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Supplementary Materials

Effect of Temperature on the Functionalization Process of Structural Self-Healing Epoxy Resin

Luigi Vertuccio [1], Elisa Calabrese [2], Marialuigia Raimondo [2], Michelina Catauro [1], Andrea Sorrentino [3], Carlo Naddeo [2], Raffaele Longo [2] and Liberata Guadagno [2,*]

[1] Department of Engineering, University of Campania "Luigi Vanvitelli", Via Roma 29, 81031 Aversa, Italy; luigi.vertuccio@unicampania.it (L.V.); michelina.catauro@unicampania.it (M.C.)
[2] Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II, 132, 84084, Fisciano, Italy; elicalabrese@unisa.it (E.C.); mraimondo@unisa.it (M.R.); cnaddeo@unisa.it (C.N.); rlongo@unisa.it (R.L.)
[3] Institute for Polymers, Composites, and Biomaterials (IPCB-CNR), Via Previati n. 1/E, 23900 Lecco, Italy; andrea.sorrentino@cnr.it
* Correspondence: lguadagno@unisa.it

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Section 1

Experimental Methods

FTIR Spectra of the cured epoxy resin were collected by reducing into powder parts of the samples and dispersing them in KBr pellets, used as a carrier. Infrared spectra of liquid samples were obtained by spreading a thin layer of material on the KBr pellet. The spectra were acquired using a Bruker Vertex 70 FTIR-spectrophotometer (Bruker Optics Inc. Billerica, MA, USA), in the range of 4000–400 cm^{-1}, with a resolution of 2 cm^{-1} (32 scans collected), and they were obtained in absorbance.

Thermal measurements were performed by Thermogravimetric analyses (TGA) and Differential Scanning Calorimetry (DSC). In TGA analysis, the weight loss was recorded as a function of the temperature. The scan rate was fixed at 10°C/min, and performed in the range between 25° and 900°C, after having dispersed about 7-10 mg of samples in ceramic crucibles. DSC measurements were performed in order to evaluate the curing degree (DC) of the epoxy materials by using Equation 1,

where ΔH_T is the total heat of the reaction of the uncured material and ΔH_{Res} is the residual heat of reaction of the partially cured epoxy resin. ΔH_T was determined by per

$$DC = \frac{\Delta H_T - \Delta H_{Res}}{\Delta H_T} \times 100 \quad (1)$$

forming the tests on uncured formulations and ΔH_{Res} was determined from the measurement carried out on cured samples. All samples were scanned with a rate of 10 °C/min, in the temperature range from 0 °C to 300 °C.

Thermogravimetric analyses (TGA) were performed through a Mettler TGA/SDTA 851 thermal analyzer, in airflow.

Differential Scanning Calorimetry (DSC) analyses were carried out by using a Mettler DSC 822/400 (Mettler-Toledo Columbus, OH, USA) thermal analyzer.

To perform Dynamic Mechanical Analysis (DMA), solid samples with dimensions 3×4×35 mm^3, were tested by applying a flexural deformation in three points bending geometry. The displacement amplitude was set to 0.1% and the frequency to 1 Hz. The range of temperature analyzed was from 30 °C to 300 °C at the constant scanning rate of 3 °C min^{-1}. The glass transition temperatures were obtained from the maximum in the loss

tangent spectrum (tan δ versus temperature) by taking the derivative of tan δ with respect to temperature.

To evaluate the Self-healing efficiency (η) using the fracture test with a tapered double cantilever beam (TDCB) geometry method, samples characterized by shape and dimensions shown in Figure S1 have been employed.

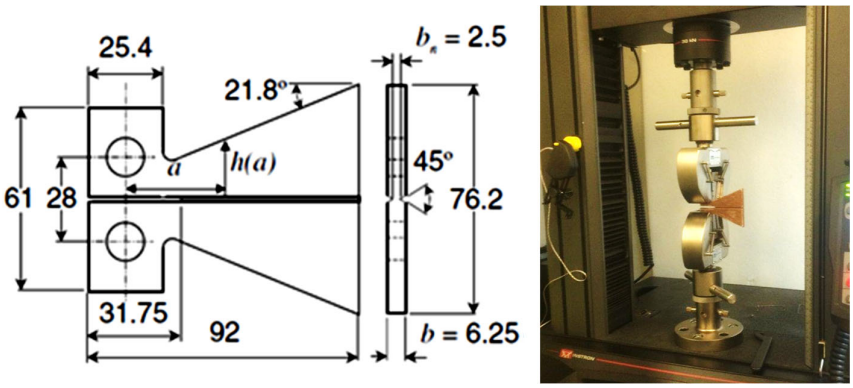


Figure S1. Dimensions of the TDCB geometry specimen (on the left); EP-R-160 sample located in the INSTRON instrument (on the right). Numerical values of the lengths are expressed in mm.

Section 2

DSC Results

Figure S2 shows the DSC curves of the samples EP-R-160, EP-R-160-DBA, EP-R-160-T, EP-R-160-M, before the curing process (after the functionalization reaction) and after the curing process.

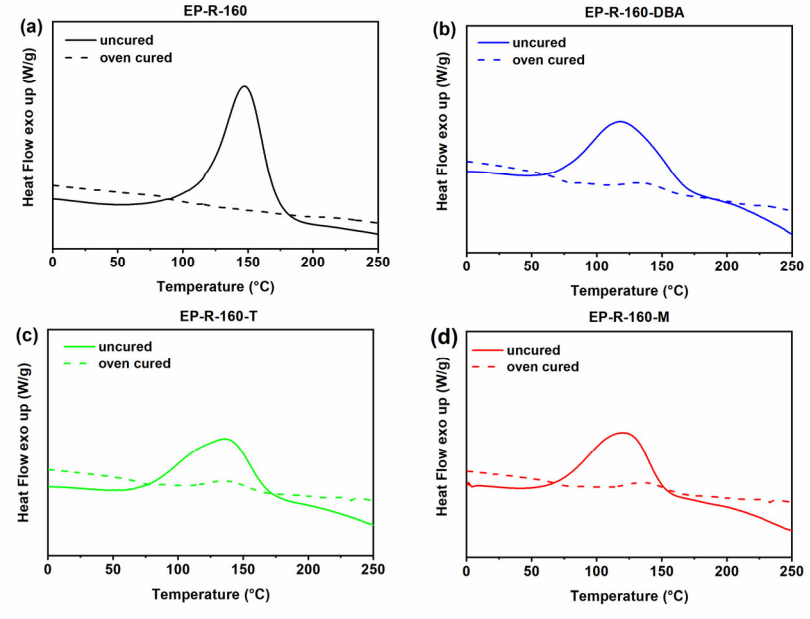


Figure S2. DSC curves of the samples EP-R-160, EP-R-160-DBA, EP-R-160-T, EP-R-160-M, before the curing process (after the functionalization reaction) and after the curing process.

Section 3

Solubility tests

Solubility of self-healing fillers in the components of the epoxy formulation before and after the curing cycle.

Before deciding on the chemical composition of the formulation and the order in which to mix the components, the authors carried out many experimental tests. In particular, solubility tests of the self-healing fillers were carried out at different concentrations of fillers in the epoxy precursor and in the hardener used for the epoxy mixture.

Initially, a much larger number of self-healing fillers were tested (nine compounds have been identified as possible self-healing fillers on the basis of their chemical structure). Many of these (6) have been discarded based on the solubility results in the components of the epoxy formulation under investigation. Ultimately, the choice fell on the three fillers (1,3-Dimethylbarbituric acid (DBA); 2-Thiohydantoin (T); and Murexide (M)), investigated in this work because of their complete or high solubility (M filler) in the matrix formulation.

Concerning the question of the filler concentration, the self-healing filler percentage of 1% by wt. was selected based on solubility kinetics. (It is worth noting that this 1% by wt. corresponds to the weight percentage of 0.42% calculated with respect to all the components of the final epoxy mixture, as described in the main text.

Solubility tests have ensured rapid and complete solubilization at room temperature only for the DBA filler. For T and M fillers, solubility tests at higher temperatures were performed. Figure S3-1 shows photos of the three fillers after their mixing into the Gurit precursor ECC (at room temperature).

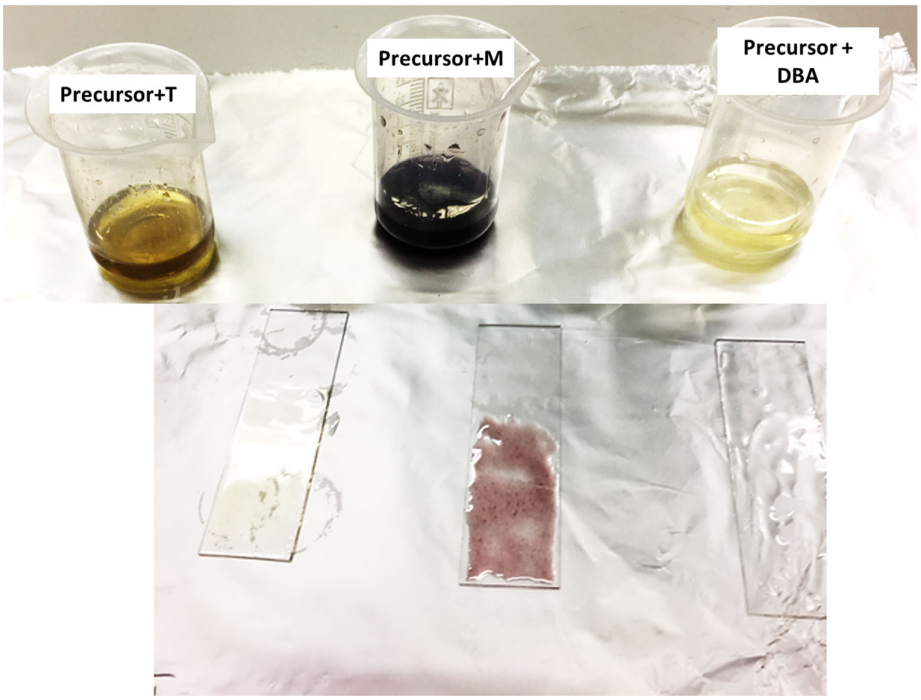


Figure S3-1. Photos of the self-healing fillers after incorporation into the Gurit precursor ECC at room temperature.

Optical images, evidenced a complete solubilization at room temperature for DBA and T fillers. A more in-depth investigation, carried out by optical microscopy, still highlighted the presence of small crystallites of T fillers (invisible to the naked eye).

As described before, the solubility tests were also performed in the hardener.

The solubility tests in the Gurit hardener MHHPA have been carried out at room temperature since at higher temperatures the Gurit hardener starts to give rise to cross-linking phenomena. In the following, we show photos of the fillers before (see Figure S3-2) and after incorporation into the hardener (see Figure S3-3).

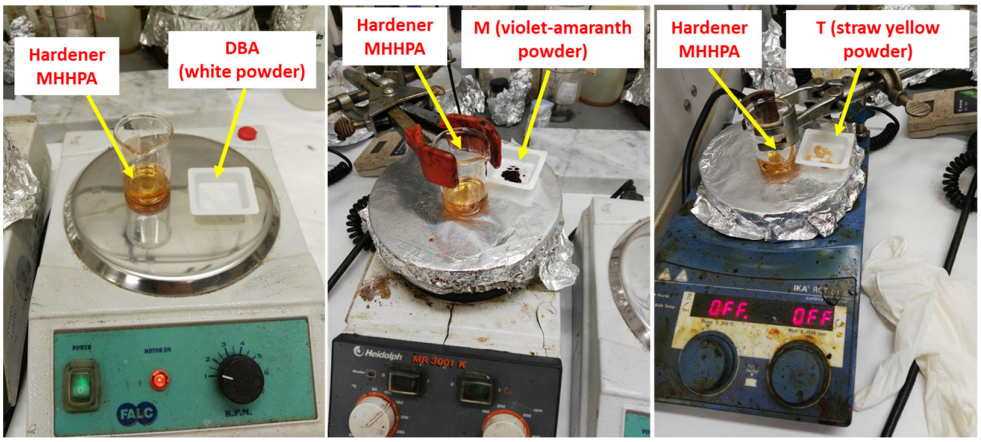


Figure S3-2. Photos of the self-healing fillers before incorporation into the Gurit hardener MHHPA.

The dissolution of self-healing fillers was carried out through mechanical agitation using a magnetic stirrer (400 rpm).

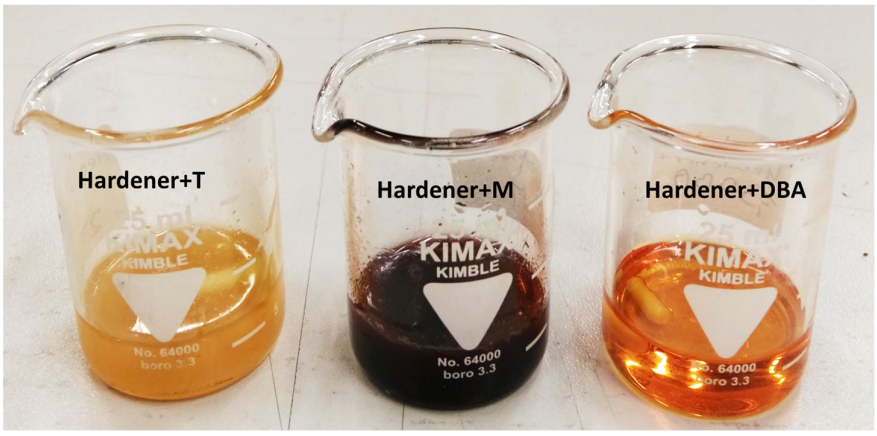


Figure S3-3. Photos of the self-healing fillers after incorporation into the Gurit hardener MHHPA.

Solubility tests carried out at room temperature in the Gurit hardener MHHPA highlight that, under these conditions, only the filler DBA is completely solubilized just after 5 minutes. In contrast, instead, for the other two fillers (T and M), at room temperature and after 5 minutes, even though no complete solubilization was observed, a substantial reduction in particle size was found. After a time of at least 20 minutes at room temperature, a complete solubilization was also obtained for the other two fillers, T and M, as is evident by observing the fluid mixtures stratified, after the solubility test, on a slide for light microscopy, where substantially no particles are visible to the naked eye (see Figure S3-4).

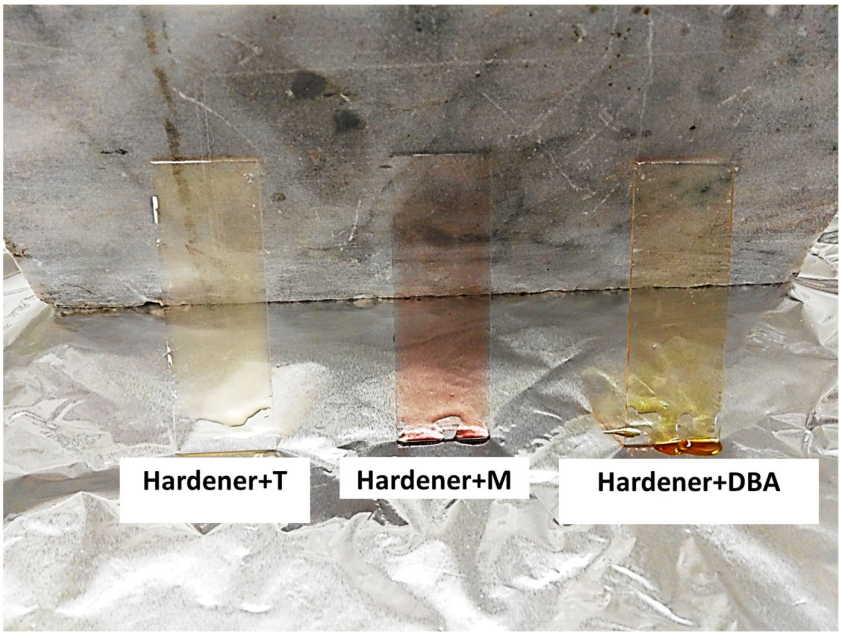
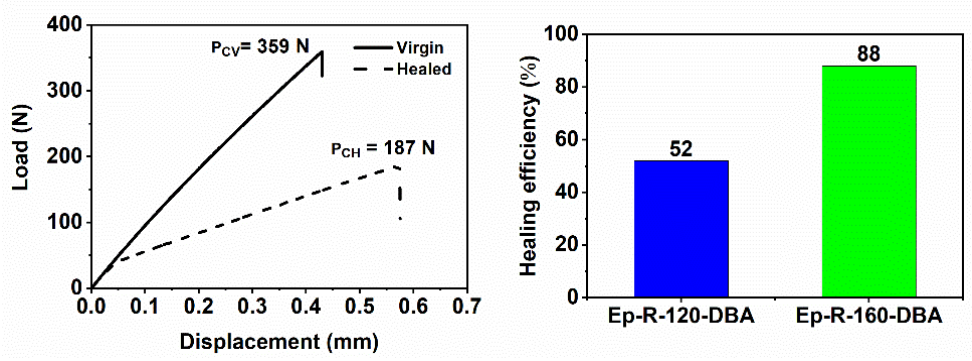


Figure S3-4. Visualization of the complete solubilization of the self-healing fillers in the Gurit hardener MHHPA.

The solubility of the self-healing fillers has also been investigated after the curing cycle for the final composites.

It is worth noting that, as final results, after the curing cycle of the samples, no trace of the crystallites DBA and T have been observed (see SEM image in Figure 13 of the main text). In fact, after all the mixing operations, the treatments at 120°C and 160°C, to carry out the functionalization process, and the cure cycle adopted to solidify the final formulation, very small crystallites (observable in the SEM images in the form of thin crystals) have been observed only for M filler.

Section 4



(**a**) (**b**)

Figure S4. (**a**) Load-Displacement curves for the sample Ep-R-120-DBA; and (**b**) histogram illustrating the healing efficiency values for the samples Ep-R-120-DBA and EP-R-160-DBA.