

## UV Curable Self-Healing Structural Epoxy Composite Materials Interfacial Polycondensation Microencapsulation of Healing Agent and Photo-Initiator

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### Abstract

The ability of polymeric coatings to self-heal itself from mechanical damage is explored in this paper. Polymeric coatings with self-healing property is one of the important aspects in modern science. It can be used in industries such as oil industry (protection against corrosion), mechanical engineering, aircraft, etc. The polyurethane (PU) microparticles were synthesized on the basis of polypropyleneglycol (PPG) and toluene diisocyanate (TDI) with a method of interfacial polycondensation at the interface water-benzene. Further to study the surface morphology of the microcapsules with healing agent (trimethylolpropanetriacrylate–TMPTA) obtained PU was applied the method of scanning electron and atomic force microscopy. The PU microparticles hollow inside have regular spherical shape with a diameter of 5-10  $\mu\text{m}$  with a dense and smooth polymeric shell. The resulting polyimide–polyurethane (PI–PU) composites have high potential to regenerate damaged surfaces not only on the surface and also in the volume of composite within several minutes.

### Introduction

Developments of advanced materials have paced the evolution of technologies for the last 50 years and their importance in the advancement of global growth is essential. The recent decade brought about new dimensions to materials developments; stimuli-response materials capable of responding to internal or external stimuli. And most promising property is the ability of materials to autonomously self-heal [1].

The number of publications that appeared in the past decade concerning the self-repair of polymeric materials is quite extensive. They cover different fields of research, including thermoplastic and thermoset polymers, polymer composites, and coatings. The first ideas already started to develop in the 1990s, when scientists started to look at nature to solve the recurring problem of damage to materials. If biological systems are used as the benchmark of regeneration, self-healing, and reproduction, mimicking these processes is not trivial because they ex-

hibit highly coordinated and complex cellular and molecular level metabolic activities, enabling coordination of defense responses by assembly–disassembly of heterogeneous morphologies [1-4].

The self-healing concept envisages a similar recovery of material properties, such as fracture toughness, corrosion resistance, or conductivity, to improve the durability and reliability of the polymer materials. Damage due to impact, wear or fatigue initiates a healing mechanism that preferentially without external stimulus can recover any functionality. Researchers working in the field of self-healing polymeric materials mainly focus on high-end applications where the added value outweighs the cost of production. Such applications can, for example, be found in the transport sector, electronics, and structural materials. Car coatings, structural composites in airplanes, conductive polymers in sensors are only some examples of many targeted applications. Repair of damage in these materials is often laborious, not cost-efficient and only detected on the

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macroscopic level when it is too late. On the other hand, self-healing materials try to avoid macroscopic failure by responding immediately or at least fast enough to damage.

Macroscopic damage to materials generally starts as microcracks. In most self-healing systems, this is the stage where the healing action takes place. In order to efficiently heal the material, fast inhibition of crack propagation is favorable to limit the crack volume to be healed. When the crack surfaces are in close proximity to each other, liquid healing agents or dangling functional groups can bridge the gap to restore at least partially the physical properties of the polymeric materials and composites. In this field, a whole range of crosslinking chemistries have been applied with varying results [5-8].

Here, we demonstrate a self-healing structural composite system with two-component healant. The difference of the present work from those reported previously is the use of photo-initiator instead of the catalyst. The photo-initiator is encapsulated with epoxy healing agent together in polyurethane microcapsules, which in case of damage can heal itself under the influence of UV beam. The microparticles were synthesized on the base of segmented polyurethane (PU) using the interfacial polycondensation method at water-benzene interface. The feasibility of the developed self-healing methodology was tested by encapsulating multifunctional acrylates, i.e. trimethylol propane triacrylate (TMPTA) in the presence of a radical photo-initiator (Darocur® 1173). In the self-healing polyimide film structural polymer matrix composite, a microencapsulated monomer (healing agent) and photo-initiator are dispersed. Consequently, higher adhesion strength and better repair effect can be expected.

## Experimental

### Materials and Reagents

There are several constituent materials which, when combined, function as a self-healing materials system: healing agent (TMPTA—trimethylolpropane triacrylate, molecular weight 296.32), for microcapsule shell (polyurethane) was used TDI (toluene diisocyanate, molecular weight 174.16) and PPG (polypropylene glycol, average  $M_n \sim 425$ ), chemical photoinitiator (Darocur®1173—2-hydroxy-2-methylpropiophenone, 97%, molecular weight 164.20), epoxy polymer matrix (polyimide resin), and emulsion stabilizer (Tween 20—polyoxyethylene sorbitan monolaurate, molecular weight  $\sim 1228$ ). All the materials are used without further purification [9] and were purchased from Sigma Aldrich and were used as received.

### Synthesis of Microcapsules

TDI was dissolved in benzene as dispersed organic phase. The organic phase is added to the PPG containing aqueous phase, under magnetic stirring during 5 min and pH was systematically monitored in order to estimate the hydrolysis of the NCO groups during the emulsification process. An emulsion stabilizer (Tween 20) was added to the formulation to stabilize the emulsion. The ultrasonification time was chosen equal to 20-30 sec. The turbidity of the preparation increase very rapidly in the first seconds of ultrasonification, becomes milky and then remains constant. The reaction then subsides under magnetic stirring during 4 h at 60 °C. After 4 h of continuous stirring, the mixer was cooled; particles are filtered on Büchner filtration and are washed with a water/ethanol solution (50 wt.%/50 wt.%). Then, particles are dried in air at room temperature for about 24-48 h. The reproducibility of the encapsulation reaction was verified in terms of size and size distribution with a SEM. Both techniques attested to the presence of submicrometer capsules [10].

The external wall of the microcapsules appeared smooth, in accordance with the typically observed morphology of the external wall of microcapsules obtained by an interfacial polycondensation process from normal emulsion. We can see the smooth external wall in Fig. 4, where the microcapsules are visible on surface of the polyimide film. The morphology of the external wall is explained by the formation mechanism and kinetics of the primary membrane. Many parameters can influence the interfacial polycondensation kinetics. The reactivity of the both monomers, the viscosity of the external phase depending on the molecular weight and the chemical structure of the diol and the nature of the dispersed phase. The latter must concurrently induce the precipitation and the swelling of the growing membrane. The length of the diol will also influence the morphology of the capsules. These aliphatic and aromatic compounds will induce the formation of completely spherical capsules with clear and smooth surface. Thus, the spherical shape and the smooth surface of the microcapsules observed by scanning electron microscopy (SEM) [10].

### Microencapsulation of the Healing Agent and Photo-Initiator

As it was mentioned previously in our study TMPTA was used as a healing agent and Darocur®1173 was used as a UV radiation curable photoinitiator. An appropriate amount of TMPTA and photoinitiator with the organic phase (TDI/benzene) were added to the aqueous phase (PPG/water). Af-

ter 4 h of stable stirring at 60 °C the mixture was cooled, filtered and washed with a water/ethanol solution. Further the dried polyurethane microcapsules with the TMPTA and photoinitiator was tested in an epoxy polymer matrix.

## Results and Discussion

### Research Methods and Experimental Techniques

Purification of starting materials and solvents were performed by standard methods. Images of the polyimide films surface were obtained on a microscope «Leica». Thermogravimetric analysis of polymers was held on derivatograph of «Mettler Toledo» company and the temperature rise rate is 8 °C/min. Polyurethane capsules were prepared in inverse emulsion based on TDI and PPG, substances for encapsulation (healing agent monomer) were TMPTA and UV initiator Darocur®1173. In 5 ml of benzene were dissolved 1 ml of TDI, 1 ml of TMPTA and 0.05 ml of Darocur®1173, and in aqua phase were dissolved in 5 ml of PPG, 4 ml benzene and 0.05 ml Tween 40 (surfactant). The solution of TDI and monomer TMPTA were added (drop wise) to the aqua phase of PPG solution. The solution was stirred at 60 °C for 1 h. After synthesis of microcapsules the solution was washed with 50% isopropanol solution (100 ml) in a Büchner funnel, then the microcapsules were placed in a drying oven to dry at 90 °C. The capsules had a milky white color, weight of capsules was 3.59 g.

Resettable (or self-healing) films were prepared by mechanically mixing of microcapsule with 25% solution of alicyclic polyimide in dimethylacetamide, followed by coating on the glass surface uniformly as 20-100 microns thin layer. Further, the epoxy film was dried at 1100 °C for 24 h to obtain a solid (stable) of the polyimide film.

TGA and CDTA datas in Fig. 2 show the correlation between the concentration of microcapsules (with TMPTA monomer) in the PI film and thermal decomposition. It is explained by the fact that the decomposition temperature of the monomer TMPTA is around 460 °C (Fig. 1), and hence an increase in the monomer concentration decreases the decomposition temperature of the PI [11-14].

### The Healing Process of the Composite

The monomer is allocated outside at destruction of the microcapsules containing TMPTA which are within PI volume. After exposure of film samples under the influence of UV-radiation of a DR-500M quartz lamp at current intensity on a throttle 4A, a change of thickness of films cut is noticeable in

Fig. 3. For the best fixation of “self-healing” effect we fixed changes after 10 min of exposition under UV-radiation.

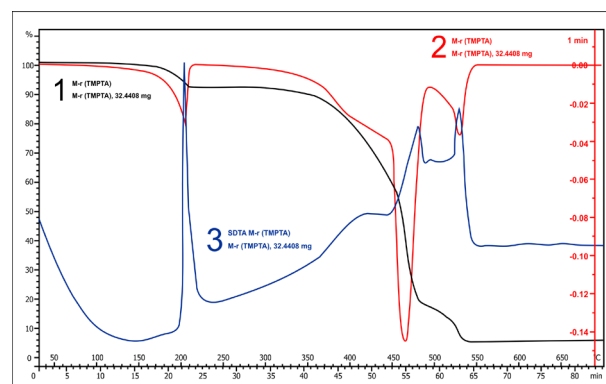


Fig. 1. TGA (1), TGA derivative (2), and SDTA (3) of TMPTA monomer.

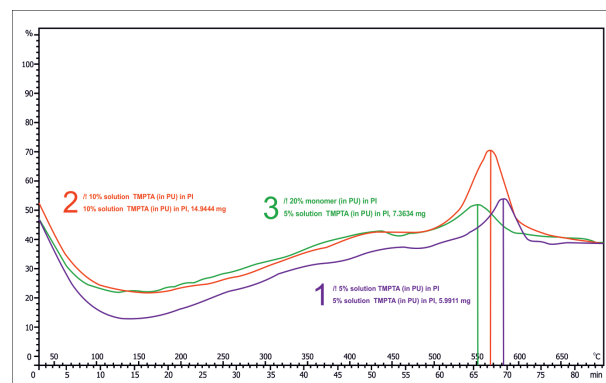
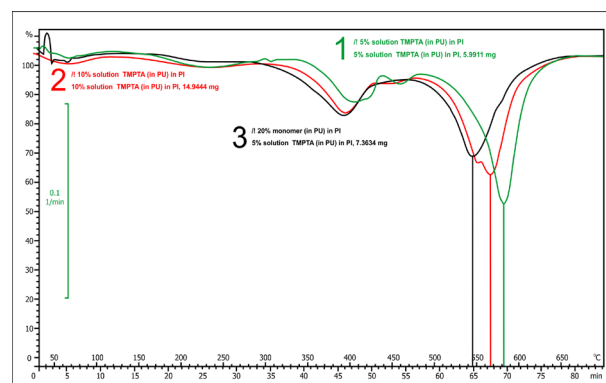


Fig. 2. TGA derivative (a) and SDTA (b) of PI films, containing: 1 – 5%; 2 – 10%; and 3 – 20% TMPTA monomer encapsulated in PU microcapsules.

The study concluded that films containing 5% encapsulated monomer “overrun” is better than the same film with a high content of microcapsules. The flexibility of a film decreases as the concentration of the encapsulated monomer increases, so it makes the film less prone to the “self-healing”. This pattern is observed in films containing TMPTA monomer encapsulated in PU.

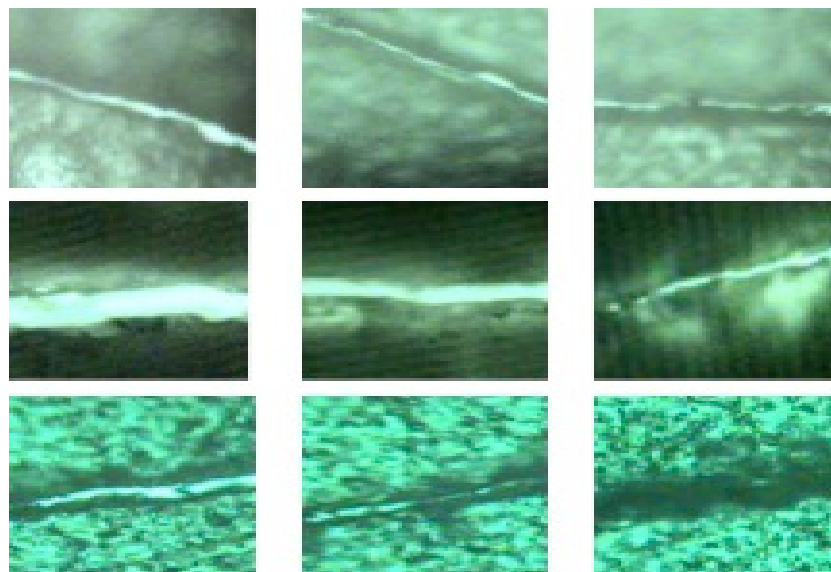


Fig. 3. Self-healing polyimide film under UV radiations. Various quantities of microcapsules loaded in TMPTA and Darocur®1173 incorporated into a polyimide film.

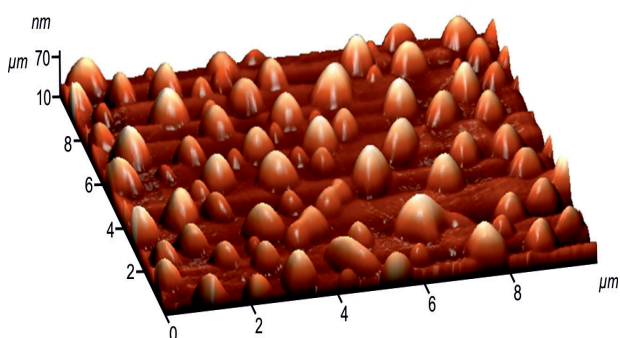


Fig. 4. PU Microparticles distribution in polyimide films.

Thus, the “self-healing” films have a high potential to regenerate damaged surfaces not only on the surface but also in volume of the composite. These films having photopolymerizable composites can be used in those fields of technology and engineering, where it is not necessary to use a wear-resistant coating films.

### Conclusions

Our studies showed that films containing 5% of encapsulated monomer “grow” better, than the same films, with high (10–15%) microcapsules content. The increase of encapsulated monomer concentration resulted in a decreases of the film flexibility which makes it less prone to the “self-healing”. We found that the optimized polyimide–polyurethane composites have high potential to regenerate damaged films not only on the surface but also in-

the volume of the composite. Such films, based on photopolymerizable healing agents can find number of technological and engineering applications as wear-resistant coatings.

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### References

- [1]. Y. Yang, M.W. Urban, *Chem. Soc. Rev.*, 42 (17) (2013) 7446–7467.
- [2]. R.F. Diegelmann, C.M. Evans, *Front. Biosci.*, 9 (2004) 283–289.
- [3]. R. Han, K.P. Campbell, *Curr. Opin. Cell Biol.*, 19 (4) (2007) 409–416.
- [4]. R. Paris, L. Lamattina, C.A. Casalongue, *Plant Physiol. Biochem.*, 45 (2007) 80–86.
- [5]. S. Billiet, X.K.D. Hillewaere, R.F.A. Teixeira, F.E. Du Prez. *Macromol. Rapid Commun.* 34 (2013) 290–309.
- [6]. B.J. Blaiszik, S.L.B. Kramer, S.C. Olugebefola, J.S. Moore, N.R. Sottos, S.R. White, in *Annual Review of Materials Research*, Vol 40, (Eds: D. R. Clarke, M. Ruhle, F. Zok), Annual Reviews, Palo Alto 2010, p 179.
- [7]. T.C. Mauldin, M.R. Kessler, *Int. Mater. Rev.* 55 (2010) 317–346.

- [8]. E.B. Murphy, F. Wudl, *Prog. Polym. Sci.* 35 (2010) 223–251.
- [9]. A.A. Périchaud, R.M. Iskakov, A. Kurbatov, T.Z. Akhmetov, O.Y. Prokohdko, I.V. Razumovskaya, S.L. Bazhenov, P.Y. Apel, V.Yu. Voytekunas, M.J.M. Abadie. Auto-Reparation of Polyimide Film Coatings for Aerospace Applications Challenges & Perspectives, *Intech* (216-243) C:11 (2012).
- [10]. T. Yin, M.Z. Rong, M.Q. Zhang, G.Ch. Yang. *Compos. Sci. Technol.* 67 (2007) 201–212.
- [11]. B.A. Zhubanov, V.D. Kravtsova, K.H. Bekmagambetova. *Polym. Sci.* 2003. Ser. B. V. 45/3. № 4. P. 76–81.
- [12]. B.A. Zhubanov, V.D. Kravtsova, K.A. Zhubanov et al., *Eurasian Chemico-Technological Journal* 6 (2004) 45–50.
- [13]. S. Kudaikulova, Z. Musapirova, N. Sobarina, M. Umerzakova, R. Iskakov, B. Zhubanov, M. Abadie, *Eurasian Chemico-Technological Journal* 6 (1) (2004) 7–10.
- [14]. S. Kudaikulova, Z. Musapirova, N. Sobarina, M. Umerzakova, R. Iskakov, B. Zhubanov, M. Abadie, *Eurasian Chemico-Technological Journal* 6 (1) (2004) 11–16.

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