Effect of carbon nanotubes addition on the interface property of titanium-based fiber metal laminates

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ABSTRACT

In this study, diverse weight fractions of carbon nanotubes were dispersed in PMR polyimide adhesives by ultrasonic dispersion method to bond titanium sheets. Single lap shear test samples were prepared and average shear strengths were experimentally measured to characterize the interface bonding strength between titanium and polyimide. The shear strength of PMR polyimide adhesive was further enhanced by incorporating carbon nanotubes, with over 87.5% improvement for the carbon nanotubes toughened adhesive joints with concentration up to 5wt%. The influence of carbon nanotubes on the interlaminar shear strength (ILSS) of Ti/Cf/PMR polyimide was investigated through the short-beam three-point-bending test. The incorporation of carbon nanotubes into PMR polyimide evidently improved the interlaminar shear strength.by 36%. Furthermore, Scanning Electron Microscopy (SEM) images revealed failure morphologies such as pull-out, fracture and bridging of carbon nanotubes. The results indicated the strengthening mechanism that carbon nanotubes strengthen the shear strength of fiber metal laminates.

1. INTRODUCTION

Fiber metal laminates (FMLs) are hybrid materials based on alternating layers of thin metal sheets and fiber reinforced composite plies[1]. As the new generation of FMLs, TiGr is manufactured by unidirectional carbon fiber reinforced polyimide and titanium, receiving special attention owing to its unique properties such as high temperature processing condition[2]，superior fatigue properties, and excellent mechanical properties. With these outstanding characteristics, TiGr laminates can be candidate materials for next generation aircrafts. Unfortunately, delamination is often encountered due to the existence of several interface layers [3], which may result in austere reduction of overall structural strength and stiffness. Moreover, delamination normally occurs between metal and fiber layers. Whether the delamination occurs or not between metal and fiber layer depends on the bonding properties between the metal and the resin. In order to achieve better adhesion properties between the metal and resin, chemical and mechanical treatments (e.g., anodizing [4], grit-blasting [5, 6], coupling agent [7, 8] and mechanical patterning[9-11]) on metal surface are mainly used to enhance the adhesion properties. However, these techniques create adhesion mainly based on mechanical interlocking that is rather weak, especially when the structures operate in extreme environment of high temperature and high pressure[12].

On the other hand, numerous researches on nano-fillers (nanoclays, carbon nanofiber, carbon nanotubes, nanosilica, grapheme sheets) with excellent mechanical properties are considered as an ideal reinforcement candidate to the interface of FRP laminates based composites have shown nano-fillers increase the interfacial bond strength of the composites [13-18]. For instance, Jen et al. [18] have observed that the incorporation of 1.0wt% SiO2 nanoparticles into interfaces among CFRP plies can induce the increase of the overall in-plane tensile strength and stiffness of CFRP, but little improvement in fatigue behavior. Kim[19] had investigated the effect of bucky paper interleaves made from carbon nanofibers on interlaminar mechanical properties of CFRP, which demonstrated the interlaminar shear strength were increased by 31%. Some researches indicate the excellent properties of carbon nanotubes, such as high Young's modulus, large aspect ratio and high failure stress, make them ideal for reinforcing the resin adhesive [20, 21]. Binghua Wang et al. [22] have added multi-walled carbon nanotubes (CNTs) and Kevlar fiber into the epoxy adhesive joints lead to the shear strength increased almost 70%. The tensile strength, stiffness and fatigue life of composite are further enhanced by incorporating multi-walled carbon nanotubes at the fiber/fabric–matrix interfaces over the laminate cross-section [23]. Hong Xu et al. [24] have interleaved continuous carbon nanotubes film between laminates of composites. The flexural strength and interlaminar shear strength (ILSS) of the composite initially increased with carbon nanotubes film content. Among above researches, although carbon nanotubes have already been proved possess the capability of improving interface property and mechanical property of conventional composites, published data of fiber metal laminates are still rather meagre.

In this study, we investigated the effect of carbon nanotubes on the shear strength between PMR polyimide and titanium and the mechanism of the strength enhancement. The interface bonding strength was examined via Single lap shear test and interlaminar shear test. The failure modes and mechanism of the laminates were discussed in this paper.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

The PMR type polyimide was provided by Institute of Chemistry, Chinese Academy of Science. Carbon fiber was TR50S 6L obtained from Mitsubishi Rayon Co., Ltd. The titanium was 0.3mm thick layers from BAOJI Titanium Industry Co., Ltd. The Carbon nanotubes used were multi-walled carbon nanotubes with average diameter 30 nm and average length 20um, supplied by Nanjing XFNANO Materials Tech Co., Ltd.

2.2. Dispersion of carbon nanotubes

In this work, an ultrasonic mixer (TJS-3000 Intelligent Ultrasonic Generator V6.0) was used to disperse carbon nanotubes. Carbon nanotubes at concentration of 0wt%, 2.5wt%, 5wt%, 7.5wt% were incorporated into PMR polyimide. The PMR polyimide resins and carbon nanotubes were carefully weighted and mixed together in a breaker. A high intensity, ultrasonic probe was employed for the mixing process. In order to avoid overheating and reaggregation, the mixture was kept in low temperature by submerging the container in an ice bath. The sonication experimental conditions were 2h of sonication and 50% sonication amplitude [25].

2.3. Sample preparation process

Interlaminar shear test samples were unidirectional FMLs plates with the configuration 3/2 (three titanium layers and two composite layers) by manufacturing in a mold. Prior to laminating, titanium layers were treated with the NaTESi anodizing process[2] and painted with mixture of PMR polyimide resins and carbon nanotubes as primer in order to improve the inherently weak interlaminar bond strength between the titanium and the prepreg, as shown in Fig.1. The mold was then put into a hot press system according the following process shown in Fig.2, after cooling slowly to the room temperature. The single lap shear test samples were manufactured by stacking two titanium sheets using the mixture as adhesives, as shown in Fig. 3. The samples were curing based on the above curing curve, as shown in Fig.2.

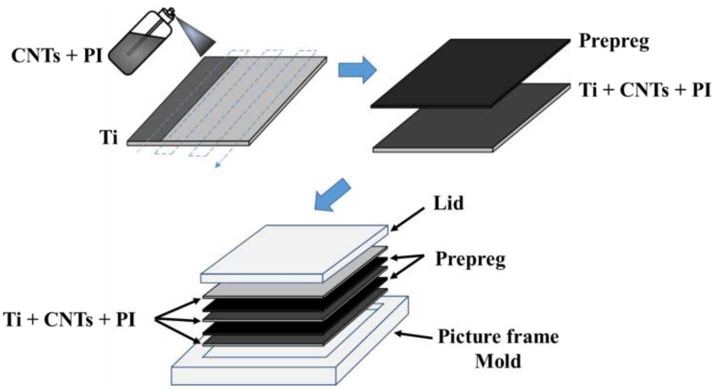


Fig.1. Schematic illustration of specimen fabrication process

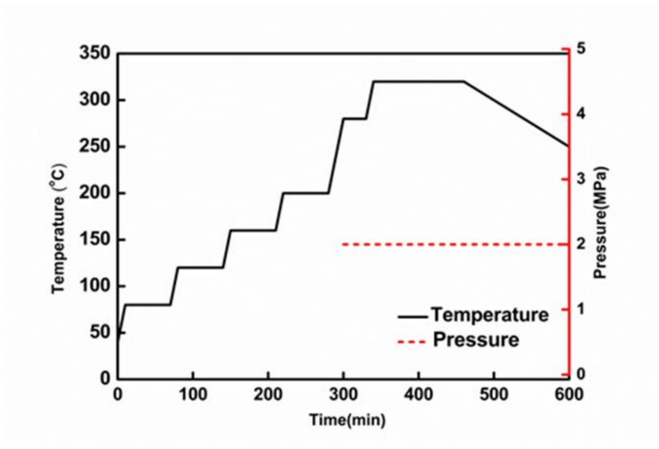


Fig.2. Curing process curve of the FMLs

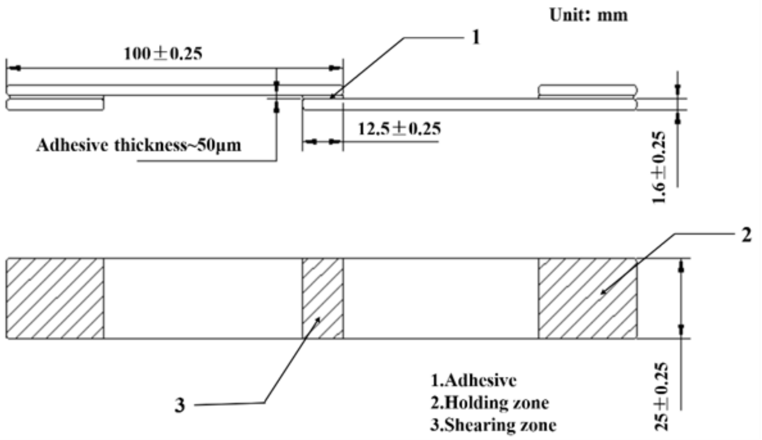


Fig.3. Schematic diagrame of single lap shear test samples.

2.4. Mechanical test

The single lap shear tests were performed according to the ASTM 1002 standard. The displacement rate was 2 mm/s at room temperature. The tests were stopped after the adhesive joints were invalid and the peak loads were recorded.

Interlaminar shear tests were conducted according to Liu [26] by using a three-point loading fixture with a constant span-to depth ratio of 8. The specimen size was 20 mm x 10 mm (length x width). The rate of loading was 1 mm/min, seeing Fig. 4. The failure mode and the interlaminar shear strength of the specimens were obtained according to the test.

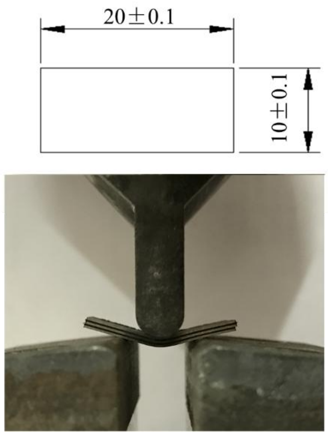


Fig.4. Mechanical tests setup of ILSS test fixture

3. RESULTS AND DISCUSSION

3.1. Single lap shear test

The specimen details are listed in Table 1, and the average shear strength of the specimens were calculated and shown in Fig. 5. Significant improvement in the average adhesive shear strength was observed after adding carbon nanotubes. The addition of medium amount of carbon nanotubes, i.e. 5wt%, in PMR polyimide resin had a positive effect on shear behavior and an 87% increasing of shear strength could be achieved compared to pure PMR polyimide. To understand how the carbon nanotubes improve the adhesion, we used the schematic diagram of titanium-polyimide interface to explain the mechanism, as shown in Fig. 6.

Titanium was treated by the NaTESi anodizing process to increase surface roughness in order to improve the interlaminar property between titanium layer and matrix. Yang[27] pointed out that the interface of the composite was not a single surface of contact between the matrix and reinforcement, but a transitional region of tens of nanometers to tens of microns. So we infer that the typical interface of titanium-polyimide thickness is a few microns to tens of microns as illustrated in Fig. 6a, the typical carbon nanotubes length is very small in comparison with the interface of titanium-polyimide as illustrated in Fig. 6b. The carbon nanotubes may be pressed and irregular arrangement, which could deflect crack growth path into the adhesive joint away from the interface of the titanium and polyimide. Moreover, the excellent mechanical features of the carbon nanotubes improved the properties of the interface as well. Therefore, the interface of the titanium-polyimide was toughened and strengthened with the carbon nanotubes addition. However, it was also observed that the shear strength had a decrease tendency when carbon nanotube concentration addition up to 7.5wt%. This results suggest that the excessive carbon nanotubes concentration leads to the agglomeration of carbon nanotubes in the polyimide.

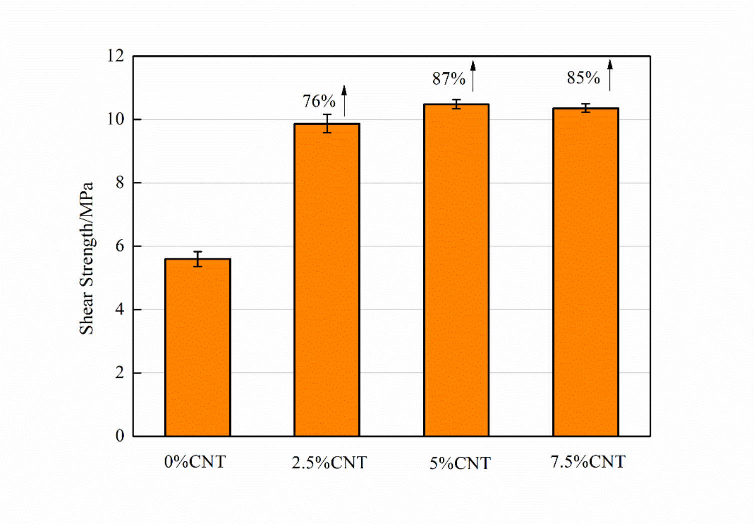


Fig.5 The trend of the Lap-shear tensile behavior with respect to the carbon nanotubes concentration

Table 1 Specimen details and test result

Specimen Category	Maximum shear stress(MPa)	Minimum shear stress(MPa)	Average shear stress(MPa)	Standard deviation (MPa)
Pure PMR polyimide	5.81	5.42	5.6	0.196
2.5wt%	10.23	9.65	9.87	0.26
5wt%	10.63	10.34	10.48	0.12
7.5wt%	10.52	10.16	10.36	0.18

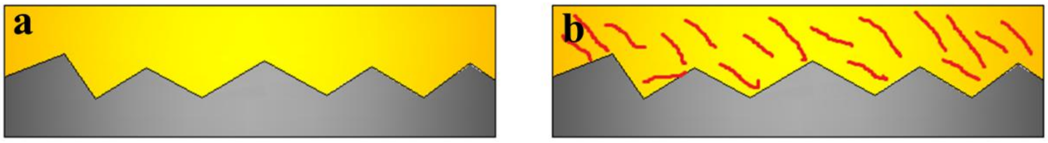


Fig.6. (a) Cross-section view of Ti/PMR polyimide interface; (b) Cross-section view of Ti/PMR polyimide/carbon nanotubes interface

Figure7 shows the images of the samples' surface status on the failure areas after the single lap shear testing. In common, visual examination indicated a mix of cohesive failure and interfacial failure. As shown in Fig. 7a, the specimen with 0wt% carbon nanotubes shows more than 50% failure area is interfacial failure. From Fig 7b after adding 2.5wt% carbon nanotubes into polyimide, 70% failure area is cohesive failure area, whereas 30% is the interfacial failure area. As shown Fig. 7c, the failure morphology not only show almost 90% cohesive failure area after adding 5wt% carbon nanotubes, but also the cohesive failure area is uniform. From Fig. 7d, although the specimen added with 7.5wt% carbon nanotubes still displays 90% cohesive failure area, the cohesive failure area is nonuniform. Meanwhile, the shear strength was inferior to specimen with 5wt% carbon nanotubes. For the reason that in this content the carbon nanotubes are agglomerate. This phenomenon indicated that the incorporation of carbon nanotubes played a role in promoting the macro-interface failure mode and the interface bonding strength.

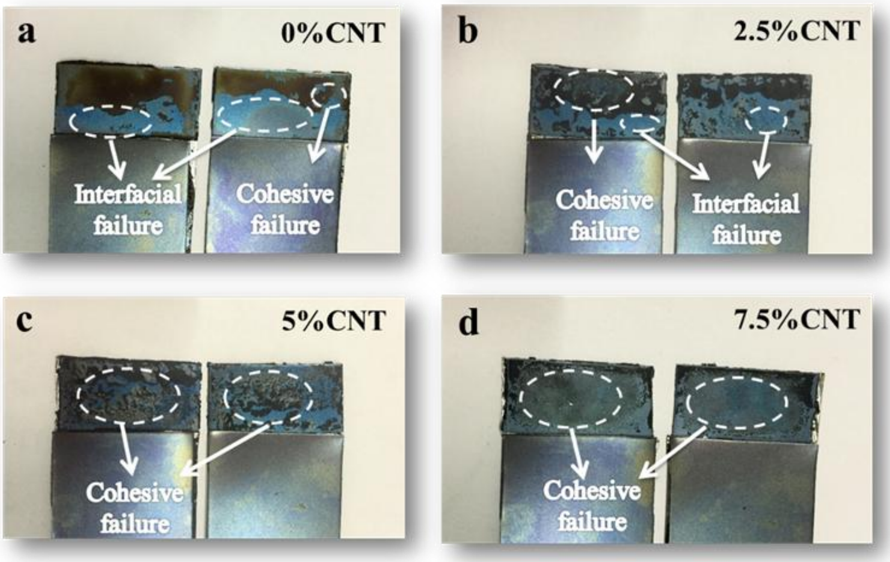


Fig.7. Images of the sample surface data on the failure areas after single lap shear testing (a) 0wt%carbon nanotubes; (b) 2.5wt%; (c) 5wt%carbon nanotubes; (d) 7.5wt%carbon nanotubes

The SEM images of single lap shear failure area are illustrated in Fig. 8. From Fig. 8 (a), the dispersion of carbon nanotubes in the polyimide matrix. It demonstrated that carbon nanotubes were uniformly dispersed into the polyimide after the dispersing process by sonication and mechanical stirrer. Figure 8 (b) is enlarged view of the encircled area in 8 (a), it can be clearly seen that details of presence of protruding carbon nanotubes, such as pull-out and bridging[28] as shown in arrow1 and arrow 3. When a load was applied to the sample the carbon nanotubes were failure in the above two forms to absorb partial energy, and thereby toughened the matrix and increased the shear strength. Although some carbon nanotubes protruded from the facture surface during the fracture of the adhesive, there remained large numbers fracture carbon nanotubes in the CNT-polyimide fracture surface (as shown in arrow 2) which was indicative of strong adhesion between the matrix and CNTs.

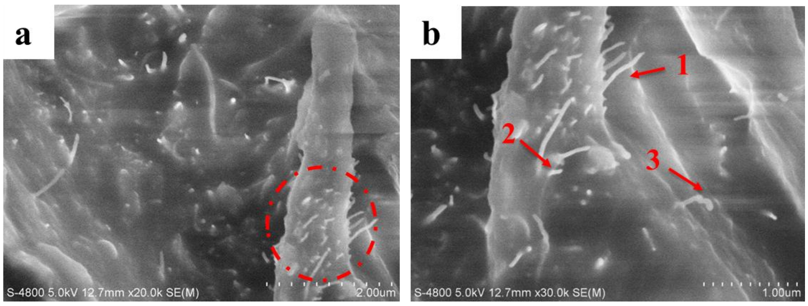
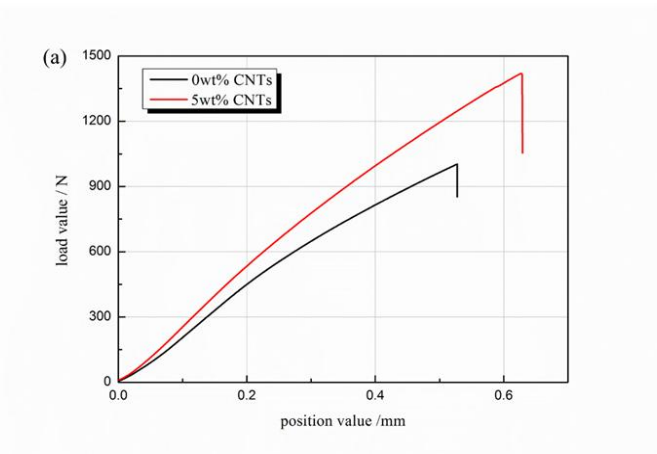


Fig.8 Detailed shear failure features on substrate, where PMR polyimide adhesive with carbon nanotubess reinforcement: (a) overview of shear failure area, (b) enlarged view of the encircled area in (a)

3.2. Interlaminar shear tests

As mentioned above, the addition of 5% carbon nanotubes had the best effect on the enhancement of interfacial strength, so in the following research the carbon nanotubes with the content of 5wt% were added into the primer of fiber metal laminates to measure the interlaminar shear property. Figure 9a shows the load-displacement curve of the ILSS tests. It is clearly observed that the peak load of the ILSS is improved after carbon nanotubes added. The normalized interlaminar shear stress was calculated based on the equation of ILSS according to ASTM-D2344. Figure 9b presents the average interlaminar strength of the laminates. It was evident that the ILSS of the FMLs achieved a 32.6% improvement after carbon nanotubes added. The strong role of carbon nanotubes in matrix was related with the fact that the failure mechanism was controlled by interlaminar performance.



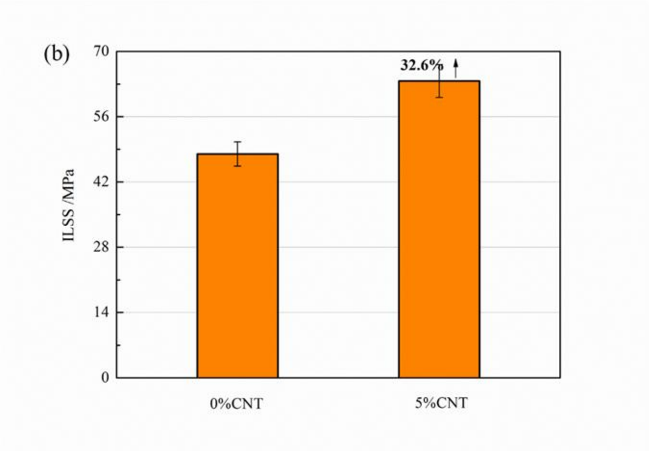


Fig. 9 Load-position of specimen (a) and interlaminar shear strength of specimen (b)

To understand how the carbon nanotubes improve the adhesion, we used the schematic diagram of fiber metal laminates interface to explain the mechanism, as shown in Fig. 10. The typical fiber metal laminates interlaminar structure of fiber prereg and titanium as illustrated in Fig. 10a. The structure contains five different regions, of which two are interfacial regions, e.g. Ti/polyimide interface and fiber prereg/polyimide interface. Majority of the cracks propagated from the Ti/polyimide interface region. When the crack (blue curve) expanded in the Ti/polyimide interface region, most of the failure occurred along the bonding interface. The fiber metal laminates with carbon nanotubes interlaminar structure as illustrated in Fig.10b. The structure contains three interphases which are Ti/CNT-polyimide interface, CNT/polyimide interface and carbon fiber/polyimide interface. The polyimide layer was an overflowing polyimide in the prepreg during the process of hot pressing. When the crack (black curve) expaned in the Ti/CNT-polyimide interface, the polyimide matrix had fractured. We suspected the carbon nanotubes fractured and pulled out from the matrix, which absorbed fracture energy. On the other hand, when the crack propagated the carbon nanotubes could bridge in the matrix to prevent crack propagating, and the crack was transferred from the titanium-polyimide interface, which enhanced the Ti/CNT-polyimide interface strength.

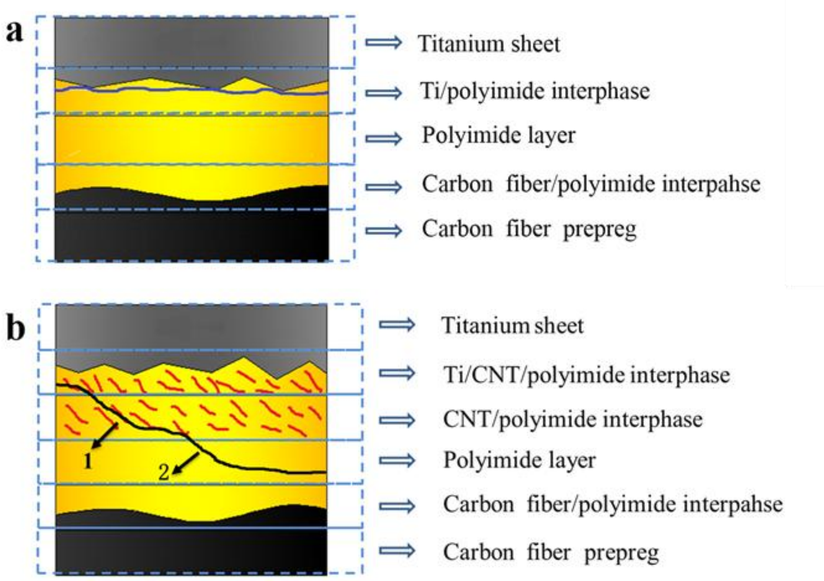


Fig. 10 Cross-section view of fiber metal laminates interfacial structure: (a) 0wt%Carbon

nanotubes; (b) 5wt%Carbon nanotubes

The SEM images of interlaminar shear failure cross-section diagrams of the laminates with and without carbon nanotubes are shown in 11 (a) to 11 (b), respectively. The two types of interlaminar shear failure modes were different. The interlaminar shear failure of lamiantes without carbon nanotubes occurred along the bonding surface of the titanium-polyimide. Visual examination indicated that the cross section of titanium existed uneven jagged structure and without fracture resin adhering to it. On the contrary, carbon nanotubes were incorporated, the shear failure along the polyimide resin layer and Ti/polyimide interface layer had not been destroyed. Titanium plate surface attached of a fractured polyimide resin layer. It was obvious that carbon nanotubes reinforced the Ti/polyimide interface and promoting the interlaminar shear strength. Figure 12 (a) to 12 (b) combined with the actual failure to prove the above enhancement mechanism. In order to demonstrate that the carbon nanotubes were uniformly dispersed in the resin matrix, we used the acid to etch the superficial titanium .The result shown that carbon nanotubes were uniformly dispersed in the polyimide, as illustrated in Fig.12 (a). The marked regions number 1 and 2 by arrows in figure 10 (b) correlate to the location of the crack as shown in the cross-section schematic of crack path in figure 12 (b). As mentioned previously, carbon nanotubes had a role in preventing crack propagation. It was observed that the crack path changed from the Ti/CNT-polyimide interface in the sample to the CNT/polyimide interface and eventually expanded in the polyimide layer. It should be noted that a small amount of carbon nanotubes could be observed in arrow 1 which was the region of Ti/CNT-polyimide or CNT/polyimide interface, as shown in Fig. 12(b). Due to the effect of carbon nanotubes the crack was transmitted to the polyimide layer referred by arrow 2. The behavior of the crack expanded from arrow 1 to arrow 2 proved that the Ti/CNT-polyimide interface performance was superior to polyimide layer. In another word, the carbon nanotubes enhanced the Ti/CNT-polyimide interface strength

Fig. 11 Interlaminar shear failure Cross-section view of the FMLs: (a) 0%Carbon nanotubes; (b) 5% Carbon nanotubes

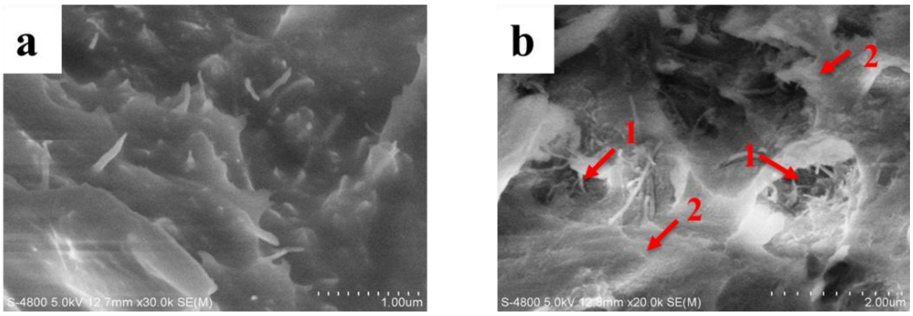


Fig. 12 Image of substrate where PMR polyimide adhesive with carbon nanotubes reinforcement: (a) the laminates surface after remove the surface of titanium; (b) interlaminar shear failure feature

4. CONCLUSION

Within the limitations of this study, the following conclusions were drawn:

(1) In conjunction with the reinforcement of carbon nanotubes at concentration of 5wt% the single lap shear strength of PMR polyimide-bonded NaTESi anodizing Titanium substrates and ILSS of laminates were improved over 87.5% and over 32.6%, respectively.

(2) SEM analysis of the fracture surface was used to assist in determining the mechanism responsible for improving interface bonding strength. The carbon nanotubes fractured and pulled out from the matrix, which absorbed fracture energy. And the carbon nanotubes could bridge in the polyimide to prevent crack propagating. Meanwhile, the crack was transferred from the titanium-polyimide interface, which enhanced the Ti/CNT-polyimide interface strength.

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