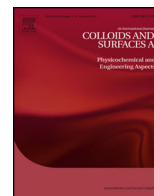




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## Research Paper

# Polyurethane matrix incorporating PDMS-based self-healing microcapsules with enhanced mechanical and thermal stability



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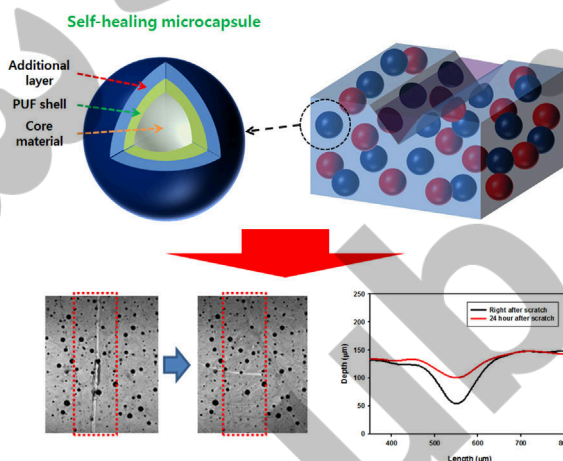
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## HIGHLIGHTS

- Mechanically and thermally stable self-healing microcapsules were prepared.
- Resultant microcapsules could contain PDMS-based healing agents.
- Microcapsule-embedded self-healing PU matrices were prepared.
- Self-healing PU matrix could repair the scratch by releasing healing agents.

## GRAPHICAL ABSTRACT



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## ABSTRACT

For the purpose of developing self-healing skin layers of instrument panels in automobiles, mechanically and thermally stable microcapsules containing healing agents were prepared and incorporated into a polyurethane (PU) matrix. Two different poly(urea-formaldehyde) (PUF) microcapsules containing either a polydimethylsiloxane (PDMS)/Pt catalyst (Pt) blend or crosslinker were synthesized using *in situ* emulsion polymerization. However, the resulting microcapsules were mechanically and thermally weak. More than 40% of the microcapsules were broken during the washing/drying process, and capsule decomposition began at 200 °C. These properties of microcapsules were greatly enhanced by decreasing the capsule size and depositing an additional urea-formaldehyde (UF) layer onto pre-formed PUF microcapsules. The former was accomplished by tuning the stirring speed during the reaction and the latter by adding more urea components. Under optimized conditions, only approximately 10% of microcapsules were broken after the same washing/drying process, and the decomposition temperature was raised to 250 °C. The two different optimized microcapsules were successfully embedded in a PU matrix and could

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be broken upon matrix cracking, thereby releasing the healing agent to the target areas via capillary effects. Subsequently, it was confirmed that the cracked portions were repaired through chemical and/or physical interactions within the healing system.

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## 1. Introduction

The self-healing materials, inspired by biological systems, exhibit the ability to repair minor damage without the need for detection or any type of manual intervention. Self-healing materials incorporated in various polymeric products are increasingly used in structural applications in the space, automobile, defense and construction industries. These smart materials can significantly increase the lifetime and safety of polymer-based products and components [1–4]. While several extrinsic (capsule-based, vascular) and intrinsic self-healing strategies have been investigated, self-healing based on microencapsulated healing agents is more likely to be successful in the near future because microcapsules can easily be incorporated into the polymer matrix using existing blending techniques without changing the original chemical structure of the polymers. In addition, this self-healing can heal large-volume cracks [5–8]. Typically, mechanical damage in a material ruptures the microcapsules and releases healing agents into the damaged area. Then, the crack is repaired by polymerization via the reaction between different agents.

Recently, several efforts have been made to apply self-healing materials to automobile interiors and exterior components such as plastic panels or paint because emotional engineering has become important for customer satisfaction [9–11]. For example, if an automobile user encounters a scratch in the skin layer of the instrument panel (which consists of an outermost skin layer, interlayer and core layer), the visual and tactile emotion of the user may worsen. Among various polymeric materials in automobiles, PU resin consisting of a urethane bond ( $-\text{NH}-\text{COO}-$ ) has mainly been used for the skin layer because it can decrease the scratch probability due to its intrinsic elasticity [12]. However, external damage such as scratches on the PU-based skin layer is still unavoidable, which may degrade the user's emotional state. To protect the PU layer from scratches, two approaches have been explored. The first is enhancing the scratch resistance of the skin layer by using nano-sized ceramic particles to improve the hardness of the clear coating and the second is recovering or healing the scratches by enhancing the elastic property of PU resins [13–16]. However, the first approach is not effective once a scratch has occurred, and the second approach may also be limited depending on the extent of the scratch. Therefore, the incorporation of microcapsule-based self-healing materials into PU resin may be a better way to minimize the presence of scratches and subsequently prevent customer dissatisfaction.

PU-based skin layers are produced by either reaction injection molding (RIM) or powder slush molding (PSM) processes, which typically involve high shear stress and/or high temperature [17,18]. Furthermore, in order for self-healing microcapsules to incorporate into PU resin, a severe washing and subsequent drying process should be conducted because moisture (water) can react with PU resin and generate urethane foam with a rough surface. Therefore, self-healing microcapsules must have adequate mechanical and thermal properties to withstand the molding and washing/drying processes, which can be achieved by increasing the shell thickness or introducing inorganic materials into the shell [19–23].

In this study, a PU-based matrix with a self-healing capability was prepared by incorporating two different microcapsules

into the matrix for future application in the skin layers of instrument panels in automobiles. One microcapsule was filled with poly (dimethyl siloxane) (PDMS) and platinum catalyst (Pt) blend, and the other microcapsule was filled with a crosslinker. To improve the mechanical and thermal properties, additional urea-formaldehyde (UF) layers were deposited on the newly-prepared poly(urea-formaldehyde) (PUF)-based microcapsules, and the microcapsule size was tuned. After analysis of various microcapsule properties, the self-healing capacity of PU matrix was evaluated.

## 2. Experimental

### 2.1. Materials

Polydimethylsiloxane (HSF-40), a Pt catalyst (CATA 12070) and crosslinker (TSF 484) were purchased from Hansol E&C (Korea). Dicyclopentadiene (DCPD) was purchased from Sigma-Aldrich (Milwaukee, WI, USA). Urea, ammonium chloride and formaldehyde were purchased from Samchun chemical (Korea). Sodium lauryl sulfate (SLS) was purchased from Duksan Pharmaceutical Co. (Korea). Resorcinol was obtained from Junsei chemical (Japan). The polyol component and isocyanate component (diphenylmethane diisocyanate, MDI) solutions were obtained from Kangnam Chemical Co. (Korea).

### 2.2. Preparation of self-healing microcapsules

In this study, two different microcapsules containing either a blend of PDMS/Pt or a single crosslinker were fabricated by *in-situ* polymerization in an oil-in-water emulsion using a method similar to that described in previous studies [24,25]. At room temperature, 1.25 g of SLS was dissolved in 125 ml of deionized water in a beaker (1 wt.%). After that, 2.5 g of urea, 0.25 g of ammonium chloride and 0.25 g of resorcinol were dissolved in the solution. After 5 min of agitation with a digital mixer (Eurostar, IKA Labortechnik, München, Germany), a slow stream of 20 ml of the blended solution of PDMS and Pt catalyst (PDMS:Pt = 9:1, weight ratio) or crosslinker solution was added to form an emulsion. The pH was adjusted to 3.5 by drop-wise addition of formic acid. At this point, the stirring speed of the digital mixer ranged from 500 to 2000 rpm for 5 min to adjust the microcapsule size, and one or two drops of 1-octanol were added to eliminate surface bubbles. Finally, 7 g of 37 wt.% aqueous solution of formaldehyde was added. The emulsion was heated at a rate of 1 °C/min to a target temperature of 60 °C. After a one-hour reaction between formaldehyde and urea with continuous agitation, PUF microcapsules containing the PDMS/Pt catalyst or crosslinker were produced.

### 2.3. Mechanically and thermally enforced microcapsules

To improve the microcapsule mechanical and thermal stability, an additional urea component was sequentially added to the pre-formed PUF microcapsules. The amount of sequentially added urea component varied from 0 to 20 wt% urea added in the original PUF microcapsule. Three hours after the urea addition, the microcapsule suspension was separated and washed with deionized water under vacuum with a coarse-fritted filter and was then allowed to air dry

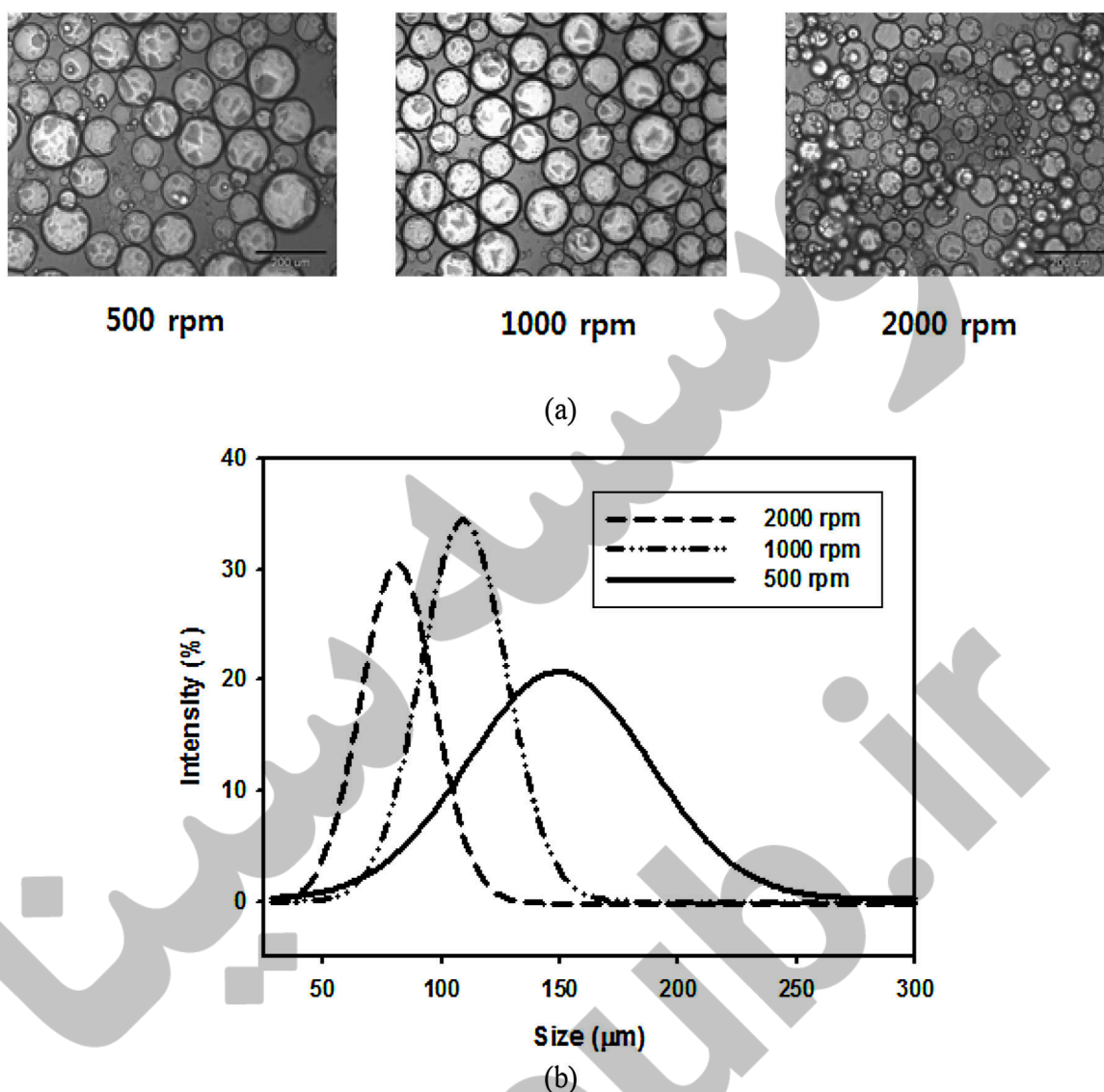


Fig. 1. Preparation of PUF-based microcapsules. (a) Optical images and (b) size distribution of microcapsules prepared at different stirring speeds. (scale bar: 200 μm).

for 24 h. To visualize the microcapsule shells with scanning electron microscopy (SEM), the core material within the microcapsules was changed to DCPD, which is more volatile than either the PDMS/Pt blend or crosslinker. The microcapsules that contained a DCPD core were poured onto a carbon tape, chopped with a razor blade, and heated on a hot plate at 180 °C overnight to evaporate the core materials [26].

#### 2.4. Microcapsule-embedded polyurethane (PU) matrix

The prepared self-healing microcapsules containing PDMS/Pt blend or crosslinker were embedded into a PU matrix. The PU matrix was commonly synthesized by mixing polyol and isocyanate. First, the microcapsule mixture (PDMS/Pt blend and crosslinker capsules) was poured into the polyol component solution and then thoroughly mixed. In this step, the weight ratio between two microcapsules was 9:1 (PDMS/Pt blend: crosslinker) with 10 wt.% microcapsules in the PU matrix. After the microcapsule mixture was fully mixed into polyol component solution, the isocyanate component solution was added and placed in a hot oven for 24 h to initiate the polyurethane reaction.

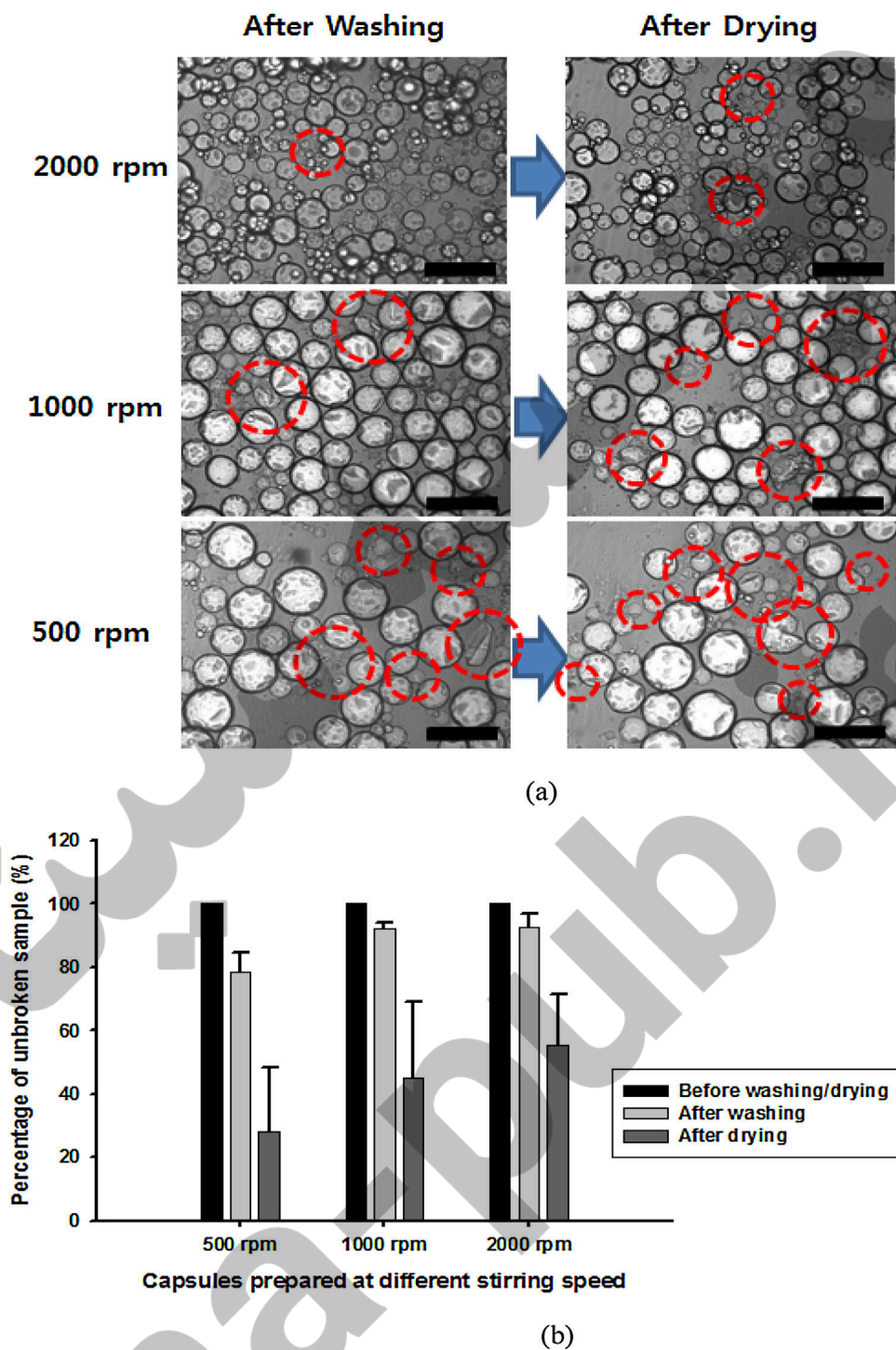
#### 2.5. Evaluation of self-healing performance

The self-healing performance of the microcapsule-embedded PU matrix was investigated after a scratch was applied to the PU matrix using a cross hatch cutter. The cuts were made by a knife-shaped tip with a 15 N force [27]. After the cuts were made, core materials of microcapsules flew out and filled the crack. Changes in morphology of PU matrix after scratch were confirmed by optical microscope and depth profiles were measured by a digital microscope.

#### 2.6. Characterization

The microcapsule size was measured with a laser light scattering analyzer (X-100, Microtac, Inc., Montgomeryville, PA, USA), and the thermal decomposition behavior of the microcapsules was determined using thermogravimetric analysis (TGA, Q50, TA Instrument, United States). The surface morphology and shell wall thickness of the microcapsules were analyzed using SEM (JSM-7001F, JEOL, Japan). The amount of formaldehyde was analyzed using gas chromatography-mass spectrometry (GC-MS,



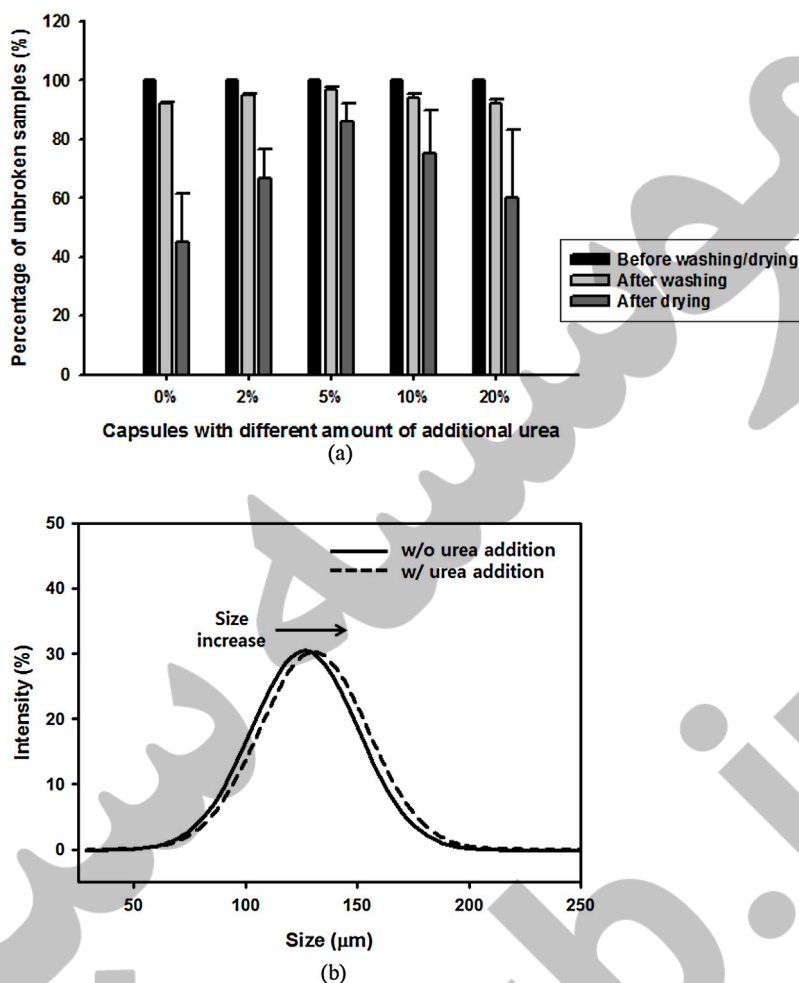


**Fig. 2.** Rupture of microcapsules after the washing and drying process. (a) Optical images of microcapsules prepared at different stirring speeds after the washing and drying process. (b) Percentage of unbroken microcapsules after the washing and drying process. (scale bar: 200  $\mu\text{m}$ ).

Agilent 7890B-GC/5977A-MS/GC sampler 80, Agilent Technologies, USA). Here, formaldehyde is analyzed by derivatization with *o*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) as described in the literature [28]. A cross hatch cutter (430P, Erichsen, Germany) was used to perform the scratch and self-healing tests. After the scratches were applied, optical and digital microscopes (VHX-5000, Keyence, Japan) were used to investigate the changes in surface morphology and depth profiles of the PU matrix, respectively.

### 3. Results and discussions

PUF microcapsules encapsulating PDMS/Pt or crosslinker agent were prepared by *in-situ* emulsion polymerization. The size of the microcapsules could be tuned by changing the stirring speed, as shown in Fig. 1a (the microcapsule size decreased as the stirring speed increased). The size analysis revealed that microcapsules with diameters of 165, 120, and 80  $\mu\text{m}$  were produced with stirring speed of 500, 1000, and 2000 rpm, respectively (Fig. 1b). Fig. 1b also shows that the microcapsule size distribution was narrower with



**Fig. 3.** PUF microcapsules deposited with additional UF layers. (a) Percentage of unbroken microcapsules after the washing and drying process. (b) Size distribution of pre-formed and PUF UF-deposited PUF microcapsules. Microcapsules were prepared at 1000 rpm.

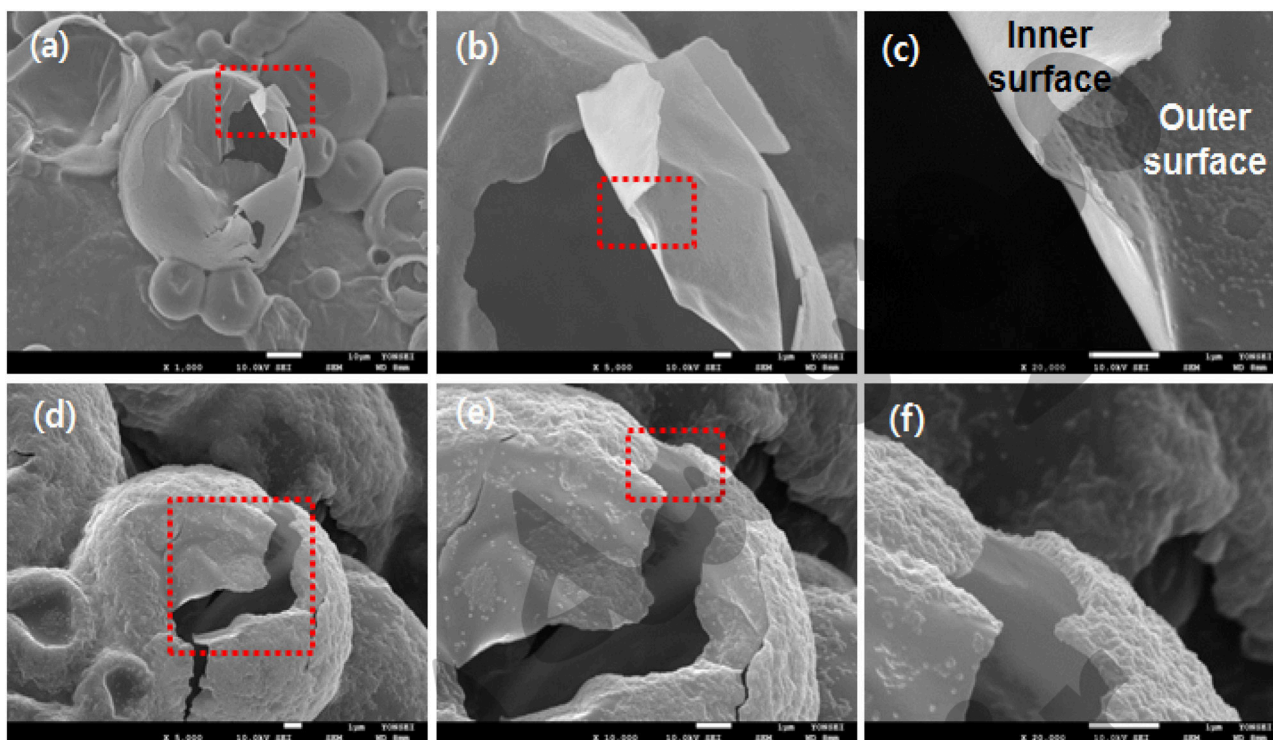
an increase in stirring speed. This is possibly because the higher stirring speed can facilitate the formation of a homogeneous emulsion, leading to a narrower size distribution. For practical applications, the microcapsules should undergo a washing and drying process before incorporation into various matrixes such as PU. However, the resultant microcapsules were mechanically weak and easily broken during these processes, as shown in Fig. 2a. The quantitative data (Fig. 2b) show that a higher percentage of unbroken capsules after the washing and drying steps was observed as the microcapsule size decreased, indicating that smaller microcapsules possess better mechanical stability. Higher stirring speed than 2000 rpm could produce smaller microcapsules with narrower size distribution, which had a positive influence on the capsule stability. However, as microcapsule size became smaller, efficiency of PDMS encapsulation within microcapsule decreased. Therefore, lower healing efficiency was observed for microcapsules prepared using higher stirring speed than 2000 rpm.

To further improve the mechanical stability of the microcapsules, additional urea components were added to PUF microcapsules. In theory, a 1:2 molar ratio of urea to formaldehyde is utilized to form PUF microcapsules [29]. However, in this experiment, the optimized initial molar ratio was approximately 1:2.1, which suggests that residual formaldehyde remains after the formation of PUF shells. Therefore, the subsequent addition of a urea component can react with excess formaldehyde in the continuous phase and generate an additional UF layer on the preformed PUF shells, which would enhance the mechanical properties of the

microcapsules. Various amounts of urea (2, 5, 10, and 20 wt% of the initially added urea) were added to the reacting batch solution, and the mechanical stability of resultant microcapsules were evaluated by counting the broken capsules during the washing and drying processes. As the amount of urea increased (up to 5 wt%), the mechanical stability of the microcapsules improved, as shown in Fig. 3a. However, excessive urea (10 and 20 wt%) significantly decreased the microcapsule production yield due to urea precipitation. Under optimized conditions (2000 rpm and 5 wt% additional urea), approximately 10% of the microcapsules were broken after the washing and drying process. Therefore, we concluded that 5 wt% additional urea was an optimal amount for this study, which might result from the fact that the molar ratio of urea to formaldehyde was close to the 1:2 theoretical value with added urea. The deposition of an additional UF layer caused a slight increase in the microcapsule size (Fig. 3b).

The morphology and shell thickness were investigated with SEM, as shown in Fig. 4. The additional UF layer-deposited PUF microcapsules had rougher surfaces and thicker shells than the original PUF microcapsules. From the SEM images in Fig. 4, the shell thickness of microcapsules with 110 μm diameter was about 100 nm, which is very thin compared with overall size of microcapsules. Therefore, the increase of shell thickness (from 100 nm to 210 nm) by urea addition did not have a significant effect on the size change of microcapsules as shown in Fig. 3b.

The thermal properties of PDMS-containing microcapsules were characterized by TGA. The TGA curves indicate that both microcap-



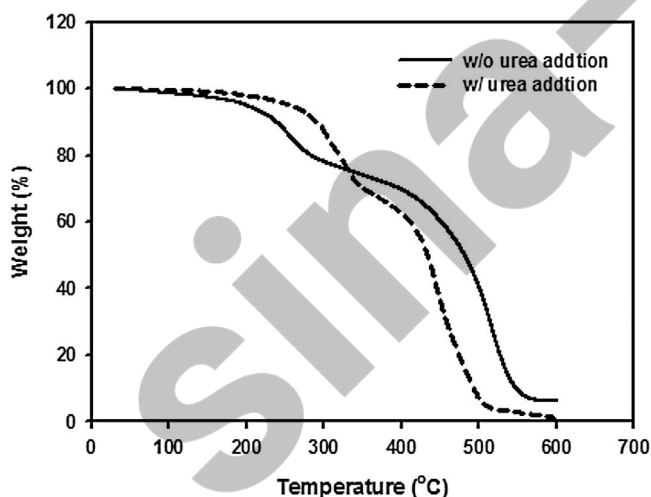
**Fig. 4.** SEM images of microcapsules. SEM images of PUF microcapsules (a–c) and PUF microcapsules deposited with additional UF layers (d–f) at different magnifications.

sules had two weight loss stages corresponding to the capsule shells at 200–300 °C and core PDMS at 450–550 °C (Fig. 5). Compared with the original PUF that started to degrade at 200 °C, the additional UF layer-deposited PUF shells showed an elevated decomposition temperature (260 °C). This result demonstrates that the thermal stability of the microcapsules greatly improved by the deposition of an additional UF layer. For automobile applications, a thermal stability over 250 °C would allow the PSM process, which is conducted at 240 °C.

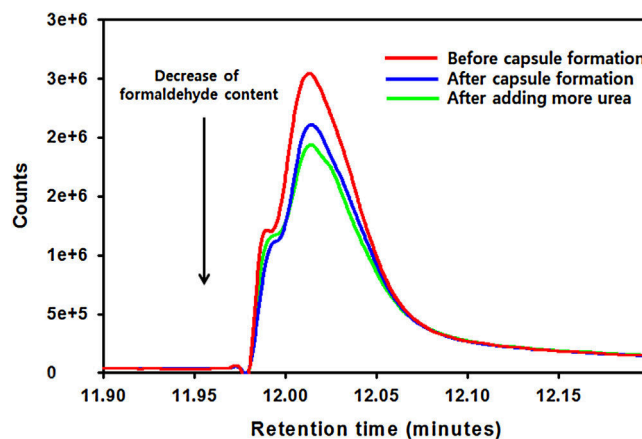
To verify our hypothesis that sequentially added urea components react with residual formaldehyde, the amount of formaldehyde before and after the addition of urea was analyzed using GC–MS. This analysis was performed using PFBHA reagent solution to derivatize the formaldehyde in the samples. As shown

in Fig. 6, the amount of formaldehyde decreased after the formation of PUF microcapsules and further decreased with the addition of urea components. These results confirm that the reaction between urea and formaldehyde generated microcapsules, and the residual formaldehyde further reacted with additional urea components, forming a sequentially deposited UF layer on the original PUF microcapsules.

For self-healing coating or matrix applications, a multi-capsule system was utilized in this study. The most mechanically stable microcapsules (2000 rpm and 5 wt% urea addition) that encapsulated both the PDMS/Pt blend and cross-linker agent were embedded into PU matrix. Prior to using the double capsule system, we also tried a single microcapsule system, where only PDMS/Pt blends were encapsulated within the microcapsules, and the crosslinker was dispersed in PU matrix without encapsulation. However, the dispersed crosslinker seriously slowed down the formation of PU matrix by interrupting the reaction between polyol

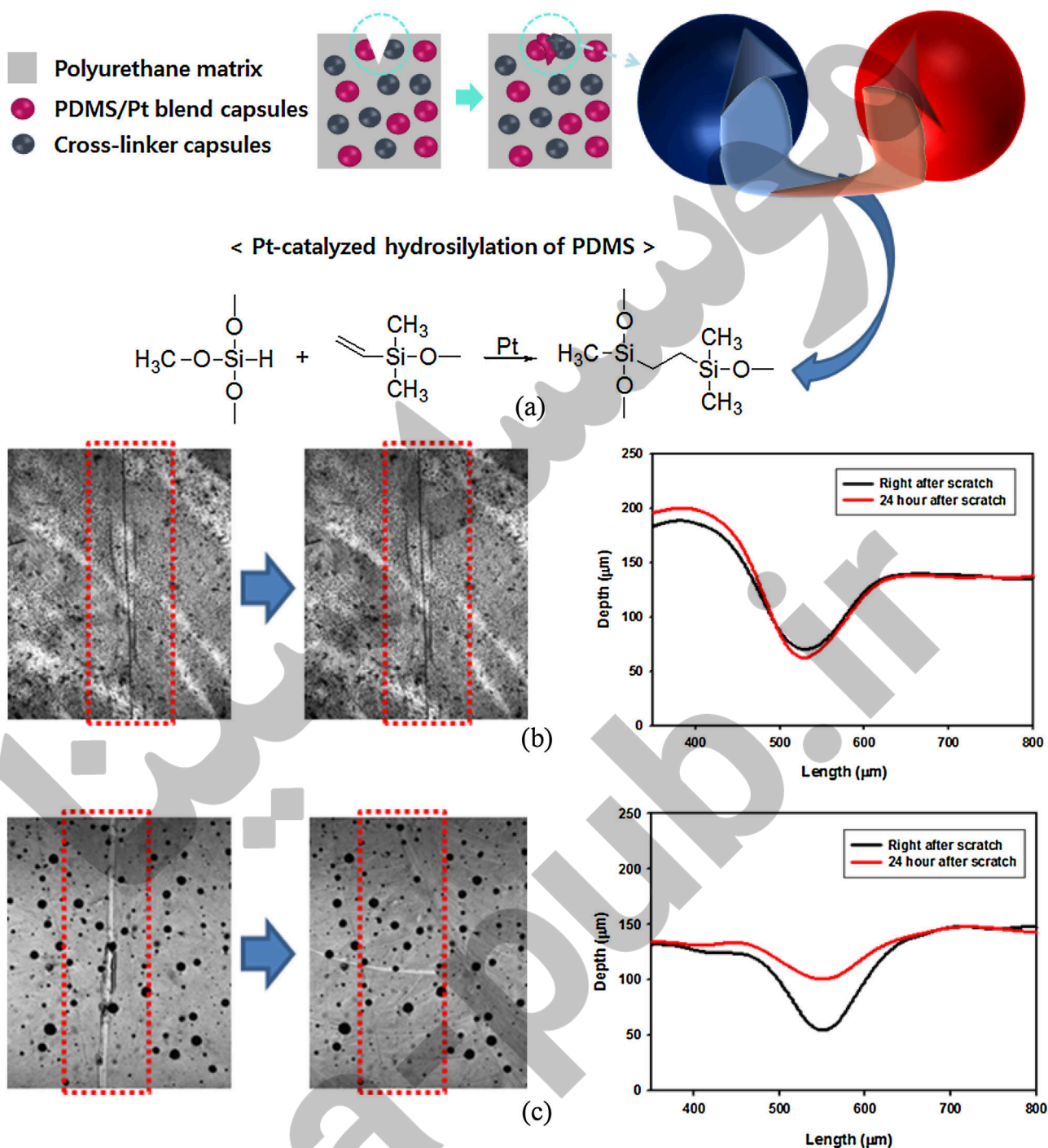


**Fig. 5.** TGA weight loss curve of the PUF microcapsules and UF-deposited PUF microcapsules.



**Fig. 6.** GC–MS chromatograms for quantification of formaldehyde in the reactor.





**Fig. 7.** Self-healing performance of the PU matrix after embedding two different microcapsules. (a) Schematic illustration of the self-healing mechanism. Optical images and surface profiles of PU matrix before and after applying scratches to the PU matrix (b) without microcapsules and (c) with embedded microcapsules.

and isocyanate. A schematic of microcapsule-embedded PU matrix and its self-healing process is described in Fig. 7a. An external scratch induces the rupture of the microcapsules and subsequent release of core materials. In this system, the healing reaction is a Pt-catalyzed hydrosilylation of vinyl-terminated PDMS resin, which is achieved by the combination of core materials (PDMS, Pt, and crosslinker). The self-healing performance was evaluated by post-mortem observation using optical microscopy. A 9:1 (PDMS/Pt: crosslinker) weight ratio between the two different capsules was fixed, and 10 wt% of the total microcapsules were embedded in the

PU matrix. The optical images and surface profiles show that the scratches of the PU matrix without microcapsules did not show healing capability (Fig. 7b), while scratches in the PU matrix with microcapsules were filled with core materials (Fig. 7c) and healed. Under this condition, the healing efficiency (the number of healed scratches/the number of total scratches) was approximately 82%. These results confirm that the deposition of additional UF layers onto PUF microcapsules improve their mechanical and thermal stability and can initiate self-healing after the rupture and release of encapsulated materials by external scratches.

#### 4. Conclusion

To improve the mechanical and thermal stability of PUF self-healing microcapsules, the microcapsule size was tuned and an additional UF layer was sequentially deposited onto the preformed PUF capsules by adding an extra urea component. The smaller-sized, microcapsules had better mechanical stability, while the addition of the urea component enhanced both the mechanical and thermal stability of microcapsules. Two different microcapsules, one filled with PDMS/Pt and the other filled with a crosslinker, were successfully embedded in PU matrix without a significant change in physical properties of matrix. The optimized self-healing microcapsules were strong enough to withstand the washing and drying process but also weak enough to be ruptured by an external scratch and release healing materials when embedded in the PU matrix. Therefore, the resultant microcapsule-embedded PU matrix can be used for the scratch-resistant skin layer of instrument panels, which would satisfy automobile consumer expectations in terms of emotional engineering.

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#### References

- [1] B.J. S.L.B. Blaiszik, S.C. Kramer, J.S. Olugebefola, N.R. Moore, S.R. Sottos, S.R. White, Self-healing polymers and composites, *Annu. Rev. Mater. Res.* 40 (2010) 179–211.
- [2] N. Sottos, S. White, I. Bond, Introduction: self-healing polymers and composites, *J. R. Soc. Interface* 4 (2007) 347–348.
- [3] Y.C. Yuan, M.Z. Rong, M.Q. Zhang, G.C. Yang, J.Q. Zhao, Self-healing of fatigue crack in epoxy materials with epoxy/mercaptan system, *Express Polym. Lett.* 5 (2011) 47–59.
- [4] S.H. Cho, S.R. White, P.V. Braun, Self-healing polymer coatings, *Adv. Mater.* 21 (2009) 645–.
- [5] H.L. Huang, G. Ye, Z.H. Shui, Feasibility of self-healing in cementitious materials—by using capsules or a vascular system? *Constr. Build. Mater.* 63 (2014) 108–118.
- [6] H.P. Wang, M.Z. Rong, M.Q. Zhang, Self-healing polymers and polymer-based composites containing microcapsules, *Prog. Chem.* 22 (2010) 2397–2407.
- [7] D.Y. Zhu, M.Z. Rong, M.Q. Zhang, Self-healing polymeric materials based on microencapsulated healing agents: from design to preparation, *Prog. Polym. Sci.* 49–50 (2015) 175–220.
- [8] L. Gao, J.L. He, J. Hu, C. Wang, Photoresponsive self-healing polymer composite with photoabsorbing hybrid microcapsules, *ACS Appl. Mater. Interface* 7 (2015) 25546–25552.
- [9] M.G. Helander, M.P. Tham, Hedonomics—affective human factors design, *Ergonomics* 46 (2003) 1269–1272.
- [10] M.D. Hager, P. Greil, C. Leyens, S. van der Zwaag, U.S. Schubert, Self-healing materials, *Adv. Mater.* 22 (2010) 5424–5430.
- [11] J. Seonho, J. Hotak, J. Kiyeon, J. Soonjoon, A study on the scratch self-healing coating for automobile interior parts, *Korean Soc. Automot. Eng.* (2013) 1165–1166.
- [12] R.B. Seymour, G.B. Kauffman, Polyurethanes—a class of modern versatile materials, *J. Chem. Educ.* 69 (1992) 909–910.
- [13] C. Seubert, K. Nietering, M. Nichols, R. Wykoff, S. Bollin, An overview of the scratch resistance of automotive coatings: exterior clearcoats and polycarbonate hardcoats, *Coatings* 2 (2012) 221–234.
- [14] L.P. Sung, J. Comer, A.M. Forster, H. Hu, B. Floryancic, L. Brickweg, R.H. Fernando, Scratch behavior of nano-alumina/polyurethane coatings, *J. Coat. Technol. Res.* 5 (2008) 419–430.
- [15] R.A. Ryntz, B.D. Abell, G.M. Pollano, L.H. Nguyen, W.C. Shen, Scratch resistance behavior of model coating systems, *J. Coating. Technol.* 72 (2000) 47–53.
- [16] C. Xiang, H.J. Sue, J. Chu, B. Coleman, Scratch behavior and material property relationship in polymers, *J. Polym. Sci. Pol. Phys.* 39 (2001) 47–59.
- [17] J.M. Castro, C.W. Macosko, Studies of mold filling and curing in the reaction injection-molding process, *AIChE J.* 28 (1982) 250–260.
- [18] J.A. Grande, Slush-molded TPUs challenge PVC for auto instrument-panel skins, *Mod. Plast.* 75 (1998) 28–29.
- [19] H.H. Jin, C.L. Mangun, A.S. Griffin, J.S. Moore, N.R. Sottos, S.R. White, Thermally stable autonomic healing in epoxy using a dual-microcapsule system, *Adv. Mater.* 26 (2014) 282–287.
- [20] M.M. Caruso, B.J. Blaiszik, H.H. Jin, S.R. Schelkopf, D.S. Stradley, N.R. Sottos, S.R. White, J.S. Moore, Robust, double-walled microcapsules for self-healing polymeric materials, *ACS Appl. Mater. Inter.* 2 (2010) 1195–1199.
- [21] G. Wu, J.L. An, D.W. Sun, X.Z. Tang, Y. Xiang, J.L. Yang, Robust microcapsules with polyurea/silica hybrid shell for one-part self-healing anticorrosion coatings, *J. Mater. Chem. A* 2 (2014) 11614–11620.
- [22] C.J. Fan, X.D. Zhou, Preparation and barrier properties of the microcapsules added nanoclays in the wall, *Polym. Adv. Technol.* 20 (2009) 934–939.
- [23] Q. Li, A.K. Mishra, N.H. Kim, T. Kuila, K.T. Lau, J.H. Lee, Effects of processing conditions of poly(methylmethacrylate) encapsulated liquid curing agent on the properties of self-healing composites, *Compos. Part B: Eng.* 49 (2013) 6–15.
- [24] M.W. Keller, S.R. White, N.R. Sottos, A self-healing poly(dimethyl siloxane) elastomer, *Adv. Funct. Mater.* 17 (2007) 2399–2404.
- [25] E.N. Brown, M.R. Kessler, N.R. Sottos, S.R. White, In situ poly(urea-formaldehyde) microencapsulation of dicyclopentadiene, *J. Microencapsul.* 20 (2003) 719–730.
- [26] H.H. Noh, J.K. Lee, Microencapsulation of self-healing agents containing a fluorescent dye, *Express Polym. Lett.* 7 (2013) 88–94.
- [27] P.D. Tatiya, R.K. Hedao, P.P. Mahulikar, V.V. Gite, Novel polyurea microcapsules using dendritic functional monomer: synthesis, characterization, and its use in self-healing and anticorrosive polyurethane coatings, *Ind. Eng. Chem. Res.* 52 (2013) 1562–1570.
- [28] B. Cancho, F. Ventura, M.T. Galceran, Determination of aldehydes in drinking water using pentafluorobenzylhydroxylamine derivatization and solid-phase microextraction, *J. Chromatogr. A* 943 (2002) 1–13.
- [29] R.G. Wang, H.L. Hu, X.D. He, W.B. Liu, H.Y. Li, Q. Guo, L.Y. Yuan, Synthesis and characterization of chitosan/urea-formaldehyde shell microcapsules containing dicyclopentadiene, *J. Appl. Polym. Sci.* 121 (2011) 2202–2212.