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MARIO EDUARDO ESCOBAR RAMOS

EFFECT OF ACIDIC ETCHING AND UNIVERSAL ADHESIVE APLICATION TIME ON PEEK BOND STRENGTH TO RESIN COMPOSITE

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MARIO EDUARDO ESCOBAR RAMOS

EFFECT OF ACIDIC ETCHING AND UNIVERSAL ADHESIVE APLICATION TIME ON PEEK BOND STRENGTH TO RESIN COMPOSITE

O presente trabalho em nível de mestrado foi avaliado e aprovado por banca examinadora composta pelos seguintes membros:

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Certificamos que esta é a **versão original** do trabalho de conclusão que foi julgado adequado para obtenção do título de mestre em implantodontia.

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Este trabalho é dedicado à minha mãe

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When the power of love overcomes the love of
power, the world will know peace.

Sri Chinmoy Ghose

RESUMO

O presente estudo visa demostrar como o PEEK ao ser atacado com acido sulfúrico ao 98% e um revestimento com adesivo universal autocondicionamte pode melhorar sua adesão com a resina composta. Para este estudo foi feita uma revisão de escopo sobre modificação de superfície e métodos de adesão para estabelecer uma ligação eficaz de PEEK ao composto de resina para seu uso na odontologia. Uma pesquisa em Medline foi realizada para artigos científicos relacionados publicados a partir de 1995 até 2018. Para o estudo in vitro foi avaliado os efeitos do pré-tratamento superficial com uma concentração de ácido sulfúrico e adesivo universal sobre propriedades de superfície e ligação entre Polyetheretherketone (PEEK) e uma resina composta. Sete grupos, (A) ácido sulfúrico a 98% por 60 s, (B) ácido sulfúrico a 98% por 60 s com adesivo por 1min, (C) 3min e (D) 5 min antes da foto polimerização, (E) PEEK sem condicionamento ácido pré-tratamento com 1min, (F) 3min, (G) 5 min antes de fotopolimerizar foram analisados. Após o tratamento de superfície, foram realizados os testes de rugosidade com a análise Topográfica 2D, 3D e MEV, medida do ângulo de contato, FTIR (espectroscopia de infravermelho). Para o teste de resistência ao cisalhamento (SBS), o composto de resina foi montado em cada grupo de espécimes PEEK e fotocurado por 60s. Os dados de cisalhamento foram analisados estatisticamente usando One-way ANOVA e Tukey's post hoc test. (P <, 05). O ataque com ácido sulfúrico a 98% + 5 minutos de contato com o adesivo alcançou a maior valor de cisalhamento (p <0,05). SEM demonstrou superfícies gravadas com poros largos e profundos. O condicionamento com ácido sulfúrico a 98% foi sugerido como a concentração ótima para melhorar a adesão mecânica entre o PEEK e o compósito de resina.

Palavras Chaves: PEEK. Adesivo Dental. Resina Composta.

ABSTRACT

The present study aims to demonstrate the performance of PEEK when attacked with 98% sulfuric acid and a self-etching universal adhesive coating improving its adhesion with resin composite. A scoping review on surface modification and adhesion methods to establish an effective bond of PEEK to resin composite for restorative dentistry was performed. A Medline search was employed for related scientific articles published from 1995 up to 2018. For the in vitro study, seventy PEEK specimens were assigned randomly to 7 groups (n=10), was evaluated the effects of surface pretreatment with a concentration of sulfuric acid etching at 98% and universal adhesive on surface properties and work of adhesion between Polyetheretherketone (PEEK) and a resin composite. Groups were nominated by (A) 98% sulfuric acid for 60 s, (B) 98% sulfuric acid for 60 s with adhesive for 1min, (C) 3min and (D) 5 min before foto-cured, (E) PEEK without etching pretreatment with 1min, (F) 3min, (G) 5 min before fotocured. After surface treatment surface roughness with SEM analysis and Topographical 2D and 3D analysis, contact angle measure, and FTIR (Fourier transform infrared spectroscopy) were analyzed. For the shear bond strength test (SBS), resin composite was mounted on each PEEK specimen groups and fotocured for 60s. One-way ANOVA and Tukey's post hoc tests (P<,05). The 98% sulfuric acid etching + 5 min adhesive contact achieved the highest SBS ($p<0.05$). SEM demonstrated etched surfaces with wide and deep pores. The 98% sulfuric acid etching were suggested to be the optimal concentration to improve mechanical adhesion between PEEK and the resin composite.

Keywords: PEEK. Dental Adhesive. Resin Composite.

FIGURE CHART

TABLE CHART

LISTA DE ABREVIATURAS E SIGLAS

PAEK – Poli-aril-eter-cetona

PEEK – Poli-éter-éter-cetona

FTIR – Fourier-transform infrared spectrscopy

SPEEK – Poli-éter-éter-cetona sulfonado

SEM – Scanning electron microscope

TEGDMA – triethylene glycol dimethacrylate

BisGMA – bisphenylglycidyl dimethacrylate

BisEMA – bisphenol-A dimethacrylate

H_2SO_4 – Sulfuric Acid

CO_2 – Carbon dioxide

MMA – Methylmethacrylate

SEM – Scanning Electron Microscopy

SBS – Shear Bond Strength

GPS – geometrical product specification

HEMA – 2- hydroxyethyl methacrylate

MDP – methacryloyloxydecyl dihydrogen phosphate

SUMMARY

RESUMO EXPANDIDO

O poli (éter éter cetona) (PEEK) é um polímero termoplástico e semicristalino de alto desempenho. Entre os polímeros poli (arilo éter cetonas) (PAEKs), PEEK tem sido amplamente utilizado desde 1987 para fabricar implantes ortopédicos e próteses (KURTZ e DEVINE, 2007). As propriedades mecânicas vantajosas do PEEK, como o baixo módulo elástico (3-4 GPa), que é muito próximo ao registrado para o osso humano (3-8 GPa), e alta resistência à tração de cerca de 90 MPa tornaram-se propriedades-chave para aplicações biomédicas (JUNG e colab., 2016; KURTZ e DEVINE, 2007). Além disso, os compósitos PEEK podem atingir um módulo elástico em torno de 15-18 GPa e resistência à tração de 200 MPa, que são mais apropriados para estruturas protéticas (NAJEEB e colab., 2016). De fato, um fósforo no módulo elástico e a força entre materiais restaurativos, dentes, e estruturas do osso podem realçar o desempenho a longo prazo de estruturas restaurativas e protéticas (KURTZ e DEVINE, 2007). A aderência de compósitos de resina ao PEEK ainda é uma questão relativa ao desempenho a longo prazo de estruturas restauradoras baseadas em PEEK devido a uma superfície hidrofóbica e energia livre de superfície baixa (CAGLAR e colab., 2018; , A.; ÖZKIR, SERHAT EMRE, SAHIN, 2017; KURTZ e DEVINE, 2007; SCHMIDLIN, Patrick R. e colab., 2010; STAWARCZYK, BOGNA e colab., 2015, 2018). Assim, os métodos convencionais de adesão de compósitos de resina a infraestruturas protéticas não têm sido efetivos em relação aos materiais à base de PEEK. Estudos prévios relataram métodos de modificação de superfície envolvendo jateamento, condicionamento de ácido sulfúrico, jateamento e outros, melhorando a molhabilidade do PEEK e sua força de aderência aos cimentos de resina (HENRIQUES e colab., 2018; KERN, Matthias e LEHMANN, 2012a; LIEBERMANN, KEUL e colab., 2014; STAWARCZYK, BOGNA e colab., 2015).

Os valores de resistência de cisalhamento entre PEEK e compósitos de resina superiores a 10 MPa foram relatados como clinicamente aceitáveis (ABU BAKAR e colab., 2003; BEHR e colab., 2003, 2011; HALLMANN e colab., 2012b; NAJEEB e colab., 2016; RATNER, 1995; ROCHA e colab., 2016; SCHMIDLIN, Patrick R. e colab., 2010; STAWARCZYK, BOGNA e BEUER e colab., 2013; STAWARCZYK, BOGNA e KEUL e colab., 2013). Estudos prévios relataram baixos valores de força de aderência entre o PEEK não tratado e compósitos de resina que podem ser aprimorados por uma modificação das superfícies PEEK antes da colagem com compósitos de resina (LIEBERMANN, KEUL e colab., 2014; LOUROPOULOU e colab., 2012; LÜMKEMANN e colab., 2017; MONICH, Patricia R e colab., 2013; ROSENTRITT e

colab., 2015; STAWARCZYK, BOGNA e colab., 2014; STAWARCZYK, BOGNA e KEUL e colab., 2013; ZHOU e colab., 2014a). Além disso, a composição química e a viscosidade de um adesivo podem aumentar a aderência de compósitos de resina contendo monômeros de metacrilatos como TEGDMA, BisEMA e BisGMA (CAGLAR e colab., 2018; , A.; ÖZKIR, SERHAT EMRE, SAHIN, 2017; STAWARCZYK, BOGNA e colab., 2018; STAWARCZYK, BOGNA e KEUL e colab., 2013).

O objetivo deste trabalho foi realizar uma revisão de literatura sobre a modificação de superfície e métodos de colagem para estabelecer uma adesão efetiva de PEEK a compósitos de resina para odontologia restauradora.

Para fornecer um método eficaz para realçar a adesão composta da resina à superfície do PEEK por uma combinação de uma superfície do PEEK pre-tratado e de um adesivo universal, com uma hipótese que o diferente tempo de ação do adesivo auto condicionante pode afetar a adesão do PEEK /resina composta.

OBEJETIVOS

Desta forma, o objetivo deste estudo foi melhorar a aderência do material compósito de resina a uma superfície pré-tratada PEEK, enquanto os objetivos específicos foram obtidos identificando qual aplicação do tempo adesivo será melhor para melhorar a força de aderência. O desenvolvimento da superfície porosa de PEEK um material viscoso foi interessante basicamente para a razão da hidrofilicidade de PEEK adquirida pelo pré-tratamento de superfície.

ESTRUTURA E METODOLOGIA

Este estudo consiste em três capítulos que incluem a presente introdução, com uma abordagem ampla aos temas abordados, um justificativo e os objetivos do projeto.

O capítulo 2 abrange um artigo de uma revisão de literatura, que pretende apresentar as propriedades e características do PEEK, mais focada nas características superficiais; a importância de como o tratamento de superfície pode melhorar a adesão aos compósitos de resina; e, finalmente, um resumo de como as propriedades do adesivo auto condicionante podem melhorar a aderência à superfície PEEK.

O capítulo 3 abraça o segundo artigo, que mostra um estudo experimental para produzir um tratamento de superfície na superfície do PEEK para aumentar a porosidade, e um revestimento com adesivo auto condicionante para melhorar a força de ligação ao composto da resina.

RESULTADOS

ANÁLISES TOPOGRÁFICAS

As superfícies pré-tratadas do PEEK revelaram as modificações de superfície e as irregularidades como poços e pores que não foram notados no PEEK não tratado.

As superfícies do PEEK gravadas com 98% de acido sulfúrico, poros revelaram que foram preenchidas parcialmente com o adesivo auto condicionante. Os poros podem evitar o fluxo dos compósitos de resina nas superfícies PEEK levando a regiões de concentração de tensão na interface. Assim, os poros foram completamente preenchidos quando o tempo de aplicação de adesivo auto condicionante foi aumentado.

O teste de Shapiro Wilk não apresentou distribuição normal e, portanto, os dados de ra foram conduzidos por uma análise estatística não-paramétrica usando o teste de Kruskal-Wallis, indicando significância. A comparação Pair-Wise para o tratamento de superfície (grupos A, B, C, D) usando o teste U de Mann-Whitney revelou diferenças entre grupos ($p < 0001$).

No grupo controle, o PEEK gravado (A) mostrou grande largura e profundidade de arranhões, como mostrado em manchas escuras. As superfícies geradas pela superfície gravada mais adesivo (grupo B, C, D) apresentaram características topográficas semelhantes ao grupo controle.

ANÁLISES DE MOLHABILIDADE

O ângulo de contato formado entre a fase de fluido adesivo e as superfícies de PEEK são estatisticamente significantes ($p < .05$), o que indica uma maior molhabilidade do PEEK após o processo de sulfonação da superfície.

FORÇA DE ADERÊNCIA AO CISALHAMENTO

O teste de Shapiro-Wilk foi utilizado para testar a normalidade da distribuição dos dados. O SBS foi analisado utilizando-se a ANOVA One-Way e os testes post hoc de Tukey (SPSS versão 23,0, Chicago, IL, EUA). O nível de significância estatística foi fixado em um nível de 0, 5.

ANALISIS DE FLAHA

As superfícies dos substratos foram examinadas após testes de resistência ao cisalhamento, as imagens do MEV revelaram dois tipos de falha, (1) adesiva e (2) coesiva entre o PEEK e o compósito de resina.

Os espécimes do grupo A (controle), mostraram uma falha coesiva livre de resina composta nos poros do PEEK. A resina composta remanescente foi detectada nas superfícies PEEK dos grupos A, B, C e D. O remanescente de resina composta foi detectado sobre as superfícies do PEEK, mostrando uma maior falha coesiva, tendo uma adesão totalmente mecânica. No entanto, nenhum compósito de resina foi notado sobre as superfícies PEEK sem condicionamento ácido (grupos E, F, G).

CONCLUSÃO

Dentro das limitações do presente estudo in vitro, o principal desfecho da modificação do PEEK para adesão a compósitos de resina pode ser desenhado da seguinte forma:

-A rugosidade PEEK aumentada após condicionamento em 98% de ácido sulfúrico em função do tempo de condicionamento ácido;

-Os poros e os poços foram detectados após a gravura ácida que igualmente realça a molhabilidade do PEEK ao adesivo Self-gravura e consequentemente ao revestimento adesivo penetrado nos pores. Isso conduziu a um bloqueio mecânico preliminar para realçar a adesão do auge aos materiais resina-baseados;

-O efeito sinérgico da gravura ácida adequada de superfícies PEEK em ácido sulfúrico seguido de revestimento adesivo auto condicionante melhorou a resistência de cisalhamento das superfícies PEEK modificadas aos compósitos de resina. O tempo de condicionamento ácido e revestimento adesivo determinou a resistência de aderência de cisalhamento do PEEK ao compósito de resina que estabeleceu um bloqueio mecânico efetivo;

-Estudos adicionais sobre o pH, composição química e tempo de condicionamento do adesivo self-etch devem ser realizados em combinação com a funcionalização do PEEK por sulfonação e tratamentos de superfície mecânicos.

Palavras Chaves: PEEK. Adesivo Dental. Resina Composta.

INTRODUCTION

Poly (ether ether ketone) (PEEK) is a thermoplastic and semi-crystalline high-performance polymer. Among the poly (aryl ether ketones) (PAEKs) polymers, PEEK has been widely used since 1987 to manufacture orthopedic implants and prostheses(KURTZ e DEVINE, 2007). The advantageous mechanical properties of PEEK such as low elastic modulus (3-4 GPa), which is very close to that recorded for human bone (3-8 GPa), and high tensile strength of around 90 MPa have become key properties for biomedical applications (JUNG e colab., 2016; KURTZ e DEVINE, 2007). Also, PEEK composites can reach an elastic modulus at around 15-18 GPa and tensile strength of 200 MPa, which are more appropriate for prosthetic structures (NAJEEB e colab., 2016). In fact, a match in elastic modulus and strength among restorative materials, teeth, and bone structures can enhance the long-term performance of restorative and prosthetic structures(KURTZ e DEVINE, 2007).

The adhesion of resin composites to PEEK is still an issue concerning long-term performance of PEEK-based restorative structures due to a hydrophobic surface and low surface free energy(CAGLAR e colab., 2018; ÇULHAOĞLU, AHMET KÜRŞAT; ÖZKIR, SERHAT EMRE, SAHIN, 2017; KURTZ e DEVINE, 2007; SCHMIDLIN, Patrick R. e colab., 2010; STAWARCZYK, Bogna e colab., 2015, 2018). Thus, the conventional methods for adhesion of resin composite to prosthetic infrastructures have not been effective regarding PEEK-based materials. Previous studies have reported surface modification methods involving grit-blasting, sulfuric acid etching, gritblasting and others, enhancing PEEK wettability and its bond strength to resin cements(HENRIQUES e colab., 2018; KERN, Matthias e LEHMANN, 2012a; LIEBERMANN, KEUL e colab., 2014; STAWARCZYK, Bogna e colab., 2015).

Shear bond strength values between PEEK and resin composites higher than 10 MPa have been reported as clinically acceptable (ABU BAKAR e colab., 2003; BEHR e colab., 2003, 2011; HALLMANN e colab., 2012b; NAJEEB e colab., 2016; RATNER, 1995; ROCHA e colab., 2016; SCHMIDLIN, Patrick R. e colab., 2010; STAWARCZYK, Bogna e BEUER e colab., 2013; STAWARCZYK, Bogna e KEUL e colab., 2013). Previous studies have reported low bond strength values between untreated PEEK and resin composites that can be enhanced by a modification of PEEK surfaces prior bonding to resin composites (LIEBERMANN, KEUL e colab., 2014; LOUROPOULOU e colab., 2012; LÜMKEMANN e colab., 2017; MONICH, Patricia R e colab., 2013; ROSENTRITT e colab., 2015; STAWARCZYK, Bogna e colab., 2014; STAWARCZYK, Bogna e KEUL e colab., 2013; ZHOU e colab., 2014a). Also, the

chemical composition and viscosity of an adhesive can enhance the adhesion of resin composites containing methacrylates monomers such as TEGDMA, BisEMA and BisGMA (CAGLAR e colab., 2018; ÇULHAOĞLU, AHMET KÜRŞAT; ÖZKIR, SERHAT EMRE, SAHIN, 2017; STAWARCZYK, Bogna e colab., 2018; STAWARCZYK, Bogna e KEUL e colab., 2013).

The aim of this work was to perform a literature review on surface modification and bonding methods to establish an effective adhesion of PEEK to resin composites for restorative dentistry.

PEEK exhibits a low surface energy, which is responsible for weak adhesion to resin cements and composites (HALLMANN e colab., 2012b). Thus, the improvement of PEEK surface properties has become a research topic for biomedical applications. There are several physicochemical methods to modify PEEK surfaces such as plasma, ultraviolet/ozone, gritblasting, etching, and radiation-induced (plasma gas, laser, electron and ion-beam) treatment and coatings (KURTZ e DEVINE, 2007; RATNER, 1995).

The roughness of the substrate is an important factor for adhesion, once it increases the contact surface area leading to enhanced mechanical interlocking of the adhesive (KURTZ e DEVINE, 2007). Several studies reported the use of grit-blasting with 50 or 110 µm alumina particles, to increase the PEEK average roughness of PEEK at around 2.6 µm for mechanical anchorage to resin composite adhesive and cements (ÇULHAOĞLU e colab., 2017; LIEBERMANN, KEUL e colab., 2014; ROCHA e colab., 2016; ROSENTRITT e colab., 2015; STAWARCZYK, Bogna e BEUER e colab., 2013; STAWARCZYK, Bogna e colab., 2015). Several acidic solutions have been studied to increase the Ra roughness of PEEK surface ranging from 0.18 up to 0.74 µm(CHAIJAREENONT e colab., 2018; KERN, Matthias e LEHMANN, 2012a; MONICH, Patricia R e colab., 2013). The conditioning of PEEK surface with Piranha solution, composed of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) results in an increase of functional groups on the surface for bonding (HALLMANN e colab., 2012a; LIEBERMANN, KEUL e colab., 2014; ROSENTRITT e colab., 2015; UHRENBACHER e SCHMIDLIN e KEUL e EICHBERGER e ROOS e GERNET e DRHC e colab., 2014). Previous studies reported that the use of 98% sulfuric acid as a PEEK surface pretreatment to modify PEEK surface has a positive effect , that resultings in a highly porous and permeable surface (CHAIJAREENONT e colab., 2018; FURBINO e colab., 2016; ROSENTRITT e colab., 2015; UHRENBACHER e SCHMIDLIN e KEUL e EICHBERGER e ROOS e GERNET e DRHC e colab., 2014; ZHOU e colab., 2014b). A previous study compared the bond strength between CO_2 laser structured and acid-etch (sulfuric acid) PEEK to and resin cement. with laser

patterning (CO_2 laser) treatment and acid-etch (sulfuric acid) treatment. They used PEEK, glass fiber reinforced with glass fibers and carbon fiber reinforced-PEEK reinforced with carbon fibers were used as substrates and adhesion was assessed by shear bond strength (SBS) tests. Acid etched surfaces resulted in the highest as a base material to treat and SBS test was used to evaluate the efficacy of the surface treatments. As results the acid-etch treatment on unfilled PEEK had de highest SBS values while laser structuring failed to improve the SBS values due to the presence of entrapped air at the cavities, which hindered the resin to flow inside (HENRIQUES e colab., 2018).

Different surface treatment and adhesives for PEEK have been mainly studied using shear and tensile bond strength tests (CHAIJAREENONT e colab., 2018; ÇULHAOĞLU, AHMET KÜRŞAT; ÖZKIR, SERHAT EMRE, SAHIN, 2017; ÇULHAOĞLU e colab., 2017; FURBINO e colab., 2016; HENRIQUES e colab., 2018; MONICH, Patricia R e colab., 2013; PATRICK e colab., 2014; SCHMIDLIN, Patrick R. e colab., 2010; SCHMIDLIN, Patrick R e colab., 2010; TSUKA e colab., 2017; UHRENBACHER e SCHMIDLIN e KEUL e EICHBERGER e ROOS e GERNET e STAWARCZYK, 2014). A major concern is noted in literature (CAGLAR e colab., 2018; ÇULHAOĞLU e colab., 2017; FURBINO e colab., 2016; LIEBERMANN, KEUL e colab., 2014; STAWARCZYK, Bogna e colab., 2018; STAWARCZYK, Bogna e KEUL e colab., 2013; ZHOU e colab., 2014b) concerning the adhesion of untreated PEEK surfaces to resin composites as seen in Table 1. On the untreated PEEK to resin composite assemblies, the shear bond strength values ranged from 0 up to 12 MPa(CAGLAR e colab., 2018; LIEBERMANN, KEUL e colab., 2014). On the other hand, the highest shear bond strength values at 27 MPa were found for PEEK treated by sulfuric acid treatment (CHAIJAREENONT e colab., 2018; ÇULHAOĞLU e colab., 2017; FURBINO e colab., 2016; STAWARCZYK, Bogna e KEUL e colab., 2013; ZHOU e colab., 2014b) while the shear bond strength for PEEK treated by air abrasion achieved 19 MPa (CAGLAR e colab., 2018; LIEBERMANN, KEUL e colab., 2014; STAWARCZYK, Bogna e colab., 2015, 2018; TSUKA e colab., 2017; ZHOU e colab., 2014a). However, shear bond strength results were influenced by the time and concentration of acid etching. Also, the particle size and pressure influence the air abrasion treatment and resultant PEEK roughness for mechanical interlocking to resin composites (CAGLAR e colab., 2018; CHAIJAREENONT e colab., 2018; ÇULHAOĞLU e colab., 2017; FURBINO e colab., 2016; MONICH, Patricia R e colab., 2013). Other results of surface treatment mechanism was the use of CO_2 and ER:YAG laser that showed no resin bonding to PEEK, leaving low SBS values less that 10 MPa and reaveling an exposure of fibers after laser ablation that will increase the contact surface area for bonding,

but without any experimental analisis been performed(BEHR e colab., 2003, 2011; CAGLAR e colab., 2018; HENRIQUES e colab., 2018); another type of laser the Yb:PL laser that may be considered a viable surface treatment modality for the PEEK material in regard of the obtained SBS values higher than 10 MPa(BEHR e colab., 2003, 2011; ÇULHAOĞLU e colab., 2017).

The use of adhesives to enhance PEEK bonding has also been explored. Adhesives containing multifunctional methylmethacrylate (MMA) monomers has been showing enhanced adhesion on any treated surface (KERN, Matthias e LEHMANN, 2012a; STAWARCZYK, Bogna e KEUL e colab., 2013). The highest PEEK to resin composites adhesion values were reported for PEEK conditioned with adhesive systems composed of methylmetacrylate, dimethacrylates, and pentaerythritol triacrylate displayed (LIEBERMANN, KEUL e colab., 2014; LÜMKEMANN e colab., 2017; STAWARCZYK, Bogna e colab., 2014; TEKIN e colab., 2018; TSUKA e colab., 2017).

To provide an effective method to enhance resin composite adhesion to PEEK surface by a combination of a PEEK surface pretreated and a Universal Adhesive, a hypothesis that the different time appliance of the self-etch adhesive may affect the bond strength of the PEEK/resin composite adhesion was made.

OBJECTIVES

In this way the aim of this study was to enhance the adhesion of the resin composite material to a pretreated PEEK surface, while specific aims were obtained identifying which adhesive time application will be better to enhance the bond strength.

The development of porous surface of PEEK under a viscous material was interesting basically for the reason of hydrophilicity of PEEK gained by the surface pretreatment.

STRUCTURE AND ORGANIZATION

This study consists of three chapters that include the present introduction, with a broad approach to the themes addressed, a justificative and the objectives of the project.

Chapter 2 encompasses an article of a literature review, which intends to present the properties and characteristics of PEEK, most focused on surface characteristics; the importance of how surface treatment can improve adhesion to resin composites; and finally, a summary of how properties of self-etch adhesive can improve the adhesion to PEEK surface.

Chapter 3 embraces the second article, which shows an experimental study to produce a surface treatment on PEEK surface to increase porosity, and a coating with self-etch adhesive to improve the bond strength to resin composite

CHAPTER 2

ADHESION OF RESIN COMPOSITES TO PEEK USED IN DENTISTRY: A REVIEW ON SURFACE MODIFICATION AND BOND STRENGTH

INTRODUCTION

Poly (ether ether ketone) (PEEK) is a thermoplastic and semi-crystalline high-performance polymer. Among the poly (aryl ether ketones) (PAEKs) polymers, PEEK has been widely used since 1987 to manufacture orthopedic implants and prostheses(KURTZ e DEVINE, 2007). The advantageous mechanical properties of PEEK such as low elastic modulus (3-4 GPa), which is very close to that recorded for human bone (3-8 GPa), and high tensile strength of around 90 MPa have become key properties for biomedical applications (JUNG e colab., 2016; KURTZ e DEVINE, 2007). Also, PEEK composites can reach an elastic modulus at around 15-18 GPa and tensile strength of 200 MPa, which are more appropriate for prosthetic structures (NAJEEB e colab., 2016). In fact, a match in elastic modulus and strength among restorative materials, teeth, and bone structures can enhance the long-term performance of restorative and prosthetic structures(KURTZ e DEVINE, 2007).

The adhesion of resin composites to PEEK is still an issue concerning long-term performance of PEEK-based restorative structures due to a hydrophobic surface and low surface free energy(CAGLAR e colab., 2018; ÇULHAOĞLU, AHMET KÜRŞAT; ÖZKIR, SERHAT EMRE, SAHIN, 2017; KURTZ e DEVINE, 2007; SCHMIDLIN, Patrick R. e colab., 2010; STAWARCZYK, Bogna e colab., 2015, 2018). Thus, the conventional methods for adhesion of resin composite to prosthetic infrastructures have not been effective regarding PEEK-based materials. Previous studies have reported surface modification methods involving grit-blasting, sulfuric acid etching, gritblasting and others, enhancing PEEK wettability and its bond strength

to resin cements(HENRIQUES e colab., 2018; KERN, M e LEHMANN, 2012; LIEBERMANN, KEUL e colab., 2014; STAWARCZYK, Bogna e colab., 2015).

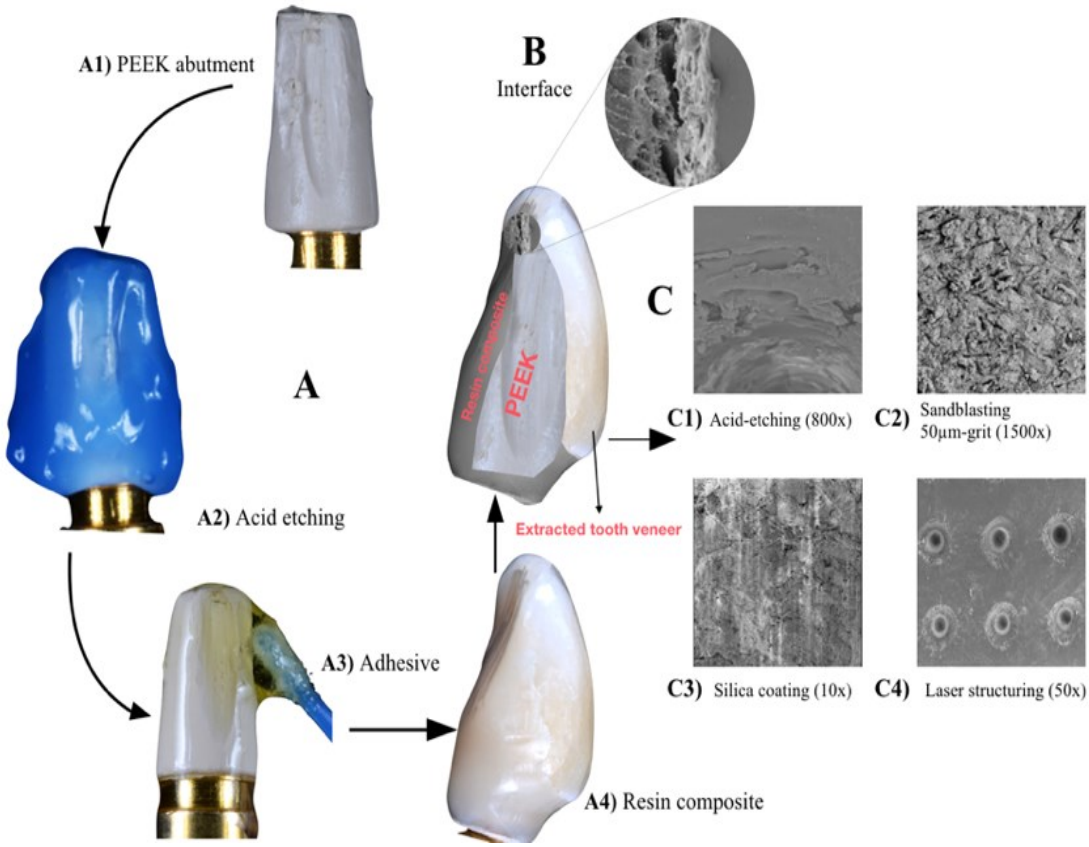
Shear bond strength values between PEEK and resin composites higher than 10 MPa have been reported as clinically acceptable (ABU BAKAR e colab., 2003; BEHR e colab., 2003, 2011; HALLMANN e colab., 2012b; NAJEEB e colab., 2016; RATNER, 1995; ROCHA e colab., 2016; SCHMIDLIN, Patrick R. e colab., 2010; STAWARCZYK, Bogna e KEUL e colab., 2013). Previous studies have reported low bond strength values between untreated PEEK and resin composites that can be enhanced by a modification of PEEK surfaces prior bonding to resin composites (LIEBERMANN, KEUL e colab., 2014; LOUROPOULOU e colab., 2012; LÜMKEMANN e colab., 2017; MONICH, Patricia R e colab., 2013; ROSENTRITT e colab., 2015; STAWARCZYK, Bogna e colab., 2014; STAWARCZYK, Bogna e KEUL e colab., 2013; ZHOU e colab., 2014a). Also, the chemical composition and viscosity of an adhesive can enhance the adhesion of resin composites containing methacrylates monomers such as TegDMA, BisEMA and BisGMA (CAGLAR e colab., 2018; ÇULHAOĞLU, AHMET KÜRŞAT; ÖZKIR, SERHAT EMRE, SAHIN, 2017; STAWARCZYK, Bogna e colab., 2018; STAWARCZYK, Bogna e KEUL e colab., 2013).

The aim of this work was to perform a literature review on surface modification and bonding methods to establish an effective adhesion of PEEK to resin composites for restorative dentistry. A Medline bibliographical search of articles from 1995 to 2019 was carried out using the following search items: “PEEK” AND “adhesion” OR “resin composite”, OR ‘’bond strength”, OR “surface treatment”, OR “adhesive”. The selection criteria used were: articles written in English; meta-analysis and prospective cohort studies. For this study, only papers focusing on PEEK surface modification to enhance the adhesion to resin composites were considered.

PEEK SURFACE TREATMENT

PEEK exhibits a low surface energy, which is responsible for weak adhesion to resin cements and composites (HALLMANN e colab., 2012b). Thus, the improvement of PEEK surface properties has become a research topic for biomedical applications. There are several physicochemical methods to modify PEEK surfaces such as plasma, ultraviolet/ozone, gritblasting, etching, and radiation-induced (plasma gas, laser, electron and ion-beam) treatment and coatings (KURTZ e DEVINE, 2007; RATNER, 1995). Physicochemical modification methods of PEEK surfaces are illustrated in Figure 1.

Figure 1. Schematic illustration of a peek-resin composite implant provisional restoration. a) experimental sequence: peek provisional abutment; peek surface pretreatment by acid etching; adhesive application to peek surface; resin composite veneering. b) detailed view of peek/adhesive/resin composite interface. c) peek surface morphology after different pretreatments: acid-etching; sandblasting 50µm; silica-coating; laser structuring.



The roughness of the substrate is an important factor for adhesion, once it increases the contact surface area leading to enhanced mechanical interlocking of the adhesive (KURTZ e DEVINE, 2007). Several studies reported the use of grit-blasting with 50 or 110 µm alumina particles, to increase the PEEK average roughness of PEEK at around 2.6 µm for mechanical anchorage to resin composite adhesive and cements (ÇULHAOĞLU e colab., 2017; LIEBERMANN, KEUL e colab., 2014; ROCHA e colab., 2016; ROSENTRITT e colab., 2015; STAWARCZYK, Bogna e BEUER e colab., 2013; STAWARCZYK, Bogna e colab., 2015). Several acidic solutions have been studied to increase the surface roughness (Ra) of PEEK surface ranging from 0.18 up to 0.74 µm(CHAIJAREENONT e colab., 2018; KERN, M e LEHMANN, 2012; MONICH, Patricia R e colab., 2013). The conditioning of PEEK surface with Piranha solution, composed of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) results in an increase of

functional groups on the surface for bonding (HALLMANN e colab., 2012a; LIEBERMANN, KEUL e colab., 2014; ROSENTRITT e colab., 2015; UHRENBACHER e SCHMIDLIN e KEUL e EICHBERGER e ROOS e GERNET e STAWARCZYK, 2014). Previous studies reported that the use of 98% sulfuric acid as a PEEK surface pretreatment to modify PEEK surface has a positive effect , that resulting in a highly porous and permeable surface (CHAIJAREENONT e colab., 2018; FURBINO e colab., 2016; ROSENTRITT e colab., 2015; UHRENBACHER e SCHMIDLIN e KEUL e EICHBERGER e ROOS e GERNET e STAWARCZYK, 2014; ZHOU e colab., 2014a). A previous study compared the bond strength between CO_2 laser structured and acid-etch (sulfuric acid) PEEK to and resin cement. with laser patterning (CO_2 laser) treatment and acid-etch (sulfuric acid) treatment. They used PEEK, glass fiber reinforced with glass fibers and carbon fiber reinforced-PEEK reinforced with carbon fibers were used as substrates and adhesion was assessed by shear bond strength (SBS) tests. Acid etched surfaces resulted in the highest as a base material to treat and SBS test was used to evaluate the efficacy of the surface treatments. As results the acid-etch treatment on unfilled PEEK had de highest SBS values while laser structuring failed to improve the SBS values due to the presence of entrapped air at the cavities, which hindered the resin to flow inside (HENRIQUES e colab., 2018).

PEEK ADHESION TO RESIN COMPOSITES

Different surface treatment and adhesives for PEEK have been mainly studied using shear and tensile bond strength tests (CHAIJAREENONT e colab., 2018; ÇULHAOĞLU, AHMET KÜRŞAT; ÖZKIR, SERHAT EMRE, SAHIN, 2017; ÇULHAOĞLU e colab., 2017; FURBINO e colab., 2016; HENRIQUES e colab., 2018; MONICH, Patricia R e colab., 2013; PATRICK e colab., 2014; SCHMIDLIN, Patrick R. e colab., 2010; TSUKA e colab., 2017; UHRENBACHER e SCHMIDLIN e KEUL e EICHBERGER e ROOS e GERNET e STAWARCZYK, 2014). A major concern is noted in literature (CAGLAR e colab., 2018; ÇULHAOĞLU e colab., 2017; FURBINO e colab., 2016; LIEBERMANN, KEUL e colab., 2014; STAWARCZYK, B e colab., 2013; STAWARCZYK, Bogna e colab., 2018; ZHOU e colab., 2014a) concerning the adhesion of untreated PEEK surfaces to resin composites as the minimum or tolerable SBS value should be 5 MPa according to the ISO 10477 and the results reported in Table 1 for this condition are far below this reference. On the untreated PEEK to resin composite assemblies, the shear bond strength values ranged from 0 up to 12 MPa (CAGLAR e colab., 2018; LIEBERMANN, KEUL e colab., 2014). On the other hand, the

highest shear bond strength values at 27 MPa were found for PEEK treated by sulfuric acid treatment (CHAIJAREENONT e colab., 2018; ÇULHAOĞLU e colab., 2017; FURBINO e colab., 2016; STAWARCZYK, B e colab., 2013; ZHOU e colab., 2014a) while the shear bond strength for PEEK treated by air abrasion achieved 19 MPa (CAGLAR e colab., 2018; LIEBERMANN, KEUL e colab., 2014; STAWARCZYK, Bogna e colab., 2015, 2018; TSUKA e colab., 2017; ZHOU e colab., 2014a). However, shear bond strength results were influenced by the time and concentration of acid etching. Also, the particle size and pressure influence the air abrasion treatment and resultant PEEK roughness for mechanical interlocking to resin composites (CAGLAR e colab., 2018; CHAIJAREENONT e colab., 2018; ÇULHAOĞLU e colab., 2017; FURBINO e colab., 2016; MONICH, Patricia R e colab., 2013). Surface treatments of PEEK and PEEK composites using CO_2 and Er:YAG lasers have also been studied. The structured surfaces and the fibres exposure (seen in fibre-reinfoced PEEK) did not result in the expected adhesion improvement, mainly due to the presence of entrapped air at the dimples, which hinder the resin flow and the mechanical retention of the resin. The reported SBS results were lower than 10 MPa (BEHR e colab., 2003, 2011; CAGLAR e colab., 2018; HENRIQUES e colab., 2018). Alternatively, surface irradiation with Yb:PL laser resulted in SBS values higher than 10 MPa (BEHR e colab., 2003, 2011; ÇULHAOĞLU e colab., 2017).
The use of adhesives to enhance bonding to PEEK has also been explored. Some adhesives contain methacryloxydecyl dihydrogen phosphate (MDP), which is known to enhance the adhesion between resin composites and inorganic materials such as alumina, zirconia and metallic alloys by improving the wettabilty of these materials surfaces (reduction of the contact angle) (KERN, Matthias e LEHMANN, 2012b). However, the same effect was not observed for PEEK and it can be explained by the fact that one functional group of the bifunctional MDP monomer is occupied by a phosphate group, which cannot further chemicaly react with the PEEK substrate (LIEBERMANN, KEUL e colab., 2014). On the other hand, adhesives containing multifunctional methylmethacrylate (MMA) monomers has been shown enhanced adhesion on any treated surface by a mechanism in which the adhesive slips in the voids made by the surface treatment (KERN, Matthias e LEHMANN, 2012a; STAWARCZYK, Bogna e KEUL e colab., 2013). The highest PEEK to resin composites adhesion values were reported for PEEK conditioned with adhesive systems composed of methylmetacrylate, dimethacrylates, and pentaerythritol triacrylate displayed (LIEBERMANN, KEUL e colab., 2014; LÜMKEMANN e colab., 2017; STAWARCZYK, Bogna e colab., 2014; TEKIN e colab., 2018; TSUKA e colab., 2017). In addition, several studies on PEEK-resin cement adhesion have followed the aging protocol reported in ISO 10477, which consists in 5000 thermal cycles

between 5 to 55 C° for 20s of dwell time that will correspond to approximately 4 to 5 years of clinical service(GALE e DARVELL, 1999; STAWARCZYK, B e colab., 2014; UHRENBACHER e SCHMIDLIN e KEUL e EICHBERGER e ROOS e GERNET e STAWARCZYK, 2014; YOUNIS e colab., [S.d.]).

Table 1. Mean. Standard deviation of TBS and SBS (Mpa) of resin composites on treated PEEK specimens.

Author/Year	Assemblies	Surface Treatment	Bond strength	
			TEST	Mean +/- Standard Deviation (MPa)
Stawarczyk, et al 2013	PEEK/ HEMA adhesive 3M ESPE Germany/ veneering resin composites (Sinfony, 3M, USA)	No treatment	shear bond strength	0.52 ± 0.31
		Acid etched		18.56 ± 2.74
		Air abraded Al_2O_3 50µm		1.69 ±1.49
		Air abraded Al_2O_3 110µm		8.88 ± 2.31
		Silica coated		11.52 ± 3.56
	PEEK/ HEMA adhesive 3M ESPE Germany/ veneering resin composites (Gradia, GC, USA)	No treatment		0.33 ± 0.30
		Acid etched		14.30 ± 1.80
		Air abraded Al_2O_3 50µm		0.42 ± 0.33
		Air abraded Al_2O_3 110µm		9.33 ± 2.41
		Silica coated		7.67 ± 2.02
Zhou, et al 2014	PEEK/NanoSiO2 (7wt%) -SE BOND/Clearfil AP-X- Veneering Resin composites	No treatment	shear bond strength	5.2 ± 0.6
		Sulfiric Acid 60s		8.7 ± 0.2
		Hydrofluoric acid 60s		2.8 ± 0.2
		Argon plasma13.56MHz		6.8 ± 0.7
		Air abrasion Al_2O_3 50µm		5.3 ± 0.6
		mean cement		5.8 ± 2.0
	PEEK/NanoSiO2 (7wt%) -RelyX Unicem - Veneering Resins	No treatment		0.0 ± 0.0
		Sulfiric Acid 60s		7.4 ± 0.6
		Hydrofluoric acid 60s		0.0 ± 0.0
		Argo n plasma13.56MHz		4.0 ± 0.2
		Air abrasion Al_2O_3 50µm		1.4 ± 0.2
		mean cement		2.6 ± 2.9
	PEEK/monobond Ivoclar Vivadent; Lichtenstein/ Heliobond/ resin composite	Air abrasion		18.4 ± 4.5
		Piranha solution H_2SO_4 98% H_2O_2		3.7 ± 6.5
		Air abrasion+ Piranha solution H_2SO_4 98% H2O2		17.1 ± 4.5
		No treatment		6.5 ±10.0

Keul, et al 2014	PEEK/Signum Composite A3/Visiolink Bredent; Germany MMA.	Air abrasion	tensile bond strength	16.5 ± 8.0
		Piranha solution H_2SO_4 98% H_2O_2		23.4 ± 9.9
		Air abrasion+ Piranha solution H_2SO_4 98% H_2O_2		19.9 ± 8.0
		No treatment		14.1 ± 10.7
	PEEK/Signum Composite A3 /Clearfil Ceramic PrimerKuraray Noritake Dental; Japan	Air abrasion		3.6 ± 3.9
		Piranha solution H_2SO_4 98% H_2O_2		0 ± 0
		Air abrasion+ Piranha solution H_2SO_4 98% H_2O_2		1.8 ± 2.9
		No treatment		0 ± 0
	PEEK/ Signum Composite A3 Heraeus Kulzer; Germany/ Sgnum PEEK bond I + II Heraeus Kulzer; Germany	Air abrasion		14.7 ± 4.6
		Piranha solution H_2SO_4 98% H_2O_2		5.8 ± 6.3
		Air abrasion+ Piranha solution H_2SO_4 98% H_2O_2		11.1 ± 7.9
		No treatment		8.1 ± 7.1
	PEEK/ Signum Composite A3 Heraeus Kulzer; Germany / no treatment	Air abrasion		0 ± 0
		Piranha solution H2SO4 98% H_2O_2		0 ± 0
		Air abrasion+ Piranha solution H_2SO_4 98% H_2O_2		0 ± 0
		No treatment		0 ± 0
	PEEK/ Signum Ceramis Dentin A3 Heraeus Kulzer; Germany/ monobond/Heliobond	Air abrasion		20.7 ± 7.6
		Piranha solution H_2SO_4 98% H_2O_2		0 ± 0
		Air abrasion+ Piranha solution H_2SO_4 98% H_2O_2		22.6 ± 8.3
		No treatment		0 ± 0
	PEEK/ Signum Ceramis Dentin A3/ Visiolink	Air abrasion		12.8 ± 12.1
		Piranha solution H_2SO_4 98% H_2O_2		15.2 ± 10.6
		Air abrasion+ Piranha solution H_2SO_4 98% H_2O_2		19.7 ± 10.6
		No treatment		13.9 ± 11.5
	PEEK/ Signum Ceramis Dentin A3/ Clearfil Ceramic Primer	Air abrasion		1.3 ± 2.3
		Piranha solution H_2SO_4 98% H_2O_2		0 ± 0

		Air abrasion+ Piranha solution H_2SO_4 98% H_2O_2		1.4 ± 3.1
		No treatment		0 ± 0
	PEEK/ Signum Ceramis Dentin A3/ Sgnum PEEK bond I + II	Air abrasion		11.2 ± 10.9
		Piranha solution H_2SO_4 98% H_2O_2		11.9 ± 7.3
		Air abrasion+ Piranha solution H_2SO_4 98% H_2O_2		18.2 ± 13.8
		No treatment		0 ± 0
	PEEK/ Signum Ceramis Dentin A3/ no treatment	Air abrasion		0 ± 0
		Piranha solution H_2SO_4 98% H_2O_2		0 ± 0
		Air abrasion+ Piranha solution H_2SO_4 98% H_2O_2		0 ± 0
		No treatment		0 ± 0
Rocha, et al 2016	PEEK/ Adper™ Single Bond 2, 3M™ ESPE; Brazil/ RelyX™ ARC, 3M™	Sulfiric Acid 5s	shear bond strength	2.28 ± 1.75
		Sulfuric Acid 30s		1.80 ± 0.85
		Sulfuric Acid 60s		1.67 ± 0.94
		Alumina Oxide		2.37 ± 0.86
		Rocatec		2.12 ± 1.12
culhaoglu et al. 2017	PEEK/ visio.link; Bredent; Germany/ pretreated surface/ resin composite combo.lign; Bredent; Germany	Silicoating (Co Jet system)	shear bond strength	8.07 ± 2.54
		Acetone (99%/60s)		5.98 ± 1.54
		acid etching (sulfuric acid 98%/60s)		15.82 ± 4.23
		untreated		5.09 ± 2.14
		airborne particle abrasion (110µm Al_2O_3)		10.81 ± 3.06
		laser irradiation (Yb:PL laser, 5W)		11.46 ± 1.97
	PEEK (VESTAKEEP, tooth colored), Dailvcel-EVONIK (Panavia V5)	No treatment		0.8± 0.4
		no treatment		5.2±1.3
		no treatment		3.7±1.4
		no treatment		8.2 ±1.3
		sandblasting		0.6 ± 0.5
	PEEK (VESTAKEEP, tooth colored), Dailvcel-EVONIK(RelyX Ultimate Resin Cement)	sandblasting		6.8 ± 1.2
	PEEK (VESTAKEEP, tooth colored), Dailvcel-EVONIK (G-CEM Link Force)	sandblasting		9.2 ± 2.0

	PEEK (VESTAKEEP, tooth colored), Dailvcel-EVONIK(Super-Bond C&B)	sandblasting		11.2 ± 2.6
Stawarczyk et al 2018	PEEK/Visio.link; Bredent; Germany/ composite; Schütz dental; Germany	Air abrasion Al_2O_3 50 µm 0.5bar	tensile bond strength	28.58 ± 6.27
		Air abrasion Al_2O_3 50 µm 3.5bar		29.52 ± 52.9
		Air abrasion Al_2O_3 110 µm 0.5bar		29.82 ± 8.64
		Air abrasion Al_2O_3 110 µm 3.5bar		28.52 ± 5.59
		Rocatec		29.61 ± 7.72
	PEEK/ scotchbond universal; 3M; Germany/ composite; Schütz dental; Germany	Air abrasion Al_2O_3 50 µm 0.5bar		10.58 ± 9.09
		Air abrasion Al_2O_3 50 µm 3.5bar		29.52 ± 52.9
		Air abrasion Al_2O_3 110 µm 0.5bar		5.83 ± 79.49
		Air abrasion Al_2O_3 110 µm 3.5bar		25.76 ± 7.92
		Rocatec		20.44 ± 8.28
	PEEK/ monobond plus Ivoclar Vivadent; Liechtenstein/ composite; Schütz dental; Germany	Air abrasion Al_2O_3 50 µm 0.5bar		1.57 ± 4.28
		Air abrasion Al_2O_3 50 µm 3.5bar		5.90 ± 10.50
		Air abrasion Al_2O_3 110 µm 0.5bar		2.28 ± 5.68
		Air abrasion Al_2O_3 110 µm 3.5bar		12.68 ±12.01
		Rocatec		5.96 ± 8.51
	PEEK/ dialog bonding fluid Schütz dental; Germany/ composite;Schütz dental; Germany	Air abrasion Al_2O_3 50 µm 0.5bar		1.80 ± 4.46
		Air abrasion Al_2O_3 50 µm 3.5bar		27.86 ± 6.12
		Air abrasion Al_2O_3 110 µm 0.5bar		12.20 ± 8.01
		Air abrasion Al_2O_3 110 µm 3.5bar		28.52 ± 5.59
		Rocatec		17.83 ± 12.69
Chaijareenon t et al 2018	PEEK/ Heliobond; Ivoclar Vivadent; Liechtenstein/ pretreated surface/ resin composite; Filtek™ Z350XT Flowable restorative; 3M ESPE USA	Control	shear bond strength	1.75 ± 0.66
		70% Sulfuric acid		1.37 ± 1.37
		80% Sulfuric acid		17.47 ± 17.47
		85% Sulfuric acid		21.53 ± 21.53
		90% Sulfuric acid		26.68 ± 26.88
		98% Sulfuric acid		27.36 ± 27.36
		no surface pretreatment		5.58 ± 0.38

Caglar et al 2018	PEEK Bredent GmbH & Co KG/ no adhesive/ resin cement	sandblastaed 50 µm Al2O3 particles	shear bond strength	11.65 ± 2.09
		silica coated CoJet System		9.59 ± 1.58
		Er: YAG laser 1.5W		5.71 ± 1.24
		No surface pretreatment		12.54 ± 2.19
		sandblastaed 50 µm Al_2O_3 particles		19.86 ± 2.52
		silica coated CoJet System		18.76 ± 1.97
		Er: YAG laser 1.5W		9.69 ± 1.69
		No surface treatment		12.31 ± 1.74
		sandblastaed 50 µm Al_2O_3 particles		11.86 ± 0.93
		silica coated CoJet System		10.55 ± 2.23
		Er: YAG laser 1.5W		6.30 ± 0.77
Henriques et al 2018	PEEK (TECAPEEK, Ensinger)	H_2SO_4	shear bond strength	12.45 ±8.87
		D2E4		6.29 ±4.35
		D2E6		1.69 ±1.74
		H_2SO_4 D2E4		1.24 ±1,27
		H_2SO_4		9.42 ± 3.42
	PEEK reinforced with glass fibers (30%vol) (TECAPEEK GF30, Ensinger)	D2E4		5.36 ± 1.66
		D2E6		6.08 ± 2.00
		H_2SO_4 D2E4		2.56 ± 2.60
		H_2SO_4		2.25 ± 2.67
		D2E4		5.78 ± 4.84
	PEEK reinforced with carbon fibers (30%vol) (TECAPEEK CF30, Ensinger)	D2E6		7.41 ± 4.03
		H_2SO_4 D2E4		1.47 1.27

CONCLUDING REMARKS AND PERSPECTIVES

Surface treatment methods of PEEK and the adhesion of PEEK to resin composites has been discussed in this review. Among the surface treatment reported in literature, 98% sulfuric acid etching and air abrasion treatment have shown to increase the adhesion of PEEK to resin composites. Nevertheless, the adhesion of PEEK to resin composites is still weak and brings a current issue in clinical practice. Several factors related to the etching acid and air abrasion proceduce should be evaluated considering time and chemical composition of materials. Methacrylate-based adhesives has been also assessed to enhance the adhesion of PEEK to resin

composites or esthetic veneer ceramics. Further studies on novel surface treatment and adhesive materials are relevant to address the lack of chemical interaction of PEEK to other restorative veneer materials and a proposal of using a low viscosity veneering material that may result in a better penetration into the micropores created after pretreatment.

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CHAPTER 3

EFFECT OF ACIDIC ETCHING AND UNIVERSAL ADHESIVE APLICATION TIME ON PEEK BOND STRENGTH TO RESIN COMPOSITE

INTRODUCTION

Poly (ether ether ketone) (PEEK) is a thermoplastic and semi-crystalline high-performance polymer. Is a high temperature polymer of the family of the poly (aryl ether ketones) (PAEKs). The advantageous mechanical properties of PEEK, such as low elastic modulus (3-4 GPa), which is very close to that recorded for human bone (3-8 GPa), and high tensile strength (around 90 MPa) have become key properties for medical applications (JUNG e colab., 2016; KURTZ e DEVINE, 2007). Also, PEEK composites reinforced by carbon fibers can reach an elastic modulus at around 15-18 GPa and tensile strength of 200 MPa, that provide indications for manufacturing prosthetic structures (KURTZ e DEVINE, 2007; NAJEEB e colab., 2016).

The adhesion of resin composites to PEEK is still an issue concerning long-term performance of PEEK-based restorative structures due to a lack in functionalization meethdos for PEEK surfaces (CAGLAR e colab., 2018; ÇULHAOĞLU, AHMET KÜRŞAT; ÖZKIR, SERHAT EMRE, SAHIN, 2017; KURTZ e DEVINE, 2007; SCHMIDLIN, Patrick R. e colab., 2010; STAWARCZYK, Bogna e colab., 2015, 2018). Thus, the conventional methods for adhesion of resin composite to prosthetic infrastructures have not been effective regarding PEEK-based materials. Previous studies have reported a few methods of surface modification involving grit-blasting, sulfuric acid etching that slightly enhance PEEK wettability and bond strength to resin cements (HENRIQUES e colab., 2018; KERN, Matthias e LEHMANN, 2012a; LIEBERMANN, KEUL e colab., 2014; STAWARCZYK, Bogna e colab., 2015). Shear bond strength (SBS) values between PEEK and resin composites higher than 10 MPa have been reported as clinically acceptable (ABU BAKAR e colab., 2003; BEHR e colab., 2003, 2011; HALLMANN e colab., 2012b; NAJEEB e colab., 2016; RATNER, 1995; ROCHA e colab., 2016; SCHMIDLIN, Patrick R. e colab., 2010; STAWARCZYK, Bogna e BEUER e colab., 2013; STAWARCZYK, Bogna e KEUL e colab., 2013). Previous studies have reported low bond strength values for untreated PEEK to resin composites that can be enhanced by a modification of PEEK surfaces prior bonding (LIEBERMANN, KEUL e colab., 2014; LOUROPOULOU e colab., 2012; LÜMKEMANN e colab., 2017; MONICH, Patrícia R. e colab., 2017; ROSENTRITT e colab., 2015; STAWARCZYK, Bogna e colab., 2014;

STAWARCZYK, Bogna e KEUL e colab., 2013; ZHOU e colab., 2014a). Also, the chemical composition and viscosity of adhesives can enhance the adhesion of resin composites containing methacrylates monomers such as TEGDMA, BisEMA and BisGMA (CAGLAR e colab., 2018; ÇULHAOĞLU, AHMET KÜRŞAT; ÖZKIR, SERHAT EMRE, SAHIN, 2017; STAWARCZYK, Bogna e colab., 2018; STAWARCZYK, Bogna e KEUL e colab., 2013).

Thus, the improvement of PEEK surface properties has become a research topic for biomedical applications. There are several physicochemical methods to modify PEEK surfaces such as plasma, ultraviolet/ozone, grit-blasting, etching, and radiation-induced (plasma gas, laser, electron and ion-beam) treatment and coatings (KURTZ e DEVINE, 2007; RATNER, 1995). In fact, the roughness of the substrate is an important factor for adhesion, once it increases the contact surface area leading to enhanced mechanical interlocking of the adhesive (KURTZ e DEVINE, 2007). Several studies reported the use of grit-blasting with 50 or 110 μm alumina particles, to increase the PEEK average roughness (*Ra*) at around 2.6 μm for mechanical anchorage to resin composite adhesive and cements (ÇULHAOĞLU e colab., 2017; LIEBERMANN, KEUL e colab., 2014; ROCHA e colab., 2016; ROSENTRITT e colab., 2015; STAWARCZYK, Bogna e BEUER e colab., 2013; STAWARCZYK, Bogna e colab., 2015). The particle size and pressure influence the air abrasion treatment and result in varable PEEK roughness for mechanical interlocking to resin composites (CAGLAR e colab., 2018; CHAIJAREENONT e colab., 2018; ÇULHAOĞLU e colab., 2017; FURBINO e colab., 2016). Several acidic solutions have been studied to increase the *Ra* roughness of PEEK surface ranging from 0.18 up to 0.74 μm (CHAIJAREENONT e colab., 2018; KERN, Matthias e LEHMANN, 2012a). Previous studies reported that the use of 98% sulfuric acid as a PEEK surface pretreatment to modify PEEK surface has a positive effect, that results in a highly porous, permeable surface and in the appearance of H_2SO_4 functional groups on PEEK surface (CHAIJAREENONT e colab., 2018; FURBINO e colab., 2016; ROSENTRITT e colab., 2015; UHRENBACHER e SCHMIDLIN e KEUL e EICHBERGER e ROOS e GERNET e DRHC e colab., 2014; ZHOU e colab., 2014a).

Different surface treatment and adhesives for PEEK have been mainly studied using shear and tensile bond strength tests (CHAIJAREENONT e colab., 2018; ÇULHAOĞLU, AHMET KÜRŞAT; ÖZKIR, SERHAT EMRE, SAHIN, 2017; ÇULHAOĞLU e colab., 2017; FURBINO e colab., 2016; HENRIQUES e colab., 2018; PATRICK e colab., 2014; SCHMIDLIN, Patrick R. e colab., 2010; SCHMIDLIN, Patrick R e colab., 2010; TSUKA e colab., 2017; UHRENBACHER e SCHMIDLIN e KEUL e EICHBERGER e ROOS e GERNET e STAWARCZYK, 2014). Adhesives containing multifunctional

methylmethacrylate (MMA) monomers has been showing enhanced adhesion on every treated surface (KERN, M e LEHMANN, 2012). The highest PEEK to resin composites adhesion values were reported for PEEK conditioned with adhesive systems composed of methylmetacrylate, dimethacrylates, and pentaerythritol triacrylate displayed (LIEBERMANN, KEUL e colab., 2014; LÜMKEMANN e colab., 2017; STAWARCZYK, Bogna e colab., 2014; TEKIN e colab., 2018; TSUKA e colab., 2017). Nevertheless, the time of application, physical properties, and chemical composition of the adhesives are the key factors to affect the adhesion of PEEK to resin composites.

The aim of the present study was to evaluate the effect of the modification of PEEK substrates by acidic conditioning and self-etching adhesive on the shear bond strength of resin composite. It was hypothesized that the combined effect of 98% sulfuric acid treatment and self-etch adhesive coating can enhance the shear bond strength of PEEK t resin composites.

MATERIALS AND METHODS

PREPARATION OF PEEK TO RESIN COMPOSITE SAMPLES

Seventy specimens (8.5 mm diameter and 3 mm thick) were milled from PEEK rods (TECAPEEK, Ensinger, Germany). The specimens were wet ground down to 2500 grit silicon carbide papers (3M, USA). Polished specimens were ultrasonically cleaned in distilled water bath for 5 min and randomly divided into seven groups for further surface treatment procedures, as seen in Table 7.2.1.. Specimens from the groups A-D were acid etched with 98% sulfuric acid (CAS 7664-93-9, SigamAldrich, Brazil) for 60 seconds and then rinsed with deionized water for 10 min. All test PEEK surfaces (Groups B-G) were coated with an self-etch adhesive (Ambar Universal Adhesive, FGM, Brasil); after coating, adhesive excess were removed in different time appliance(1min, 3min and 5min) with 99,8% ethylic alcohol (SigamAldrich, Brazil) and polymerized for 60s (RadiiCal, SDI BRASIL INDUSTRIA E COMERCIO LTDA., São Paulo, SP, Brasil).

Table 2. Treatment procedures and chemical composition of the different treated groups.

Group	Surface treatment	Adhesive system(time)	Composition
A (Control)	Acid etched with H_2SO_4	No adhesive	-
B	Acid etched with H_2SO_4	Ambar Universal, FGM (1min)	Methacrylate monomers (UDMA and 10-MDP), photoinitiators, co-initiators, stabilizers, inert silica nanoparticles and ethanol.
C	Acid etched with H_2SO_4	Ambar Universal, FGM (3min)	Methacrylate monomers (UDMA and 10-MDP), photoinitiators, co-initiators, stabilizers, inert silica nanoparticles and ethanol.
D	Acid etched with H_2SO_4	Ambar Universal, FGM (5min)	Methacrylate monomers (UDMA and 10-MDP), photoinitiators, co-initiators, stabilizers, inert silica nanoparticles and ethanol.
E	PEEK without treatment	Ambar Universal, FGM (1min)	Methacrylate monomers (UDMA and 10-MDP), photoinitiators, co-initiators, stabilizers, inert silica nanoparticles and ethanol.
F	PEEK without treatment	Ambar Universal, FGM (3min)	Methacrylate monomers (UDMA and 10-MDP), photoinitiators, co-initiators, stabilizers, inert silica nanoparticles and ethanol.
G	PEEK without treatment	Ambar Universal, FGM (5min)	Methacrylate monomers (UDMA and 10-MDP), photoinitiators, co-initiators, stabilizers, inert silica nanoparticles and ethanol.

TOPOGRAPHICAL ANALYSES OF THE SURFACES

Arithmetic absolute average roughness (*Ra*) of the specimens was measured using a profilometer (Taylor Hubson Form Talysurf i-series, UK) with a cutoff set of 0.8 mm. Five surface measurement were performed for each specimen (n = 35).

3D topographical analyses were performed using an optical white light interferometry machine (NewView 7300 Zygo, Middlefield, USA). One specimen from each surface treatment procedure was randomly selected and each specimen was analyzed in a scanning area of 1500×1500 μm and a data analysis software (MountainsMap® Universal 7.1.7204, Besançon, France) was used to analyze 3D topographical data. Topographical 3D parameters were calculated according to the following standard, defining Geometrical Product Specification (GPS): ISO 25178.

Morphological analyses were also performed using a scanning electron microscope (SEM) (TM-3030 Hitachi, Krefeld, Germany). One specimen from each surface treatment procedure was randomly selected for SEM. PEEK surfaces were coated with 200A˚ of gold in 5 min at a current pressure of 10 mA and examined at magnification from x100 up to x1k. After the shear bond strength tests, the fractured surfaces were analysed to identify the failure mode of each group of specimens.

WETTABILITY ASSAYS

The effect of the surface treatment on the wettability of PEEK specimens was measured with a remote computer controlled liquid contact angle goniometer system (Ramé-Hart Instrument Co.- model Ramé-Hart 250, Succasunna, USA). For each specimen Ten measurements (n = 10) of adhesive contact angle (θ) were performed for each specimen under controlled conditions (T = 22 ± 1°C, RH= 40 ±5%) using a sessile drop measure machine containing the adhesive fluid. Mean adhesive contact angle value for each group was was considered as indicative of a wettability of the specimen.

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

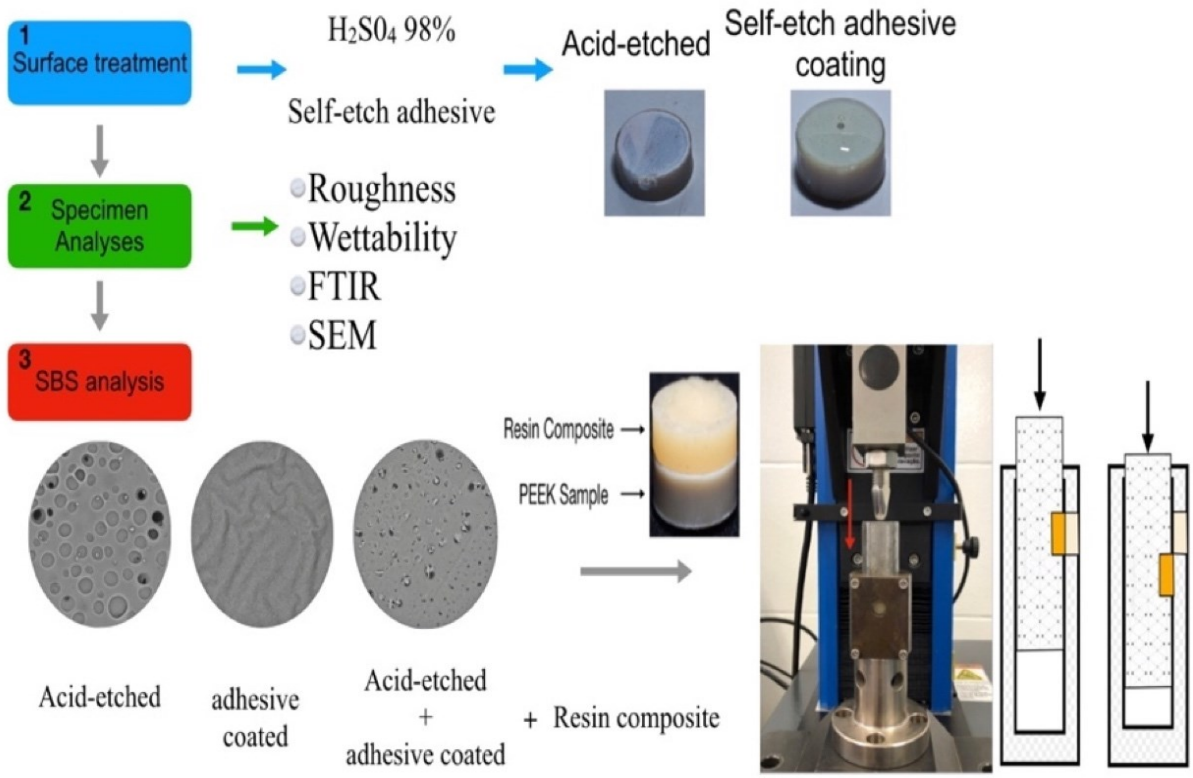
FTIR spectra were performed by the attenuated total reflectance method using FTL 200 spectrometer (Bomem, Canada) with resolution of 4 cm−1 and the wavenumbers ranged from

500 to 4000 cm^{-1}. The methacrylate monomer and PEEK bands were the functional groups assessed on the FTIR spectra.

SHEAR BOND STRENGTH TESTS

A resin composite (8.5 mm in diameter and 2 mm in thickness) (Opallis composite, FGM, Brasil) was applied on the test surfaces and polimerized using a light-curing unit (bre.Lux Power Unit; Bredent, Senden, Germany) at wavelength range 370 - 400 nm for 60 sec except. Shear bond tests were carried out within an universal test machine (INSTRON EMIC 23-5S, S.J. dos Pinhais, PR, Brasil) at a crosshead speed of 1 mm/min. The following equation was used to measure the shear bond strength of the PEEK to resin composites: σ =F/S (σ =shear bond strength, F = the load [N] at failure, S = surface area of the PEEK core/veneering resin interface [mm2]) as shown in Figure 2.

Figure 2. Schematic diagram showing the followed methodology for SBS analyses.



STATISTICAL ANALYSIS

Statistical analyses were conducted with the statistical software (SPSS version 23.0, Chicago, IL, USA). Data distribution were evaluated primarily with the Shapiro-Wilk test, and then analyzed by an equality of groups with Levene test. For the determination of significant differences between the tested groups, one-way ANOVA with the post-hoc Tukey test and non-parametric Kruskal-Wallis and Mann-Whitney tests were used. A statistical significance level of $p<0.05$ was considered for all tests.

RESULTS

TOPOGRAPHICAL ANALYSES

The surface topography of the PEEK surfaces is shown in Figure 3. The pretreated PEEK surfaces revealed surface modifications and irregularities like pits and pores (Fig. 3) that was not noted on unpretreated PEEK (Fig. 4).

Figure 3. SEM images revealing morphological aspects of PEEK surfaces at different magnifications (x100, x500, x1k). (A, B, C) PEEK and (D, E, F) PEEK etched within 98% H2SO4.

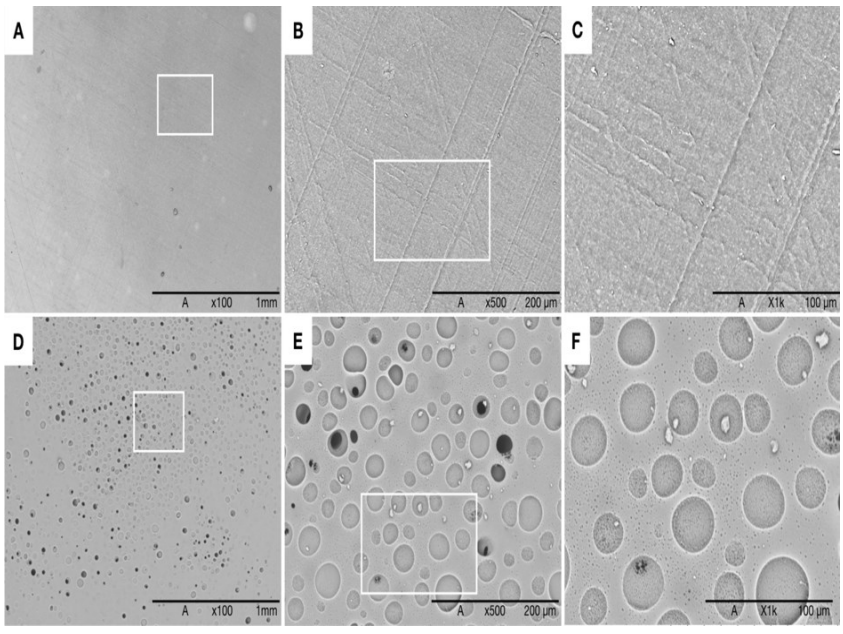


Figure 4. SEM images revealing morphological aspects of PEEK surfaces coated with self-etch adhesive at different magnifications (x100, x500, x1k) (A-C) for 1min, (D-F) for 3min, and (G-I) for 5min.

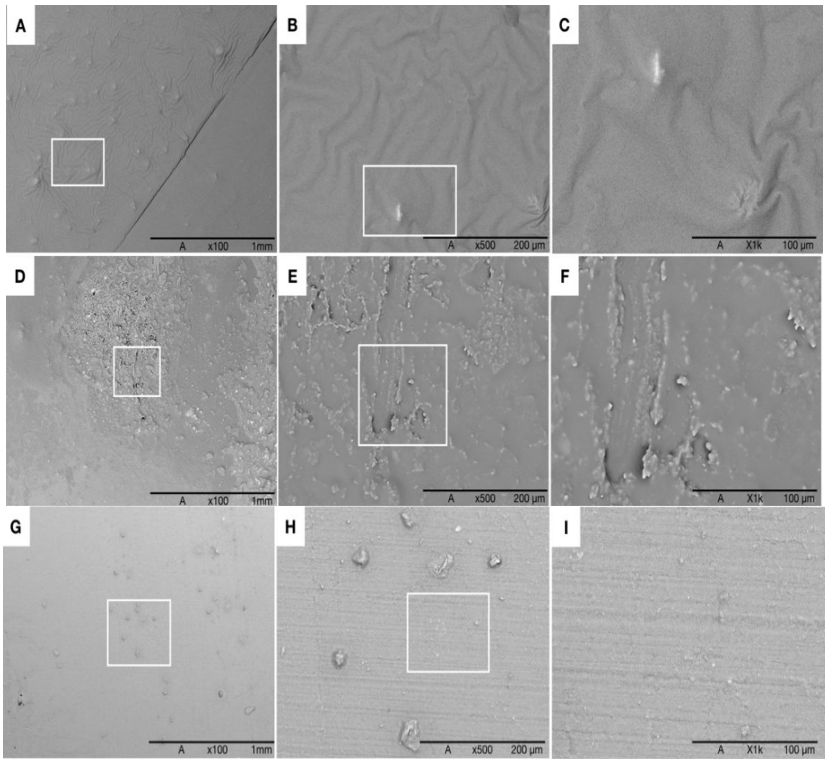
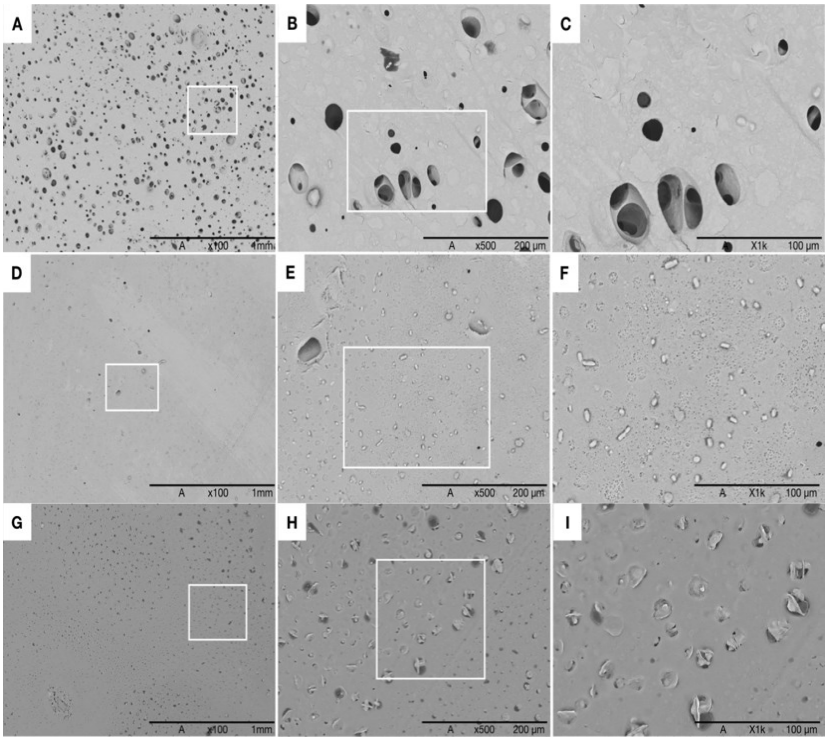


Figure 5. SEM images revealing morphological aspects of PEEK surfaces etched with 98% H2SO4 and coated with self-etch adhesive at different magnifications (x100, x500, x1k) for (A-C) 1min, for (D-F) 3min, and for (G-I) 5min.



PEEK coated with self-etch adhesives revealed a smooth surface free of pores that could cause by the adhesive application. That morphological aspect of the surface is proper for despotion and bonding of the resin composite.

PEEK surfaces etched within 98% H_2SO_4 revealed pores which were partially filled with self-adhesives. The pores can avoid the flowing of the resin composites on the PEEK surfaces leading to stress concentration regions at the interface. Thus, the pores were completely filled when the time of self-etch adhesive application was increased.

Ra mean values for all groups are shown in Table 3. Shapiro Wilk test did not show a normal distribution and therefore Ra data were conducted by a non-parametric statistical analysis using Kruskal–Wallis test, indicating significance was found. Pair-wise comparison for surface treatment (groups A, B, C, D) using Mann–Whitney U-test revealed differences between groups ($p < 0,001$).

Table 3. Mean, standard deviation and median for PEEK roughness values (μm).

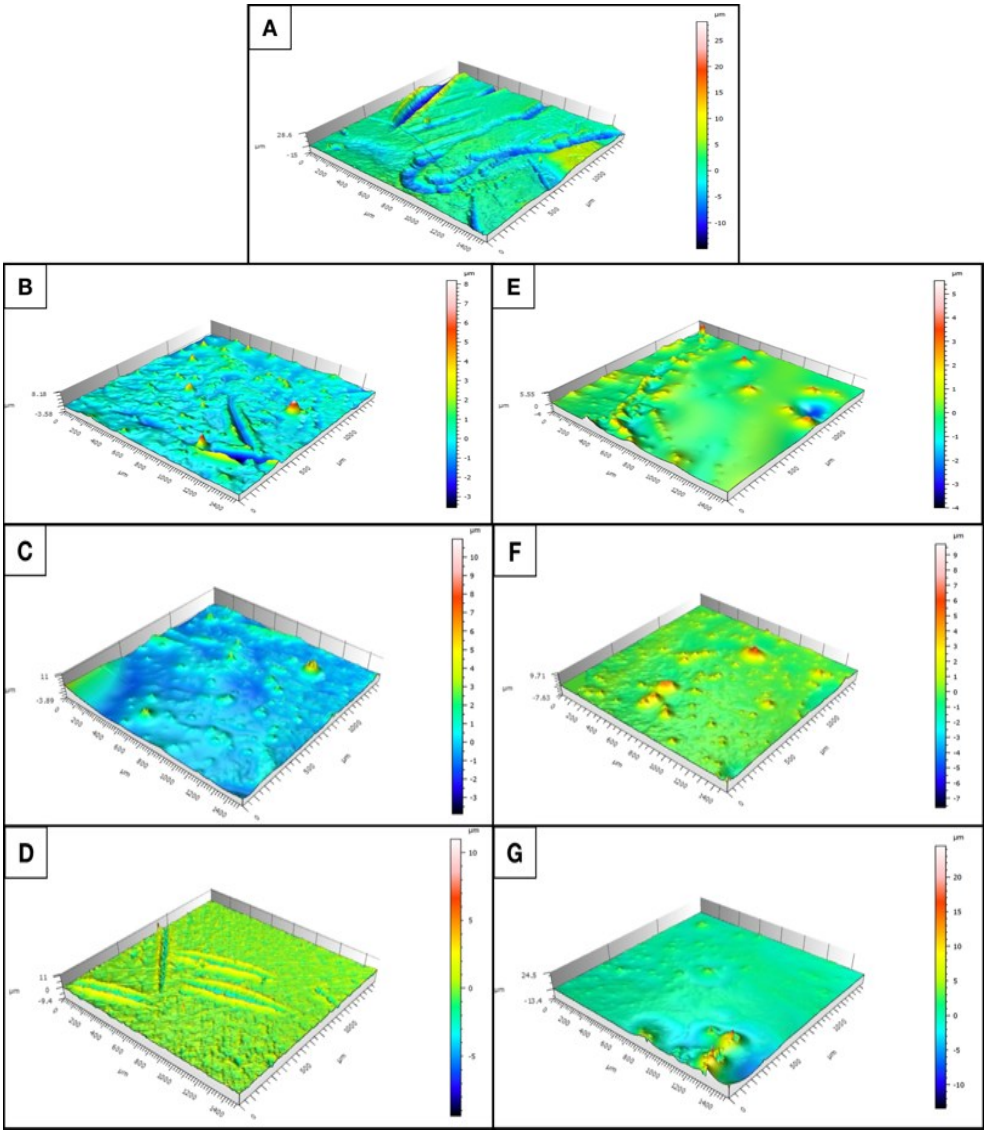
Group	*Ra* roughness (μm)		
	Mean (SD)	Median	*p*-Value*
Control	1.05 (±0,59)	1.05a	<0.001
PEEK+H2SO4+Ad 1min	0.86 (±0,29)	0.77a	
PEEK+H2SO4+Ad 3min	0.70 (±0,25)	0.65a	
PEEK+H2SO4+Ad 5min	1.26 (±0,51)	1.08a	
PEEK+Ad1min	0.06 (±0,01)	0.06b	
PEEK+Ad3min	0.06 (±0,01)	0.06b	
PEEK+Ad5min	0.06 (±0,00)	0.06b	

*Kruskal–Wallis test, statistically significant difference $p<0.05$.

Identical letters indicate non-significant difference values (Mann–Whitney U-test; $p>0,05$).

Topographical 3D images are shown in Figs. 5. In the control group the acid etched PEEK (A) surface showed large width and depth of scratches as shown in dark spots. The surfaces generated by the etched surface plus adhesive (Group B, C, D) had similar surface topographical characteristics with respect to the control group.

Figure 6. Representative 3D topographical images of PEEK surfaces. (A) PEEK etched within 98% H2SO4, (B) PEEK etched within 98% H2SO4 and coated with adhesive for 1min, (C) for 3min, (D) for 5min. PEEK surfaces free of etching and coated with self-etch adhesive



FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR spectra recorded for PEEK are shown in Figures 7-8. The transmittance bands at 1010 cm^{-1}, 1380 cm^{-1}, 1450 cm^{-1}, and 1552 cm^{-1} corresponding to SO_3H groups can be identified in the FTIR spectra recorded for the sulfonated PEEK. The transmittance bands at 840 cm^{-1}, 1720 cm^{-1}, and 1638 cm^{-1} are characteristic for methacrylate ((Bis- GMA) C_6H_4, C=O, C=C

functional groups) which compose the adhesive matrix. After applying the adhesive layer, the PEEK and sulfuric acid functional groups cannot be perceived, making impossible to differentiate test groups (Group B-G), that shows methacrylate functional groups (image 7.3.6.).

Figure 7. Transmittance photoacoustic spectrum acquired from PEEK comparing with PEEK+H2SO4 with the functional groups identified.

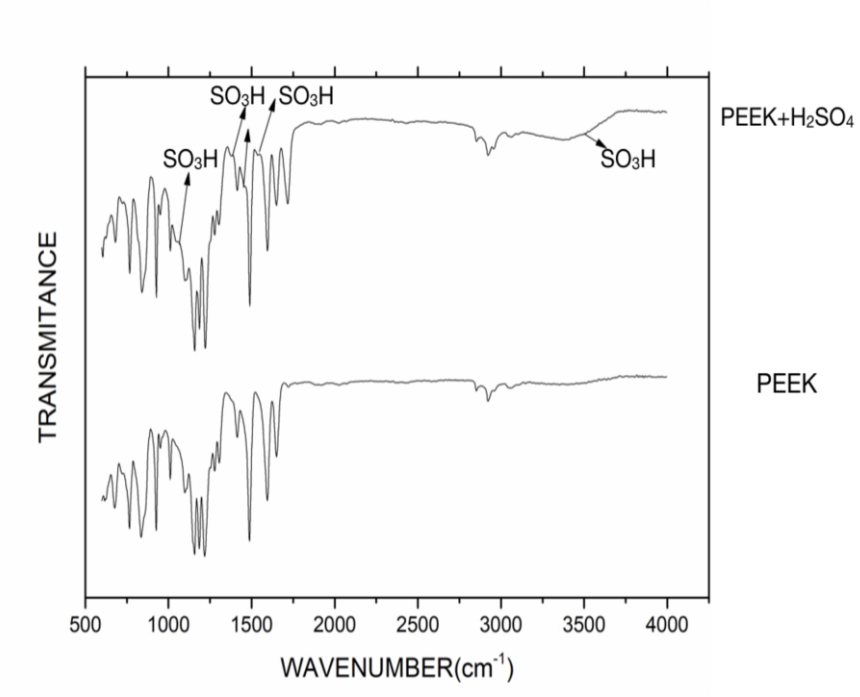
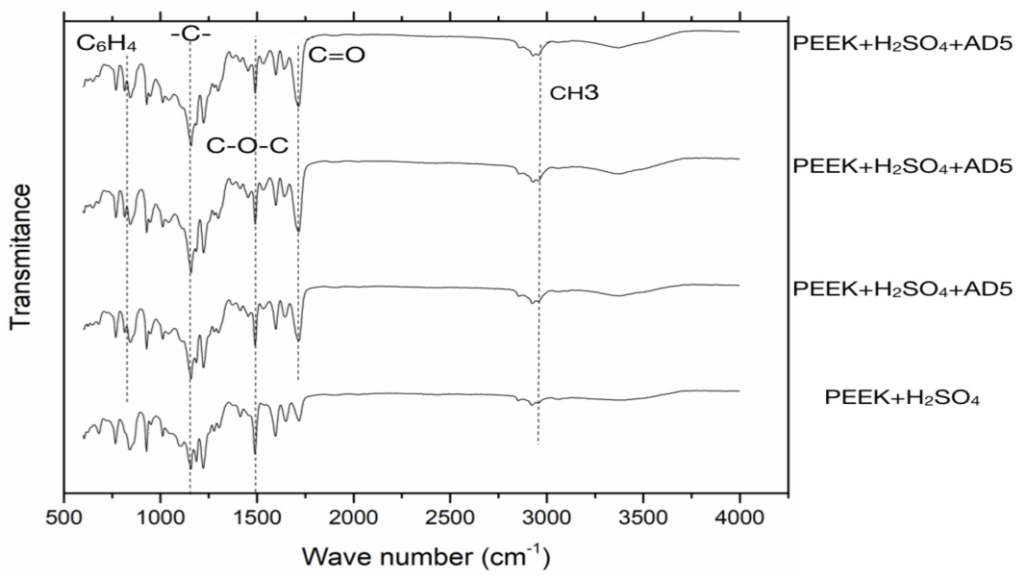
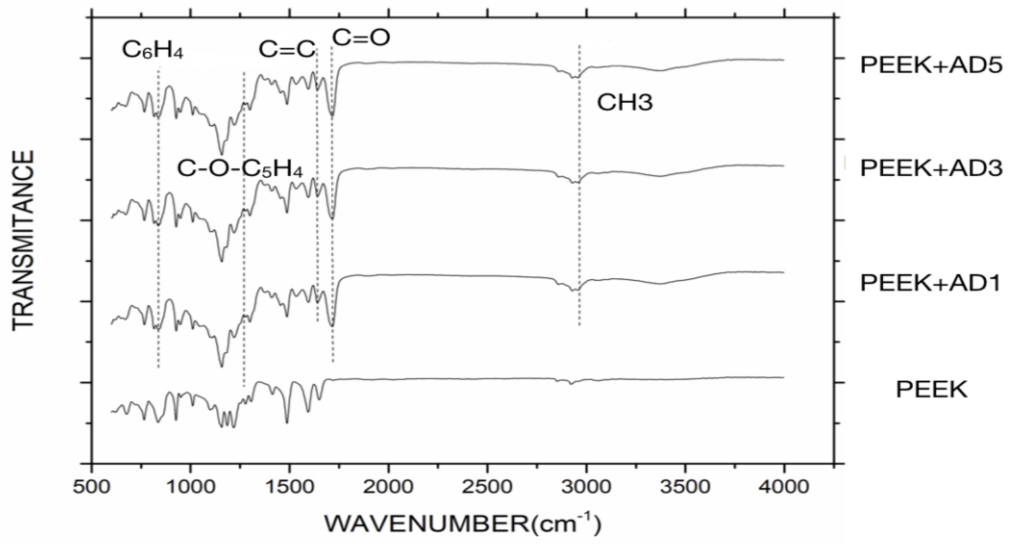


Figure 8. Transmittance photoacoustic spectrum acquired from adhesive at different time appliance on PEEK and PEEK+H2SO4 with the functional groups identified.



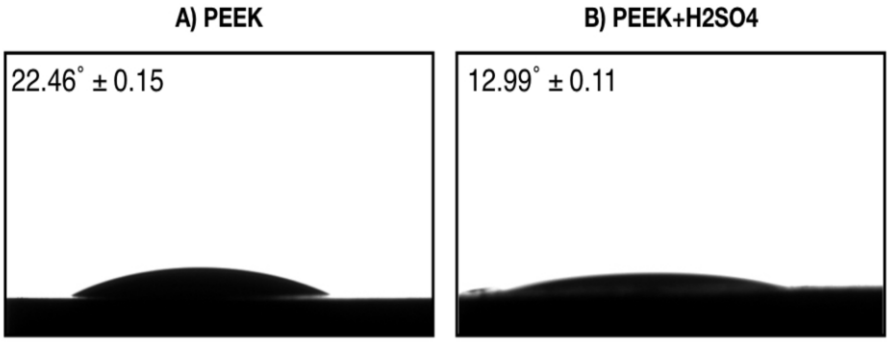


WETTABILITY ANALYSES

Adhesive contact angles values recorded in the fluid phase of the self-etch adhesive droplet on PEEK surfaces are shown in Figure 9. The contact angle formed between the adhesive fluid phase and the PEEK surfaces are statistically significant ($p < .05$) lower for PEEK etched within

98% H_2SO_4 when compared to PEEK free of acidic conditioning. That indicates a higher wettability of the PEEK after the sulfonation process of the surface.

Figure 9. Adhesive contact angle formed at surfaces of (A) PEEK and (B) PEEK etched within 98% H2SO4.



SHEAR BOND STRENGTH

Shear bond strength (SBS) data are revealed in Table 4. The Shapiro-Wilk test was used to test the normality of data distribution. SBS were analyzed using the One-way ANOVA and Tukey's post hoc tests (SPSS version 23.0, Chicago, IL, USA). The statistical significance level was set at a level of 0.05.

Table 4. Mean, SD for shear bond strength values of test groups (Mpa).

Group	Shear Bond Strength (SBS)	
	Mean (SD)	***p*-Value**
Control	5.58 (±3.27)[a]	<0.001*
PEEK+H2SO4+Ad 1min	10.55 (±2.55)[a]	
PEEK+H2SO4+Ad 3min	20.14 (±3.18)[b]	
PEEK+H2SO4+Ad 5min	24.18 (±5.65)[b]	

*One-way ANOVA, statistically significant difference p<0.05.

Identical letters indicate non-significant difference values (Tukey test; p>0,05).

FAILURE ANALYSIS

The surfaces of the substrates were examined after shear bond strength tests (Figure 10-11)SEM images revealed two failure types (1) Adhesive and (2) cohesive failure mode between PEEK and the resin composite.

Specimens from Group A (control), showed cohesive failure free of remnant resin composite in the PEEK pores. Remnant resin composite was detected on the PEEK surfaces from groups A, B, C, and D. Remnant resin composite was detected over the PEEK surfaces showing mostly cohesive failure, that suggested a mechanical interlocking effect. However, no resin composite was noticed over the PEEK surfaces free of acidic etching process (groups E, F, G) as see in Figure 11.

Figure 10. SEM images (x40 and x500) on the fracture surfaces after shear bond strength test. Acid etching pretreatment (A) compared with the pretreated group: acid etch + adhesive 1min (B), acid etch + adhesive 3min (C), acid etch + adhesive 5min (D).

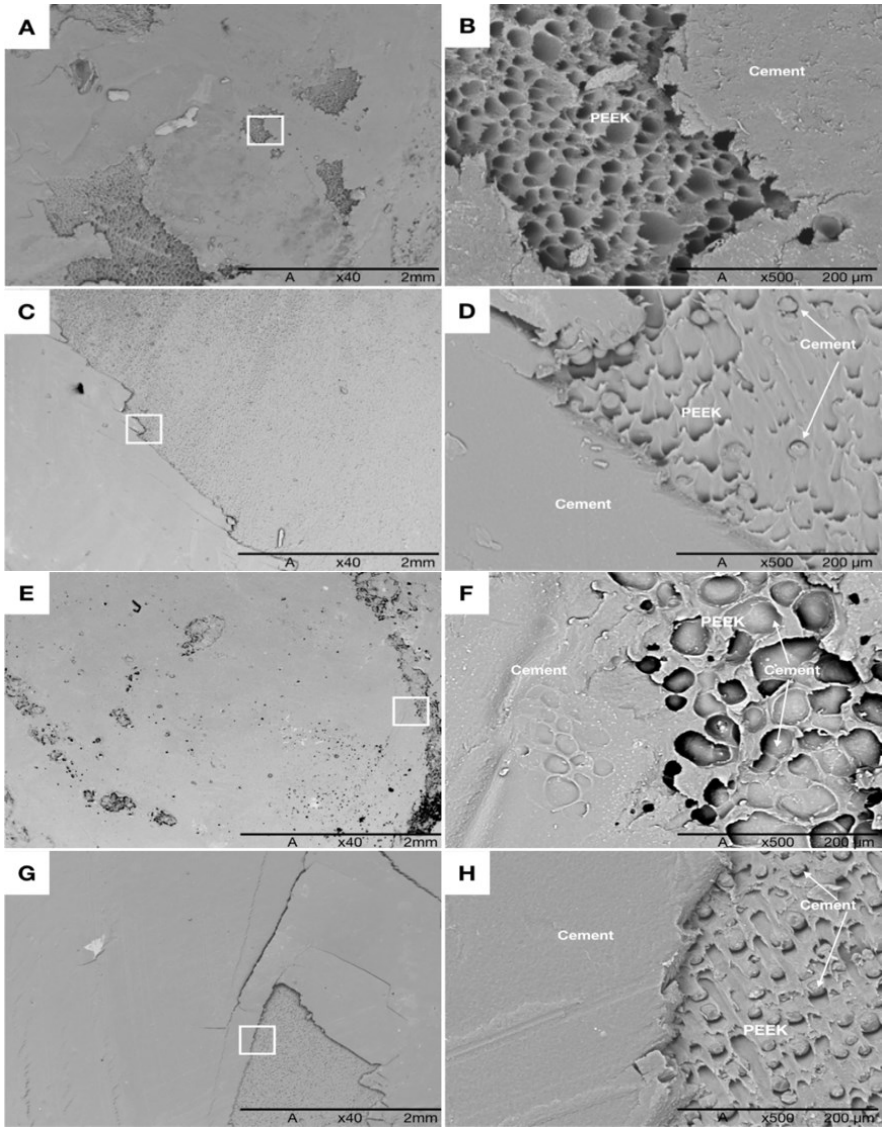
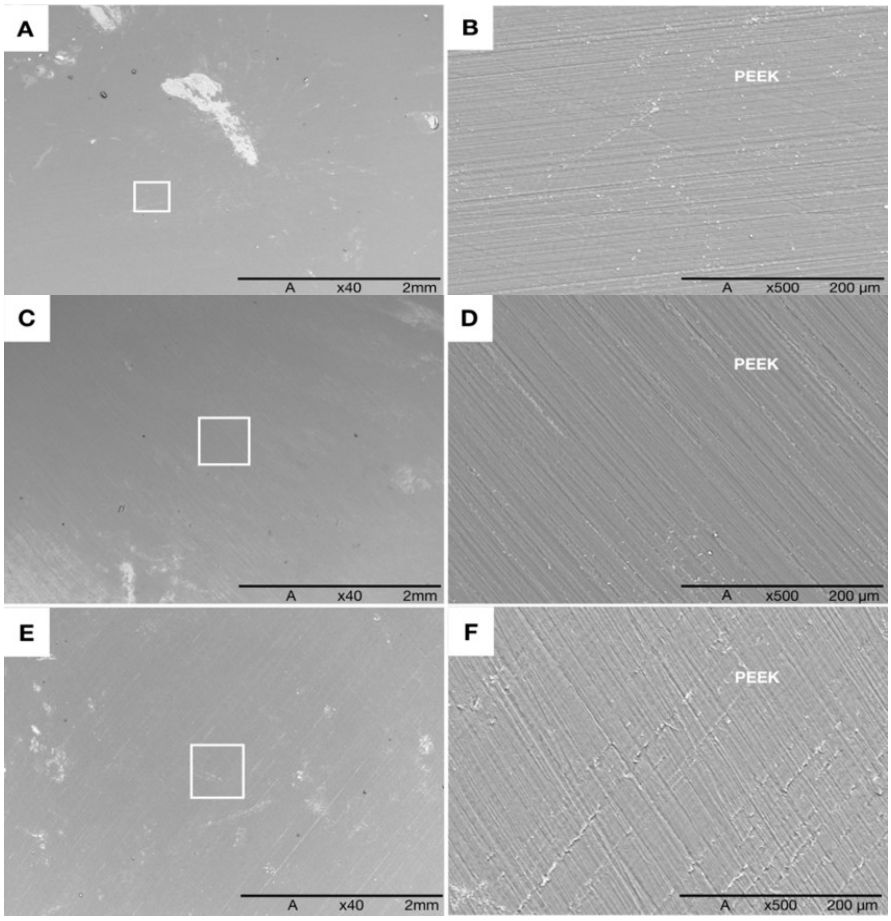


Figure 11. SEM images (x40 and x500) on the fracture surfaces after shear bond strength tests. Acid etching pretreatment (A) compared with the untreated group: adhesive 1min (E), adhesive 3min (F), adhesive 5min (G).



DISCUSSION

The results of this study support the rejection of the null hypothesis. They showed that the acidic etching in 98% H_2SO_4 followed by self-etch adhesive coating increased the shear bond strength of PEEK to resin composites. The time of acidic etching play a significant role on the roughness, morphological aspect, and on the wettability of PEEK to the self-etching adhesive that enhanced the adhesion of the resin composite.

Surfaces analyses by FTIR revealed that the PEEK surface was modified after acidic etching in 98% H_2SO_4 by the presence of SO_3H functional groups as compared with other studies that the sulfonation of SPEEK are determined by the presence of SO_3H into the functionalization of PEEK (MONTERO e colab., 2017; ZHAO e colab., 2013). Additionally, the time of exposure of PEEK to the acidic etching determined the morphological aspect of the surfaces. As described by Brum et al, 2018 when H_2SO_4 is in contact with PEEK surface, the inter chain interactions are higher due to the presence of the polar group SO3H, which can make polymer chains reorganized and form new structures (MONICH, R S Brum P R e colab., 2018). Considering time exposure, previous studies confirm that one of the principal factors

commanding the sulfonation rate is the acid strength and that acid etching rate decrease with the reaction time (DAOUST e colab., 2001).

As seen in the topographical images, morphological aspect of the surfaces changed in function of the acidic etching time and self-etching adhesive coating. Pores and pits were detected on PEEK etched by H_2OS_4 that could be filled by the self-etching adhesive coating. Previous studies reported that increasing etching duration, the overall surface topography remained constant, but with dipper pits and that prolonging the etching duration the surface became dispersed (SPROESSER e colab., 2014). Previous reported treating PEEK surface with 98% concentrated sulfuric acid, producing a highly porous surface and increasing PEEK permeability for adhesive penetration through pores (ZHOU e colab., 2014a). Schmidlin et al. 2010; confirm that sulfuric acid has led to a highly porous and permeable surface, providing pronounced undercuts, which could be more easily penetrated by the adhesives, but with no tags observed in SEM failure images.

The highest roughness mean values of PEEK were recorded after etching in 98% H_2SO_4 and self-etch adhesive coating for 5 min. On the other hand, the PEEK free of acidic etching procedure showed smooth surfaces which are unproper for mechanical interlocking of resin composite cements or adhesives. The application of 98% sulfuric acid etching for 60 s and self-etch adhesive coating in this study showed a higher SBS compared with previous studies which employed the same protocol but with no time appliance recorded for the adhesive (CHAIJAREENONT e colab., 2018; SCHMIDLIN, Patrick R. e colab., 2010). It seems that topographical changes of PEEK surface after sulfuric acid etching enhanced the penetration of the resin adhesive, resulting in the increased SBS. Differences on PEEK surfaces after sulfuric acid etching were due to the dissolution of the PEEK matrix by sulfonation reaction (CHAIJAREENONT e colab., 2018).

In fact, the fluid adhesive flowed throughout the micro-scale valleys and filled the pits and pores leading to a irregular methacrylate-based surface for resin composite deposition. The solvent of the adhesive penetrates into the porous surface of the PEEK etched in H_2SO_4 leading to the removal of remnant water molecules that could promote voids at the interface. Other previous studies reported the improvement of PEEK wettability to adhesives containing HEMA and solvents (LEE e colab., 2017; ZHOU e colab., 2014a). Considering viscosity, the resin composite could not be capable to filled those micro-scale irregularities that could form stress concentration spots during loading. Furthermore, the physical properties of the bonding area

are important for the work of adhesion. If the acid-etching creates a humid surface after application and ultrasonic cleaning, adhesive penetration would be troubled because methacrylate in the adhesive system is hydrophobic, and sufficient bonding would not be achieved on the moisture surface (CAGLAR e colab., 2018; SCHMIDLIN, Patrick R. e colab., 2010). Rosentritt et al, 2014 had shown that the combination of a high surface roughness with flowable bonding did not result in increased initial shear bond strength (ROSENTRITT e colab., 2015). In essence, the consistency of the material seemed to have no influence on bonding quality.

Thus, the shear bond strength of PEEK to resin composites was increased with an increase in PEEK roughness corroborating with previous findings in literature (CHAIJAREENONT e colab., 2018; LIEBERMANN, KEUL e colab., 2014; ROSENTRITT e colab., 2015; SCHMIDLIN, Patrick R. e colab., 2010; ZHOU e colab., 2014a). The time of acidic etching and adhesive application affected the shear bond strength values since the etching increased the PEEK roughness and the adhesive coating enhanced the adhesion between PEEK and resin composite. PEEK surfaces free of acidic etching and adhesive application revealed the lowest shear bond strength values (around 5 MPa) that is above the clinical application threshold. Previous studies had shown that high concentrations of sulfuric acid promoted deeper porous surface, therefore, higher resin tag length and higher SBS. The increase of exposure time to sulfuric acid promotes an increase of pits sizes (CHAIJAREENONT e colab., 2018). However, the longer the exposure time, the greater the decay of the PEEK surface, which could lead to cohesive failures (FURBINO e colab., 2016; SPROESSER e colab., 2014).

Previous studies found that adhesive systems that contain MMA monomers caused higher bond strength values between PEEK and resin (CAGLAR e colab., 2018; CHAIJAREENONT e colab., 2018; ROSENTRITT e colab., 2015; SCHMIDLIN, P R e colab., 2010; ZHOU e colab., 2014a). A study reported that seven of the test adhesive systems which include MDP components enhanced the shear bond strength of resin to PEEK surface (ROSENTRITT e colab., 2015). However, the effect of the MDP molecule on the PEEK to resin adhesion should be also studied. Taking into consideration that the adhesive system containing the functional monomer 10-MDP used in this study demonstrated chemical affinity for hydroxyapatite as state by Oliveira et al. 2017 (OLIVEIRA e colab., 2017). PEEK has no organic components so there is no reactive groups between adhesive and substrate. There is a exchange between the substrates and the adhesive. A strong bond takes place, when the adhesive is anchored into the

substrate and dissipates most of the energy, so the roughness of the substrate is an important factor adhesion improving the mechanical anchorage of the adhesive due to the increase of surface contact (HALLMANN e colab., 2012b; ZHOU e colab., 2014a).

CONCLUSION

Within the limitations of the present in vitro study, the main outcome of the PEEK modification for adhesion to resin composites can be drawn as follows:

- The PEEK roughness increased after conditioning in 98% sulfuric acid in function of the acidic etching time;
- Pores and pits were detected after the acidic etching that also enhance the wettability of the PEEK to self-etching adhesive and therefore the adhesive coating penetrated into the pores. That resulted in a primary mechanical interlocking to enhance the PEEK adhesion to resin-based materials;
- The synergistic effect of the proper acidic etching of PEEK surfaces in sulfuric acid followed by self-etching adhesive coating enhanced the shear bond strength of the modified PEEK surfaces to resin composites. The time of acidic etching and adhesive coating determined the shear bond strength of PEEK to resin composite that established an effective mechanical interlocking;
- Further studies on the pH, chemical composition, and conditioning time of self-etch adhesive should be performed in combination with PEEK functionalization by sulfonation and physical surface treatments.

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