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Development of conductive CFRPs using PANI-P-2M thermoset polymer matrix

Santwana Pati[a,b*], Sukanta Das[a], Teruya Goto[c], Tatsuhiro Takahashi[c] & Tomohiro Yokozeki[a]

[a]Department of Aeronautics and Astronautics, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113 8656, Japan

[b]CSIR-National Physical Laboratory, Dr. K. S. Krishnan Marg, New Delhi 110012, India

[c]Department of Organic Device Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992 5810, Japan

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This research article presents the analysis of a conductive carbon-fiber-reinforced plastic (CFRP) prepared using the new thermoset resin of polyaniline (PANI) applying 2-Methacryloyloxyethyl acid phosphate (P-2M) as a curable dopant. The results of this study established a conductive CFRP with easy synthesis route employing the prepreg technology. This work shows a successful fabrication of CFRP using the new resin developed using a curable dopant for PANI. This is a significant step forward at producing lightning strike protection (LSP) technologies with large scale manufacturing potential, and the future work aims at investigating this CFRP for lightning strike effectiveness.

Keywords: Conductive thermosetting composites, Polyaniline, Carbon fiber-reinforced plastic, Electrical conductivity

1 Introduction

CFRP continues to provide new avenues for innovation to satisfy the never-ending demand of a stronger, lighter, and safer material. Nowadays, aircraft design employs CFRP structures extensively. Recently Diamond aircraft in Austria introduced an all Carbon airframe that provides several features for safety, efficiency, and low emission levels[1,2]. Similarly, the Aeronautical University in Mexico reported about a fuselage made from composites for the first time for a two-seater jet aircraft[3,4]. Therefore, aero composites are becoming the new face of aircrafts manufacturing. However, as the primary resin material, epoxy is insulating in nature, additional lightning strike protection (LSP) and fire retardant are mandatory for CFRP based aircraft[5]. Bolts of lightning can severely damage the structural integrity of the plane and disturb the avionics. So, a metal mesh LSP is required to protect the exterior surfaces. Metal mesh LSPs are mostly aluminium or copper. Aluminum increases the risk of galvanic corrosion, and copper adds extra weight to the CFRP aircraft. Consequently, new multifunctional approaches are necessary.

Haydale composite solutions, a leading company for nanomaterials production recently reported pristine monolayer graphene integrated with the epoxy resin in CFRP to get rid of the need for copper mesh as LSP[6]. This opened the door for mass production and extensive research on high-quality nanomaterials to replace copper mesh LSPs[7]. Nevertheless, the nanotechnology integration into aero composite comes with its limitations; complicated synthesis procedure, high cost of production, and difficult to control agglomeration[8]. Hence, the next forward step is to eliminate the need for LSP by replacing epoxy with an inexpensive conductive resin. Polyaniline has been one of the most extensively studied polymers to synthesize new conductive resin for CFRP. Many reports on polyaniline with various types of do pants have been shown to have LSP properties[9,10]. Yokozeki *et al.* have reported multiple kinds of PANI based conductive resin for structural applications[11–15]. Each resin is an improvement over the other or possesses various multifunctional properties. The first reported PANI/DBSA/DVB resin showed excellent conductivity but with scope for a simpler synthesis route[11,16]. The recently published PANI/P-2M resin showed a single material synthesis technique[17,18]. This article introducesa novel conductive CFRP, manufactured using the simple prepreg technology implementing the PANI/P-2M resin. P-2M is a curable dopant added for the simultaneous doping and curing of polyaniline applying a single material. This makes the process quite simple to manufacture, and the steady-state viscosity makes it easier to store and transport. The resin synthesis and the optimization have been well studied and reported in

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*Corresponding author (E-mail:santwana1990@gmail.com) the previous publications[17,18]. This article focusses on the next step; CFRP fabrication and optimization with the electrical and mechanical properties analysis. Conductive CFRPs are a prime research focus to find a new resin that can replace epoxy with high conductivity, mechanical properties, and easy to fabricate synthesis route.

2 Experimental Methodology

The complete experimental methodology includes resin preparation and then CFRP fabrication using the resin.

2.1 Materials

Polyaniline (PANI) in powder form was procured from Regulus Co. Ltd., Tokyo, Japan. P-2M in gel form, which is a curable dopant for PANI, was supplied by Kyoeisha chemicals. The curing initiator Perbutyl-E in liquid form was provided by NOF Corporation. The carbon fibers used are of the following specification:TR3110M, TR30-3K fibers, 200 g/m^2 from the Mitsubishi Rayon Co., Ltd.

2.2 Resin preparation

In the first step, PANI was heated for 24 hours at 60 ℃ to eliminate the previously retained moisture due to storage. This dried PANI was then mixed with P-2M in the weight ratio of PANI (30 wt %) and P-2M (70 wt %) using a centrifugal mixture at 2000 rpm for a few minutes to prepare a homogenous mixture. This mixture is then heated at 80 °C for 2 hours and is named as Doping complex, and the thermal treatment stage is further called the semi doping process. The purpose of this stage is to enhance the conductivity of the resin and was designed after a series of optimization.

Further, this doping complex was mixed with a calculated amount of P-2M to get the specific wt % of PANI in the resin. Different batches of the resin were synthesized with various PANI content and are hereby termed as the following: 0 wt %, 5 wt %, 10 wt %, 15 wt % of PANI. At the final stage, 10 wt % of the crosslinking catalyst Perbutyl-E was added, thereby finishing the resin synthesis phase.

2.3 CFRP (carbon-fiber-reinforced plastic) fabrication

The prepared resin was impregnated on the carbon fibers cut in the dimension of 200 × 200 mm, and these impregnated fibers (prepregs) could be stored for a long period of time. This property of this resin with long term stability as a prepreg is a big leap over the other conductive resins. Eight plies of these prepregs were stacked and cured at 120 ºC at 3 MPa pressure for 2 hours in a hot press. The exact temperature and pressure with the time duration were optimised with a series of experiments varying these factors and finally the one with minimum residual heat of reaction was considered the most preferred condition for complete curing. The resultant cured CFRPs were 2 ±0.4 mm thick.

2.4 CFRP(carbon-fiber-reinforced plastic) characterisation

The results and analysis of these fabricated CFRPs required proper samples in various dimensions. The electrical conductivity measurement was done using the LCR meter (3522-50 LCR Hi TESTER, Hioki E.E. Corporation, Ueda, Japan) by four-probe method. The sample dimensions were 25 × 25 mm for the conductivity measurement. The flexural properties of the samples were measured using the Universal Testing machine (UTM, Instron - 5582) by three-point bending method. The machine used a load cell of the range of 5 kN and the crosshead speed was set at 1 mm/min. The sample dimensions were 80 mm in length, 12-13 mm in width, and 2 mm in thickness, and the span distance is taken as 32 times the thickness as prescribed by the standard. Finally, for the morphological analysis, the samples were cut into size of 15 × 20 mm and put inside clear plastic rings. CLEARPOXY resin (Sankei, co. ltd) was mixed with CLEARPOXY hardener (Sankei, co. ltd) in weight ratio 100:13 and vacuumed to bleed air out of the resin. The epoxy resin was then poured into the clear plastic ring with specimens inside. The liquid epoxy was let to harden for 24 hours. The ring with hardened epoxy and specimens was polished using grinder-polisher machine (Buehler EcoMet® 250, Buehler AG) with five steps of polishing plates. The high-resolution cross-sectional images were captured using the LEICA MC170HD. Figure 1 Illustrates the various stages of this research article. It starts with resin synthesis and then finally characterization of the CFRP. The lightning strike protection effectiveness of these samples are under further scope in this line of research.

3 Results and Discussion

This section describes all the properties of the CFRP with various wt. % of PANI. The mechanical properties show that the flexural modulus decreases with the increase in the amount of PANI. With the same curing profile, the resin with more amount of PANI was less cured, as it required more curing

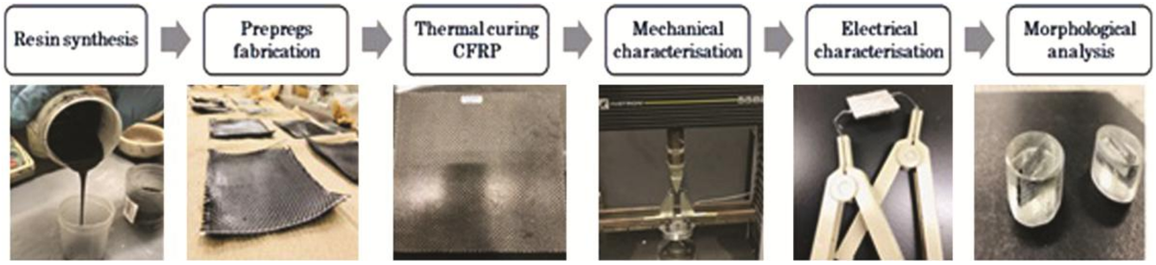

Fig. 1 — Experimental flowchart from synthesis to characterization.

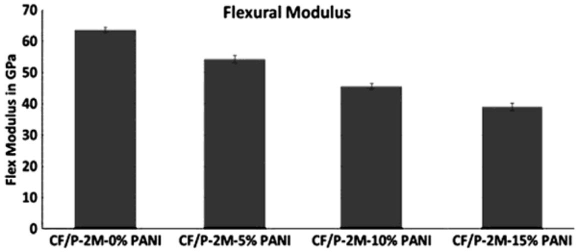

Fig. 2 — Flexural modulus of the CF/P-2M samples with various wt% of PANI.

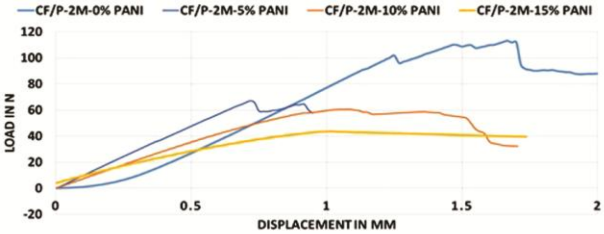

Fig. 3 — Load-Displacement curves for the CFRP samples with various wt % of PANI in the resin.

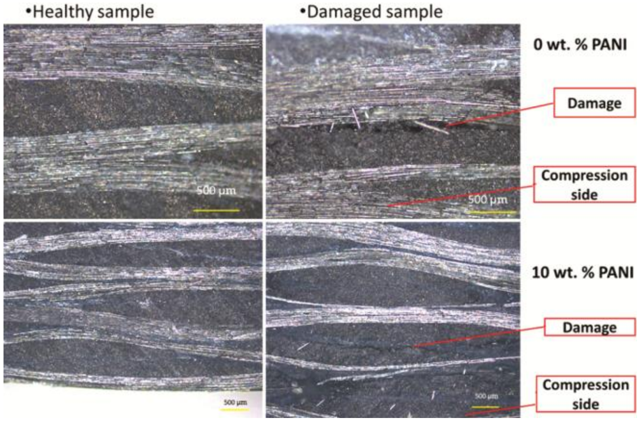

Fig. 4 — Optical microscope images of the CFRP samples showing the damage sites for samples with 0 wt % and 10 wt % PANI.

energy. Figure 2 illustrates how the modulus changes for various constitution of the resin. P-2M aids in both the curing of the resin and doping of the PANI. Therefore, with the increase in the amount of PANI, lesser amount of P-2M is available for the curing. And thereby the reduction in the modulus in the final composite. Further the long chain of PANI may also hinder the radical curing mechanism that P-2M follows for the composite hardening[15]. However, this is a theoretical assessment and the confirmation can be done by deeper analysis into the curing chemistry of the resin.

Figure 3 encompasses the load-displacement curve for all the samples. As the amount of PANI increased, the slope of the curve decreased. The breakage was not one shot but gradual. The flexural modulus summarised in Fig. 2 was obtained from the linear portion of the load-displacement curve. The nonlinear extended portion after the first breakage was quite unique for PANI based resin and is not shown by epoxy resin[19].

The morphological analysis of the samples is necessary to understand the mechanical properties inside the CFRP. The samples before and after the bending test were analyzed using an optical microscope, and Fig. 4 illustrates the analysis. The details of sample preparation have been explained under CFRP Characterisation. The damage is shown in the diagram and visibly it is more significant in the sample with 10 wt % PANI. The orientation of the sample is also mentioned in the figures. The damages were due to resin failure as the modulus of the resin was much lower than that of fibres. The failures were caused due to fibre-matrix debonding at the vicinity of the load. This results in gradual failure and no catastrophic damage as expected in epoxy[20]. In this case, the load gradually drops rather than sudden failure (as in fibre failure). Therefore, the damage is mostly dominated by debonding and cracks. The sample with a higher amount of PANI shows damages owing to the matrix failure. The sample with 0 wt % PANI has clear fiber-matrix debonding. This is the reason the load-deflection curves experience long and gradual failure rather than a sudden drop in the load. The morphological analysis explains how PANI/P-2M based CFRPs are different from epoxy based CFRPs

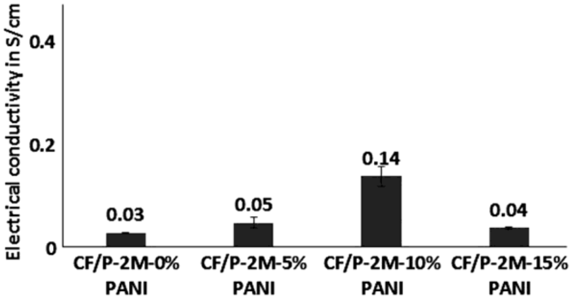

Fig. 5 — Electrical conductivity in S/cm of the samples with various wt % of PANI.

and therefore show a dissimilar load-deflection curve. However, epoxy being dielectric in nature does not offer any conductivity to its CFRPs. The electrical conductivity of the PANI/P-2M CFRPs is the biggest benefit over epoxy-based CFRPs.

Figure 5 demonstrates the conductivity (through plane) for all the samples used in this study. PANI provides conductivity owing to its long chain of alternate double bonds. The trend shows an increase in conductivity with the PANI amount. However, the sample with 15 wt % PANI could not be fully cured. The mechanical properties also showed a significant drop in the modulus. This was because the amount of curing energy and doping energy required to completely fabricate the 15 wt % PANI CFRP sample was not provided by the uniform curing profile followed for all the samples. Apart from that, the samples showed an increase in conductivity with an increase in the amount of PANI. The sample with 10 wt % PANI exhibited 0.14±0.02 S/cm. The conductivity is much higher than epoxy based CFRP samples. However, it is lower than previous resin of PANI (PANI/DBSA/DVB) developed by our team[10,16]. But on the positive side, the ease of fabrication using the prepreg fabrication method gives amore significant rise in this research.

Hence the developed conductive CFRP offers good mechanical and electrical properties with a simple synthesis route. A very few polymers have been studied as a potential thermo set resin for aircraft grade CFRP fabrication. PANI/P-2M resin as a new focus of research for aircraft applications is full of scope. The lightning strike tests on these samples are covered in the further range of this research.

4 Conclusions

The present study examines the CFRP fabricated using a newly developed conductive thermo set resin named PANI/P-2M. The resin comprises of PANI as the conductive polymer and P-2M as the curable dopant. The conductive CFRP prepared by using various combinations of wt % of PANI in the resin were analyzed for electrical and mechanical properties. The CFRP with the resin constitution of 10 wt % PANI exhibits flexural modulus of 45±1 GPa and conductivity of 0.14±0.02 S/cm. The sample shows good mechanical and electrical properties and may successfully resist lightning strike discharges. Therefore, this conductive CFRP developed using PANI/P-2M matrix can be considered as a potential LSP candidate for aircraft applications.

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