fig. 2d and e). There was a carbonyl absorption band of the amide group at 1735  $\text{cm}^{-1}$  and C-H stretching/bending vibrations of a long alkyl chain's methylene groups at 2950 and 1470  $\text{cm}^{-1}$  in the PU urethane paint, thus, demonstrating that the core material had been encapsulated and released. 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. 3). 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 a 62–76  $\mu\text{m}$  average diameter and a 17–4  $\mu\text{m}$  wall thickness.

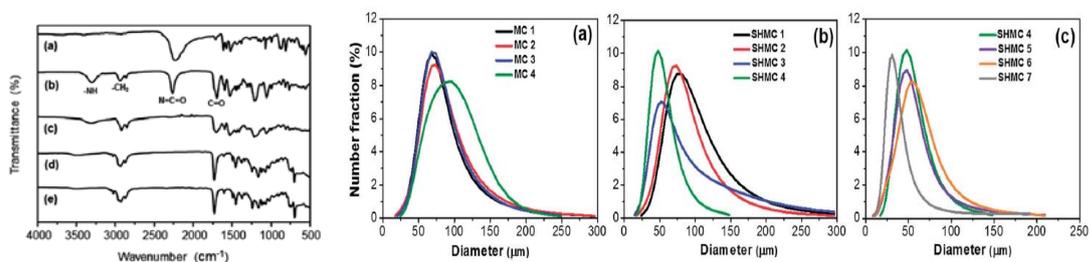


Figure. 2: FTIR Spectra of (a) toluene-1,4-diisocyanate (TDI), (b) BD-TDI prepolymer, (c) PU microcapsule wall, (d) capsule core compound released from the ruptured microcapsule (SHMC 4), and (e) pure water-borne PU paint.

Figure. 3: 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.

**Morphology of microcapsules;** As seen in Fig. 4, 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 in the range of added core material amounts (8–40 wt%) and at all agitation rates in the range 2000–8000 rpm. It was possible to control the shell thickness by adjusting the amount 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.

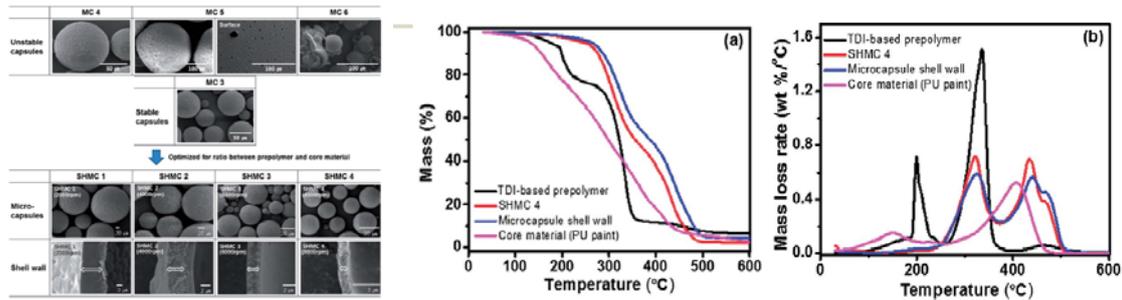


Figure. 4: Surface and shell morphology of PU microcapsules obtained according to initially added core amount and at various agitation rates

**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 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, in comparison 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.

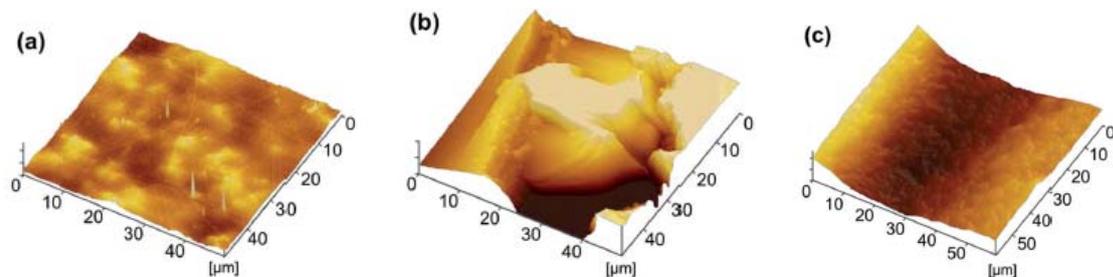


Figure. 5 AFM images of (a) unscratched paint layer containing capsules on a carbon steel plate (P-4-35), (b) partially recovered paint layer on a plate (P-4-10), and (c) fully self-healed paint layer on a panel (P-4-35).

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. Fig. 5b and c show the partially recovered paint layer, which has a rough surface that has an efficiency of 47%.

*Paint protection study;* A scanning electron microscopy (SEM) image of the repaired scratch area (SHMC 4) reveals the morphology of the selfhealing paint coating (Fig. 5). 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. There was hardly any uncovered trace in the PU paint coated cross-sectioned sample, 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<sup>TM</sup>.

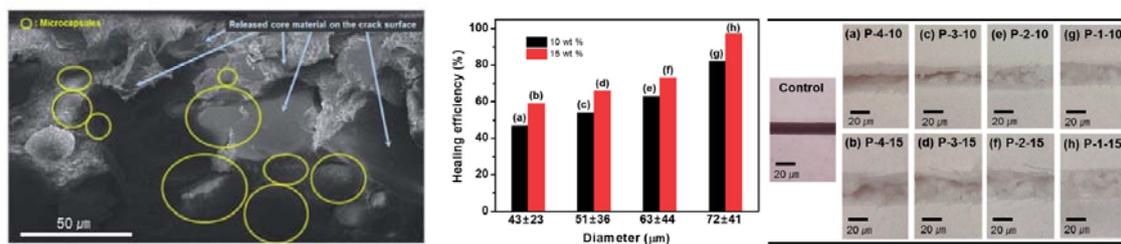


Figure. 6: A cross-section SEM image of a paint self-coated layer using 35 wt% microcapsule concentration.

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 showed 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 (Fig. 6a–h). Healing efficiency increased as the diameter of the capsules was enlarged, therefore, we assumed that larger capsules would contain more core material.

#### 4 CONCLUSION

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 FTIR. Spherical microcapsules, with diameter in the range 39–72 mm and shell wall thickness in the range 4–6 mm, 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 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 selfhealing protection coating for industrial paint applications

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