coatings

MDPI

Article

Comparative Study of Resin and Silane Coupling Agents Coating Treatments on Bonding Strength Improvement of Titanium and Carbon Fiber Composites

Shihao Zuo [1], Lin Wang [1], Jinheng Zhang [1], Guangming Yang [1], Yang Xu [1], Yunsen Hu [2], Fei Cheng [1,3,*] and Xiaozhi Hu [4]

[1] School of Materials and Chemistry, Southwest University of Science and Technology, Mianyang 621010, China; zsh13683403560@163.com (S.Z.); wl195799@163.com (L.W.); zjh20001106@163.com (J.Z.); yangswust@outlook.com (G.Y.); xy1300849930@163.com (Y.X.)
[2] School of Mechanical Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China; huyunsen33@foxmail.com
[3] Department of Mechanical Engineering, University of Western Australia, Perth, WA 6009, Australia
[4] Engineering Research Center of Biomass Materials, Ministry of Education, Southwest University of Science and Technology, Mianyang 621010, China; xiao.zhi.hu@uwa.edu.au
* Correspondence: feicheng@swust.edu.cn; Tel.: +86-18280755750

Abstract: In this study, anodizing treatment was utilized to etch titanium (Ti) substrates' surface to prefabricate nano-cavities. Resin pre-coating (RPC) and three silane coupling agents' coating (CAC) techniques were further applied to porous Ti substrates surface to compare the reinforcement effect of adhesive bonding strength. SEM images show that nano-cavities have been prepared to create a greater contact area and vertical volume on Ti substrate surface, fully covered by resin coatings via RPC. A higher surface roughness and better surface wetting are also obtained by the testing results of atomic force microscope and contact angles. Single lap shear tests results indicate that specimens with "anodizing + RPC" treatment yield the best average shear strength of 20.73 MPa, increased by 31.7% compared to anodizing base strength and at least 63.0% higher than silane KH-550/560/792-coated specimens. A dominant cohesive failure and fiber-tearing on CFRP's shallow surface, instead of adhesive debonding failure, are shown in the appearances of damaged specimens, proving that the RPC technique has a more effective bonding strength reinforcement in titanium and carbon fiber-reinforced polymer (Ti-CFRP) composites' toughening. Thus, the simple RPC technique can be regarded as a new-type alternative to adhesive joint toughening to manufacture high-performance composites for aerospace applications.

Keywords: resin pre-coating (RPC); coupling agents' coating (CAC); anodizing; adhesive bonding strength improvement

check for updates

Citation: Zuo, S.; Wang, L.; Zhang, J.; Yang, G.; Xu, Y.; Hu, Y.; Cheng, F.; Hu, X. Comparative Study of Resin and Silane Coupling Agents Coating Treatments on Bonding Strength Improvement of Titanium and Carbon Fiber Composites. *Coatings* **2023**, *13*, 903. https://doi.org/10.3390/coatings13050903

Academic Editor: Mariaenrica Frigione

Received: 16 April 2023
Revised: 28 April 2023
Accepted: 2 May 2023
Published: 11 May 2023

1. Introduction

Carbon fiber-reinforced polymer (CFRP) has been gradually used as a dominant alternative to lightweight design in important equipment fields (aerospace, ships, transportation equipment, etc.) because of its high strength-to-weight ratio, good corrosion resistance and excellent designability [1–4]. However, CFRP is very vulnerable to out-of-plane loads resulting from impacts during maintenance and service operations [5]. In actual industry, metal frames are often joined with CFRP to manufacture hybrid structures [6,7]. Titanium (Ti) and its alloys are used as important bonding substrates [8]. They show high strength, low density, sufficient ductility, and are completely resistant to galvanic corrosion when bonding with carbon fiber composites [9,10]. Although adhesive bonding can appropriately avoid issues including substrate structure damage, local stress concentration and potential galvanic corrosion at the Ti-CFRP connection surface caused by mechanical fasteners (bolts, rivets and screws), it may lead to debonding failure due to its poor wetting and compatibility, and weak mechanical occlusion on the bonding interface between epoxy resin and substrates [11,12].

It is well-known that etching substrate surfaces to create vertical channels can promote adhesive bonding based on the mechanical interlocking theory. Mechanical treatments [13–15] such as sanding, grinding and abrasive blasting, and chemical and electrochemical treatments [16–20] such as alkaline etching, anodizing and micro-arc oxidation, are very effective methods to prefabricate micro- or nano- channels, and anodizing surface treatment has been proven to form a better channel structure and distribution for interfacial adhesion than other treatments on a variety of metal substrate surfaces. Cheng [21] used a mixing solution of H_2SO_4 and $H_2C_2O_4$ to etch aluminum alloys; hard pores with a uniform aperture and depth ranging from 3 to 5 μm were prepared; the CNTs/resin/acetone mixture was further applied to treat the adhesive surface so that an improvement in shear strength of 130% was obtained. Hu [18] adopted the H_2SO_4 solution and NaOH solution to treat the substrate; a porous oxide film with a thickness of several microns was formed on the both substrate surfaces and significant increases in adhesive bonding strength were also realized.

It should be noted that the anodized substrate cannot directly bond with adhesive for the better development of bonding strength, since epoxy resin must have high viscosity to avoid easily flowing into the root of those micro- or nano- channels [21]. Coupling agents (e.g., silane coupling agents) are commonly used to modify the substrate surface before adhesive bonding [22–24], containing chemical functional groups that could form a covalent bond with a silanol group or molecules on the surface of substrates to achieve bonding strength reinforcements. A simple and novel technique named resin pre-coating (RPC) was pertinently developed to efficiently solve interface defects [25]. This is carried out using evaporable organic dispersants to dilute pure high-viscosity epoxy resin without reacting chemically with resin; in this way, more liquid RPC solution can guide diluted resin (or add reinforcing fiber) into pre-fabricated porous channels. Resin coatings at the root of micro-cavities can be obtained with the full volatilization of organic dispersant [26]. The RPC technique has been used multiple times in the ordered or disordered porous structures of metal [27], wood [28], bamboo [29], sandstone and granite [30], and even resin-based composites [31], which are demonstrated to significantly improve bonding interface properties. The main advantages of RPC are as follows: (i) The substrate surface remains wet because no hardener is mixed into the RPC solution; thus, better wettability can be acquired so that air entrapments are not easy to generate at the root of micro-cavities. A normal epoxy mixture (epoxy resin + hardener) enables a better wetting and compatibility with pre-coated resin in the micro-cavities, which may eliminate potential void defects, as shown in Figure 1b. (ii) Reinforcing additives (or fibers) can be dispersed into RPC solution, and dragged into pre-fabricated channels, together with diluted resin, which is volatilized during acetone, and this thin layer of epoxy + reinforcing additives (or fibers) in the micro-cavities can promote the formation of quasi-Z directional fiber bridging at the adhesive stage [32]. Compared with the common pre-coated coupling agents, RPC treatment may remain as a single resin system, allowing for adhesive bonding without introducing other impurity components.

In this study, coupling agents and resin are designed to treat anodized Ti alloys via RPC-like and RPC methods to form a coating on the substrate surface with same surface condition. Microstructure, roughness and contact angle are characterized to investigate surface performance, and single lap shear tests are conducted to compare bonding strength following treatments of CAC and RPC. This is the first the comparison of resin pre-coating and coupling agents' pre-coating techniques on the substrate surface under the same conditions; it will provide a great reference and alternative for the adhesive manufacturing processes of Ti-CFRP composites and even other metal–CFRP hybrid composites.

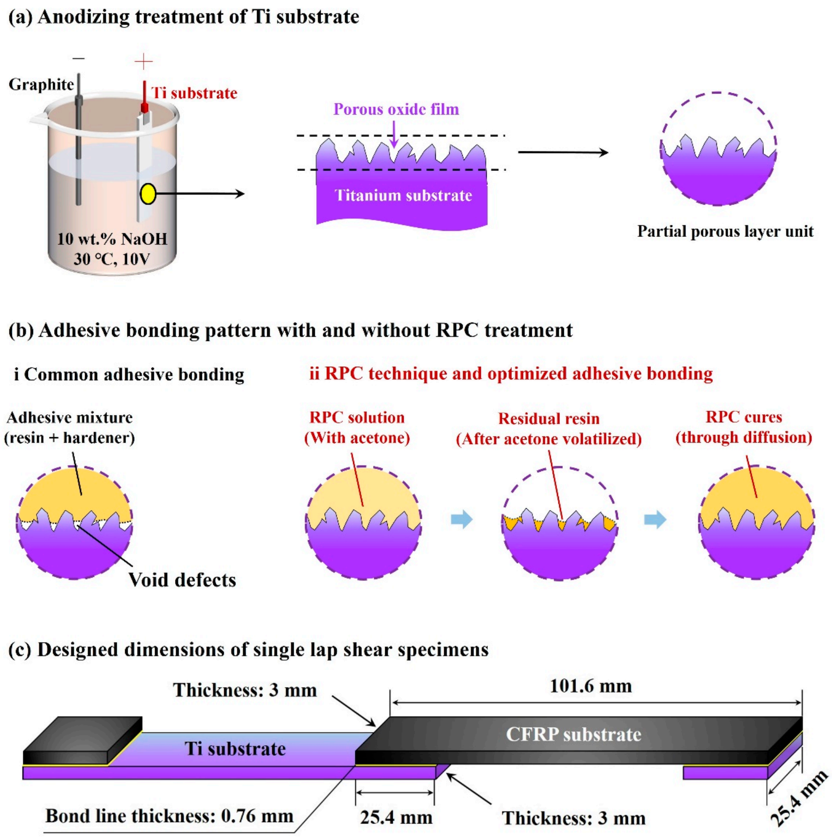

Figure 1. Schematic image of Ti substrate surface treatments and Ti-CFRP composites' manufacturing: (**a**) anodizing treatment of Ti substrate; (**b**) patterns of common adhesive bonding and optimized adhesive bonding via RPC technique; (**c**) designed dimensions of single lap shear specimens based on ASTM D5868 [33].

2. Composites Preparation and Characterization

2.1. Composites Design and Preparation

Ti-6Al-4V Titanium alloy plates (composed of 5.5–6.75 wt.% Al, 3.5–4.5 wt.% V, $\leq$0.3 wt.% Fe, $\leq$0.2 wt.% O, $\leq$0.08 wt.% C, $\leq$0.05 wt.% N, $\leq$0.015 wt.% H and Ti balance, supplied from Wuxi Shengtai Technology Ltd., Wuxi, China), were first cleaned by 3 wt.% HF solution for 3 min and 30 wt.% H_2SO_4 solution for 1 h at ambient temperature to remove passive oxide films. They were further electrochemically etched by 10 wt.% NaOH solution at 30 °C with a constant voltage of 10 V; the anodizing process lasted for 15 min to obtain the required surface microstructure for adhesion. The cross-ply $[0/90]_{10s}$ CFRP plates (101.6 mm × 25.4 mm × 3.0 mm, purchased by Carbonwiz Technology Ltd., Shenzhen, China) were grinded by DL6391 electric handheld grinder. Then, grinded CFRP were ultrasonically cleaned in acetone for 10 min to remove the produced dust particles.

Anodized Ti and grinded CFRP substrates were further immersed into RPC solutions consisting of 90 wt.% acetone and 10 wt.% epoxy resin (without hardener), brought out after 10 s to form resin coatings when acetone fully volatilized. Other anodized Ti substrates were coated by three coupling agent solutions composed of 8 wt.% silane KH-550/560/792 (bought from Kangjin New Material Technology Co., Ltd., Dongguan, China) and 92 wt.% ethylalcohol for 10 s, and their coatings were formed by the volatilization of ethylalcohol.

The adhesion process was carried out using normal epoxy resin + hardener mixture (obtained from Huntsman Advanced Chemical Materials Co., Ltd., Guangzhou, China) with a ratio of 50 vol.%: 50 vol.%; relative specimen dimensions, bonding line thickness and area based on ASTM D5868 [33] are exhibited in Figure 1c. After adhesive bonding, all the specimens stayed in their original location for 12 h, and then were placed in the drying oven at 60 °C to cure for 72 h. A total of 6 group specimens with different treatment conditions on Ti substrate surfaces, namely acid pickling, anodizing, anodizing + coating KH-550/560/792 and anodizing + RPC, were manufactured and detailed designations are summarized in Table 1.

Table 1. Detailed designations of adhesive bonding composites according to different treatments on Ti alloy and CFRP panel surfaces.

Specimen Groups	Surface Treatments of Ti Alloys	Surface Treatments of CFRP Panels	Specimen Number
Acid pickling	Acid pickling	Acetone ultrasonic cleaning	6
Anodizing	Anodizing	Grinding + RPC	6
Coating KH-550	Coating KH-550	Grinding + RPC	6
Coating KH-560	Coating KH-560	Grinding + RPC	6
Coating KH-792	Coating KH-560	Grinding + RPC	6
Anodizing + RPC	Anodizing + RPC	Grinding + RPC	6

2.2. Composites Test and Characterization

The morphologies of anodized Ti substrates and resin-coated ones were examined by a scanning electron microscope (SEM, Thermo Fisher Scientific Inc., Waltham, MA, USA) with an Everhart-Thornley detector (ETD). The compositions of net-shaped nano-cavities on anodized Ti substrates were analyzed using an energy-dispersive X-ray spectroscopy (EDX) detector equipped for the SEM. Surface height profiles and roughness parameters of anodized Ti surfaces were obtained using the Bruker Dimension Icon atomic force microscope (AFM, Bruker Corp., Belica, MA, USA) operated in contact mode. The contact angles between anodized Ti surfaces and ultrapure water were measured by the Krüss DSA30 drop shape analyser (Krüss GmbH, Hamburg, Germany). Six measurements were conducted for each surface condition. A single lap shear of specimens was measured using a WANCE ETM105D universal mechanical testing machine with a 150 KN load cell. The tensile tests were conducted, and the loading displacement speed was controlled at 2 mm/min; the tests were immediately ended following a precipitous decline in load. The detailed parameters of detected specimens, including the dimensions, bonding line thickness and bonding area shown in Figure 1c, were assigned to ASTM D5868 [33].

3. Results and Discussions

Figure 2 shows the surface morphologies of Ti substrates after anodizing and RPC treatment, and the EDX spectrum of nano-cavities on the Ti substrate surface. The anodized Ti substrates exhibit ant-nest-like nanostructured surfaces resembling the surface appearances of alkaline-anodizing titanium in previous research [34,35]. Disorderly stacked rock-like oxide particles can be observed clearly, which may be attributed to the insufficient etching. Porous net-structures of a few hundred nanos are below protuberant particles at channel roots in Figure 2b, capable of creating greater volumes for RPC and CAC treatments. The compositions of net-shaped nano-cavities are examined by EDX, and the related spectrum is shown in Figure 2d. As the oxide film mainly comprises TiO_2 [16] forms on the Ti substrate surface, the element wt% of O (17.52 wt.%) is higher than that of original Ti substrate ($\leq$0.2 wt.%). As displayed in Figure 2e,f, protuberant oxide particles can hardly be identified because the porous surface is completely covered by coated resin after RPC.

Figure 3 presents the representative AFM images of anodized Ti substrates and acid-pickled specimens, revealing the arithmetical mean roughness (Ra) and root mean square roughness (Rq). The anodized substrate evidently has a greater average Ra and Rq values than the acid-pickled one, exhibiting an improved surface roughness. It also possesses a contact angle ($36.35 \pm 3.71°$) that is twice as small as that of the latter ($75.16 \pm 3.81°$), as displayed in Figure 4a,b, indicating the anodizing treatment contributes to a greater surface roughness and better substrate wetting. Rougher surfaces may be beneficial to increase the contact area between water and substrates for a better wettability. As RPC and silane KH-550/560/792 coatings are further applied to the surface, their contact angles increase, except for silane KH-560, since coated resin (without hardener) and silane coupling agents are hydrophobic and inhibit substrate wetting to aqueous solutions [36]. This illustrates that the ultra-thin coatings remain on the substrate surface; however, it cannot be confirmed that resin and silane KH-550/560/792 pre-coated substrate surfaces are not good for adhesive bonding. Since the normal epoxy resin + hardener mixtures are used as the bonding adhesive, resin-coated substrate can even promote the wetting of adhesive, owing to the better compatibility of homogenous material.

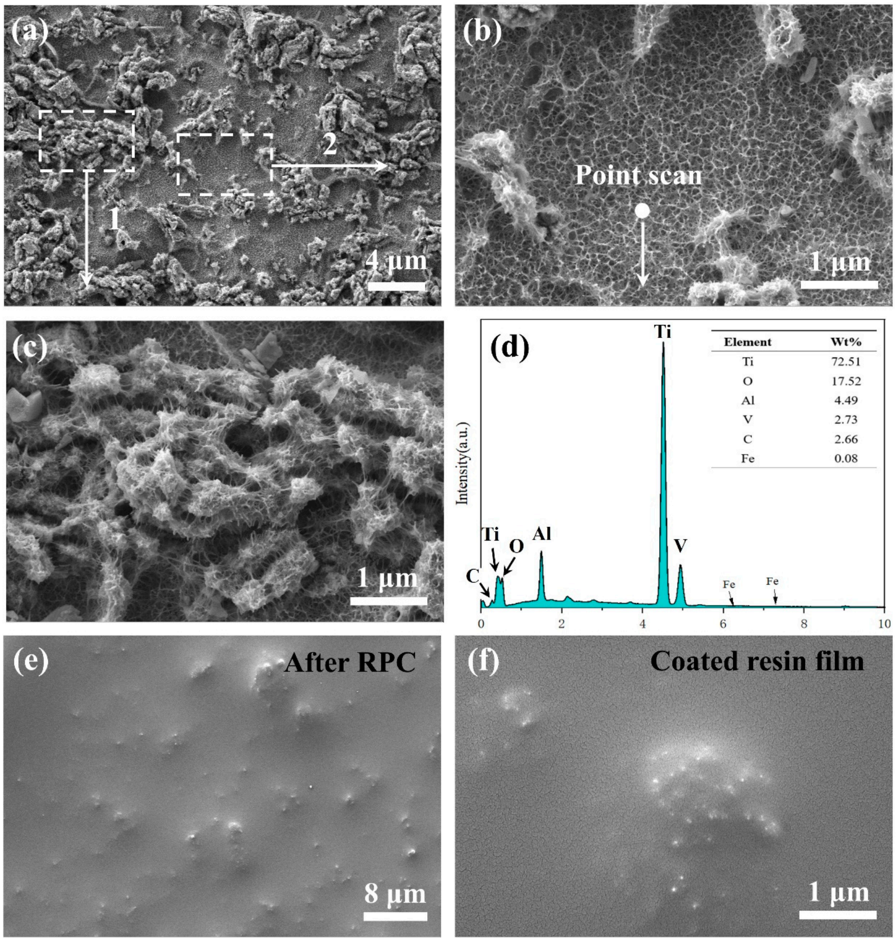

Figure 2. SEM images of Ti substrates via using SE2 signal: (**a**–**c**) anodizing, (**e**) and (**f**) anodizing + RPC; EDX spectrum of net-structure nano-cavities in (**b**).

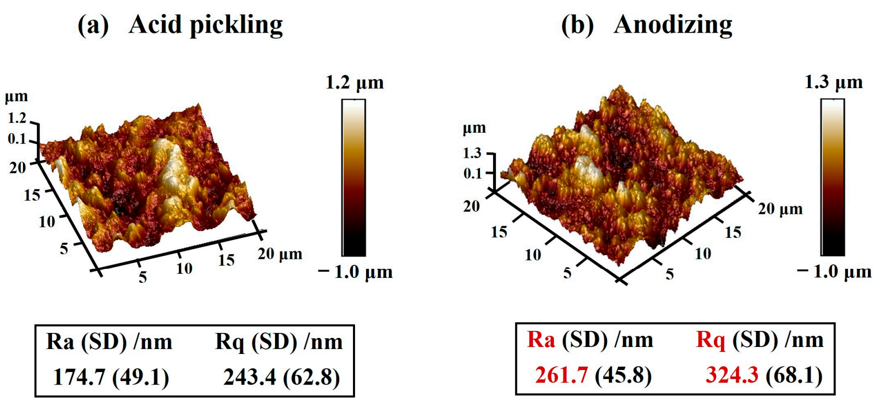

Figure 3. Representative AFM images and average Ra/Rq values of Ti substrate: (**a**) acid pickling, (**b**) anodizing.

The representative load-displacement curves and the average adhesive bonding strength of each specimen group after the shear tests are shown in Figure 5; the detailed testing and calculated results are listed in Table 1. Noticeable linearly increasing regions and nonlinear regions can be recognized from the load-displacement curves in Figure 5a, and can be attributed to the elastic deformation of composites, plastic deformation of adhesive and even localized interface de-bonding [37].

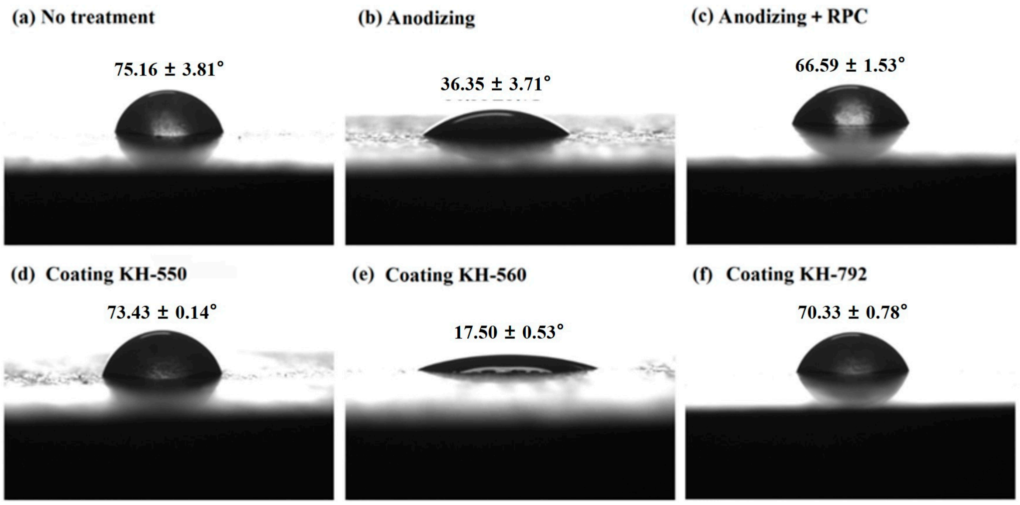

Figure 4. Contact angles of Ti substrate with different conditions: (**a**) no treatment; (**b**) anodizing; (**c**) anodizing + RPC; (**d**–**f**) anodizing + coating KH-550, KH-560 and KH-792, respectively.

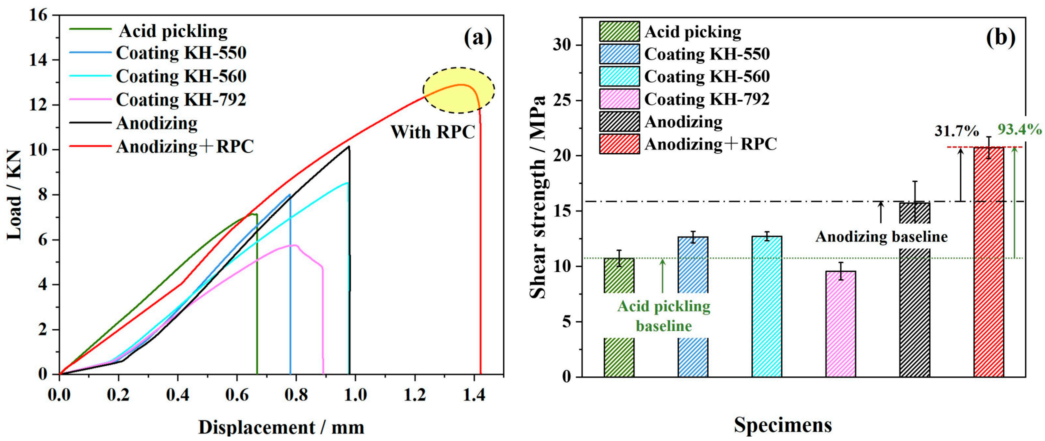

Figure 5. Single lap shear testing results of Ti-CFRP composites with different conditions: (**a**) representative load versus displacement curve, (**b**) average bond strength (error bars show the standard deviations).

As revealed in Figure 5b, anodized specimens have an average shear strength of 15.74 MPa, 75% higher than the acid pickling base, and silane KH-550/560-coated specimens also have a greater shear strength. However, all three silane-coated specimens evidently exhibit a decreasing bonding performance, the maximum values of 12.72 MPa yielded by the KH-560 coated specimen are around 19.2 % lower than the only anodized specimen. However, RPC treatment causes the shear strength to increase to 20.73 MPa, a remarkable 93.4% and 31.7% improvement compared to the acid-pickled and only anodized specimens, respectively. This indicates that RPC treatment has a better reinforcing effect in terms of bonding strength compared to silane-coated coupling agents.

Figure 6a–d shows specimens coated by KH-792, KH-550, KH-560 and resin after single lap shear tests, and detailed parameters including average Pmax and shear strength were exhibited in Table 2. The residual quantities of the cured resin remaining on Ti substrate surface show a continuous increasing trend from KH-792 to resin-coated specimens. KH-792- and KH-550-coated specimens exhibit a complete and dominant adhesive failure on the Ti substrate surface, respectively. The resin-coated specimen has maximum resin residues that are slightly attached by some torn carbon fibers, indicating a cohesive failure and carbon fiber tearing on the CFRP shallow surface. A weaker Ti/epoxy adhesive interface causes a typical adhesive failure [18] compared to the CFRP/epoxy interface because CFRP uses the epoxy component to achieve better wetting and compatibility, which can be improved by anodizing and RPC treatment. This explains why the resin-coated specimen has the best shear strength.

Even if silane KH-550/560/792 can be dragged into the nano-cavities or submicron-cavities via coating treatment, their various functional groups (especially the –CH(O)CH– group of KH-560) can form a covalent bond and also bond with the polymer molecule to obtain a good interface combination, acting as a connecting bridge between the adhesive and inorganic porous surface of the Ti substrate. However, guiding the epoxy resin via RPC causes a single homogenous resin system to remain in the nano-cavities [38], which is more prone to be wetted, compatible with the normal epoxy + hardener adhesive, and forms a stronger integrated Ti/epoxy bonding interface.

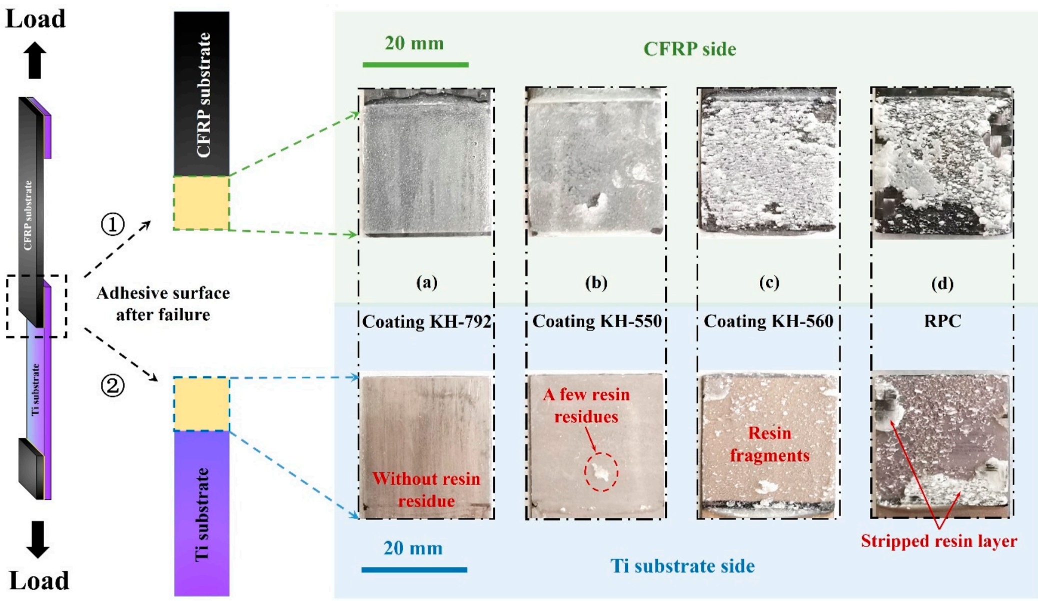

Figure 6. Adhesive bonding region appearance images of CFRPs and Ti substrates with different surface conditions after failure: (**a**) coating KH-792, (**b**) coating KH-550, (**c**) coating KH-560 and (**d**) RPC.

Table 2. Detailed parameters including average P_{max} and shear strength of Ti-CFRP composites after single lap shear testing.

Specimens	Average P_{max}/N	Standard Deviation/N	Shear Strength/MPa	Standard Deviation/MPa
Acid pickling	6871.14	498.14	10.72	0.73
Anodizing	10,157.04	668.82	15.74	1.96
Coating KH-550	8164.72	259.41	12.66	0.52
Coating KH-560	8208.32	636.43	12.72	0.40
Coating KH-792	6176.75	503.22	9.57	0.78
Anodizing + RPC	13,375.86	639.41	20.73	0.99

4. Conclusions

This study compares a simple RPC technique and three silane CAC treatments on a porous Ti substrate surface for adhesive bonding strength reinforcement. An anodizing treatment was adopted to prefabricate nano-cavities to create enough volume, resin and coupling agent coatings, which will be further formed on an anodized Ti substrate surface. The AFM and contact angle results showed the increased surface roughness and improved wettability of an anodized Ti substrate compared with the untreated specimens. Single lap shear tests results demonstrated that the shear strengths of silane KH-550/560/792 coated specimens are at least 19.2% lower than those of only anodized ones. Specimens with anodizing + RPC have an average strength of 20.73 MPa, 10.5% higher than the anodizing base and much higher than silane KH-550/560/792-coated specimens. Post-failure appearances indicated that resin-coated specimens show a cohesive failure and carbon fiber-tearing on the CFRP shallow surface compared to the adhesive failure of KH-550/560/792-coated specimens. In summary, the simple RPC technique has a more effective reinforcement than coating silane KH-550/560/792 in the Ti-CFRP composites' toughening system, and can be regarded as a new alternative for adhesive joint-toughening applications.

Author Contributions: Conceptualization, F.C. and Y.H.; methodology, S.Z.; software, G.Y.; validation, J.Z. and Y.X.; formal analysis, S.Z. and L.W.; investigation, S.Z.; resources, L.W.; writing—original draft preparation, S.Z.; writing—review and editing, F.C. and X.H.; visualization, J.Z.; supervision, F.C.; project administration, S.Z.; funding acquisition, F.C. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported financially by the National Natural Science Foundations of China (Grant No. 52102115), the Natural Science Foundations of Sichuan Province (Grant No. 2023NSFSC0961) and the Overseas High-end Talent Introduction Project of Sichuan Province (Grant No. 2023JDGD0013).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors thank Shiyanjia Lab "www.shiyanjia.com (accessed on 1 September 2016)" for the SEM and AFM analysis. The authors also wish to thank the editor and reviewers for kindly giving revision suggestions.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Geier, N.; Davim, J.P.; Szalay, T. Advanced cutting tools and technologies for drilling carbon fibre reinforced polymer (CFRP) composites: A review. *Compos. Part A Appl. Sci. Manuf.* **2019**, *125*, 105552. [CrossRef]
2. Cheng, F.; Hu, Y.S.; Yuan, B.Y.; Hu, X.Z.; Huang, Z.H. Transverse and longitudinal flexural properties of unidirectional carbon fiber composites interleaved with hierarchical Aramid pulp micro/nano-fibers. *Compos. Part B Eng.* **2020**, *188*, 107897. [CrossRef]
3. Yuan, B.Y.; Tan, B.; Hu, Y.S.; Shaw, J.; Hu, X.Z. Improving impact resistance and residual compressive strength of carbon fibre composites using un-bonded non-woven short aramid fibre veil. *Compos. Part A Appl. Sci. Manuf.* **2019**, *121*, 439–448. [CrossRef]
4. Hassan, M.; Mubashar, A.; Masud, M.; Zafar, A.; Ali, M.U.; Rim, Y.S. Effect of Temperature and Al_2O_3 NanoFiller on the Stress Field of CFRP/Al Adhesively Bonded Single-Lap Joints. *Coatings* **2022**, *12*, 1865. [CrossRef]
5. Hu, Y.S.; Wei, Y.; Han, G.; Zhang, J.H.; Sun, G.Y.; Hu, X.Z.; Cheng, F. Comparison of impact resistance of carbon fibre composites with multiple ultra-thin CNT, aramid pulp, PBO and graphene interlayers. *Compos. Part A Appl. Sci. Manuf.* **2022**, *155*, 106815. [CrossRef]
6. Kaiser, I.; Tan, C.; Tan, K.T. Bio-inspired patterned adhesive single-lap joints for CFRP and titanium. *Compos. Part B Eng.* **2021**, *224*, 109182. [CrossRef]
7. Mu, W.L.; Qin, G.F.; Na, J.X.; Tan, W.; Liu, H.L.; Luan, J.Z. Effect of alternating load on the residual strength of environmentally aged adhesively bonded CFRP-aluminum alloy joints. *Compos. Part B Eng.* **2019**, *168*, 87–97. [CrossRef]
8. Aravindakshan, R.; Saju, K.K.; Aruvathottil Rajan, R. Investigation into Effect of Natural Shellac on the Bonding Strength of Magnesium Substituted Hydroxyapatite Coatings Developed on Ti6Al4V Substrates. *Coatings* **2021**, *11*, 933. [CrossRef]
9. Pantović Pavlović, M.R.; Eraković, S.G.; Pavlović, M.M.; Stevanović, J.S.; Panić, V.V.; Ignjatović, N.L. Anaphoretical/oxidative approach to the in-situ synthesis of adherent hydroxyapatite/titanium oxide composite coatings on titanium. *Surf. Coat. Technol.* **2019**, *358*, 688–694. [CrossRef]
10. Faudree, M.C.; Uchida, H.T.; Kimura, H.; Kaneko, S.; Salvia, M.; Nishi, Y. Advances in Titanium/Polymer Hybrid Joints by Carbon Fiber Plug Insert: Current Status and Review. *Materials* **2022**, *15*, 3220. [CrossRef]

11. Xu, J.Y.; Lin, T.Y.; Li, L.F.; Ji, M.; Davim, J.P.; Geier, N.; Chen, M. Numerical study of interface damage formation mechanisms in machining CFRP/Ti6Al4V stacks under different cutting sequence strategies. *Compos. Struct.* **2022**, *285*, 115236. [CrossRef]
12. Cao, S.; Zhang, K.; Hou, G.; Luo, B.; Cheng, H.; Li, Y.; Li, X.; Liu, C. Experimental analysis of entrance and exit damage mechanism affected by the structural dynamic deformation characteristics during drilling of thin-walled CFRP. *Thin-Walled Struct.* **2022**, *180*, 109870. [CrossRef]
13. Kim, Y.-W. Surface Modification of Ti Dental Implants by Grit-Blasting and Micro-Arc Oxidation. *Mater. Manuf. Process.* **2010**, *25*, 307–310. [CrossRef]
14. He, P.G.; Chen, K.; Yang, J.L. Surface modifications of Ti alloy with tunable hierarchical structures and chemistry for improved metal–polymer interface used in deepwater composite riser. *Appl. Surf. Sci.* **2015**, *328*, 614–622. [CrossRef]
15. Sun, Z.; Hu, X.Z.; Chen, H.R. Effects of aramid-fibre toughening on interfacial fracture toughness of epoxy adhesive joint between carbon-fibre face sheet and aluminium substrate. *Int. J. Adhes. Adhes.* **2014**, *48*, 288–294. [CrossRef]
16. Hu, Y.S.; Yuan, B.Y.; Cheng, F.; Hu, X.Z. NaOH etching and resin pre-coating treatments for stronger adhesive bonding between CFRP and aluminium alloy. *Compos. Part B Eng.* **2019**, *178*, 107478. [CrossRef]
17. Yu, Y.-S.; Xie, L.-S.; Chen, M.-H.; Wang, N.; Wang, H. Surface characteristics and adhesive strength to epoxy of three different types of titanium alloys anodized in NaTESi electrolyte. *Surf. Coatings Technol.* **2015**, *280*, 122–128. [CrossRef]
18. Hu, Y.S.; Zhang, J.H.; Wang, L.; Jiang, H.Y.; Cheng, F.; Hu, X.Z. A simple and effective resin pre-coating treatment on grinded, acid pickled and anodised substrates for stronger adhesive bonding between Ti-6Al-4V titanium alloy and CFRP. *Surf. Coatings Technol.* **2022**, *432*, 128072. [CrossRef]
19. Chen, Q.Z.; Jiang, Z.Q.; Tang, S.G.; Dong, W.B.; Tong, Q.; Li, W.Z. Influence of graphene particles on the micro-arc oxidation behaviors of 6063 aluminum alloy and the coating properties. *Appl. Surf. Sci.* **2017**, *423*, 939–950. [CrossRef]
20. Wang, R.T.; Xu, H.; Yao, Z.P.; Li, C.X.; Jiang, Z.H. Adhesion and Corrosion Resistance of Micro-Arc Oxidation/Polyurethane Composite Coating on Aluminum Alloy Surface. *Appl. Sci.* **2020**, *10*, 6779. [CrossRef]
21. Cheng, F.; Hu, Y.S.; Lv, Z.F.; Chen, G.; Yuan, B.Y.; Hu, X.Z.; Huang, Z.H. Directing helical CNT into chemically-etched micro-channels on aluminum substrate for strong adhesive bonding with carbon fiber composites. *Compos. Part A Appl. Sci. Manuf.* **2020**, *135*, 105952. [CrossRef]
22. Ding, G.Y.; Yu, X.; Dong, F.Q.; Ji, Z.Z.; Wang, J.Y. Using Silane Coupling Agent Coating on Acidic Aggregate Surfaces to Enhance the Adhesion between Asphalt and Aggregate: A Molecular Dynamics Simulation. *Materials* **2020**, *13*, 5580. [CrossRef]
23. Zhu, W.; Xiao, H.; Wang, J.; Li, X.D. Effect of Different Coupling Agents on Interfacial Properties of Fibre-Reinforced Aluminum Laminates. *Materials* **2021**, *14*, 1019. [CrossRef]
24. Deng, S.H.; Li, Z.Q.; Liu, Z.Z. Study on the modification of epoxy matrix by coupling agent in glass fiber composite. *Thermosetting Resin.* **2017**, *32*, 45–50.
25. Wang, B.H.; Hu, X.Z.; Lu, P. Improvement of adhesive bonding of grit-blasted steel substrates by using diluted resin as a primer. *Int. J. Adhes. Adhes.* **2017**, *73*, 92–99. [CrossRef]
26. Han, X.Y.; Yuan, B.Y.; Tan, B.; Hu, X.Z.; Chen, S. Repair of subsurface micro-cracks in rock using resin pre-coating technique. *Constr. Build. Mater.* **2019**, *196*, 485–491. [CrossRef]
27. Tan, B.; Hu, Y.S.; Yuan, B.Y.; Hu, X.Z.; Huang, Z.H. Optimizing adhesive bonding between CFRP and Al alloy substrate through resin pre-coating by filling micro-cavities from sandblasting. *Int. J. Adhes. Adhes.* **2021**, *110*, 102952. [CrossRef]
28. Tan, B.; Ji, Y.; Hu, Y.S.; Yuan, B.Y.; Hu, X.Z.; Huang, Z.H. Pretreatment using diluted epoxy adhesive resin solution for improving bond strength between steel and wood surfaces. *Int. J. Adhes. Adhes.* **2020**, *98*, 102502. [CrossRef]
29. Liu, W.; Xu, H.; Hu, X.Z.; Yuan, B.Y.; Tan, B.; Xu, F. Strengthening and repairing of engineered bamboo-steel epoxy adhesive joints with carbon nanotube on the basis of resin pre-coating method. *Eur. J. Wood Wood Prod.* **2020**, *78*, 313–320. [CrossRef]
30. Han, X.Y.; Liu, W.; Zhang, Q.; Chen, Y.; Hu, X.Z.; Xiao, Q.; Chen, S. Effect of resin pre-coating method on repairing subsurface micro-defects in sandstone and granite. *Constr. Build. Mater.* **2020**, *264*, 120144. [CrossRef]
31. Ji, Y.; Yuan, B.Y.; Hu, X.Z.; Jiang, H.Y.; Qiao, Y. Repairing sharp delamination cracks in CFRP through capillary action of acetone-diluted resin solution. *Compos. Sci. Technol.* **2022**, *219*, 109249. [CrossRef]
32. Cheng, F.; Hu, Y.S.; Zhang, X.G.; Hu, X.Z.; Huang, Z.H. Adhesive bond strength enhancing between carbon fiber reinforced polymer and aluminum substrates with different surface morphologies created by three sulfuric acid solutions. *Compos. Part A Appl. Sci. Manuf.* **2021**, *146*, 106427. [CrossRef]
33. *ASTM D5868*; Standard Test Method for Lap Shear Adhesion for Fiber Reinforced Plastic (FRP) Bonding. ASTM International: West Conshohocken, PA, USA. [CrossRef]
34. Ye, J.; Wang, H.; Dong, J.L.; Liu, C.; Gao, Y.; Gong, B.W.; Su, B.; Peng, H.X. Metal surface nanopatterning for enhanced interfacial adhesion in fiber metal laminates. *Compos. Sci. Technol.* **2021**, *205*, 108651. [CrossRef]
35. Huang, X.; Liu, Z. Growth of titanium oxide or titanate nanostructured thin films on Ti substrates by anodic oxidation in alkali solutions. *Surf. Coatings Technol.* **2013**, *232*, 224–233. [CrossRef]
36. Cheng, F.; Xu, Y.; Zhang, J.H.; Wang, L.; Zhang, H.H.; Wan, Q.; Li, W.P.; Wang, L.; Lv, Z.F. Growing carbon nanotubes in-situ via chemical vapor deposition and resin pre-coating treatment on anodized Ti-6Al-4V titanium substrates for stronger adhesive bonding with carbon fiber composites. *Surf. Coatings Technol.* **2023**, *457*, 129296. [CrossRef]

37. Zhang, J.H.; Cheng, F.; Wang, L.; Xu, Y.; Zhou, Z.T.; Liu, X.Y.; Hu, Y.S.; Hu, X.Z. Reinforcement study of anodizing treatment with various temperatures on aluminum substrates for stronger adhesive bonding with carbon fiber composites. *Surf. Coatings Technol.* **2023**, *462*, 129473. [CrossRef]
38. Wang, B.H.; Hu, X.Z.; Hui, J.; Lu, P.; Jiang, B. CNT-reinforced adhesive joint between grit-blasted steel substrates fabricated by simple resin pre-coating method. *J. Adhes.* **2018**, *94*, 529–540. [CrossRef]