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PII: S1359-8368(16)31194-5

DOI: 10.1016/j.compositesb.2016.12.059

Reference: JCOMB 4915

To appear in: *Composites Part B*

Received Date: 1 July 2016

Revised Date: 25 October 2016

Accepted Date: 16 December 2016

Please cite this article as: Gaztelumendi I, Chapartegui M, Seddon R, Flórez S, Pons F, Cinquin J, Enhancement of electrical conductivity of composite structures by integration of carbon nanotubes via bulk resin and/or buckypaper films, *Composites Part B* (2017), doi: 10.1016/j.compositesb.2016.12.059.

Enhancement of Electrical Conductivity of Composite Structures by Integration of Carbon Nanotubes Via Bulk Resin and/or Buckypaper Films

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Abstract

This study describes two approaches for the incorporation of carbon nanotubes (CNTs) in carbon fibre reinforced polymer (CFRP) composites, through the addition of the CNTs in the bulk resin and by the addition of CNT-based buckypaper (BP) in the CFRP structure. Several laminates were successfully manufactured integrating these two approaches, where a significant improvement of the electrical conductivity (EC) values was found. Additionally, in order to compare different surface preparations and testing methods, a cross check of EC test was carried out among different laboratories. This characterization was complemented with scanning electron microscopy (SEM) analyses, results of which were used to rule out a complete filtering effect of the CNTs. Furthermore, interlaminar shear strength (ILSS) tests were also performed, with the aim of assessing the mechanical behavior of the different configurations.

Keywords: A. Polymer-matrix composites; B. Electrical properties; Buckypaper.

1. Introduction

In recent years, the implementation of non-metallic materials in aircraft structures has increased in order to meet new technological and ecological requirements which has led to the manufacturing of light-weight and environmentally friendly components. However, a significant drawback exhibited by composite materials, when compared to metallic structures, relates to their lower electrical conductivity and reduced ability to perform different electrical functions such as edge glow, lightning strike, direct effect protection, short-circuits and electrical bonding [1]. The objective of this work is to investigate if these electrical functions could be met through the use of nanotechnologies, by incorporating carbon nanotubes (CNTs) into the common composite manufacturing processes. The CNTs contribute to the development of improved composite materials by enhancing the combined electrical, mechanical and thermal properties of the composite structure [2-5]. It is also important to highlight that the testing methodology for electrical conductivity measurement on composite materials is an important parameter to control [6]. In the last two decades, the use of CNTs has been widely studied for polymer reinforcement, due to their unique combination of superior properties [7]. In particular, the discovery of their electrically conductive behavior dominated by percolation at low filler loadings has led to wide interest in the interplay between the processing and the electrical response of CNT based nanocomposites [8-12]. However, critical issues still need to be overcome, especially related to the processing of CNTs using conventional CFRP composite manufacturing methods, such as liquid injection technologies (resin infusion, RTM). The incorporation of CNTs into the resin leads to an increase in its viscosity, thereby modifying its flow properties, which in turn can affect the impregnation of the fibres. In addition, CNTs introduced via doped resin can be trapped by the carbon fibres during the infusion process causing a filtration effect, leading to inhomogeneity across the composite [13]. Furthermore, the required increase in temperature during the processing and curing steps reduces the viscosity of the CNT doped resin, which can result in the re-agglomeration of the CNTs. To avoid these issues, an optimal and stable dispersion of CNTs within the resin is essential. This enables a suitable nanofiller/resin interfacial bonding and preserves the integrity of the nanoreinforcements during the dispersion process [13]. In this context, the use of CNT based buckypapers (BP) can overcome some of these problems. A BP is a film like sheet consisting of a highly dense network structure of entangled CNTs [14]**,** manufactured by filtration of nanotube suspensions that have been stabilized with surfactants or binders in order to produce thin porous mats. The distribution, high aspect ratios and strong inter-tube Van der Waals attractions of the CNTs, provide sufficient resistance to enable good handling of the sheet form. As a nanostructured preform, the BP can be incorporated into a composite preform and then infiltrated with resin using traditional methods, such as LCM (Liquid Composite Moulding), autoclave, etc. These structures can then be subsequently cured to give composites with high CNT content, leading to superior electrical conductivities. Using this method, the CNTs remain well distributed within the final composite structure. The previously mentioned problems associated with high viscosity (particularly at high CNT loadings levels) are mitigated. The use of this BP technology can therefore enable an easier integration of CNTs into selective areas of the composite. The introduction of BPs could also be envisaged for applications in a number of industrial sectors including aeronautic, aerospace, automotive, defense, electronics and energy. In aeronautics, BP based solutions can be used to replace or reduce the weight of the current metallic mesh used to disperse lightning strikes at the surface of the composite structure of the aircraft [15, 16]. The reduction of metallic structures in composite aircraft can help lead to an important reduction in global weight. BP films can also be interspersed between the fibre layers to help enhance the through thickness electrical properties of the composite structure. For energy storage and conversion applications, the most important advantages of BPs include their high conductivity, large surface area and tailorable porosity for use in fuel cells and batteries. However, the results on CNT-BP based composites reported in literature have shown that some additional issues, such as difficulties for full resin infiltration, can affect the final properties [17]. In this study, BPs have been developed and optimized to be further incorporated into existing CFRP laminates manufacturing processes. Furthermore, the introduction of BPs along with CNT doped resin has also been assessed, in order to solve the previously described issues. This has been done using technical solutions such as adding lower CNT contents (above the percolation threshold) and also optimizing the processing temperatures, to enable a suitable flow during the resin infusion process whilst maintaining the dispersion properties.

2. Experimental

2.1. Materials

MVR444 epoxy resin, provided by Cytec, was selected as the matrix. It consists of a single component resin for the manufacturing of aerospace-quality composite components by infusion processes. However, this resin was received in two parts (MVR444R+ MVR444H), in order to make the CNT dispersion process easier. Graphistrength C100 multi-walled carbon nanotubes (MWCNT) were provided by

Arkema (outer diameter 10-15 nm and length 0.1-10 µm). For the BP manufacturing, MWCNTs were used in powder format, whereas for the doping of the epoxy resin, a masterbatch containing 25 wt.% Graphistrength C100 in MVR444R was developed by Arkema. For the manufacturing of the laminates via infusion process, carbon fibre was used as reinforcement (274 gsm UD fabric from Saertex).

2.2. Manufacturing of CNT doped resin

A two-step dispersion method was applied to disperse the CNTs in the epoxy matrix. The first step consisted of the dilution of the 25 wt.% CNT masterbatch down to 3 wt.% CNT, through the addition of MVR444R, using a three roll calendar mill EXAKT80E. This step was made using a protocol consisting of a progressive reduction of the gaps between the rolls [10, 18], starting at the maximum gap (GAP1=135µm/GAP2= 100µm) and finishing at GAP1=45µm/GAP2=15µm, at a constant speed of 250rpm. A second dilution then reduced the CNT content down to 0.1% wt. This was carried out in a shear mixer DISPERMAT CA-60 by further addition of MVR444R. The MVR444H hardener was then preheated at 80ºC and mixed with the dispersion using mechanical stirring under vacuum. The mixture was then cast in a metallic mould, degassed in a vacuum chamber to eliminate the air trapped in the mixture and cured in an oven using a curing cycle of 75min at 160ºC followed by 2h at 180ºC. The CNT percentage was determined according to the performed rheological study as described in Section 3.

2.3. Manufacturing of Buckypapers

Buckypapers were manufactured using a filtration method, following protocols previously defined by our group [19, 20]. However, several improvements were implemented that enabled the manufacture of BPs up to 245mm in diameter and with a controlled thickness of 80 µm. For improved resin impregnation, the BPs were perforated using a multiple pinned roll creating holes of 1,5mm diameter at a fixed distance of 10mm between holes. The study on the influence of the presence of holes in the final electrical conductivity of the BP is presented in Section 3.2.

2.4. Manufacturing of carbon fibre based laminates

The composite laminates were manufactured via lateral resin infusion process, with stacking sequence $[(+45/0/-45/90)_2]_s$. Three laminates were manufactured, based on the following configurations:

Configuration 1: Undoped resin + carbon fabric (Reference)

Configuration 2: Undoped resin + carbon fabric + BP layer on top surface

Configuration 3: Doped resin (0.1 wt.% CNT) + carbon fabric +BP layer on top surface

For the infusion of undoped resin, the mould and resin temperatures were maintained at 80ºC and 70ºC respectively, according to the conditions suggested by the resin supplier [21]**.** However, for the infusion of the doped resin, processing conditions were adjusted to use a mould temperature of 88ºC and a resin temperature of 77ºC, to counteract the increased resin viscosity caused by the addition of the CNTs (see Section 3). The curing cycle was set at 160ºC for 75 min followed by a post-curing cycle of 2h at 180ºC.

2.5. CNT doped resin characterization

2.5.1. Rheological analyses

Continuous flow and small amplitude oscillatory flow measurements were carried out in a Haake Rheostress 6000 rheometer using plate-plate geometry with 20 and 60mm diameter and 0.5-1 mm gap. In particular, viscosity profiles were analysed, and the gel time of the samples was obtained through the assessment of the crossing of storage (G') and loss (G'') moduli.

2.5.2 Electrical conductivity measurements

Electrical conductivity measurements were carried out at room temperature on cured CNT doped resin samples (90mm x70mm x 2mm). In this case, according to the conductivity range of the sample, a two probe method was employed [22], according to the ASTM D257 standard test, using a Keithley 2410 as the source/meter and a resistivity chamber Keithley 8009.

2.6. Buckypaper characterization

For the electrical characterization of BP, a four probe Van der Pauw method [23] was employed, using the Keithley 2410 source/meter with an applied current intensity of 10mA. Sample dimensions were 45x45mm. Three specimens were tested for each material and the mean values were considered. Dimensions and weight of BPs were also measured to calculate the areal weight.

2.7. Carbon fibre based laminates characterization

In order to assess the possible filtering effect of the CNTs in the doped resin during the infusion process, SEM analyses (JEOL JSM-5910LV) were performed on samples from the outlet area of the doped resin based laminate. Additionally, a visual inspection of the resin in the outlet area was carried out, to confirm the presence of CNTs after the infusion process. Furthermore, the dispersion quality was evaluated by SEM on the inlet and outlet areas of the laminates. SEM analyses were also carried out also on BP based laminates in order to evaluate the impregnation of the BP by the resin. The EC was measured in the through-thickness direction using 40x40mm samples taken from four different zones of the laminates, where Zone 1 corresponds to the area nearest to the inlet part and Zone 4 corresponds to the area nearest to the outlet part of the laminate. A four wire methodology was used to eliminate the effect of the electrical resistance of the wires, according to the AITM2-0065 standard test. As conductivity values can be influenced by the testing method, alternative measurement methods were considered. The compression method, applies pressure (50MPa) on the electrode plates placed on top and bottom of the sample, with the aim of minimizing the contact resistance between the electrode and the sample by assuring a full contact between them [6]. In order to minimize these effects, the upper and lower faces of the samples were metalized, depositing a conductive material on the surfaces to act as electrodes. Two different types of metallization were considered and compared in this work:

- Silver conductive paint, commercially available (RS 186-3600, RS Online).

- Nickel Electrodeposition, using an electrochemical process. This process consists of two steps. Firstly, an electro-less nickel deposition (5µm to 10µm) is carried out, followed by an electrolytic nickel plating (20µm to 50µm) (according to AITM2-0065).

In order to have a good contact between the outer carbon fibres and the metallic deposition, prior to the metallization step, both surfaces were sanded to remove surface resin. With the aim of assessing the influence of the metallization type, the different testing methods as well as the test equipment used, a cross-check was performed amongst several laboratories: Airbus Group Innovations (former EADS-IW-France), Airbus France (AIR-F) and Tecnalia. A summary of the cross check tests can be found in Table 1. ILSS tests, according to the UNE EN 2563 standard test, were also carried out using an Instron 5500 universal testing machine. Five specimens were tested for each laminate, cut from different zones from the inlet through to the outlet area.

3. Results and discussion

3.1. CNT doped resin- results

For an adequate impregnation of CNT based buckypaper with epoxy resin, several authors suggest a maximum viscosity value of the resin of 100 cP [24]. In addition, for resin injection technologies, the viscosity of the resin is usually limited to 100–500 cP [25]. In this context, the evolution of viscosity with temperature was studied to select the optimum processing conditions. Table 2 shows the resin viscosity values for the processing temperatures suggested by Cytec [21].

Although the viscosity of the doped resin is lower than 500 cP at these temperatures (Fig. 1), the doped resin and mould temperatures were increased to 77ºC and 88ºC respectively in order to lower the viscosity of the doped resin to that of the neat resin. In this way, the same processing conditions were used. The influence of CNTs in the curing behavior of the epoxy resin was evaluated by isothermal curing at T=140ºC. The evolution of storage (G´) and loss (G´´) moduli with time was studied (Fig. 2), with the gel time considered to be the time at which crossing of the moduli curves is observed, i.e. G´=G´´ [26-29]. When adding 0.1 wt.% CNT to the epoxy resin, the gel time decreased by 6 minutes (from 162min to 156min). This accelerating effect has been observed by several authors and is attributed to the catalyst impurities of the carbon nanotubes [30, 31]. Regarding the electrical conductivity, 0.1 wt.% CNT doped resin showed an electrical conductivity of 1.10^{-6} S/m, which is five orders of magnitude higher than that of the neat resin. This result indicates that an electrical path is formed within the matrix by the CNTs [32]. The CNTs are surrounded by the insulating epoxy resin, so in theory the electron transport could be based on the tunneling effect. Tunneling has to be taken into account for the electrical conductive behavior of CNT-filled composites. When nanotubes reach the electrical percolation threshold in a polymeric matrix, they need not physically touch each other, as long as they are just close enough to allow the hopping/tunneling process [11, 33, 34].

3.2. Buckypaper- results

The manufactured BPs presented areal weights in the range of 40-80g/m^2 with thicknesses in the range of 50- 100µm. Electrical conductivity values were in the range of 3000-5000 S/m. The BP is an already formed network of CNTs and this network is not significantly altered after resin infusion [35, 36]. However, owing to the high natural density of the vacuum filtered BP and its natural low permeability [20], a higher level of porosity is needed in the BP sheets for its use in composite applications, in order to improve the resin flow [17]. Several BPs were manufactured and mechanically perforated, using a punching method, in order to vary the overall number of “introduced” holes. The BP perforation percentage is calculated with respect to the surface loss resulting from the generation of these holes. Each perforated BP was tested for its Van der Pauw electrical conductivity as described in Section 2.6. Figure 3 shows the Van der Pauw electrical results. According to Fig. 3, an 8% of additional mechanical perforation of the BP resulted in an EC of 3100 S/m. This corresponded to a 20% reduction in EC value compared to the baseline BP (EC 3800 S/m). Based on this analysis, it was established that the introduction of 1.5% added perforation, lead to just a 2-3% decrease in EC. For this purpose, a pinned roller system with holes of 1.5mm maximum diameter at 10mm spacing was introduced. This system is also better suited to continuous production methods.

3.3. Carbon fibre based laminates characterization- results

3.3.1. SEM

During the infusion process of the doped resin, both with and without BP, no evidence of the filtering effect was visually detected. There was no change in filling time with respect to the neat resin, however, the distribution of the CNTs at the inlet and outlet regions, as well as the impregnation of the BP were investigated by SEM. For BP based laminates (Fig. 4-6), it can be observed in all cases that the BP was well impregnated by the resin in both the inlet and the outlet part. These analyses and findings are supported by previous work studying the ability of the BP to be impregnated by a resin [19]. Laminates manufactured with doped resin (Fig. 5 and 6) show good dispersion of CNT in the resin. The presence of CNTs in the outlet part of the laminate confirmed again the absence of any significant filtering effect during infusion.

3.3.2. Electrical conductivity

For all the three laminates, EC tests were performed according to different parameters such as testing zone, electrode type, testing method, equipment and laminate configuration.

a) Testing zone

Four different zones, from the inlet to the outlet area were studied in each laminate. Figure 7 shows the EC test results, performed according to the AITM2-0065 standard test which used the nickel electrodeposition as electrode type. These measurements were made using a Keithley 2410 source/meter. Slight differences can be observed between the different zones, especially in the case of the reference laminate (Fig. 7a).

b) Electrode type

Figure 8 presents a comparison between the two electrode types, silver paint and nickel electrodeposition, for each configuration. The tests used the Keithley 2410 as the source/ meter and were performed according to the AITM2-0065 standard. As can be seen in the figures, similar values were found using both electrode types.

c) Equipment

A comparison was made between the EC results for the BP based laminates using nickel electrodeposited sample tested according to the AITM2-0065 standard. For the comparison, the samples were measured using different equipment (Keithley 2410 and Burster Resistomat 2316 series) with the results shown in Fig. 9. It can be concluded that the use of different measurement equipment does not affect the final EC results.

d) Test method

The different test methods were also compared (AITM2-0065 and compression method). In this case, nickel electrodeposited samples from the reference laminate were studied. Since the equipment type is not a parameter that affects the EC values (as concluded above), Keithley 2410 and Multimeter Agilent 34 420A were used. As can be seen in Fig. 10, the results were not strongly influenced by the testing method.

e) Laminate configuration

Figure 11 shows the EC results for the different laminate configurations. The results show the mean values resulting from the four studied zones for each laminate configuration. All the samples were tested according to the AITM2- 0065 standard test using the nickel electrodeposition for the electrode and the Keithley 2410 as the source/meter. The reference laminate showed a high scattering of results that could be attributed to the typical variations derived from the infusion process. Resin infusion can affect the level of contact between the fibres in the Z direction, which is the dominant parameter in the through thickness electrical conductivity properties. The EC values were not seen to be affected by the BP layer on the surface. Nevertheless, the highest EC values were found in the laminate which combined the BP and the 0.1 wt.% CNT doped resin. This combination has led to a 30% increase in through-thickness electrical conductivity. The presence of CNTs plays a significant role in the resin rich areas [37], contributing to the electron transport by forming a conductive path between the fibres.

3.3.3. Mechanical characterization.

ILSS test results, corresponding to the different testing zones are shown in Fig. 12. No significant variations were found in the different tested areas for the studied laminates. When introducing the BP, the laminate exhibited no change in strength with respect to the reference laminate, whereas the BP+doped resin laminate showed a slight decrease in strength. These small differences could be due to the variability usually found in the infusion process, especially when adding CNTs [38, 39]. In Fig. 13 a summary of the ILSS results can be seen for each laminate configuration.

4. Conclusions

A combination of CNT doped resin and CNT buckypaper layered nanomaterials were successfully integrated into CFRP composites using an infusion process. The original composite mechanical properties were maintained. Good dispersion of CNTs was achieved, as confirmed by rheological analyses, which revealed an accelerating effect of the CNTs in the curing of the epoxy resin. CNT doped resin showed a significant improvement in electrical conductivity, compared to undoped resin, and reached values up to 1.10^{-6} S/m. The doped CFRP laminates exhibited good dispersion of CNTs and the SEM analysis confirmed that a filtering effect did not occur in the laminates. Good impregnation of the buckypaper by the resin was also observed. The through thickness EC values were significantly improved in the laminate manufactured with both BP and CNT doped resin. An increase of 30% was observed with respect to the reference samples, close to the requirement for the edge glow protection of composite structures. It is important to pay attention to the high dispersion of results in the reference laminate, which revealed the low repeatability of the infused laminates, even in the undoped samples. The cross-check performed in this study reveals that the surface preparation method has no influence on the through thickness EC values and similar results were obtained when either electrodeposition or silver paint metallization were used. This study has also confirmed that the EC values are not dependent on the testing method used (AITM vs Compression). The results of this study could potentially be used to help implement the introduction of CNTs in both sheet and doped resin form in the manufacturing of larger composite structures. The CNT based technologies have been developed with the consideration of their scaling up to industrial processes.

5. Acknowledgments

We gratefully acknowledge the financial support from FP-7 EU project ELECTRICAL: Novel Aeronautical Multifunctional Composite Structures with Bulk Electrical Conductivity and Self-Sensing Capabilities (ACP8-GA-2010-265593), especially project partners CYTEC and ARKEMA for the material supply and technical support.

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7. Figure Captions

Fig. 1. Evolution of viscosity with T for undoped and doped epoxy resin

Fig. 2. Evolution of G´ and G´´ with time at T=140ºC for undoped and doped resin

Fig. 3. Influence of mechanically added holes on BP electrical behavior

Fig. 4. SEM images of CFRP laminates: Configuration 2. a) Inlet zone b) Outlet zone

Fig. 5. SEM images of CFRP laminates: Configuration 3, Inlet zone: a) BP b) CNTs in resin

Fig. 6. SEM images of CFRP laminates: Configuration 3, Outlet zone: a) BP b) CNTs in resin

Fig. 7. EC results vs testing zone for: a) Configuration 1 b) Configuration 2 c) Configuration 3

Fig. 8. EC results vs electrode type for: a) Configuration 1 b) Configuration 2 c) Configuration 3

Fig. 9. EC results vs equipment for: a) Configuration 2 b) Configuration 3

Fig. 10. EC results vs test method for Configuration 1

Fig. 11. EC results vs laminate configuration

Fig. 12. ILSS results vs testing zone for: a) Configuration 1 b) Configuration 2 c) Configuration 3

Fig. 13. ILSS results vs laminate configuration

8. Tables

Laminate	EC Test		
	Electrode Type	Method	Equipment
Reference	Silver Paint	AITM2-0065	Keithley 2410
	Nickel electrodeposition	AITM2-0065	Keithley 2410
	Nickel electrodeposition	Compression	Multimeter Agilent
BP+Undoped	Silver Paint	AITM2-0065	Keithley 2410
	Nickel electrodeposition	AITM2-0065	Burster Resistomat 2316 series
	Nickel electrodeposition	AITM2-0065	Keithley 2410
BP+Doped	Silver Paint	AITM2-0065	Keithley 2410
	Nickel electrodeposition	AITM2-0065	Burster Resistomat 2316 series
	Nickel electrodeposition	AITM2-0065	Keithley 2410

Table 1. EC tests on carbon fibre based laminates - cross checking details

Neat Resin		Doped Resin
T (ºC)	**Viscosity (cP)**	**T (ºC)**
70 (resin)	280	77 (resin)
80 (mould)	150	88 (mould)

Table 2. Resin and mould temperatures according to the viscosities suggested by Cytec

FIGURES

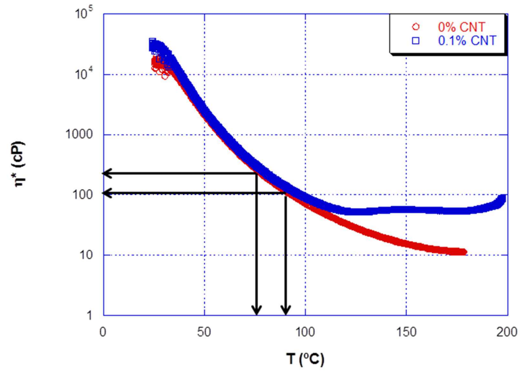

Fig. 1. Evolution of viscosity with T for undoped and doped epoxy resin

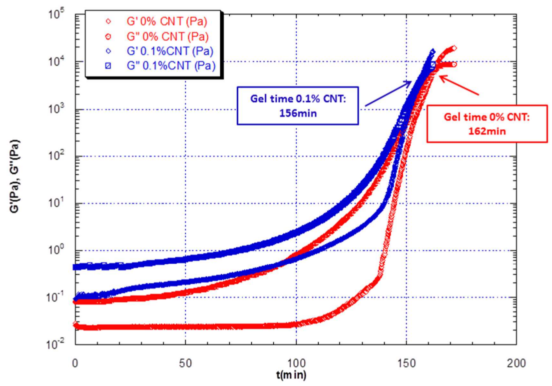

Fig. 2. Evolution of G´ and G´´ with time at T=140ºC for undoped and doped resin

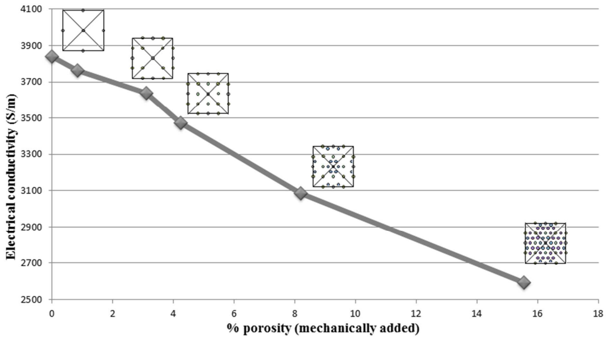

Fig. 3. Influence of mechanically added holes on BP electrical behavior

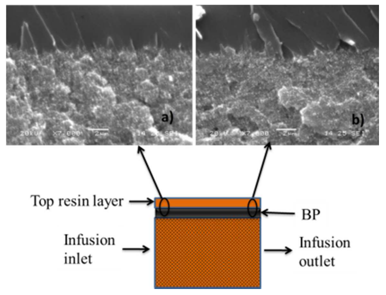

Fig. 4. SEM images of CFRP laminates: Configuration 2. a) Inlet zone b) Outlet zone

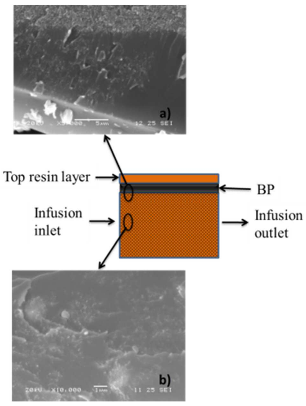

Fig. 5. SEM images of CFRP laminates: Configuration 3, Inlet zone: a) BP b) CNTs in resin

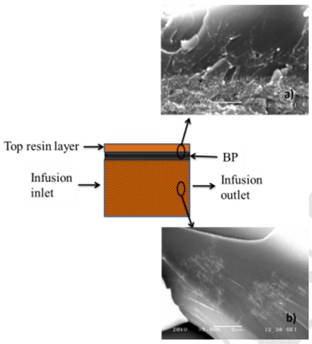

Fig. 6. SEM images of CFRP laminates: Configuration 3, Outlet zone: a) BP b) CNTs in resin

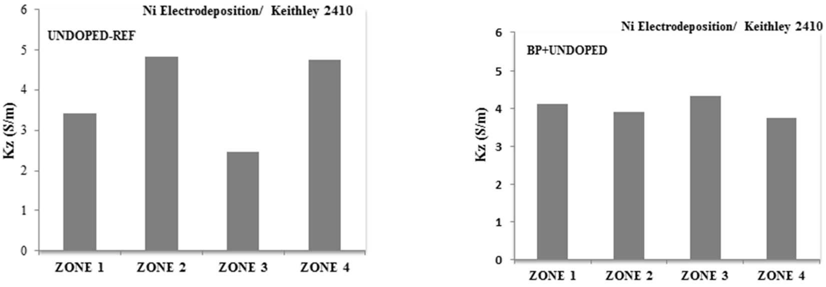

Fig. 7. EC results vs testing zone for: a) Configuration 1 b) Configuration 2

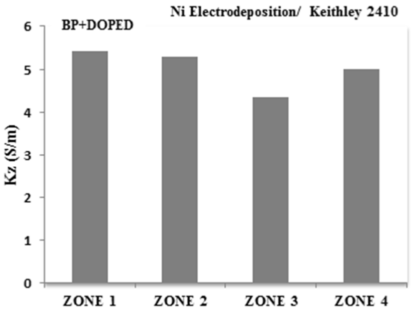

Fig. 7c) EC results vs testing zone for Configuration 3

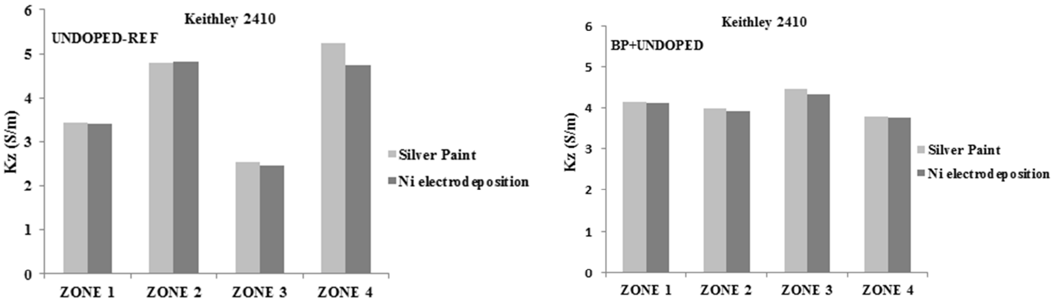

Fig. 8. EC results vs electrode type for: a) Configuration 1 b) Configuration 2

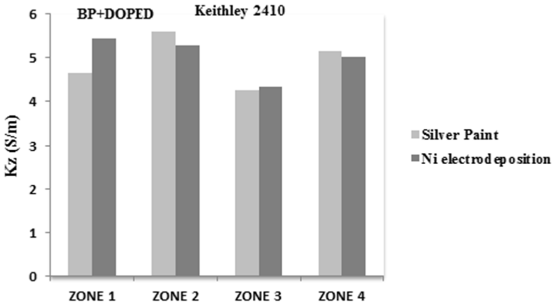

Fig. 8c) EC results vs electrode type for Configuration 3

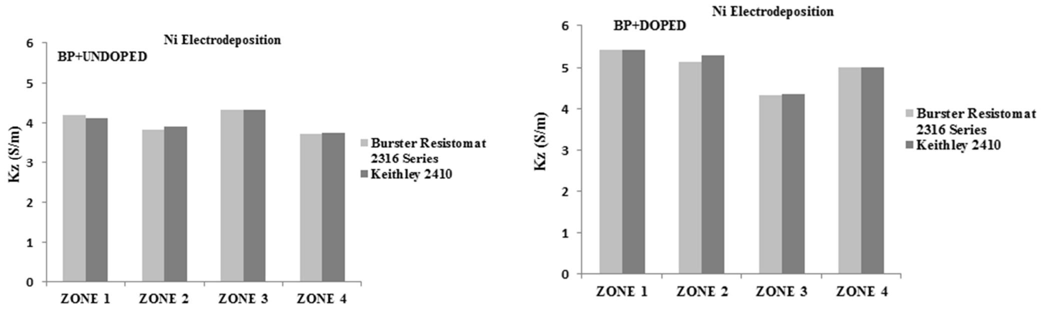

Fig. 9. EC results vs equipment for: a) Configuration 2 b) Configuration 3

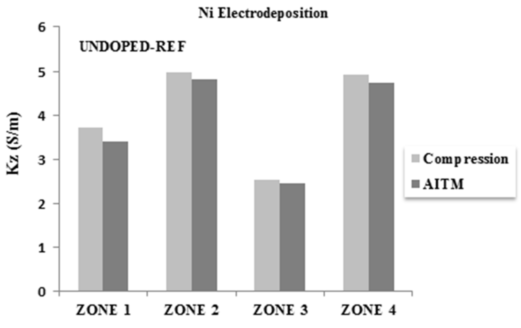

Fig. 10. EC results vs test method for Configuration 1

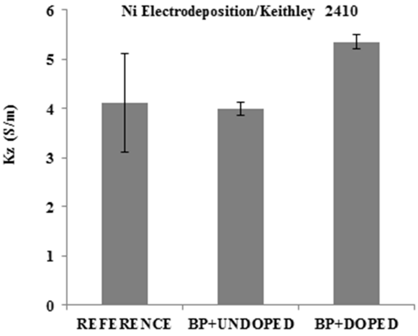

Fig. 11. EC results vs laminate configuration

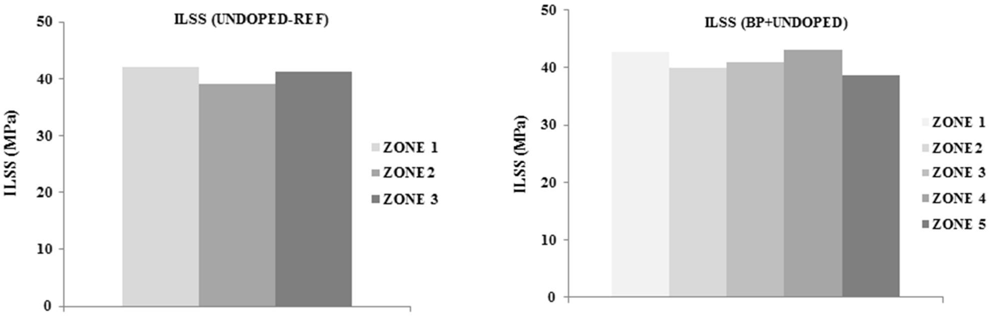

Fig. 12. ILSS results vs zone for: a) Configuration 1 b) Configuration 2

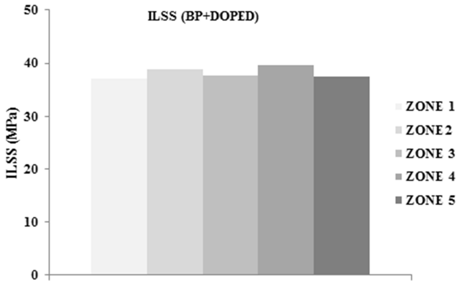

Fig. 12c) ILSS results vs zone for Configuration 3

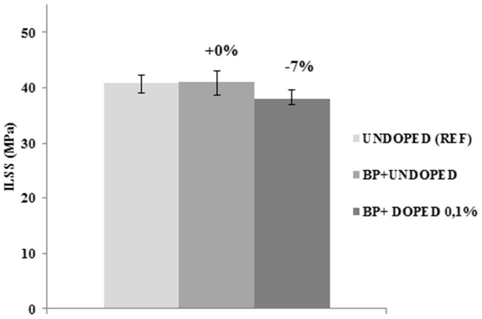

Fig. 13. ILSS results vs laminate configuration