

Effect of TiO₂ nanotubes developed on pure titanium substrates on the mechanical performance of titanium-titanium single-lap adhesive joints

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Abstract

The aim of the present work is to study the combined effect of TiO₂ nanotubes, developed by means of electrochemical anodization on pure titanium adherends, and of the adhesive epoxy resin reinforced with carbon nanotubes (CNTs), on the quasi-static three-point bending behaviour of titanium-titanium single lap adhesive joints. A specific combination of parameters, namely time, type of electrolyte and voltage, has been selected in order to develop nanotubes with optimum geometry in an effort to achieve single lap adhesive joints with enhanced mechanical strength. The mechanical performance of the single lap joints as well as the bonding efficiency of the nano-composite adhesive were studied by means of three point bending and tensile shear tests, while the nano-structural topography was investigated through Scanning Electron Microscopy (SEM) observations. Following the above procedure an increase on the order of 82% in flexural strength for the thus manufactured single-lap adhesive joints was achieved, while the flexural modulus of the joints remained unaffected.

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Keywords: single lap joints; titania nanotubes; CNTs reinforced adhesive.

1. Introduction

Adhesive bonding gains day by day more and more popularity in modern structural engineering due to several advantages as compared to other joining methods. Traditional joining methods such as riveting or bolting, include the introduction of holes in the structure which under working conditions create premature failure of the joint. With the application of adhesive bonding these problems can be avoided, since stress distribution in the joint is improved, while, at the same time, a simultaneous reduction in the weight and cost of the final product can be achieved. For the reasons mentioned above, adhesive joints find a great number of applications in the automotive, aerospace and marine industry [1-4].

Since many years, a particular type of adhesive joint, i.e. the single lap joint configuration, is on the focus of

many researchers. Due to the simplicity of geometry and relatively easy construction, single lap joints are preferred over other more complex and more expensive adhesive joint configurations. Despite of its geometrical simplicity, there are several parameters affecting the working performance of single lap joints. Amongst these parameters one can mention the adhesives' thickness, the overlap length, the adherends' nature and their surface treatment, the environmental conditions etc. [6-11].

The inclusion of additives in polymeric matrices is a common technique for the improvement of the composites properties. Carbon nanotubes (CNTs), because of their unique and diverse nature and their great mechanical, thermal and electrical properties, are an ideal choice for inclusion in an epoxy adhesive. CNTs have already been utilized in adhesive lap joints for in situ sensing and health monitoring of the adherends damage [12-15]. Simultaneously the incorporation of CNTs inside an epoxy matrix also results in the increase of the adhesive joint's strength and durability [16-20]. However, the combined effect

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of both *CNTs reinforced adhesive and adherent surface modification* for an improved adhesive-adherent interphase performance has not been thoroughly studied yet.

In the present investigation the simultaneous combined effect of an epoxy adhesive reinforced with CNTs and of titania nanotubes synthesized on the titanium adherends overlap surfaces on the mechanical performance of Ti-Ti single lap joints was studied.

2. Materials and Methods

2.1. Materials

The epoxy resin system used as adhesive material for the single lap joints was a resin type RenLam CY219 (Bisphenol A) combined with a curing agent type HY 5161 (Diamine) at a ratio 2: 1 by weight. Gelling time was 24 hours at 50°C with a mass density of the cured polymer 1.1gcm⁻³. The viscosity of the system CY219 and HY 5161 was 1-1.2Pas at 25°C. Multiwall carbon nanotubes supplied by Nanothinx were used as filler. The MWCNTs had an outer diameter in the range 15-35nm with a total length lower than 10 microns and purity 97%. A 99% industrial grade titanium plates were used as adherends. Four different types of single lap Ti-Ti adhesive joints, as shown in Fig. 1, were manufactured; namely:

1. Pure Ti/Neat Epoxy Resin/Pure Ti (reference)
2. Pure Ti/Epoxy with 1 wt% CNTs/Pure Ti
3. Anodized Ti/Neat Epoxy Resin/Anodized Ti
4. Anodized Ti/Epoxy with 1 wt% CNTs/Anodized Ti

2.2. Pre-treatment of titanium adherends

In order to increase the Ti adherends surface roughness and achieve a better joint performance, adherends overlap surfaces were anodized using the electrochemical anodization method. Following this method, the titanium plate was mounted as an anode, and a graphite bar was used as a cathode. Three anodization parameters were important; namely: (i) electrolyte type (ii) time of anodization, and (iii) applied voltage. Several combinations of these parameters have been checked in an effort to obtain a highly organized titanium dioxide nanotubes layer on the titanium adherends surface. As it was experimentally found, the optimum combination of these parameters was as following: the electrolyte was 0.4% (w/w) HF in 1:1 (w/w) water-glycerol, while the anodization had a duration of 14 hours and the applied voltage was 25V. After anodization, samples were

carefully cleaned in ethanol and subsequently air dried. Finally, adherends were studied by means of SEM in order to observe the developed TiO₂ nanotubes layers.

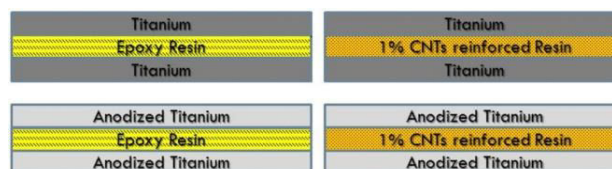


Fig. 1. The four different types of manufactured single lap joints.

2.3. Preparation of carbon nanotube reinforced epoxy adhesive

The resin was firstly placed in an oven for 10 minutes at 40°C in order to decrease its viscosity. Carbon nanotubes were added to the hardener in a plastic beaker and preliminary mixed by means of an electrical stirrer. Next, the mixture was placed in a sonicator, type Bandelin Sonopuls HD 2200 sonicator homogenizer, for 5 minutes, at 10 kHz. In order to avoid temperature rise during sonication, external cooling was employed by submerging the mixing beaker in a mixture of ice and salt water. The beaker containing the resin was also submerged in a mixture of ice and salt water and the CNTs-hardener system was added in the resin and mixed via an electric stirrer until homogeneity was achieved. The final mixture was placed in a vacuum chamber for 5–6 minutes to reduce the amount of entrapped air.

2.4. Preparation of double reinforced single lap titanium joints

The CNTs reinforced epoxy adhesive was uniformly applied, with a thickness of approximately 40µm, on one adherend surface and subsequently bonded to the second adherend in a continuous process under controlled pressure at room temperature conditions. Single lap joints were mounted with an overlap length of 20 mm. The overall dimensions of the metal adherends were 140 × 18 × 1.6mm, which is in accordance to ASTM D0790-03 standards. As already mentioned and shown in Fig. 1, four different types of single lap adhesive joints were manufactured.

3. Experimental

Both, the formation of titania nanotubes (TNTs) on the anodized titanium adherends and the distribution of the CNTs in the polymeric adhesive were observed by means of Scanning Electron Microscopy (SEM device, Model Zeiss SUPRA 35VP) in the absence of any conductive sputtering.

The flexural strength of the joints was determined in accordance with ASTM D0790-03 and an applied displacement rate of 1mm/min (Instron 4301).

The apparent shear strength of the adhesive was determined through tensile loading of the joint in accordance with ASTM D1002-01 standard, with a displacement rate of 1mm/min (Instron 4301).

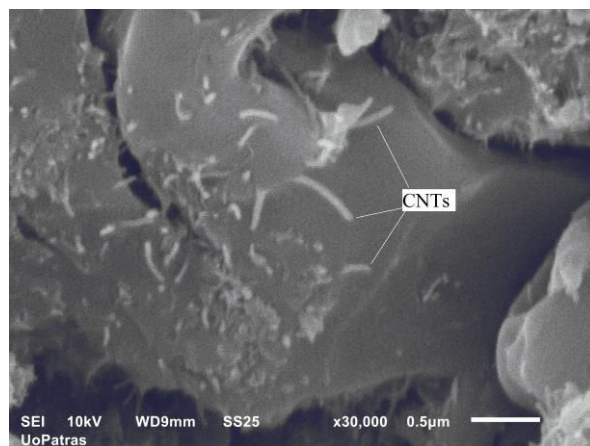
The geometry and dimensions of the manufactured single lap joints according to the ASTM standards are given in Fig. 2.

Five or more specimens were manufactured per each combination of adherends and adhesives.

4. Results and Discussion

4.1. Dispersion of CNTs into the epoxy matrix

The degree of dispersion of the CNTs into the epoxy adhesive was studied by means of SEM photomicrographs. As it can be deduced from photomicrographs shown in Fig. 3, a good dispersion of CNTs has been achieved (Fig. 3a), although in some places nanotubes agglomerations can be observed (Fig. 3b).



(a)

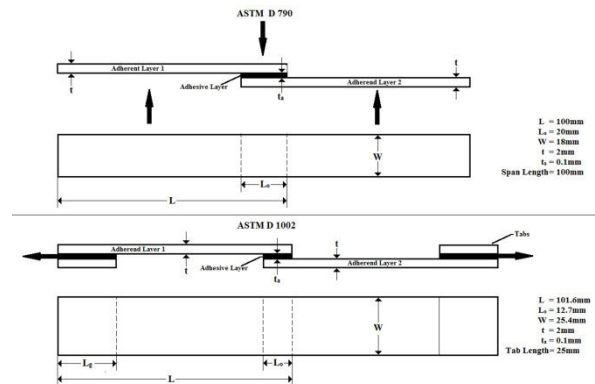
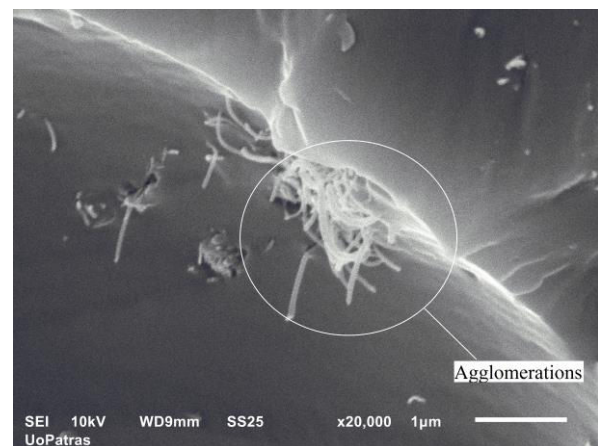


Fig. 2. Geometry and dimensions of the single lap joints manufactured according to the ASTM standards.

4.2. Anodization of the adherends

The electrochemical anodization method is considered an effective method used for processing titanium surfaces. Through the electrochemical anodization of titanium, molecular self-organizing processes can be enabled, and organized TiO_2 nanotube layers can be synthesized on its surface. Although this method is not an expensive one while at the same time it is quite simple in applying, the result dependency on a great number of manufacturing parameters require deep knowledge of the phenomena taking place and careful selection of the parameters controlling the resulting surface structure. Research on synthesizing titania nanotubes usually involves pure titanium plates



(b)

Fig. 3. SEM micrographs of 1% CNTs/epoxy composites.

provided by specific suppliers. However, most of the titanium grades used in industrial sectors such as in aeronautics, ship-building and medicine, are usually of lower quality and purity and as a result, of lower price.

On the other hand development of TiO₂ nanotubes on 99.9% pure titanium surfaces is an easy task while on Ti-surfaces characterized by a lower purity this procedure becomes quite difficult due to the additional elements/impurities contained into the titanium structure. Small differences in the metal's structure (purity, density, porosity) may totally alter the anodization results. Thus, in the present work we have decided to apply the anodization method onto plates made out of industrial grade titanium.

From electrochemical point of view, an important aspect in the anodization process is the electrolyte homogeneity. In this study, it has been concluded that proper ions activation and balance in the electrolyte is achieved after repeatedly using the same electrolytic solution in successive experiments.

Fig. 4 shows a number of industrial titanium plates used as adherends in the single lap joints manufacturing that were anodized under the same conditions with the only difference that the same electrolyte was reused; the samples where nanotubes layers were developed on their surfaces are the two ones shown on the right side of the image (i.e. specimens 5 and 6).

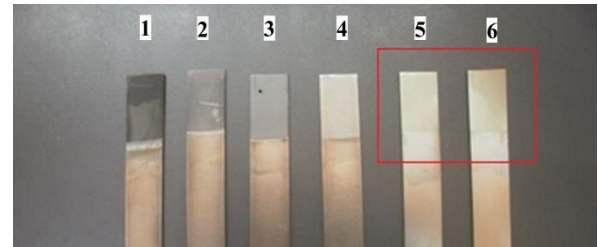
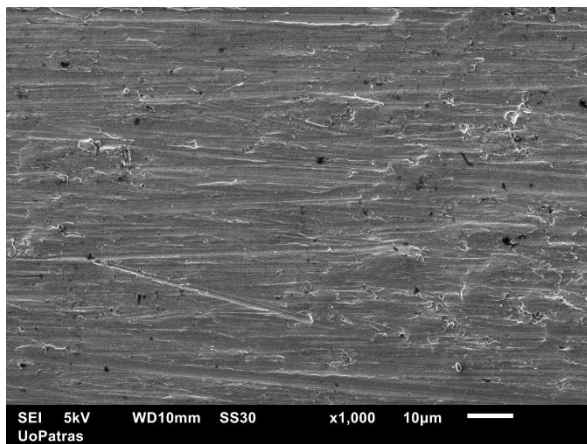
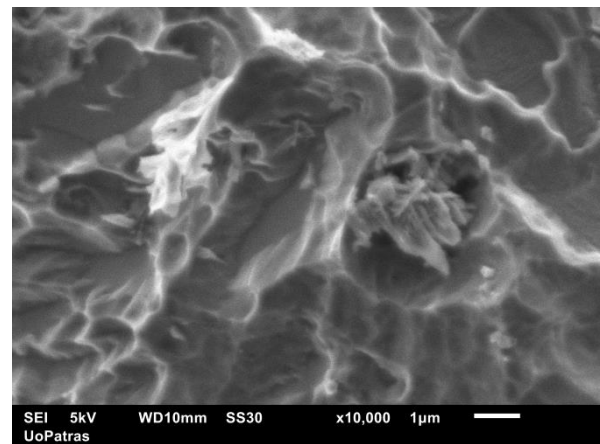


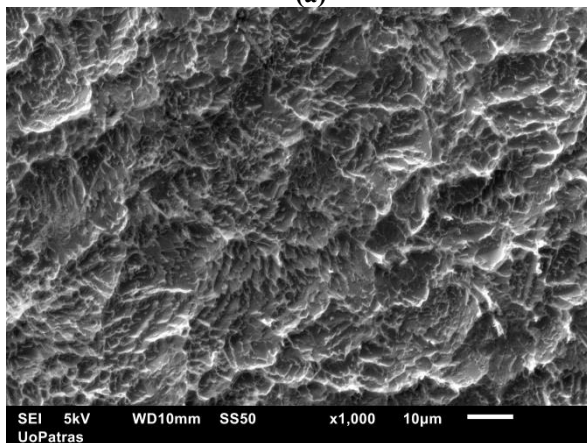
Fig. 4. Several industrial titanium samples, anodized under the same conditions, in a reused electrolyte.



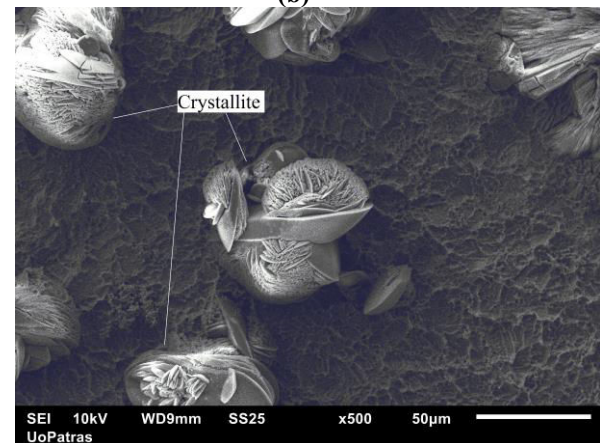
(a)



(b)



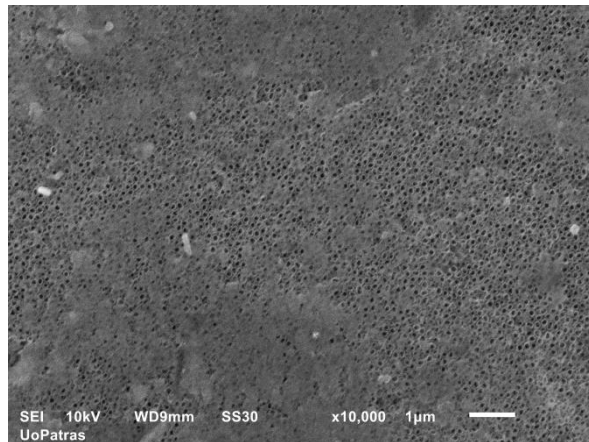
(c)



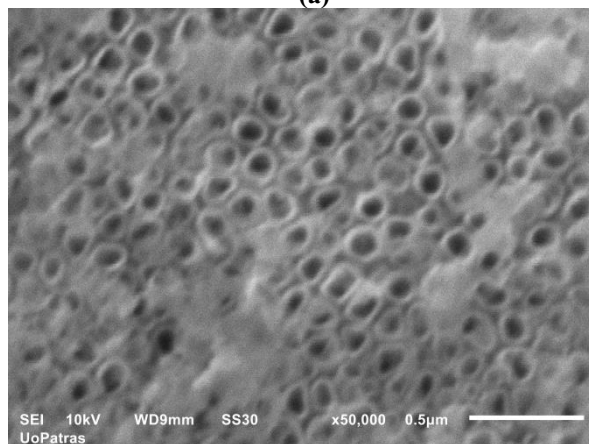
(d)

Fig. 5. SEM images of samples anodized in different conditions (electrolyte, voltage, time): (a) Reference specimen (b) 1% (w/w) HF, in 1:1 (w/w) glycerol – water, 25 V, 8 hrs (c) 0.4% (w/w) HF, in 1:1 (w/w) glycerol – water, 25 V, 8 hrs (d) 1% (w/w) HF, in 1:1 (w/w) diethylene glycol – water, 40 V, 8 hrs.

Also, as observed in Fig. 4, the four samples on the left side of the image have a dark colour, some appearing black (specimen 1) while others grey (specimen 2, 3 and 4), indicating that the material has been aggressively corroded. On these four samples there were no nanotubes formed. On the contrary, on



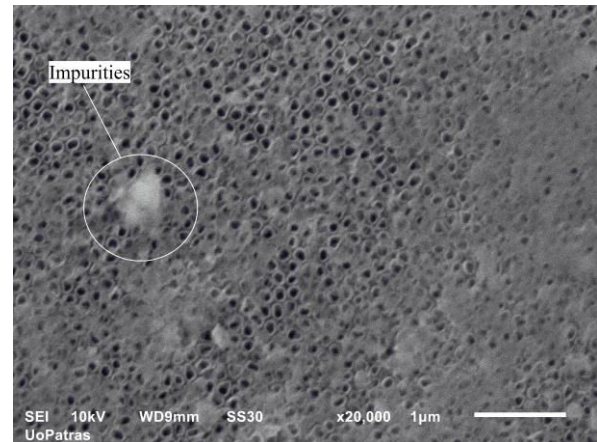
(a)



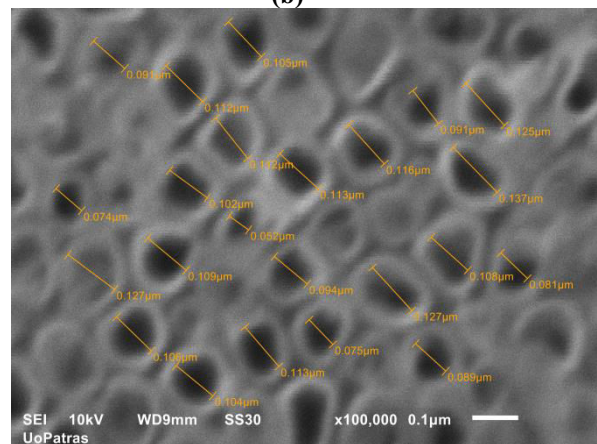
(c)

compared to the reference specimen (not anodized) in Fig. 5.

Fig. 5a shows the surface of the virgin (reference) specimen, while Fig. 5b, 5c, and 5d show the effect of the different parameters combinations on the surface topography of the titanium specimens. More precisely,



(b)



(d)

Fig. 6. SEM micrographs of the industrial titanium plates anodized under optimum conditions.

the two samples surfaces on specimens 5 and 6, a highly organized nanotubes layer was synthesized in the anodization region. As mentioned above, anodization conditions were the same, with the only difference that the electrolyte has been reused several times; thus its intensity as a corrosive agent has been minimized, while ions concentration was stabilized. In order to develop TiO_2 nanotubes on the Titanium surfaces, several combinations of parameters were checked. These include anodization time, applied voltage and type of electrolyte. SEM micrographs of industrial titanium surfaces anodized under different conditions are shown and

initially, the only effect observed using specific parameters combination, was the creation of a rough surface (Fig. 5b,5c) while, under different conditions, as described below the figure, the formation of microstructures was achieved using diethylene glycol in the electrolyte solution at an electromotive force of 40V. Crystallite shaped microstructures were synthesized as a result of an intense chemical dissolution which dominated the electrochemical process (Fig. 5d).

At this point we must stress our attention to the specific mechanisms responsible for the creation of nanotubes and/or micro-crystallites. Nanotubes are shaped through a carving process, while on the

opposite; micro-crystallites are shaped into the titanium layer as a result of an intense dissolution.

As a consequence, some local oxidation picks are produced which end up in the formation of the crystallite-shaped microstructures after the dissolution of the surrounding titanium layer.

After several successive trials, it was found that the optimum conditions for the formation of a highly organized titanium dioxide nanotubes layer on the industrial titanium plates surface used in the present investigation for the titanium-titanium single lap joints are:

- Anodization time: 14 hours
- Anodization Voltage: 25 volt
- Anodization electrolyte: 0.4% (w/w)HF in 1:1 (w/w) water-glycerol

SEM images showing the surface of the industrial titanium after anodization under optimum conditions can be seen in Fig. 6. As observed, highly organized nanotubes having a mean diameter on the order of 100nm were developed on the titanium surface. Apart from this, traces of impurities which may be caused by the salts in the water (existing in the electrolyte) or by some other elements which weren't removed by the ethanol and distilled water, exist on top of the nanotubes layer. These types of impurities can be eliminated through ultrasonication in distilled water or ethanol.

4.3. Shear properties of the adhesive

Tensile shear experiments were performed on the manufactured joints in order to determine the shear strength of the adhesives used. Five or more specimens were manufactured per each combination of adherends and adhesives. In Fig. 7 the variation of the adhesive shear strength as a function of the adhesive type used at the time, is shown. From the bar diagram shown in Fig. 7 it becomes clear that the adhesive shear strength is significantly reduced after the addition of 1 wt% of CNTs into the epoxy adhesive. More specifically shear strength reduces from the value of 5.7MPa for the neat epoxy resin to 2.83MPa for the CNTs/epoxy system. This drop can be translated to a 50% reduction in shear strength once the CNTs were introduced into the epoxy adhesive.

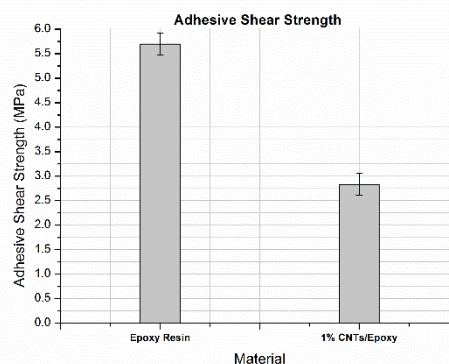


Fig. 7. Shear strength of the two different adhesives.

In very general terms, the fluid's viscosity relates the strain rate and the viscous stress. In the Newtonian fluid model, the relationship is by definition linear. Non-Newtonian fluids exhibit a variety of different correlations between shear stress and shear rate. In all cases, shear strength variation depends on respective viscosity changes. For a constant strain rate, the higher the viscosity, the higher the shear stress.

As stated in [21], for long sonication periods, a decrease in the viscosity can be observed, which can be attributed to the breakage/damage (with a possible decrease in average length) of the CNTs. Also, on the other hand, a higher amount of CNTs could favour the contact between the epoxy molecules and the nanotubes, causing some orientation of those molecules and, consequently, a reduction in viscosity; besides, the release of trapped solvent traces could also lead to a reduction in viscosity [22]. Thus, we can conclude that the inclusion of CNTs reduces the viscosity of the epoxy adhesive facilitating its application onto the titanium surfaces as well as within the free space in-between the TiO₂ nanotubes.

4.4. Flexural properties of the single lap joint

Three point bending tests were performed on the manufactured composites, in order to determine the flexural properties of the joints. Five or more specimens were manufactured per each combination of adherends and adhesives. In Fig. 8 we can observe the variation of flexural strength, depending on the constituents of the single lap joint.

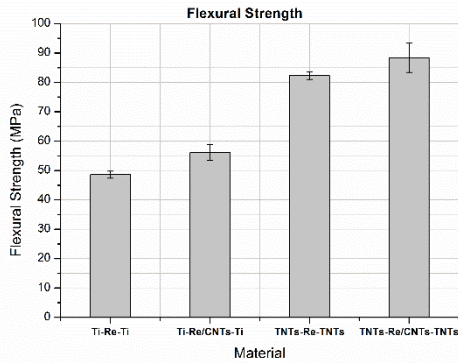


Fig. 8. Flexural strength of the four different single manufactured lap joints.

The single lap joint used as reference consists of pure titanium and neat epoxy resin as adhesive. At first, carbon nanotubes (1% wt) were added in the epoxy matrix, slightly increasing the flexural strength. The next step was the surface treatment of titanium via electrochemical anodization. The goal was to increase the contact area between the adherend and the adhesive and this was achieved through the creation of TiO_2 nanotubes on the surface of the titanium plates. Combined pure epoxy resin with anodized titanium, resulted in a great increase of flexural strength (Fig. 8), much larger than the one achieved with the inclusion of CNTs in the epoxy matrix alone.

Finally, the combination of anodized titanium and epoxy resin reinforced with CNTs yielded the higher increase in flexural strength. In order to observe the improvement in flexural strength in terms of percentage increase, the normalized flexural strength with respect to the reference joint (Ti/neat epoxy resin/Ti) was plotted in Fig. 9.

As it becomes clear from the bar diagram shown in Fig. 9, the epoxy reinforcement with CNTs alone, leads to a slight increase on the order of 15.5% in the joint flexural strength. Then, a higher increase in flexural strength (69.5%) was achieved in joints where the surface was electrochemically treated so that TiO_2 nanotubes were created on the adherends, while a neat epoxy resin was used as adhesive. Finally, the combination of CNTs in the epoxy resin adhesive and of the TNTs on the titanium surface results in the highest observed increase in flexural strength (81.9%) relative to the reference joint.

The increased contact area between substrate and adhesive due to the TNTs formation allows the epoxy resin to bind better with the titanium plate. On the other hand, the addition of CNTs into the epoxy

adhesive displays all the advantages already studied and presented in a series of articles found in literature. Thus, the combination of the above two factors leads to an optimized joint structure with superior performance.

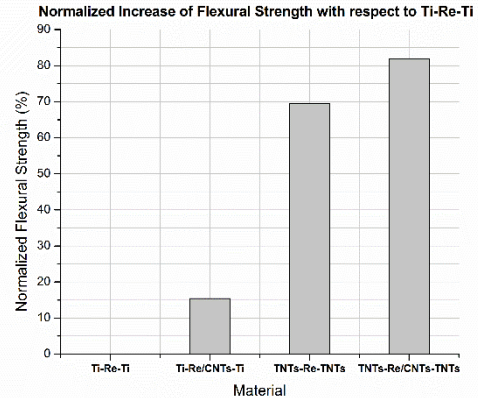


Fig. 9. Normalized increase of flexural strength with respect to the reference single lap joint of the four different single manufactured lap joints.

Table 1. Normalized flexural modulus and normalized flexural strength of the joints manufactured with respect to Ti-Re-Ti.

Materials	Flexural Modulus (GPa)	Normalized Flexural Modulus (%)	Normalized Flexural Strength (%)
Ti-Re-Ti	20.83	0	0
Ti-Re/CNTs-Ti	20.62	-1.01	15.5
TNTs-Re-TNTs	20.01	-3.91	69.5
TNTs-Re/CNTs-TNTs	19.68	-5.54	81.9

A very important observation is that despite the great increase in flexural strength the flexural modulus of the joint remains almost constant. In Table 1 the variation of the flexural modulus for the different types of joints manufactured and tested in the present work is given. From the figures shown in Table 1 it is clear that the maximum observed loss in the flexural modulus was on the order of 5.5%. Stiffness loss is due to the partial adhesive bond fracture by accounting for the shorter overlap length due to cracking [23]. In our case, the observed stiffness loss is too small (maximum observed stiffness loss on the order of 5.5%) and is within the experimental error. The small stiffness loss observed proves the high degree of adhesion developed between the joint components. Thus, we can conclude that an increase in flexural strength on the order of 81.9% was achieved, without

sacrificing the flexural modulus of the single lap joints under investigation.

5. Conclusions

The aim of the present work was to study the combined effect of TiO₂ nanotubes, developed by means of electrochemical anodization on pure titanium adherends, and of the adhesive epoxy resin reinforced with carbon nanotubes (CNTs), on the quasi-static three-point bending behaviour of titanium-titanium single lap adhesive joints.

In an attempt to optimize single lap adhesive joints flexural strength, four different types of single lap Ti-Ti adhesive joints, were manufactured as follows:

1. Pure Ti/Neat Epoxy Resin/Pure Ti (reference)
2. Pure Ti/Epoxy with 1 wt% CNTs/Pure Ti
3. Anodized Ti/Neat Epoxy Resin/Anodized Ti
4. Anodized Ti/Epoxy with 1 wt% CNTs/Anodized Ti

From the whole work the following conclusions can be derived:

- The electrochemical method of anodization can be successfully applied for the synthesis of highly organized nanostructures on industrial titanium dedicated to lap joints manufacturing.
- To apply this method it is essential to find the optimum combination of parameters (anodization time, electrolyte type and applied voltage) depending on the material's nature and the specific application the material is going to be used for.
- By optimizing the above parameters, a highly organized layer of TiO₂ nanotubes was developed on the surface of industrial grade titanium adherends.
- The inclusion of 1 wt% CNTs into the epoxy resin adhesive resulted in a 50% decrease in adhesive shear strength.
- In pure Ti/Epoxy with 1 wt% CNTs/Pure Ti adhesive joints a small increase on the order of 15.5% was achieved.
- In Anodized Ti/Neat Epoxy Resin/Anodized Ti adhesive joints flexural strength increase reached the level of 69.5% as compared to the reference joint.
- Finally, in the combined case of Anodized Ti/Epoxy with 1 wt% CNTs/Anodized Ti adhesive joint a maximum of 82% relative increase in the joint flexural strength was achieved.
- In all cases, flexural modulus value remained practically unaffected.
- Besides the high flexural strength increase already

achieved, parameters such as adhesive thickness, CNTs concentration, overlap length, etc. remain for further investigation in order to achieve a much better mechanical performance of the joints considered.

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