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MANUFACTURING OF COMPOSITES SAMPLES WITH GRAPHENE

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Abstract

The article presents the state of knowledge within the scope of graphene production used in polymer matrices composites, as well as methods of obtaining graphene for these composites, including chemical method. The way of obtaining graphene in form of planes with dimensions of 90 x 100 mm and the method of manufacturing multilayer composite with graphene were presented. Composites were produced from carbon fiber-epoxy resin prepregs in out of autoclave process. The adhesive film were used as an additional component which allows to transfer of graphene plane on carbon-epoxy resin prepregs and facilitate the consolidation process. In terms of the quality analysis of prepared composite samples results of ultrasonic tests of composites plate without the graphene and with graphene as an A-scan, B-scan, C-scan, S-scan were shown. The use of ultrasonic methods of registration: C-scan type amplitude of the echo and bottom echo signal amplitude,that allows to detect manufacturing defects caused by the mismatch of parallel edges of carbon prepregs, were engaged. The analysis of C-scan images allows to determine the accuracy of the angular orientation of the carbon layers.
Keywords: composite, graphene, composites with grapheme.

1. INTRODUCTION

Carbon-epoxy composites are materials widely used as structural components in the automotive and aerospace industries [1÷3]. The attractiveness of such materials is associated with their favorable properties: high stiffness and resistance to fatigue loading conditions. The low weight of composites as compared to conventional construction materials, such as metal alloys, is also important [4]. However, polymer composites also have limitations in application due to the fragility of the matrix. This leads to the appearance of delamination and cracks particularly manifested due to destruction by impact. Hence, attempts to refine the material further by including additional reinforcement to polymer matrix in the form of nanofillers are widely taken. Nanofillers can significantly improve the mechanical and electrical properties of the material [5]. Next to well-studied carbon nanofillers such as: carbon nanotubes, nanofibers or carbon black, the possibility of using graphene in polymer composites is also considered [5].

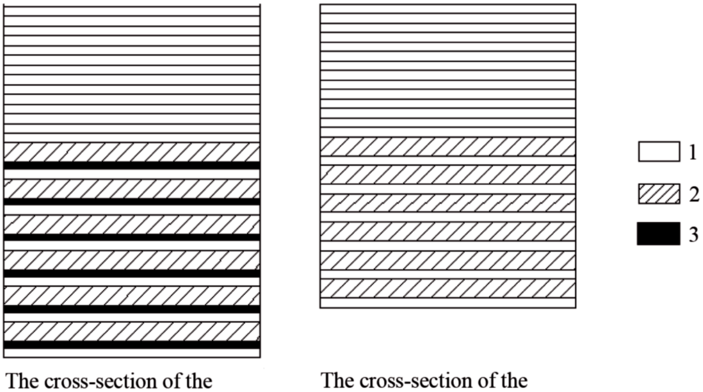
The unique structure of graphene as the lightest and most durable material gives the great potential to reduce the weight of the means of transport construction, thereby reducing fuel consumption. Additionally, the incorporation of graphene is connected with the improvement of electrical properties, thermal conductivity, and mechanical properties of composites by reinforcing the connection between the fiber and the matrix [6]. In aviation resins doping with graphene or graphene oxide is used mainly to improve the strength properties of the material, changing the penetrability of gases, and to increase the chemical and resistivity of construction [7].

Work on graphene reinforced carbon-epoxy composites consists mainly of doping the polymer matrix with graphene flakes of small, nanometer sizes. Flakes of graphene are obtained from reduced graphene oxide with the use of the cheapest and simultaneously the most effective chemical method (and it is called chemical graphene) [8]. Graphene planes of large scale can be produced by metallurgical method from liquid phase on the surface of Cu-Ni alloy. This method can provide graphene with high mechanical strength [9, 10, 11].

The aim of this study was to determine the effect of graphene on the structure and properties of carbon fiber-epoxy resin composite. To realize the task design and technology of composite panels with adhesive film and adhesive film with graphene were developed and non-destructive ultrasonic tests were conducted.

2. THE METHOD OF GRAPHENE REINFORCED COMPOSITES PANELS MANUFACTURING

The construction and technology of composites panels fabrication from unidirectional prepreg MTM46 / HTS (12K) -150-35% RW type were developed. Composites samples with adhesives films only and with graphene plane on adhesives film measuring 100×150 mm were prepared. Each composite panel consisted of 20 layers of prepreg, 6 layer of film adhesives with graphene and without graphene plane for comparison purpose (Fig. 1).



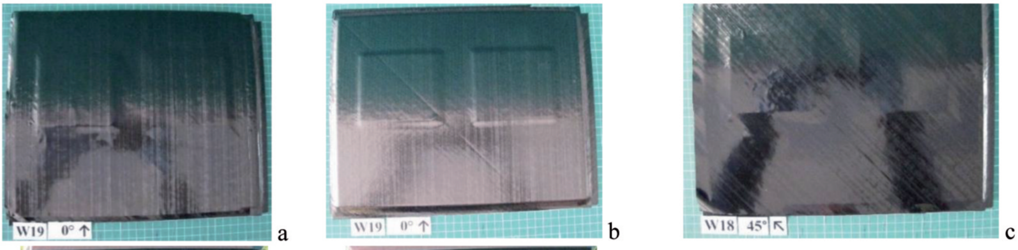
The cross-section of the composite panel with graphene plane

The cross-section of the composite panel without graphene plane

Fig. 1. Schematic arrangement of adhesive film and graphene layers between carbon fiber-epoxy resin in cross-section view of composite panels:
1 – prepreg layer,
2 – adhesive film,
3 – graphene plane.

Examples of arrangement of the prepreg layers at various angles before and after vacuum pressing process are shown in Figure 2. Graphene planes, because of a smaller size (90×90 mm) than the composite panels, cover only part of the sample (Fig. 2). Samples, which were cut from the fabricated composite panels, were designated as:

1. samples without graphene – G-O.2-CAI-KB-RTA-01,
2. samples with graphene – G-O.3-CAI-GKB-RTA-01.



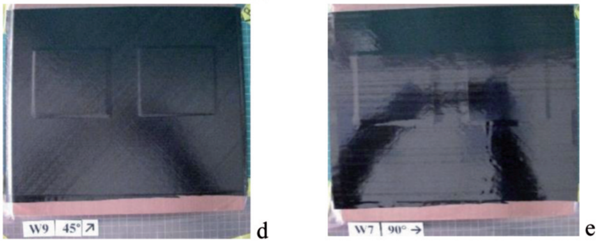


Fig. 2. Examples of arrangement of prepreg layers at various angles before vacuum press:
a – 0°,
and after vacuum press:
b – 0°,
c – -45°,
d – +45°,
e – +90°

Examples of setting layers of adhesives film on prepreg and the final panel with adhesive film (KB) and graphene on adhesive film (GKB) is shown in Figure 3.

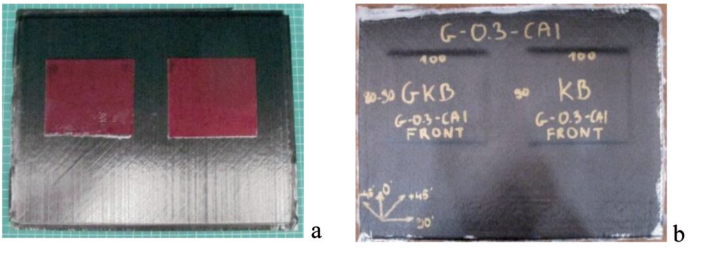


Fig. 3. View from the front of composite panels:
a – with two layers of adhesives film,
b – finished panel with adhesives film (KB) and adhesives film with graphene (GKB)

For composite panels fabrication the adhesive film of a thickness of 0.24 mm was used, on which, as on the media, graphene plane was transfered.

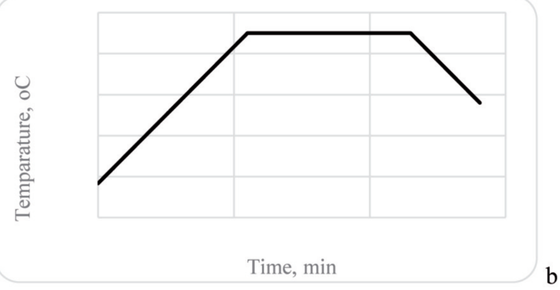
The production of graphene plane and the transfer process was performed by the Team of Łódź University of Technology. The high strength metallurgical graphene (HSMG™) sheets were manufactured in an thermochemical facility based on the process described in previous papers [9, 10, 11]. Structural adhesive film (3M Scotch-WeldTM AF 163-2) was used for transfer process of graphene as a graphene support. *Adhesive film/Graphene/Metallic substrate* stack was placed in a $FeCl_3$ solution (1M), 4°C for 24 h. After etching process adhesive-film with graphene was rinsed in cold deionizer water and in this form graphene was introduced into composites structures. Six layers of adhesives film were positioned on every composites plane under six the most outer prepreg sheets, which was presented in Figure 1. On the composite panel applied to the adhesive layer 6 disposed on one side into the outer layers of prepregs as positioning adhesive and the adhesive between the graphene layers of prepreg are shown in Figure 1.

The example of preparting layer system with adhesive film (KB) without graphene - G-0.2-CAI panel and with graphene (GKB) - G-0.3-CAI panel is following:

1. G-0.2-CAI plane – [45/KB/0/KB/-45/KB/90/KB/90/KB/-45/KB/0/45/45/0/-45/-45/0/45/,
2. G-0.3-CAI plane – [45/KBG/0/KBG/-45/KBG/90/KBG/45/KBG/0/KBG/-45/90/45/0/-45/90/45/0/.

Composite panels were prepared from MTM46/HTS(12K)-150-35%RW unidirectional prepreg, which were cured (Fig. 4a) in a special oven adapted for this purpose (Fig. 4b).


a



b

Fig. 4. The process of thermal curing of composite panels with adhesive films and with graphene on adhesives film made from MTM46/HTS(12K)-150-35%RW carbon fiber epoxy/resin prepreg: a – chamber of oven dedicated for curing process; b – diagram of temperature change in the function of heating and cooling time of composite panels.

3. NONDESTRUCTIVE ULTRASONIC TESTS OF COMPOSITE PANELS

After curing composite panels ultrasonic tests were submitted. The amplitude of the ultrasonic C-scan were determined from the smooth surface side:

1. sample (1) G-0.2-CAI (Fig. 5, 6) consisted of prepregs and 6 layers of adhesive film without graphene,
2. sample (2) G-0.2-CAI consisted of prepregs and 6 layers of adhesive film with graphene (Fig. 5, 6)

and the following results were obtained:

1. sample without graphene (1) – *SNR* coefficient = 9 dB; the average amplitude of the bottom echo *Aev* = 59 % FSH with a standard deviation of 9.8 % FSH,
2. sample with graphene (2) – *SNR* coefficient = 9.8 dB, the average amplitude of the bottom echo *Aev*=73.5 % FSH with a standard deviation 6.8 % FSH.

NDT research and obtained SNR coefficient show that sample with graphene has lower level of noises (higher value of SNR coefficient) and significantly lower amplitude decrease relative to reference amplitude, the value of which was taken as 80 %. Noises are always caused by inhomogeneity and discontinuity of the material. Since the samples are made of the same materials and in the same production process can therefore deduce that graphene can, to same extend, reduce the loss in amplitude. Moreover, graphene suppresses and disperses the ultrasonic wave to a lesser degree then material consist only with prepregs and adhesive films. From the NDT investigator point of view quality of the samples with graphene is greater than those without graphene.

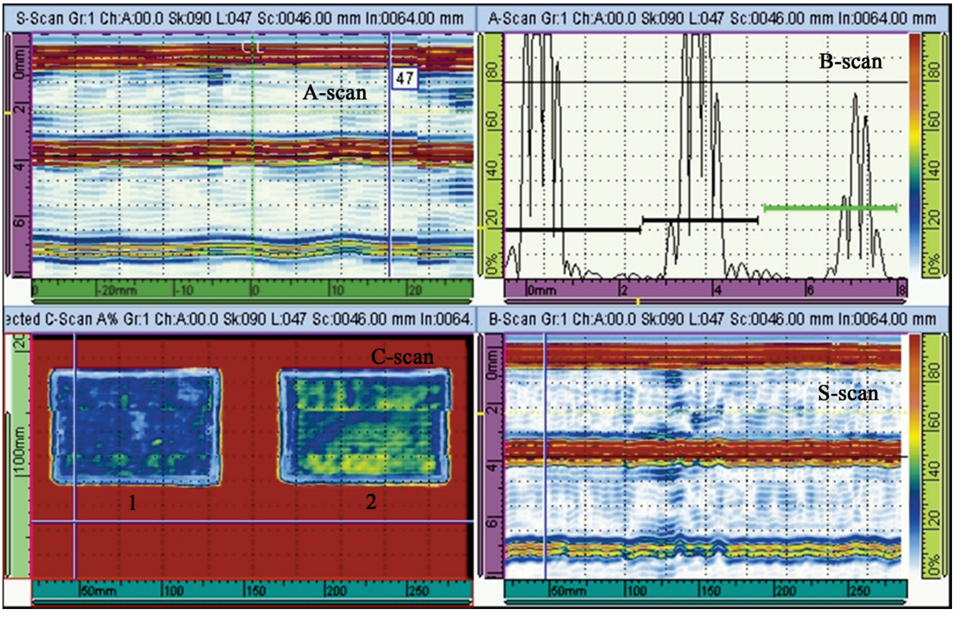


Fig. 5. A-scan, B-scan, C-scan i S-scan of G-0.2-CAI panel: 1 – sample without graphene, 2 – sample with graphene

In view of C-scan echo amplitude and the amplitude of the echo bottom the purple line at an angle of 44.8° is visible (Fig. 6), which shows the manufacturing defect arising from mismatch of the parallel edges of carbon fiber/epoxy resin prepreg. The defect could be a result of the lack of surplus material.

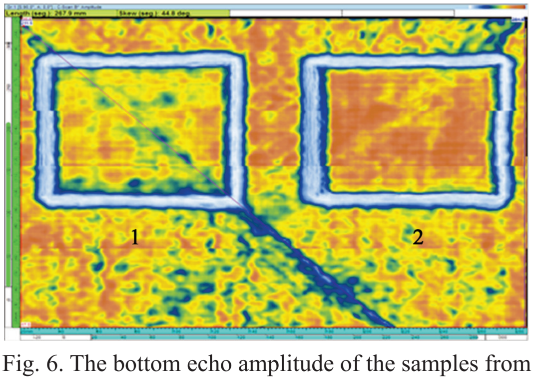


Fig. 6. The bottom echo amplitude of the samples from G-0.2-CAI panel: 1 – sample without graphene, 2 – sample with graphene

Higher taint temperature in figure 6 indicates a higher amplitude of the signal reflected from the bottom of the tested samples of carbon composite.

Figure 7 (C-scan of the echo and echo bottom view) shows the purple line at 45º/-45º; it is a manufacturing defect caused by the mismatch between the parallel edges of prepreg carbon. The defect could be a result of the lack of surplus material.

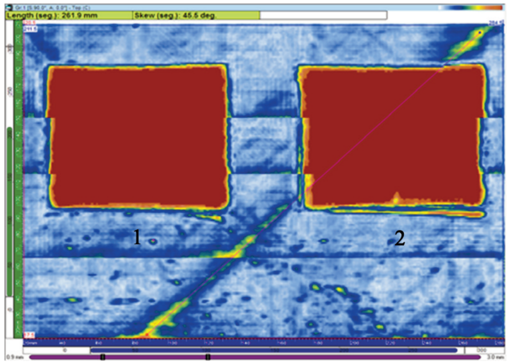


Fig. 7. The bottom echo amplitude of the samples from G-0.2-CAI panel: 1 – sample without graphene, 2 – sample with graphene

Purple line shows the defect cause by edges mismatch of two pieces of prepreg. The angle of located layers was 45º, and the measured angle of this edges was 45.5°.

Figures 8 and 9 shown the smooth side of the test samples from panel G-0.3-CAI in view of the C-scan technique. Sample (1) contains a prepreg and 6 layers of adhesive film without graphene. Sample (2) from the same panel G-0.3-CAI contains carbon prepreg with the adhesive film with graphene. The following results from C-scan test were obtained:

1. sample without graphene (1) – *SNR* coefficient = 7.2 dB; the average amplitude of the bottom echo *Aev*=61.8 % FSH with a standard deviation of 9 % FSH,
2. sample with graphene (2) – *SNR* coefficient = 8,1 dB, the average amplitude of the bottom echo *Aev*=73.5 % FSH with a standard deviation 6.8 % FSH.

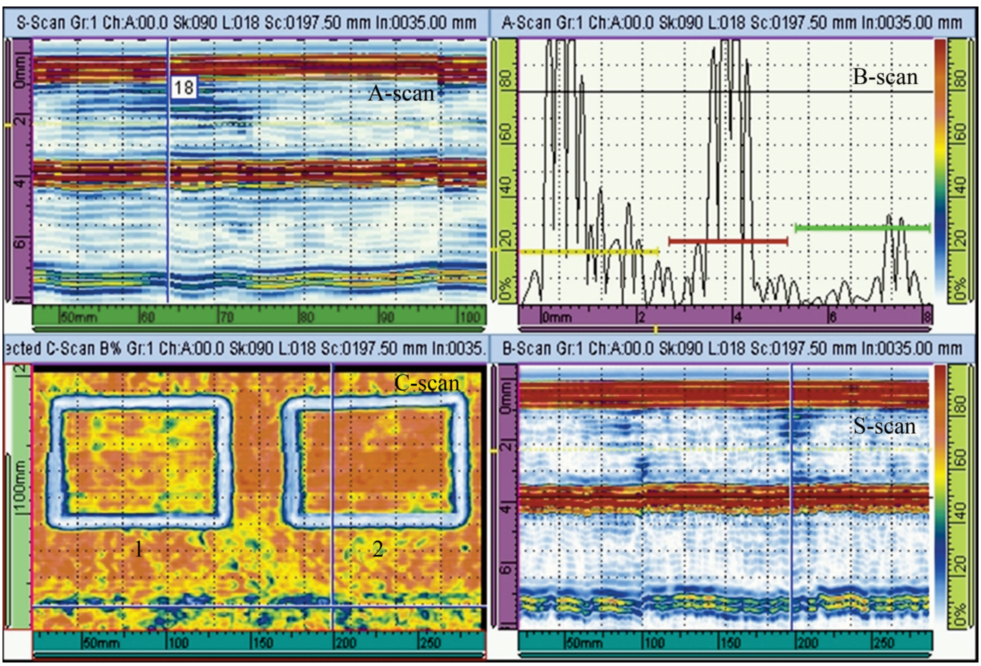


Fig. 8. A-scan, B-scan, C-scan and S-scan view of G-0.3-CAI panel: 1 – sample without graphene, 2 – with graphene

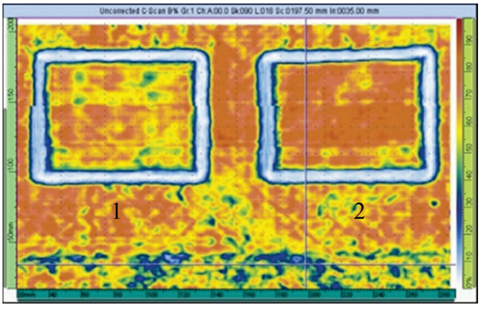


Fig. 9. Echo bottom amplitude of samples from G-0.3-CAI panel: 1 – sample without graphene; 2 – sample with graphene

Higher taint temperature in Figure 9 indicates a higher amplitude of the signal reflected from the bottom of the tested samples of carbon composite.

The view of C-scan amplitude (Fig. 10) shows the purple line at 45º/-45º. It is a manufacturing defect caused by the mismatch between the parallel edges of prepreg carbon. The defect could be a result of the lack of surplus material.

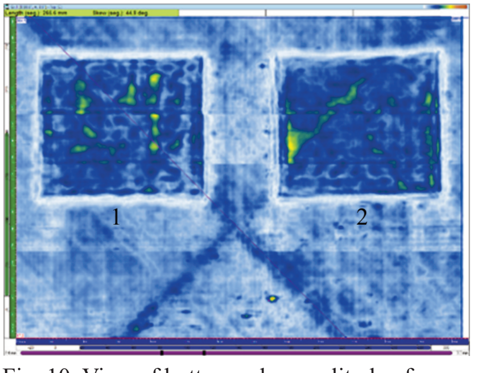


Fig. 10. View of bottom echo amplitude of G-0.3-CAI panel: 1 – sample without graphene, 2 – sample with graphene

Purple line shows the defect caused by mismatch of prepregs edges. The angle of located layers was -45º and 45º, and the measured angle of this edges were: -45.5° and 45.3°.

4. CONCLUSIONS

Based on the carried tests the following conclusions can be drawn:

1. Adhesive film is a good media for graphene transfer on carbon fiber-epoxy resin prepreg – the obtaining composite panels are free from delamination in the area, where the graphene plane edges met with prepreg.
2. The use of nondestructive ultrasonic methods of registration C-scan echo amplitude and the amplitude of the bottom echo allows to detect manufacturing defects caused by the mismatch prepreg edges (as evidenced by the purple line).
3. Higher SNR and C-scan echo amplitude of samples with graphene (SNR=9.8 dB) than of samples without graphene (SNR=9 dB) indicates that graphene reduces noises caused by material defects.

4. An analysis of images such as ultrasonic C-scan allows to specified angular alignment of prepreg layers with accuracy of ± 0.5°.
5. The demonstrated tests show the necessity of consideration the changes in the structure of the sample by use of an adhesive film over the entire surface of the composite panel, which will compensate the sample thickness and uniformity and eliminate the presence of weaker place in the sample.

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WYTWARZANIE KOMPOZYTOWYCH PRÓBEK Z GRAFENEM

Streszczenie

W artykule przedstawiono stan wiedzy w zakresie wytwarzania grafenu do zastosowania w kompozytach o osnowach polimerowych, a także metody pozyskiwania grafenu dla tychże kompozytów, w tym metodę chemiczną. Przedstawiono sposób pozyskiwania grafenu w formie płaszczyzn o wymiarach 90x100 mm, a także metodę wytwarzania wielowarstwowego kompozytu z grafenem. Kompozyty wytwarzano z preimpregantów węglowo-epoksydowych w procesie bezautoklawowym. Zastosowano klej błonkowy, jako dodatkowy składnik kompozytu pozwalający na przeniesienie płaszczyzn grafenowych na preimpregnat węglowo-epoksydowy oraz ułatwiający proces konsolidacji kompozytu. W zakresie wykonanych analiz jakości przygotowanych próbek kompozytowych przedstawiono wyniki badań ultradźwiękowych płyt kompozytowych bez grafenu i z grafenem w postaci: A-scan, B-scan, C-scan i S-scan. Przedstawiono użycie metody ultradźwiękowej z rejestracją typu C-scan amplitudy echa oraz amplitudy echa dna, która pozwala na wykrycie wad produkcyjnych powstałych w wyniku niedopasowania równoległego krawędzi preimpregnatu węglowego. Z analizy obrazów typu C-scan określono dokładność kątową ułożenia warstw węglowych.

Słowa kluczowe: kompozyt, grafen, kompozyty z grafenem.