EFFECTS OF ELECTROPHORETICALLY DEPOSITED GRAPHENE OXIDE ON THE SURFACE OF TA2 ON THE BONDING STRENGTH OF TI/PEEK

Lv yunfei, Pan lei*, Zhang Aiai, Wang Yifan, Ding Wenye, Ma Wenliang, Hu Jingling, Tao jie
College of Material Science and Technology, Nanjing University of Aeronautics and Astronautics, 210016 Nanjing, China
*E-mail address: bettypan@nuaa.edu.cn

Keywords: Ti/PEEK, Electrophoretic deposition, GO, Interface adhesive strength, Single lap tensile shear

Summary: The GO was deposited on the surface of Ti sheet to reinforce the joint adhesive strength of Ti/PEEK. The deposition was realized by the anodic electrophoretic deposition method in the aqueous dispersions of GO.

Abstract

In order to improve the adhesive strength of Ti/PEEK interfacial adhesive in Ti/PEEK/Cf fiber metal super-hybrid laminates, the graphene oxide (GO) was deposited on the titanium plate surface by electrophoretic deposition method. Firstly, the anodic electrophoretic deposition method was used in the water dispersion solution of GO, then the morphology and properties of titanium plate surface before and after GO deposited were characterized by SEM, contact angle. And the properties change of GO after heated under 390 ℃ were characterized by Raman spectrum and FTIR spectrum. According to the result of Raman spectrum, GO dispersed on the titanium plate surface with no apparent reunion. After 390 ℃ heated 1h, the oxygen functional group of GO lost apparently. The observation of surface topography by scanning electron microscope showed that the GO distribution of titanium plate surface deposition was relatively uniformly. While the GO surface has a large number of folds, which is beneficial to increase the contact area of resin peek. According to the results of single lap tensile shear test, the adhesion strength of Ti/PEEK interface after deposition GO was 32.54MPa, compared to the non-deposited 27.04MPa increased by 20.3%. It indicated that the Ti/PEEK interfacial adhesive strength can be obviously improved after the deposition of GO.

1. INTRODUCTION

There is a strong demand for lightweight, high-strength, high-modulus and damage-tolerant structural materials with the development of large aircraft all over the world. The fiber-metal hybrid laminates (FMLs) has high specific strength and specific rigid, outstanding impact resistance, high damage tolerance, and good resistance performance to fatigue crack propagation, which has been widely used as the cover and structural materials in many types of airplane[1,2]. The fourth generation hybrid laminates, Ti/C_f/PEEK (TiGr) hybrid laminates are alternating lay up of titanium sheets and carbon fiber reinforced polyetheretherketone (PEEK) prepreg, then cured under certain conditions. Because the lightweight titanium and the high modulus of carbon fiber reinforced thermoplastic

polyetheretherketone resin prepreg were used, the TiGr has been applied on some commercial aircraft and military aircraft since its excellent flame retardant property, high damage tolerance and corrosion resistance, and good impact resistance, easy forming and recyclable property, and has received widespread attention[3-5].

There are many interfaces in hybrid laminate composites, and the interfacial bonding strength between metals and resins is a key factor to restrict the overall strength of the material[6]. A layer of peek adhesive film is added between metallic Ti and carbon fiber reinforced prepreg in Ti/Cf/PEEK hybrid laminates, so the interface of Ti and peek resins is essential to the development and application of TiGr laminates. The adhesive strength of the Ti/PEEK interface can be improved by the surface treatment of titanium to constract special structures or graft substances containing specific functional groups. Commonly used titanium alloy surface treatment methods can be divided into the following three categories: 1) mechanical method, such as sandblasting, shot blasting; 2) chemical or electrochemical treatment, such as acid or alkali corrosion, anodic oxidation; 3) coupling agent graft, which form a layer of substances containing specific functional groups on the metal surface[7]. There are other methods such as lithography, micro-arc oxidation etc. But there are problems with those methods, such as poor heat and humidity durability, unfriendly environment, hydrogen embrittlement, non-high temperature resistance, etc[8-12].

In this study a new method was adopted which was environment friendly and efficient. The graphene oxide (GO) nano-powder was added into the interface of Ti/PEEK after the surface the anodizing of Ti sheet. With large specific surface area and a lot of -OH,-COOH,-C=O and other functional groups, GO is a two-dimensional material with the similar carbon structure, very excellent mechanical properties, thermal conductivity as graphene. Used as nano-enhancer, a small amount of the addition of GO can make the performance of resin or metal a great increase[13-16]. But there is no research about the interface bonding strengthen by the adding of GO. This study is aimed at the problems existing in the TiGr laminate, electrophoretic deposition method was used to deposit GO on the TA2 surface to improve the Ti/PEEK interfacial adhesive strength.

In this study, the TA2 sheets after anodizing and the pristine TA2 were used as the metal to observe the change of surface properities, which was deposited with GO. Contact angle was tested by contact angle measurement machine, scanning electron microscope (SEM) and Raman spectroscopy were used to characterize the surface energy, surface morphology and properties of GO after deposited. The properties of original GO, GO dispersed in water and after hot pressing were characterized by Fourier transform infrared spectroscopy (FTIR). Moreover, the effect of deposition GO on the adhesive strength of Ti/PEEK interface was evaluated by comparing the value of single lap tensile shear strength.

2. EXPERIMENTAL PROCEDURE

2.1 Materials and samples preparation

Commercially pure titanium sheets (TA2) from Baoji Titanium industry Co., Ltd. with a thickness of 1.6mm were cut into 100×25mm2. The PEEK, from Victrex , was cut into 12.5×25 mm2 and the physical properties are summarized in Table1. Graphene oxide (GO) with the concentration of 1.0mg/ml was dispersed into deionized water. GO was synthesized by improved Hummer’s method[17].

Table 1: Physical properties of PEEK

Physical properties	Value
Melt point(℃)	343
Glass transition temperature(℃)	143
Shrinkage Rate(%)	<2
Coefficient of linear thermal expansion($\alpha/10^{-6}/℃^{-1}$)	47
Dielectric constant	3.5

2.2 Pretreatment of TA2 surface

There are oil and uneven oxidation film on the original TA2 surface due to processing and air oxidation. So the surface oil and original oxidation film should be removed at the beginning. First, TA2 sheet was immersed into acetone at 60℃water bath heating environment, then cleaned with deionized water. At last, the original oxidation film of the TA2 surface was removed by pickling in mixed acid (85% of nitric acid, 15% hydrofluoric acid) at 40℃ for 40s. Deionized water was used to clean the remaining acid.

2.3 Anodizing and Electrophoretic deposition

The TA2 sheets after removing the original oxide film and oil contamination were anodized immediately. The electrolyte was alkaline NaTESi solution (NaOH 300g/L, EDTA 30g/L, Sodium tartrate 65g/L, Sodium silicate 6g/L). Anodization was performed under constant voltage (DC) supply and temperature. The temperature, voltage and the duration time were 35 ℃, 10V and 10min, respectively. TA2 sheets were used as anode while the sheets of stainless steel with same area of TA2 sheets were used as cathode.

The GO powder was scattered in deionized water and dispersed for 30min in ultrasonic environment. Then anode deposition method was applied and the experimental device was identical to the above-mentioned anodizing device. Deposition ambient temperature, deposition voltage and the deposition duration were 35 ℃, 10V and 3min, respectively.

2.4 Contact angle test

The contact angle between the TA2 surface and liquid was measured by using the Lying drop method. The measured average was selected at multiple points, and the droplet size was 6 μL. Produced Shanghai Chen Digital Technology Equipment Co., Ltd., The JC2000D7M contact angle measuring instrument was used to do this test. Water and ethylene glycol are used to test the contact angle of different liquids with TA2. According to the formula (1), the surface energy of the titanium plate was calculated. The surface energy parameters of water and ethylene glycol are shown in table 2 below.

$$\gamma_{Lv}(1+\cos\theta)=2\sqrt{\gamma_{SV}^{d}\gamma_{LV}^{d}}+2\sqrt{\gamma_{LV}^{p}\gamma_{SV}^{p}} \quad (1)$$

θ is the measuring contact angle;

γ_{SV}^{d} and γ_{SV}^{p} are the polar parts of the free energy of solid and liquid surface, and the dispersion portions of γ_{LV}^{d} and γ_{LV}^{p} are free energy of solid and liquid surfaces;

The γ_{Lv} and γ_{sv} are the free energy of the liquid-gas and solid-gas interface of the unit area respectively.

The surface of the solid should be:

$$\gamma_{SV} = \gamma_{SV}^{p} + \gamma_{SV}^{d} \tag{2}$$

Table 2：Surface energy parameters of two liquids

Surface energy (mN/m) / Liquid	γ_{Lv}	γ_{LV}^{d}	γ_{LV}^{p}
Water	72.8	21.8	51.0
Ethylene glycol	48.3	29.3	19

2.5 Surface morphology

Hitachi S-4800 Type Scanning electron microscope was used to observe the surface morphology of titanium sheet. The GO was tested by LabRAM HR Evolution Raman spectrometer from HORIBA Scientific Company before and after deposition. The IR spectra of the TA2 sheets with different treatments were observed by NEXUS 870 Fourier infrared spectrometer. For each spectrum, 32 scans in the wave number range of 400–4000 cm^{-1} were accumulated at a spectral resolution of 2 cm^{-1}.

2.6 Single lap tensile shear experiment

According to ASTM D1002, the test of TA2/PEEK bonding interface strength was carried out. The specimen size was shown in figure 1. Peek adhesive film was cut into 25x12.5mm^2, and three-layer peek adhesive film was placed in the middle of each specimen. The Φ 0.2mm steel wire was used to control the thickness of the adhesive layer.

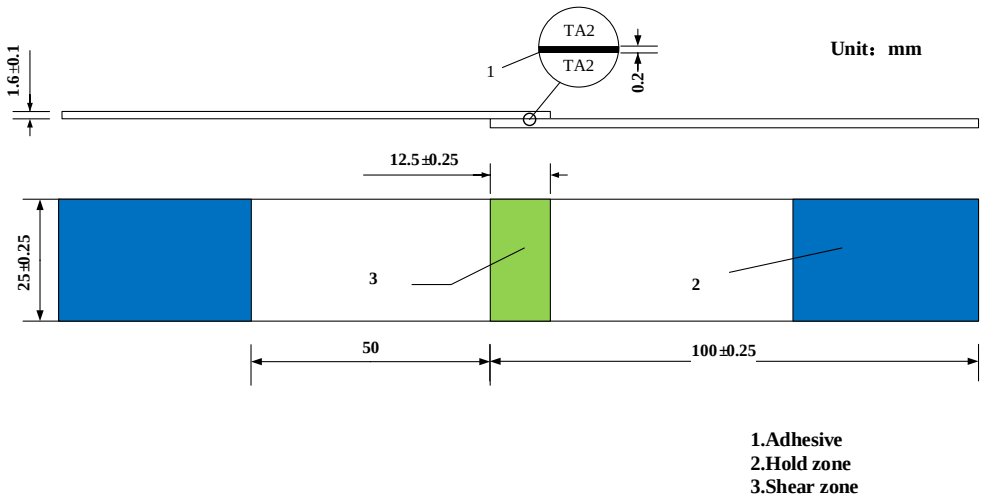

Figure 1: Sketch of single lap tensile shear specimen.

2.7 Hot pressing process of laminate

The hot pressing process is shown in figure 2. The specimen is placed at 390 ℃ hot pressing machine and made the PEEK film melted fully, then give pressure of 0.6MPa. The heat process finished after temperature and pressure preservation for 15min. The load was released when cooling down to 340 ℃. Sample was taken out for water-cooled when temperature reached 180 ℃.

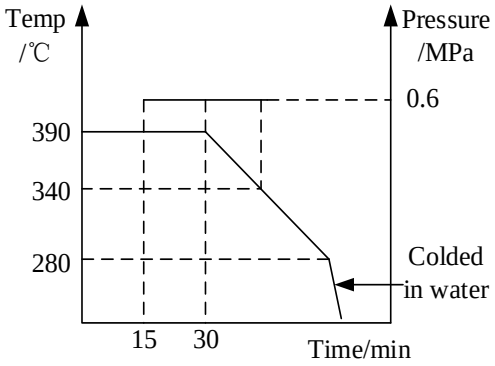

Figure 2: Sketch of hot pressing process curves of laminate

3. RESULTS AND DISCUSSION

3.1 Raman Spectrum

Raman spectrum of GO deposited on the titanium after anodic oxidation is shown in Figure.4 below. There are two sharp peaks in the Raman spectrum, which are D peak at 1295cm^{-1} and G peak at 1580 cm^{-1}. The D peak originates from the vibration of the carbon atom in the sp3 orbit, which reflects the structural defects in the carbon plane and the disordered structure of the region; G-peak corresponds to the first-order scattering of the E_{2g} phonon in-plane vibration of the carbon atom sp2 orbit. The I_D/I_G value of original GO is 1.10 while the I_D/I_G of deposited GO is 0.92. The ratio decreases while the number of defects in the structure are increased; the distance between layers also increased.

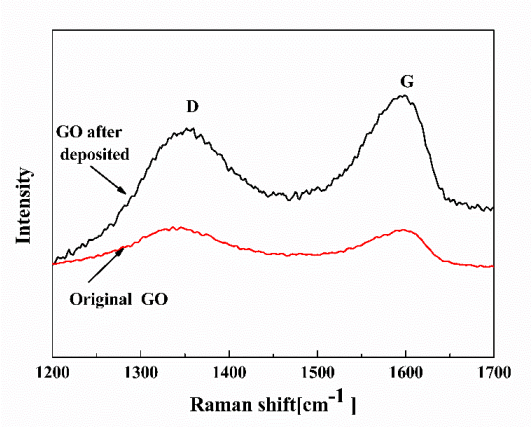

Figure 3: GO Raman spectrum

3.2 FTIR Spectrum

There are plenty of oxygenated functional groups, such as the -OH, -C=O, and -COOH, in the interlayer and edges of GO which has the same carbon structure with graphene. The existence of these groups makes it easy for GO dispersed in water, which also decides that GO can improve the wettability between TA2 and PEEK adhesive and enhance the interfacial adhesive strength. The change of functional groups of GO before and after different treatments was observed by FTIR spectroscopy since these groups are sensitive to temperature.

According to the FTIR spectrum shown in figure 4, peaks at 3400cm^{-1}, 1727 cm^{-1}, 1600 cm^{-1}, 1400 cm^{-1}and 1200 cm^{-1} correspond to -OH, -C-O, C=C, -COH,-C-O-C functional groups [18-20] respectively. The -OH telescopic vibration corresponding to 3400cm^{-1} and 1400cm^{-1} peaks increased because of the increase of the content of water molecules after GO dispersed in the water. After heat treatment under 390 ℃ for 1h, the intensity of C=O telescopic vibration peak and -C-OH peak decreased, which indicates that heat treatment cause the oxygenated functional groups loss. The reduction of the corresponding peak of -OH is the result of the disappearance of water between layers and the loss of -OH functional groups[21].

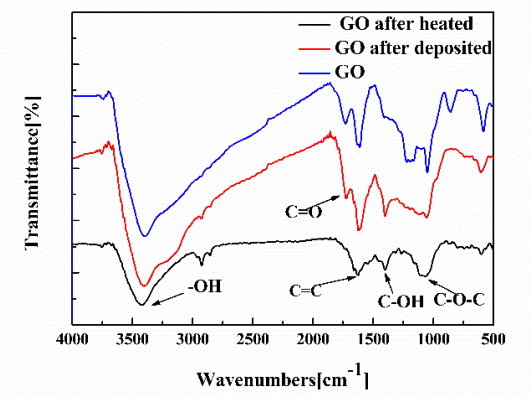

Figure 4: The FTIR spectrum of GO after different treatment

3.3 Contact angle and Surface energy

The contact angle of TA2 surface and with water and ethylene glycol are shown in figure 5. The contact angle after deposition of GO decreased markedly. The contact angle of the titanium with the water and ethylene glycol only by anodic oxidation treatment is 44.02 °and 28.11 °respectively, while after deposition of GO decreased to 28.41 °and 19.34 °respectively. According to the contact angle, the surface energy can be obtained which is shown in Tab.3. Only anodized, TA2 surface energy is 56.01mN/m but increase to 72.32mN/m after GO deposited. As GO has a large number of oxygenated functional groups, it can greatly improve the surface activity of TA2. The increase of surfaces activity can improve the wettability of titanium and PEEK resin, which lead to interface bonding strength increased also.

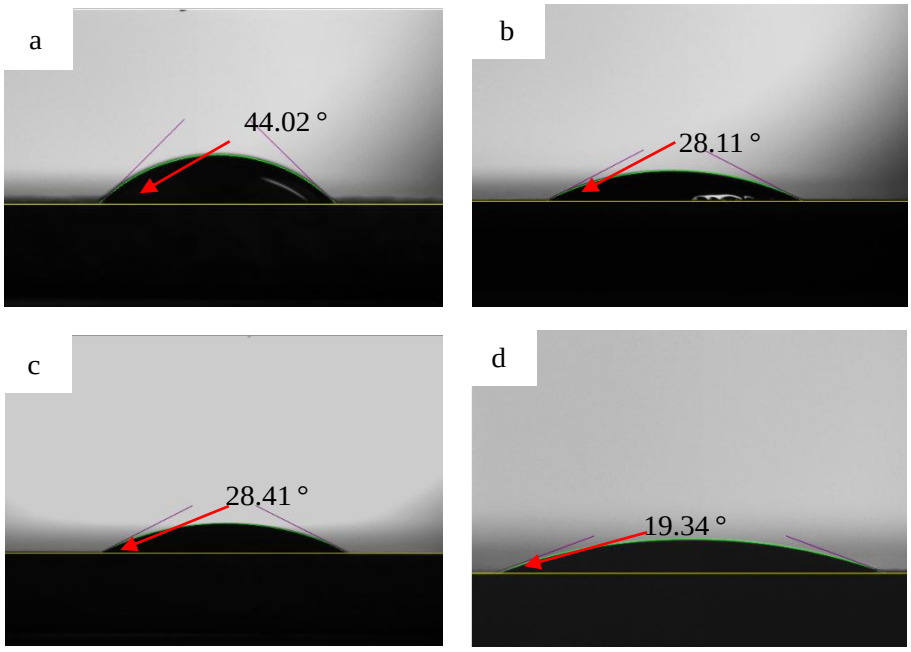

Figure 5: Contact Angle (a) anodic oxidation + water, (b) anodic oxidation + ethylene glycol (c) GO+ water, (d) GO+ glycol

Table 4: Surface energy of TA2 with different treatment

Treatment	Water（°）	ethylene glycol（°）	Surface energy（mN/m）
Anodizing	44.02	28.11	56.01
Anodizing + GO	28.41	19.34	72.32

3.4 SEM

Under the effect of external electric field, the anode TA2 sheet loses the outer electron and then reacts with the ions in the solution which generates a rough layer of TiO_2 film on the TA2 surface when TA2 anodized in alkaline NaTESi solution. GO is easy to disperse in the water and present the electro-negative because of a large number of -COOH and other oxygenated groups. GO migrates to the anode TA2 and deposited on the surface under the effect of the electric field.

Figure 6 shows SEM observation results of TA2 surface topography after different treatment. The surface of pure titanium has few macroscopic rough surface topography which caused by mechanical machining process, but the overall performance is smooth. After anodized in alkaline NaTESi electrolyte, there is a layer of homogeneous nodular oxide film formed on the TA2 surface shown in figure 6(b). The surface roughness increased markedly and the oxide film surface appeared the size of nanometer particles whose diameter is 10-20nm. After deposited on TA2, as shown in figure 6(c), GO distribute not really even on the TA2 surface. There is a large number of folds on GO nano-layer surface which are conducive to increase the TA2 surface roughness value, and increase the mechanical inlay between adhesive resin and TA2. At the same time, when GO deposited on TA2 after anodizing, slight reunion of GO will cause blockage of the anodizing holes which is unconducive to glue resin immersion.

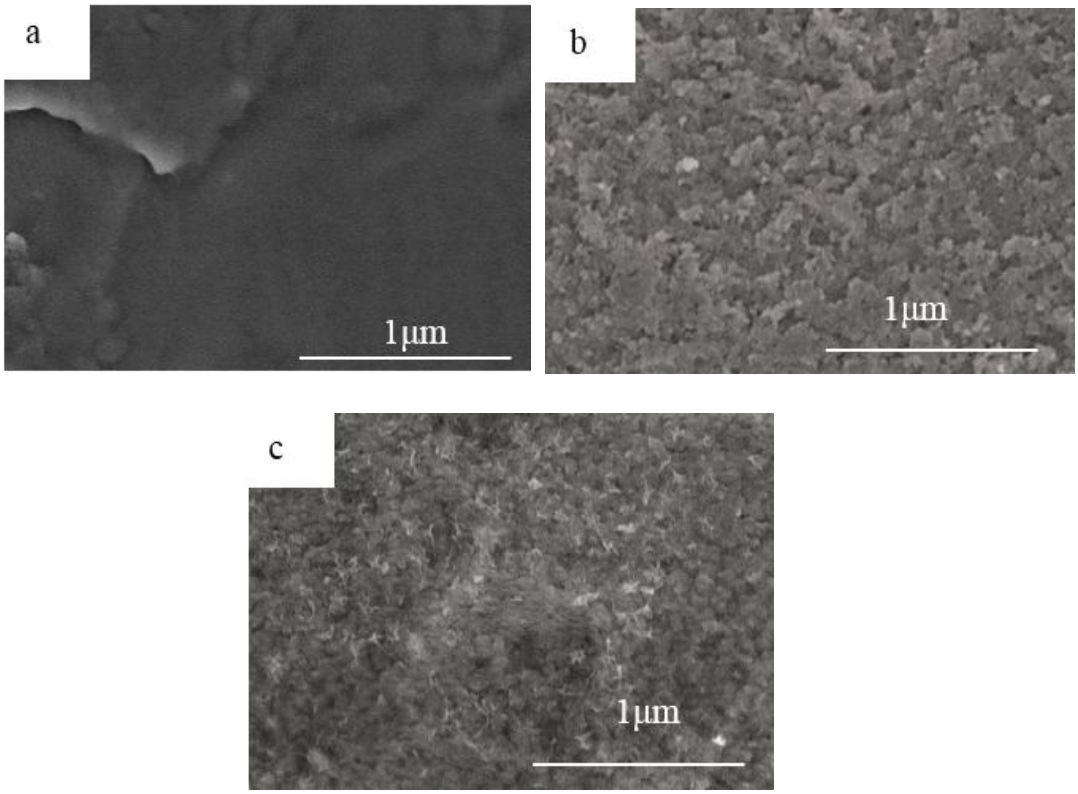

Figure 6: The SEM images (a):Pure TA2; (b): TA2 after anodizing ; (c) TA2 after anodizing and deposition

3.5 Single lap tensile shear strength

The strength value of the single lap tensile shear of the specimen after GO deposited is 32.54MPa, compared to the 27.04MPa of that only anodized increased by 20.3%. The single lap tensile shear strength increased apparently after the deposition of GO after anodic oxidation when compared with only anodized one.

figure 7 shows the surface morphology of the broken specimen following a single lap shear. It can be found that failure was the result of the cohesive failure and interfacial failure. After the deposition of GO, both sides of the sample have a large number of resin residue after the joint fracture, which indicates failure is mainly caused by cohesive failure. As for the sample only anodized, the proportion of interface failure is higher than cohesive failure, and it is higher than the sample that after GO deposited, too. The cohesive failure is caused by the bond destruction between the resins, the interfacial failure is simply the debonding of mechanical embedding between PEEK and TA2, which require less force than the damage of the covalent bond. As shown in figure 7 (c) and (d), after the deposition of GO, the resin adhesive has the cohesive failure, resulting in more plastic deformation after the specimen rupture, so the single lap tensile shear strength with sediment of GO is higher than only anodized one. GO is beneficial to the wetting of resin and TA2, and the strength value of the bonding interface is further enhanced due to the increase of the contact area of the resin and the folds of the GO surface increasing the mechanical lock.

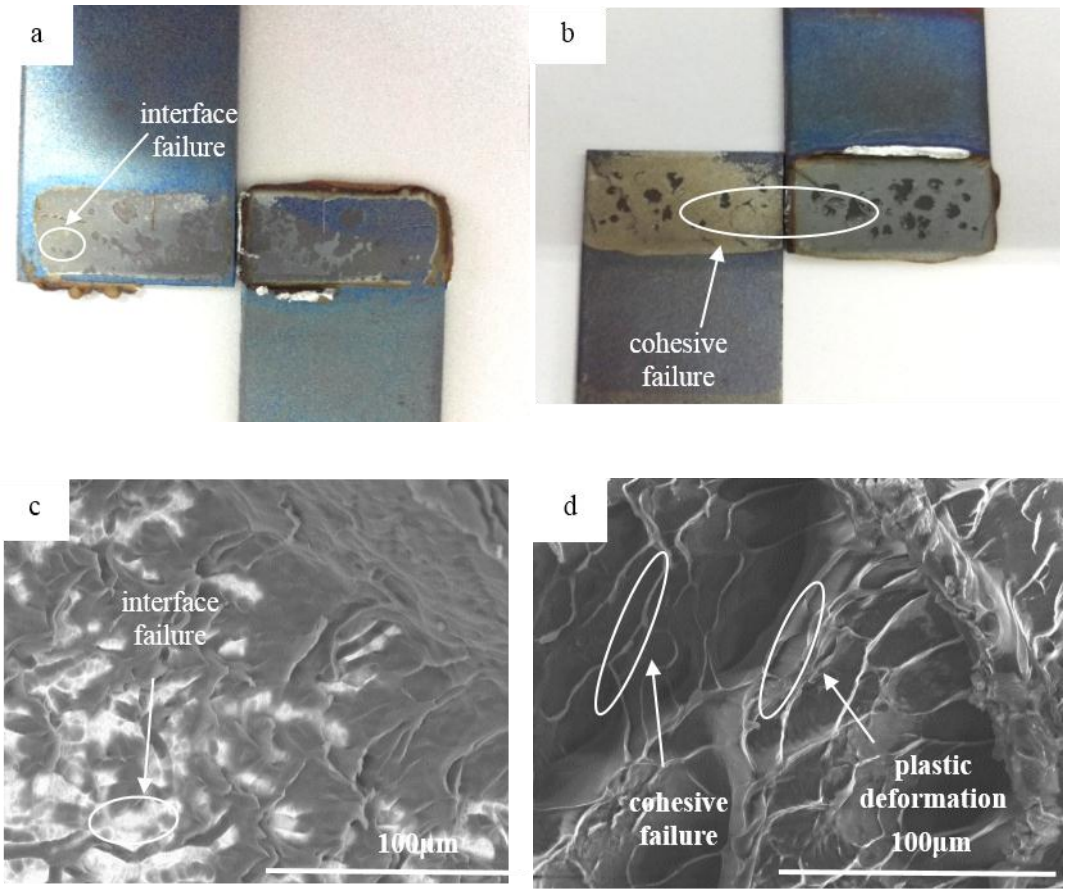

Figure 7: Morphology after fracture of single lap tensile shear specimens
(a) (c) only anodic oxidation treatment, (b) (d) anodic oxidation +GO

4. CONCLUSIONS

The SEM, Raman spectrum and contact angle measurement proved that the GO was deposited on the surface of TA2 sheet successfully by electrophoretic deposition. And the FTIR spectra showed that after heated under 390℃, GO lost some oxygenated functional groups, and there was the new bonding Ti-O-C formed which was beneficial to the reinforcement of the joint of TA2 sheet and PEEK resin.

The adhesive strength of Ti/PEEK interface was investigated by single lap tensile shear test to study the effect of GO deposition. It showed that the interface adhesive strength after GO deposited increased by 20.3% than that only do the anodizing.

ACKNOWLEDGMENTS

This work was supported by the Fundamental Research Funds for the Central Universities (Grant No. NS2014059); the National Natural Science Foundation of China (Grant No. 51503099); the National Shipbuilding Project (New type of liquefied natural gas (LNG) ship cargo containment system research in advance) and a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

REFERENCE

[1] Pawar, Omanath A., Gaikhe, Yogesh S., Tewari Asim, Sundaram Ramesh, Joshi, Suhas S., Analysis of hole quality in drilling GLARE fiber metal laminates. *Composite Structures*, **123**, 2015, pp. 350-365. (doi:10.1016/j.compstruct.2014.12.056)

[2] Kolesnikov, B., L. Herbeck, and A. Fink, CFRP/titanium hybrid material for improving composite bolted joints. *Composite Structures*, **83**, 2008, pp. 368-380. (doi:10.1016/j.compstruct.2007.05.010)

[3] Asundi A, Choi A Y N. Fiber metal laminates: an advanced material for future aircraft[J]. *Journal of Material Processing Technology*, **63**, 1997, pp. 384~394. (doi:10.1016/S0924-0136(96)02652-0)

[4] Park, S.Y., W.J. Choi, and H.S. Choi, A comparative study on the properties of GLARE laminates cured by autoclave and autoclave consolidation followed by oven postcuring. *The International Journal of Advanced Manufacturing Technology*, **49**, 2009, pp. 605-613. (doi:10.1007/s00170-009-2408-x)

[5] Pan, Lei, Duan, Lixiang, Zheng, Zengmin, Hu, Yubing, Aamir, Ali, Bhuwan, Sapkota, Tao, Jie, Zhao, Tong and Du Zhengyang, Surface characteristics and adhesive strength to polyetheretherketone of titanium electrografted with aryl diazonium salt. *Materials & Design*, **95**, 2016, pp. 555-562. (doi:10.1016/j.matdes.2016.01.076)

[6] Martinelli, E. and A. Caggiano, A Unified Theoretical Model for the Monotonic and Cyclic Response of FRP Strips Glued to Concrete. *Polymers*, **6**, 2014, pp. 370-381 (doi:10.3390/polym6020370)

[7] Glyn Lawcock, Lin Ye, Yiu Wing Mai and Chin-Teh Sun, The effect of adhesive bonding between aluminum and composite prepreg on the mechanical properties of carbon-fiber-reinforced metal laminates. *Composites Science and Technology*, **57**, 1997, pp. 35-45. (doi:10.1016/S0266-3538(96)00107-8)

[8] Abedi, R. and A. Akbarzadeh, Bond strength and mechanical properties of three-layered St/AZ31/St composite fabricated by roll bonding. *Materials & Design*, **88**, 2015, pp. 880-888. (doi:10.1109/5.771073)

[9] Liu Yuan, Zhang Xue, Song Chenchen, Zhang Yuanyuan, Fang Yichao, Yang Bin and Wang Xinling, An effective surface modification of carbon fiber for improving the interfacial adhesion of polypropylene composites. *Materials & Design*, **88**, 2015, pp. 810-819. (doi:10.1016/j.matdes.2015.09.100)

[10] Yu YongShui, Xie LanSheng, Chen MingHe, Wang Ning and Wang Hui, Surface characteristics and adhesive strength to epoxy of three different types of titanium alloys anodized in NaTESi electrolyte. *Surface and Coatings Technology*, **280**, 2015, pp. 122-128. (doi:10.1016/j.matdes.2015.09.100)

[11] Kurtovic, A., Brandl, E., Mertens, T. and Maier, H. J., Laser induced surface nano-structuring of Ti–6Al–4V for adhesive bonding. *International Journal of Adhesion and Adhesives*, **45**, 2013, pp. 112-117. (doi:10.1016/j.ijadhadh.2013.05.004)

[12] Goushegir, S.M., J.F. dos Santos, and S.T. Amancio-Filho, Influence of process parameters on mechanical performance and bonding area of AA2024/carbon-fiber-reinforced poly (phenylene sulfide) friction spot single lap joints. *Materials & Design*, **83**, 2015, pp. 431-442. (doi:10.1016/j.matdes.2015.06.044)

[13] Paul, D.R. and L.M. Robeson, Polymer nanotechnology: *Nanocomposites. Polymer*, **49**, 2008, pp. 3187-3204. (doi:10.1016/j.polymer.2008.04.017)

[14] Mahmood, Haroon, Tripathi, Manoj, Pugno, Nicola and Pegoretti, Alessandro, Enhancement of interfacial adhesion in glass fiber/epoxy composites by electrophoretic deposition of graphene oxide on glass fibers. *Composites Science and Technology*, **126**, 2016, pp. 149-157. (doi:10.1016/j.compscitech.2016.02.016)

[15] Goushegir, S.M., J.F. dos Santos, and S.T. Amancio-Filho, Influence of process parameters on mechanical performance and bonding area of AA2024/carbon-fiber-reinforced poly (phenylene sulfide) friction spot single lap joints. *Materials & Design*, **83**, 2015, pp. 431-442. (doi:10.1016/j.matdes.2015.06.044)

[16] Huang, Sheng-Yun, Wu, Gang-Ping, Chen, Cheng-Meng, Yang, Yu, Zhang, Shou-Chun and Lu, Chun-Xiang, Electrophoretic deposition and thermal annealing of a graphene oxide thin film on carbon fiber surfaces. *Carbon*, **52**, 2013, pp. 613-616. (doi:10.1016/j.carbon.2012.09.062)

[17] WILLIAM S. HUMMERS, JR., and RICHARD E. OFFEMA, Preparation of Graphitic Oxide. *Journal of the American Chemical Society*, **80**, 1958, pp. 1339-1339. (doi:10.1021/ja01539a017)

[18] Jeong, Hae Kyung, Lee Yun Pyo, Jin Mei Hua, Kim Eun Sung, Bae Jung Jun and Lee Young Hee, Thermal stability of graphite oxide. *Chemical Physics Letters*, **470**, 2009, pp. 255-258. (doi:10.1016/j.cplett.2009.01.050)

[19] Yanwu Zhu, Meryl D. Stoller, Weiwei Cai, Aruna Velamakanni, Richard D. Piner, David Chen, and Rodney S. Ruoff, Exfoliation of Graphite Oxide in Propylene Carbonate and Thermal Reduction of the Resulting Graphene Oxide Platelets. *ACS nano*, **2**, 2010, pp. 1227-1233. (doi:10.1021/nn901689k)

[20] Ziyin Lin, Yagang Yao, Zhuo Li, Yan Liu, Zhou Li, and Ching-Ping Wong, Solvent-Assisted Thermal Reduction of Graphite Oxide. *The Journal of Physical Chemistry C*, **114**, 2010, pp.14819-14825. (doi:10.1021/jp1049843)

[21] Saeimi Sadigh, M.A. and G. Marami, Investigating the effects of reduced graphene oxide additive on the tensile strength of adhesively bonded joints at different extension rates. *Materials & Design*, **92**, 2016, pp. 36-43. (doi:10.1016/j.matdes.2015.12.006)