An Acad Bras Cienc (2023) 95(Suppl. 2): e20230337 DOI 10.1590/0001-3765202320230337
Anais da Academia Brasileira de Ciências | *Annals of the Brazilian Academy of Sciences*
Printed ISSN 0001-3765 I Online ISSN 1678-2690
www.scielo.br/aabc | www.fb.com/aabcjournal

ENGINEERING SCIENCES

Synthesis and characterization of Poly(urea-formaldehyde) microcapsules with 5-ethylidene-2-norbornene as self-healing agent and potential use in polymeric composites

SABRINA SARA ROSSI, ALEXANDRE ESTEVÃO CARRARA, MARIA CAROLINA B. COSTA, CAIO LUCAS G.P. MARTINS, RITA DE CÁSSIA L. DUTRA & JORGE CARLOS N. DUTRA

Abstract: This study describes a methodology to prepare and characterize PUF [poly(urea formaldehyde)] microcapsules containing 5-ethylidene-2-norbornene (ENB) as self-healing agent, as well as the compatibility evaluation of ENB in the presence of Grubb's catalyst with an epoxy matrix. First, the results of an adhesion assay by lap shear proved chemical compatibility between the epoxy matrix and self-healing agent in the presence of Grubb's catalyst. After evaluating the chemical compatibility, microcapsules with ENB were synthesized in an oil-in-water emulsion system. Thereafter, the microcapsules were morphologically, chemically and thermally characterized in which a granulometric dispersion between 30-140 μm and an average size of 69.8 ± 4.9 μm were observed. The SEM (scanning electron microscope) results showed that the average thickness of microcapsules shell was 3.6 ± 0.4 μm. The thermogravimetric analysis (TGA) showed that microcapsules are susceptible to rupture and consequent ENB release in temperatures greater than 230 °C, demonstrating that microcapsules are suitable for applications in materials with self-healing capacity.

Key words: characterization, composites, microcapsules, self-healing, synthesis.

INTRODUCTION

The technological evolution of society demands the development of novel materials or specific technological combinations. In this context, the synthesis of self-healing materials can be addressed. Based on the natural self-repair mechanism of living bodies (Ghosh 2009, Lee et al. 2018), the self-healing concept was developed for manufacturing a new category of materials: self-healing materials. The unavoidable damage events caused during manufacturing and application are repaired on a microscopic scale (Huynh et al. 2017, White et al. 2001).

Several denominations are used in researching materials with self-repair capacity such as: self-healing, self-repairing, autonomic-repairing or autonomic-healing. The basic principle of self-repair is the presence of a self-healing agent and catalyst in a polymer matrix. These materials can be defined as materials with the capacity to locally self-repair damage suffered and recover the initial properties (totally or partially) in the affected zone, with or without external stimuli (Hager et al. 2010).

The classification of self-repair capacity depends on stimuli and the self-healing process mechanism. Materials regarding stimuli are classified as autonomous or non-autonomous.

Non-autonomous self-healing materials require external stimuli, in contrast to autonomous materials in which the damage suffered is the healing trigger (Hager et al. 2010).

Materials regarding the self-healing mechanism are classified as intrinsic and extrinsic. Intrinsic materials do not require any intervention and the healing is based on forming chemical bonds and physical interactions between damage ends, whereas extrinsic self-repair needs external recovery agents. A typical example of this process is the addition of microcapsules containing healing agents with a catalyst in matrix polymers (van der Zwaag 2007, Carvalho et al. 2019, Rodrigues et al. 2019, Carrara et al. 2023), which causes microcapsules to rupture when suffering damage events and consequent release of healing agent, in turn advancing to completely or partially seal damage, as illustrated in Figure 1 (Dry et al. 1992, Brown et al. 2002, Wu et al. 2008, Yang et al. 2008).

Emulsion polymerization is the most common microcapsule synthesis process. A catalyst is normally used to promote the polymerization of self-healing during damage sealing. The most effective catalyst reported is Grubb's catalyst, despite its high cost and low versatility. Several parameters can influence the morphology, size and physico-chemical characteristics of microcapsules during the synthesis step, for example: temperature, medium pH, stirring rate, and emulsification (among others), which mainly affect the microcapsule characteristics and its applicability (Rodrigues et al. 2019, Fan & Zhou 2010, 2011, Fan et al. 2013, Nesterova et al. 2012).

The effect of synthesis conditions on the formation of urea-formaldehyde microcapsules was evaluated by Katoueizadeh, Zebarjad & Janghorban (2019). To do so, they conducted syntheses under different conditions by *in situ* polymerization. The evaluated synthesis parameters were: the formaldehyde to urea molar ratio (0.94, 1.88, 2.81), time (1, 4, 7 h), temperature (25, 55, 85 °C) and pH (3, 7, 11). The results showed that the formation of microcapsules is highly dependent on these factors, the ideal pH should be below 7 (acidic) and the F/U molar ratio should exceed 0.94. The study also showed that microcapsules obtained from a low F/U molar ratio degraded at lower temperatures, while microcapsules produced with a high F/U molar ratio and high synthesis temperature showed thermal stability at a higher temperature due to the formation of more crosslinks.

A review work by Ullah et al. (2016) addressing the potential of microencapsulated self-repairable materials for recovering microcracks in composite systems showed the influence of several aspects related to self-healing using microcapsules. The effect of synthesis parameters on the size of microcapsules, the healing efficiency and the potential of

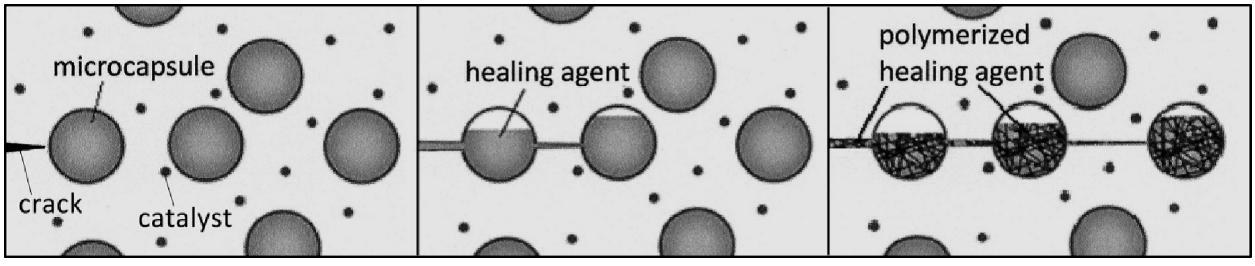


Figure 1. Self-healing system as developed: (a) microcapsules and catalyst embedded in polymeric host material, (b) crack ruptures microcapsules, the healing agent distributes into the crack plane, and (c) healing agent reacts with catalyst to heal the crack (White et al. 2001).

microencapsulated agents were evaluated. The authors generalized that melanin-formaldehyde (MF) microcapsules displayed better properties than UF microcapsules, however no self-healing evaluation was done for the composite system in question. Thus, an evaluation of different systems involving different microcapsules (shell and core) must be continuously studied.

Most studied self-healing catalytic systems address the use of poly(urea formaldehyde) (PUF) microcapsules containing encapsulated dicyclopentadiene (DCPD), both dispersed in epoxy matrixes (White et al. 2001), which in presence of Grubb's catalyst, polymerizes in the presence of Grubb's catalyst by ring-opening metathesis polymerization (ROMP). Despite the success of this technique, the scientific community has taken interest in studying novel agents with healing capacity since DCPD has a low melting point. Among the different agents, 5-ethylidene-2-norbornene (ENB) has the most studies reported due to its higher reactivity which promotes faster polymerization with lower quantities of catalyst, as well as its lower viscosity which eases diffusion in the damaged area (Zhang & Rong 2011).

Hia et al. (2016) carried out a review study comparing the efficiency of self-healing polymer composites, as well as their possible applications across various industries such as aerospace, automotive, coating, and energy, etc. This study presents a comparison of the self-healing efficiency between PUF microcapsules filled with DPCD and PUF microcapsules filled with ENB. Microcapsules containing ENB showed superior efficiency (95% versus 56% cured during the same time).

In the current world economic scenario, the demand for more efficient and sustainable technologies brings up new scientific challenges. Self-healing materials are part of this scope and have had significant evolution in the scientific community in recent years. This technology is particularly essential for polymeric materials applied in space and aeronautics in the development and application of solid fuels, thermal protection, structural composites, adhesive and interfaces, etc., to inhibit crack propagation, thereby increasing the lifecycle and reliability of devices, structures, and materials (Rodrigues et al. 2019, Das et al. 2016, Carlson & Goretta 2006, Semprimosching 2006).

Synthesized microcapsules need to have a thick and rigid shell to provide a protective barrier to support the synthesis process conditions and the dispersion in the matrix polymer in order to successfully self-heal, but at the same time they have to be fragile enough to break during the formation of matrix damage. Furthermore, microcapsules need to have enough impermeability to avoid diffusion of the repairing agent, which has to easily diffuse and has to present enough adhesion to the polymer matrix (Carvalho et al. 2019, Brown et al. 2003).

Marinho et al. (2021) evaluated the effect of seven input variables of the synthesis process on the properties of the obtained microcapsules. The evaluated responses were average diameter, the encapsulated content, synthesis yield, thermal stability temperature and degradation temperature. It was observed that the stirring speed and the emulsifier amount presented the most significant effects for all analyzed parameters on the analyzed response variables. Like so, from the results obtained in this previous article, it was possible to obtain here, PUF microcapsules filled with ENB presenting more satisfactory characteristics, through a more adequate control of the synthesis conditions. Beside this, in this work, microcapsules obtained were characterized with different techniques to evaluate their loading capacity and thermal resistance. It is also important to highlight that the compatibility between the cured epoxy

matrix and the poly (EBN) in the presence of Grubbs' catalyst has not been previously evaluated. Results of an adhesion assay by lap shear proved chemical compatibility between the epoxy matrix and self-healing agent in the presence of Grubb's catalyst, indicating that the microcapsules obtained have high potential for self-healing. In summary, the evaluation of the effect of synthesis variables on the properties of microcapsules, carried out in the previously published article, made it possible to obtain microcapsules with more optimized properties in this work and the results obtained here indicate that the microcapsules obtained have potential application in self-healing systems, since it was possible to prove the compatibility between the cured epoxy matrix (used in several polymeric composite materials) and poly (EBN), in the presence of Grubbs' catalyst. A new work is being developed by our research group to evaluate quantitatively the efficiency of self-healing through mechanical tests.

Thus, PUF microcapsules containing ENB were synthesized and characterized dimensionally through optical microscopy (OM), morphologically through scanning electron microscopy (SEM), chemically through Fourier transform infrared spectroscopy (FT-IR) and thermally through thermogravimetric analysis (TGA). The reaction yield was determined, as well as the ENB efficiency as an adhesive in sealing epoxy composites. Thus, lap shear tests were performed to evaluate the ENB adhesive compatibility as a self-healing material in the presence of Grubb's catalyst in the epoxy matrix. ENB was chosen because it cures quickly, especially when compared to other healers. The evaluation was carried out to investigate whether the encapsulated agent (ENB) would give adhesion to the epoxy matrix upon finding the catalyst once the microcapsule is broken.

MATERIALS AND METHODS

Microcapsule synthesis

The materials used to synthesize the microcapsule PUF shell were: urea, resorcinol and ammonium chloride (Synth), formaldehyde (Êxodo Científica), maleic anhydride (EMA) (Sigma-Aldrich P.A.) to emulsify and water. Next, 1-octanol (Synth P.A.) was used as the solution stabilizer. Sodium hydroxide (NaOH) 10% w/w (correction to basic medium) or chloridric acid (HCl) 10% w/w (correction to acid medium) were used to control the pH medium close to 3.5, both provided by Synth P.A. Ethanol was used to wash synthesized microcapsules.

ENB (boiling point 148 °C) was donated by Sigma-Aldrich (St. Louis, MO, USA) and was used as the core agent.

Grubb's catalyst 1st generation (benzylidenebis (tricyclohexylphosphine) dichlororuthenium) was also donated by Sigma-Aldrich (St. Louis, MO, USA, P.A. 97%). Both ENB and Grubb's catalyst were considered as the self-repairing system.

Reagents were weighed in a Shimadzu AUY 220 analytical scale. Heating was performed using a heating plated with magnetic stirring (model IKA RH basic 1) and the temperature was measured with a mercury thermometer coupled to the reaction system. The pH was measured using a suitable portable equipment KASVI model K39-0014PA device.

PUF was chosen as the microcapsule shell composition and ENB as the core agent in this study. The synthesis methodology was conducted as proposed proposed by Zhang et al (2019) in which a urea-formaldehyde reaction occurs in acidic medium without the need to have a pre-condensed phase, as shown in Figure 2.

Microcapsules were synthesized by an *in situ* oil-in-water polymerization process. The reagents were weighed in the following quantities:

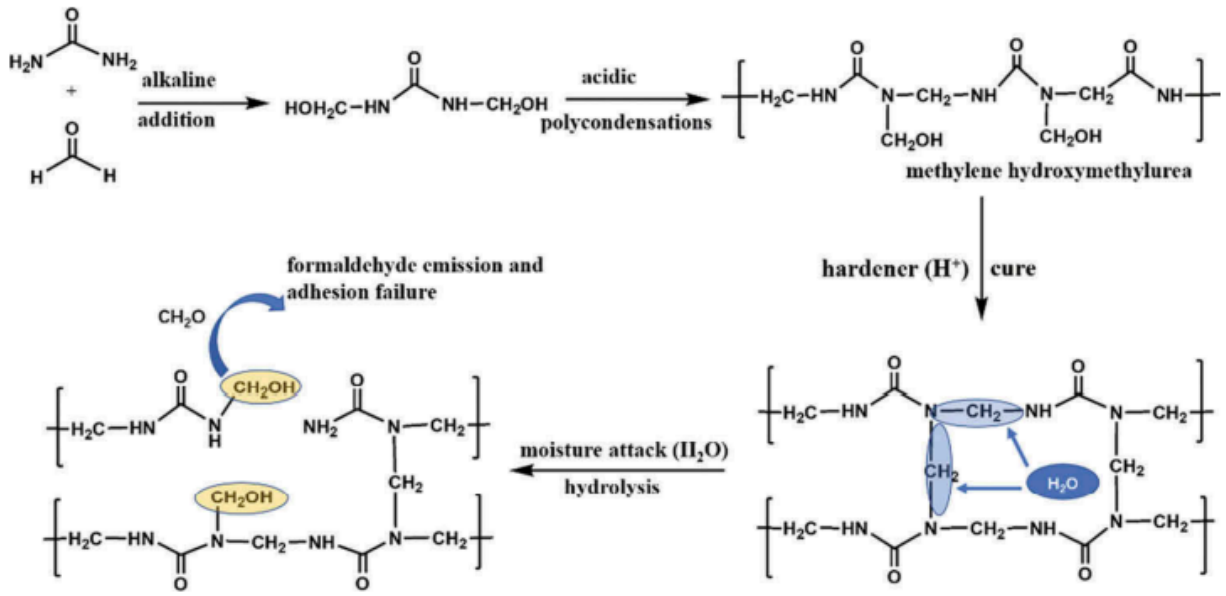


Figure 2. Polymerization reaction to obtain PUF.

2.5 g of urea, 0.25 g of ammonium chloride, 0.25 g of resorcinol and 0.5 g of polyethylene maleic anhydride, which were added to 200 mL of deionized water at room temperature. The pH of the solution after 10 minutes of magnetic stirring at 500 rpm was 2.5. Next, 20 drops of NaOH 10% were added to adjust the pH to 3.5, and 2 drops of 1-octanol to avoid the formation of bubbles in emulsion. Thereafter, 5.8 mL of formaldehyde and 20 mL of ENB were slowly added (drop by drop) under magnetic stirring to control the rate fixed in 500 rpm for more than 4h at a controlled temperature of 55 °C. The product obtained from the polymerization reaction between urea and formaldehyde, which is extremely exothermic, is presented in Figure 3.

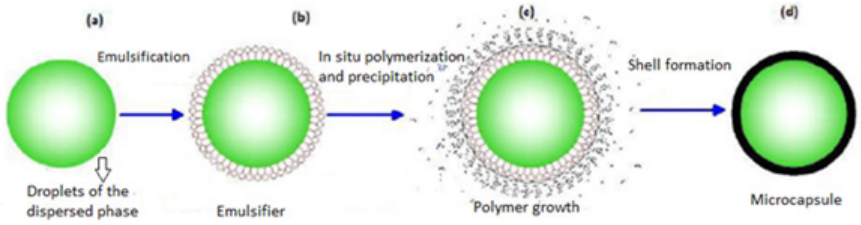
After finishing the synthesis, the material was cooled to room temperature during 24h and then washed with ethanol and filtered using filter paper (Quanty) with a pore size of 25 µm and air dried. The synthesized microcapsules present a white powder aspect.

Microcapsules without a core agent were subsequently synthesized following the same procedures presented above. These hollow microcapsules were synthesized to check the ENB influence on the final characteristics of the microcapsules.

Compatibility between a cured epoxy matrix and poly(EBN) + Grubb´s catalyst

An epoxy matrix (Ampreg 26 High Tg) (Barracuda Advanced Composites) was used as support to certify the compatibility of the adhesion mixture (ENB + Grubb's catalyst disperses 5% w/w). Surfaces to be adhered were cleaned with ethanol:water solution (50:50) in controlled temperature (23 °C). After drying, the adhesion mixture was applied on both contact surfaces and contact between interfaces was performed. Lap shear assays were conducted after 24h of curing at room temperature based in ASTM D1002 standard.

The ASTM standard specifies that "the testing machine shall conform to the requirements of Practices E 4." For this test the Instron 5569 electromechanical test frame was configured with a 50 kN load cell and 30 kN capacity mechanical wedge action grips with coarse serrated faces. The standard further specifies



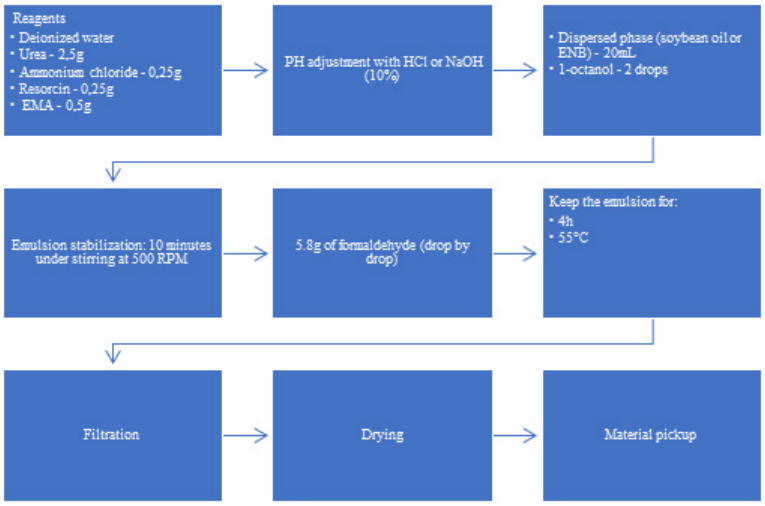


Figure 3. PUF microcapsule synthesis route.

that "the long axis of the test specimen coincide with the direction of applied pull through the center line of the grip assembly." In order to insure that the load be applied in exactly the same direction as the center line, spacers were inserted into the grips and clamped very tightly to prevent slipping. The test was run at a crosshead speed of 1.3 mm/min until failure.

Yield reaction calculation

The reaction yield to obtain PUF microcapsules containing ENB was calculated based on the study of Huang & Yang (2011), according to Equation 1:

$$Yield\,(\%) = (Wmc)/(Wure + Wform + Wagen)\,x\,100\,\% \quad (1)$$

In which: Wmc is related to the microcapsule weight, Wure to urea weight, Wform to formaldehyde weight, and Wagen to the core agent weight (dispersal phase) used in the synthesis, in this case, ENB.

Characterization techniques

Morphologic analysis and microcapsules shell thickness determination – OM and SEM

Granulometric determination was conducted using an optical microscope (Model Quimis Q780MIT) after filtering the samples in filter paper (Quanty), drying and random collection of 300 microcapsules, whereas morphologic analysis, shell thickness determination and the surface aspect were analyzed using SEM equipment (Hitashi TM-3000 Tabletop Microscope).

FT-IR spectroscopy

The FT-IR analysis was conducted by collecting data in the medium infrared spectral region (MIR) (4000 a 550 cm^{-1}) through the use of a PerkinElmer SpectrumOne FT-IR spectrophotometer with a resolution of 4 cm^{-1} and 20 scans by reflection technique using universal attenuated total reflection (UATR). The sample was analyzed as received.

Thermogravimetric analysis (TGA)

The TGA analysis was performed in inert nitrogen atmosphere in a temperature range of 30-700 °C, applying a heating rate of 10 °C/min and using a TGA/DTA analyser (6300 SII EXSTAR 6000).

RESULTS AND DISCUSSION

ENB and epoxy matrix compatibility

Figure 4 shows the lap shear results equivalent to 1.08 ± 0.41 N/mm^2 and adhesive cohesive failure in the bonding region of samples containing ENB and catalyst as adhesive. These tests proved excellent adhesion of the product resulting from the polymerization of ENB with the epoxy matrix, showing that the matrix cohesion strength was higher than the adhesive strength. Furthermore, these results indicate that the ENB monomer is polymerized in the fracture surface when there is damage in the matrix and consequent microcapsule rupture with the release of the ENB healing agent in contact with the dispersal catalyst, as represented in Figure 4, which interrupts the propagation of this damage, as the ENB acts as a repairing agent.

After confirming the compatibility between epoxy matrix and poly (ENB), the challenge is to synthesize the microcapsules with efficient ENB encapsulation. As the main objective of this test is to evaluate the functionality of the self-healing system, it was decided not to carry out new tests varying the amount of Grub's catalyst in the adhesive.

Yield reaction calculation

Considering the adopted synthesis parameters, the quantity of reagents, stirring speed (500 rpm) and the type of agitation, the resulting yield for filled PUF microcapsules with ENB was 15%. This value corresponds to 25% of the value reported by Brown et al. (2003) and Then et al. (2011), in which DCPD was used as the self-healing agent. This low yield must have been due to the process conditions, mainly in conditions of constant pH throughout the process.

Characterization techniques

Morphologic analysis and microcapsules shell thickness determination – OM and SEM

Morphological and dimensional aspects of the microcapsules were determined through analysis by OM and SEM.

OM enables calculating the average diameter by randomly selecting 300 microcapsules and the ImageJ software program was used to count microcapsules and determine the size distribution profile, as shown in Figure 5.

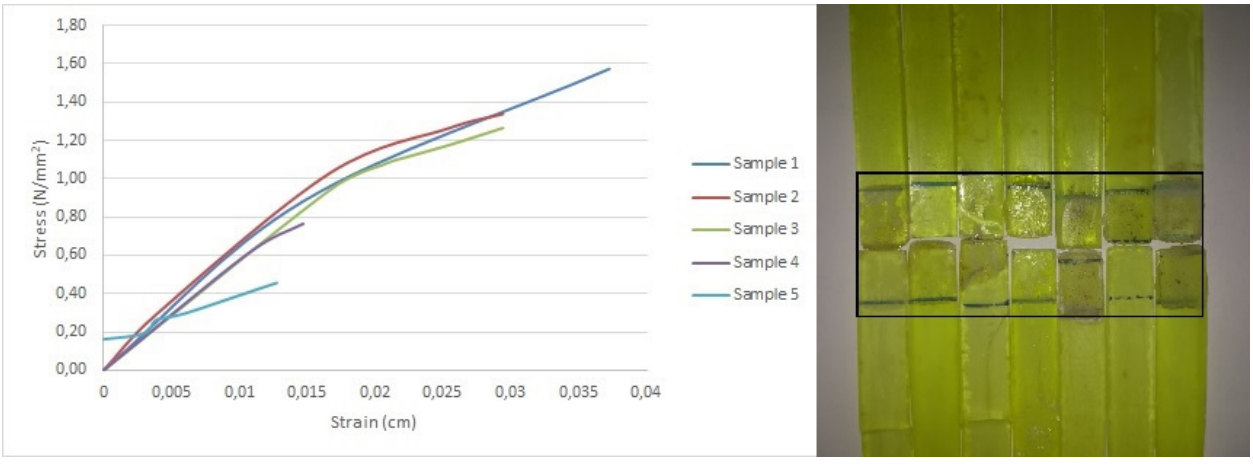


Figure 4. Lap shear results and adhesive cohesive failure in the bonding region.

The results present a dispersion between 30-140 µm with an average value of 69.8 ± 4.9 µm, mostly frequent in the range of 50 and 90 µm. The image obtained by SEM randomly represents an agglomeration of microcapsules, which have a spherical aspect and a rough surface (Figure 6).

Fan & Zhou (2010) studied several reaction parameters during poly urea-formaldehyde (PUF) microcapsule synthesis, and found that a lower pH in the reaction medium collaborates for fast polymerization between urea and formaldehyde. On the other hand, higher pH contributes to forming a smoother external surface.

In the SEM results presented in Figure 7, the average shell thickness could be determined (3.6 ± 0.4 µm) by 10 distinct measures.

According to Brown et al. (2003), PUF microcapsules with an average thickness of 1.6-2.2 µm are robust enough to support synthesis parameters and handling, and are suitable for application in materials with self-healing capacity.

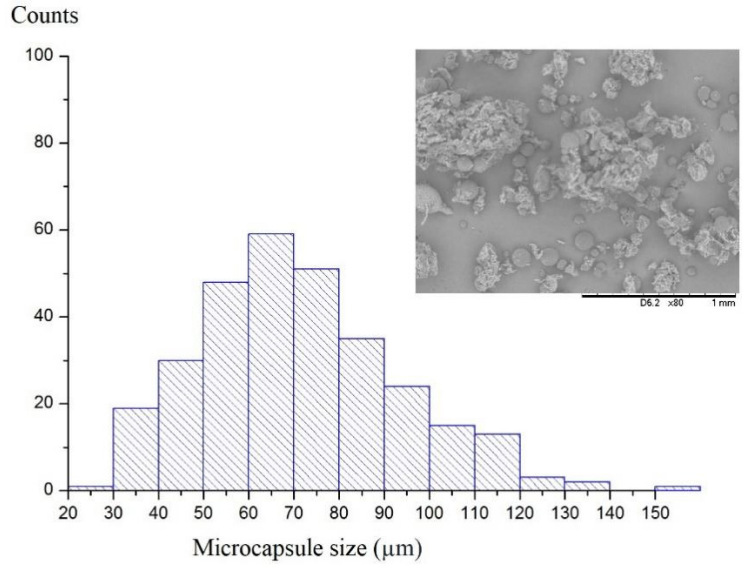


Figure 5. Microcapsules size distribution.

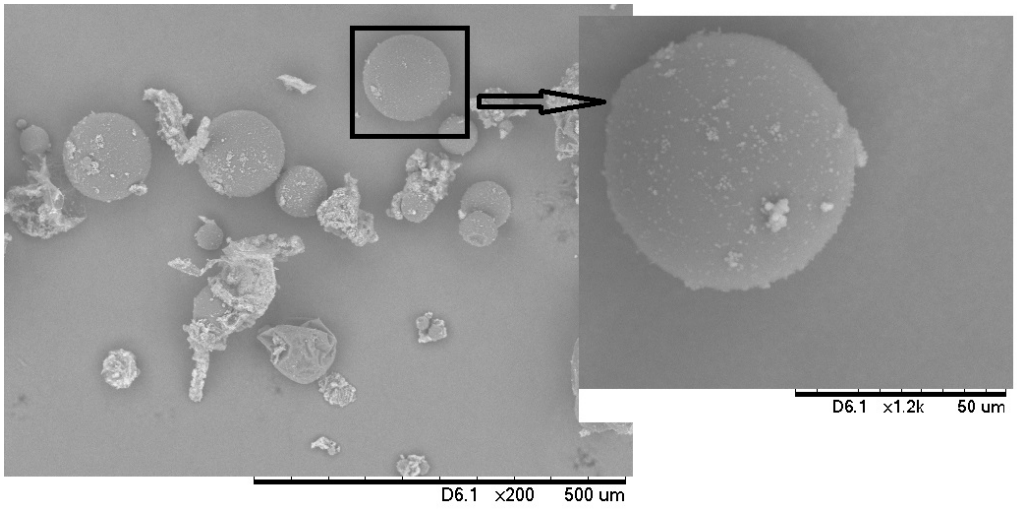


Figure 6. Filled PUF microcapsules with ENB 200x.

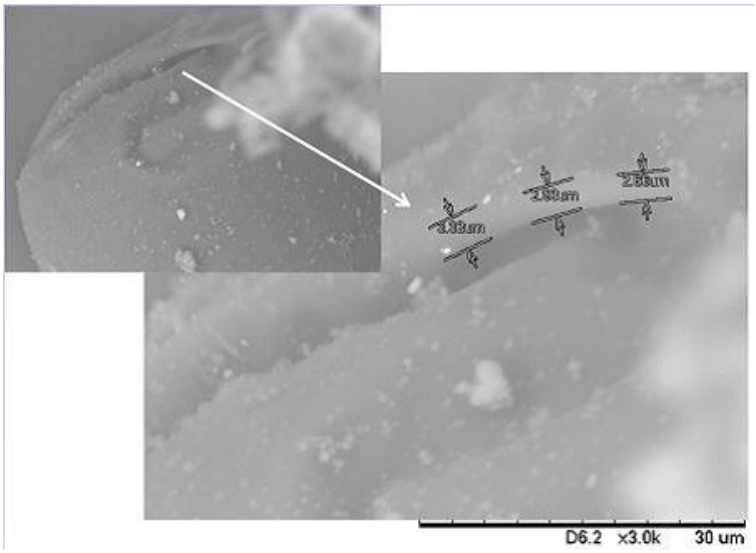


Figure 7. Shell thickness values of some microcapsules filled with ENB (ethylidene norbornene) 3.0Kx.

FT-IR spectroscopy

Figure 8 shows the FT-IR-UATR spectra obtained for hollow microcapsules and for filled microcapsules with ENB.

Characteristic bands of PUF microcapsules were observed. The broad absorption at 3340 cm^{-1} is assigned to stretching of–O-H and –N-H groups. According Zorba et al. 2008, this broadening probably is due to excess PUF prepolymer by-products, such as water and formaldehyde, which allow the formation of hydrogen bond with–NH, -NH_2, and –CH_2OH groups. The band at 1650 cm^{-1} corresponds to stretching of the –C=O group, while the absorption around 1550 cm^{-1} corresponds to the stretching of the –CN and –C=O and bending of NH groups (Smith 1979).

A band at 1700 cm^{-1}, also observed in the hollow microcapsule of PUF spectrum in the stretching range of C=O group, may be assigned to a formaldehyde excessive amount, in accordance with Zorba et al. 2008, or may be assigned to different chemical structures formed. The band at 1650 cm^{-1} should be closer to NH group, resulting in a resonance effect between coupled C=O and N-H, where the electrons pair of N is shared with the C of C=O group, then the double bond assumes a simple bond characteristic, which are in lower wavenumbers than the double ones (Pires et al. 2009, Smith 1979).

The differences of wavenumbers and band shapes between UATR spectra of hollow and filled microcapsule are associated to the different nature of both compounds, but also to the characteristics of analysis by reflection, which has variable path length, influencing the absorption intensity. Lower wavenumbers bands are more intense than higher wavenumbers bands (Magalhães et al. 2020, Ferrão 2001). A recent study (Gao et al. 2022) applied infrared spectroscopy, among other analytical techniques, to evaluate self-healing processes. Although satisfactory results are presented, the data collection procedure is not clarified by the authors and, as discussed in this work, could be a relevant topic in spectra interpretation.

According to ENB characteristics [an organic compound basically formed by ethylene and norbornene (cyclic hydrocarbon)], the absorption at 844 cm^{-1} was assigned to–C=C olefin bond present in the structure of ENB (Figure 9) (Zhaoguo et al. 2008). Shchapin et al. (2007) described that the absorption at 700-910 cm^{-1} characterizes the material. The more

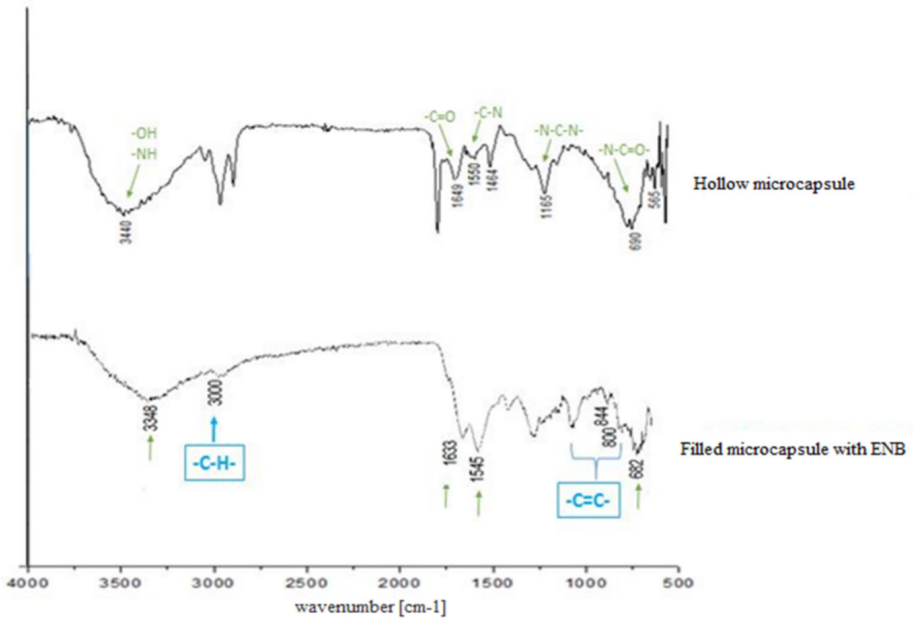


Figure 8. FT-IR-UATR spectra of hollow and filled microcapsules (ENB).

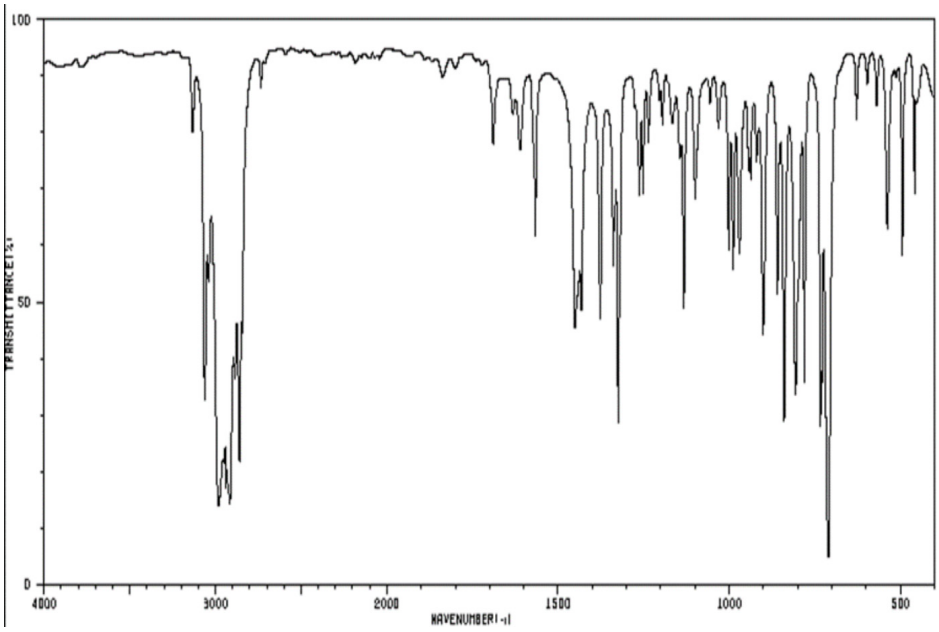


Figure 9. FT-IR-UATR spectrum of ENB (Matsuyama et al. 2009).

intense band at 713 cm^{-1} corresponds to the vibration out of the cis-CH-CH bond plane of the norbornene ring, which can be observed in Figure 9. The band at 3060 cm^{-1} represents carbon (sp^2)-hydrogen bonds, corroborating the presence of norbornene. As observed in Figure 9, some ENB bands were not visible in the spectrum as ENB was encapsulated, then similar spectra were obtained for hollow and filled microcapsules.

As ENB is not an easily handling material due to fast evaporation, the authors opted for evaluate its bands though a literature spectrum (Matsuyama et al. 2009).

PUF bands were highlighted considering the characteristics of UATR technique, which is suitable for surface analysis. However, it was possible to indicate the presence of ENB in the spectrum PUF + ENB, as commented above.

Thermogravimetric analysis (TGA)

According to the results obtained by TGA (Figure 10), the weight loss of hollow and filled microcapsules with ENB presented similar behaviour when submitted to the proposed analysis conditions. Both samples lost around 12% of weight before 130 °C due to the evaporation of residues of small molar weight, probably formaldehyde, in addition to loss of humidity inherent to synthesis, demonstrating the relevance of a pre-drying step before the application. Both samples had a similar profile from 130 °C until the temperature of 230 °C. Microcapsules with ENB lost around 40% of weight in this step, while hollow microcapsules lost 20%.

Despite ENB presenting a boiling temperature of 148 °C, microcapsules filled with ENB had considerable weight loss, around 95% at 230 °C, while hollow microcapsules lost around 25%. This abrupt weight loss occurred due to ENB evaporation, triggered by the increase in the internal pressure, exploding almost all of the microcapsules at the same time. The fact that this explosion occurs in an isotherm is an indication of the thickness homogeneity and consequently the mechanical resistance of the microcapsule shells.

An insignificant weight loss value was observed for the microcapsules until the end of analysis at 700 °C, with 98% lost for filled microcapsules and 85% for hollow microcapsules. Only the PUF degradation reaction occurred in this temperature range as ENB was already evaporated, even in an inert atmosphere (Figure 10).

According to the results obtained for microcapsules filled with ENB, it was possible to quantitatively estimate the weight lost due to the presence of humidity and synthesis residue around 30% up to a temperature of 230 °C. The abrupt explosion of microcapsules occurred as an isotherm around this temperature, releasing around 60% of encapsulated ENB. The weight loss from that point was around 8% due to thermal decomposition of PUF shell, while the final residue for hollow microcapsules was close to 15%.

The use of this system for self-healing application is limited to conditions which do not exceed temperatures of 230 °C, as higher

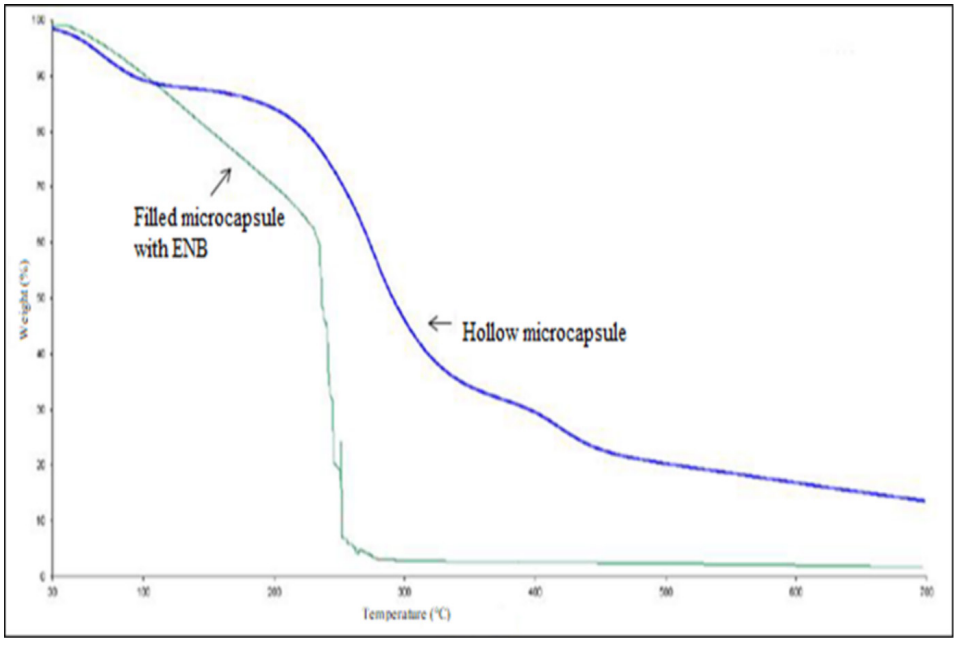


Figure 10. TGA curves for hollow and filled microcapsules.

temperatures can trigger the microcapsules' rupture and the ENB release. The obtained results are similar to those reported by Lee et al. (2004).

CONCLUSION

The compatibility between cured epoxy matrix and poly(ENB) in the presence of Grubb's catalyst was confirmed through a lap shear adhesion test. The synthesis process by oil-in-water emulsion was efficient enough to encapsulate ENB with an average yield of 15%, forming microcapsules with an average size of 69.8 ± 4.9 µm and average shell thickness of 3.6 ± 0.4 µm, enabling the process to occur without rupture. The encapsulation of ENB was proven through FT-IR analysis, while TGA demonstrated that the microcapsules filled with ENB has a limited application in conditions which do not exceed 230 °C, as higher temperatures can trigger the rupture of the microcapsules and ENB release. Based on these results discussed, it is possible to state that the microcapsules are robust enough to support synthesis and handling parameters, and are therefore suitable for applications in materials with self-healing capacity.

Acknowledgments

The authors would like to thank EMBRAER S. A. for the support.This study was also financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brazil (CAPES) - Finance Code 001 and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) - Finance code 301626/2022-07.

REFERENCES

BROWN EN, KESSLER MR, STTOS NR & WHITE SR. 2003. In situ poly(urea-formaldehyde) microencapsulation of dicyclopentadiene. J Microencapsul 20: 719-730.

BROWN EN, SOTTOS NR & WHITE SR. 2002. Fracture testing of a self-healing polymer composite. Exp Mech 42: 372-379.

CARLSON HC & GORETTA KC. 2006. Basic materials research programs at the US Air Force office of scientific research. Mater Sci Eng Part B: Solid State Mater Adv Tech 132: 2-7.

CARRARA AE, RODRIGUES VHS, DUTRA RCL & DUTRA JCN. 2023. Impact assessment of synthesis parameter stirring speed in final physicochemical properties of PU microcapsules incorporated into epoxy matrixes. An Acad Bras Cienc 95: e20201518.

CARVALHO ACM, FERREIRA EPC, BOMIO M, MELO JDD, BARBOSA APC & COSTA MCB. 2019. Influence of synthesis parameters on properties and characteristics of poly (urea-formaldehyde) microcapsules for self-healing applications. J Microencapsul 36: 410-419.

DAS R, MELCHIOR C & KARUMBAIAH KM. 2016. Self-healing composites for aerospace applications. Adv Compos Mater Aerospace Engineering, p. 333-364.

DRY CM & SOTTOS NR. 1992. Passive smart self-repair in polymer matrix composite materials. In: Conference On Recent Advances In Adaptive And Sensory Materials And Their Applications. Albuquerque, NM. *Proceedings* [...]. Bellingham, WA: SPIE, 438-444.

FAN C, TANG J & ZHOU X. 2013. Role of ammonium chloride in preparing poly (urea-formaldehyde) microcapsules using one-step method. J Appl Polym Sci 29: 2848-2856.

FAN C & ZHOU X. 2010. Influence of operating conditions on the surface morphology of microcapsules prepared by in situ polymerization. Colloids Surf A: Physicochem Eng Asp Colloids and Surface A: Phys and Eng Asp 363: 49-55.

FAN C & ZHOU X. 2011. Effect of emulsifier on poly (urea–formaldehyde) microencapsulation of tetrachloroethylene. Polym Bull 67: 15-27.

FERRÃO MF. 2001. Técnicas de Reflexão no Infravermelho Aplicadas na Análise de Alimentos. Tecnol 5: 65-85.

GAO X, SU JF, WANG S & YANG P. 2022. Smart Self-Nourishing and Self-Healing Artificial Skin Composite Using Bionic Microvascular Containing Liquid Agent. Polym 2022 14: 1-20.

GHOSH SK. 2009. Self-healing materials: fundamentals, design, strategies, and applications. Weinheim: Willey-VCH Verlag, 306 p.

HAGER MD, GREIL P, LEYENS C, VAN DER ZWAAG S & SCHUBERT US. 2010. Self-healing materials. Adv Mater 22: 5424-5430.

HIA IL, VAHEDI V & PASBAKHSH P. 2016. Self-Healing Polymer Composites: Prospects, Challenges, and Applications. Polym Rev 56: 225-261.

HUANG M & YANG J. 2011. Facile Microencapsulation of HDI for self-healing anticorrosion coatings. J Mater Chem 21: 11123-11130.

HUYNH TP, SONAR P & HAICK H. 2017. Advanced Materials for Use in Soft Self-Healing Devices. Adv Mater 29: 1-14.

KATOUEIZADEH E, ZEBARJAD SM & JANGHORBAN K. 2019. Investigating the effect of synthesis conditions on the formation of urea–formaldehyde microcapsules. J Mater Res Technol 8: 541-552.

LEE JK, HONG SJ & LIU X. 2004. Characterization of dicyclopentadiene and 5-ethylidene-2-norbornene as self-healing agents for polymer composite and its microcapsules. Macromol Res 12: 478-483.

LEE J, PARK SJ, PARK CS, KWON OS, CHUNG SY, SHIM J, LEE CS & BAE J. 2018 Effect of a surfactant in microcapsule synthesis on self-healing behavior of capsule embedded polymeric films. Polymers 10: 1-13.

MAGALHÃES RF, BARROS AH, TAKEMATS, MM. SANCHES NB, QUAGLIANO JCA & DUTRA RCL. 2020. FT-IR surface analysis of poly [(4-hydroxybenzoic)-ran-(2-hydroxy-6-naphthoic acid)] fiber – A short review. Polym Test 90: 106750.

MARINHO TMA, PONTES VS, MELO JDD & COSTA MCB. 2021. Evaluation of the synthesis variables' effect on the properties of PUF/ENB microcapsules using experimental design. J Polym Res 28: 136. https ://doi.org/10.1007/s10965-021-02494-1.

MATSUYAMA S, KINUGAS S, TANABE K & TAMURA T. 2009. Spectral Database for Organic Compounds, SDBS. National Institute of Advanced Industrial Science and Technology (AIST): Japan.

NESTEROVA T, DAM-JOHANSEN K, PEDERSEN LT & KIIL S. 2012. Microcapsule-based self-healing anticorrosive coatings: capsule size, coating formulation, and exposure testing. Prog Org Coat 75: 309-318.

PIRES DC, STOCKLER-PINTO DVB, SCIAMARELI J, COSTA JR, DINIZ MF, IHA K & DUTRA RCL. 2009. Síntese e caracterização por espectroscopia no infravermelho de agente de ligação à base de hidantoína, utilizado em propelentes compósitos. J Aerosp Technol Manag 1: 177-184.

RODRIGUES VHS, CARRARA AE, ROSSI SS, SILVA LM, DUTRA RCL & DUTRA JCN. 2019. Synthesis, characterization and qualitative assessment of self-healing capacity of PU microcapsules containing TDI and IPDI as a core agent. Mater Today Commun 21: 100698.

SEMPRIMOSCHING C. 2006. enabling self-healing capabilities: a small step to bio-mimetic materials. Noordwijk: European Space Agency, 2006. (Materials Report Number 4476).

SHCHAPIN YUI, MAKHNACH OV, KLOCHIKHIN VL, OSOKIN YUG & NEKHAEV AI. 2007. Chemical behavior of 5-vinyl-2-norbornene, 5-ethylidene-2-norbornene, and related compounds as a key to understanding the specifics of radiation-chemical processes: 2. The structure of polymeric products according to IR data. Pet Chem 47: 92-98.

SMITH AL. 1979. Applied Infrared Spectroscopy, J Wiley & Sons. New York, 314 p.

THEN S, NEON GS & KASIN NHA. 2011. Optimization of Microencapsulation Process for Self-Healing Polymeric Material. Sains Malays 40: 795-802.

ULLAH H, AZIZLI KAM, MAN ZB, ISMAIL MBC & KHAN MI. 2016. The Potential of Microencapsulated Self-healing Materials for Microcracks Recovery in Self-healing Composite Systems: A Review. Polym Rev 56(3): 429-485.

VAN DER ZWAAG S. 2007. Self-Healing Materials - an Alternative Approach to 20 Centuries Materials Science, Springer, Dordrecht, The Netherlands, Ch.1.

WHITE SR, SOTTOS NR, GEUBELLE PH, MOORE JS, KESSLER M, SRIRAM SR & VISWANATHAN S. 2001. Autonomic healing of polymer composites. Nature 409: 794-797.

WU DY, MEURE S & SOLOMON D. 2008. Self-healing polymeric materials: a review of recent developments. Prog Polym Sci 33: 479-522.

YANG J, KELLER MW, MOORE JS, WHITE SR & SOTTOS NR. 2008. Microencapsulation of Isocyanates for Self-Healing Polymers Microencapsulation of Isocyanates for Self-Healing Polymers. Macromolecules 41: 9650-9655.

ZHANG B, JIANG S, DU G, CAO M, ZHOU X, WU Z & LI T. 2019. Polyurea-formaldehyde resin: a novel wood adhesive with high bonding performance and low formaldehyde emission. J Adhes 97(5): 477-492. DOI: 10.1080/00218464.2019.1679631.

ZHANG MQ & RONG MZ. 2011. Self-healing polymers and Polymer composites, Published by J Wiley & Sons, Inc., Hoboken, New Jersey.

ZHAOGUO J, WANG Y, LIU J & YANG Z. 2008. Synthesis and properties of paraffin capsules as phase change materials. Polymer 49: 2903-2910.

ZORBA T, PAPADOPOULOU E, HATJIISSAAK A, PARASKEVOPOULOS KM & CHRISAAFS K. 2008. Urea-formaldehyde resins

characterized by thermal analysis and FTIR method. J Therm Anal Calorim 92: 29-33.

How to cite

ROSSI SS, CARRARA AE, COSTA MCB, MARTINS CLGP, DUTRA RCL & DUTRA JCN. 2023. Synthesis and characterization of Poly(urea-formaldehyde) microcapsules with 5-ethylidene-2-norbornene as self-healing agent and potential use in polymeric composites. An Acad Bras Cienc 95: e20230377. DOI 10.1590/0001-3765202320230337.

Manuscript received on March 25, 2023;
accepted for publication on July 30, 2023

SABRINA SARA ROSSI[1]
https://orcid.org/0000-0002-8779-0257

ALEXANDRE ESTEVÃO CARRARA[2]
https://orcid.org/0000-0002-6286-1493

MARIA CAROLINA B. COSTA[3]
https://orcid.org/0000-0003-3347-7916

CAIO LUCAS G.P. MARTINS[4]
https://orcid.org/0000-0002-4261-1331

RITA DE CÁSSIA L. DUTRA[2]
https://orcid.org/0000-0001-9958-1279

JORGE CARLOS N. DUTRA[2]
https://orcid.org/0000-0002-0923-620X

[1]Embraer, Rodovia Presidente Dutra, s/n, Km 134, 12247-004 São José dos Campos, SP, Brazil

[2]Instituto Tecnológico de Aeronáutica (ITA), Departamento de Ciência e Tecnologia Aeroespacial, Praça Marechal Eduardo Gomes, 50, Vila das Acácias, 12228-900 São José dos Campos, SP, Brazil

[3]Universidade Federal do Rio Grande do Norte, Departamento de Engenharia de Materiais, Campus Universitário Lagoa Nova, Caixa Postal 1524, 59078-970 Natal, RN, Brazil

[4]Universidade Federal de São Carlos, Departamento de Engenharia de Materiais, Rodovia Washington Luiz, s/n, 13565-905 São Carlos, SP, Brazil

Correspondence to: **Jorge Carlos Narciso Dutra**
E-mail: jorge@ita.br

Author contributions

Conceptualization and Methodology: Rossi SS, Costa MCB and Dutra JCN. Investigation: Rossi, SS, Martins CLGP, Carrara AE. Writing – Original Draft: Rossi, SS, Costa MCB and Dutra JCN. Writing – Review and Editing, Carrara AE, Dutra RCL, Costa MCB and Dutra JCN. Funding Acquisition, Costa MCB. Resources: Rossi SS, Costa MCB and Martins CLGP. Supervision: Carrara AE, Dutra RCL, Costa MCB and Dutra JCN.