Composites Science and Technology 127 (2016) 1–7

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

# Lightning damage suppression in a carbon fiber-reinforced polymer with a polyaniline-based conductive thermoset matrix

Yoshiyasu Hirano [a], [*], Tomohiro Yokozeki [b], Yuichi Ishida [a], Teruya Goto [c], Tatsuhiro Takahashi [c], Danna Qian [d], Shoji Ito [d], Toshio Ogasawara [e], Masaru Ishibashi [f]

[a] Advanced Composite Research Center, Japan Aerospace Exploration Agency, Japan
[b] Department of Aeronautics and Astronautics, The University of Tokyo, Japan
[c] Department of Polymer Science and Engineering, Yamagata University, Japan
[d] Central Research Institute, Mitsubishi Plastics Inc., Japan
[e] Department of Mechanical Systems Engineering, Tokyo University of Agriculture and Technology, Japan
[f] GSI Creos Corporation, Japan

ARTICLE INFO

*Article history:*
Received 11 November 2015
Received in revised form
9 February 2016
Accepted 13 February 2016
Available online 18 February 2016

*Keywords:*
Lightning damage
Conductive thermosetting composite
Electrical properties (B)
Thermal properties (B)
Mechanical properties (B)

ABSTRACT

In this paper, the effectiveness of lightning damage suppression by a carbon-fiber-reinforced polymer (CFRP) laminate with a newly developed polyaniline (PANI)-based conductive thermosetting resin was experimentally examined by conducting simulated lightning and residual strength tests. We developed the PANI-based conductive thermosetting resin using dodecylbenzenesulfonic acid (DBSA) and *p*-toluenesulfonic acid (PTSA) as dopants and divinylbenzene (DVB) as a crosslinking agent, which improved the electrical conductivity and homogeneity of the resin. The electrical conductivity values for the PANI-based composite were 148 and 0.73 S/cm in the in-plane and out-of-plane directions, which are 5.92 times and 27.4 times greater than that of a conventional carbon fiber (CF)/epoxy composite, respectively. As a result, the PANI-based composite, when subjected to simulated lightning currents of −40 and −100 kA, showed dramatic improvements in lightning damage resistance compared to the conventional CF/epoxy composite. The residual strength examined by 4-point flexural testing after the simulated lightning test at −100 kA revealed only a 10% reduction from its initial strength, whereas the damaged CF/epoxy specimen tested at −40 kA showed a 76% reduction. Thus, the superior electrical conductivity of the CF/PANI composite quite effectively suppressed lightning damage without applying any lightning strike protection (LSP).

## 1. Introduction

Carbon fiber-reinforced polymer (CFRP) composites are widely employed in large structures such as airframes, wind turbine blades, and automobiles to reduce weight and maintenance costs, because of their superior mechanical and fatigue/corrosion resistance properties as compared to conventional metal materials [1,2]. However, because of the inferior electrical and thermal conductivity of CFRPs as compared to conventional metal materials, their lower lightning damage resistance becomes a major issue. Lightning current attachment causes serious damage due to a number of factors, including the Joule heating effect, matrix resin decomposition, acoustic shock, and electromagnetic force [2–7]. Especially in composite airframe design, special attention should be focused on the problem of lightning strikes. In general, a lightning strike protection (LSP) system comprises a metallic mesh or metallic foil that is applied on the surface of the composite structure to prevent excessive lightning damage. However, applying the LSP increases the total structural weight as well as the manufacturing costs. Furthermore, even if the LSP is applied to a composite structure, it is still difficult to completely protect it from lightning damage. Complicated repair processes that increase maintenance costs and downtime are often required for damaged structures. Therefore, a

---

*Abbreviations:* CF, carbon fiber; CNF, carbon nanofiber; DBSA, dodecylbenzenesulfonic acid; DSC, differential scanning calorimetry; DVB, divinylbenzene; LSP, lightning strike protection; PANI, polyaniline; PTSA, *p*-toluenesulfonic acid; TG/DTA, thermogravimetric analysis/differential thermal analysis; VaRTM, vacuum-assisted resin transfer molding.

[*] Corresponding author. 6-13-1 Osawa, Mitaka-shi, Tokyo, 181-0015 Japan. Tel.: +81 5033626308; fax: +81 422401451.
*E-mail address:* hirano.yoshiyasu@jaxa.jp (Y. Hirano).

http://dx.doi.org/10.1016/j.compscitech.2016.02.022

new solution which could improve the lightning-damage resistance of the composite material itself would be highly desirable.

Several approaches have been pursued to improve the electrical conductivity of insulating matrix resins. One strategy is to mix a conductive nanomaterial (i.e., carbon nanotubes, carbon nanofibers (CNFs), metal nanoparticles, or graphene) with the matrix resin as a filler [8–12]. Our previous research showed a certain degree of effectiveness and the potential to improve the lightning-damage resistance of a CFRP with cup-stacked CNFs as conductive fillers [13]. A general deficiency in this approach, however, lies in the manufacturing process of the nano-composite comprising the conductive filler and polymer.

One promising approach to solving these problems is the use of a conductive polymer instead of applying conductive nanofillers. Polyaniline (PANI) and its derivatives are one of the most-studied classes of intrinsically conductive polymers in recent years [14–22] because of their high conductivity, good environmental stability, and low-cost manufacturing processes. We recently developed a highly conductive thermosetting polymer system comprising PANI, dodecylbenzenesulfonic acid (DBSA) as a dopant, and divinylbenzene (DVB) as a crosslinking polymer [23,24]. The proposed polymer system exhibits ideal properties for use as a matrix in a CFRP to enhance electrical properties and improve manufacturability [25]. However, neither the effectiveness of a conductive polymer-based composite against lightning damage, nor the effect of improving the electrical conductivity of the matrix resin in the absence of an LSP, have been verified experimentally or reported in the literature.

In this study, therefore, a newly developed PANI-based conductive thermosetting composite was proposed for improved lightning damage resistance properties, and its effectiveness was experimentally examined with a simulated lightning current test. The resulting lightning damage was examined both visually and through ultrasonic inspection. The residual strength after the exposure to simulated lightning was evaluated by a four-point flexural test. The effectiveness of the lightning-damage suppression by changing the material properties was discussed based on the experimentally measured electrical and thermal characteristics of the composite material.

## 2. Materials and specimens

### 2.1. Conductive polymer system

We previously developed a conductive thermosetting polymer system consisting of PANI with the dopant DBSA and crosslinking polymer DVB to enhance rigidity [23,24]. Typically, preparing a PANI-based conductive thermoset resin requires a complex process, involving the mixing of PANI and the dopant, doping, the mixing of the PANI/dopant/polymer/curing agent, and subsequent curing by heating [14,15]. Our previous study [24] proposed a one-step process for the preparation of the PANI-based composites. Because DBSA can act as both a dopant and a curing agent, the doping reaction of the PANI/DBSA and the curing of the composite simultaneously proceed with a single heating process. To achieve homogeneous and high quality blends of PANI/DBSA/DVB, a three-roll milling machine was applied for the mixing process [25]. The mixing time must be selected carefully to achieve good dispersion. In addition to DBSA, *p*-toluenesulfonic acid (PTSA) was also used as a dopant to increase the electrical conductivity of the cured resin. DBSA mainly acts as a dopant for PANI and a curing agent for DVB, whereas PTSA contributes to the increased electrical conductivity. The blending weight ratio of PANI/DBSA/PTSA/DVB was fixed at 15/31/4/50 wt% in this study. A detailed description of the chemical reaction, conductivity mechanism, and development process of the PANI-based composite is provided in Ref. [25].

### 2.2. Specimen preparation

Laminated composites were cured by a conventional prepreg-based process with the prepreg sheets comprising the PANI-based conductive resin and plain-woven carbon fiber sheets (TR3110M, TR30-3K fibers, 200 g/m$^2$, Mitsubishi Rayon Co., Ltd.). The prepreg sheet was prepared using the new process described in Section 2.1. PANI (Regulus Co. Ltd.), DBSA (Kanto Chemical Co., Inc.), and PTSA (Tokyo Chemical Industry Co., Ltd.) were mixed to form a PANI/DBSA/PTSA blend by the three-roll milling process in the ratio of 30/62/8 in percentage by weight. This blend was subsequently mixed with DVB (Sigma-Aldrich Co.) at room temperature in a 50/50 wt% ratio. A single layer of the plain-woven carbon fabric was impregnated with the resin to make the CF/PANI prepreg.

Eight plies of the prepreg sheets were stacked and cured at 110 °C for 2 h with a hot press. The stacking sequence was $[0°/90°]_8$, and the thickness and specific gravity of the resultant laminate were 1.6 mm and 1.46, respectively. For comparison, a conventional CF/epoxy laminate was also fabricated using the identical carbon fiber fabric and XNR/H6815 epoxy resin (Nagase ChemteX Corp.), using a vacuum-assisted resin transfer molding (VaRTM) process [26]. The specific gravity of the resultant laminate was 1.44. The carbon fiber fabrics employed for both the CF/PANI and CF/epoxy laminates were identical, with the aim of avoiding any effects from mechanical property differences between the carbon fibers. The specimens were trimmed to 150 × 150 mm$^2$ from both the PANI-based and CF/epoxy laminates. In this study, the PANI-based thermosetting composite and the conventional epoxy composite are referred to as the CF/PANI and CF/epoxy composites, respectively.

## 3. Experimental

### 3.1. Simulated lightning current test

A simulated lightning current was applied to the specimens using an impulse current generator (developed by Otowa Electric Co., Ltd., owned by National Composite Center Japan at Nagoya University) (Fig. 1(a)) capable of applying a standard combination waveform of components A, B, and C, as defined in SAE ARP-5412 [27]. Fig. 1(b) presents the testing setup consisting of a support jig and discharge electrode. Specimens were fixed with a picture-frame-type copper jig, which was connected with the ground of the impulse current generator. In this setup, only the edge of the specimen was retained by the base plate and cover frame, which were screw-clamped together. The applied impulse current was measured with a current transducer (Model 1423, Pearson Electronics, Inc.) connected to a ground line and a digital oscilloscope (DPO 3034, Tektronix, Inc.).

In this study, a modified simulated current of Component A, as defined in SAE ARP-5412 [26], was applied. Whereas the original Component A waveform has a peak current of −200 kA, in this study, peak currents of −40 kA (A/5) and −100 kA (A/2) were applied. The current waveform was exponential, and could be characterized by the time-to-peak current ($t_1$) and the time to decay to fifty percent of its maximum amplitude ($t_2$). Fig. 2 presents a typical result for the simulated lightning current measured by the oscilloscope connected to the current monitor. Table 1 presents the testing conditions for the simulated lightning current, where the action integral shows the applied electrical specific energy. The simulated current was applied in the center of the specimen surface as arc entry; the gap between the tip of the discharge probe and the specimen surface was 2 mm.