



Influence of laser structuring of PEEK, PEEK-GF30 and PEEK-CF30 surfaces on the shear bond strength to a resin cement

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ABSTRACT

Objectives: The aim of this study was to evaluate the influence of a surface conditioning technique using laser ablation and acid etching on PEEK substrate on its bonding strength to a resin cement.

Materials and methods: Cylindrical specimens of unfilled PEEK, 30% glass fiber reinforced PEEK and 30% carbon fiber reinforced PEEK were separated in four groups according to the following surface treatments: acid etching with H₂SO₄, laser ablation with 200 µm holes spaced 400 µm apart (D2E4), laser ablation with 200 µm holes spaced 600 µm apart (D2E6), and laser ablation (D2E4) followed by acid etching. A dual-curing resin cement (Allcem CORE) was then applied to the PEEK surface. Specimens were aged in distilled water at 37 °C for 24 h. Shear bond strength tests were performed to the fracture of the samples. Two-way ANOVA statistical analysis was performed with a significance level of 0.05. Scanning electron microscopy analysis was performed to analyse the conditioned and fracture surfaces.

Results: SEM images of the test interfaces showed that the resin cement could not flow in the holes designed by the laser ablation on the PEEK surface. The shear bond strength of PEEK to resin cement was not improved by the surface modification of the PEEK. Also, there was a statistically significant decrease in shear bond strength for unfilled PEEK specimens. On carbon or glass reinforced PEEK, the change was not significant. SEM images of the fracture surfaces revealed that the failure mode was mainly adhesive.

Conclusions: Although laser ablation promoted the PEEK surface modification by the formation of retentive holes, the test resin cement could not thoroughly flow on the rough modified surfaces to establish an effective mechanical interlocking. That negatively affected the shear bonding strength of PEEK to the resin cement. Further studies should be carried out to increase the bonding between PEEK and resin cements.

1. Introduction

Polyether-ether-ketone (PEEK) is a polymer with increasing interest for biomedical applications due to its attractive properties, such as high strength, wear and fatigue resistance, and toughness (Hallmann et al., 2012; Henriques et al., 2017; Kern and Lehmann, 2012; Monich et al., 2017, 2016; Sampaio et al., 2016, 2015). Additionally, PEEK can be processed without additives that guarantee a high biocompatibility (Katzer et al., 2002). PEEK also is compatible with many reinforcement fillers (e.g. carbon and glass fibers) that has increased the strength of PEEK composites. Although unfilled PEEK has an elastic modulus of approximately 4 GPa, PEEK composites can match the elastic modulus of the cortical bone (9–18 GPa) (Kurtz and Devine, 2007). PEEK is a

versatile biomaterial that can be manufactured with a wide range of physical properties (Kurtz, 2012) for different clinical situations in the field of orthopaedics and prosthodontics. In dentistry, PEEK has been used for short-term applications, such as temporary abutments, clasps and healing caps (Hallmann et al., 2012; Kern and Lehmann, 2012; Najeeb et al., 2016). The long-term performance of PEEK still needs to be improved.

The elastic modulus of PEEK and its composites is a key advantage. The stress distribution through stiff titanium implants can result in peri-implant stress shielding and bone resorption (Huiskes et al., 2000; Lee et al., 2012). PEEK and its PEEK have elastic moduli that match the human bone, enamel or dentin, decreasing the stress shielding around alternative dental implants.

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Table 1
Types of surface conditioning methods applied to specimens.

Group	Surface treatment
Group A	Acid etching with H ₂ SO ₄
Group B	Laser patterning (D2E4)
Group C	Laser patterning (D2E6)
Group D	Laser patterning (D2E4) + Acid etching with H ₂ SO ₄

However, the bonding of PEEK to resin composites and cements is still a challenge once the procedures for surface modification can not provide an effective morphological aspect for mechanical interlocking (Noiset et al., 2000). Several surface treatments, such as conventional abrasive treatments, acid etching, laser and plasma techniques, have been studied to improve PEEK wettability and its bond strength to luting resin cement. Although air abrasion can significantly increase the roughness of PEEK, previous studies have reported only a slightly increase in shear bond strength (SBS) of PEEK to resin-based materials when compared with other techniques (Stawarczyk et al., 2013a). There is no consensus on the influence of acid etching over PEEK. Even though most studies have shown a beneficial effect of acid etching with sulfuric acid on the bonding of PEEK (Schmidlin et al., 2010; Stawarczyk et al., 2013a), some studies revealed no effect of acid etching on the fracture load of veneered PEEK (Stawarczyk et al., 2015). Therefore, no significant differences were found between the effect of acid etching and air abrasion in the SBS of PEEK to resin-based materials (Uhrenbacher et al., 2014). Plasma treatment offers another approach to improve the PEEK wettability and its adhesion to resin-

based materials. The extremely energetic environment of the plasma promotes chemical changes on the material surface, leading to a deposition of free radicals to improve bonding (Liston, 1989). However, studies show that plasma treatment did not improve the adhesive bonding of stable polymers, such as PEEK and PMMA (Liebermann et al., 2013; Stawarczyk et al., 2015).

Laser treatment is a promising alternative that can offer high resolution, high operating speed and low cost, without alter the bulk material (Riveiro et al., 2012). Studies have shown that excimer laser radiation (UV laser) below the ablation threshold can significantly improve the adhesive bonding properties of PEEK. The fracture energy of PEEK to epoxy adhesives can be increased in 10 times by using UV laser (Laurens et al., 1998). Morphological changes such as removal of weak boundary layers through evaporation, modification of surface chemistry and increase in roughness, are some phenomena induced by UV laser (Rotel et al., 2000). Excimer lasers also increase the surface wettability of PEEK, forming polar and reactive chemical groups on the treated surfaces (Laurens et al., 2000). However, laser ablation also can be used to increase roughness and mechanical interlocking to enhance bonding strength (Ceballo et al., 2002). This technique consist in remove materials by melting generated by the laser pulses, creating cavities on the material surface. In this work, small holes were shaped by laser ablation, forming regions where the mechanical interlocking of resin cement would take place.

The aim of this study was to evaluate the influence of acid etching and laser patterning of PEEK surfaces on the bond strength between PEEK and resin cement. Three different PEEK-based materials were tested (unfilled PEEK, glass-reinforced PEEK and carbon-reinforced

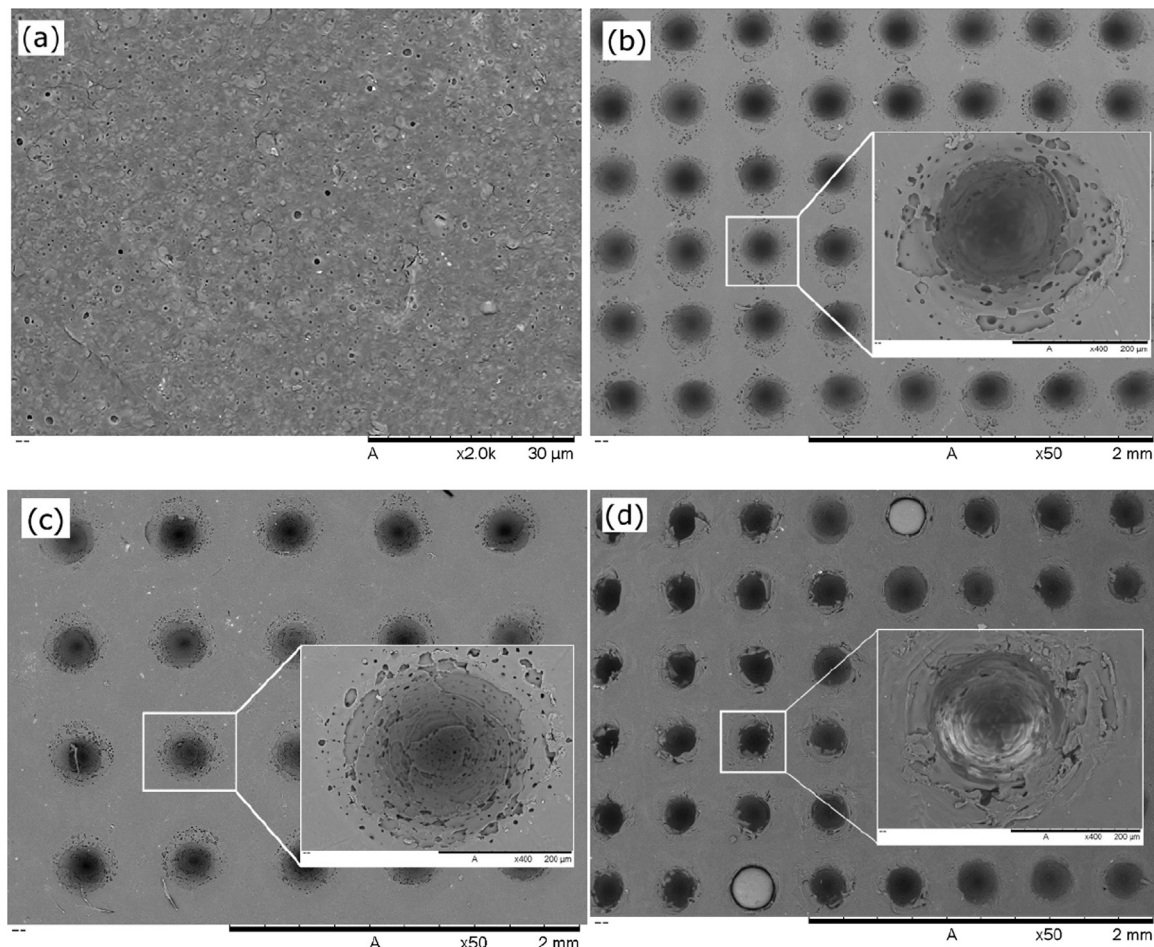


Fig. 1. SEM images revealing morphological aspects of unfilled PEEK surfaces from group A (a), group B (b), group C (c) and group D (d).

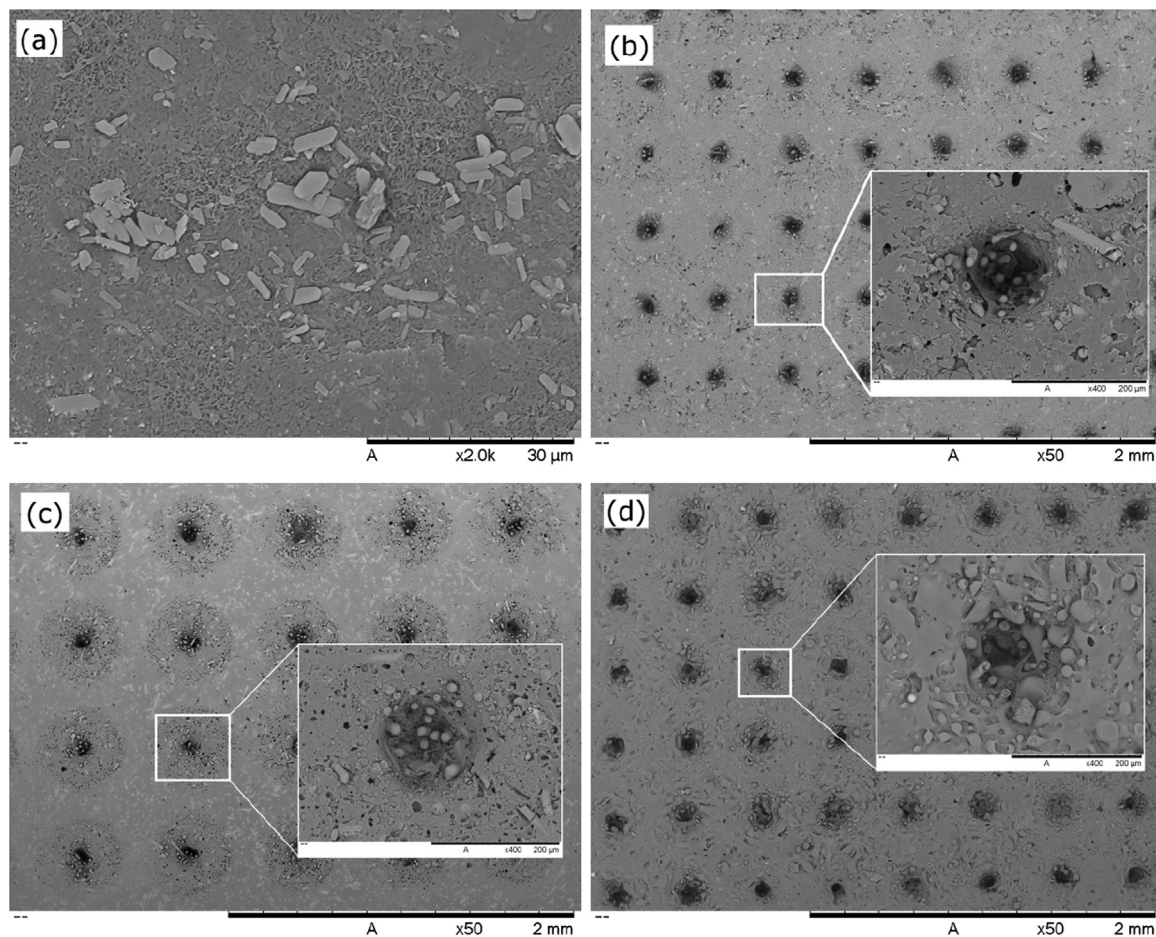


Fig. 2. SEM images revealing morphological aspects of glass-reinforced PEEK surfaces from group A (a), group B (b), group C (c) and group D (d).

PEEK). The null hypothesis was that laser patterning would not increase the adhesion of PEEK to resin cements.

2. Materials and methods

2.1. Specimens preparation

The base materials used in this study were PEEK (TECAPEEK, Ensinger), PEEK reinforced with glass fibers (30%vol) (TECAPEEK GF30, Ensinger) and PEEK reinforced with carbon fibers (30%vol) (TECAPEEK CF30, Ensinger). Cylindrical specimens were prepared with a diameter of 8 mm and a thickness of 4 mm. For each material, specimens were separated into four groups with different surface treatments, according to Table 1. Acid etching with sulfuric acid (H_2SO_4) was used to functionalize the PEEK surface. For laser patterning, a CO_2 laser (BD-50C, Bende Machine, China) was used with wavelength at 1064 nm, laser power at 50 W, input power of 1000 W, and frequency at 50 Hz. Laser patterned specimens were separated in three groups: the first with 200 μm holes spaced 400 μm apart (D2E4) and the second one with 200 μm holes spaced 600 μm apart (D2E6). The specimens of the latter group were firstly micromachined with laser ablation (D2E4) and then acid etched. After the surface conditioning, all the specimens were ultrasonically cleaned with distilled water for 60 s.

A dual-curing resin cement (Allcem CORE, FGM, Joinville, Brazil), containing methacrylates monomers such as TEGDMA, BisEMA and

BISGMA, was then applied to the PEEK surface. Specimens were light-cured for 40 s using a LED dental curing light equipment (1200 mW/cm², 44–480 nm, Radii-cal – SDI). The bonded specimens were then aged in distilled water at 37 °C for 24 h.

2.2. Shear bond strength measurements

Shear bond strength was measured using a universal testing machine (Instron 8874, MA, USA) with a load cell of 25 kN capacity. The tests were performed in a custom-made apparatus consisting in two sliding components, each one with a hole aligned to the other component. Such apparatus and method were previously reported by Henriques et al. (2011). The load was applied with a crosshead speed of 0.5 mm/s. The shear bond strength (MPa) was obtained by relationing the highest recorded fracture force (N) per the cross sectional area of the specimen (mm²).

2.3. SEM analysis

PEEK substrates were inspected after the surface conditioning by scanning electron microscopy (SEM) (TM-3030 - Hitachi). Then, PEEK to resin cement interfaces were also inspected by SEM. After the shear bond strength tests, the fractured surfaces were analysed to identify the failure mode of each group of specimens.

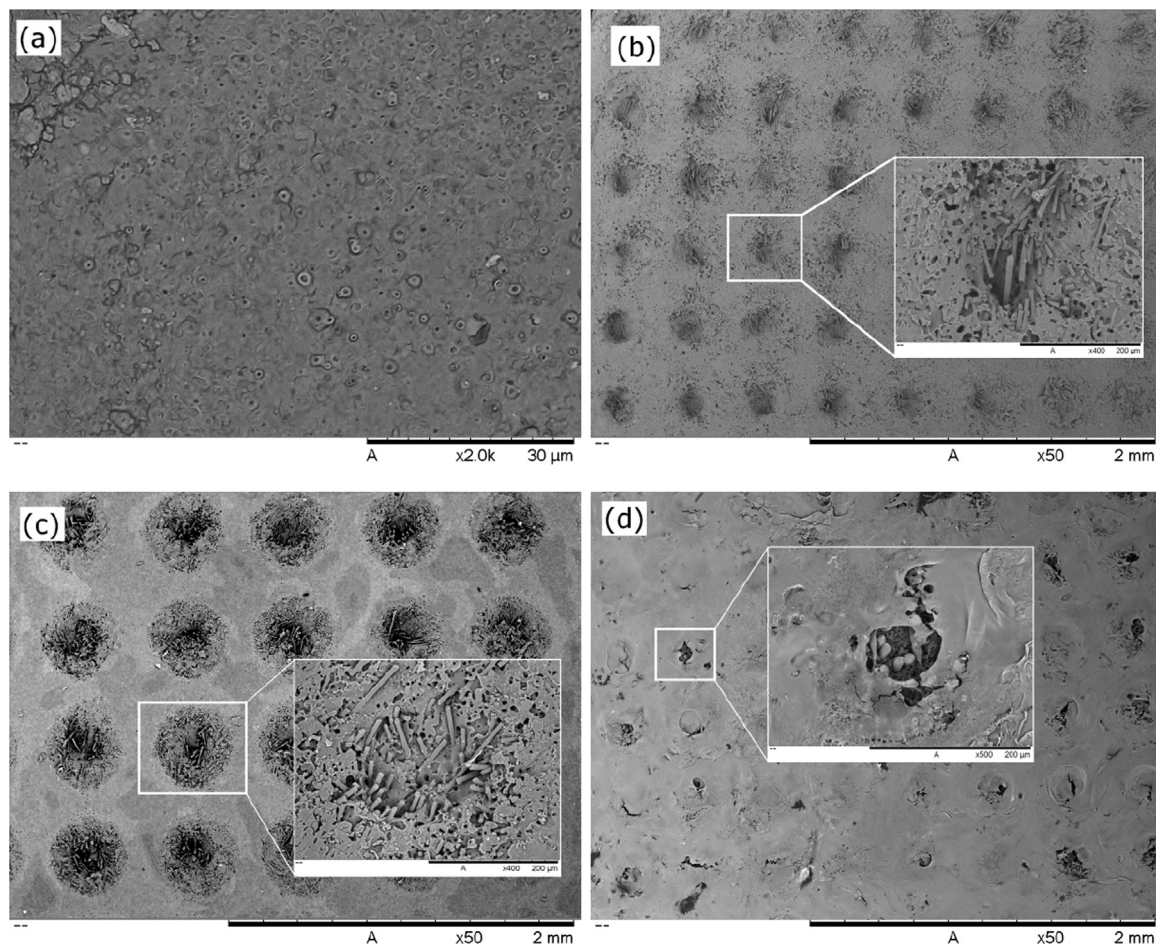


Fig. 3. SEM images revealing morphological aspects of carbon-reinforced PEEK surfaces from group A (a), group B (b), group C (c) and group D (d).

2.4. Statistical analysis

A two-way ANOVA test was performed to evaluate the influence of the material and the surface treatment on the SBS results for each group of samples. Tukey post hoc test was also performed to compare each group of samples and analyse the interaction between groups. One-way ANOVA test was also used to compare the groups for each material. The level of significance was set at 0.05.

3. Results

3.1. Surface morphology

The morphological aspects of the conditioned surfaces obtained by scanning electron microscopy are shown in Figs. 1–3. Sulfuric acid etching resulted in micropores on the unfilled PEEK (Fig. 1(a)), that increased roughness. The laser patterning (groups B and C) resulted in well-designed and reproducible holes for all the materials. The heat affected zone around the holes resulted in a porous region. On the group D (Fig. 1(d)), the acid etching smoothed the surface of the samples, decreasing the number of pores and irregularities mainly at the heat affected zone.

Although acid etching did not result in pores on the glass-

reinforced PEEK, that increased roughness and exposed some of the fibers, as shown in Fig. 2(a). The laser melted the polymer region of the groups B, C and D, maintaining the integrity of the fibers, which are clearly visible in Fig. 2(b), (c) and (d). A heat affected zone around the holes also occurred during laser ablation, which was clearly noticeable in the group C (Fig. 2(c)). The surfaces of the samples from group D were also smoothed by the acid etching after the laser treatment (Fig. 2(d)).

Pores were also noticed on the acid etched carbon-reinforced PEEK surface (Fig. 3(a)). A porous region on the heat affected zone was also detected in the laser treated samples. On the glass-reinforced PEEK, the laser melted the polymer region of the carbon-reinforced PEEK, maintaining the fibers, as seen in Fig. 3(b), (c) and (c). On group D (Fig. 3(d)), the acid etching smoothed the surface of the samples, decreasing the number of pores and irregularities mainly at the heat affected zone.

SEM images of the interface showed microgaps between the resin cement (upper region in the SEM images) and the PEEK in some regions (Fig. 4(a)). Microgaps were noted in the interface of all groups. The resin cement also did not properly flow in the laser holes as shown in Fig. 4(c). Laser treated and acid etched specimens (group D) did not reveal any improvement regarding the bonding between the materials, as seen in Fig. 4(d).

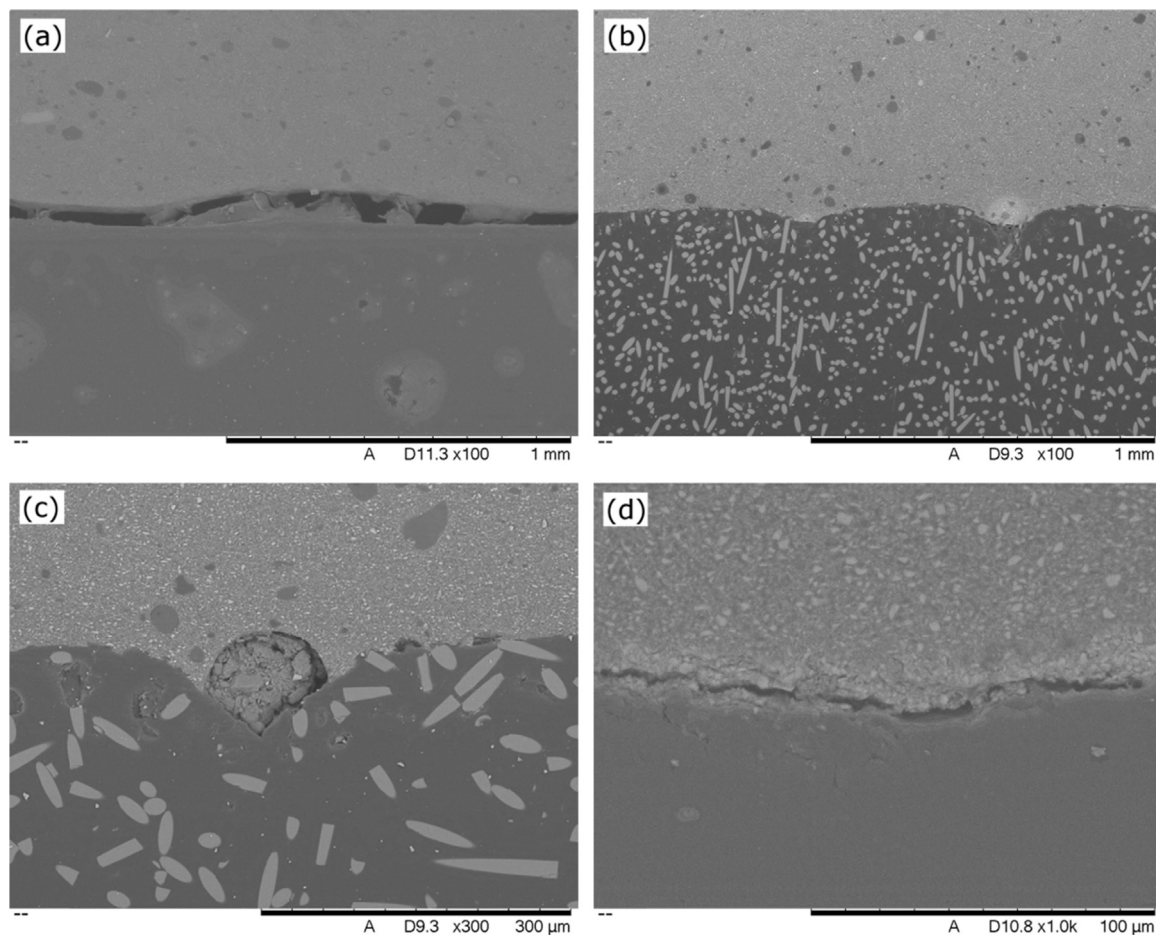


Fig. 4. SEM images of the interfaces between resin cements (upper region) and acid etched PEEK (a), glass-fiber reinforced PEEK with laser treatment (b and c), or PEEK (d).

3.2. Shear bond strength analysis

Results of shear bond strength (SBS) for resin cement to PEEK substrates are shown in Fig. 5. The unfilled PEEK samples treated only with acid etched showed the highest SBS mean values. The lowest values were found on the samples treated with both acid etching and laser patterning. ANOVA tests showed that the surface treatments affected significantly ($p < 0.05$) the SBS of the test specimens. Although the SBS values were not significantly affected by the materials, the interaction between material and surface treatments influenced the SBS of PEEK to resin.

Within the unfilled PEEK groups, the laser treatment negatively affected the SBS values of PEEK to resin cement. The influence of the size of the holes was not significant. Surface conditioning with laser showed insignificant influence in the glass-reinforced samples. The carbon-reinforced samples showed a different behaviour. However, the samples from group C (laser treated) showed a significant increase in the bond strength compared with the specimens treated by ordinary acid etching treatment. The acid etched specimens had a substantial decrease in the SBS comparing with the unfilled and glass-reinforced samples.

3.3. Failure analysis

Specimens from group A of unfilled PEEK showed mostly cohesive failure, which confirmed a high bond strength. Remnant PEEK was

detected on the resin cement portion of the fractured surfaces while some content of resin cement continued bonded to the PEEK region, as seen in Fig. 6(a) and (b). The fractured specimens of group B and C of unfilled PEEK revealed remnant resin cement on some pores, which partially validate the mechanical interlocking effect (Fig. 6(c)). Residual PEEK can also be found in the resin cement region (Fig. 6(d)). Similarly, samples from group D showed residual resin in the PEEK substrate microholes (Fig. 6(e)). A small quantity of PEEK can be found in the resin cement region as well, as shown in Fig. 6(f). Groups B, C and D showed both cohesive and adhesive failure modes.

The acid etched specimens of glass-reinforced PEEK also showed mostly cohesive failure, with remnant PEEK attached to the resin cement part, as shown in Fig. 7(a). Unlike the samples of PEEK, specimens from groups B and C of glass-reinforced PEEK did not show any sign that the resin has penetrated into the laser holes. However, residual resin cement was found on the PEEK region (Fig. 7(b)) as well as a fraction of PEEK was found on the resin cement region (Fig. 7(c)). Specimens from group D showed little remnant resin cement on the PEEK region (Fig. 7(d)), revealing mostly an adhesive failure.

The failure mode of the carbon-reinforced PEEK was predominantly adhesive. Specimens from group A showed resin cement remnant on the PEEK region (Fig. 8(a)), although almost no evidence of PEEK was found on the resin cement region. Even though some residual resin can be found on the laser treated PEEK surfaces (Fig. 8(b)), a significant portion of PEEK remained attached to the resin. Some carbon fibers

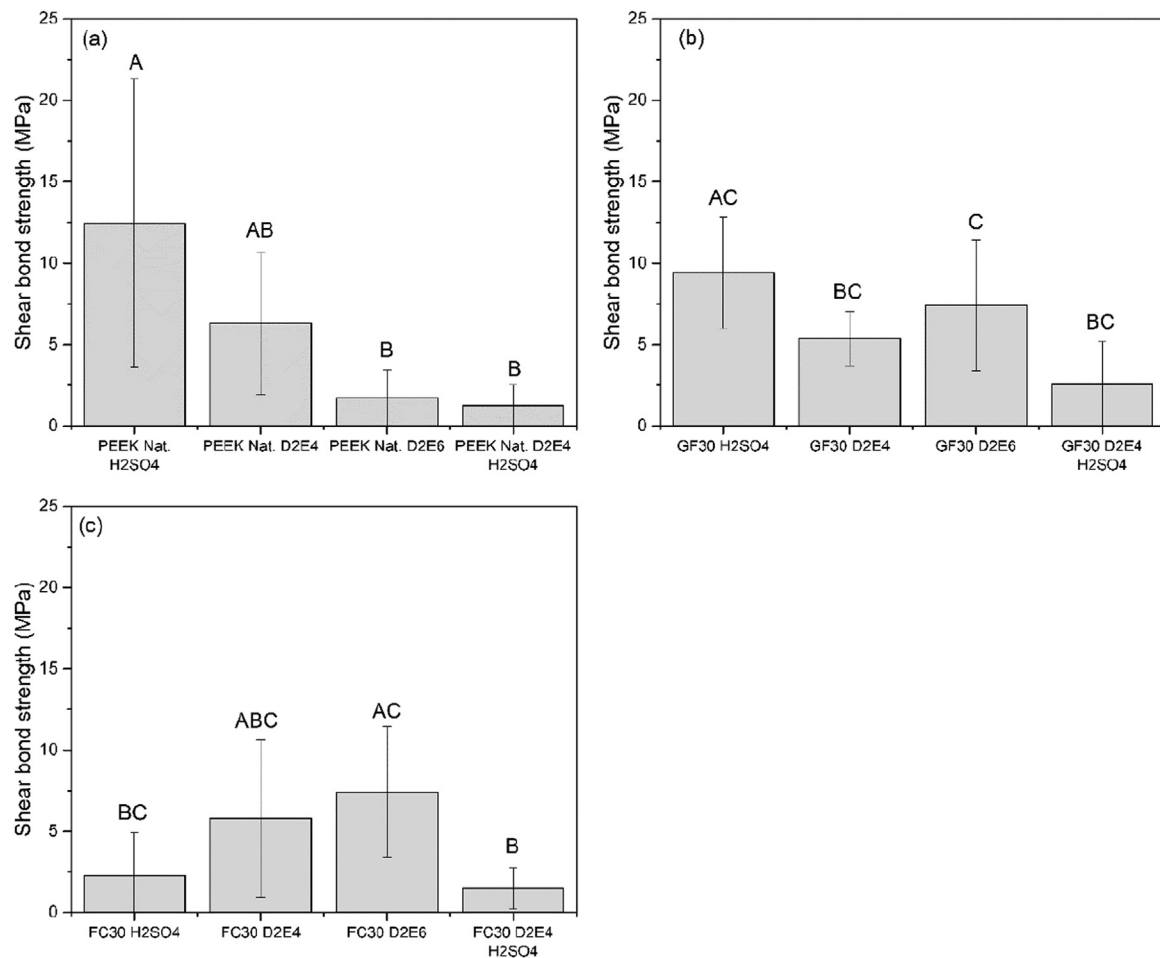


Fig. 5. Shear bond strength (SBS) of resin cement to PEEK (a), glass-reinforced PEEK (b) and carbon-reinforced PEEK (c). The capitals represent significant difference between groups. Groups with the same letter did not reveal significant differences in SBS.

were also transferred to the resin region, as seen in Fig. 8(c). On specimens from group D, some resin was attached to the PEEK substrate, mainly at the carbon fibers (Fig. 8(d)).

4. Discussion

The null hypothesis of this work was accepted. In fact, there was no clear evidences that the laser treatment increased the bonding strength of PEEK to the resin cement.

The surface treatment used in this work was effective regarding the morphological modification of the PEEK-based surfaces, as shown in Figs. 1–3. The acid etching resulted in pits on the PEEK surface as shown by other previous studies (Hallmann et al., 2012; Schmidlin et al., 2010). The laser conditioning promoted standard spaced holes by material ablation. However, laser micromachining of polymer materials can thermally induce defects, such as change in chemical composition and molten (Moreno et al., 2006). Femtosecond pulsed laser can decrease such detrimental defects. In our study, a thermally affected zone with a porous region was mainly detected at the reinforced PEEK, although its influence at the bonding strength to resin cement could not be evaluated.

Regarding mechanical and chemical properties, PEEK reveals itself as a suitable and promising material for dental applications. However, the bond strength of PEEK to veneering resins is still a concern that

should be further studied to ensure low failure rates. Surface conditioning has been studied to increase the PEEK wettability and its bonding to resin cements. In this study, acid etched PEEK was used as control group. Acid etching can chemically modify the PEEK surface, since sulfuric acid binds to the carbonyl and ether groups from PEEK. That provides functional groups on PEEK surface, increasing its reactivity to the resin-based adhesive (Ha et al., 1997; Hallmann et al., 2012). Besides the functionality of the PEEK surface, the bond strength also relies on the chemical composition of the resin-based materials. Resin cements with multifunctional methacrylates (MMA) are capable to establish a chemical bonding to PEEK, even without a surface functionalization (Kern and Lehmann, 2012; Stawarczyk et al., 2013b). A recent study has found that the highest shear bond strength values of PEEK to resin cements was achieved using an adhesive which contains pentaerythritol triacrylate (PETIA) in solution, MMA monomers, and additional dimethacrylates (Keul et al., 2014). Another previous study corroborated the benefits of using a methacrylate-based adhesive on PEEK surfaces (Stawarczyk et al., 2014). Since the bonding strength depends heavily on the resin-based adhesive, a large deviation in shear bond strength can be found due to the use of different resin-based materials.

Although chemical bonding is important to ensure a long-term resistance, the enhancement of the morphological aspects of the surfaces can increase the contact area for chemical bonding, and therefore

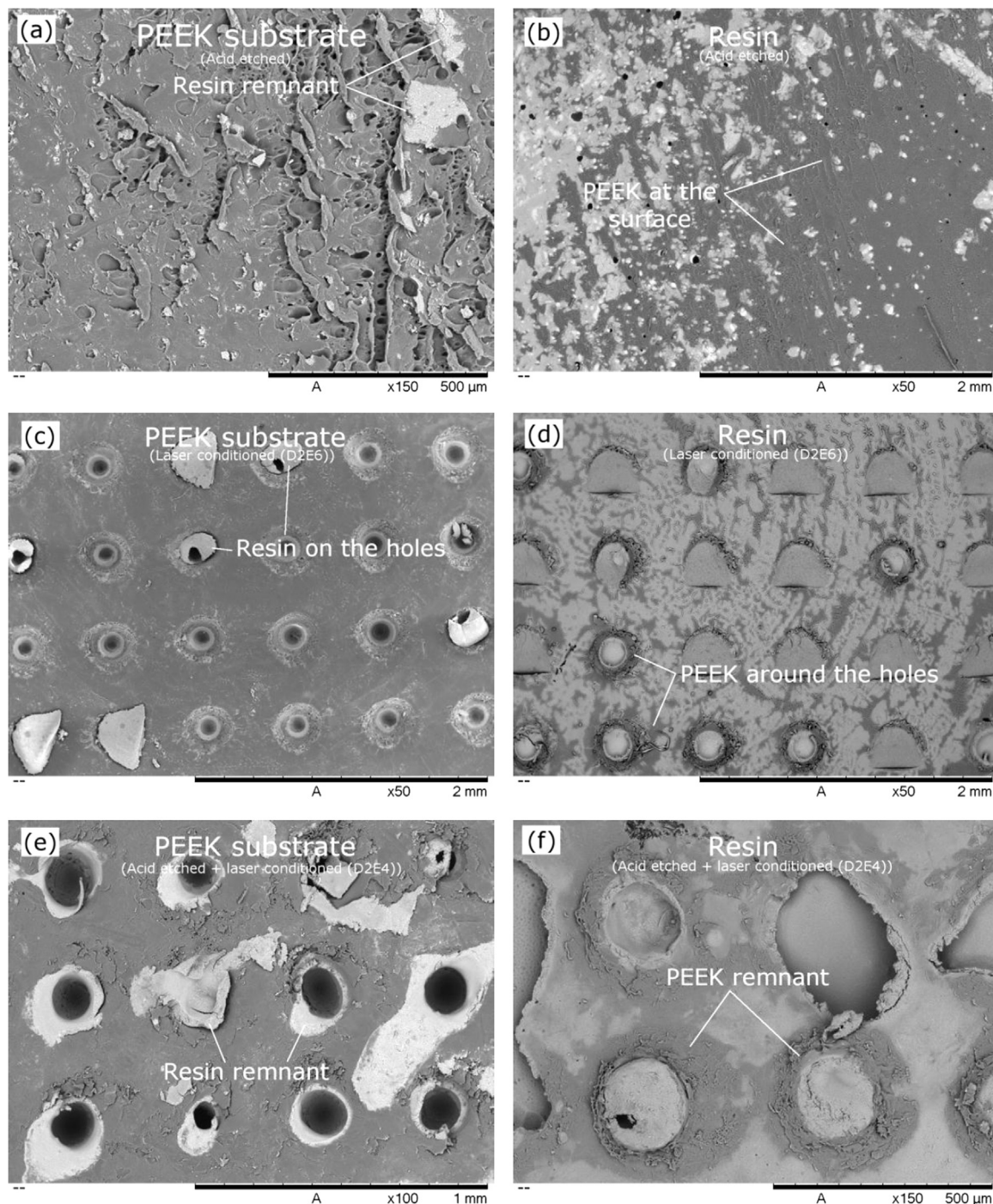


Fig. 6. SEM images for fractured surfaces of unfilled PEEK treated with acid etching (PEEK region (a) and resin cement region (b)), laser ablation (PEEK region (c) and resin cement region (d)) and laser ablation + acid etching (PEEK region (e) and resin cement region (f)).

accomplish the mechanical anchorage effect for the bonding strength (Hallmann et al., 2012). In this work, the resin cement could not properly flow in the holes designed by the laser patterning, thus that did not promote the desired mechanical interlocking effect. This lack of flowing decreased the contact surface area, as noticed in Fig. 4. However, the carbon-reinforced PEEK revealed an exposure of fibers after laser ablation that increased the contact surface area for bonding. Further studies should be performed considering different laser ablation

parameters on PEEK and other resin cements. The variation in viscosity, chemical composition, mechanical properties, polymerization shrinkage, are key factors for adhesive restorative materials.

SEM images of the fracture surfaces corroborated with the shear bond strength results. Specimens of unfilled and glass-reinforced PEEK from group A revealed cohesive failure modes and also showed the highest SBS values. The laser conditioned samples revealed mainly adhesive failure, which explain their low SBS. In some samples of laser

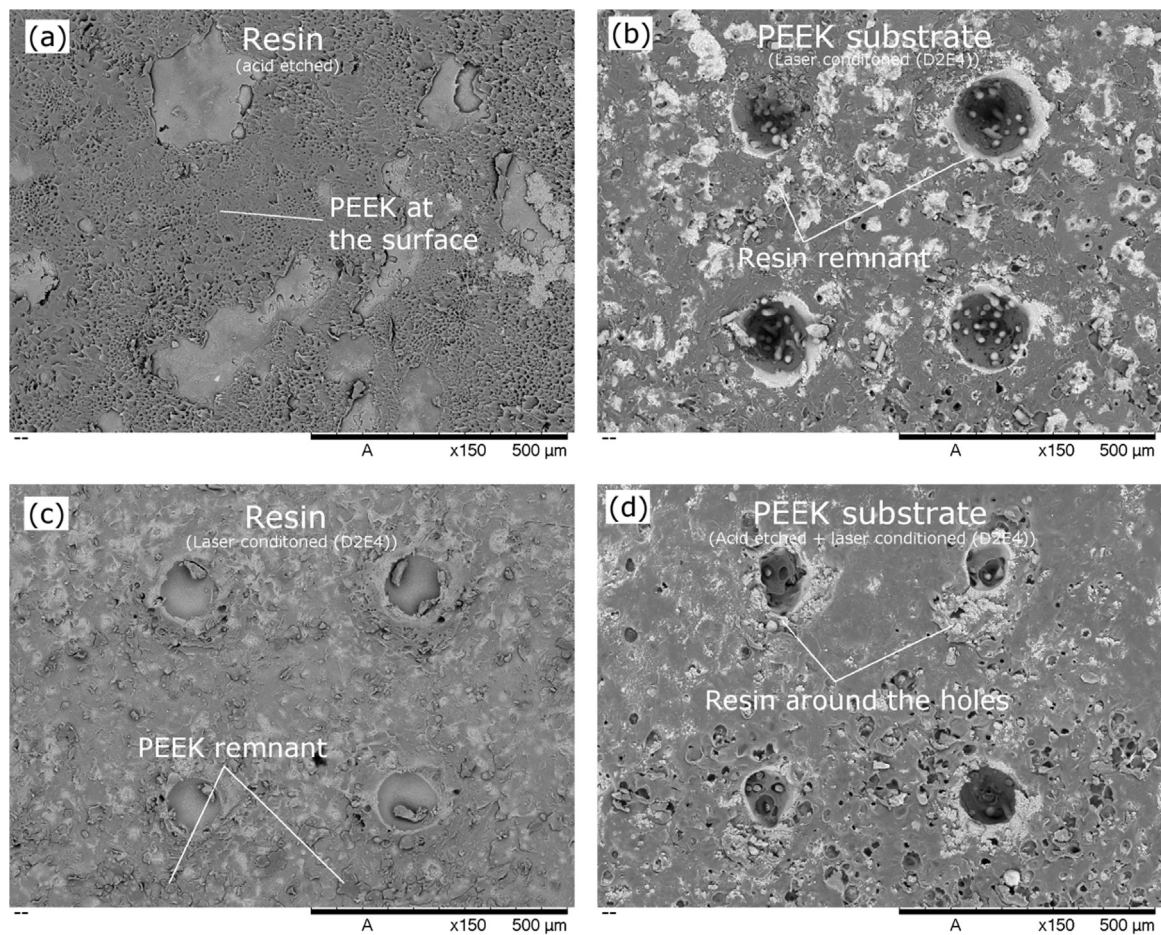


Fig. 7. SEM images for glass-fiber reinforced PEEK fractures, showing the resin portion of the acid etched specimen (a), the PEEK (b) and resin (c) regions of the laser treated sample and the PEEK region of a sample from group D (d).

treated PEEK, remnant resin cement was found on a few PEEK holes. That indicated a partially resin flowing although it was not sufficient to establish the mechanical interlocking to the PEEK structure.

4.1. Adhesion mechanisms of PEEK and Fiber reinforced-PEEK composites to composite resin cements

The strength of the adhesion between PEEK-based substrates and resin-based materials depends on the type of substrate and veneering materials. Several bonding mechanisms are available that may contribute to an effective connection between the resin-based materials to PEEK-based substrates such as macro-mechanical retention, micro-mechanical retention, and interpenetrating polymer networks (IPN) or covalent bonds (Deng et al., 2015).

PEEK is a thermoplastic polymer that can provide IPNs with the resin cement. Despite there is a lack in literature concerning the IPN bonding between PEEK and resin cements, the bonding pathways between these two materials are expected to be similar to those existing between the linear polymer poly(methyl methacrylate) (PMMA) and the resin-based materials (Vallittu and Shinya, 2017; Vallittu, 2009). In this case, the bonding process is based on the dissolution of the base polymer with the monomers contained in the resin composite adhesives (e.g. bisphenol- A-diglycidyl dimethacrylate (bisGMA), triethyleneglycol dimethacrylate (TEGDMA) or ethyleneglycol dimethacrylate (EGDMA)), or with a separate solvent. Thus, those adhesive could

establish a strong bond between both materials after the resin polymerization, without any presence of other toxic chemicals from surface treatment procedures (Fig. 9) (Perea et al., 2014; Vallittu, 1995; Vallittu et al., 1994). The accomplishment of IPN occurs within polymerization of the cross-linking monomers in the presence of swelled and dissolved polymer chains of the PMMA. The polymer surface dissolved by the molecules of the monomer turns into a gel promoting the penetration of the monomers (Lastumäki et al., 2002). The characteristics of the IPN bonding layer is dependent on several factors, namely: the capability of PMMA dissolution by dimethacrylate monomers like bisphenol- A-diglycidyl dimethacrylate (bisGMA) or triethyleneglycol dimethacrylate (TEGDMA), or ethyleneglycol dimethacrylate (EGDMA); the contact wetting time of the liquid dimethacrylate monomers; temperature; and the penetration depth of the cross-linking monomers into the PMMA.

When considering the adhesion of the resin composite cement to the Fiber Reinforced PEEK substrates (PEEK-GF30 and PEEK-CF30), the bonding mechanism can show slight variations considering the polymer matrix and also the exposed fibers. Therefore, the adhesion properties of the fibers themselves must be accounted in adhering the resin composite cement to the PEEK-GF30 or PEEK-CF30 substrates, where the adhesion of the resin composite to the fibers can be improved by silanization (Vallittu, 2009). Thus, the surface modification of PEEK is a current challenge concerning those issues. Further scientific research and clinical trials are still necessary to indicate PEEK and their composites for reliable clinical use in the field of restorative dentistry.

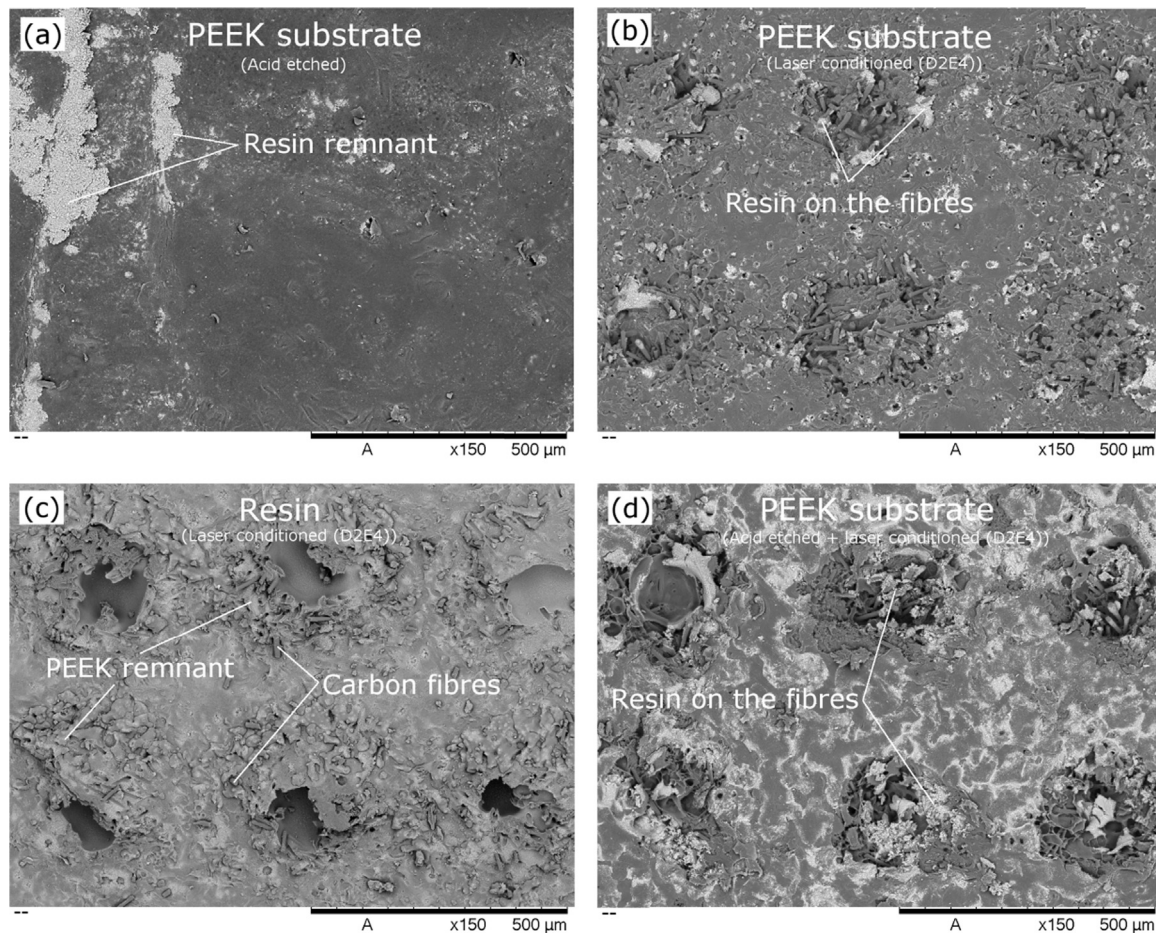


Fig. 8. SEM images for fracture of the carbon-reinforced PEEK, showing the PEEK region of a specimen from group A (a), the PEEK (b) and resin (c) regions of a sample from group B and the PEEK region of a sample from group D (d).

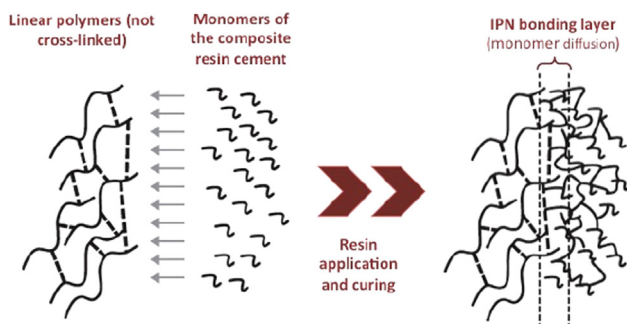


Fig. 9. Schematics of bonding mechanisms between linear polymers (e.g. PMMA, PEEK) and monomers of the resin-based materials by the formation of an Interpenetrating Polymer Network (IPN) bonding layer. Adapted from (Vallittu and Shinya, 2017).

5. Conclusion

The following conclusions can be drawn from the results of this work:

- Patterned holes were shaped by laser ablation to enhance the mechanical interlocking of veneering adhesive materials;
- Different laser ablation parameters should be tested concerning retentive depth of holes and contact surface area for adhesion of resin-based materials. Also, PEEK composites such as carbon- or glass-reinforced PEEK should be modified by a combination of chemical and physical methods due to the presence of fibers;

- Further studies should also be carried out using different resin cements and adhesives to increase the bonding strength between PEEK and dental resin composites.

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