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Synthesis and Testing of a Conducting Polymeric Composite Material for Lightning Strike Protection Applications

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Abstract. Lightning strike protection is one of the important issues in the modern maintenance problems of aircraft. This is due to the fact that the most of exterior elements of modern aircraft is manufactured from polymeric composites which are characterized by isolating electrical properties, and thus cannot carry the giant electrical charge when the lightning strikes. This causes serious damage of an aircraft structure and necessity of repairs and tests before returning a vehicle to operation. In order to overcome this problem, usually metallic meshes are immersed in the polymeric elements. This approach is quite effective, but increases a mass of an aircraft and significantly complicates the manufacturing process. The approach proposed by the authors is based on a mixture of conducting and dielectric polymers. Numerous modeling studies which are based on percolation clustering using kinetic Monte Carlo methods, finite element modeling of electrical and mechanical properties, and preliminary experimental studies, allow achieving an optimal content of conducting particles in a dielectric matrix in order to achieve possibly the best electrical conductivity and mechanical properties, simultaneously. After manufacturing the samples with optimal content of a conducting polymer, mechanical and electrical characterization as well as high-voltage testing was performed. The application of such a material simplifies manufacturing process and ensures unique properties of aircraft structures, which allows for minimizing damage after lightning strike, as well as provide electrical bounding and grounding, interference shielding, etc. The proposed solution can minimize costs of repair, testing and certification of aircraft structures damaged by lightning strikes.

Keywords: Electrically conducting polymers; Lightning strike protection; Polyaniline; Aircraft structures.

PACS: 61.41.+e, 62.20.-x, 65.60.+a.
INTRODUCTION

Modern aircraft industry intensively uses polymeric composites in construction of vehicles. The content of polymeric composites in the newest passenger aircraft exceeds 50% of a whole mass. The growing tendency of application of polymeric composites gives numerous advantages like lightweightness and good mechanical properties of the composite elements simultaneously. However, these materials are essentially dielectric which causes a necessity of protection of composite elements from lightning strike consequences. When the lightning strikes to a polymeric composite element, the electrical energy is dissipated in the form of heat and the rapid growth of temperature to even few thousands Kelvins in the epicenter of a strike occurs due to high electrical resistance of polymers. Additionally, the lightning causes an appearance of an acoustic wave which also loads mechanically a structure subjected to a lightning strike. These phenomena lead to the occurrence of structural damage in such elements in the form of local burns and evaporation of a matrix of a composite as well as to mechanical damage such as cracks and delamination. Despite a fact that lightning strikes do not cause catastrophic damaging of aircraft (the last failure caused by the lightning strike was noticed in 1967 [1]), exterior elements of aircraft damaged during lightning strike need to be repaired and certified which significantly increases the costs of their maintenance.

In order to overcome this problem or at least minimize the consequences of lightning strikes several solutions have been developed to date. Such lightning strike protection (LSP) solutions are generally based on integration of metallic meshes or foils into the composite structure (such solutions have been applied in the newest passenger aircraft, in Boeing 787 Dreamliner and in Airbus A350 XWB). These solutions allow decreasing damage caused by lightning strikes significantly, which was conducted in numerous experimental studies [2-5]. However, the process of integration of metallic mesh (or foil) significantly complicates manufacturing procedures of composite elements which, in turn, increases manufacturing costs. Moreover, the application of such solutions increases a mass of an aircraft which causes an increase of fuel consumption, and the maintenance cost.

In the performed study the authors decided to minimize the mentioned problems by proposing the novel material which does not contain metals. The general approach applied in this study is to substitute a dielectric matrix of a composite material with an electrically conductive mixture of conducting and dielectric polymers. The consideration of a mixture of polymers is essential since the compromise between mechanical and electrical properties of a mixture should be reached. On the one hand the polymers used in aircraft application (primarily epoxy resin) have good mechanical properties, but very high electrical resistance, while on the other hand electrically conductive polymers are good electrical conductors, but have poor mechanical properties which eliminates them from constructional applications. In order to obtain appropriate content of electrically conductive polymer in the mixture the percolation theory was used, which allows for evaluation of such a content of conducting particles that the whole structure becomes electrically conductive, and simultaneously mechanical properties of a mixture do not decrease significantly. The detailed
The following paper focuses on recent attempts on preliminary computational studies as well as on synthesis and characterization of a novel material. It covers numerical modeling of percolation processes and electromechanical interactions in the material, characterization of the selected conducting polymer and selection of solvents in order to increase electrical conductivity, and finally synthesis and characterization of a resulting mixture of conducting and dielectric polymers with description of static tests, thermodynamic tests as well high-voltage tests that simulated lightning strike.

**PRELIMINARY CALCULATIONS**

Before starting the synthesis of the conducting composite material several numerical studies were performed in order to model the desired properties of the resulting mixture. These numerical studies were addressed to the evaluation of a content of conducting particles in the resulting polymeric mixture as well as modeling its material properties.

The first studies were performed using the own-developed Matlab routines which were based on modified Dijkstra’s algorithm and Monte Carlo simulation method in order to simulate electrical percolation in various combinations of conducting polymers with a dielectric one. In order to evaluate the percolation threshold, which denotes in this case the volumetric content of conducting particles in the mixture, the hard-core soft-shell model was assumed (for instance see [7]). This model assumes that particles cannot interpenetrate (a hard-core in the model representing a physical particle), while their shells, which represent tunneling between particles can. The tunneling phenomenon, which can be considered as the electron transferring between neighboring particles in dielectric medium without a direct contact between these particles, plays an important role in such models. The tunneling ability allows decreasing significantly percolation thresholds and initiates the jump-wise change of properties at much smaller concentration of conducting particles (or occupied sites in general). The percolation problem was modified with respect to its classical formulation, i.e. the all-sided percolation clusters where considered, which means that the percolation cluster should connect all sides of the domain (4 in the 2D case, 6 in the 3D case). This modification originated from the physics of the considered problem, i.e. the elementary cells of the modeled material should have an ability to conduct current in order to consider the whole material as a conductive one.

In the performed study three types of conducting polymers were considered: polyaniline (PANI), polypyrrole (PPy), and polythiophene (PTh) [7]. Simulations were performed based on literature data, and resulted in percolation threshold for PANI of 35.7%, for PPy of 0.1%, and for PTh of 38.3%. Further finite element analysis (FEA) of PPy/epoxy mixture show that the threshold should be ca. 10% for this case [8] in order to obtain fully conductive material. Due to the stability and the best processing properties PANI was selected for further studies. Using the software developed by A. Herega [9] the percolation threshold was determined also for various configurations of aspect ratios of sides of a 3D domain in order to evaluate the influence of different geometries of a domain onto the value of the percolation threshold. The results of
simulation show that the influence of aspect ratios is negligible, and the resulting percolation threshold was slightly above 30% [10]. This was confirmed by the previously obtained results described in [6].

**DOPING and CHARACTERIZATION of the CONDUCTING POLYMER**

Polyaniline base, PANI (MW = 50 000 g/mol, Sigma-Aldrich), 10-camphor sulfonic acid, CSA (98%, TCI Chemicals), m-cresol (98%, TCI Chemicals), N-methyl-2-pyrolidone, NMP (99%, TCI Chemicals) were used as received. To increase its conductivity, PANI was doped with camphorsulfonic acid, CSA, according to the literature report [11]. N-Methyl-2-Pyrolidone and m-cresol were used as solvents.

PANI (0.067 g), CSA (0.088 g) and m-cresol (2 ml) as well as the same set with NMP (2 ml) were delivered into the vial (4 ml), placed in ultrasonic bath for 30 min, heated in a water bath (temp. 70°C) and continuously stirred (magnetic stirrer) for 60 min. After this time, black-dark green suspension of high viscosity was obtained.

After the process of doping, PANI:CSA:solvent mixture was placed on the surface of glass slides and dried in the oven. After 3 days, the samples were characterized by means of bipotentiostat (Autolab PGSTAT302N + BA), 4 point probe and scanning electron microscope, SEM (Phenom ProX) equipped with EDS detector and 3D Roughness Reconstruction application. PANI:CSA:m-cresol formed thin uniform and continuous polymer film; it could be removed from the glass substrate and act as a self-standing membrane. The surface of doped PANI was covered with needle-type crystals of CSA. PANI:CSA:NMP turned into black powder covering the glass slide in a non-uniform way. The polymer particles were easily observed on the surface. Among doped PANI chains, crystallites of CSA were detected. The SEM images for the considered solvents are presented in Figures 1 and 2, while the corresponding 3D Roughness profiles are presented in Figure 3. Further details can be found in [12].

The conductivities of PANI:CSA:m-cresol measured by means of different techniques were comparable: 21 S/cm (4 point probe), 26 S/cm (cyclic voltammetry) and 30 S/cm (chronoamperometry). The conductivities of PANI:CSA:NMP differed when measured by means of 4 point technique and bipotentiostat. 4 point probe showed that polymer films were not conducting, however, both types of bipotentiostatic measurements proved that PANI is conducting with the conductivity equal to 18 S/cm (cyclic voltammetry), and up to 48 S/cm (chronoamperometry). The reason of this behavior is in the difference in geometry of the measurements. The distance between probes is 2 mm in 4 point probe technique and 5 μm in bipotentiostat. Because of the non-uniformity of polymer film, 2 mm was too long distance to ensure electrical connection between PANI particles [12].
Figure 1. PANI doped with CSA in the presence of NMP – various magnifications.
SYNTHESIS and CHARACTERIZATION of the CONDUCTING COMPOSITE

SYNTHESIS PROCEDURE

The synthesis of polyaniline (PANI) consisted of the dissolution of aniline in H$_2$SO$_4$ and the addition of (NH$_4$)$_2$S$_2$O$_8$ (oxidant) at the temperature below −3°C. The resulting precipitation was washed with deionized water until neutral pH and purified in the Soxhlet apparatus. PANI was then deprotonated in NH$_3$ aq solution, filtrated and washed with deionized water until neutral pH. The resulting dark-blue precipitate of polymer was dried under vacuum. The overall reaction yield was equal to 63.6%.
The chemical structure of synthesized PANI was verified and compared with commercial PANI (Sigma Aldrich) by means of Raman spectroscopy (Figure 4a) and IR spectroscopy (Figure 4b). From the presented spectra one can observe that the semi-industrial synthesis of PANI match the properties of commercially available PANI.

To increase its conductivity, PANI was doped with camphorsulfonic acid, CSA, with the use of vibrational mill LMW (Testchem) which is supposed to increase the protonation degree of PANI [13]. Water was used as a solvent. After the process of doping, PANI:CSA mixture was placed on the surface of glass slides, dried in the oven and characterized by means of scanning electron microscope (Phenom ProX) (see Figure 5a) and bipotentiostat (Autolab PGSTAT302N + BA) (see Figure 5b).

The morphology of PANI:CSA films was uniform and homogeneous. The conductivities of PANI:CSA measured for mixtures blended for 5, 10 and 15 minutes were comparable and equal to $6.93 \pm 1.38$ S/cm (5 min), $7.61 \pm 1.35$ S/cm (10 min) and $6.14 \pm 2.51$ S/cm (15 min). CSA-protonated PANI was further used to prepare epoxy/PANI composites. The epoxy resin was made from commercially available epoxide Epidian 6 and amine hardener IDA. The samples of epoxy/PANI composites with different volume percentage of PANI were prepared.

The conductivity measurements performed by means of four point probe indicated high resistance for the composites with lower volume percentage of PANI than 50%. To verify the experimental procedure, bipotentiostatic approach (Autolab PGSTAT302N + BA) was used to measure the conductivity of epoxy/PANI samples having 30% and 50% content of PANI:CSA molded in the presence of water (see Figure 6). These two values of content of PANI in the mixture were selected due to the optimal cross-linking and a coincidence with a theoretical values in the first case, and due to the fact that the volume concentration of PANI equal to 50% was found to be the highest amount of conductive filler to obtain liquid composition and enable the process of molding. Scanning electron microscope (Phenom ProX) was used to collect the images of the profiles of epoxy/PANI composites (Figure 7). SEM images indicate
that PANI is mixed with the epoxy component of the composite and forms one phase with Epidian and IDA.

**Figure 5.** a) SEM image of PANI:CSA; b) Chronoamperometric curve for PANI:CSA blended for 5 min, recorded in bipotentiostatic mode for \( E = -0.5\) V and \( E_{\text{offset}} = 0.01\) V.

**Figure 6.** Chronoamperometric curve for PANI:CSA (50% PANI), recorded in bipotentiostatic mode for \( E = -0.5\) V and \( E_{\text{offset}} = 0.01\) V.
The synthesized epoxy/PANI composites were characterized by means of Raman spectroscopy, scanning electron microscopy. According to the parallel studies on the conductivity of epoxy/PANI composites, it was found that the composites with volume percentage of PANI lower than 50% are characterized with high resistance. Basing on SEM images of cross-sections of epoxy/PANI composites with different amount of conductive filler it can be observed that PANI tends to agglomerate and form clusters within the composite materials, increasing the amount of conductive filler necessary to fulfill the percolation requirements.

According to the conductivity studies, the resistivity of epoxy/PANI composites was substantially decreased when the surface of composite was polished with the abrasive paper. This indicated that the epoxy resin tends to form the outer shell of the composite and isolate PANI from the surrounding. To verify this hypothesis, Raman spectra of the surface and cross-sections of epoxy/PANI composites with 30% and 50% content of conductive filler were collected (Figure 8). It can be seen that the major difference between epoxy/PANI(30%) and epoxy/PANI(50%) is the chemical composition of the surface of these composite materials, while the chemical composition of their profiles is the same. There is also a substantial difference in chemical composition of surface and cross-section within one type of composite. This proves the hypothesis of the effect of insulating epoxy layer covering the composite material on its conductivity.

Due to the coincidence of epoxy/PANI(30%) composite with theoretical results as well as the high degree of its cross-linking (which has a direct influence on mechanical properties of a material) this solution was selected for further studies and tests. The determined density of the material equals 1.149 g cm$^{-3}$. The mechanical properties
were determined in the tensile test for the specimens with the gauge length of 40 mm and the speed of tension of 0.5 mm min$^{-1}$. The resulting values averaged for four tested specimens are as follows: the ultimate tensile strength of 13.75 MPa, and the maximum force of 0.2075 kN.

![Figure 8. Influence of insulating epoxy layer: a) Raman spectra for surface; b) Cross-section.](image)

**LIGHTNING STRIKE PROTECTION ABILITY: SIMULATION and EXPERIMENTS**

In order to evaluate the effectiveness of the developed material preliminary calculations of its thermal response during lightning strike were performed [14]. The mechanical, thermal and electrical properties were assumed based on the literature survey. During this study the Carbon Fiber-Reinforced Polymer, CFRP (typically used in manufacturing of aircraft components of the exterior fuselage), and the newly developed material (epoxy/PANI) also reinforced by carbon fiber, were compared. The obtained results show that the thermal flux in the case of the developed material is three orders lower than the weakly electrically conductive CFRP. This means that due to the electrical conductivity of the developed material the electrical potential can dissipate in the material which decreases a temperature accompanied the dissipation processes.

Additionally, in order to evaluate the thermal resistance of the developed material the thermogravimetric analysis (TGA) was performed. The results of the analysis show that the decomposition temperature of the epoxy/PANI composite equals 617.1°C, which is higher than the decomposition temperature of epoxy in CFRP (reported in [15] based on TGA) by more than 100°C. This denotes that thermal degradation processes of the epoxy/PANI composite initiate at higher temperatures than for CFRP, and thus, the lightning current may cause damage with lower extent than in the case of a traditional CFRP.

Finally, the high voltage tests for the epoxy/PANI composite were performed. The generator of lightning voltage impulses used in this study with the epoxy/PANI composite specimen placed between the wire electrode and the flat electrode is
presented in Figure 9. The generated voltage impulse of 1.2 / 50 μs and with a maximum voltage value in average of 32 kV was delivered to the tested specimen. At the charge voltage of the generator of 15.5 kV the obtained avalanche breakdown current equaled ca. 1 kA. These results indicated that the developed epoxy/PANI composite has an electrical conductivity as high as to conduct the current between electrodes through the material (i.e. not in the form of surface currents characteristic for dielectrics). The moment of the current strike is presented in Figure 10a. Due to the concentration of the electric current on the wire electrode, which significantly exceeds the average value, the degradation of the tested specimen can be observed (see Figures 10b and 10c). This phenomenon occurs due to the very high local electric current (around the wire electrode) which, in consequence, causes the rapid increase of a temperature and burning out the material on the current path between the electrodes.

CONCLUSION

The presented paper deals with the synthesis and characterization of a novel all-polymeric electrically conductive composite material which is dedicated as a matrix of CFRP composite for lightning strike protection applications in the aircraft industry. The synthesis stage was preceded by calculations and numerical simulations which resulted in evaluation of a content of a conducting polymer in the resulting mixture as well as evaluation of the fundamental electromechanical behavior of the material. Next, the conducting polymer based on PANI was synthesized and tested. At this stage various solvents were applied in order to select the solvent which ensures the highest value of electrical conductivity. Further, the experiments on the content of PANI in the resulting mixture were performed. These experiments proved the value of a content of 30% of PANI as the most appropriate, which was in agreement with theoretical results obtained from Monte Carlo simulation of the percolation. The synthesized epoxy/PANI composite was then characterized by means of Raman spectroscopy, which reveals the occurrence of insulating shells covering the conducting particles. This problem was partially solved by polishing the surface of specimens. Then, the mechanical and thermal properties of the composite were tested. These tests revealed acceptable ultimate tensile strength as well as high decomposition temperature, which is important property in the case of lightning strike. High voltage tests confirmed the conductivity of the developed composite and the ability to carry high voltage and high current charges. The next studies will be focused on addition of the carbon reinforcement which should improve significantly the mechanical, thermal and electrical properties of the composite.
Figure 9. Experimental test rig for high voltage tests.
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