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Healing agent for the activation of self-healing function at low temperature

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The development of smart composites capable of self-repair in aeronautical structures is still at the planning stage owing to complex issues to overcome. It is critical that self-healing activity functions at low working temperatures which can reach values as low as −50 °C. Also, another problem concerns the components' stability of the proposed composites which are compromised at the cure temperatures necessary for good performance of the composite. Here, we show a multifunctional autonomically healing composite with self-healing function capable at very low temperatures (−50 °C). The self-repair function in this self-healing system is based on the metathesis polymerization of 5-ethylidene-2-norbornene/dicyclopentadiene (ENB/DCPD) blend activated by Hoveyda-Grubbs'1st generation (HG1) catalyst, dispersed at molecular level in the matrix. The formulated material shows a self-healing efficiency of about 72%.

Keywords: self-healing materials; epoxy matrix; ring-opening metathesis

Introduction

Advances in the growing use of polymer composites in aerospace applications explore the possibility in the development of smart materials capable of self-repair. Many realistic strategies have been formulated in the development of self-healing materials; a very promising system for thermosetting resin was proposed by White et al. [1]. It consists of incorporating a microencapsulated healing agent and a catalytic chemical trigger within an epoxy matrix. An approaching crack ruptures embedded microcapsules releasing the polymerizer agent into the crack plane through capillary action. Polymerization of the healing agent is triggered by contact with the embedded catalyst, bonding the crack faces. In these systems, the efficiency of self-repair function in terms of trigger, speed, and yield is related to ring-opening metathesis polymerization (ROMP) of the healing agent by appropriate catalysts. The healing agent is a microencapsulated liquid monomer that must include a long shelf life, prompt deliverability, high reactivity, and low volume shrinkage upon polymerization,[2] but also a high degree of cross-linking. This last aspect was analyzed in detail in this paper also considering that, for aeronautic applications, it is critical that the self-healing activity functions at low working temperatures which can reach values as low as −50 °C.

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In this work, ring-opening metathesis polymerizations activated at very low temperatures have been studied in order to apply these reactions in the development of self-healing aeronautic materials. The self-repair function is based on the metathesis polymerization of a healing agent based on the blend of two polyolefins (ENB/DCPD blend) activated by Hoveyda-Grubbs'1st generation catalyst. DCPD was added to ENB with the aim of increasing the cross-linked fraction of the metathesis products. Issues related to phase separation of the blend (ENB/DCPD) at low temperatures were also analyzed.

Experimental

Materials

The blend investigated in this work to be used as 'healing agent' is a mixture of ENB and DCPD. Two different compositions were investigated: ENB(97.5%)/DCPD(2.5%) and ENB(95%)/DCPD(5%).

Cross-linked fraction of metathesis polymer was determined, according to the ASTM method D2765-84, as the percent of the original weight of the sample extracting for 6 h in boiling decahydronaphthalene (decaline, a mixture of cis and trans isomers). The extraction was followed by drying at 150 °C in a vacuum oven. As suggested by this standard method, to avoid polymer degradation during the extraction procedure, an antioxidant agent has to be used. In particular, 2,2′-methylene-bis-(4-methyl-6-tert-butyl phenol) was dissolved in decaline (1 wt%) before the extraction tests. To carry out the phase separation tests, the following procedure was used: a thermostatic bath was prepared by dipping a cooling coil (cryogen-cooled) in a dewar flask containing ethanol (temperature set point = −50 °C). Control of the temperature was performed by immersion in the dewar flask of a thermocouple directly connected to the cryostat. Once the set point temperature was reached, two vials containing the ENB/DCPD blends (2.5 and 5% by wt of DCPD) were immersed in the thermostatic bath. Periodically the vials were removed from the thermostatic bath for visual inspection.

Ispired by Brown, White et co. studies, for the manufacturing of self-healing samples in this research, we used a modified version of tapered double-cantilever beam (TDCB) geometry with the dimensions indicated in Figure 1.[3–5]

Fracture tests for self-healing efficiency evaluation were conducted by a dynamometer INSTRON 4301 with a constant crosshead speed of 0.5 mm/min.

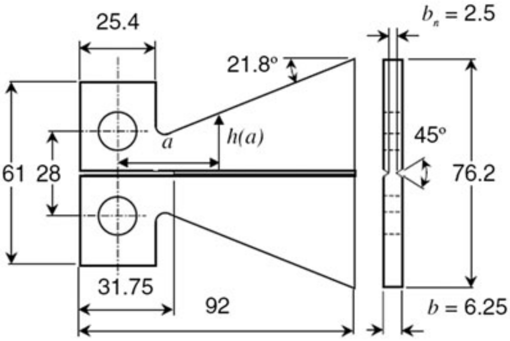

Figure 1. TDCB geometry and dimensions (mm).

The ^{1}H NMR spectra were recorded at room temperature, using a Bruker AVANCE-III 400 instrument.

Results and discussion

Healing agent: phase separation tests

At low temperatures, it was necessary to carry out phase separation tests on this blend because the two monomers have very different melting points.

Phase Separation Tests for DCPD + ENB blends with different percentage of DCPD (2.5 and 5% of DCPD) at −50 °C were performed.

Figure 2 shows the blends (at −50 °C) after 1 h. The blends were observed for another 4 h and no phase separation was observed at this temperature.

These tests were also performed increasing the weight percentage of DCPD in the blends. The results have demonstrated phase separation after 1 h at −50 °C for ENB (90%)/DCPD(10%) and ENB(85%)/DCPD(15%) blends; for this reason our attention was focused on blends with a lower percentage of DCPD.

Healing agent: evaluation of cross-linked fraction of metathesis products

An important aspect concerning the ROMP of healing agent is related to the degree of cross-linking of the metathesis products. In this paper, the degree of cross-linking was evaluated using HG1 catalyst, making extraction of the insoluble fraction in cis-trans decahydronaphthalene (decaline) as described in the experimental part.

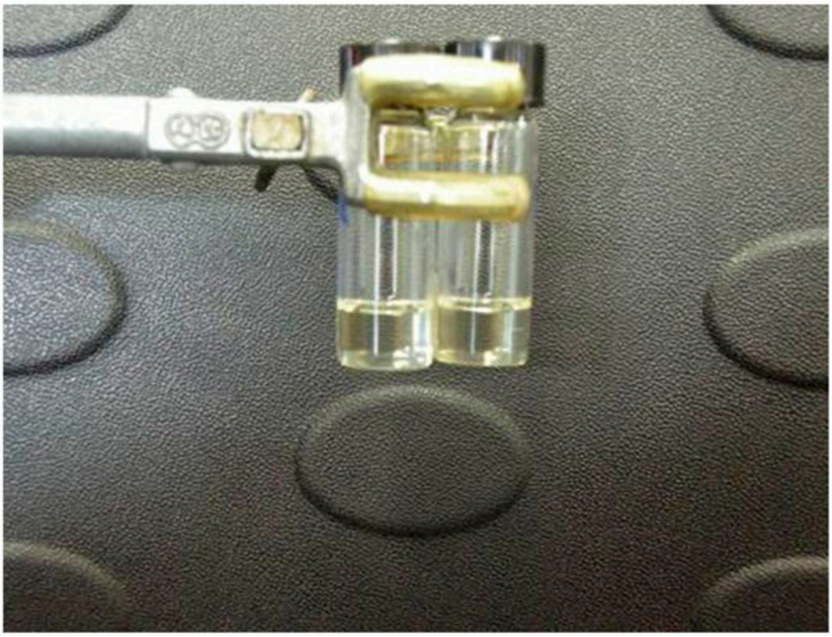

Figure 2. ENB(97.5%)/DCPD(2.5%) and ENB(95%)/DCPD(5%) after 1 h at –50 °C.

Table 1. Cross-linked fraction of metathesis product of ENB/DCPD blends.

Blend	Temp. (°C)	Reac. time (min)	DCPD (%)	Yield (%)	Insoluble fract. (%)	Soluble fract. (%)
(ENB 100%)	25	0.5	0	96	60	40
(ENB 97.5%)	25	0.66	2.5	99	81	19
(ENB 95%)	25	0.66	5	99	87	13
(ENB 100%)	−50	450	0	99	10	90
(ENB 97.5%)	−50	450	2.5	80	76	24
(ENB 95%)	−50	450	5	77	75	25

Table 1 shows the cross-linked fraction of metathesis products of ENB/DCPD blends for ROMP reaction carried out at different temperatures.

Table 1 shows that the cross-linked fraction at 25 °C for the blend with 5% of DCPD is 87%, whereas for ENB(100%) is 60%; at low temperature (−50 °C), the cross-linked fraction for the same blend is 75%, whereas for ENB(100%) is 10%. In conclusion, the blend ENB(95%)/DCPD(5%) seems to meet all the requirements to be used as healing agent for self-healing function at very low temperature. This healing agent has been encapsulated in nanometric vessels to formulate self-healing epoxy resins.

Microcapsule manufacture

The microcapsules, with the outer shell containing poly(urea-formaldehyde) and the inner shell of ethylene maleic anhydride copolymer (EMA), were prepared by *in situ* polymerization in an oil-in-water emulsion in accord with a procedure already described in previous papers [6]. The only change, with respect to the aforementioned synthesis procedure, consisted of using a blend ENB/DCPD. According to such a procedure, a desired dimension range can be selected by a suitable variation of the process parameters during the synthesis stage, and/or with the use of molecular sieves. For example, by setting the process parameters as described by other authors [6–8], we obtained the microcapsules used for our self-healing epoxy specimen. The efficiency of the healing agent microencapsulation was verified by ^{1}H NMR and a gas chromatography analysis of the chloroform solution obtained from the extraction of the pounded microcapsules.

The capsules used to manufacture the self-healing system are shown in Figure 3.

The analysis of the capsule size distribution shows that the largest part is characterized by a spherical form with average diameter of about 500–600 nm.

Self-healing sample

T*he epoxy matrix composite* was prepared by mixing an epoxy (Bisphenol A diglycidyl ether – Acronym BADGE) (Trade name Epon 828) with a reactive diluent (1,4-Butanediol-diglycidyl ether – Acronym BDDGE) which was used in small percentage to reduce the viscosity of the material, to improve handling and ease of processing, and to optimize consequently performance properties. These resins, both containing an epoxy, were obtained by Sigma-Aldrich. *The curing agent* investigated for this study is an anionic initiator phenol, 2,4,6-tris[(dimethylamino) methyl] (Trade name Ancamine K54). This hardener agent was already used for self-healing formulations.[1,9–13] The HG1 catalyst also obtained from Aldrich was used to manufacture the epoxy matrix. It

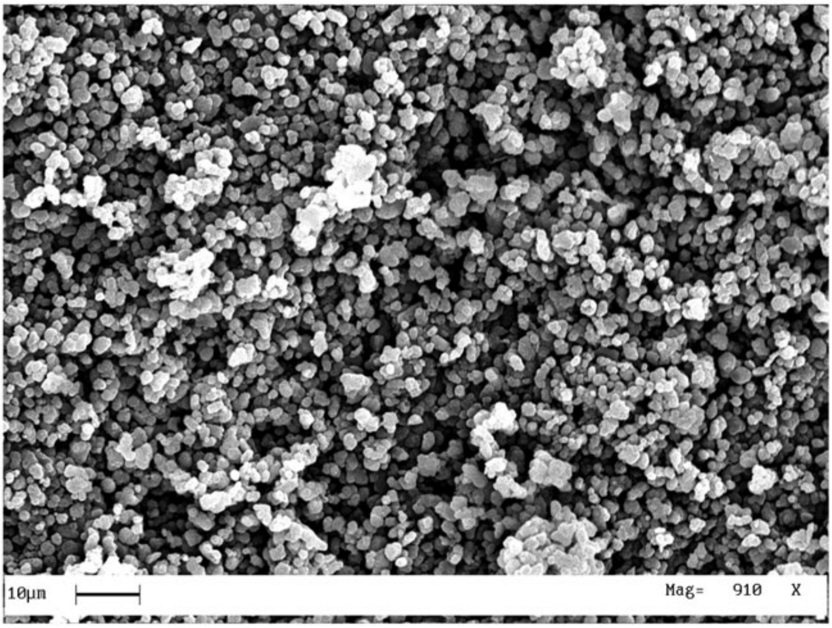

Figure 3. Scanning electron microscope (SEM) image of micro- and nanocapsules at magnification 910$^{\times}$.

was dispersed at molecular level into the epoxy matrix. This last choice is due to the need to overcome a drawback in the employment of the ROMP catalysts which is related to the local availability of the catalyst particles. In particular, the catalyst for the metathesis reaction is embedded in the precursors of the epoxy matrix in the form of solid particles, i.e. powders with different morphology and crystallographic modifications.[14] In practice, the effective concentration of the catalyst depends on the availability of the aforesaid particles at the level of the fracture and on the rate of dissolution of the catalyst in the reactive monomer (healing agent) within the polymer matrix. Even with high concentrations of catalyst particles exposed at the level of the fracture, the effective concentration of the catalyst could be relatively low because of limited rates of dissolution of the catalyst. The rate of dissolution of the catalyst depends not only on the chemical nature of the various components, but also on morphological and structural characteristics of the catalyst particles. It has been found in practice that the presence of the catalyst in the form of crystalline powders has some critical aspects relating to the uniform availability of the catalyst in all the zones in which a microcrack can potentially develop, compromising the effectiveness of the self-healing process.[15]

The self-healing samples were obtained with the following procedure:

(1) preparation of the blend composed of epoxy precursor (E) and reactive diluent (B) – mechanical stirring at 60 °C for 10 min;
(2) solubilization of HG1 catalyst particles in EB mixture – mechanical stirring at 90 °C until complete solubilization of the catalyst;
(3) addition of ENB/DCPD-filled nanocapsules – mechanical stirring at 60 °C for 10 min;

(4) addition of the hardener (ancamine K54) – mechanical stirring at 60 °C for 5 min;
(5) pouring of the mixture into molds;
(6) two-stage curing cycle: a first isothermal stage at 125 °C (1 h) and a second isothermal stage at 170 °C (2 h).

In this paper, EBA indicates the epoxy matrix composed of E (epoxy precursor – Epon 828), B (reactive diluent – BDDGE), and A (hardener – Ancamine K54); while EBA-HG1 indicates the epoxy formulation containing HG1 (Hoveyda Grubbs 1st generation catalyst) particles; EBA-HG1-CAP ENB/DCPD (170) indicates the formulation of EBA-HG1, where ENB/DCPD-filled nanocapsules were added and the number between the brackets indicates the temperature in the second step of the curing cycle.

A simplified scheme of the self-healing formulation is shown in Figure 4.

In order to avoid adhesion phenomena that normally are established between the resin and mold, and to facilitate the extraction of the sample after the curing process, silicone rubber molds were manufactured to obtain TDCB specimens.

Self-healing efficiency assessed by fracture test

For quasi-static fracture conditions crack healing efficiency, η (see Equation (1)) is defined as the ability of a healed sample to recover fracture toughness [16]:

$$\eta = \frac{K_{\text{IChealed}}}{K_{\text{ICvirgin}}} \tag{1}$$

where K_{ICvirgin} is the fracture toughness of the virgin specimen and K_{IChealed} is the fracture toughness of the healed specimen. Using the protocol already established in literature [1,17] healing efficiency is measured by carefully controlled fracture experiments

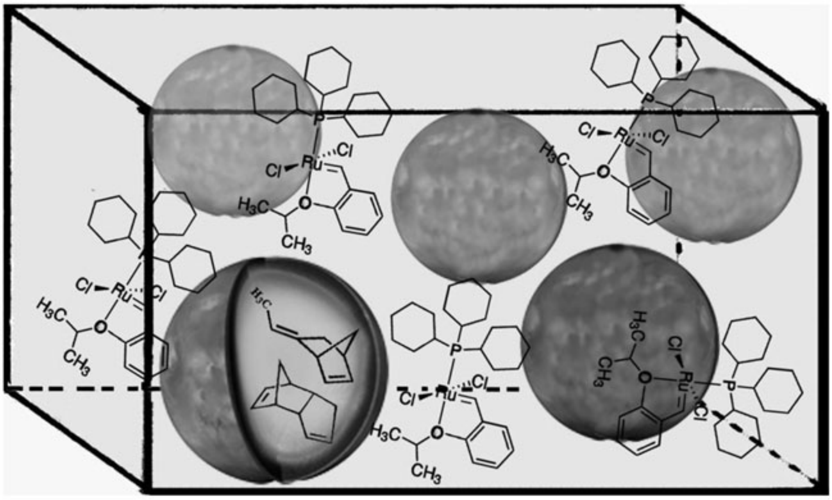

Figure 4. Scheme of self-healing formulation which includes capsules containing the blend (ENB/DCPD) and a catalyst for the polymerizer (HG1).

for both the virgin and the healed sample. These tests utilize a TDCB geometry [3] which ensures controlled crack growth along the centerline of the specimen and provides a crack length independent measure of the fracture toughness. Healing evaluation begins with a virgin fracture test of an undamaged TDCB sample. A precrack is introduced to sharpen the crack tip. The sample is then mounted on a load frame and loaded under displacement control causing the precrack to propagate along the centerline of the sample until failure.

The crack is then closed and allowed to heal at room temperature with no external intervention. After healing, the sample is loaded again until failure. With this geometry, the efficiency measurement simply requires knowledge of the critical fracture load, P_C, of virgin and healed specimen (Equation (2)):

$$\eta = \frac{P_{\mathrm{Chealed}}}{P_{\mathrm{Cvirgin}}} \tag{2}$$

Equation (2) can be derived from Equation (1) by considering that $K_{IC} = \alpha P_C$ where $\alpha = 11.2 \times 10^3\ \mathrm{m}^{-3/2}$, for the TDCB used geometry. This procedure has been recognized to be very effective to measure the healing efficiency by many authors [1,16,18–22].

Values of healing efficiency (η) were calculated using equation 2. Figure 5 shows the load-displacement curves for a self-healing sample cured up to 170 °C. The sample was manufactured with a percentage of microcapsules and catalyst of 20 wt% and 5 wt %, respectively, and as healing agent a blend of ENB/DCPD with a percentage of DCPD 5 wt% was used.

The calculated healing efficiency was found to be 72% for the sample of Figure 5. Other three tests of the self-healing efficiency on the same formulation showed healing efficiencies of 71, 66, and 69%. This value of 69 ± 3 was lower than the healing efficiencies found for self-healing epoxy resins manufactured using solid catalyst particles (also using microcapsules with different healing agents and morphological parameters).[13,20–23] Additional experiments were performed on this issue for better understanding the reason for the lower efficiency. Our tests have evidenced that solid catalyst particles in the epoxy mixtures at high temperature (between 130 and 170 °C) retain an intact heart of catalyst particles, which are not deactivated in contact with the oxirane rings of the epoxy matrix. In the case of the catalyst particles solubilized at molecular level, the catalyst particles which are locally in contact with the oxirane rings (during the curing reactions) deactivate; hence, reducing the actual amount of active catalyst as described in the next paragraph.

Study of the catalytic activity of HG1 in presence of oxirane rings

HG1 catalyst powder was solubilized at molecular level in cyclohexene oxide to test HG1 reactivity with the epoxy groups in high concentration (without other components of the resin). To better analyze the behavior of the epoxides with the catalyst, we have used a simpler monomer as an epoxide: the cyclohexene oxide. The reactivity of this monomer with the catalyst was analyzed at different compositions and temperature by means of ^{1}H NMR.

The ^{1}H NMR spectra of Hoveyda-Grubbs I, cyclohexene oxide, and of mixtures containing both HG1 and cyclohexene oxide in a molar ratio 1/1 were recorded at room

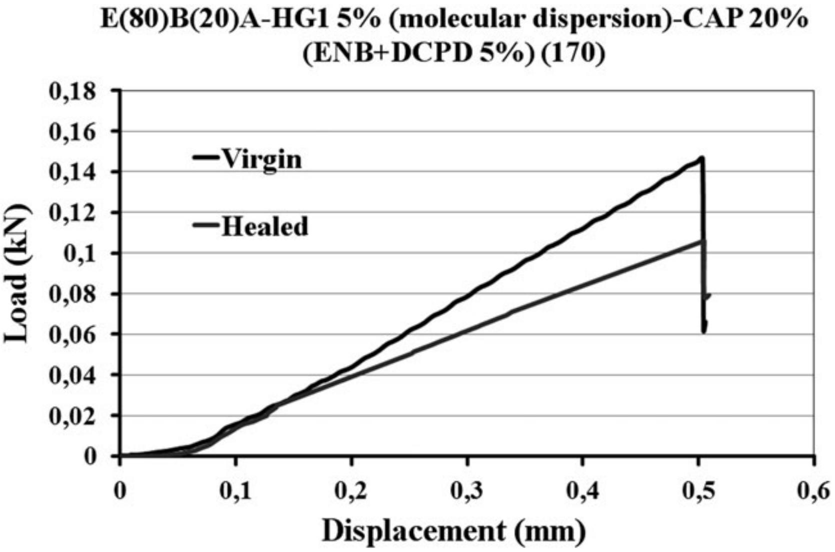

Figure 5. Load-displacement curves for virgin (black curve) and healed (grey curve) samples.

temperature; the δ values were given in ppm, on samples dissolved in 1,1,2,2-tetrachloroethane-d2 (TCDE). Figure 6 shows the spectra of Hoveyda-Grubbs I and cyclohexene oxide recorded at room temperature.

In Figure 7, variable-temperature (VT) ^{1}H NMR experiments in the range $80 < T < 140$ °C of the mixture containing HG1 and cyclohexene oxide in a molar ratio 1:1 are reported. Spectrum at 80 °C (Figure 7(a)) shows all the signals characteristics of HG1 and cyclohexene oxide, highlighting that no reaction take place between these two compounds.

At higher temperatures, the signal at 17.45 ppm due to proton on alkylidene carbon of HG1 decreases, as well as the signal at 3.09 ppm attributable to protons of methine carbons of cyclohexene oxide, evidently because a reaction occurs between the alkylidene and the epoxide ring. At 140 °C (Figure 7(d)), the reaction is practically completed, being the signals of the proton on alkylidene carbon of HG1 and the signal of protons of methine carbons of cyclohexene oxide barely noticeable.

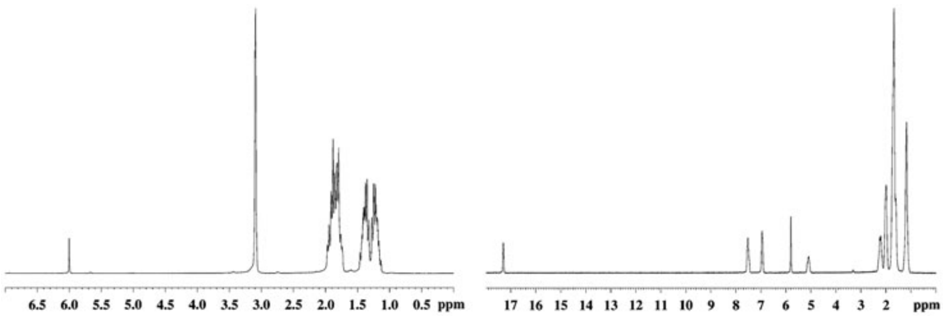

Figure 6. ^{1}H NMR spectra of Hoveyda-Grubbs I catalyst (on the right side) and cyclohexene oxide (on the left side) dissolved in 1,1,2,2-tetrachloroethane-d2 TCDE.

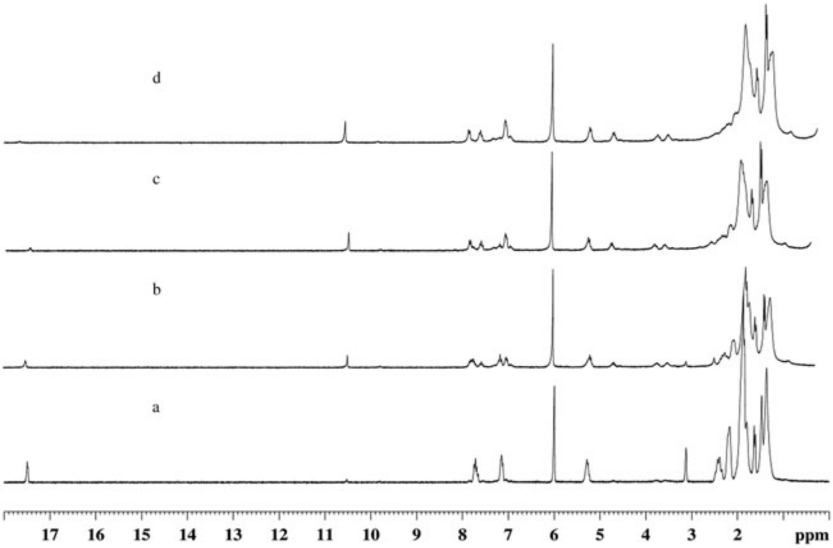

Figure 7. VT ^{1}H NMR experiments on a mixture containing HG1 and cyclohexene oxide in a molar ratio 1:1 ((a) 80 °C, (b) 100 °C, (c) 120 °C, and (d) 140 °C).

It is worth to note that NMR spectra of both the HG1 catalyst and cyclohexene oxide kept for 35 min at 140 °C show all the characteristic signal indicating that no thermal decomposition occurs.

The effect of the concentration on the ^{1}H NMR results with increasing the epoxy compound has also been analyzed and ^{1}H NMR spectrum of a mixture of Hoveyda-Grubbs I catalyst with cyclohexene oxide (molar ratio 1/35) after a permanence for 1 hour at 140 °C is shown in Figure 8.

In this case, we observe the absence of the characteristic resonance signal of the benzylidene proton (Ru = CH-Ph) at 17.45 ppm. Moreover, we again observe the resonance signal at 3.09 ppm due to the protons on the epoxy carbons; this result is obvious considering that the cyclohexene oxide is in large excess. Evidently, the reaction between epoxide ring and alkylidene of rutenium compound is equimolecular.

The addition of a drop of healing agent (5-ethylidene-2-norbornene – ENB) to this mixture shows that the catalyst is deactivated, as can be seen from the absence of the solid film formation due to the metathesis reaction. We consistently observed catalyst deactivation with the complete disappearance of the alkylidene signal in the ^{1}H NMR spectrum.

Thus, the last results highlight that a deactivation of the HG1 catalyst occurs at 140 °C due to a reaction between the catalyst and the cyclohexene oxide.

Of course, the deactivation of the catalyst due to the oxirane rings is facilitated in the mixture HG1/cyclohexene oxide with respect to the deactivation of the catalyst due to the contact with oxirane rings in the mixture HG1/ epoxy mixture, due to the higher concentration of oxirane rings in the mixture with cyclohexene oxide. In the epoxy mixture, part of the catalyst particles can survive up to 170 °C, due the accidental lack of direct contact between molecules of the complex (catalyst) and oxirane rings of the epoxy mixture. Therefore, even if the deactivation of the HG1 catalyst occurs at 130 °C due to a reaction between the catalyst and the oxirane rings, for catalyst molecules in which contact does not occur, the self-healing mechanisms can be active up to

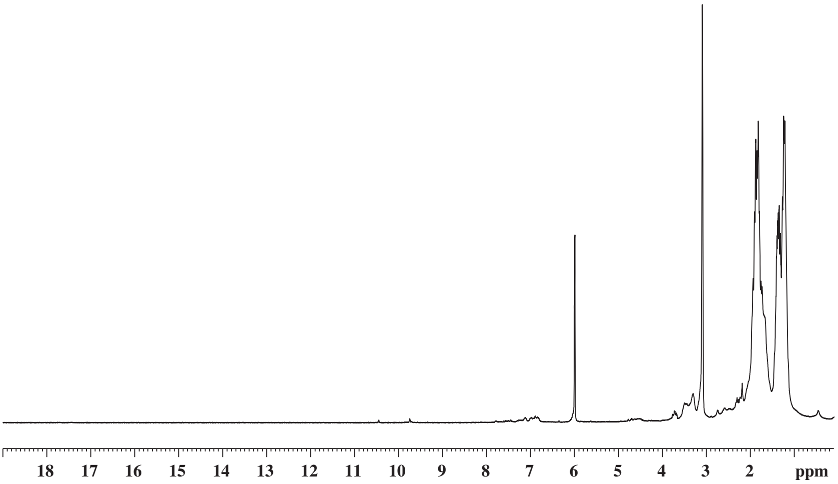

Figure 8. ^{1}H NMR spectra of HG1 and cyclohexene oxide in TCDE kept for 35 min at 140 °C.

170 °C with a reduced self-healing efficiency because of the reduction in the actual amount of catalyst.

Conclusions

We have formulated, prepared, and characterized a multifunctional autonomically healing composite with a self-healing efficiency of 72%. The self-repair function in this new self-healing system is based on the metathesis polymerization of a blend ENB/DCPD activated by Hoveyda-Grubbs'1st generation catalyst solubilized at molecular level inside the epoxy matrix. The self-healing epoxy mixture was cured up to 170 °C to explore the possibility to use high temperatures for the curing reactions. The results demonstrate lower healing efficiency with respect to the catalyst embedded in the form of solid particles in the microencapsulated self-healing epoxy mixtures.[13,20–23] Experimental analysis highlighted that solid catalyst particles in the epoxy mixtures at high temperature retain an intact heart of catalyst particles, which are not deactivated in contact with the oxirane rings of the epoxy matrix. Instead, in the case of the catalyst particles solubilized at molecular level, the catalyst particles which are locally in contact with the oxirane rings (during the curing reactions) deactivate; hence, reducing the actual amount of catalyst active in the ROMP reactions.

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References

[1] White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, Sriram SR, Brown EN, Viswanathan S. Autonomic healing of polymer composites. Nature. 2001;409:794–797.

[2] Keller MW, White SR, Sottos NR. A Self-healing poly(dimethyl siloxane) elastomer. Adv. Funct. Mater. 2007;17:2399–2404.

[3] Brown EN, Sottos NR, White SR. Fracture testing of a self-healing polymer composite. Exp. Mech. 2002;42:372–379.

[4] Rule JD, Sottos NR, White SR, Moore JS. The chemistry of self healing polymers. Educ. Chem. 2005;42:130–132.

[5] Brown EN, White SR, Sottos NR. Retardation and repair of fatigue cracks in a microcapsule toughened epoxy composite-Part II: In situ self-healing. Compos. Sci. Technol. 2005; 65:2474–2480.

[6] Brown EN, Kessler MR, Sottos NR, White SR. In situ poly(urea-formaldehyde) microencapsulation of dicyclopentadiene. J. Microencapsul. 2003;20:719–730.

[7] Yin T, Rong MZ, Wu J, Chen H, Zhang MQ. Healing of impact damage in woven glass fabric reinforced epoxy composites. Compos. Part A: Appl. Sci. Manuf. 2008;39:1479–1487.

[8] Brown EN, White SR, Sottos NR. Microcapsule induced toughening in a self-healing polymer composite. J. Mater. Sci. 2004;39:1703–1710.

[9] Guadagno L, Longo P, Raimondo M, Mariconda A, Naddeo C, Sorrentino A, Vittoria V, Iannuzzo G, Russo S, Calvi E. Process for preparing a self-healing composite material. US patent 20100168280 A1. 2010 Jul 1.

[10] Guadagno L, Raimondo M. Infrared spectroscopy – materials science, engineering and technology, “Use of FT/IR analysis to control the self-healing functionality of epoxy resins”. In: Infrared spectroscopy – materials science, engineering and technology. Theophanides T, editor. Rijeka: InTech; 2011. p. 285–300.

[11] Guadagno L, Longo P, Raimondo M, Naddeo C, Mariconda A, Vittoria V, Iannuzzo G, Russo S. Use of Hoveyda-Grubbs’ second generation catalyst in self-healing epoxy mixtures. Compos. Part B: Eng. 2011;42:296–301.

[12] Guadagno L, Longo P, Raimondo M, Naddeo C, Mariconda A, Sorrentino A, Vittoria V, Iannuzzo G, Russo S. Cure behavior and mechanical properties of structural self-healing epoxy resins. J. Polym. Sci., Part B: Polym. Phys. 2010;48:2413–2423.

[13] Guadagno L, Raimondo M, Naddeo C, Longo P. Self-healing polymers: from principles to applications, “Application of Self-Healing Materials in Aerospace Engineering”. In: Self-healing polymers: from principles to applications. Binder WH, editor. Weinheim: Wiley-VCH Books; 2013. p. 401–412.

[14] Wilson GO, Caruso MM, Reimer NT, White SR, Sottos NR, Moore JS. Evaluation of ruthenium catalysts for ring-opening metathesis polymerization-based self-healing applications. Chem. Mater. 2008;20:3288–3297. “Supporting Information”.

[15] Guadagno L, Raimondo M, Naddeo C, Mariconda A, Corvino R, Longo P, Vittoria V, Russo S, Iannuzzo G. Process for preparing self-healing composite materials of high efficiency for structural applications. US Patent 20110118385 A1. 2011 May 19.

[16] Mostovoy S, Croseley PB, Ripling EJ. Use of crack-line-loaded specimens for measuring plain-strain fracture toughness. J. Mater. 1967;2:661–681.

[17] Wool RP, O’Conner KM. A theory of crack healing in polymers. J. Appl. Phys. 1981;52:5953–5963.

[18] Kirkby EL, Rule JD, Michaud VJ, Sottos NR, White SR, Månson JAE. Embedded shape-memory alloy wires for improved performance of self-healing polymers. Adv. Funct. Mater. 2008;18:2253–2260.

[19] Guadagno L, Raimondo M, Iannuzzo G, Russo S. Self-healing structures in aerospace applications. AIP Conf. Proc. 2010;1255:267–269.

[20] Raimondo M, Guadagno L. Healing efficiency of epoxy-based materials for structural applications. Polym. Compos. 2013;34:1525–1532.

[21] Guadagno L, Raimondo M, Naddeo C, Longo P, Mariconda A. Self-healing materials for structural applications. Polym. Eng. Sci. 2014;54:777–784.

[22] Raimondo M, Guadagno L. Healing efficiency of epoxy-based materials for structural application. AIP Conf. Proc. 2012;1459:223–225.

[23] Guadagno L, Raimondo M, Naddeo C, Longo P, Mariconda A, Wolfgang WH. Healing efficiency and dynamic mechanical properties of self-healing epoxy.systems. Smart Mater. Struct. 2014;23:045001 (11 p.).