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EFFECT OF MICROCAPSULE STABILITY ON SELF-HEALING ABILITY OF POLYURETHANE DISPERSIONS

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Abstract. Self-healing coatings have attracted great research interest during the last years. One methodology for development of self-healing materials is based on the dispersion of adequately designed microcapsules, containing an active self-healing agent into a polyurethane matrix. The development of polyurea microcapsules containing isocyanate compounds for use as self-healing agents in waterborne polyurethane coatings is reported, in the present work. The stability of the isocyanates in the core of the capsules was studied, as well as the most suitable storage conditions of the capsules (solid or aqueous dispersion form) based on the ASTM D2572 standard. To test their self-healing ability, content of 3 and 4.5 wt.% $AcMCs_{solid}$ / PUD_{solid} capsules in the polyurethane matrices was studied, while different kinds of self-healing stimuli of the coatings (water addition or temperature application) were also evaluated.

Keywords: Polyurea Microcapsules, Stability of isocyanate, Aqueous dispersion, Self-healing tests.

1 INTRODUCTION

Self-healing phenomenon on synthetic materials enables the restoration of their initial properties, recovering from damage. In this field, a number of materials have been developed that exhibit self-healing abilities. [1-4] The two main categories for materials with self-healing abilities are intrinsic [5] and extrinsic. [6] Materials with intrinsic self-healing ability are those in which functional groups are added from the beginning to the matrix of the material. Functional groups can either interact with neighbouring groups via H-bonds [7-10] and/or react through chemical reactions, restoring damage of the material [11]. The materials with extrinsic self-healing abilities, it is based on micro-containers (microcapsules, fibers, vascular networks), which are integrated into the matrix of the material from the beginning. The micro-containers include a healing agent, which can de released when a scratch occurs. Then the gap created by the damage is filled and the material heals. [12-19]

The most studied choice for materials with extrinsic self-healing ability, are those composed of microcapsules. Working in this direction, in the present study, it was chosen to synthesize polyurea microcapsules that have isocyanate derivatives trapped in their core, while for the self-healing tests, coatings of water-based polyurethane dispersions were chosen such as coatings are gaining increasing attention in many applications due to their versatility and environmentally friendly character [5]. The mechanism of self-healing of the materials is based on the microcapsule technology with entrapped the isocyanate compounds. Isocyanates react quickly with various

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groups and mainly with water, forming polyurethane structures, achieving thus the self-healing of the surfaces.

In a previous study, the synthesis and characterization of polyurea microcapsules containing isophorone isocyanate (IPDI) and modified Novolac resin were presented, as well as some encouraging initial self-healing tests. The Novolac modification of choice was acetylation. Thus, the hydroxyl groups of the resin become ester groups, decreasing the chances of reacting with the reactive function groups of the isocyanates (NCO). [20] In the present study, we focus on the same type of polyurea microcapsules, giving more emphasis on the self-healing ability, as well as on capsule stability issues with respect to coating matrix self-healing stimulus (water addition, temperature).

2 MATERIALS AND METHOD

2.1 Materials

Poly(vinyl alcohol) (PVOH, Mw = 130,000 with 88 % hydrolysis degree), Methylene diphenyl diisocyanate (MDI), Isophorone Diisocyanate (IPDI), Diethylenetriamine (DETA) and Cyclohexanone were obtained from Merck. All chemicals in this study were used as received without additional purification.

The procedure reference for Novolac synthesis and modification (benzylation or acetylation processes) have been presented in previous work. [20]

Waterborne polyurethane dispersions were kindly provided by Megara Resins S.A. (Greece). Three dispersions of polyurethane polycarbonate (PUDs), PUD-P47 (1000), PUD-P40 (2000) and PUD-P48 (2000) were used, where the molecular weights of the polyols used as chain extenders were 1000 and 2000.

2.2 Synthesis of Acetyl Microcapsules (Ac MCs)

IPDI-loaded polyurea microcapsules were prepared using a previously described procedure, containing a PVOH-polyurea composite shell and a core containing IPDI monomer [20].
More specifically, a 2.5 wt.% PVOH aqueous solution was used as emulsifier. The emulsifier phase was left to homogenize for 10 minutes with a stirring rate of 5,000 rpm. Next, the organic phase containing MDI, IPDI and the modified Novolac resin (9/45.5/45.5 wt.%) in Cyclohexanone (56 wt.%) was prepared under inert conditions. Finally, the organic phase was added dropwise to the emulsifier phase. DETA was then added as a shell chain extender to proceed with the emulsion polymerization. The reaction was completed at three hours at room temperature (RT). The capsules were obtained as solid material after filtration of the emulsion polymerization mixture, washed three time with water and dried at RT for two days.

2.3 Study of Microcapsules core

To confirm the stability of isocyanate compounds in the microcapsule core, the dispersions of microcapsules in water were studied during the time using the ASTM D2572 standard. [21-22]

0.2 g of solid AcMCs (from aqueous dispersion) were crushed in an agate mortar and sonicated in acetone for 1 h. The mixture was centrifuged at a speed of 7,000 rpm for 20 min. This process was repeated two times and, finally, the supernatant and the precipitate were collected. The obtained precipitate, considered to be shell, was dried at room temperature (RT), while the core was extracted with acetone. The supernatant was titrated according to the ASTM D2572 standard.

2.4 Preparation of self-healing coatings

The desirable amount of white solid microcapsules was dispersed in an aqueous solution to a final concentration of 10 wt.% under gentle magnetic stirring at room temperature (RT) for 10 min. The dispersion was added dropwise into the water-soluble polyurethane matrices (PUD) to prepare the self-healing coatings with polyurea microcapsules as additives. Two AcMCs solid contents (wt%) were tested about the solid polyurethane of the water-soluble polyurethane matrices (PUD) solution. A Teflon film was coated with the mixture and left to dry at RT for 5 days during the film-casting process. After drying, the films were removed from the Teflon substrate to study their self-healing abilities. Self-healing tests were performed by applying scratches to these films using a scalpel. An optical microscope was used to observe the evolution of the scratches during the time.

3 RESULTS AND DISCUSSION

3.1 Stability of the Microcapsule core

The healing ability of microcapsules containing isocyanate reagents is greatly affected the long term stability of the encapsulated active materials. Thus the organic medium as well as the capsules shell play a critical role on the final healing property. The used microcapsule shell consists of polyurea groups, which are formed through surface polymerization in the emulsion as shown in Fig. 1. [20] Acetyl polyurea microcapsules have been synthesized by the reaction of MDI and DETA to form the polyurea shell, while the healing agent, IPDI, is trapped inside, and the Acetyl modified Novolac resin participates as an organic substrate in the emulsion polymerization.

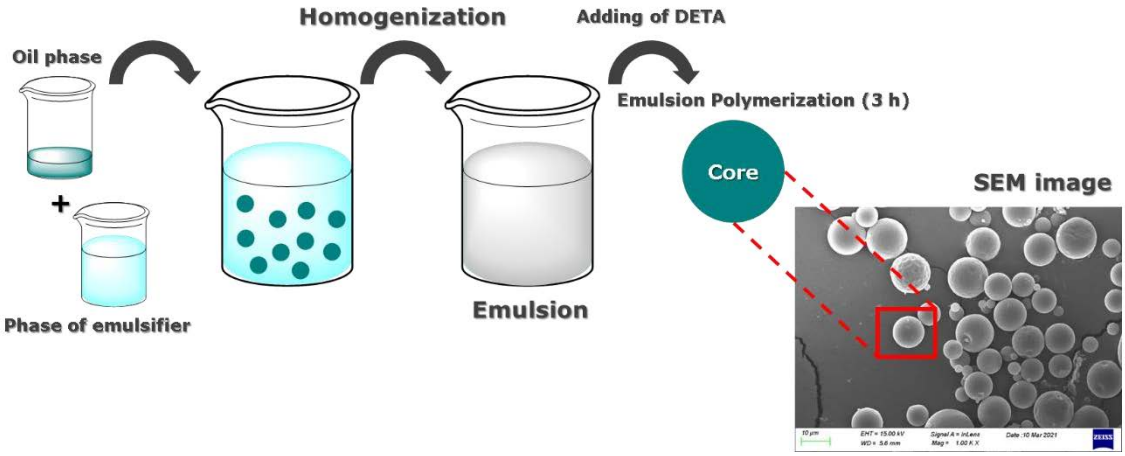

Figure 1: Schematic image of the formation process of microcapsules via interfacial polymerization in an oil-in-water emulsion.

The characterization of the final product was performed are given through FTIR-ATR spectroscopy. In Fig. 2 the spectrum of AcMCs is presented. The characteristic signal at 1630 cm^{-1}, 1545 cm^{-1} and 1450 cm^{-1} of the carbonyl group (C=O), the N-H group and the C-N bond were observed, indicating the formation of a polyurea shell. The Acetyl capsules also show the characteristic peak of the resin at 1760 cm^{-1} for the carbonyl group and at 1306 cm^{-1} for the C-O bond of the ester formed after acetylation. The intense peak of NCO at 2250 cm^{-1} supports the high IPDI content in the synthesized capsules. The peak was also used for the further study of the active healing agent after storage or use.

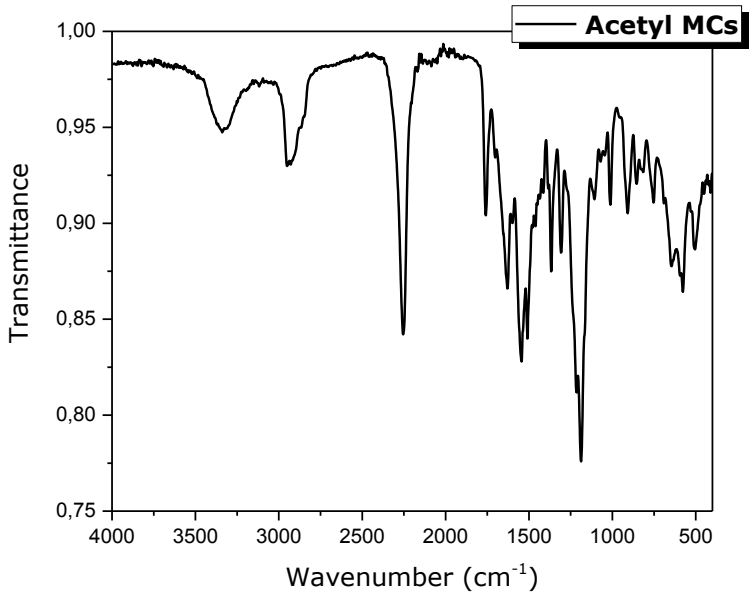

Figure 2: FTIR-ATR spectra of AcMCs,

Three ways of storing the capsules were chosen to be studied: as a solid (a) in ambient conditions or (b) in inert conditions and (c) or as aqueous dispersion, so that a comparison study could be performed. To test the importance of ambient conditions, the microcapsules were kept in vials, which were sealed with a stopper and stored in the laboratory cabinet. For inert conditions, the microcapsules were kept in vials which were first filled with N_2 gas and finally stored in a desiccator. The microcapsules dispersion is the amount of microcapsule solid in a water dispersion of final concentration 10 wt.%.

For the analysis of the extracted fraction isocyanate functional groups in supernatant acetone solution were modified to urea using dibutylamine diluted in dry toluene. After that, the excess amine titrates with hydrochloric acid for the quantitative determination of NCO groups. [22]

Fig. 3 shows the comparison of the evaluation of NCO wt.% content for the three storing conditions (aqueous dispersion and solid of microcapsules under RT and inert conditions storage). In all cases for a period of about 15 days minor changes of the NCO content is noticed. Furthermore, the results showed that it is more beneficial for the microcapsules to be stored in the form of a solid and not an aqueous dispersion, as it is

observed that at 45 days the amount of NCO wt.% has decreased at almost half of the initial amount. At 120 days, all the amount of NCO wt.% has practically been consumed in the case of aqueous dispersion. At 130 days, NCO content in case of the microcapsule solid, it is observed that there are minor differences between their storage conditions. More specifically, NCO content under the inert conditions was almost 60% of the initial amount, while at RT condition was almost 80%.

The above study gives the answer to whether the capsules should be stored in solid form and not as an aqueous dispersion. Now regarding the addition of the capsules to the PUDs matrices, it would be preferable that at the time the addition is desired to be made they are dispersed in water and quickly added to the matrix to prevent decreases in the NCO wt.% content.

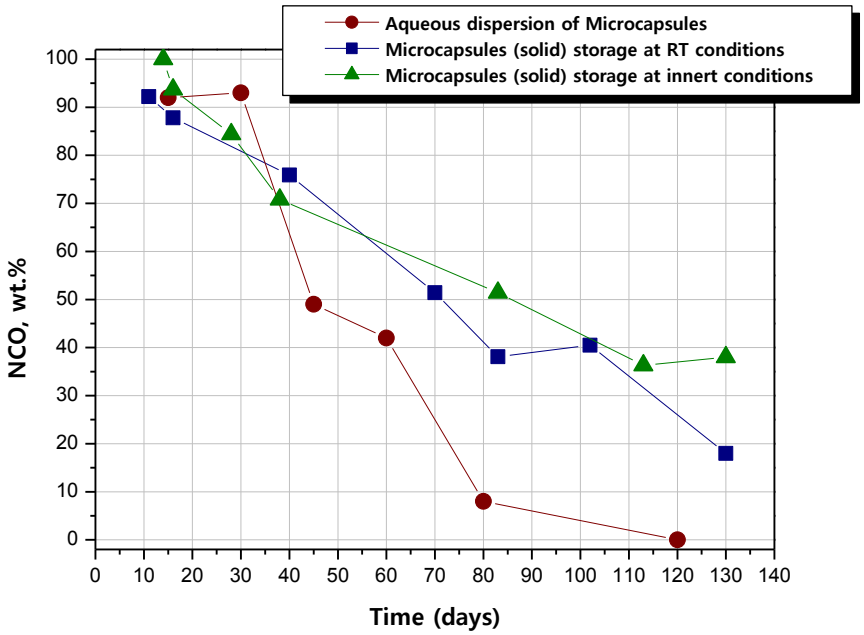

Figure 3: Evaluation of NCO wt.% with time for microcapsules stored as an aqueous dispersion (sphere), as a solid at RT conditions (cube) and under an inert atmosphere (triangle).

3.2 Evaluation of polyurethane films onto self-healing tests

The healing property of polycarbonate polyurethane dispersions containing 3 and 4.5 wt.% of solid AcMCs over the polyurethane mass was studied. Three polycarbonate polyurethane dispersions, namely PUD-P40, PUD-P47 and PUD-P48, were used. The content of the microcapsules dispersion in water was 10 wt.%. The microcapsules are easily dispersed in water through magnetic stirring, and they are introduced dropwise into polyurethane matrices to prepare the final coatings. The mixture was then applied onto a Teflon substrate where the solvent slowly evaporates at RT. This process lasts 5 days. When the AcMCs-loaded films were dried, they were peeled off from the Teflon film to facilitate the self-healing studies.

A scratch was created on the surface of the polyurethane films, neat or loaded with microcapsules, using a scalpel. The depth of the scratch, using the scalpel, is ~ (100–120) μm. The evolution of the scratches was followed by optical microscopy using a

10× magnification. The healing ways which were tested are: (a) the samples were left under ambient conditions (RT), (b) drops of water were added to samples and (c) the samples were left under 40 ºC overnight.

Fig. 4 presents the tests for the self-healing ability of the polyurethane matrix, PUD-P40. Fig. 4 (A) shows the results of PUD film which containing 3 wt.% $AcMCs_{solid}$ / PUD_{solid}. The sample is left at ambient conditions after applying the scratch to the surface and is studied over time. For samples (B) and (C) in Fig. 4 the content increases to 4.5 wt.% $AcMCs_{solid}$ / PUD_{solid}. The samples are left at ambient conditions (B) after applying the scratch to the surface, while in (C) drops of water are added and studied over time. The results showed that the samples left at ambient conditions present encouraging self-healing abilities for a long period of time (21 days), while in the sample to which water drops were added, an immediate weakening of the crack is observed (1st heal).

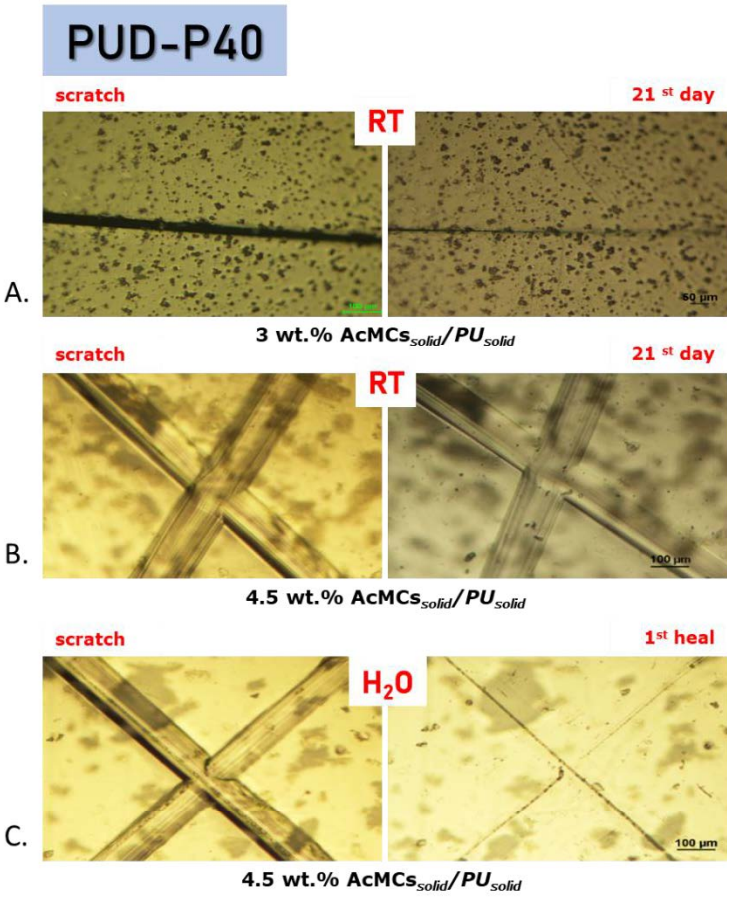

Figure 4: Evaluation of scratches on polyurethane films of PUD-P40 entering (A) 3 wt.% $AcMCs_{solid}$ / PUD_{solid} left under ambient conditions (B) 4.5 wt.% $AcMCs_{solid}$ / PUD_{solid} left under ambient conditions and (C) 4.5 wt.% wt.% $AcMCs_{solid}$ / PUD_{solid} adding drops of water.

Fig. 5 shows the tests for the self-healing ability of the polycarbonate polyurethane matrix, PUD-P48. The samples contain 4.5 wt.% $AcMCs_{solid}$ / PUD_{solid}. Drops of water are added to the sample (A) after applying the etching to the surface, while (B) is left at 40 ºC overnight and studied over time. The results showed that both samples show a significant decrease of the thickness of the crack (3rd heal).

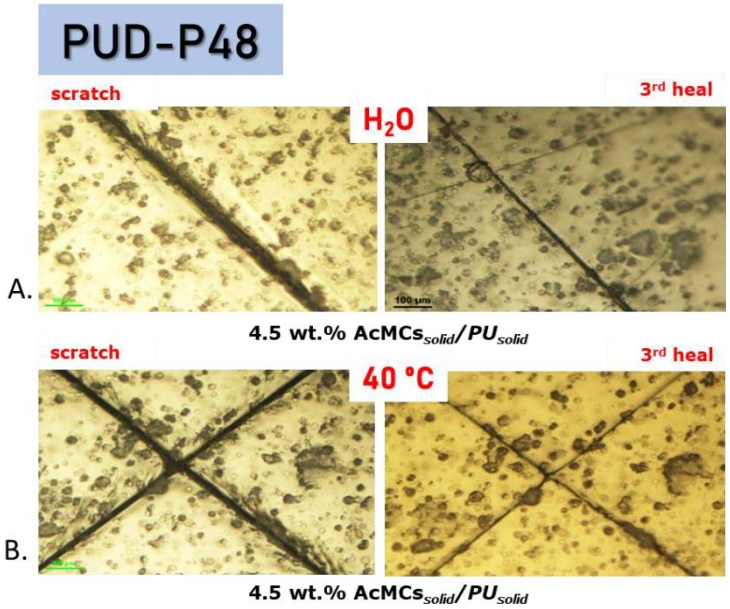

Figure 5: Scratches on polyurethane films of PUD-P48 (A) with 4.5 wt.% AcMCs solid / PUDsolid adding drops of water and (B) with 4.5 wt.% AcMCs solid / PUDsolid left at 40 ºC overnight.

Fig. 6 shows the tests for the self-healing ability of the polycarbonate polyurethane matrix, PUD-P47, which had a lower molecular weight polyol used in its composition. The samples contain 4.5 % wt.% $AcMCs_{solid}$ / PUD_{solid}. Drops of water are added to the sample (A) after applying the scratch to the surface, or they were left at 40 ºC overnight (B) and studied over time. The results showed that both samples present an improved image for the self-healing ability of the layers of each membrane (3rd heal).

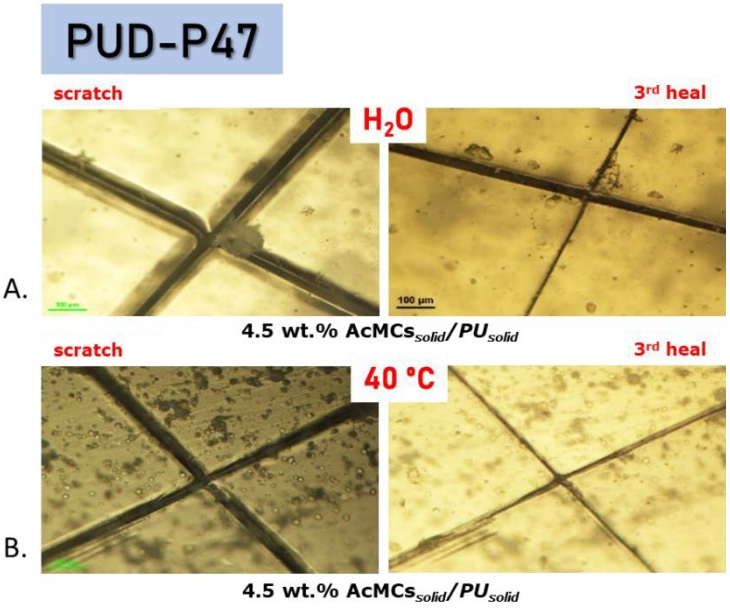

Figure 6: Scratches on polyurethane films of PUD-P47 (A) with 4.5 wt.% AcMCs solid / PUDsolid adding drops of water and (B) with 4.5 wt.% AcMCs solid / PUDsolid left at 40 ºC overnight.

4 CONCLUSION

The main objective of the present work was to study and evaluate the stability of the core contents of the capsules leading to the best way to store the capsules over time, as well as the application of self-healing ability tests of the polyurethane coatings loaded with the polyurea microcapsules that were composed. The conclusions drawn, regarding the stability of the contents of the core of the capsules, were that the capsules stored at solids show good stability over time which, however, decreases considerably over the period of two months. As for the capsules which are stored in aqueous dispersion, their core content decreases significantly of around 40 days. Thus, it becomes clear that the best way to store the capsules is in the form of a solid powder under inert conditions. Finally, the self-healing ability of polyurethane coatings loaded with polyurea microcapsules seems to give encouraging results. A critical role is played by the self-healing stimuli that were tested, mainly the addition of water drops, or the left of membranes at 40 ^{o}C overnight.

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5 REFERENCES

1. Wen, N., Song, T., Ji, Z., Jiang, D., Wu, Z., Wang, Y. and Guo, Z. Recent advancements in self-healing materials: mechanicals, performances and features (**2021**) *Reactive and Functional Polymers*, 168, 105041 https://doi.org/10.1016/j.reactfunctpolym.2021.105041
2. Wang, S., and Urban, M.W. Self-healing polymers (**2020**) *Nat. Rev. Mater.*, 5, 562–583 https://doi.org/10.1038/s41578-020-0202-4
3. Hager, M. D., van der Zwaag, S. and Schubert, U.S. Self-healing Materials (**2016**) *Springer International Publishing*, https://doi.org/10.1007/978-3-319-32778-5
4. Song, T., Jiang, B., Li, Y., Ji, Z., Zhou, H., Jiang, D., Seok, I., Murugadoss, V., Wen, N. and Colorado, H. Self-healing materials: a review of recent developments (**2021**) *ES Mater. Manuf.,* 14, 1-19 https://doi.org/10.30919/esmm5f465
5. Willocq, B., Odent, J., Dubois, P., Raquez, J.-M. Advances in intrinsic self-healing polyurethanes and related composites (**2020**) *RSC Advances*, *10 (23)*, 13766-13782. https://doi.org/10.1039/D0RA01394C

6. Keller, M.W. and Crall, M.D. Self-healing composite materials, (**2018**) *Comprehensive Composite Materials II, Elsevier*, 431–453 https://doi.org/10.1016/B978-0-12-803581-8.10026-8
7. Cordier, P., Tournilhac, F., Soulie-Ziakovic, C. and Leibler, L. Self-healing and thermoreversible rubber from supramolecular assembly (**2008**) *Nature,* 451, 977–980 https://doi.org/10.1038/nature06669
8. Zhao, D., Feng, M., Zhang, L., He, B., Chen, X. and Sun, J. Facile synthesis of self-healing and layered sodium alginate/polyacrylamide hydrogel promoted by dynamic hydrogen bond (**2021**) *Carbohydr. Polym.*, 256, 117580 https://doi.org/10.1016/j.carbpol.2020.117580
9. Zhao, M., Tang, Z., Zhang, X., Li, Z., Xiao, H. Zhang, M., Liu, K. Ni, Y., Huang, L. Chen, L. and Wu, H. A self-healing, stretchable, and conductive Poly(Nvinylpyrrolidone)/gallic acid composite hydrogel formed via hydrogen bonding for wearable electronic sensors, (**2020**) *Compos. Sci. Technol.,* 198, 108294 https://doi.org/10.1016/j.compscitech.2020.108294
10. Gadwal, I. A brief overview on preparation of self-healing polymers and coatings via hydrogen bonding interactions (**2021**) *Macromol 1,* 18–36 https://doi.org/10.3390/macromol1010003
11. Tzoumani, I., Soto Beobide, A., Iatridi, Z., Voyiatzis, G. A., Bokias, G. and Kallitsis, J. K. Glycidyl Methacrylate-Based Copolymers as Healing Agents of Waterborne Polyurethanes (**2022**) *Int. J. Mol. Sci.*, 23 (15), 8118 https://doi.org/10.3390/ijms23158118
12. Wilson, G.O., Moore, J.S., White, S.R., Sottos, N.R. and Andersson, H.M. Autonomic healing of epoxy vinyl esters via ring opening metathesis polymerization, (**2008**) *Adv.Funct. Mater.,* 18, 44–52 https://doi.org/10.1002/adfm.200700419
13. Jin, H., Mangun, C.L., Stradley, D.S., Moore, J.S., Sottos, N.R. and White, S.R. Self-healing thermoset using encapsulated epoxy-amine healing chemistry (**2012**) *Polymer,* 53, 581–587 https://doi.org/10.1016/j.polymer.2011.12.005
14. Zhu, D.Y., Wetzel, B., Noll, A., Rong, M.Z. and Zhang, M.Q. Thermo-molded self-healing thermoplastics containing multilayer microreactors, (**2013**) *J. Mater. Chem. A 1*, 7191–7198 https://doi.org/10.1039/C3TA11008G
15. Jin, H., Mangun, C.L., Griffin, A.S., Moore, J.S., Sottos, N.R. and White, S.R. Thermally stable autonomic healing in epoxy using a dual-microcapsule system, (**2014**) *Adv. Mater.*, 26, 282–287 https://doi.org/10.1002/adma.201303179
16. Hillewaere, X.K.D., Teixeira, R.F.A., Nguyen, L.-T.T., Ramos, J.A., Rahier, H. and Prez, F.E. Autonomous self-healing of epoxy thermosets with thiol-isocyanate chemistry (**2014**) *Adv. Funct. Mater.*, 24, 5575–5583 https://doi.org/10.1002/adfm.201400580
17. McIlroy, D.A., Blaiszik, B.J., Caruso, M.M., White, S.R., Moore, J.S. and Sottos, N.R. Microencapsulation of a reactive liquid-phase amine for self-healing epoxy composites (**2010**) *Macromolecules,* 43,1855–1859 https://doi.org/10.1021/ma902251n
18. White, S.R., Sottos, N.R., Geubelle, P.H., Moore, J.S., Kessler, M.R., Brown, E.N., Sriram, S.R. and Viswanathan, S. Autonomic healing of polymer composites (**2001**) *Nature,* 409, 794-79

https://doi.org/10.1038/35057232
19. Yi, H., Yang, Y., Gu, A.X., Huanga, J. and Wang, C.H. Multilayer composite microcapsules synthesized by Pickering emulsion templates and their application in self-healing coating (**2015**) *J. Mater. Chem. A*, 3, 13749–13757 https://doi.org/10.1039/C5TA02288F
20. Avdeliodi, E., Soto Beobide, A., Voyiatzis, G.A., Bokias, G. and Kallitsis, J.K. Novolac-based microcapsules containing isocyanate reagents for self-healing applications (**2022**) *Progress in Organic Coatings*, 173, 107204 https://doi.org/10.1016/j.porgcoat.2022.107204
21. Sun, D., An, J., Wu, G. and Yang, J. Double-layered reactive microcapsules with excellent thermal and non-polar solvent resistance for self-healing coatings (2015) *J. Mater. Chem. A*, 3(8), 4435-4444 https://doi.org/10.1039/c4ta05339g
22. Moghimi, A., Omrani, I., Khanmiri, R.H., Bahadorbeigi, R., Mahmoodi, M. Determination of NCO content of the urethane prepolymers by 19F NMR spectroscopy (**2014**) Polymer Testing, 33, 30-33 https://doi.org/10.1016/j.polymertesting.2013.11.002