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Multifunctional graphene/POSS epoxy resin tailored for aircraft lightning strike protection

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A B S T R A C T

This paper presents a first successful attempt to obtain a conductivity mapping at nanoscale level of a new multifunctional fire retardant graphene/polyhedral oligomeric silsesquioxane (POSS) epoxy resin using Tunneling Atomic Force Microscopy (TUNA) that is a very sensitive mode by which ultra-low currents ranging from 80 fA to 120 pA can be measured. The multifunctional material, specifically designed to meet structural aeronautical requirements, such as suitable thermal stability, fire resistance, mechanical performance and electrical conductivity, has proven to be a promising candidate in the field of aeronautic and aerospace composites. The results also highlight the great potentiality of TUNA technique to analyze conductive networks at nanodomain level. Through simultaneous topographic and current images acquisition, this technique enables a direct correlation of local topography with electrical properties of the nanofiller based samples. The intrinsic electrical conductivity of the manufactured polymeric systems allows TUNA measurements without using electrical conductive paint, which is usually employed for polymeric systems to ensure effective electrical contacts to the ground.

1. Introduction

Aeronautic structures differ from other structures as they need to meet two challenging criteria: high performance and lightweight. In this contest, graphene-based composites may play a game-changing impact in terms of performance and efficiency of future airframe. This is due to the electrical and other unique physical properties of graphene [1–9] that could allow smart integration into lightning strike protection, flame retardancy, impact resistance and others [10–24]. Engineered materials are required to resist degradation [25,26] during an unlikely event of fire in many critical applications such as skyscrapers, boats, or airplanes [27]. Materials used in aviation should be designed to inhibit, suppress, or delay the production of flames to prevent the spread of fire [28]. Epoxy based thermosetting nanocomposites are one of the most commonly used aeronautic materials in the aviation industry because of their excellent mechanical performance, chemical and electrical resistance, fire retardant properties and low shrinkage on curing [29–46] and they can be designed to be applied as multifunctional resins [10,28,43,47]. Materials of this kind offer *whopping* potential to impact future structural performance of advanced engineered composites with easy integration into current processing schemes [10] by reducing size, weight cost, power consumption and complexity while improving efficiency, safety and versatility. Successful strategies to reduce the flammability of epoxy resins [24,48,49], simultaneously increasing the electrical conductivity, are extremely important in the field of aeronautic and aerospace applications [28,37,43]. Currently, in the field of conductive lightweight resins, the material scientists have the possibility "to use" the advantages of the recent discoveries about nanofillers and nanotechnologies that can help to project materials working as multifunctional systems, in addition to the classical methods to protect the materials. Improvements in electrical percolation and mechanical performance have been obtained by a combined action due to a nice balance between the exfoliation degree and the chemistry of graphene edges which promotes the interfacial interaction between polymer and carbon layers [37]. Current chemical technology aimed at increasing the flame resistance of polymeric and composite materials and providing, at the same time, new tools for chemical and materials research is based on cage-like POSS

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nanostructured molecules composed of silicon and oxygen [28,43] with the empirical formula $RSiO_{1.5}$, where R attached to the corners of the cage may be a hydrogen atom or an organic functional group, e.g., alkyl, alkylene, acrylate, hydroxyl or epoxide unit [50–54]. The organic pendent groups can be designed to achieve the desired affinity with the host polymeric matrix [55]. Lightning strike to aircraft, where there is a direct contact between the aircraft surface and the lightning arc, represents a possible safety hazard. Lightning is a discharge of electricity that occurs in the atmosphere and can be thought of as a high-current — about 20,000 A — electric spark associated with thunderstorms. The effects of a lightning strike on aircraft are classified into two main categories: while direct effects are associated with physical damages occurring at the attachment point and in equipment, the indirect effects concern the interferences due to the electromagnetic coupling with the systems and the cabling [56].

Actually, several lightning strike protection (LSP) strategies have been adopted for composite aircrafts [57]. The goal of lightning protection is to prevent accidents and increase the reliability of aircraft. Aeroplanes have metal shells that prevent passengers being affected by lightning strikes. One of the main drawbacks arising from the transition from electrically conductive metals to insulating or semi-conducting composites is the higher vulnerability of the aircraft to lightning strike damage. Aircraft structures are being redesigned to use fiber-reinforced composites mainly due to their high specific stiffness and strength [58]. It is well known that carbon fiber composites are used extensively in aircraft applications such as fuselages, leading edges and wing surfaces because the carbon fibre is light and strong thus allowing for aircraft to consume less fuel. Unfortunately, the fiber reinforced polymer (FRP) composites are unable to conduct the high electrical currents and electromagnetic forces sufficiently to prevent structural damage. When lightning strikes or lightning currents pass through these composite structures, the result can be embrittlement, delamination, and/or structural failure [59]. There is a need for a lightning strike protection (LSP) solution that enables lightning currents and electromagnetic interference (EMI) forces to flow through the aircraft's protection system harmlessly, and exit at the other end towards the ground. The most severe damage usually occurs at the entrance or exit of lightning strikes where the energy density is highest. Major aerospace companies are dealing with the issue of LSP by investigating methods in order to enhance LSP protection on composite parts so that damages are reduced or eliminated. The current protection approach consists of bonding a metal mesh to the surface of the composite structure, but this weight increase negatively impacts on the fuel efficiency and as a consequence on the environmental pollution. The main challenge to replace the current metallic mesh technology is to find a material with a higher conductivity/density ratio or a solution that makes use of lightning physics to avoid damage to the aircraft. In this regard, recently, there is an enormous increase of research and development activities on graphene-reinforced polymers [57] and many research projects are funded with the goal of exploiting the wonderful graphene's electricity-conducting properties that can be incorporated into the carbon fibre. It is known that the addition of small quantities of graphene materials can simultaneously provide significant improvements in strength, toughness, electrical and thermal conductivity, and chemical inertness to a number of polymers [5–8,57,60,61].

Hence, the exploitation of a new generation of aerospace nano-reinforced composite systems with additional functionalities which combine enhanced mechanical and thermal properties with flame retardant abilities without compromising structural integrity represents a peremptory aspect in the current aerospace technology [28,36–43,62]. Furthermore, in order to dissipate lightning currents without employing conductive metal fibers or metal screens, the electrical conductivity of structural parts such as aircraft fuselages has to reach 1–10 S m^{-1} [42,46]. Surface science and nanotechnology have both grown rapidly in the past decades, and are still among the most active fields of research. Simultaneously, the semiconductor technology was significantly enhanced by account of the implementation of novel approach which rely on the application of surface properties.

Besides, the need for electrical characterization of surfaces on the nanometer scale in order to improve local conductivity measurements has led quickly to a variety of scanning probe microscopy based techniques. For this type of measurements, usually, two different setups performed in contact mode are used; conductive atomic force microscope (C-AFM) [63–66] and tunneling AFM (TUNA) [67,68] depending on the range of currents involved. The first is used to measure current in the range of sub-nA to μA (in particular, higher currents can be measured ranging from 1 pA to 1 μA), the latter for the range between sub-pA to nA (in particular, ultra-low currents (< 1 pA) ranging from 80 fA to 120 pA can be measured). In this work, TUNA which utilizes a conductive probe during the measurement process was used.

Our recent research focused on developing high performance polymer nanocomposites, with the benefit of carboxylated partially exfoliated graphite (CpEG) and flame retardant glycidyl polyhedral oligomeric silsesquioxane (GPOSS) nanoparticles, to achieve a novel multifunctional epoxy resin. This paper presents the first successful attempt to obtain a conductivity mapping of a new multifunctional epoxy resin by TUNA. This novel technology allows to simultaneously map the topography and conductivity of advanced material by applying controlled, low forces on the tip during imaging, which allows a direct comparison between the morphology and the electrical properties at the nanoscale [67,69–72].

In this technique, that uses a conductive AFM probe in contact mode, the sensor signal is the electric current between the AFM tip and the conductive sample for an applied DC bias. This non-contact technique helps in carrying out various non-destructive measurements on electrical conductive nanoparticles to obtain point measurement scan of the sample topography and its corresponding electrical data. On the basis of our knowledge, there are currently few works that report a characterization based on this new technique. The multifunctional system has been specially designed so as to meet specific aeronautical requirements through tailored properties by identifying the best strategy for improving its thermal, fire resistance and electrical conductivity. In particular, this paper focus on electrical characterization at nanoscale level using Tunneling AFM (TUNA) and flammability behavior of a new multifunctional nanocomposite. The increase of limiting oxygen index (LOI) value, the decrease of the peak of heat release rate (PHRR) value, observed when GPOSS is used, and the increase of the time of ignition due to the inclusion of CpEG in epoxy systems, together with the high electrical and mechanical properties and the good thermostability imparted by self-assembly blocks of CpEG nanofiller, support the possibility of creating a true multifunctional composite.

2. Experimental and methods

2.1. Materials and epoxy specimens manufacture

The two dimensional (2D) predominant shape CpEG nanoparticles were prepared starting from high surface area of natural low density flake graphite (FG) (Asbury graphite grade 3759, Asbury Carbons, NJ) that is characterized by the following parameters: Carbon purity % = 98.6, Size 1” × 8 mesh, Bulk Density (g/100 mL) = 17.80, Sulfur (%) = 0.056 and Resistivity (Ω cm) = 0.0316. The elemental analysis of the CpEG graphitic sample highlighted an oxygen content of 8.5 wt %. [37]. The sample CpEG was prepared as follows: a mixture containing nitric and sulfuric acid and natural graphite was used. After 24 h of reaction, intercalation within graphene sheets took place to form intercalated graphite compound (IG). Then the mixture was filtered, washed with water, and dried in an oven at low temperatures. The intercalated graphite compound was subjected to sudden heat treatment temperature of 900 °C and rapid expansion then occurred. The expansion ratio was as high as 300 times. Changes in the degree of exfoliation was obtained by varying the resident time in the fluidized