Development of aeronautical epoxy nanocomposites having an integrated self-healing ability

Liberata Guadagno[1*], *Luigi* Vertuccio[1], *Carlo* Naddeo[1], *Elisa* Calabrese[1], *Giuseppina* Barra[1], *Marialuigia* Raimondo[1], *Andrea* Sorrentino[2], Wolfgang *H*. Binder[3], *Philipp* Michael[3], and *Sravendra* Rana[3-4].

[1]Department of Industrial Engineering, University of Salerno, Fisciano, SA 84084, Italy
[2]Institute of Polymers, Composites and Biomaterials (IPCB-CNR), Via Previati n. 1/E, 23900, Lecco, Italy
[3]Macromolecular Chemistry, Institute of Chemistry, Faculty of Natural Science II, Martin Luther University Halle-Wittenberg, Von-Danckelmann-Platz 4, 06120 Halle (Saale), Germany
[4]Department of Chemistry, University of Petroleum and Energy Studies (UPES), Bidholi Dehradun, 248007, India

Abstract. Functionalized multi-wall carbon nanotubes (MWCNTs) have been embedded in a rubber-toughened epoxy formulation in order to explore the possibility to impart an auto-repair function to the epoxy matrix. The nanofiller has been covalently functionalized with hydrogen bonding moieties able to act as donor and acceptor of hydrogen bondings. Healing efficiencies have been evaluated for nano charged epoxy formulations at a loading of 0.5% wt/wt of functionalized MWCNTs bearing barbituric acid and thymine-based ligands. For both the performed functionalizations, a self-healing efficiency higher than 50% has been found. Dynamic Mechanical Analysis (DMA) highlights that the inclusion of nanofiller increases the storage moduli. Furthermore, DMA analysis evidences the presence of a phase characterized by a greater mobility of the epoxy chains, which promotes the activation of self-healing mechanisms.

1 Introduction

Global competition and the need to maintain global leadership in the field of structural materials (air transport field, aircraft, ships, wind turbine blades, satellite control boards, electronic devices, etc.) dictate the need for cost-efficient, environmental friendly aviation products and services, while at the same time maintaining top quality. The demonstrated benefits of composite materials, compared to metallic one, have led to the recent trend of increased use of the former with respect to metal alloys, most of all in the field of primary aeronautical structures. As an instance, in aeronautics, the design of new materials and applied technologies for their manufacturing is driven towards solutions to fulfill the

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* Corresponding author: lguadagno@unisa.it

following requirements: (i) weight reduction - to maximize the performance; (ii) strict requirements to pollution control during manufacturing process and their use in service; (iii) low consumption of fuel and resources; (iv) reduction of the manufacturing and operating costs (life-cycle costs) etc.

Furthermore, structural systems for aeronautical materials experience a broad spectrum of environmental and operational loads and atmospheric hazards (hail, lightning, storms etc.). Severe and/or prolonged load exposures may trigger the damage accumulation process even in recently deployed structures. An important contribution to the increased exploitation of composite materials can be given by an implementation of a strategy of damage auto-repairing, and other specific functions integrated into the material structure, to contrast the reduced electrical conductivity, flame resistance, thermal conductivity etc.

The research activity, discussed in this paper, is aimed at developing self-healing, load-bearing materials and structures with different functionalities integrated into a single load-bearing material.

In particular, based on recent developments in the field of nanotechnologies, and successful strategies recently identified in the literature, promising multifunctional resins able to simultaneously increase flame resistance, electrical conductivity and to impart regenerative ability can be employed as structural materials in many fields of structural materials [1-8]. As an instance, Carbon Fiber Reinforced Panels (CFRPs), impregnated using multifunctional resin, have been manufactured by Resin Film Infusion (RFI) using a non-usual technique to infuse a nano-filled resin into the carbon fiber dry preform [9-10]. Several flat panels have been produced and tested. The manufactured panels have been tested with respect to all the integrated functionalities. The electrical conductivity was found to be about $2x10^4$S/m in the direction parallel to the fibers, whereas a value between 3.0 and 4.0 S/m was found in the directional orthogonal to the fibers. The panels also highlighted enhanced flame resistance properties. Furthermore, due to hydrogen reversible bonding interactions, a significant decrease in the fatigue crack growth rate by approximately 80 % was found [11-13]. This last result suggests that this strategy can be used to impart the self-healing function to the resin impregnating CFRPs.

In particular, in this field, two innovative approaches have been recently considered to impart self-healing function to multifunctional resins. The first approach is based on microencapsulated systems. An advancement of this kind of self-healing systems, for application requiring high mechanical performance, has been recently proposed. A new ruthenium catalyst has been designed and developed. It has been used in the form of molecular complex inside epoxy mixtures allowing a strong reduction of the manufacturing costs and a relevant enhancement in the mechanical properties. Its chemical stability allows to use aromatic primary amines (such as the DDS, which is used as a common hardener in aeronautical resins) without undergoing deactivation [6]. Concerning the second approach, relevant recent achievements, in the field of supramolecular chemistry and hybrid material formulations, can provide an effective strategy for developing new self-healing composites, able to manifest multiple auto repair mechanisms [13-14]; also restoring other functionalities. Thus, a large variety of SH-systems have been prepared, which auto-repairing function at a different time and length-scales [15], and crosslinked [16] or even blend-systems, which allow the mixed-composition of different polymeric systems [17-18].

In this work, MWCNTs functionalized with thymine and barbituric acid-based ligands, prepared via "click" reaction [13] have been dispersed in an aeronautical epoxy mixture. The solidified resin has proven to be a promising candidate to impart auto-repair mechanisms to aeronautical resins.

2 Experimental section

2.1 Materials

2.1.1 Epoxy matrix TCTBD

The epoxy mixture TCTBD was prepared by mixing the epoxy precursor tetraglycidyl methylene dianiline (acronym T) with 12.5 phr of carboxyl-terminated butadiene acrylonitrile (acronym CT) and 10 phr of the catalyst triphenylphosphine (PPh₃). The chemical formulas of the liquid rubber CT and of the catalyst PPh₃ are shown in Fig. 1a. This mixture was heated and stirred at 170 °C for 24 h. The reaction between the epoxy groups of the precursor T and the carboxylic groups of the liquid rubber CT is shown in Fig. 1b and was studied by FT-IR analysis [19]. The obtained TCT mixture was cooled at 120 °C and the reactive epoxy diluent 1,4-butane dioldiglycidylether (acronym B) was added at a concentration T/B of 80%:20% by wt, obtaining the mixture TCTB. An amount of curing agent 4,4′-diamino diphenyl sulfone (acronym D) of 55 phr with respect to precursor T was added to the mixture TCTB to activate the curing reactions, obtaining the epoxy mixture TCTBD. The epoxy TCTBD was mixed at 120 °C for 1 h and was degassed afterward in vacuum at 100 °C for 1 h. The mixture was cured by two-stage curing cycles: a first isothermal stage at the lower temperature of 125 °C for 1 h followed by a second isothermal stage at the higher temperatures of 200 °C for 3 h.
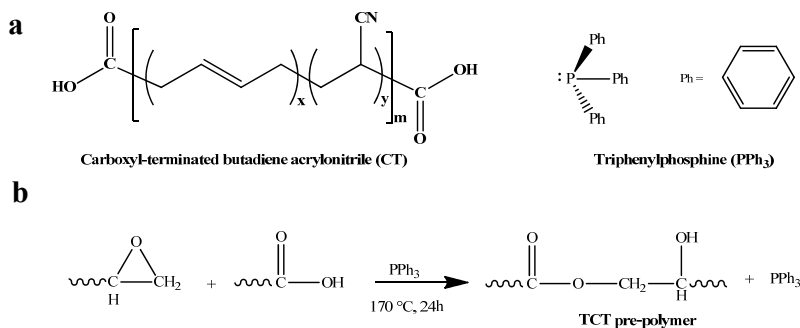

Fig. 1. a) Chemical formulas of CT and PPh₃; b) Reaction related to the formation of the TCT pre-polymer.

2.1.2 Epoxy matrix TCTBD loaded with functionalized and unfunctionalized MWCNTs

The epoxy formulations TCTBD+0.5%CNT, TCTBD+0.5%CNT-Barbiturate, and TCTBD+0.5%CNT-Thymine were prepared by adding the nano-fillers into the matrix TCTBD and sonicating the same by using an ultrasonication for 20 min (Hielscher model UP200S-24 kHz high power ultrasonic probe) in order to improve dispersion of the nanofiller. All the mixtures were cured by two-stage curing cycles: a first isothermal stage at the lower temperature of 125 °C for 1 h followed by a second isothermal stage at the higher temperatures of 200 °C for 3 h (as already done for the unfilled formulation). The chemical structures of the functionalized MWCNTs are shown in figure 2 [13]
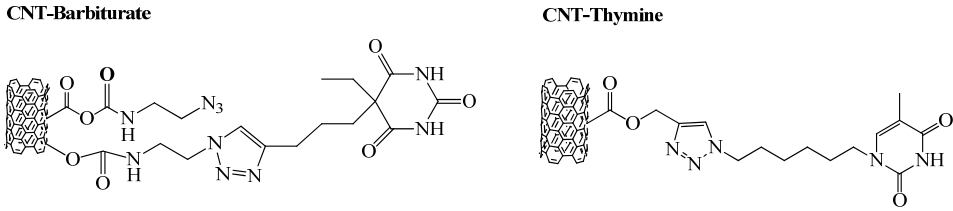
CNT-Barbiturate   **CNT-Thymine**

Fig. 2. Chemical structures of CNT-Barbiturate and of CNT-Thymine.

2.2 Methods

2.2.1 Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical properties, as a function of temperature, of the samples, were investigated by means of DMA 2980 (TA instrument). Samples were analyzed in dual cantilever in bending mode, with a displacement amplitude of 0.1% and a frequency of 1Hz. A constant heating rate of 3 °C min^{-1} was used.

2.2.2 TDCB test for self-healing efficiency evaluation

Tapered double cantilever beam (TDCB) test was performed on the samples in order to evaluate the healing efficiency η. For quasi-static fracture conditions crack healing efficiency is defined as the ability of a healed sample to recover fracture toughness, according to Equation (1), where $K_{ICvirgin}$ is the fracture toughness of the virgin specimen and $K_{IChealed}$ is the fracture toughness of the healed specimen. Using a protocol already established in the literature [20], the efficiency (η) was determined for the virgin and the healed sample by controlled fracture experiments. Samples with a TDCB geometry (figure 3a) were used for these tests to ensure a controlled crack growth along the centreline of the specimen and a crack length independent measure of the fracture toughness. The specimens of shape and size defined in figure 3a were prepared in a metallic mold (figure 3b) from which they were extracted after the curing cycle and subsequently tested.

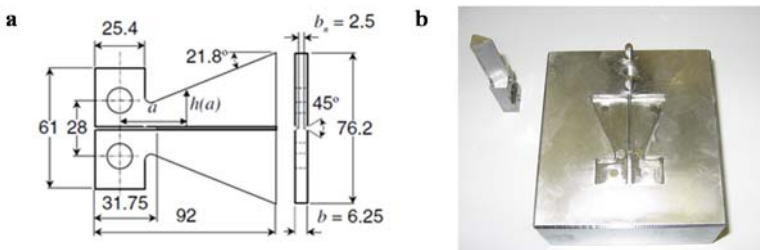$$\eta = \frac{K_{IChealed}}{K_{ICvirgin}} \tag{1}$$

Fig. 3. a) TDCB geometry and dimensions (mm) [20]; b) Metallic mould for sample preparation.

Healing evaluation was firstly performed with a virgin fracture test of an undamaged sample with TDCB geometry. A pre-crack was introduced to sharpen the crack-tip. Afterward the sample was mounted on a load frame and loaded under displacement control causing the propagation of the pre-crack along the centreline of the sample. Subsequently, the crack was

closed and allowed to heal at room temperature without external intervention. After healing, the sample was loaded again until failure. Due to the TDCB geometry, the healing efficiency measurement depends only on the critical fracture load, Pc, of virgin and healed specimen (Equation (2)).

$$\eta = \frac{P_{IChealed}}{P_{ICvirgin}}$$ (2)

Equation (2) can be derived from Equation (1) by considering that $K_{IC}=\alpha P_C$; where $\alpha=11.2\times10^3 m^{-3/2}$, for the used TDCB geometry. This procedure has been recognized to be very effective to measure the healing efficiency [7, 20–23]. In the current work, fracture specimens were tested by INSTRON mod. 5967 Dynamometer under displacement control using a load cell of 30 KN and a 250 µm/min displacement rate and measuring load and displacement values. Samples were loaded at first failure and then unloaded allowing the crack face to come back into contact. After 24 h, the sample was retested and the healing efficiency was calculated using Equation (2).

3 Results and discussion

3.1 Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical properties (DMA) of the filled and unfilled TCTBD modified epoxies are reported in figure 4. As expected, the incorporation of functionalized and unfunctionalized MWCNTs into the epoxy matrix increased the storage modulus of samples. However, the amount of improvement depends on the filler nature. Unfunctionalized MWCNTs show a greater improvement compared to the functionalized MWCNTs. The different effects observed are probably due to the different distribution of the filler in the matrix. The loss tangent (tan δ, Fig. 4) shows a typical behavior for an epoxy-based composite. Two distinct peaks, indicative of two different relaxation phenomena are clearly observed in all samples. The peak located in the in the region between 170 and 200 °C, corresponds to the glass transition temperature. Incorporation of filler into the epoxy matrix results in a lower glass transition temperature. The matrix - MWCNTs cluster interactions could be of two different types: (i) polar cluster - nonpolar polymer backbone, which is similar to the interaction involving epoxy matrix and reinforcing fillers, (ii) polar-polar groups of the matrix, which should result in an increase in the glass transition temperature. While the rubber-filler interaction involving the non-polar polymer backbone is of weak van der Waals' type; the same due to functionalized aggregates (polar cluster), which is of much stronger type. The incorporation of functionalized MWCNTs into the matrix may cause a reinforcing effect as well. The decrease in the intensity of the peak, at low temperature, further supports that the non-functionalized MWCNTs are reinforcing. The appearance of both, at low and high temperature, for the functionalized MWCNTs samples may be considered as an evidence for the micro-phase or the "physical cross-links".
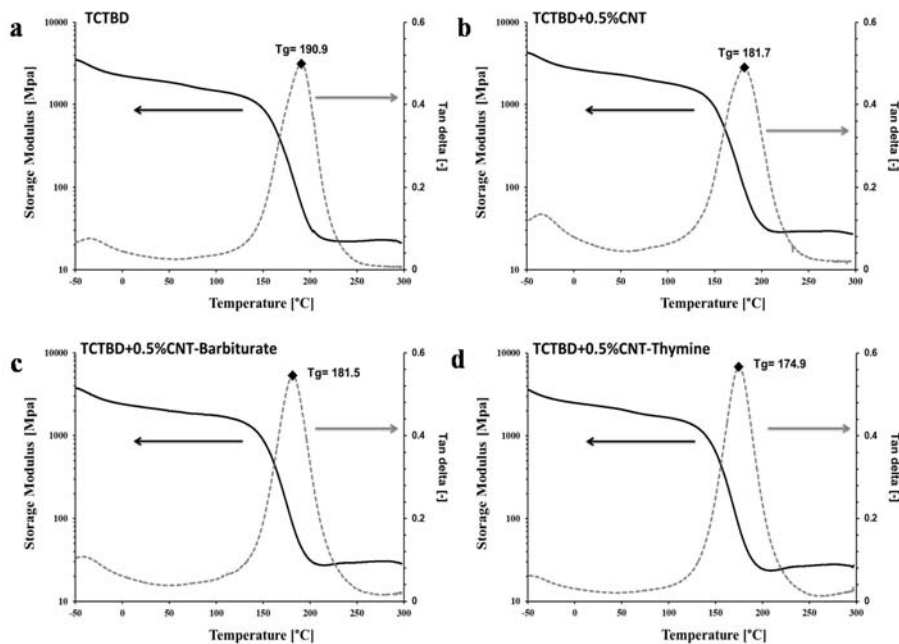
Fig. 4. DMA data of the filled and unfilled formulations: a) TCTBD; b) TCTBD+0.5%CNT; c) TCTBD+0.5%CNT-Barbiturate; d) TCTBD+0.5%CNT-Thymine.

3.2 TDCB test for self-healing efficiency evaluation

Values of healing efficiency η have been calculated using Equation (2), as described in the Experimental Section "TDCB test for self-healing efficiency evaluation". The histogram in figure 5 shows the values of healing efficiency for the analyzed formulations. Healing efficiencies have been found to be 52% and 55% for the samples containing embedded functionalized MWCNTs. The sample filled with MWCNTs functionalized with thymine-based ligand tend to manifest values in the healing efficiency slightly higher than the sample filled with MWCNTs functionalized with the barbiturate-based ligand. The healing efficiencies calculated for the sample TCTBD+0.5%CNT-Barbiturate (on five virgin samples) have been found to be 51%, 52%, 52% and 53% and 54% respectively (average value = 52.4%). Similarly, for TCTBD+0.5%CNT-Thymine samples values in the healing efficiency of 54%, 53%, 55% 55% and 57% have been found (average value = 54.8%).
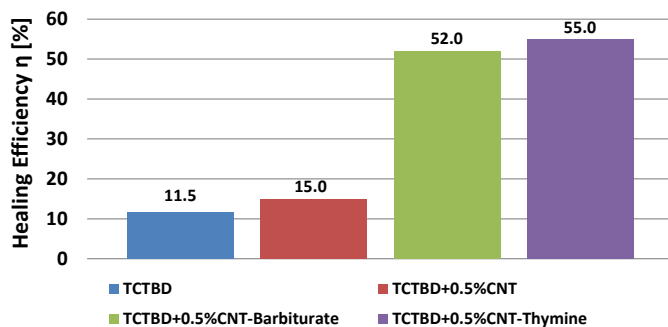

Fig. 5. Values of healing efficiency after the first healing cycle (24 h).

Fig. 6 shows the sites where the dynamic hydrogen bonds (see dotted lines) are active for conferring auto-repair mechanisms to the epoxy formulations.
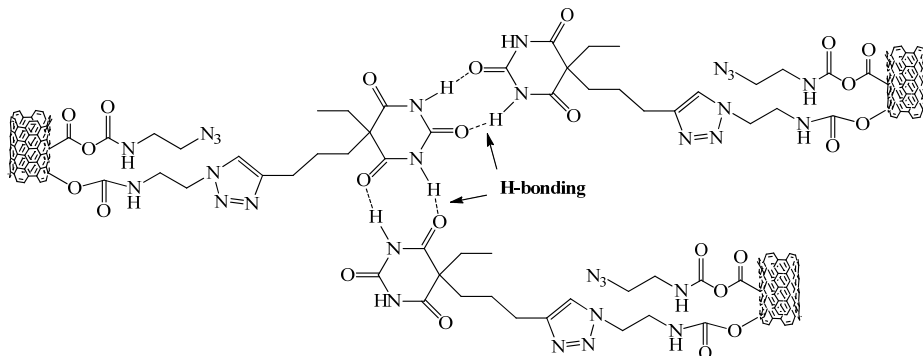

Fig. 6. Example showing the formation of hydrogen bonds between the moieties of MWCNT-Barbiturate.

4 CONCLUSIONS

MWCNTs functionalized with barbituric acid and thymine-based moieties have been embedded in a rubber-toughened epoxy formulation to transfer auto-repair function, based on attractive reversible hydrogen bonding interactions, to thermosetting resins. The design here proposed combines highly dynamic properties, like a reversible, "sticker-like" bond opening and closing behavior to enable a de-and subsequent reconnection, and thus supramolecular network formation with the possibility to also restore different functionalities based on the electrical properties of the nanofiller. One of biggest challenge encountered to apply this strategy is the limited dynamic properties of thermosetting matrix segments. In this work, the rigidity of the matrix has been reduced implementing a rubber material to modify the phase composition. The reversibility of hydrogen bonds can be enhanced by a fine interpenetration of small rubber domains in the matrix. The higher mobility of this rubber phase, finely distributed in the composite, is most likely responsible for favoring the arrangement of hydrogen bonding interactions to activate self-healing mechanisms. The healing efficiency of nanocomposites filled with MWCNTs functionalized with barbituric acid has been found between 51% and 54%, whereas for MWCNTs functionalized with thymine-based moieties, η ranges between 53% and 57%. The self-healing ability has been imparted to an epoxy formulation characterized by high values in the storage modulus (between 2000 and 3000 MPa up to 100 °C) and in the main glass transition temperature (between 175 °C and 191 °C). Further improvements can be achieved suitable tuning the concentration of the functional groups on MWCNT walls. The proposed strategy allows to also restore other properties (as an instance several self-responsive functions) directly conferred to the resin through the conductive nanofiller.

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