LIGHTNING DAMAGE SUPRESSION IN A CFRP WITH A POLYANILINE-BASED CONDUCTIVE THERMOSET MATRIX

Yoshiyasu Hirano[1], Tomohiro Yokozeki[2], Yuichi Ishida[1], Teruya Goto, Tatsuhiro Takahashi[3], Danna Wian, Shoji Itoh, Toshio Ogasawara, and Masaru Ishibashi[3]

[1]Structures and Advanced Composite Research Unit, Aeronautical Technology Directorate, Japan Aerospace Exploration Agency, 6-13-1 Ohsawa, Mitaka, Tokyo 181-0015, Japan
Email: hirano.yoshiyasu@jaxa.jp, Web Page: http://www.jaxa.jp
[2]Department of Aeronautics and Astronautics, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
Email: yokozeki@aastr.t.u-tokyo.ac.jp, web page: http://www.aastr.t.u-tokyo.ac.jp/index_e.html
[3]Department of Polymer Science and Engineering, Yamagata University,
4-3-16 Jonan, Yonezawa, Yamagata, 992-8510 Japan
Email: t-goto@yz.yamagata-u.ac.jp, effort@yz.yamagata-u.ac.jp ,
web page: http://yone.yz.yamagata-u.ac.jp/#hpb-container
[4]Central Research Institute, Mitsubishi Plastics Inc.,
5-8 Mitsuyacho, Nagahama, Shiga, 526-8660 Japan
Email: sen.tanna@ms.mpi.co.jp, ito.shoji@md.mpi.co.jp web page: http://www.mpi.co.jp/english/
[5]GSI Creos Corporation, 2-3-1 kudanminami, choyoda-ku, Tokyo, Japan
Email: m.ishibashi@gsi.co.jp, web page: http://www.gsi.co.jp/en/

Keywords: Lightning damage, Conductive CFRP, Polyaniline, NDI

Abstract

The effectiveness of lightning damage suppression by a carbon-fiber-reinforced polymer (CFRP) laminate with polyaniline (PANI)-based conductive thermosetting resin was experimentally examined by conducting lightning test and residual strength tests in this study. 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 was developed. As a result, the PANI-based composite, when subjected to impulse 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).

Excerpt from ISBN 978-3-00-053387-7

1. Introduction

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 for airflame structure application. 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 [1-5]. 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 aften required for damange structures. To solve this problem, new solution which could improve the lightning-damage resistance of the composite material is highly desirable.

One promising approach to solving these problems is the use of a conductive polymer to improve an electricao conductivity of CFRPs. Polyaniline (PANI) and its derivatives are one of the most-studied classes of intrinsically conductive polymers in recent years [6-14] 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 [15, 16]. The proposed polymer system exhibits ideal properties for use as a matrix in a CFRP to enhance electrical properties and improve manufacturability [17].

In this study, the developed PANI-based conductive thermosetting composite was proposed for improved lightning damage resistance properties, and its effectiveness was experimentally examined with a 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 fexural 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 materials.

2. Experimental

2.1. Materials and specimens

A material system used in this study is CFRP with conductive thermosetting polymer consisting of PANI with the dopant DBSA and crosslinking polymer DVB to enhance rigidity we have developed previously [15, 16]. 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/m2, Mitsubishi Rayon Co., Ltd.). 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 specie gravity of the resultant laminate were 1.6mm 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 [18]. The specific gravity of the resultant laminate was 1.44. The specimens were trimmed to 150 × 150 mm from both the PANI based and CF/epoxy laminates.

2.2. lightning current test

A modified impulse lightning current of Component A , as defined in SAE ARP-5412 [19], was applied by using an impulse current generator (developed by Otowa Electric Co., Ltd., owned by National Composite Center Japan at Nagoya University). Whereas the original Component A waveform has a peak current of -200 kA, the modified lightning current with peak currents of -40 kA (A/5) and -100 kA (A/2) were applied. 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 (Figure 1). 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). Figure 2 presents a typical result for the impulse lightning current measured by the oscilloscope connected to the current monitor. Table 1 presents the testing conditions of lightning current, where the action integral shows

Excerpt from ISBN 978-3-00-053387-7

the applied electrical specific energy. The lightning 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.

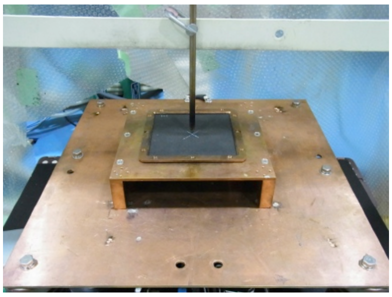


Figure 1. Schematic of support jig and discharge electrode

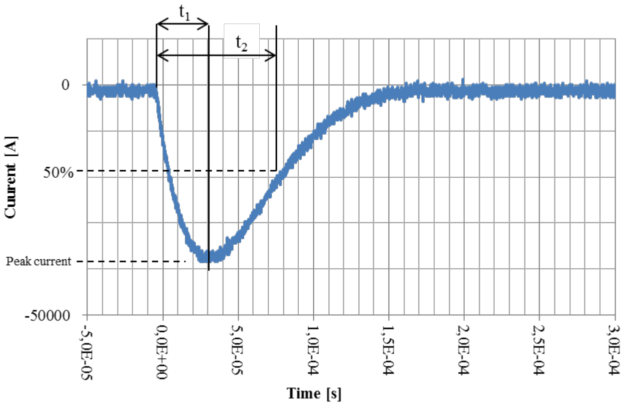


Figure 2. typical result of measured applied simulated lightning energy

Table 1. Testing conditions of applied simulated lightning current

S/N	Material	Peak current [kA]	Wave form[μs]	Action integral [A^2s]
E-1	CF/Epoxy	-40.0	29.6/78.6	76,103
E-2	CF/Epoxy	-38.8	34.1/79.5	72,991
E-3	CF/Epoxy	-99.2	29.1/79.2	512,599
P-1	CF/PANI	-41.2	30.9/77.8	82,141
P-2	CF/PANI	-41.2	26.7/76.2	82,410
P-3	CF/PANI	-99.2	33.9/83.3	528,558

2.3. Residual strength test

The residual strength after the lightning current test was examine with a four-point flexural test in accordance with JIS K 7074 [20]. The specimen size was 100 mm × 15 mm. The crosshead speed was 5 mm/min. Both intact and damaged specimens were cut from the tested specimens to compare the strength before and after lightning damage. The loading span and the support span were 27 mm and 81 mm, respectively. A conventional electrically driven testing machine (INSTRON 5582, Instron Inc.) was used.

Excerpt from ISBN 978-3-00-053387-7

3. Results and discussion

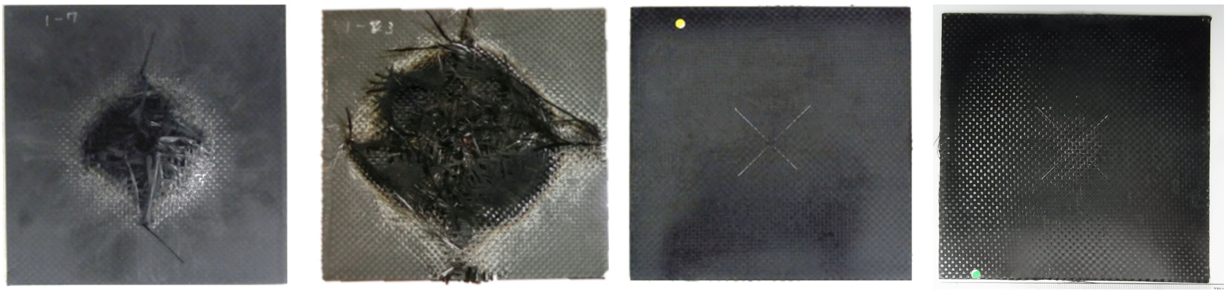
3.1. Lightning current test

The typical damage incurred by applying the lightning current is shown in Figure 3, which presents a top view of the specimen at the site of the impulse current attachment. The CF/epoxy laminate tested at -40 kA (Figure 3(a)) shows a large amount of damage consisting of broken fibers as well as resin evaporation and deterioration, which developed from the center of specimen. The CF/epoxy laminate tested at -100 kA (Fig. 3(b)) shows a higher degree of catastrophic failure. In the case of the CF/PANI laminate, the specimens tested at both -40 and -100 kA show barely visible resin deterioration only around their centers (Figure 3 (c),(d)).

The CF/epoxy laminate tested at -40 kA shows circular fiber damage in a diameter of 70mmin the center of the specimen. Inside this damaged area, although the epoxy resin had evaporated totally, the laminate was not penetrated in the thickness direction. At -100 kA (Figure 3(b)), it is difficult to assess the size of the damage because of its extent. The fiber damage and resin deterioration reached the specimen edge where it was clamped by the support jig; the applied lightning current energy was too large for the specimen size.

Internal damage was examined with an ultrasonic flaw detector (HIS3 HF, Krautkramer GmbH) having a 3.5 MHz transducer. The obtained C-scan results are shown in Figure 4. The CF/epoxy laminate shows extensive internal damage beyond the fiber damage and resin deterioration area (See Figure 4(a)). The damaged area was circular in shape, with a diameter of about 125 mm. The damage extends 0.8 mm in depth, which corresponds to 4 plies from the top layer.

The CF/PANI laminates tested at -40 and -100 kA (Figure 4(b) and (c), respectively) show no defects in the thickness direction, but rather, only limited surface damage which corresponds to the barely visible surface resin deterioration which was previously described. The detected damage area increased with the increasing energy of the applied lightning current: 113 mm^2 at -40 kA versus 741 mm^2 at -100 kA. The lightning damagewas proportional to the action integral of the applied lightning current, as reported in previous work [5].



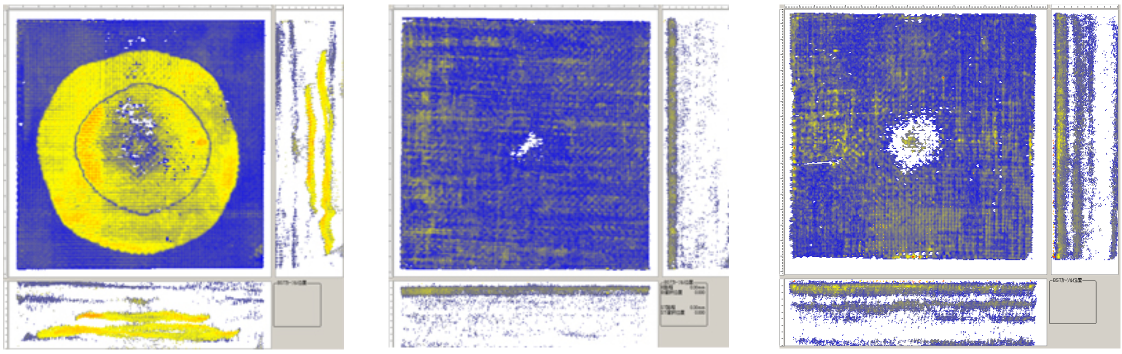
a) CF/Epoxy, -40kA (E-1)

b) CF/Epoxy, -100kA (E-2)

c) CF/PANI, -40kA (P-1)

d) CF/PANI, -100kA (P-2)

Figurure 3 Damaged specimen after lightning test



a) CF/Epoxy -40kA (E-1)

b) CF/PANI -40kA (P-1)

c) CF/PANI -100kA (P-3)

Figure 4 Results of ultrasonic scanning after simulated lightning current test

Excerpt from ISBN 978-3-00-053387-7

3.2. Residual strength test

The residual strength after the lightning damage was examined by 4-point flexural testing. Both intact and damaged specimens were prepared. Two damaged specimens were extracted from one lightning test specimen so that each beam specimen had a damaged area in its center. During the tests, the specimens were oriented such that the damaged surface was on the compression (upper) side.

The results of the four-point bending tests are shown in Table 2, as the average strength of the two specimens for each testing condition. The residual strength of the CF/epoxy specimen tested at -40 kA simulated lightning current is decreased to 24% of that of the intact specimen, whereas the CF/PANI specimen retains 90% of the initial strength after the lightning current was applied at either -40 or -100 kA. The damaged area of the CF/PANI specimen tested at -100 kA simulated lightning current is 6.6 times greater than that at -40 kA. The surface resin deterioration/damage due to the lightning current in the CF/PANI specimen has a limited effect on the residual strength. Thus, the newly designed CF/PANI composite achieves superior lightning damage resistance versus the conventional CF/epoxy composite.

Table 2 Comparison of flexural strength before and after lightning damage between CF/PANI and CF/Epoxy

Flexural strength	CF/PANI	CF/Epoxy
Intact [MPa]	267	610
Damaged [MPa] -40kA (Residual ratio)	240 (0.90)	147 (0.24)
Damaged [MPa] -100kA (Residual ratio)	239 (0.90)	N/A

3.3. Discussion

The major causes of lightning damage in CFRP laminates are 1) fiber sublimation due to Joule heating, 2) delamination caused by resin decomposition, and 3) delamination development by interlaminar resin gas evaporation [4,5]. As shown in the lightning current tests and the subsequent ultrasonic testing results, the CF/PANI laminate could effectively suppress lightning damage. Examining the damage morphology of the CF/PANI laminate, only limited surface damage in the form of barely visible surface resin deterioration can be observed. If the thermal stress had a much greater effect on damage behavior, a large degree of internal damage (especially inter-laminar) such as delamination and transverse cracks would be observed. Therefore, we focused on the contributions by the electrical and thermal properties of the CF/ PANI composite to the suppression of lightning damage.

Both the electrical and thermal properties of the composite are discussed here. Table 3 presents a comparison of the measured electrical conductivity between the CF/PANI and CF/epoxy composites in the inplane and out-of-plane directions. The conductivity was measured with an LCR meter (HiTESTER 32522-50, Hioki E.E. Corp.) with the four-probe method [17]. The CF/PANI laminate shows higher electrical conductivity both in- and out-of-plane than the CF/epoxy laminate: 5.92 times higher in the in-plane direction and 27.4 times higher in the out-of-plane direction. Although application of a general LPS adds much higher in-plane electrical conductivity values of 350-700 S/cm than CF/PANI, CF/PANI showed excellent lightning protection ability without applying LPS. The out-of-plane conductivity could plays an important role in suppressing lightning damage.

To distinguish the contribution of the electrical property changes on lightning damage prevention from those from thermal property changes, the thermal properties of the CF/PANI and CF/epoxy composites were also evaluated. The experimentally measured thermal conductivity,

Excerpt from ISBN 978-3-00-053387-7

specific heat, and initiation temperature for thermal decomposition of both the CF/PANI and CF/ epoxy composites are shown Table 4.

The thermal conductivity was measured by the steady-state method with a GH-1 thermal conductivity measurement system (ULVAC-RIKO, Inc.). The specimen size was 25 mm × 25 mm, and the results are represented as the average value of 5 specimens for each condition. The thermal conductivity in the in-plane direction shows no significant difference between the CF/PANI and CF/epoxy laminates; both increase with the increase in temperature. This indicates that the thermal conductivity in the in-plane direction for both materials is governed by that of the carbon fibers. On the other hand, the thermal conductivity in the out-of-plane direction for both materials does not show any temperature dependence; the CF/PANI shows slightly higher thermal conductivity in the out-ofplane direction.

The differences in the specific heat and thermal decomposition behavior were also evaluated for the two materials. The specific heat was measured with a differential scanning calorimetry (DSC) measurement system (DSC Q100, TA Instruments) at a heating rate of 5 °C/min. The initiation temperature of thermal decomposition was evaluated by a thermogravimetric analysis/differential thermal analysis measurement system (TG/DTA 6300, Seiko Instruments) at a heating rate of 10 °C/min. As shown, no significant difference between the two materials was obtained (Table 4). Only the thermal conductivity in the out-of-plane direction shows slight difference, which is much smaller than the differences in the electrical conductivity and extent of lightning damage between the CF/PANI and CF/epoxy. Though the slightly higher out-of-plane thermal conductivity may produce more heat dissipation in CF/PANI, its highly improved electrical conductivity dramatically reduces the generated Joule heat and resulting extent of damage. Therefore, the differences in the thermal properties have a limited contribution to the lightning damage prevention of the CF/PANI specimen. Further detailed study is needed to clarify the effect of the thermal conductivity differences in the out-of-plane direction on lightning damage behavior.

In the case of the CF/epoxy laminate, only the carbon fiber bundles act as conducting paths, whereas the surrounding epoxy resin acts as an insulator. Thus, only the limited physical contacts between the adjacent layers of the carbon fabric lead to the conduction of electrical current in the out-of-plane direction [20]. The inferior electrical conductivity in the out-of-plane direction results in a temperature rise sufficient to evaporate the surrounding epoxy resin. The limited physical contacts, in particular, could result in the concentration of the heat that initiates inter-laminar delamination, followed by additional damage that develops with the expansion of the evaporated resin gas.

On the other hand, both the carbon fabric and the conductive polymer in the CF/PANI laminate can play a role in the conducting path, resulting in the higher in-plane and out-of-plane conductivity (Table 1). This high conductivity can prevent the concentration of the conducting paths and enable a moderate temperature rise due to the Joule heating effect, resulting in the effective suppression of lightning damage on the CF/PANI laminate.

In terms of the mechanical properties (Table 2), the intact CF/PANI composite exhibits lower flexural strength and ILSS strength than the CF/epoxy composite, although they show equivalent flexural stiffness. The ILSS results indicate that the weaker interface strength between the PANI and carbon fibers could be one of the reasons for the lower flexural strength. The surface sizing treatments of commercially available carbon fibers are optimally designed for epoxy resins rather than various polymers, and the development of suitable sizing for the PANI-based polymer is necessary to improve the interface strength. Additionally, an improvement in the mechanical properties of the PANI-based polymer would also strengthen those properties in the CF/PANI composite.

Table 3 Comparison of electrical properties of CF/PANI and CF/Epoxy [24]

	In-plane conductivity [S/cm]	Out-of-plane conductivity [S/cm]
CF/PANI	148	0.74
CF/Epoxy	25	0.027

Excerpt from ISBN 978-3-00-053387-7

Table 4 Comparison of thermal properties (CF/PANI and CF/Epoxy)

		CF/PANI		CF/Epoxy	
	Temperature [°C]	In-plane	Out-of plane	In-plane	Out-of plane
Thermal conductivity [W/mK]	50	0.349	0.618	0.36	0.419
	100	0.448	0.635	0.444	0.453
	150	0.53	0.628	0.501	0.447
Specific heat [J/gK]	RT (25)	0.857		0.875	
Initiation of resin decomposition [°C]	-	290		290	

3. Conclusions

The present study examines the lightning damage resistance of the developed CFRP with a PANI-based conductive thermosetting resin, comprising PANI as a conductive polymer, DBSA and PTSA as dopants, and DVB as a crosslinking polymer. In the simulated lightning and flexural strength tests, the CF/PANI composite shows dramatically improved lightning damage resistance compared with a conventional CF/epoxy composite, without applying any LSP. The residual strength of the CF/PANI specimen obtained by the 4-point flexural test after suffering damage at -100 kA simulated lightning current showed only a 10% reduction from the initial strength, whereas the damaged CF/epoxy specimen tested at -40 kA showed a 76% reduction. There were no significant differences between the thermal properties of the CF/PANI and CF/epoxy composites, therefore, it can be confirmed that the highly enhanced electrical properties of the CF/PANI composite are the major contributor to the improved lightning damage resistance.

Acknowledgments

This research was supported by JAXA Openlab Project. We are grateful to Prof. Takashi Ishikawa, Nagoya University and Koji Sawaki, Noriharu Takata, and Tsutomu Fukumori of the National Composite Center, Nagoya University, for use of the lightning testing facility. We thank Takeo Sonehara of Shoden Corp. and Junko Aoki and Masaaki Ichikawa of IHI Jet Service Co., Ltd., for technical support in this work.

References

[1] P. Feraboli, H, Kawakami, Damage of carbon/epoxy composite plates subjected to mechanical impact and simulated lightning. *Journal of Aircraft*, 47: 999-1012, 2010.

[2] P. Feraboli, M. Miller, Damage resistance and tolerance of carbon/epoxy composite coupons subjected to simulated lightning strike. *Composite Part A*, 40: 945-967, 2009.

[3] T. Ogasawara, Y. Hirano, A. Yoshimura, Coupled thermal-electrical analysis for carbon fiber/epoxy composites exposed to simulated lightning current, *Composite Part A*, 41: 973-981, 2010.

[4] Y. Hirano, S. Katsumata, Y Iwahori, and A. Todoroki, Artificial lightning on graphite/epoxy composite laminate. *Composite Part A*, 41: 1461-1470, 2010.

[5] G. Abdelal, A. Murphy, Nonlinear numerical modelling of lightning strike effect on composite panels with temperature dependent material properties, *Composite Structures*, 109: 268-278, 2014.

[6] W. Jia, R. Tchoudakov, E. Segal, R. Joseph, M. Narkis, A. Siegmann, Electrically conductive composites based on epoxy resin with polyaniline-DBSA fillers. *Synthetic Metals*, 132: 269-278, 2003.

Excerpt from ISBN 978-3-00-053387-7

[7] CY. Yang, P. Smith, AJ. Heeger, Y. Cao, JE. Osterholm, Electron diffraction studies of the structure of polyaniline-dodecylbenzenesulfonate. *Polymer*, 35: 1142-1147, 1994.

[8] AJ. Heeger, Polyaniline with surfactant counterious, conducting polymer materials which are processible in conducting form, *Synthetic Metals*, 57: 3471-3482, 1993.

[9] Y. Cao, P. Smith, AJ Heeger, Counter-ion induced processibility of conductive polyaniline. *Synthetic Metals*, 57: 3514-3519, 1993.

[10] BH. Jeon, S. Kim, MH. Choi, IJ. Chung, Synthesis and characterization of polyaniline-polycarbonate composites prepared by an emulsion polymerization. *Synthetic Metals*, 104: 95-100, 1999.

[11] T. Del Castillo-castro, MM Castillo-ortega, Electrical, mechanical and piezo-resistive behavior of a polyaniline/poly(n-butyl methacrylate) composite. *Composites Part A*, 40: 1573-1579, 2009.

[12] MJ. Silva, AO. Sanches, LF. Malmonge, JA. Malmonge. Electrical, mechanical and thermal analysis of natural rubber/polyaniline-DBSA composite, *Materials Research*, 17: 59-63, 2014.

[13] J. Lu, K-S. Moon, B-L. Kim, CP. Wong, High dielectric constant polyaniline/epoxy composites via in situ polymerization for embedded capacitor applications. *Polymer*, 48: 1510-1516, 2007.

[14] T. Goto, H. Awano, T. Takahashi, K. Yonetake, Thermally processable highly electrically conductive polyaniline composite, *29th International Conference of the Polymer Processing Society. Nuremberg, Germany*, July 15-19, 2013.

[15] V. Kumar, T. Yokozeki, T. Goto T, T. Takahashi, Mechanical and electrical properties of PANI-based conductive thermosetting composites. *1st Joint Turkey-Japan Workshop on Polymeric Composite Materials, Istanbul, Turkey*, May 12-13, 2014.

[16] T. Yokozeki, T. Goto, T. Takahashi, Q. Danna, S. Itou, Y. Hirano, Y. Ishida, T. Ogasawara, M. Ishibashi, Development and characterization of CFRP using polyaniline-based conductive thermoset matrix. *Composite and Science and Technology*, 117: 277-281, 2015.

[17] S. Takeda, T Mizutani, T Nishi, N. Uota, Y. Hirano, Y Iwahori, Y Nagao, N Takeda, Monitoring of a CFRP-stiffened panel manufactured by VaRTM using fiberoptic sensors, *Advanced Composite Materials*, 22: 99-107, 2013.

[18] *SAE Committee report, AE4L-97-4*, Aircraft lightning environment and related test waveforms standard, 1997

[19] J*apanese Industrial Standards, JIS K 7074*, Testing Methods for Flexural Properties of Carbon Fiber Reinforced Plastics, 1988.

[20] Y. Hirano, T. Yamane, A. Todoroki, Through-thickness electric conductivity of toughened carbon-fibre reinforced polymer laminates with resin-rich layers. *Composite Science and Technology*. 112: 67-72, 2015.

Excerpt from ISBN 978-3-00-053387-7