

FELIPE DOS ANJOS RODRIGUES CAMPOS

**REVESTIMENTO DE POLÍMEROS TERMOPLÁSTICOS COM
CERÂMICAS BIOATIVAS PARA APLICAÇÃO EM IMPLANTES
ORTOPÉDICOS: ESTUDO DAS PROPRIEDADES MECÂNICAS,
QUÍMICAS E BIOLÓGICAS SEGUNDO PARÂMETROS DE
PROCESSAMENTO**



UNIVERSIDADE FEDERAL DE UBERLÂNDIA

FACULDADE DE ENGENHARIA MECÂNICA

2025

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TESE apresentada ao Programa de Pós-graduação em Engenharia Mecânica da Universidade Federal de Uberlândia, como parte dos requisitos para a obtenção do título de **DOUTOR EM ENGENHARIA MECÂNICA**.

Área de Concentração: Materiais e Processos de Fabricação.

Orientador: Prof. Dr. Alisson Rocha Machado

Coorientadora: Profa. Dra. Leticia de Souza Castro Filice

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FELIPE DOS ANJOS RODRIGUES CAMPOS

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Área de Concentração: Materiais e Processos de Fabricação.
Linha de pesquisa: Materiais biocompatíveis

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Iniciando os trabalhos o presidente da mesa, Dr. Álisson Rocha Machado, apresentou a Comissão Examinadora e o candidato, agradeceu a presença do público, e concedeu ao Discente a palavra para a exposição do seu trabalho. A duração da apresentação do Discente e o tempo de arguição e resposta foram conforme as normas do Programa.

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CAMPOS, F. A. R. Revestimento de polímeros termoplásticos com cerâmicas bioativas para aplicação em implantes ortopédicos: estudo das propriedades mecânicas, químicas e biológicas segundo parâmetros de processamento. 2025. 183 p. Tese de doutorado. Faculdade de Engenharia Mecânica. Universidade Federal de Uberlândia, Uberlândia - MG, Brasil.

RESUMO

A crescente demanda por implantes ortopédicos personalizados e de baixo custo tem estimulado o desenvolvimento de novas tecnologias de manufatura e funcionalização de biomateriais. Nesta tese, foram investigados dois métodos inovadores para o revestimento de polímeros termoplásticos com cerâmicas bioativas — o jateamento intermitente com ar comprimido e o recozimento em leito de pó — visando aplicações em implantes ortopédicos produzidos por manufatura aditiva. Ambos os processos foram aplicados a peças de ácido polilático (PLA) impressas em 3D pelo processo Fused Filament Fabrication (FFF), sendo avaliados os efeitos de parâmetros de impressão e de revestimento sobre as propriedades mecânicas, químicas e biológicas dos componentes. O jateamento utilizou fluxo contínuo de ar quente combinado a jatos intermitentes de ar comprimido contendo partículas de hidroxiapatita (HA), permitindo a incorporação superficial dos particulados. O recozimento em leito de pó consistiu na imersão das amostras em partículas submicrométricas de HA e posterior aquecimento próximo à temperatura de fusão do polímero, favorecendo a adesão por difusão. Ensaio mecânicos (flexão, impacto, dureza e esclerometria), análises químicas (MEV/EDS, FTIR, ângulo de contato) e testes *in vitro* de citotoxicidade e diferenciação osteogênica foram realizados para caracterizar o desempenho dos revestimentos e dos substratos. Os resultados indicaram que ambos os métodos possibilitam a deposição de camadas bioativas aderentes, embora apenas no recozimento em leito de pó tenha ocorrido comprovado aumento da hidrofobicidade e manutenção de propriedades mecânicas adequadas, além do método se destacar pela uniformidade e maior espessura do revestimento, com o jateamento destacando-se negativamente pela dificuldade de execução e dano térmico deletério à geometria das amostras. Os testes biológicos confirmaram a ausência de citotoxicidade e o estímulo à diferenciação osteogênica, evidenciando o potencial clínico das técnicas. Conclui-se que os processos propostos representam alternativas de baixo custo e compatíveis com polímeros reabsorvíveis, com potencial para integração em fluxos produtivos de implantes ortopédicos personalizados. Recomenda-se a continuidade dos estudos com foco em otimização paramétrica, avaliação de durabilidade em condições simuladas e validação *in vivo*.

Palavras-chave: Implantes ortopédicos, PLA, hidroxiapatita, recozimento em leito de pó, jateamento cerâmico, manufatura aditiva.

CAMPOS, F. A. R. Coating of thermoplastic polymers with bioactive ceramics for application in orthopedic implants: a study of mechanical, chemical and biological properties according to processing parameters. 2025. 183 p. Doctoral thesis. Faculty of Mechanical Engineering. Federal University of Uberlandia. Uberlandia, MG - Brazil.

ABSTRACT

The growing demand for low-cost, customized orthopedic implants has spurred the development of new technologies for manufacturing and functionalizing biomaterials. This thesis investigated two innovative methods for coating thermoplastic polymers with bioactive ceramics—intermittent compressed air jetting and powder bed annealing—for applications in orthopedic implants produced by additive manufacturing. Both processes were applied to polylactic acid (PLA) parts 3D printed using the Fused Filament Fabrication (FFF) process, evaluating the effects of printing and coating parameters on the mechanical, chemical, and biological properties of the components. Jetting used a continuous flow of hot air combined with intermittent jets of compressed air containing hydroxyapatite (HA) particles, allowing for surface incorporation of the particles. Powder bed annealing consisted of immersing the samples in submicron HA particles and subsequently heating them close to the polymer's melting temperature, promoting adhesion by diffusion. Mechanical tests (flexural, impact, hardness, and rebound hammer), chemical analyses (SEM/EDS, FTIR, contact angle), and *in vitro* cytotoxicity and osteogenic differentiation tests were performed to characterize the performance of the coatings and substrates. The results indicated that both methods enable the deposition of adherent bioactive layers, although only powder bed annealing demonstrated increased hydrophilicity and maintenance of adequate mechanical properties. The method also stands out for its uniformity and greater coating thickness, with compressed air jetting standing out negatively due to its difficulty of execution and deleterious thermal damage to the sample geometry. Biological tests confirmed the absence of cytotoxicity and the stimulation of osteogenic differentiation, demonstrating the clinical potential of the techniques. It can be concluded that the proposed processes represent low-cost alternatives compatible with resorbable polymers, with potential for integration into production processes for customized orthopedic implants. It is recommended to continue studies focusing on parametric optimization, durability assessment under simulated conditions and *in vivo* validation.

Keywords: Orthopedic implants, PLA, hydroxyapatite, powder bed annealing, ceramic blasting, additive manufacturing.

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CAPÍTULO 1

1. INTRODUÇÃO

O desenvolvimento da tecnologia, da medicina e a melhoria da qualidade de vida da população nos países em geral tem levado ao aumento da expectativa de vida da população, que embora benéfico, tem sido acompanhado por desafios, como o crescente número de problemas ortopédicos e uma maior demanda pelo uso de implantes. Por isso, é de extrema importância a realização de pesquisas para o desenvolvimento de tecnologias que possibilitem a fabricação de implantes de forma mais acessível financeiramente, que utilizem métodos de fabricação mais práticos e que ofereçam maior capacidade de personalização de acordo com as características do paciente.

Nesse sentido, muitos estudos têm sido realizados sobre a viabilidade do uso de polímeros, cujos benefícios incluem o preço da matéria prima e módulo de elasticidade próximo ao do tecido ósseo. Outro grande diferencial de alguns polímeros, como o ácido polilático (PLA), é a sua característica reabsorvível, o que pode ser muito útil para a produção de pequenos implantes que podem se decompor com o tempo e serem absorvidos pelo organismo enquanto o tecido ósseo ao redor se regenera e toma seu lugar. Embora já exista uma boa variedade de polímeros com boa biocompatibilidade, como PLA, PCL (policaprolactona) e Nylon 12, há estudos que demonstram que a compatibilidade apresentada pelos polímeros ainda pode ser melhorada utilizando métodos de modificação da superfície da peça, visto que a rugosidade do implante influencia na diferenciação óssea, e que o uso de compostos de cálcio e dióxido de titânio na forma de revestimento estimula a neoformação do tecido ósseo.

Com esse interesse no uso de polímeros na fabricação de implantes, um processo de fabricação que acabou se aprimorando e se destacando foi a manufatura aditiva, com o processo *Fused Filament Fabrication* (FFF), que permite a fabricação rápida de peças poliméricas com alto nível de customização. No entanto, essa tecnologia tem como principal limitação sua alta anisotropia, devido à deposição camada por camada, resultando em propriedades mecânicas dependentes da adesão entre as camadas depositadas. Assim, um possível método para solucionar esse problema é realizar o processo de recozimento, para coalescer as camadas ou mesmo fundi-las, tornando a peça mais homogênea e reduzindo a anisotropia. Outro possível benefício do recozimento é a alteração do estado organizacional das moléculas em polímeros semicristalinos, como o PLA. Nesses casos, sua permanência em temperaturas acima da temperatura de transição vítrea favorece o aumento da cristalinidade, o que pode melhorar suas propriedades mecânicas, embora possa também fragilizar o polímero.

Tendo esse fenômeno em mente, foi hipotetizada neste trabalho a possibilidade de criar revestimentos biocompatíveis em polímeros reabsorvíveis impressos em 3D, com processos térmicos que não só depositassem o revestimento, mas também fizessem simultaneamente o recozimento da peça, obtendo melhoria não só das propriedades da superfície, mas também do

substrato. Considerando o jateamento intermitente com ar comprimido, combinado ao aquecimento contínuo por ar quente, utilizado para a formação de revestimentos de hidroxiapatita e dióxido de titânio em polímeros termoplásticos – tecnologia investigada durante o mestrado – esta tese busca aprofundar os estudos sobre essa técnica, além de explorar um novo método desenvolvido e patenteado durante o doutorado: o revestimento por recozimento em leito de pó. Nesse processo a peça impressa é imersa numa bandeja contendo partículas cerâmicas submicrométricas e submetida ao aquecimento em forno, permitindo que o polímero se refunda e as partículas cerâmicas penetram por difusão na matriz polimérica. Ao longo do trabalho, ambos processos foram estudados e seus resultados comparados, a fim de que os parâmetros pudessem ser ajustados e otimizados para melhoria da resistência do substrato e da qualidade dos revestimentos. Os testes realizados tinham como horizonte a possibilidade de desenvolver metodologias de fabricação inovadoras da fase de prova de conceito (para o jateamento) e de conceito teórico (no caso do recozimento em leito de pó), até fases mais avançadas da escala de tecnologia (*Technology Readiness Level-TRL*). Esses estudos poderiam então resultar na redução dos custos de fabricação de peças personalizadas para implantes ortopédicos e outras aplicações, contribuindo para a saúde geral da população.

1.1 OBJETIVOS

O objetivo geral do trabalho foi investigar a influência dos parâmetros dos processos de impressão 3D e de revestimento nas propriedades mecânicas, químicas e biológicas das peças, com vista à sua aplicação em implantes ortopédicos. Entre os parâmetros de impressão, destacam-se aqueles que influenciam na história térmica e adesão inter-camadas da amostra impressa, como a temperatura do bocal, temperatura de mesa e a altura de camada. Já no processo de revestimento por jateamento, destacam-se como variáveis a pressão e intermitência dos jatos de ar comprimido, a temperatura do ar quente, movimentação da amostra, distância do bocal à peça e tempo de jateamento, cuja seleção deve ser otimizada para obtenção de revestimentos mais espessos, uniformes, e com melhor adesão ao substrato. No processo de revestimento por recozimento em leito de pó, as principais variáveis são o tempo e temperatura de aquecimento. A partir do objetivo geral, os seguintes objetivos específicos foram elencados:

- Objetivo 1 – Investigar o padrão de variação das propriedades mecânicas das amostras ao modificar os parâmetros de impressão 3D;
- Objetivo 2 – Investigar o padrão de variação das propriedades mecânicas do revestimento e substrato das peças ao modificar os parâmetros de processamento;
- Objetivo 3 – Desenvolver e/ou adaptar equipamentos necessários aos testes mecânicos e químicos, tais como máquinas de ensaio de flexão, impacto, microdureza, esclerometria, impressão 3D, entre outras;
- Objetivo 4 – Utilizar técnicas de otimização multidimensional para modelar empiricamente as propriedades da peça de acordo com os vários parâmetros de produção;

- Objetivo 5 – Comparar as propriedades do revestimento entre o processo de jateamento e o recozimento em leito de pó;
- Objetivo 6 – Avaliar as propriedades biológicas dos materiais através de testes de citotoxicidade e biocompatibilidade *in vitro*, para comprovação da viabilidade dos materiais nas aplicações em implantes ortopédicos.

1.2 ESTRUTURA DA TESE

Uma vez que ao longo da tese foram publicados vários trabalhos em congressos e preparadas algumas publicações para revistas, nem todos os experimentos estavam diretamente correlacionados de maneira sequencial, mas todos contribuíram para um amplo entendimento do problema fundamental da tese: os processos de fabricação de revestimento inovadores propostos e seus efeitos nas propriedades mecânicas do substrato. Por este motivo, a tese foi organizada de acordo com as publicações feitas e/ou preparadas, nos seguintes capítulos:

- Capítulo 1 – Introdução: apresenta o contexto, objetivos gerais e específicos e a estrutura do trabalho.
- Capítulo 2 – Revisão bibliográfica: apresenta os principais conceitos necessários para discutir resultados da tese.
- Capítulo 3 – Metodologia: relaciona os objetivos com os grupos de experimentos realizados, os quais embasaram os artigos preparados, apresentados em cada capítulo.
- Capítulo 4 – Influência de parâmetros de impressão nas resistências ao impacto e à tração de peças produzidas pelo processo Fused Filament Fabrication.
- Capítulo 5 – Análise da influência de parâmetros térmicos na resistência mecânica de peças impressas pela técnica Fused Filament Fabrication.
- Capítulo 6 – Quantificação de incerteza e calibração de uma célula de carga com sistema de aquisição por Arduino.
- Capítulo 7 – Influência do recozimento na resistência mecânica e térmica do PLA
- Capítulo 8 – Comparação da resistência ao impacto do PLA recozido impresso em 3D de acordo com diferentes parâmetros de processo e normas Izod da ASTM
- Capítulo 9 – Produção de revestimento de hidroxiapatita em peças de PLA impressas em 3D por recozimento em leito de pó.
- Capítulo 10 – Desenvolvimento de um sistema de jateamento para deposição de particulados cerâmicos bioativos na superfície de polímeros termoplásticos e comparação com recozimento em leito de pó.
- Capítulo 11 – Otimização de propriedades mecânicas e tribológicas de peças de PLA revestidas com hidroxiapatita por recozimento em leito de pó.
- Capítulo 12 – Adesão de revestimentos de hidroxiapatita em peças de PLA impressas 3D por recozimento em leito de pó.
- Capítulo 13 – Conclusões.

Por fim, ressalta-se a participação do doutorando em todos os artigos apresentados nesta tese. Mesmo naqueles em que o mesmo não aparece como 1º autor do trabalho ou mesmo como co-autor, todos os experimentos foram planejados e analisados pelo doutorando. No entanto, uma vez que houve o apoio, em graus variados, de diversos alunos e técnicos dos laboratórios da universidade na execução de alguns dos experimentos (como testes de flexão e impacto, medição de ângulo de molhamento, quantificação de células vivas em cultura, entre outros), foi optado em alguns casos por deixar alunos de iniciação científica como primeiros autores, como forma de estímulo a participação em publicações e reconhecimento as suas contribuições. Em outros casos, o doutorando se absteve até mesmo como coautor, uma vez que os trabalhos publicados valeriam maior pontuação para os coautores restantes na avaliação em editais de pós-graduação e seleção de bolsistas de intercâmbio (onde normalmente a pontuação atribuída ao artigo na análise curricular é penalizada quanto ao número de autores).

CAPÍTULO 2

2. REVISÃO BIBLIOGRÁFICA

2.1 BIOMATERIAIS PARA IMPLANTES

Os biomateriais compreendem uma fração representativa dos produtos utilizados na área da saúde, como biossensores, materiais implantáveis (como suturas, placas, telas, substitutos ósseos, dentes), e órgãos artificiais. A caracterização de um biomaterial não é suficiente para seu uso como biocomponente, mas pode e deve ser utilizado como pré-seleção de condições a serem testadas nas etapas seguintes (da SILVA et al., 2021). Os materiais aprovados na pré-seleção terão que passar por testes laboratoriais em cultura de células (testes *in vitro*) e depois testes *in vivo* (animais), e por fim testes clínicos.

Alguns dos implantes mais comuns nos tratamentos de saúde são os dentários e de substituição da cartilagem em joelhos, quadril, ombro ou disco intervertebral, nos quais normalmente é necessário perfurar o osso até o tecido esponjoso para fixar a prótese. Por isso, a estabilidade mecânica é determinante para o comportamento do tecido ósseo na interface com o implante, sendo influenciado pela rugosidade e a natureza química da superfície do biomaterial (AGARWAL e GARCÍA, 2015). Estudos *in vitro* mostraram que as superfícies mais adequadas têm rugosidade média (Ra) de aproximadamente 1 a 2 μm , e que os óxidos de titânio são capazes de induzir a diferenciação celular e facilitar crescimento e a osseointegração com o implante (ELIAS, 2010; MATOS, 2021).

Outra característica importante é o módulo de elasticidade, que tem altos valores para os materiais metálicos em comparação ao osso, levando à distribuição desigual da tensão na interface entre osso e implante, conhecida como *stress shielding*. Este fenômeno pode acarretar estabilização mais lenta do implante e perda de densidade óssea a longo prazo (BOSCHIN et al., 2007; SOLIMAN et al., 2024). Nesse sentido, tem sido investigada a utilização de polímeros em implantes endósseos, pelo módulo de elasticidade ser mais próximo ao do osso (de RUITER et al., 2017) e pelos menores custos de manufatura, inclusive, existem vários pedidos e patentes registradas para projeto de implantes feitos inteiramente de polímeros ou de compósitos de matriz polimérica (ZHU e XU, 2018; ZHONGXIANG et al., 2013; NEVINS e BACKSTEIN, 2020). Mishra e Chowdhary (2019) mostraram o potencial do PEEK (poliéter-éter-cetona) e PEKK (poliéter-cetona-cetona) em substituir o titânio em diversas aplicações cirúrgicas, enquanto o UHMWPE (polietileno de ultra alto peso molecular) e HXLPE (polietileno altamente reticulado) já são bastante utilizados em cirurgias de artroplastia (DU et al., 2018).

Embora esses polímeros tenham estabilidade química e sejam biocompatíveis, já foi demonstrado que também pode-se obter excelentes respostas de regeneração do tecido ósseo caso a peça seja revestida ou texturizada com TiO_2 ou compostos a base de fosfato de cálcio (WALSH et al., 2016), como a hidroxiapatita (HA). A combinação de alta porcentagem de

osseointegração proporcionada pelos revestimentos cerâmicos, com diminuição do *stress shielding* e com menor custo, torna os polímeros uma excelente opção para fabricação de implantes.

2.2 POLÍMEROS

Os polímeros vêm ganhando cada vez mais atenção devido à sua versatilidade e baixo custo de fabricação. Um importante ponto de estudo desse processo é o entendimento sobre a forma de organização das cadeias no estado sólido. Dependendo da linearidade do polímero e velocidade de resfriamento a partir do estado líquido/viscoso, as cadeias podem se aproximar e formar estruturas regularmente empacotadas, caracterizando o estado cristalino. Em estruturas complexas ou no resfriamento rápido as cadeias não conseguem se organizar, levando a estruturas desorganizadas caoticamente e altamente emaranhadas (EBEWELE, 2000). De acordo com o comportamento mecânico e resposta à variação de temperatura, os polímeros podem ser do tipo elastômeros, termoplásticos e termorrígidos.

Nos termoplásticos, as cadeias adquirem maior movimentação quando são aquecidos, de forma que o alto grau de agitação leva ao desaparecimento de qualquer estrutura organizada e predominância de um estado líquido ou viscoso com a fusão do polímero, caracterizando a temperatura de fusão (T_f). A primeira faixa de temperatura durante o resfriamento é chamada temperatura de cristalização (T_c) e marca o início do empacotamento organizado das cadeias, formando cristalitos que nucleiam e crescem. Se a temperatura baixar ainda mais, chegará um limite a partir do qual a movimentação das cadeias será diminuída e conseqüentemente nucleação e formação dos cristalitos não será mais possível, “congelando” a estrutura amorfa do polímero. Esta variação ocorre numa faixa de temperatura que caracteriza a transição vítrea (T_g). Estes dois limites são importantes fatores para as propriedades mecânicas e físico-químicas do polímero. Além da maior transparência, a estrutura amorfa também está associada a maiores valores de ductilidade comparado aos polímeros cristalinos.

2.3 POLÍMEROS BIOCAMPATÍVEIS

A utilização de materiais poliméricos em cirurgias aumentou com o surgimento de materiais que aliam boas propriedades mecânicas com estabilidade química, a exemplo do PEEK, UHMWPE, HXLPE e PA-12 (poliamida 12). O processo de certificação de biocompatibilidade deve atender aos requisitos do conjunto de normas ISO 10993 (2018), que fornecem diretrizes para os testes *in vitro* e *in vivo* conduzidos antes da validação e lançamento do produto, que avaliam principalmente a citotoxicidade, sensibilização, reações inflamatórias, estabilidade química e mecânica, e resistência química ou à altas temperaturas de acordo com os métodos de esterilização. Recentemente, foram relatados também estudos com boa eficiência do PA66 (poliamida 66) misturado com HA para a osseointegração em implantes ortopédicos (XIE et al., 2021; HU et al., 2019). Diversos trabalhos também investigam a possibilidade de usar

polímeros biodegradáveis e/ou reabsorvíveis, como PLA (ácido polilático) ou PCL (policaprolactona) e seus compósitos (ORYAN et al, 2020; SANIEI e MOUSAVI, 2020), que se degradam dentro do organismo humano em compostos não tóxicos.

2.4 TRATAMENTOS DE SUPERFÍCIE PARA IMPLANTES

Vários processos são possíveis para formação de revestimento de hidroxiapatita, os quais podem ser considerados viáveis para revestimentos de outros cerâmicos, como óxidos de titânio (ZHANG, 2013). Porém, muitos deles requerem que o substrato seja eletricamente condutor, como no caso de deposição eletroquímica, ou envolvem altas temperaturas, como na operação de calcinação em revestimento por imersão. Enquanto processos de deposição por vapor do tipo PVD (*physical vapor deposition* ou deposição física por vapor) e CVD (*chemical vapor deposition* ou deposição química por vapor) podem ser usados para deposição de pós metálicos ou cerâmicos em substratos poliméricos, os mais preferidos são os por spray, com especial destaque para os processos de spray térmico a plasma (SARGIN et. al., 2017; SALITO et. al., 2017). Uma variação de menor aporte térmico é o procedimento conhecido por *cold gas shooting*, que utiliza um gás de arraste a alta pressão passando num bocal convergente-divergente para acelerar as partículas sólidas a velocidades supersônicas (LUPOI et. al., 2016; GARDON et. al., 2013), tendo esse processo sido utilizado com sucesso para deposição de partículas de titânio e de cobre em termoplásticos. Parâmetros de processo e dos materiais envolvidos são de extrema importância. Neste caso, não só para evitar erosão e garantir boa adesão no substrato, mas para evitar danos a geometria e propriedades químicas e mecânicas da peça. No caso da temperatura por exemplo, evitar canais de plasma e métodos químicos como por sol-gel podem facilitar a obtenção de estruturas cristalinas puras, sem fases amorfas ou indesejadas, que podem comprometer o desempenho do revestimento. Como exemplo, a estrutura β -TCP (beta-trifosfato de cálcio), muitas vezes formada junto com a HA, pode se dissolver rapidamente no organismo e inviabilizar a osseointegração dos implantes ortopédicos.

Em se tratando do processo de jateamento ou spray com finalidade específica de recobrimento de implantes, alguns trabalhos se destacam. Wolline et al. (2015), por exemplo, utilizaram spray de plasma a vácuo para recobrir com titânio um substrato de UHMWPE. Apesar de utilizar argônio a baixa pressão (máximo de 600 mbar), a potência de plasma entre 5 e 30 kW propiciou velocidades de 100 a 1000 m/s para as partículas de titânio em pó que impactavam o polímero, obtendo-se um revestimento poroso com espessura entre 100 e 200 μm . Cheng et al. (2018) também utilizaram esse processo numa superfície de PEEK, obtendo porosidade de 35 a 60 % numa espessura de 60 a 150 μm , com rugosidade média Ra de 22.94 μm .

Já Tailor et al. (2019) utilizaram spray térmico com chama para deposição de PEEK em pó num substrato metálico, a fim de obter uma cobertura porosa de menor módulo de elasticidade que do substrato. O combustível foi injetado a 2 bar misturado com oxigênio a 2,8 bar e ar atmosférico a 2,8 bar, a uma distância de 30,5 cm da peça e com fluxo de polímero em pó de 25 g/min, resultado numa camada de 100 μm . Um processo semelhante havia sido feito por Chebbi

e Stokes (2012), que focaram na avaliação da espessura do revestimento, adesão, ângulo de molhamento e rugosidade, otimizando o processo de acordo com o ajuste das principais variáveis do processo: a velocidade de varredura, distância do bocal à peça e número de passes. Estas técnicas têm em comum a alta temperatura, que deve ser suficiente para fundir a carga e pode assim, também danificar o substrato.

Como forma de obter melhor controle do aporte térmico foi proposto numa dissertação (CAMPOS, 2021a) uma metodologia inovadora, através de um procedimento de jateamento adaptado que possibilitasse a incorporação de particulados cerâmicos na superfície de polímeros termoplásticos. Ao invés de utilizar reações químicas, hidrogéis, canais de plasma ou chama, emprega-se um fluxo contínuo de ar quente direcionado à peça polimérica para favorecer a resposta dúctil do polímero, jateado intermitentemente com uma mistura de ar frio e particulados de hidroxiapatita e/ou dióxido de titânio. A combinação dos fluxos quente e frio evita que o termoplástico aqueça excessivamente, mas mantém a sua superfície acima da temperatura de fusão (T_f) do polímero, facilitando sua deformação e incorporação das partículas no impacto. A principal vantagem é o menor custo e simplicidade dos equipamentos necessários para deposição dos particulados indutores de osseointegração. A técnica foi estudada e validada para os polímeros termoplásticos poliamida (PA6) e policarbonato (PC), com o sistema de controle e cabine de jateamento mostrados na Figura 1. O projeto possibilitou o controle dos fluxos de ar quente contínuo e ar comprimido intermitente, repetidamente acionado em intervalos constantes, além da movimentação da amostra.

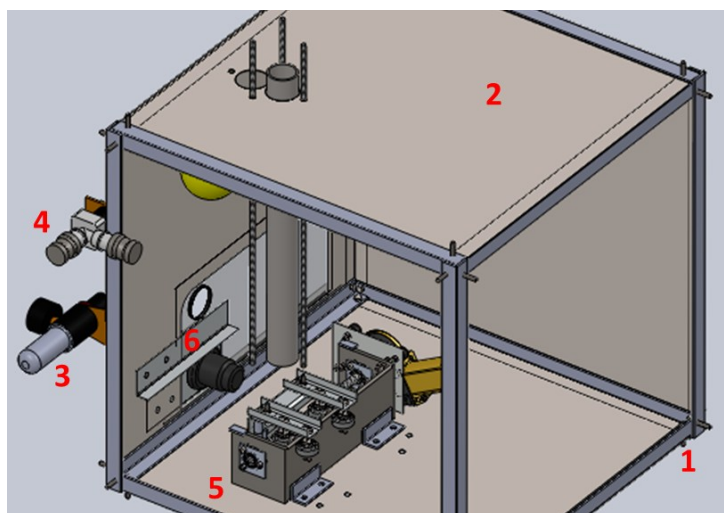


Figura 1 - Desenho da cabine de jateamento e dispositivos: (1) estrutura, (2) chapas, (3) filtro regulador de pressão, (4) válvula solenoide, (5) suporte da amostra, (6) soprador térmico.

(CAMPOS, 2021a).

O sistema de controle e aquisição de dados foi construído com base em Arduino, com sensores e atuadores compatíveis, e termopares tipo K, posicionados internamente e externamente na peça. Os primeiros medem a temperatura do polímero a 1 mm da superfície, enquanto os últimos medem a temperatura do ar que atinge a amostra, variando entre a

temperatura do ar quente e a temperatura do jato de ar comprimido, no momento em que seu fluxo é acionado.

A viabilidade de incorporação dos particulados na matriz foi investigada pelo estudo das interações entre as diversas variáveis de jateamento e as suas influências nas características mecânicas e tribológicas das peças. Na Figura 2 é mostrado o gráfico com os dados de controle e variações de temperatura dos termopares internos e externos posicionados junto às amostras durante os testes de jateamento para um ensaio (Ensaio 1). De forma geral, obteve-se boa regularidade na movimentação da amostra e acionamento intermitente dos jatos de ar comprimido, cuja pressão é mostrada na curva laranja. A curva verde, indica a corrente no motor (Imot) e, portanto, registra a direção de deslocamento da amostra (para esquerda quando Imot > 0 A e para direita quando Imot < 0 A). A curva cinza e a curva preta variam de forma sincronizada e representam, respectivamente, a corrente na resistência elétrica do soprador térmico (Isopr) e a temperatura do ar no bocal do soprador (Tsopr). As temperaturas dos termopares externos posicionados à esquerda (Text<) e à direita (Text>), representados nas curvas em azul, caem quando os jatos são liberados e sobem em seguida, na mesma frequência de oscilação da pressão. As curvas vermelha, laranja e amarela representam respectivamente, os termopares internos no lado esquerdo (Tint<), central (Tint=) e direito (Tint>) da amostra.

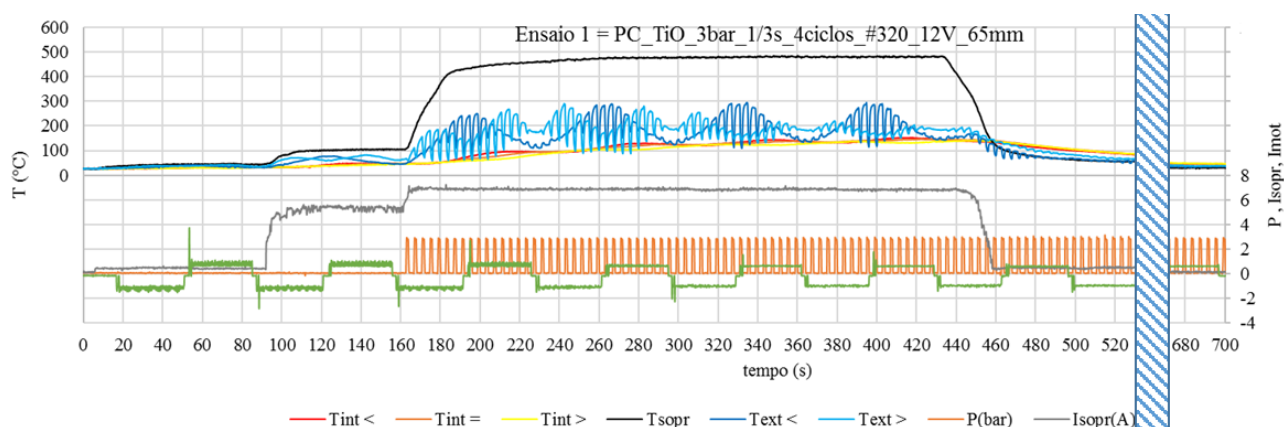


Figura 2 - Temperatura e dados de controle do ensaio de jateamento 1. (CAMPOS, 2021a).

Algoritmos de análise de imagem foram desenvolvidos no software Matlab 2018 para contagem de pixels e contabilização da espessura média das camadas depositadas nas amostras, bem como do percentual de recobrimento das superfícies por cada elemento químico. As imagens em modo BSD (Back Scattered electron Detector) e os mapas EDS (Energy-Dispersive X-ray Spectroscopy), obtidas por Microscópio Eletrônico de Varredura (MEV), foram processadas tal como mostrado nas Figuras 3 e 4, para geração dos resultados apresentados nas Figuras 5 e 6, respectivamente.

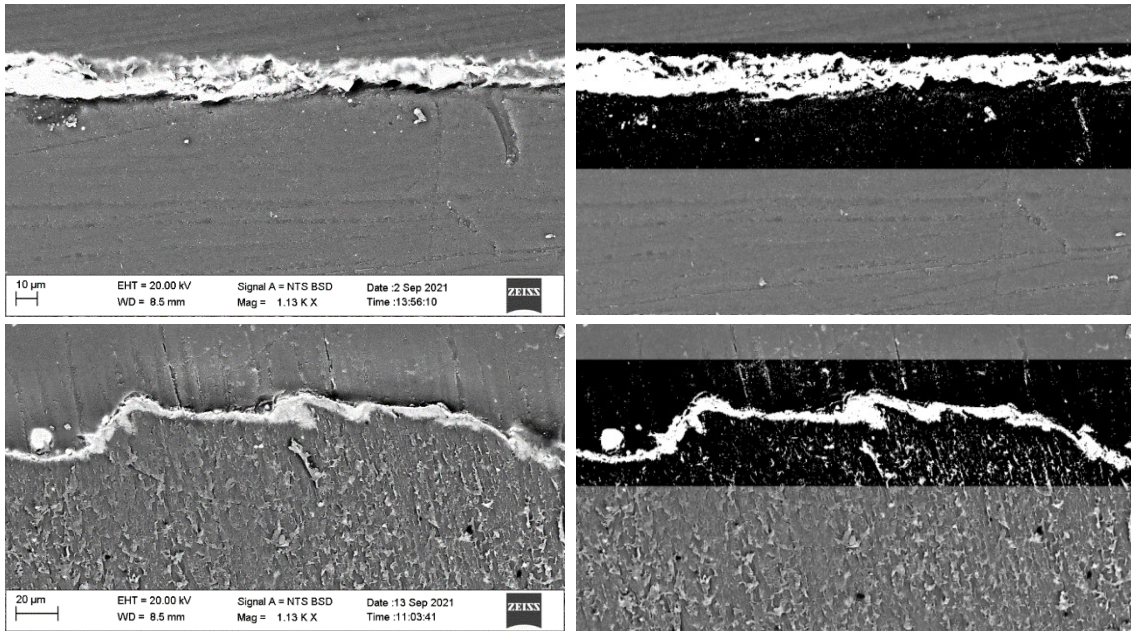


Figura 3 - Imagens da seção transversal de amostras jateadas por MEV no modo BSD, no qual a coloração da imagem varia conforme o número atômico dos átomos presentes em cada região. Nota-se a formação de uma camada distinta, devido ao sinal mais claro do Ca e Ti presentes nos particulados. Em (a) e (b), a camada depositada está entre o substrato e a resina usada no embutimento da amostra. Em (c) e (d), observa-se o processamento da imagem para contagem de pixels e cálculo da espessura média da camada. (CAMPOS, 2021a).

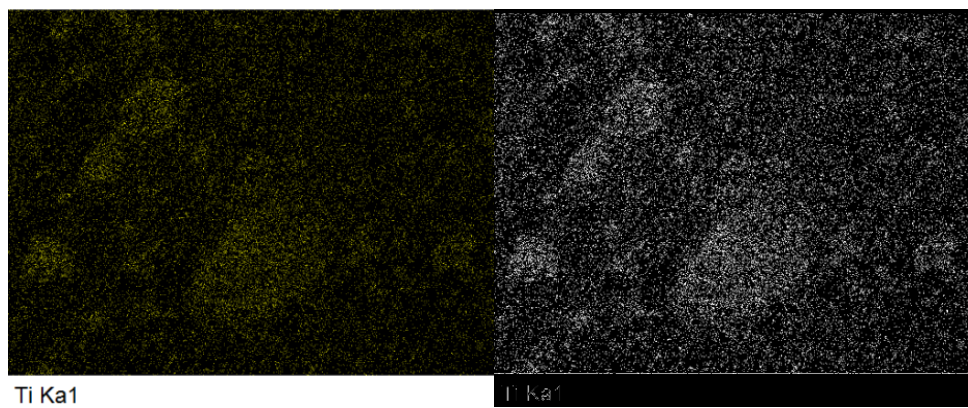


Figura 4 - Imagens em vista superior da superfície modificada, por MEV no modo EDS, mostrando o mapa de composição química para o titânio (a) em uma das amostras jateadas. (b) Imagem processada no algoritmo de análise de imagens para contagem do grau de recobrimento da superfície segundo a quantidade de pixels. (CAMPOS, 2021a).

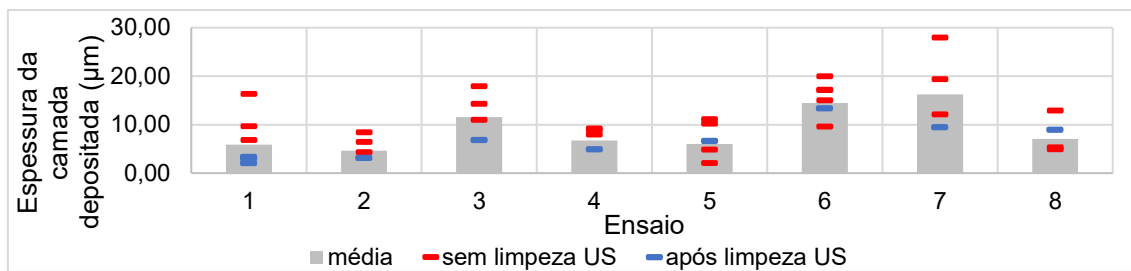


Figura 5 - Espessura da camada modificada calculada para cada foto da seção transversal obtida no MEV para as amostras jateadas. (CAMPOS, 2021a).

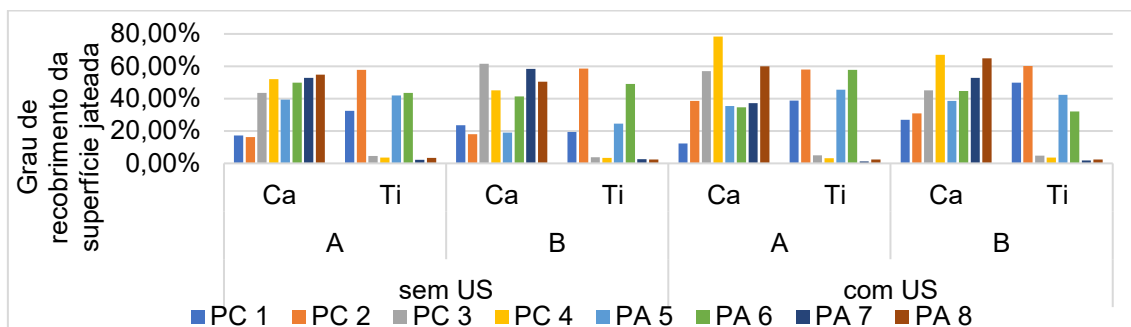


Figura 6 - Grau de recobrimento por Ca e Ti para amostras jateadas. (CAMPOS, 2021a).

Observa-se que embora o processo tenha tido sucesso na incorporação dos particulados cerâmicos, a espessura da camada depositada foi bastante irregular, variando de 2 a 28 μm dependendo da condição de jateamento. Além disso, embora os particulados tenham sido encontrados em até 78 % da área jateada, o grau de recobrimento ficou predominantemente na faixa de 40 a 60 %. Assim, fica clara a necessidade de otimização das condições de jateamento para melhoria da uniformidade e qualidade do revestimento, além de novos testes para verificar se a superfície compósita proposta teria características suficientes para promoção de osseointegração, visando a aplicação em implantes ortopédicos poliméricos.

2.5 MANUFATURA ADITIVA POR FFF E PÓS PROCESSAMENTO POR RECOZIMENTO

Um problema comum nas peças fabricadas por FFF é a menor resistência na interface entre as camadas impressas, devido à baixa adesão. Este fenômeno causa falhas sob uma variedade de condições de uso, incluindo tração (COLE et al., 2016), flexão (SUN et al., 2008), torção (RODRÍGUEZ et al., 2000) e compressão (PERCOCO et al., 2012), para os quais o carregamento pode ser estático ou de impacto. Neste último caso em especial, a falta de adesão entre as camadas facilita a nucleação e propagação de trincas entre as camadas (SHARAFI et al., 2021). Portanto, a força de ligação interlaminar de peças fabricadas aditivamente ainda é um dos principais obstáculos ao projeto e utilização das peças. Uma variedade de métodos tem sido empregada para melhorar essa adesão, incluindo otimização de parâmetros de impressão, como por exemplo: velocidade de varredura, temperatura da mesa de impressão, temperatura do bocal, taxa de deposição, entre outros (ALIHEIDARI et al., 2017). Outras alternativas incluem o

uso de algoritmos de altura de camada adaptativa (ALLEN e TRASK, 2015), adição de plastificantes (KO et al., 2019) ou espécies de baixo peso molecular (LEVENHAGEN e DADMUN, 2017) ao filamento, usar irradiação de microondas (SWEENEY et al., 2017), ou técnicas de pós-processamento, como recozimento (HART et al., 2018; BHANDARI et al., 2019).

De forma geral, o processo de adesão se relaciona com a difusão molecular das cadeias poliméricas de uma camada na outra, e por isso, depende fortemente de fatores como a fluidez e tensão superficial do polímero fundido, da temperatura da interface em relação a T_g , do tempo e pressão na interface das camadas, e de fenômenos relacionados a possível cristalização em alguns polímeros (BUTLER et al., 1998; THOMAS e RODRÍGUEZ, 2000). Durante a deposição, o polímero é aquecido a uma temperatura $T > T_g$ e, em seguida, extrudado sobre a camada previamente depositada que em muitos casos já resfriou abaixo da T_g , levando a uma variação rápida e repetida da temperatura da interface (SUN et al., 2008; SEPPALA et al., 2017). Este processo de transferência de calor é muito sensível às condições de impressão porque elas influenciam determinantemente no fluxo e distribuição do calor na peça ao longo do tempo (SEPPALA et al., 2017). A complexidade da história térmica representa assim mais um fator determinante para a boa adesão e tenacidade interlaminar. Outro ponto de interesse é o fenômeno de cristalização. Como a deformação dos polímeros depende da movimentação e estiramento das cadeias poliméricas, a resistência à tração, limite de escoamento, módulo de elasticidade e comportamento sob impacto dependem do teor de cristalinidade do material (MATYJASZEWSKI e MÖLLER, 2000).

Assim, a técnica de pós-processamento tem grande potencial para melhoria da qualidade mecânica das peças. Hart et al. (2018), por exemplo, reportaram um aumento de mais de 2700% na tenacidade à fratura interlaminar após o recozimento de peças de ABS, atingindo valores superiores a peças moldadas por injeção. Os autores construíram amostras na posição vertical, interrompendo o processo na metade para inserção de um filme fino de poliimida que funcionasse como entalhe para a propagação da trinca no ensaio de tenacidade à fratura. Devido à posição do entalhe, como mostrado na Figura 7, os autores mediram a tenacidade à fratura da interface entre camadas, obtendo assim uma boa referência para a adesão entre filamentos depositados.

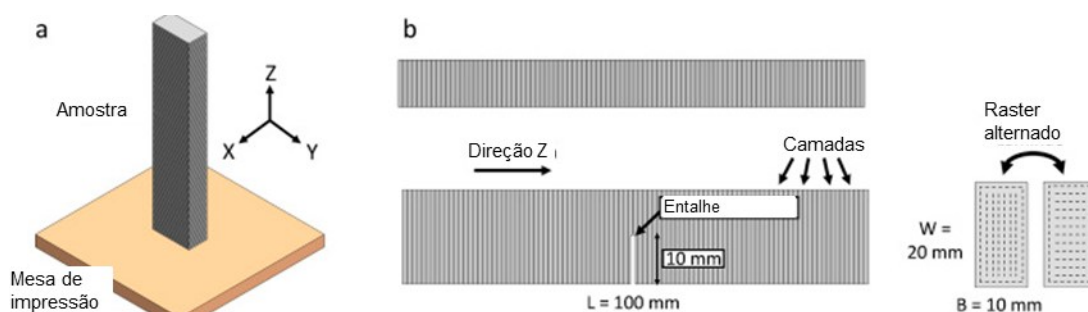


Figura 7 - (a) Posição vertical de construção do corpo de prova. (b) Posição do entalhe introduzido entre as camadas durante a fabricação das amostras, que são mostradas na posição do ensaio de tenacidade à fratura por flexão. Nota-se também o detalhe do sentido de deposição alternado nas camadas (HART et al., 2018).

Ensaio de tomografia também foram realizados antes e depois para verificar a forma dos interstícios (vazios e poros) entre as camadas e os possíveis efeitos do recozimento. Primeiramente, observa-se na Figura 8 que houve uma grande modificação na estrutura interna do material, no qual os vazios coalesceram cada vez mais à medida que o tempo e temperatura de recozimento aumentavam. Já a tenacidade à fratura passou de $260 \pm 80 \text{ J/m}^2$, com propagação de trinca instável e frágil para peça não recozida, para 7000 J/m^2 nas condições de recozimento mais agressivas, chegando a valores superiores a faixa típica de $.4000 \text{ J/m}^2$ a 6000 J/m^2 reportada na moldagem por injeção (LU et al., 1995). A análise de microestrutura revelou que os vazios e poros coalescidos provocam o desvio da trinca e reduzem a concentração de tensão pelo maior raio de arredondamento da descontinuidade, um mecanismo semelhante ao observado em alguns compósitos (HART e WETZEL, 2017). Nesse sentido, a porosidade típica do processo FFF, quando alterada para uma nova estrutura após o recozimento, pode inclusive apresentar benefícios em relação à peça maciça obtida no processo de injeção, mostrando o grande potencial do recozimento aliado à manufatura aditiva.

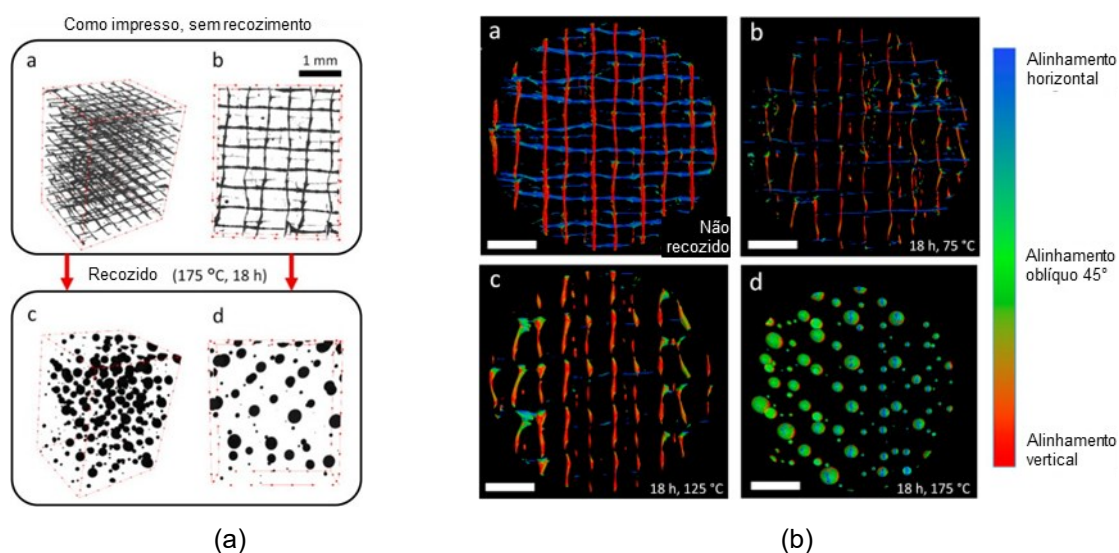


Figura 8 - (a) Estrutura dos interstícios modificada após o processo de recozimento. (b) Mudança do alinhamento dos vazios e poros, que antes orientados de acordo com o sentido de deposição e entre os filamentos depositados, coalescem e formam descontinuidades menos críticas. Adaptado de Hart et al (2018).

2.6 POLÍMEROS SEMICRISTALINOS E EFEITOS DA CRISTALIZAÇÃO

A compactação e ordenamento das cadeias poliméricas de forma paralela e lamelar diferencia os polímeros semicristalinos, que justamente devido ao menor espaço intermolecular e maior absorção da luz, apresentam-se geralmente opacos. Nem todas as cadeias conseguem se organizar, restando ainda uma porção amorfa entre os cristais (RUBINSTEIN E COLBY, 2003), que tem maior mobilidade e por isso é de grande importância para a deformação nos

polímeros. Por esse motivo, os polímeros semicristalinos apresentam em geral maior módulo de elasticidade, resistência ao desgaste, e maior resistência à tração em alguns casos (GOFMAN et al, 2013), embora isso também dependa da adesão interfacial, por exemplo. São exemplificados pelo PLA, PA, PCL, POM (poliacetal), e PEEK (VAES E PUYVELDE, 2021), todos disponíveis na forma de filamento para o processo FFF. Já os amorfos, além de terem maior resistência ao impacto pela maior capacidade de alongamento, amolecem substancialmente quando aquecidos acima da T_g, com uma ligeira queda da resistência mecânica (GOFMAN et al, 2013; KUTZ, 2011). Quando há a presença de cristais, devido a configuração de baixa entropia, estas estruturas só são desfeitas quando é ultrapassada a temperatura de fusão (T_m) do material, mantendo a rigidez desses materiais mesmo em temperaturas próximas à de fusão (MARK, 2007; PIORKOWSKA E RUTLEDGE, 2013). Isso se explica pelo fato de que os cristais servem também como barreira à deformação do material, impedindo a movimentação da fase amorfa. Sendo assim, os polímeros semicristalinos têm maior estabilidade térmica e são por isso mais desejáveis em aplicações com temperaturas de serviço elevadas (VAES E PUYVELDE, 2021). Além disso, essa propriedade permite a estimativa da cristalinidade desses polímeros através de testes semelhantes aos da norma ASTM D648 (2018), na qual é observada a partir de qual temperatura uma pequena viga bi-apoiada do polímero sofrerá deflexão para uma carga determinada. Para referência, no caso do PLA impresso 3D, sua T_g costuma situar-se em torno de 65 °C, com T_m próximo a 170 °C, embora esses valores possam modificar caso o PLA receba algum tratamento térmico (Campos et al., 2023).

Embora as técnicas de revestimento propostas tenham o objetivo primordial de criar um revestimento ou camada com particulados cerâmicos na superfície do polímero, pode-se ressaltar a possibilidade de melhoria das propriedades mecânicas devido ao calor inerente ao processo, seja no jateamento ou no recozimento em leito de pó. Dessa forma, é possível que essas técnicas de revestimento, além de melhorar a biocompatibilidade e osseointegração do polímero para uso em implantes ortopédicos, apresentem ainda incrementos na resistência à flexão e ao impacto dos implantes poliméricos impressos.

2.7 TESTES DE BIOCAMPATIBILIDADE PARA IMPLANTES POLIMÉRICOS OSSEOINTEGRÁVEIS REABSORVÍVEIS

Nos últimos anos, vários trabalhos investigaram a combinação de técnicas de manufatura aditiva para produção de *scaffolds* com compósitos reabsorvíveis, formados por mistura de polímero e particulados cerâmicos, que fornecessem uma estrutura de suporte para adesão e crescimento das células ósseas inicialmente, com degradação gradual do polímero e sua consequente substituição por matriz óssea, facilitada pela incorporação dos particulados cerâmicos. Em trabalho recente, Bernardo et al. (2022) demonstraram a viabilidade da utilização de filamentos compósitos para impressão pelo processo FFF, uma vez que o material não reduzia a viabilidade das células nos testes *in vitro*, um indicativo de que o material não provoca inflamação, sendo este um problema comum em outros tipos de implantes artificiais. Além disso,

foi verificada uma capacidade aumentada de diferenciação osteogênica das células tronco mesenquimais (CTM), fator importante para aceleração da recuperação do paciente. Para tal, diversos testes de biocompatibilidade foram feitos pelos autores, tal como o protocolo MTT no qual as CTM solubilizadas em meio de cultura foram plaqueadas sobre os materiais, avaliando-se a densidade celular pelo grau de absorção do brometo de 3-[4,5-dimetil-2-tiazol]-2,5-difenil-2H-tetrazólio (MTT). Essa substância é incorporada pelas células à medida que elas se multiplicam, e a densidade se correlaciona com o nível de absorbância óptica do fluido do meio de cultura, quando realizado o ensaio de espectrofotometria. A diferenciação das CTM em células ósseas foi verificada pela determinação da concentração da enzima fosfatase alcalina (ALP), que está associada à diferenciação osteogênica. Outro método utilizado foi a coloração com vermelho de alizarina, um corante que realça a presença da matriz óssea secretada pelos osteoblastos diferenciados a partir das células-tronco mesenquimais. A observação da matriz é feita por microscopia ótica, embora a quantificação também possa ser feita leitura da marcação por espectrofotometria. Estes são os testes *in vitro* mais utilizados para avaliação da biocompatibilidade de materiais para implantes (ALONSO-GOULART et al., 2021), tendo sido também utilizados por Medeiros et al (2021) na avaliação de *scaffolds* de nanofibras de vidro bioativo.

Existem diferentes tipos de células usadas nos testes de cultura, como osteoblastos fetais humanos (hFOB), osteoblastos humanos primários (HOB), células-tronco adultas derivadas do tecido adiposo humano (hADSCs), e linhagens de pré-osteoblastos MC-3T3-E1, entre outras. A escolha do tipo utilizado depende da finalidade do biomaterial testado e da disponibilidade das células. Os experimentos ficam cada vez mais fidedignos pela possibilidade de isolamento e cultura de células-tronco (MSCs, do inglês *Mesenchymal Stem Cells*) a partir de tecido adiposo (ADSCs), medula óssea (BMSCs) ou cordão umbilical (UC-MSCs) de humanos ou de qualquer outro animal. A capacidade de diferenciação osteogênica das ADSCs, pode variar de acordo com o meio de cultura utilizado, bem como pela adição de fatores que podem alterar as vias de sinalização e reduzir o tempo da diferenciação óssea, acelerando a osteogênese e consequente osteointegração (ALONSO-GOULART et al, 2018).

Ebrahimi et al (2022) também utilizaram estes ensaios para avaliação da biocompatibilidade de *scaffolds* de PCL produzidos por FDM e revestidos com colágeno e hidroxiapatita. A deposição foi feita por tratamento a plasma para melhoria da hidrofiliabilidade, seguido de imersão em solução de HA e colágeno para adsorção na superfície. Adicionalmente, os autores também avaliaram a composição química dos *scaffolds* por FTIR, XRD e EDS, técnicas de caracterização dos elementos químicos presentes na amostra de acordo com o espectro de radiação emitidos pelos átomos, após serem atingidos por um feixe de luz infravermelho, feixe de raios X e de elétrons, respectivamente. Embora estes testes sejam predominantemente químicos, eles também revelam informações importantes acerca do comportamento biológico dos materiais compósitos formados. Outra análise físico-química que funciona como bom indicador de biocompatibilidade é a avaliação da hidrofiliabilidade da superfície pela medição do ângulo de contato. Zhang et al (2021) utilizaram dessa técnica para caracterizar

um cilindro compósito de PLA e HA, para o qual o ângulo de contato foi de $0,7^\circ$, comparado a $90,3^\circ$ para o PLA puro. Isso evidencia o grande aumento de molhabilidade proporcionado pela presença de HA na superfície, obtendo-se alto nível de hidroflicidade, quando o ângulo de contato fica próximo a 0° . Essa característica é um bom indicativo para adesão celular em implantes osseointegráveis, já que superfícies hidrofílicas são mais favoráveis à adesão celular, embora seja possível que ângulos de contato muito baixos promovam a adesão celular, mas dificultem a motilidade celular e as funções celulares subsequentes (GITTENS et al., 2014).

Em estágios mais avançados de avaliação da biocompatibilidade, a capacidade funcional do material pode ser testada em condições *in vivo*, sobretudo através da implantação em animais, como ratos, coelhos e cabras. Cao et al. (2017) avaliaram o desempenho de implantes ortopédicos para substituição de disco vertebral, fabricados a partir de uma mistura de PLA com fosfato tri-cálcico (TCP), implantados em cabras. A fusão intervertebral foi avaliada ao longo de 12 semanas por radiografia, com posterior análise histológica por histomorfometria para quantificação da área de fusão óssea. Foi observado melhor desempenho dos materiais compósitos em relação as alternativas tradicionais, como o implante de osso autólogo e implantes comerciais em PEEK.

2.8 OTIMIZAÇÃO DE SISTEMAS MECÂNICOS

Em se tratando de processos de fabricação, frequentemente as variáveis de saída que caracterizam um produto ou processo podem ser empiricamente correlacionadas com os parâmetros de processamento. No caso do processo de jateamento, por exemplo, a espessura do revestimento poderia ser descrita como função da pressão de ar comprimido, DBCP, tempo de jateamento e intermitência do jato, para um dado conjunto de resultados experimentais. Já para o recozimento, a resistência à flexão ou ao impacto poderia ser também descrita em função do tempo e temperatura de recozimento, a partir dos dados colhidos em experimentos. Para tal, é necessário determinar um modelo matemático que modelará o experimento, podendo este ser linear, polinomial ou exponencial, por exemplo, e depois realizar uma regressão multivariável para descobrir os valores dos fatores associados a cada variável. Isso permitiria não só a previsão de como a mudança das variáveis de entrada afetaria a variável de saída, mas também a otimização do produto ou processo. Nesse sentido, o problema de otimização consiste em maximizar ou minimizar uma função no domínio real escolhendo sistematicamente valores de entrada de um conjunto permitido e computando o valor da função. Como explicado por Lobato (2008), a otimização visa determinar a melhor configuração de projeto, sem a necessidade de testar todas as condições de entrada, com o potencial de analisar uma grande quantidade de variáveis e restrições de difícil visualização gráfica. Quanto a classificação, segundo Haupt e Haupt (1998), podem ser do tipo uni ou multidimensional, mono ou multiobjetivo, restrito ou não restrito, entre outros.

Embora testes práticos ainda sejam a forma mais comum de estudar os processos de fabricação, existem várias tentativas de modelar os resultados encontrados a fim de determinar

os parâmetros ótimos de operação. Dentre as possíveis estratégias, tem-se o exemplo da Equação de Taylor para vida da ferramenta de usinagem, representada na Equação 1 (DOS SANTOS et. al., 1998), no qual a vida útil da ferramenta T é função da velocidade de corte V_c , avanço f , profundidade de corte ap , desgaste de flanco da ferramenta VB , para determinadas condições experimentais representadas pela constante K (material, ferramenta, máquina, lubrificante). Outras grandezas, como a força de corte, também podem ser modeladas através de equação similar (BARROW, 1971), fazendo-se a analogia de que variam de forma exponencial também. Essa premissa tem base nas observações experimentais, de forma que a função utilizada seja válida para todo o domínio ou pelo menos um intervalo das variáveis.

$$T = K \cdot V_c^a \cdot f^b \cdot ap^c \cdot VB^d \quad (1)$$

Com base nesse princípio, Da Silva e Campos (2021) levantaram a equação de Taylor adaptada para representar a força de corte em função da velocidade de corte, avanço e desgaste de flanco da ferramenta no torneamento do Inconel 718 em diferentes condições de refrigeração MQL, sendo registrada a força de corte através de um dinamômetro piezelétrico. Utilizando-se os métodos dos mínimos quadrados, através dos dados experimentais foi montado um problema de otimização clássica com objetivo de minimizar a diferença entre a força medida e a força calculada segundo a equação, fazendo-se um processo iterativo para ajustar os coeficientes da equação. A função objetiva foi otimizada pelo Método da função Penalidade Interna (VANDERPLAATS, 1999), o qual é utilizado para resolver problemas multidimensionais restritos e que consiste na utilização das restrições para deformação da função em torno de uma referência e sua consequente transformação num problema multidimensional irrestrito. Esse último pode ser resolvido por diferentes estratégias, como Método de Newton, das Direções Conjugadas ou da Máxima Descida, por exemplo. Neste caso foi usado Método da Variável Métrica, que consiste na transformação do problema multidimensional em um equivalente unidimensional com aproximação do inverso da matriz Hessiana durante o cálculo da direção de busca. Este último problema fica dependente apenas do passo de busca α^* , o qual foi calculado pelo Método da Seção Áurea a cada iteração.

De maneira similar, essa técnica de otimização multivariável também poderia ser aplicada aos processos de jateamento e/ou recozimento, a fim de descobrir as condições ótimas de processamento que produzissem o revestimento mais espesso, ou que levasse ao maior ganho da resistência das peças à flexão, ou ao impacto, por exemplo.

2.9 SÍNTESE E RELAÇÃO COM OS OBJETIVOS DA PESQUISA

A revisão bibliográfica apresentou os fundamentos científicos e tecnológicos que sustentam esta tese, voltada ao aprimoramento de peças poliméricas produzidas por manufatura aditiva e revestidas com cerâmicas bioativas. O conjunto de temas abordados demonstra como a combinação entre processamento térmico e funcionalização superficial pode otimizar as

propriedades mecânicas, químicas e biológicas dos materiais propostos para uso em implantes personalizados.

A análise sobre a manufatura aditiva por FFF evidenciou seu potencial na criação de dispositivos biomédicos personalizados, com elevada liberdade geométrica e baixo custo. Contudo, os desafios relacionados à adesão interlaminar, anisotropia estrutural e limitações térmicas do PLA justificam a necessidade de pós-processamentos. Nesse contexto, a discussão sobre o recozimento de polímeros semicristalinos foi fundamental para compreender como o aquecimento controlado acima da temperatura de transição vítrea pode reduzir tensões internas, aumentar o grau de cristalinidade e melhorar a estabilidade dimensional, resultando em maior rigidez e resistência térmica.

O estudo do recozimento mostrou-se particularmente relevante, pois fundamenta a abordagem inovadora desta pesquisa: combinar o tratamento térmico à incorporação de pós bioativos, obtendo simultaneamente o recozimento e o revestimento funcional da superfície polimérica. Essa estratégia elimina etapas adicionais de deposição, reduz gradientes térmicos e favorece a uniformidade do recobrimento, constituindo um avanço em relação aos métodos convencionais aplicados a substratos poliméricos.

A revisão também destacou a importância dos revestimentos bioativos, especialmente os compostos por hidroxiapatita (HA) e dióxido de titânio (TiO_2), amplamente utilizados em engenharia de tecidos por promoverem osteocondução, bioatividade e resistência à corrosão. O entendimento dos mecanismos de adesão cerâmica/polímero, das reações de interface e das alterações na rugosidade e molhabilidade é essencial para avaliar a biocompatibilidade e o desempenho das superfícies tratadas. Esses conhecimentos se alinham diretamente ao objetivo de otimizar a resposta biológica dos implantes desenvolvidos, favorecendo a interação célula-material e a integração óssea.

Assim, os conceitos revisados permitem compreender a inter-relação entre processamento, estrutura e propriedades, que é o eixo central desta tese. O recozimento atua como uma ferramenta de engenharia térmica para melhorar o desempenho mecânico do PLA, enquanto o revestimento com materiais bioativos representa uma estratégia de engenharia de superfície voltada à funcionalização biológica. A integração desses dois campos permite superar limitações intrínsecas do polímero e ampliar seu potencial de aplicação em dispositivos ortopédicos. Em síntese, a convergência entre os conhecimentos de ciência dos materiais, manufatura aditiva e bioengenharia consolida o caráter inovador e interdisciplinar desta tese.

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CAPÍTULO 3

3. METODOLOGIA

De acordo com os objetivos estabelecidos, foi traçada uma metodologia que permitisse obter as informações desejadas através de vários conjuntos de experimentos, os quais foram organizados para artigos preparados durante o doutorado (alguns já publicados). Dessa maneira, na Figura 9 é apresentado um fluxograma para facilitar o entendimento da estrutura da tese.

No Artigo 1 (Capítulo 4) foi estudado como os parâmetros de impressão – espessura de camada, espessura de casca (paredes) e *infill* – afetavam a resistência da peça. Nesse momento, a tecnologia de recozimento, aplicável apenas em peças maciças, ainda não havia sido hipotetizada, e assim julgou-se válido verificar o que contribuiria mais para a resistência das peças: o *infill* ou as paredes da amostra. No Artigo 2 (Capítulo 5), já utilizando peças maciças tendo em mente o provável enfoque do estudo no recozimento, foi investigado como os parâmetros térmicos de impressão influenciariam as peças. Com a revisão bibliográfica já feita nesse momento, sabia-se que a distribuição de temperatura durante a impressão poderia influenciar a cristalinidade, e conseqüentemente, as propriedades mecânicas.

Já o Artigo 3 (Capítulo 6), foi feito com base na necessidade de avaliar a confiabilidade de equipamentos que estavam sendo desenvolvidos, particularmente o tribômetro para execução dos testes de esclerometria de carga progressiva, para medição da adesão do revestimento. Nesse trabalho foi levantada a curva de erro e incerteza de medição das células de carga utilizadas, para verificar sua adequabilidade como instrumento de medição.

No Artigo 4 (Capítulo 7) e Artigo 5 (Capítulo 8) foi estudado como o pós-processamento por recozimento simples (com peças colocadas no forno em temperaturas menores, sem leito de pó) afetaria a resistência das peças. Nesse momento, a tecnologia de recozimento por leito de pó já havia sido pensada e os primeiros pré-testes estavam sendo feitos. Assim, considerou-se válido estudar melhor o pós-processamento por recozimento simples, que segundo a literatura, oferecia grandes potenciais de melhoria das propriedades mecânicas.

Após alguns pré-testes, estabeleceu-se as condições ideais para avaliar o processo de recozimento em leito de pó e como os parâmetros de entrada influenciariam no revestimento e substrato, levando em consideração também a biocompatibilidade das peças. Isso justificou a realização de uma investigação mais completa do que as anteriores, que culminou na produção dos Artigo 6 (Capítulo 9), Artigo 8 (Capítulo 11) e Artigo 9 (Capítulo 12). Uma vez que objetivava-se também a comparação desse processo com o jateamento idealizado em trabalhos anteriores, foi realizada a metodologia do Artigo 7 (Capítulo 10), que infelizmente não produziu amostras aceitáveis para comparação aprofundada com o recozimento em leito de pó.

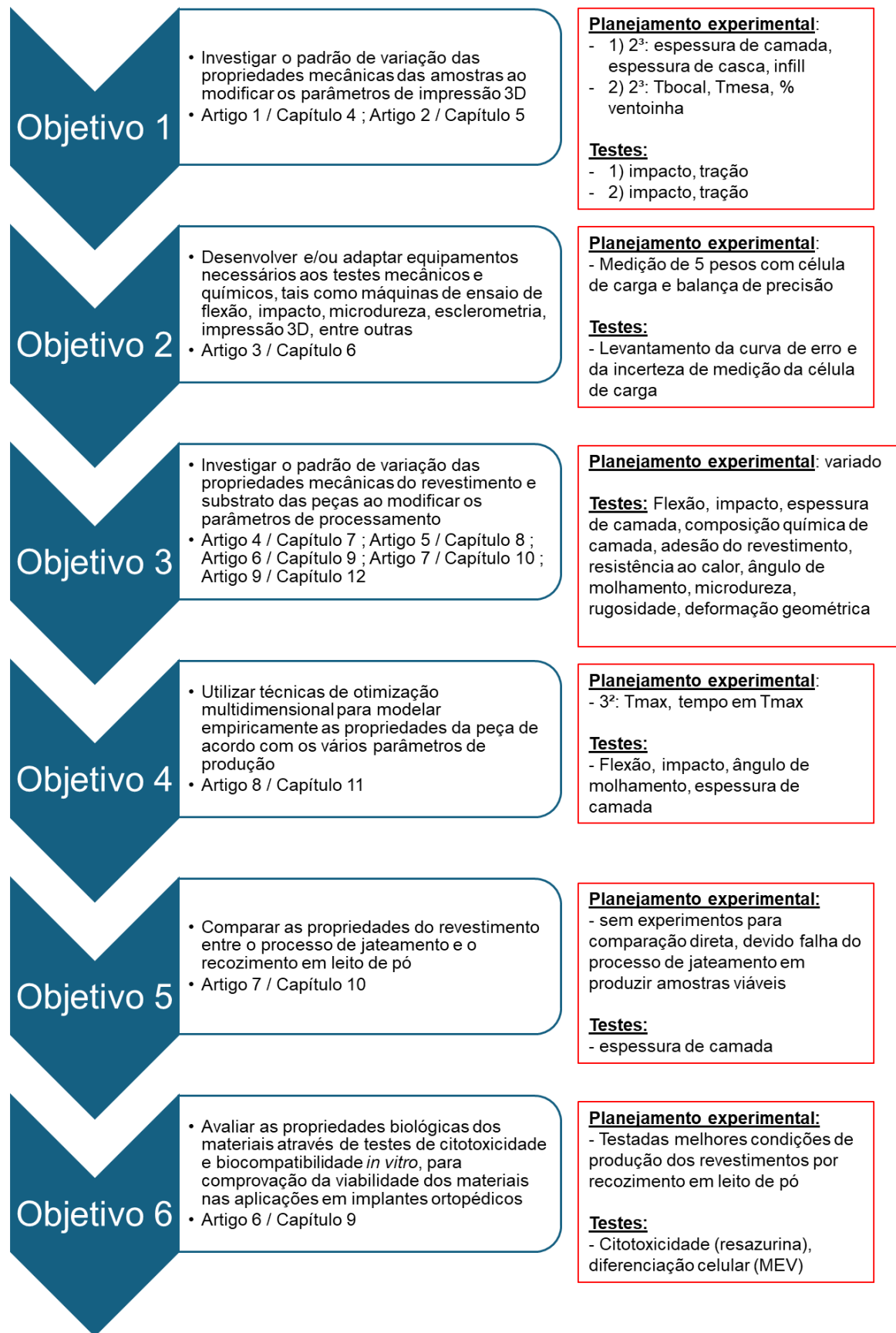


Figura 9 – Fluxograma apresentando a sequência dos objetivos e grupos de experimentos realizados, os quais embasaram os artigos preparados, apresentados em cada capítulo.

CAPÍTULO 4

4. ARTIGO 1

de Oliveira Santos, T., de Almeida, K.F., Okada, K.F.Á., Rodrigues Campos, F., da Silva, L.R.R., Machado, Á.R. (2024). Influence of Printing Parameters on Impact and Tension Resistance of Parts Produced by the Fused Filament Fabrication Process. In: de Oliveira, D., Ziberov, M., Rocha Machado, A. (eds) ABCM Series on Mechanical Sciences and Engineering. COBEF 2023. Lecture Notes in Mechanical Engineering (). Springer, Cham. https://doi.org/10.1007/978-3-031-43555-3_15

Influence of Printing Parameters on Impact and Tension Resistance of Parts Produced by The Fused Filament Fabrication Process

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Abstract. Additive manufacturing by the Fused Filament Fabrication (FFF) process is a manufacturing process that has great potential for facilitating the production of complex and customized parts quickly, with low production costs and little material waste. However, the mechanical resistance of the parts produced by this manufacturing method vary greatly according to printing parameters, especially when they are not bulk solid. It was observed in this work how the impact and tensile resistance of a part change according to the thickness of the shell, height of the printed layer and the infill since these factors alter the moment of inertia and thermal loads. For instance, it is hard to predict if the mechanical properties will improve when increasing shell thickness and reducing infill, or vice versa. Specimens were then produced following a complete factorial design for these 3 variables at 2 levels, and then an analysis of variance was performed with the data from tensile strength tests according to ASTM D638 and impact resistance according to ASTM D4508. Shell thickness was shown to be the most influential and advantageous.

Keywords: Shell Thickness, Layer Height, Infill, Mechanical Strength, Moment of Inertia.

FIRST SECTION

In recent years, with the advancement of engineering, additive manufacturing has evolved so that it is no longer used only for rapid prototyping and 3D representation of designs, but also used as a manufacturing method capable of directly producing final parts. In this way,

additive manufacturing has been benefiting several areas beyond mechanics such as dentistry [1], medicine [2] and architecture [3], with its capacity to produce parts in small quantity faster, simpler, cheaper and with less waste of material than other means of manufacturing, making it the best option for production of customized parts with a high level of complexity.

Additive manufacturing by the Fused Filament Fabrication (FFF) process consists of extruding a fused filament through a mobile nozzle responsible for designing the part layer by layer using data from a 3D computational model as a basis. The materials most used in this method of production are thermoplastic polymers due to their melting point between 150 °C and 250 °C and satisfactory mechanical properties at room temperature, with some examples of widely used materials being ABS, PLA and PETG.

Due to the part being printed layer by layer, its mechanical properties are directly related to the adhesion between the deposited filaments and between the layers formed by them, and the lack of adhesion might facilitate the nucleation and propagation of cracks that cause material premature failure [4]. Thus, parts produced by additive manufacturing have strong anisotropy, with reduced resistance in the build direction that led to failures in tensile tests [5, 6], torsion [7], compression [8, 9] and flexural tests [10]. For this reason, this remains one of the major obstacles and research topics in additive manufacturing.

The adhesion between the extruded polymeric filaments is based on the molecular diffusion of the polymer chains from one filament to the other and the intertwining between them, and this diffusion depends on the thermal history in the printed part [10]. When the filament is extruded, it loses thermal energy to the environment and to the other layers, and the longer it remains at a temperature above the glass transition temperature of the polymer, more the polymer chains will diffuse between the extruded filaments and intertwine. In addition, a higher temperature induces greater fluidity and wettability of the deposited material, which consequently generates a larger contact area between the filaments, as shown in Fig. 1a. This effect is visible in Fig. 1b, which also shows how the spaces between the deposited filaments are smaller in the bottom layers, which receive heat from the printing table for longer, ensuring more time for diffusion and adhesion of the layers.

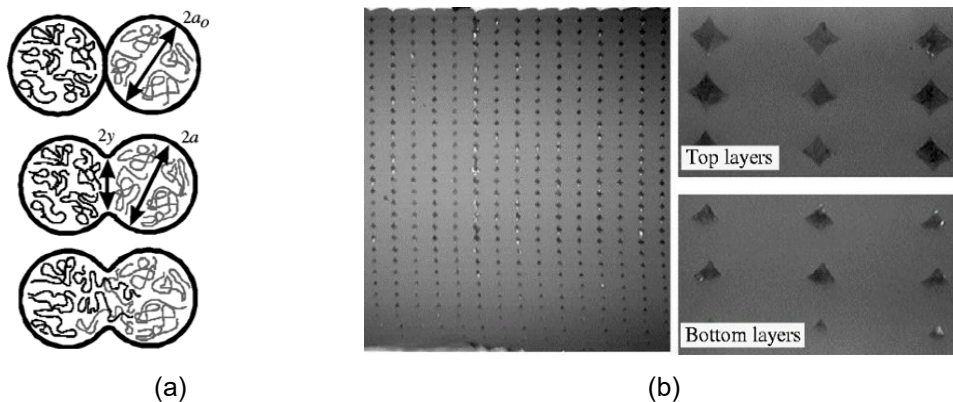


Fig. 1. (a) Mechanism of adhesion between the deposited layers, dependent on the intertwining of the polymeric chains. (b) Larger voids and lesser contact area between filaments in the top layers compared to the bottom layers. Adapted [10].

Due to this phenomenon, many researchers aim to increase the mechanical strength by other means, leaving the part less vulnerable to the thermal effects intrinsic of this manufacturing method. When designing a part to be printed, attention should be paid to the infill and the thickness of the part's shell, as one of the benefits of 3D printing is precisely the ability to produce parts without necessarily being massive. These two parameters directly influence the moment of inertia of the designed part, which is given by the integral sum of the mass of each point of the part times the square of the distance to the centroid. Thus, considering the rectangular cross section of a tensile test specimen for instance, theoretically the regions furthest from the center contribute greater for the resistance. Therefore, a greater wall thickness and increased bottom and top layer numbers may be more advantageous than a larger infill to increase mechanical strength.

In addition to these two parameters, another important parameter to evaluate when designing a part is the layer height, as observed in the literature [11, 12, 13]. It is known that a lower layer height is related to an increase in the mechanical resistance of the manufactured parts, in addition to resulting in a better finish and decreasing the interstitial spaces between the filaments shown in Fig. 1b, which consequently increases the density and mechanical resistance. However, it must also be considered that a lower layer height, just like a higher percentage of infill and thicker shell increases considerably the production time, while the last two parameters also increase the filament consumption.

In this way, as each of these parameters has its advantages and disadvantages, it necessary to study how influential they are to allow optimization of the mechanical properties, printing time and filament consumption of parts produced by the FFF process. This research employed a complete factorial design, with three variables at two levels each, to produce the tensile test and impact test specimens. It was found that the combination of these factors may lead to unforeseen results, such as lesser mechanical resistance when increasing infill. It was explained how the printing time could lead to this behavior, since it affects the thermal history of the samples.

METHODOLOGY

Sample Preparation

The impact and tensile tests were carried out with samples of polylactic acid (PLA), and the filament used was uncolored PLA from 3DFila. This is important because other works have shown that pigment loading may affect mechanical resistance of the polymer [14]. The specimens were produced FFF using a Creality Ender 3 3D printer and Ultimaker Cura Slicer Software. The input parameters evaluated were layer height, shell thickness and infill. Shell thickness is not a readily defined parameter in Cura, which allows for changing separately the wall thickness, bottom layer number and top layer number. The values were chosen so that a regular thickness could be obtained in all sides of the samples. The output parameters were the energy absorbed by the

sample, the maximum tensile strength, the printing time, and filament consumption, with the last two as yielded by the printer in the slicing software. The full factorial design resulting in the 8 printing conditions is presented in Tab. 1.

Table 1. Factorial experimental design 2³.

Condition	Layer height [mm]	Shell thickness [mm]	Infill [%]
1	0.1	0.8	40
2	0.1	0.8	60
3	0.1	1.2	40
4	0.1	1.2	60
5	0.2	0.8	40
6	0.2	0.8	60
7	0.2	1.2	40
8	0.2	1.2	60

The parameters were chosen with a difference of 50% (1.2 mm/0.8 mm of shell thickness and 60%/40% of infill) as it is already known that a much greater infill or shell thickness would increase the mechanical strength. Therefore, the intention was to observe whether small changes in these parameters would affect the results, and the significance of one parameter in relation to the others. It is noteworthy that the layer height did not change by 50%. In this case, since the test specimen thickness of 3.2 mm is suggested by the standards, this number should be a multiple of both chosen layer height values. Otherwise, the 3D slicing software could round off the values and affect the final dimension of the specimen.

For each printing condition presented in Tab. 1, three specimens were produced for the two mechanical tests performed, totaling 48 specimens produced. Although ASTM D256 and ASTM D638 recommend evaluating at least 5 samples for each test condition, there were time and resource constraints during sample fabrication.

Although printing several samples together would be faster, each part was printed individually to standardize the heat received from the table for each sample after it is printed. This is especially important because the higher thermal intake could provide more time for the polymer chains to diffuse and lead to inaccuracies in the results. In addition, the other printing parameters were fixed for all specimens, being equal to the default settings of the slicer software configured for this printer used and for generic PLA. For instance, the temperature of the extruder nozzle and the temperature of the printing table were, respectively, 200 °C and 50 °C.

Impact Tests

The Izod type C impact tests were carried out in accordance with the recommendations of the ASTM D256 standard, using specimens with the dimensions shown in Fig. 2. It is also worth noting that the impact specimens were printed with the orientation of the layers as shown in Fig. 3. Although the standard states that the notch should be machined, it was already defined in the

CAD model for printing. Since it might affect the results due to differences in residual tensions and surface integrity [15], the results should only be compared in between the conditions, and not to samples with machined notches from other works.

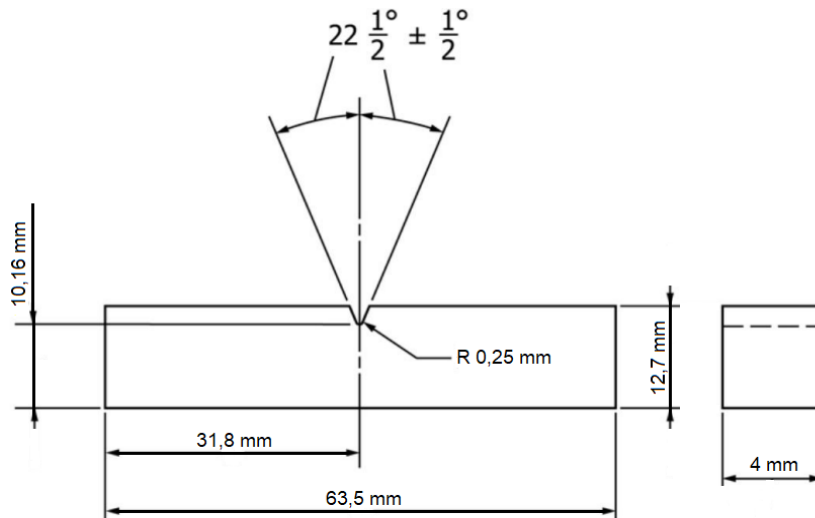


Fig. 2. Example of specimen for Izod type C tests (ASTM D256).

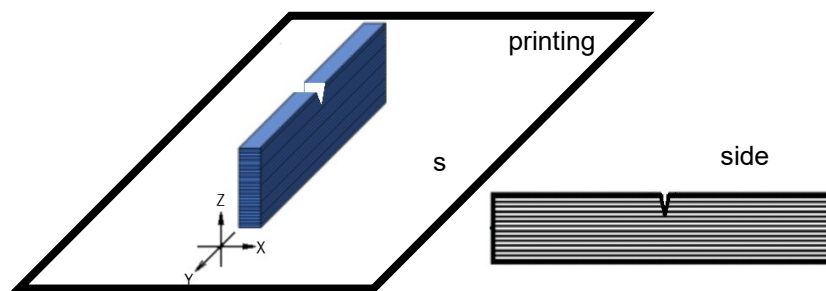


Fig. 3. Orientation of layers used in impact specimens. Adapted from Patterson et al. (2019).

The impact tests were performed on an impact testing machine adapted from other work [16], using a pendulum with a mass of 0.99 kg and a length of 0.778 m, which resulted in a pendulum energy of 1.79 J, releasing it from rest from an inclination of -30° with the horizontal, for all tests. Under these conditions, the tip of the bar impacted the samples with a velocity of approximately 4 m/s, which provides an idea of the shear rate on the material.

Tensile tests

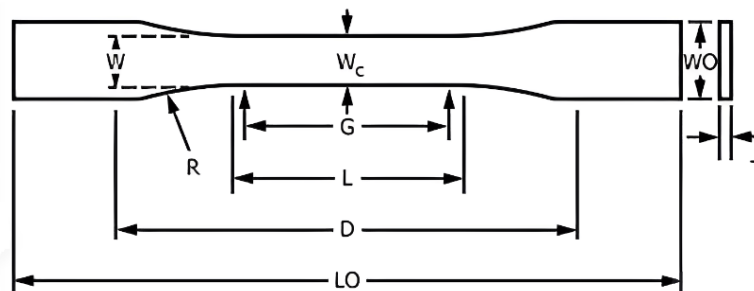


Fig. 4. Specimen for V-type tensile tests. The dimensions are defined in ASTM D638-14.

The tensile tests were carried out following the recommendations of ASTM D638-14 standard, with 4 mm thick V-type specimens, as shown in Figure 4. However, unlike the impact specimens, the tensile specimens were printed with their largest side parallel to the printing table. Even so, it is noteworthy that in both tests the main forces act in the longitudinal direction of the sample, aligned with the direction of the deposited layers. This is evident in the tensile test, and can also be seen in the impact test, where the fracture results from the flexion and stretching effect of the layers.

To carry out the tensile tests, a Pavitest 5T I-4214 hydraulic universal machine was used, with electrical control and a test speed of 0.1 mm/s. The acquisition system used was based on an adapted digital load cell, with a nominal range of 0 to 50 kg and a resolution of 0.01 kg.

RESULTS AND DISCUSSION

Impact Tests

Fig. 5 shows the energy of impact absorbed by the samples, where it can be observed that the specimens with greater shell thickness absorbed more impact energy in relation to the other specimens. This is expected, due to the thicker shell generating an increase in the resistant section and moment of inertia, with the outer regions being more important for the mechanical resistance during the bending of the sample. This becomes more evident when observing that even dividing the resistances by the masses of the test specimens, the parts with greater shell thickness had greater resistance compared to the others.

Contrary to expected, the infill did not show major changes, which may be related to how the load is distributed when applied to the specimen. It is likely that the impact of the pendulum generated greater tensions in the outer region of the part, with the filling being less relevant for part resistance.

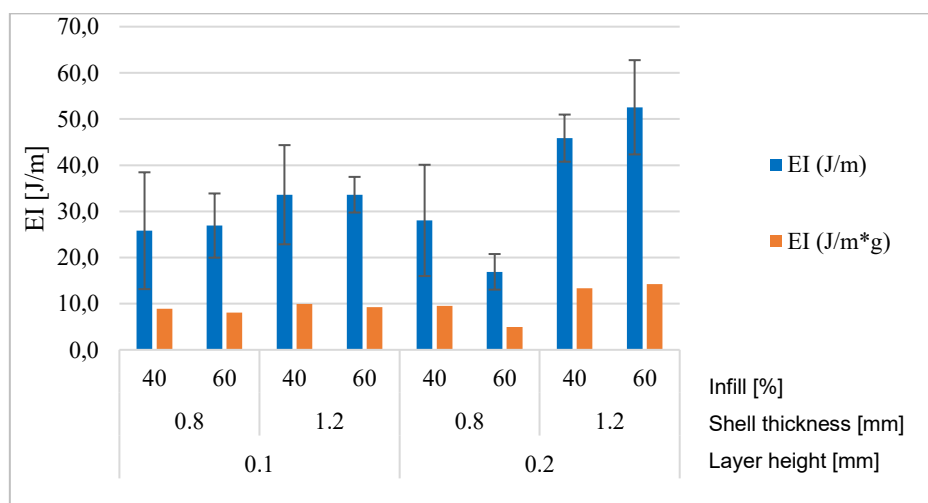


Fig. 5. Variation of energy of impact (EI) absorbed by the samples for each printing condition.

Table 2. Printing time for each combination of parameters in the impact test.

Layer height [mm]	Shell thickness [mm]	Infill [%]	Print time [min]
0.1	0.8	40	52
0.1	0.8	60	59
0.1	1.2	40	59
0.1	1.2	60	66
0.2	0.8	40	26
0.2	0.8	60	30
0.2	1.2	40	30
0.2	1.2	60	33

The influence of the layer height was different from what was expected, although it was not so significant. Instead of increasing the mechanical resistance with a lower layer height, a decrease in the resistance of some parts is observed. Initially, it was expected that a lower roughness together with smaller interstitial spaces, resulting from a lower layer height, would yield less stress concentration and better adhesion between layers due to prolonged exposure to heat, considering the longer production time of these parts. However, the higher thermal intake might have been enough to make the part less ductile due to the crystallization of the polymer chains [17], which is negative for impact strength, where ductility is important. It can be observed that the production time of the parts with lower layer height is almost twice as long as the others, which means that the material spends much more time receiving heat from the nozzle and the printing table, which could be enough to change the properties of a low glass transition temperature thermoplastic such as PLA [4].

In addition, the fact that a higher layer height did not worsen the impact resistance may be related to the build print being perpendicular to the impact direction, which would make the roughness effect insignificant, since the notch already served as a much more relevant stress concentration point. In the graph it can also be seen that in some cases with similar parameters, where the infill was the only difference, parts with 40% infill had better results, which differs from the results found in the literature and can also be explained by this greater temperature exposure time, due to longer production time with longer infill. Tab. 2 presents the printing time for each combination of parameters of the impact specimens.

These observations are in line with the effects observed in Fig. 6, obtained by analysis of variance (ANOVA), performed with Statistica 12 software. The data shows that shell thickness and the combination of shell thickness with layer height are the only factors that were significant for a confidence interval of 95 %, and shell thickness has a much greater significance than the other factors and combinations.

Also, it is interesting to note that the results of Figure 5 are much lower than other results in the literature, such as the 113.21 J/m found by Patterson et al. (2019) in Izod tests performed on PLA. Again, this can be explained by the difference in notch fabrication, since machining induces compression residual stress that difficult crack formation. However, the most important

factor in this case would be that these authors used solid samples with 100 % infill and that the Izod test used was type E, where the pendulum hits the specimen on the opposite side to the chamfer.

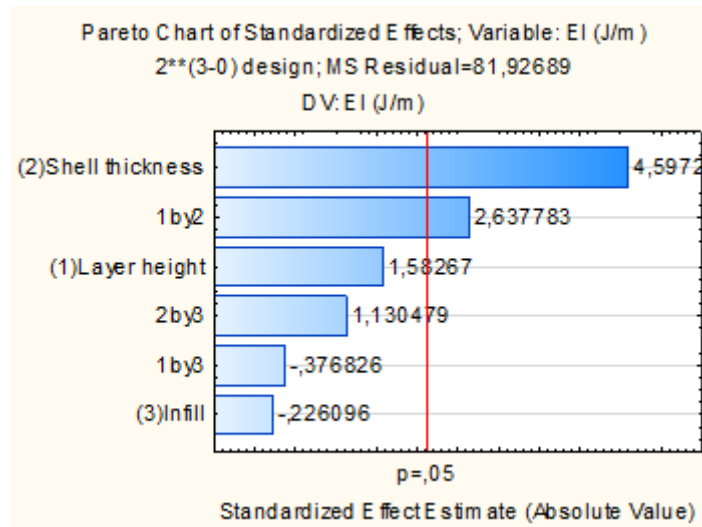


Fig. 6. Pareto chart from ANOVA showing significance of factors for energy of impact (EI).

Tensile Tests

The variations in the maximum tensile strength for the different printing conditions are shown in Fig. 7 and are within the range of values expected for PLA in the literature [18]. It is evident that all test specimens with greater shell thickness presented higher rupture stress, as previously observed with the impact tests. This is expected, since the tensile test was carried parallel to the main axis of the part, in which shell filaments are aligned. This increases the resistance due to a higher moment of inertia, regardless of the adhesion between layers. This observation is reinforced with the results obtained from ANOVA, which are shown in Fig. 8, confirming that the shell thickness really has a much greater influence compared to the other parameters.

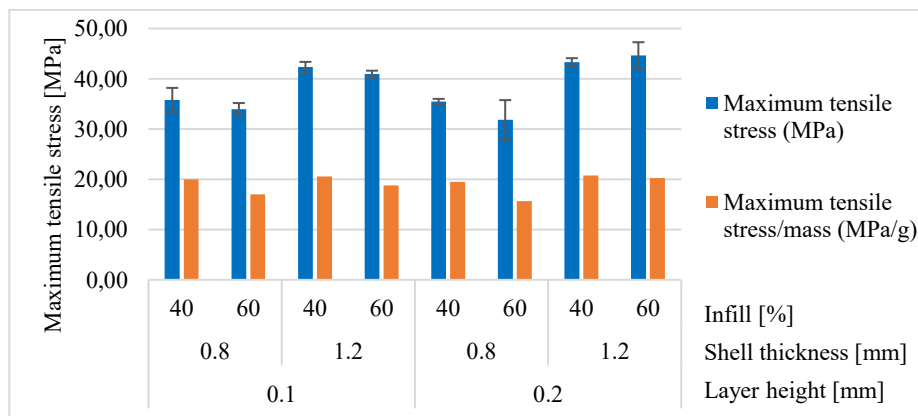


Fig. 7. Variation of maximum tensile stress for each combination of variables.

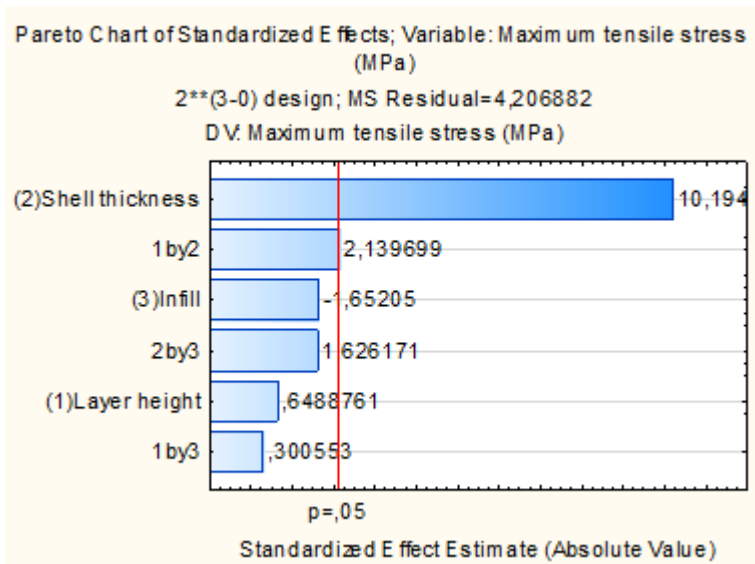


Fig. 8. Pareto chart showing significance of factors for the maximum tensile stress.

It can also be seen that shell thickness and its combination with the layer height were again the only statistically significant factors for a confidence interval of 95%. From the graph in Figure 7, it can also be noted that many parts with 40% infill showed better results compared to conditions with 60% infill and the same layer height and shell thickness, which is counter intuitive at first. In Tab. 3 it can be observed that the printing time was slightly shorter for the more resistant parts, which may indicate that exposure to temperature may have again impaired the results in the tensile tests, as well as in the impact tests. It is also possible that, since the thickness of the shell is more important for the strength of the part, the infill could have a negative effect, with the contact points between the filling and the shell serving as stress concentration points that facilitate crack nucleation and propagation.

Table 3. Printing time for each combination of parameters in the tensile test.

Layer height [mm]	Shell thickness [mm]	Infill [%]	Print time [min]
0.1	0.8	40	28
0.1	0.8	60	31
0.1	1.2	40	33
0.1	1.2	60	35
0.2	0.8	40	14
0.2	0.8	60	15
0.2	1.2	40	17
0.2	1.2	60	18

CONCLUSION

The significance analysis, based on the results obtained through the adopted methodology, allows for a better understanding of the importance of shell thickness, layer height and filling of the part when designing a part to be produced by the FFF process, and may also

serve as a comparison for future work in this area. In the tests carried out, the impact and tensile strength suffered a much greater influence from the shell thickness than for the other parameters and their combinations. One of the main factors for this is the increase in the moment of inertia, since the shell contributes more than the bulk for resistance to forces applied parallel to the axis of the filaments in the shell layers. This shows a faster and more economical way of increasing 3D printed parts mechanical properties, compared to the usual choice of increasing infill percentage. In addition, it was observed that exposure to heat from nozzle and printing table for longer periods may end up negatively influencing mechanical strength, indicating that further studies are needed to find an ideal combination of printing parameters. Also, this work found an interesting result, where higher infill could decrease both the tensile and impact resistance. This was justified with a possible stress concentration in the contact of the filling with the outer layers, which could be more relevant for mechanical strength.

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CAPÍTULO 5

5. ARTIGO 2

Pereira, L.G.A., Santos, T.O., Oliveira, P.H.V., de Souza, F.C.R., Campos, F.A.R., Castro, E.S. (2023). ANÁLISE DA INFLUÊNCIA DE PARÂMETROS TÉRMICOS NA RESISTÊNCIA MECÂNICA DE PEÇAS IMPRESSAS PELA TÉCNICA FUSED FILAMENT FABRICATION. Anais do XII Congresso Brasileiro de Engenharia de Fabricação-COBEF2023. Brasília. doi://10.26678/ABCM.COBEF2023.COF23-0277

ANÁLISE DA INFLUÊNCIA DE PARÂMETROS TÉRMICOS NA RESISTÊNCIA MECÂNICA DE PEÇAS IMPRESSAS PELA TÉCNICA FUSED FILAMENT FABRICATION

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Resumo: A manufatura aditiva, ou impressão 3D, através do processo de Fused Filament Fabrication (FFF) tem se mostrado bastante eficaz em produzir peças com geometrias diversas a um custo menor do que outras técnicas de manufatura aditiva. O método vem sendo aplicado em diversas áreas da engenharia, indústria, medicina (como próteses), entre outros. As peças produzidas por este método são fabricadas camada por camada, a partir de parâmetros programados previamente pelo computador. Devido a isso, as peças não necessariamente necessitam ser maciças, o que irá possibilitar um menor gasto de matéria prima, mas, em consequência, virá a influenciar a resistência mecânica das peças impressas. Com isso, uma problemática observada no resultado final destas peças fabricadas por FFF se dá pela menor resistência na interface das camadas impressas, devido a seu caráter anisotrópico provocado pela direção de impressão. Assim, se faz necessário discutir métodos que visam o aprimoramento das propriedades mecânicas relacionadas à resistência destas peças. No caso desta pesquisa, foram analisados três parâmetros de impressão que podem influenciar na resistência mecânica das peças, sendo eles a porcentagem de ventoinha da impressora 3D, a temperatura da mesa e a temperatura do bocal. Estes parâmetros térmicos influenciam na

adesão das camadas e a cristalinidade da peça, processos determinantes para a resistência à tração e à propagação de trincas. Dessa forma, a alteração dada pelo aumento ou diminuição destes parâmetros no momento da impressão possibilitou o conhecimento do quão relevantes estes são para a qualidade da peça impressa. Assim, para a produção dos corpos de prova foram aplicados diferentes arranjos entre as quantidades de porcentagem de ventoinha, temperatura da mesa e a temperatura do bocal, a partir de um planejamento fatorial completo em dois níveis com estas três variáveis, com a posterior realização dos testes de tração e impacto, seguindo as normas ASTM D638 e ASTM D4508, respectivamente. Com isso, os resultados obtidos nestes testes mecânicos foram submetidos à análise de variância permitindo, assim, uma melhor compreensão do processo de impressão e a influência destes parâmetros na qualidade final no que se refere à resistência mecânica das peças produzidas, contribuindo, assim, para uma aplicação mais eficaz dessa tecnologia. Palavras-chave: manufatura aditiva, impressão 3D, Fused Filament Fabrication, temperatura da mesa de impressão, temperatura do bocal, resistência mecânica.

Palavras-chave: manufatura aditiva, impressão 3D, temperatura da mesa de impressão, temperatura do bocal, resistência mecânica.

1. INTRODUÇÃO

Fused Filament Fabrication (FFF), ou Fabricação de Filamento Fundido, em português, é um processo de impressão 3D que emprega um filamento contínuo de um determinado material termoplástico. O filamento, alimentado por um longo carretel contendo o material, é encaminhado para o bocal extrusor aquecido da impressora e é depositado sobre a mesa de impressão. O bocal de impressão é movimentado a partir do computador, definindo e construindo aditivamente a peça. Uma exemplificação deste método é dada pela Fig. 1. Essa metodologia garante grande flexibilidade pela facilidade de personalização das peças, de acordo com a necessidade de cada projeto.

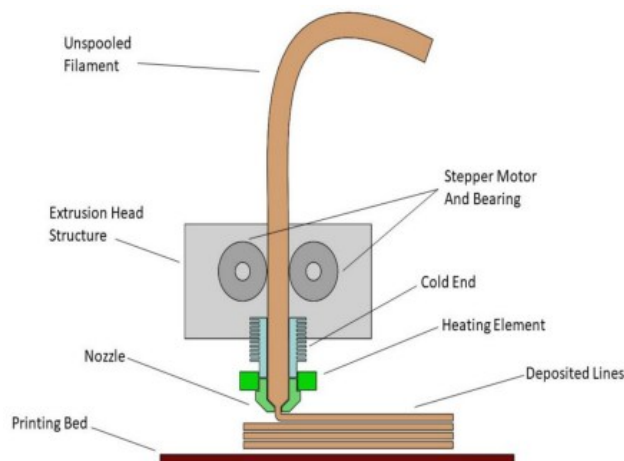


Figura 1. Demonstração do processo de Fused Filament Fabrication. (Cabreira et al, 2020)

A manufatura aditiva vem sendo cada vez mais aplicada na indústria, trazendo benefícios para diversas áreas além da engenharia mecânica, como arquitetura (Hager, 2016), odontologia (Bhargav, 2017) e medicina (Konta et al, 2017), pois, além de possibilitar a produção de peças com um alto nível de complexidade, é um método eficaz, simples, razoavelmente rápido e barato, além de evitar grandes desperdícios de material.

Porém, observa-se, nos processos de manufatura aditiva que implementam o método de impressão Fused Filament Fabrication, uma baixa resistência mecânica entre as camadas impressas. Nesse contexto, estudos anteriores revelaram que os componentes impressos em 3D possuem uma natureza anisotrópica, com propriedades de resistência mecânica mais baixas na interface das camadas (Bhandari et al, 2019), por exemplo, diminuição na resistência à tração na direção ortogonal às camadas impressas (Cole et al, 2016; Fernandez-Vicent et al, 2016), torção (Rodríguez et al, 2001), compressão (Percoco et al, 2012; Sood et al, 2012) e flexão (Sun et al, 2021). Além disso, essa baixa adesão entre os filamentos pode acarretar, também, na nucleação e propagação de trincas nas peças finais (Sharafi et al, 2021).

Nessa conjuntura, fazem-se essencialmente importantes o desenvolvimento de pesquisas que visam atenuar a problemática da baixa adesão entre as camadas impressas, bem como a questão da baixa resistência mecânica entre estas. Existem várias pesquisas focadas em diversos parâmetros que influenciam o resultado final de uma peça, boa parte deles focam nas em aspectos dimensionais e de preenchimento das peças, como o infill, isto é, o preenchimento (Fernandez-Vicent et al, 2016) e a altura de camada (Favero et al, 2017). Porém, estes aspectos não são os únicos a serem avaliados quanto a sua influência na resistência mecânica da peça produzida. Parâmetros térmicos, como a temperatura da ventoinha, que influencia na refrigeração durante a impressão, e as temperaturas da mesa e do bocal de impressão também são importantes e podem afetar consideravelmente a resistência obtida. Em vista disso, foram avaliados neste trabalho os efeitos desses parâmetros na resistência da peça, avaliada por ensaios de impacto e de tração. Um planejamento experimental do tipo fatorial completo em 2 níveis para cada uma dessas 3 variáveis foi executado, a fim de revelar a magnitude de cada fator pela análise de variância (ANOVA). A metodologia empregada permitiu a avaliação dos efeitos isolados e combinados dos diferentes parâmetros de impressão, e os resultados revelaram efeitos importantes do tempo e temperatura de impressão na resistência mecânica das peças.

2. METODOLOGIA

A primeira etapa da presente pesquisa se deu pela enumeração de quais parâmetros influenciadores, no que se refere à impressão 3D, seriam estudados. Foram, então, elencados três parâmetros, sendo eles a porcentagem da ventoinha e as temperaturas de mesa e bocal. Com estes parâmetros definidos, foram estabelecidos dois valores distintos para cada variável, simplificados por -1 e 1, como explicitado pela Tabela 1. Assim, cada teste foi nomeado por uma

letra, sendo que cada um possui uma combinação única das três variáveis, totalizando, portanto, oito testes, de A a H, como mostrado na Tabela 2.

Tabela 1. Dois níveis de valores estabelecidos para cada parâmetro.

T bocal (°C)	-1	1
	200	220
T mesa (°C)	-1	1
	40	60
Vent (%)	-1	1
	50	100

Tabela 2. Planejamento fatorial completo com três variáveis e dois níveis.

Ensaio	T mesa	T bocal	% Vent
A	-1	-1	-1
B	-1	-1	1
C	-1	1	-1
D	-1	1	1
E	1	-1	-1
F	1	-1	1
G	1	1	-1
H	1	1	1

2.1. Preparação e produção das amostras

Dessa maneira, com estes três parâmetros em mente, foi elaborado o planejamento experimental, utilizando-se da metodologia fatorial completa, isto é, tais parâmetros foram combinados de forma a obter todos os possíveis subconjuntos dos mesmos, o que levou à oito (8) combinações diferentes, sendo produzidos três (3) corpos de prova para cada combinação, a fim de verificar também a variabilidade dos resultados. Assim, foram produzidos um total de quarenta e oito (48) corpos de prova, individualmente, ao longo dessa primeira etapa da pesquisa, sendo vinte e quatro (24) corpos de prova do ensaio de impacto (ASTM D4508) e a outra metade para os corpos de prova de tração (ASTM D638), cujas dimensões estão expostas na Fig. 2 e Tab. 3. Estas peças foram produzidas na impressora Creality Ender 3, com filamento PLA (ácido polilático) comum da 3DFILA.

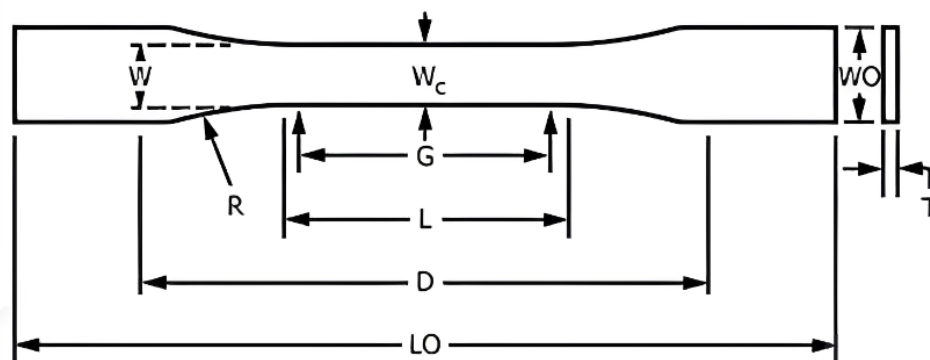


Figura 2. Corpo de prova ASTM D638 para ensaio de tração

Tabela 3. Dimensões para a norma ASTM D638 (tipo V).

Dimensões ASTM D638 (mm)	
W	3,18 ± 0,5
L	9,53 ± 0,5
W ₀	9,53 + 3,18
L ₀	63,5
G	7,62 ± 0,25
D	25,4 ± 5,00
R	12,7 ± 1

É importante salientar que os parâmetros que não estavam sendo avaliados foram mantidos constantes, para que não houvesse interferência destes nos resultados. Além disso, cada unidade de corpo de prova foi impressa individualmente, de modo que uma peça já pronta não continuasse na mesa de impressão aquecida, recebendo calor enquanto outra peça fosse produzida, o que levaria a uma maior difusão das cadeias poliméricas, podendo gerar incongruências nos resultados.

2.2. Ensaio de impacto

A resistência ao impacto das peças foi examinada por meio de ensaios de impacto Izod, com a confecção dos corpos de prova e a realização dos ensaios seguindo as recomendações da norma ASTM D4508. Nesta norma, os corpos de prova ensaiados têm formato de prisma retangular com comprimento, altura e largura de aproximadamente 19 mm, 12 mm e 3 mm, respectivamente, sem presença de entalhe. Essa condição de teste torna o corpo de prova mais sensível a parâmetros que afetem a resistência à nucleação e propagação de trincas na superfície do material, onde o nariz do pêndulo impacta. O pêndulo utilizado tem comprimento 0,778 m e massa 0,96 kg, resultando numa energia de impacto de 1,79 J disponível para a fratura das amostras. O ensaio foi feito elevando-se o mesmo até uma inclinação de -30 ° com a horizontal, que resultou numa velocidade de impacto de 4 m/s para todos os ensaios. Essa informação é importante para que se tenha uma ideia da taxa de cisalhamento a qual a amostra estava sujeita, uma vez que o comportamento mecânico pode ser mais dúctil ou mais frágil dependendo da velocidade de aplicação da carga. A energia de fratura foi calculada segundo a diferença de altura atingida pelo centro de massa do pêndulo, descontando-se a energia cinética transferida a amostra fraturada.

2.3. Ensaio de tração

A resistência à tração das peças foi examinada por meio de ensaios de tração uniaxial, com a confecção dos corpos de prova e a realização dos ensaios seguindo as recomendações da norma ASTM D638, para amostra tipo E. A velocidade de deformação das amostras foi de

0,1 mm/s, aproximando-se da condição de carga estática preconizada neste tipo de teste. A célula de carga utilizada se baseia na deformação de uma viga engastada, a fim de deformar proporcionalmente um extensômetro resistivo. O sinal é diretamente correlacionado com a tensão, utilizando-se de um sistema de aquisição digital, com resolução de 0,01 kg e faixa de medição de 0 a 50 kg para as leituras. O valor de interesse foi apenas a resistência máxima a tração neste caso. A tensão foi calculada dividindo-se a carga máxima pela área da seção transversal das amostras impressas, todas em aproximadamente 9 mm².

3. RESULTADOS E DISCUSSÕES

Para a obtenção de dados analíticos dos ensaios, foi realizada uma análise de variância utilizando o software Statistica 12.0, com um nível de confiança de 95%, tanto para o ensaio de impacto, quanto para o de tração. Com isso, foram gerados gráficos e tabelas que proporcionaram uma visualização mais clara a respeito dos dados estatísticos.

3.1. Ensaio de impacto

Foi possível perceber que os parâmetros avaliados que mais influenciaram na resistência mecânica ao impacto, por meio da absorção de energia durante o ensaio, foram, em primeiro lugar, a temperatura do bocal de extrusão, seguido pela temperatura da mesa de impressão, como é mostrado na Fig. 3, por meio de um diagrama de Pareto.

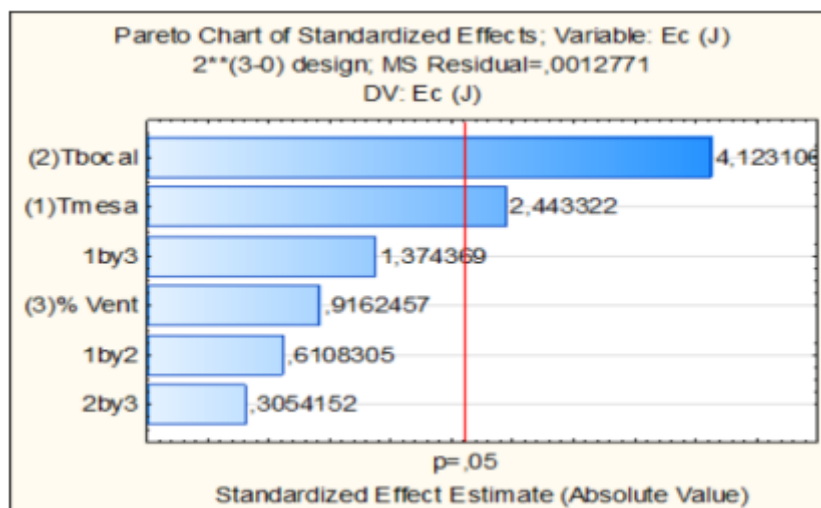


Figura 3. Significância das variáveis de entrada, segundo ANOVA, para ensaio de impacto.

Ainda, com os dados obtidos pelas análises de variância, foi montado o gráfico da Fig. 4, com os valores das médias de energia de impacto por metro (EI) de cada combinação das variáveis de entrada.

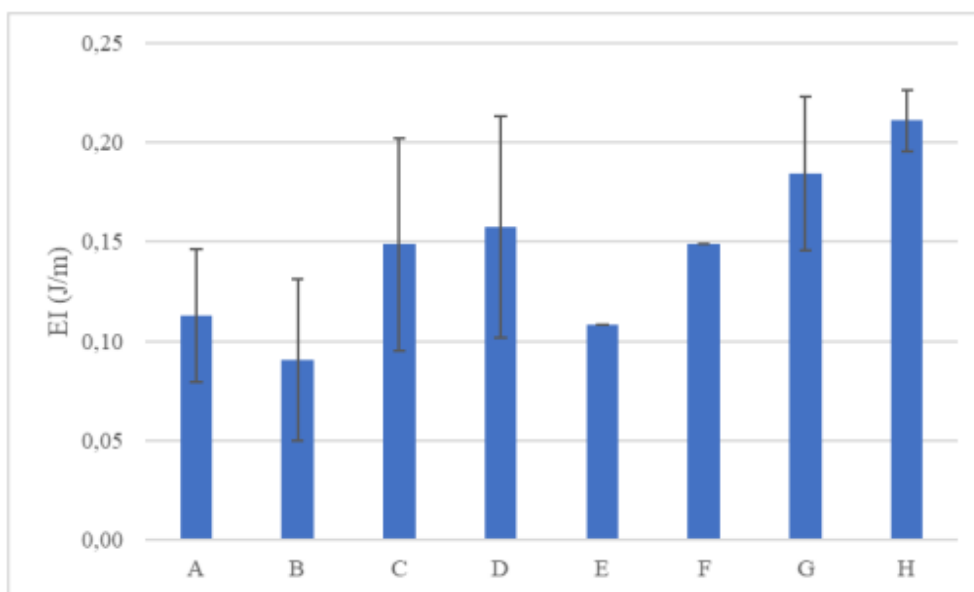


Figura 4. Gráfico com a energia absorvida (J/m) para cada teste no ensaio de impacto.

No ensaio de impacto, há a aplicação de carga de maneira muito rápida, ocasionando, conseqüentemente, uma taxa de deformação muito rápida. Dessa maneira, o tempo para o material se deformar é muito pequeno. Neste caso, a ductilidade do material tem um efeito mais relevante, no que se refere à sua resistência ao impacto. Além disso, ao aumentar as temperaturas do bocal e da mesa de impressão, confere-se uma maior adesão entre as camadas, outro fator relevante para o aumento da resistência ao impacto. Observou-se que justamente as amostras G e H, que tinham as combinações com as maiores temperaturas de bocal e mesa, obtiveram as maiores absorções de energia.

Os resultados obtidos com o ensaio de impacto são condizentes, por exemplo, com as conclusões expostas por (Wang et al, 2017), baseadas no fato de que maiores condições de temperatura de mesa e bocal de impressão podem conferir maior cristalinidade ao PLA, aumentando sua resistência. Ou ainda, é possível que o ganho de resistência se justifique pela diminuição dos interstícios graças ao coalescimento das camadas depositadas, o que aumentaria a área resistente e reduziria os concentradores de tensão.

3.2. Ensaio de tração

Como foi evidenciado pelos resultados do ensaio de tração, o aumento da temperatura do bocal e da mesa resultam em um aumento da resistência ao impacto. Todavia, estes parâmetros têm um efeito inverso quanto ao alongamento e ruptura das amostras, isto é, a aplicação de esforço de tração, com a aplicação de uma carga estática, de maneira lenta e gradual. Isso se deve pelo fato de que, ao transferir uma maior quantidade de calor para a peça que está sendo produzida, o mecanismo de cristalização é favorecido, ocasionando a diminuição de sua capacidade de deformação plástica. A princípio, isso é contra intuitivo, uma vez que nesse tipo de teste a cristalinidade favoreceria a resistência. No entanto, devido ao fenômeno pata de

elefante, típico de peças impressas por FFF, a aplicação de carga nas amostras de tração criou tensões não uniformes ao longo da seção da amostra, tracionando mais a face anterior do corpo de prova. Nessas condições, a baixa ductilidade favoreceu a ruptura precoce devido à nucleação de trincas nessa face, reduzindo os valores encontrados para a resistência máxima das peças. Esses efeitos podem ser constatados na Fig. 5. Ressalta-se que em comparação com estudos anteriores nesta área, percebe-se que os resultados e conclusões obtidos com o ensaio de tração estão de acordo com a faixa de valores esperada para o PLA (Hanon et al, 2021).

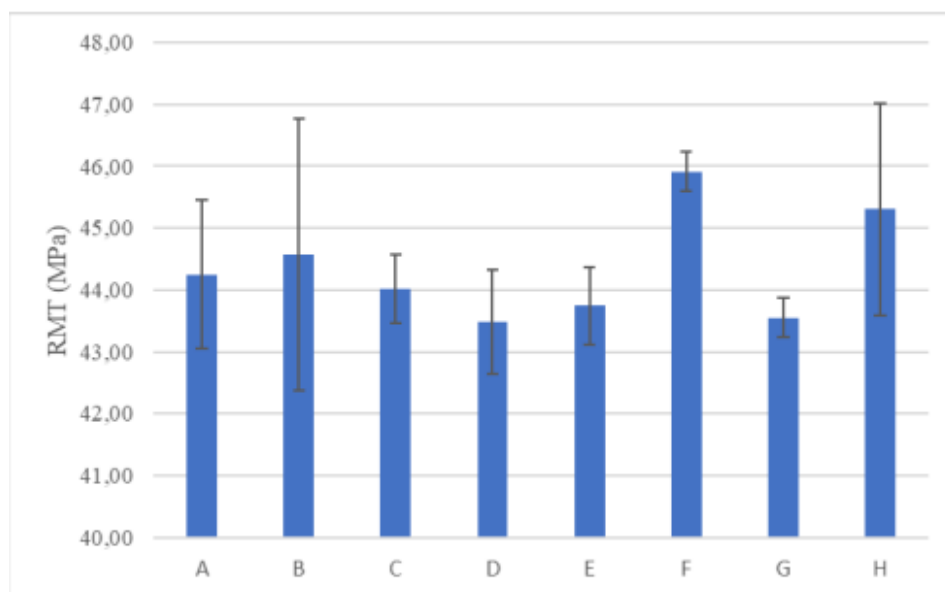


Figura 5. Gráfico com a média da resistência máxima à tração (RMT) para cada teste no ensaio de tração.

Além disso, percebeu-se, por meio do diagrama de Pareto da Fig. 6, que a porcentagem da ventoinha de refrigeração em conjunto com a temperatura da mesa, alcançaram valores de influência significativos no ensaio de tração. Porém, é importante pontuar que a impressora Creality Ender 3 utilizada nesta pesquisa, possui uma segunda ventoinha para resfriar o bocal de extrusão, além da utilizada para resfriar a peça. O resfriamento do bocal de extrusão opera sempre a 100% de sua capacidade durante toda a impressão, não sendo possível alterar seu valor. Dessa forma, parte do fluxo de ar da ventoinha de refrigeração do bocal é disperso para a peça que está sendo impressa. Portanto, mesmo abaixando a velocidade da ventoinha de refrigeração da peça, ainda ocorre o efeito de resfriamento das camadas depositadas. Assim, os resultados que envolvem este parâmetro estudado podem ser influenciados por esta especificidade da impressora.

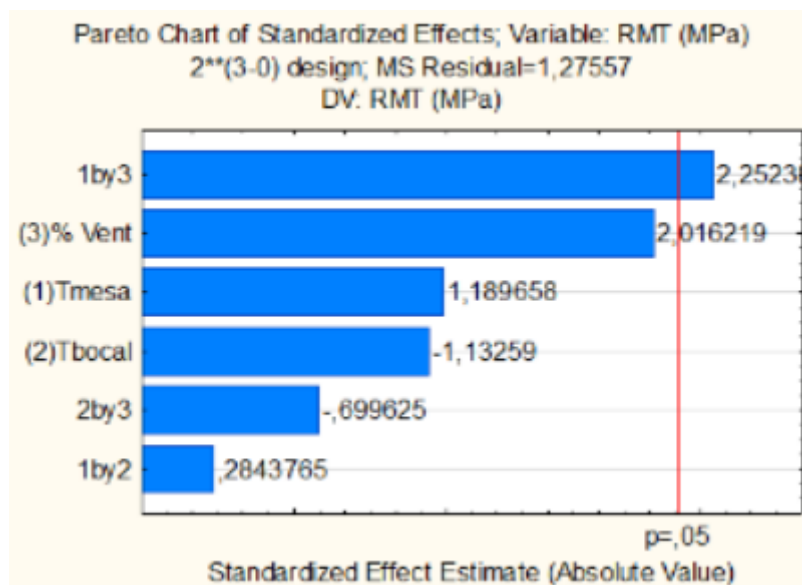


Figura 6. Significância das variáveis de entrada, segundo ANOVA, para ensaio de tração.

4. CONCLUSÃO

Observou-se, nos testes realizados, que, com o aumento da temperatura do bocal e da mesa de impressão, houve um aumento da resistência ao impacto e uma diminuição da resistência à tração. Isso provavelmente se deve, como explicado, pelo efeito de maior cristalização em condições de maior aquecimento da peça, o que causa uma perda da ductilidade do material. Estes parâmetros, portanto, de fato influenciam na resistência mecânica da peça produzida utilizando-se o método Fused Filament Fabrication, em especial com material proveniente do PLA. Este estudo também pode servir de base para testes utilizando-se outros polímeros, embora sugira-se uma variação maior nos níveis dos parâmetros. Finalmente, a resistência ao impacto, incrementada pelo aumento das variáveis térmicas do bocal e da mesa de impressão, se deu em detrimento da resistência à tração. Nessa conjuntura, faz-se importante que futuras pesquisas nesta área procurem um equilíbrio ideal entre estes parâmetros, de modo que se possa obter o maior nível de excelência em quesito de resistência mecânica.

5. AGRADECIMENTOS

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7. RESPONSABILIDADE PELAS INFORMAÇÕES

Os autores são os únicos responsáveis pelas informações incluídas neste trabalho.

CAPÍTULO 6

6. ARTIGO 3

da Silva, P.A.S., Santos, T.O., Almeida, K.F., Oliveira, P.H.V., Okada, K.F.A., Costa, E.S. (2023). QUANTIFICAÇÃO DE INCERTEZA E CALIBRAÇÃO DE CÉLULAS DE CARGA COM SISTEMA DE AQUISIÇÃO POR ARDUINO. Anais do XII Congresso Brasileiro de Engenharia de Fabricação-COBEF2023. Brasília. doi://10.26678/ABCM.COBEF2023.COF23-0031

Quantificação de incerteza e calibração de uma célula de carga com sistema de aquisição por Arduino

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Resumo: Em laboratórios e indústrias é comum encontrar processos que realizam a medição de massa ou carga para verificar a padronização da produção ou acompanhar experimentos. Entretanto, ao empregar tais métodos com sistemas de aquisição de dados para monitoramento contínuo, o custo se torna elevado, principalmente quando se necessita alta precisão e confiabilidade. A fim de contornar essa dificuldade, podem ser utilizadas células de carga, sensores de baixo custo que funcionam através da conversão da deformação de uma barra, medida por strain gages, em tensão que pode ser lida e interpretada por um sistema Arduino™. Para que esse sistema possa ser utilizado de forma confiável é necessário avaliar as incertezas de medição através de testes controlados, fazendo a calibração do sistema com base em instrumentos certificadas pelo INMETRO e desenvolvendo modelos que corrijam os erros sistemáticos. As equações para o cálculo da incerteza nas medições de massa com célula de carga e sistema de aquisição baseado em Arduino™ foram inteiramente desenvolvidas com base no método GUM, e os procedimentos descritos servem como referência para determinar as incertezas para sistemas de aquisição similares. Essa metodologia é aplicável em diversos ramos da engenharia como na padronização de processos de manufatura e construção de equipamentos mais complexos que dependem da medição de carga estática, como máquinas para ensaio de tração, compressão, flexão, ou em tribômetros. Ao utilizar uma célula de carga

com carga máxima de 5 kg conectada a um módulo HX711 e Arduino Uno, foi constatado que a estabilidade do sistema de medição foi a principal limitação, pois embora o sistema tenha resolução de 0,01 g, foram verificados desvios padrão próximos a 0,5 g e uma variação absoluta da indicação da balança de até 3 g quando a amostra era mantida na bandeja por vários minutos. No entanto, estes erros estão de acordo com os limites máximos especificados pelo fabricante de 0,1 % da carga nominal máxima. A principal vantagem foi o custo-benefício, dado que o sistema tem um custo total de aproximadamente R\$50. Dessa maneira, a estratégia utilizada configura uma alternativa interessante para medições e registro de dados de carga e massa em dispositivos laboratoriais ou industriais cujos requisitos de tolerância sejam mais esparsos. Além disso, a medição da incerteza foi transformada em rotina computacional, que permite estimar com facilidade a precisão e confiabilidade da medição, em acordo com as recomendações metroológicas do Comitê Internacional de Pesos e Medidas.

Palavras-chave: célula de carga, incerteza de medição, Arduino, calibração, curva de erro.

1. INTRODUÇÃO

Atualmente dentro de indústrias não é difícil encontrar equipamentos de medição de massa, seja eles com o objetivo de verificar a padronização no processo de produção de peças mecânicas, assim como medir componentes utilizados na produção de um determinado produto químico. No mercado é possível achar sensores de categorias de preço, confiabilidade e dimensões completamente diferentes. Geralmente esses sensores são indicados para aplicações em que a tolerância das medidas aferidas é grande. Como por exemplo na pesagem de alimentos em uma fábrica de produtos alimentícios, na construção de equipamentos de esclerometria e até na padronização de componentes mecânicos produzidos em larga escala.

Mesmo em sensores de alta precisão, um percentual de erros randômicos e sistemáticos podem ocorrer e alterar os resultados obtidos, dependendo de variáveis que são de difícil controle como: vibrações no sistema e campos eletromagnéticos, o resultado pode se tornar inválido para certas aplicações. Porém os erros sistemáticos podem ser corrigidos a ponto de viabilizar sistemas de menor custo e confiabilidade para uma pletera de projetos, já que em concordância as definições dadas pela metrologia, a medida não pode dar um valor exato daquilo que mede, mas sim um valor estimado com incerteza conhecida dado um nível de confiabilidade (Vuolo,1996).

O material conhecido como "Guide for Expression of Uncertainty in Measurement" (INMETRO, JCGM, 2008), fornece um protocolo expressivo para identificar e quantificar os diferentes fatores que podem gerar erros nas medições e suas incertezas, utilizando uma abordagem Bayesiana. Realizar esse processo de forma detalhada e controlada é importante para ter uma medição confiável e consistente. A priori uma vantagem de aplicar esse processo é dada pela capacidade de identificar individualmente as variáveis que influenciam as medições e os erros associados a cada fator de incerteza, sendo possível corrigir ou ajustar esses

parâmetros de forma personalizada para diversos processos (Arencibia et al., 2019). Outra vantagem de adotar o método GUM é a rastreabilidade que o procedimento traz consigo, por ser um processo documentado e amplamente testado, é possível fazer sua verificação em concordância com padrões internacionais, já que um estudo publicado sem validação não tem credibilidade de seus resultados devido à falta da confiabilidade nos mesmos. A medição de incerteza permite rastreamento das fontes de erro até o padrão internacional, que tem adotado definições cada vez mais precisas. A definição de massa dada pelo sistema internacional de medidas é a quilograma, e inicialmente o valor de 1 quilograma era dado por um decímetro cúbico de água destilada, no vácuo, no seu ponto de solidificação. Em 1875 o valor foi alterado para a massa de um cilindro de platina iridiada e atualmente seu valor foi alterado na Conferência Geral sobre Pesos e Medidas (CGPM), em Paris, e está relacionada com a constante de Planck.

As células de carga são sensores de massa que têm seu funcionamento baseado na deformação de uma barra de metal e extensômetro resistivos colados na mesma. Gupta (2012) define que a flexão da barra provoca a deformação do extensômetro, que varia sua resistência elétrica linearmente. Um circuito elétrico aplica uma diferença de potencial e captura a variação de corrente ou tensão resultante da mudança da resistência elétrica através de um sinal analógico, convertido em sinal digital por um módulo adequado e interpretado por um microcontrolador. Esses sensores têm seu custo baseado no limite máximo de carga que pode ser lido, sendo que a carga máxima é diretamente proporcional a resolução e precisão. Ao aliarmos as células de carga a um sistema compatível com um controlador Arduino® e seus acessórios, são notáveis as vantagens na medição devido a variações na casa de poucas unidades, assim como na extensa biblioteca de códigos compatíveis com os sensores e a alta confiabilidade proporcionada pelo método de medição das incertezas no GUM (INMETRO, JCGM, 2008), o que torna o sistema ideal para indústrias e laboratórios nas mais diversas aplicações. Segundo Muller (2010), o principal objetivo da obtenção da confiabilidade de incerteza de medição de cargas é aplicá-lo na construção de equipamentos onde o monitoramento de forças axiais seja necessário, de forma a empregar o uso combinado da célula de carga e Arduino visando os melhores resultados e custo-benefício.

2. CÁLCULO DA INCERTEZA DO SISTEMA DE MEDIÇÃO COM ARDUINO E CÉLULA DE CARGA.

As células de carga têm seu funcionamento baseado na transformação da deformação elástica do sensor em uma medida de carga, utilizando os “strain-gauges”. Esse é um método capaz de medir a deflexão de objetos sólidos, inventado por Edward E. Simmons e Arthur C Ruge, em 1938. Nessa metodologia de pequenas folhas metálicas com presença de linhas espaçadas entre si, medem a deformação de um sólido, e transmitem essa informação na forma de variação de corrente para um módulo digital. Sendo o mesmo princípio de balanças alimentícias encontradas em lojas pelo país e na medição da deformação de barras de aço em equipamentos mecânicos (Anand, 2021).

Para calibrar o sensor foi utilizada uma metodologia matemática para modelar as medições obtidas e calibrar o equipamento para a melhor obtenção de resultados. Esses modelos têm como objetivo apontar as variações nos resultados obtidos e determinar o “erro” sistemático dentro do sistema de aquisição. Algumas variações foram desconsideradas pois sua aleatoriedade advém de características inerentes aos componentes, como a influência de campos magnéticos na variação da corrente enviada pelo sensor, conseqüentemente afetando a informação que chega ao módulo de conversão. Em Da Silva e Ferreira-Oliveira (2021), é traçado um modelo matemático para a calibração de um sensor termopar em conjunto ao sistema Arduino, cujo modelo pode ser regredido a uma forma geral para determinar as incertezas do sistema de medição com um sensor qualquer. A priori as grandezas medidas podem ser diferentes, porém se o método de transmissão dos dados é feito de maneira similar (transmissão por variação de corrente) é possível definir uma forma genérica que depende da variação da média, resolução e incerteza de calibração. Ao adaptarmos as equações e modelos para a medição do sistema proposto obtemos a Eq. (1), onde ΔY é a soma das incertezas, $\overline{\Delta Y}$ é a incerteza associada a variabilidade em torno da média, ΔR é a incerteza da resolução do sistema e ΔIC é a incerteza atribuída a calibração do sistema de aquisição utilizada no processo. Em conjunto ao modelo de equações utilizamos a metodologia do Guia Internacional para Medição de Incertezas (Guide for Uncertainty Measurement – GUM), (INMETRO, JCGM, 2008), que explicita na Eq. (2) um modelo de cálculos para incerteza de medição a atribuindo a uma função de resultado Y , onde as variáveis X_1, X_2, \dots, X_N são possíveis entradas.

$$\Delta Y = \overline{\Delta Y} + \Delta R + \Delta IC \quad (1)$$

$$Y = f(X_1, X_2, \dots, X_N) \quad (2)$$

Contanto que possamos garantir a independência das variáveis determinadoras das incertezas podemos utilizar a lei de propagação de incerteza na Eq. (3) para determinar a incerteza combinada do sistema/método de medição. onde $u(x_i)$ fornece a variância de cada variável do sistema, X_i e o resultado advindo das derivadas parciais de cada incerteza nos fornecem os coeficientes de sensibilidade c_{x_i} . O cálculo da variância também depende do tipo de variável empregada, sendo que elas podem ter estimativa de incerteza do tipo A ou B, como definido pelo GUM (INMETRO JCGM, 2008).

$$U^2_c(y) = \sum_{i=1}^N \left(\frac{\partial f}{\partial x_i}\right)^2 \cdot u^2(x_i) \quad (3)$$

Pela metodologia é definida que a incerteza utilizada para resultados seja a incerteza expandida, $U(y)$, calculada pela Eq. (4), que explicita o valor expandido como o produto da incerteza determinada pela Eq. (3) e o fator de abrangência K , determinado pelo grau de liberdade efetiva ν_{eff} o qual é calculado pela equação de Welch-Satterthwaite conforme Eq. (5),

onde i é o grau de liberdade de cada variável, que quando avaliada em um intervalo de confiança nos fornece o valor de K .

$$U(y) = K \cdot u_c(y) \quad (4)$$

$$v_{eff} = \frac{u_c^4(y)}{\sum_{i=1}^N \frac{(u_i(x_i) \cdot c_{x_i})^4}{v_i}} \quad (5)$$

3. HARDWARE E SOFTWARE COMPATÍVEL COM O SISTEMA ARDUINO E CÉLULA DE CARGA.

Para a aquisição de dados foi utilizado a combinação de uma placa Arduino UNO, um módulo HX711 e a célula de carga conforme a Fig. 1. Sendo esse sistema projetado de forma que os dados foram obtidos com a célula de carga acoplada a uma superfície fixa de um lado e um bandeja de acrílico do outro, o módulo tem função de receber o sinal digital em forma de variação de voltagem e emitir um sinal analógico para o microcontrolador Arduino, que por sua vez executa um código programado em linguagem nativa para interpretar e exibir a massa captada pelo sensor. Em relação às especificações técnicas, em concordância com (Kraus, 1992) o sensor utilizado possui a carga nominal de 5 kg, sendo que pelo datasheet do fabricante a resolução mínima é de 0,001% da carga nominal, equivalente a 0,05 g. O sistema roda em uma taxa de aquisição máxima de 12 Hz, com uma comunicação de 14 bits para a porta serial do computador.

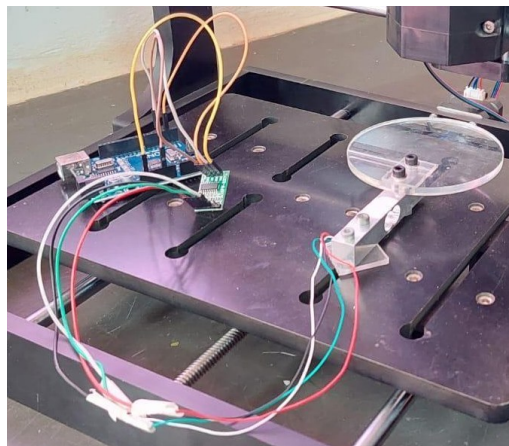


Figura 1. Conjunto de medição (Célula de carga e Arduino).

4. METODOLOGIA

4.1. Cálculo da incerteza de medição

Desenvolvendo a Eq. (1) no contexto de sistema baseado no conjunto célula de carga e Arduino, obtém-se a Eq. (6) com termos equivalentes, onde ΔM é a soma das incertezas do sistema, $\overline{\Delta M}$ é a incerteza associada a variabilidade em torno da média das massas, ΔR é a incerteza da resolução do sistema e $\Delta ICac$ é a incerteza atribuída a calibração do sistema célula de carga e Arduino, para a qual podemos afirmar a linearidade de tais variáveis em relação à incerteza total, devido a não correlação entre elas. Na Eq. (7) a propriedade de linearidade dos fatores de sensibilidade implica que todas as derivadas parciais são iguais a 1 na Eq. (8).

$$\Delta M = \overline{\Delta M} + \Delta R + \Delta ICac \quad (6)$$

$$u_c^2(\Delta M) = \left(\frac{\partial \Delta M}{\partial \overline{\Delta M}}\right)^2 \cdot u^2(\overline{\Delta M}) + \left(\frac{\partial \Delta M}{\partial \Delta R}\right)^2 \cdot u^2(\Delta R) + \left(\frac{\partial \Delta M}{\partial \Delta ICac}\right)^2 \cdot u^2(\Delta ICac) \quad (7)$$

$$c_{\overline{\Delta M}} = \frac{\partial \Delta M}{\partial \overline{\Delta M}} = 1; \quad c_{\Delta R} = \frac{\partial \Delta M}{\partial \Delta R} = 1; \quad c_{\Delta ICac} = \frac{\partial \Delta M}{\partial \Delta ICac} = 1 \quad (8)$$

Para o processo de cálculo de $\Delta ICac$ é necessário a comparação com um instrumento calibrado, de incerteza conhecida. No caso da calibração do sensor foi utilizado uma balança digital de precisão, para a qual a incerteza pode ser estimada se o operador possui conhecimento profundo sobre o sistema de medição (Vuolo, 1996). Assim, foi estipulado um fator aconselhado entre 0,5 e 2 multiplicado pela resolução Rb do instrumento. Para as aplicações desse estudo foi adotado o valor mais conservador, a fim de ter uma margem segura na incerteza estimada para o sistema.

4.2. Calibração do sistema célula de carga e Arduino.

A calibração do equipamento foi realizada com a comparação de 5 massas medidas no sistema da célula de carga e em uma balança digital de precisão Shimadzu modelo BL 3200H. Para conhecer o valor de calibração $\Delta ICac$ precisamos conhecer a maior incerteza possível que o sistema possui dentro da faixa de medição de interesse. Para isso, foram medidas 5 diferentes massas nos 2 sistemas, sendo 3 medidas para cada peso na balança digital e 3 medições para o sistema célula de carga com aquisição de 30 s em cada e taxa de 10 Hz, a fim de obter melhor confiabilidade dos dados. Após conhecidos os valores de ΔM , para um índice i de cargas variando de 1 a 5 nas Eq. (9) a Eq. (11) para as diferentes i medições, adotamos como o valor de $\Delta ICac$ a maior incerteza padrão obtida. Já o valor de ΔRb é a resolução da balança digital utilizada para calibrar o sistema e ΔICb é o valor estipulado em duas vezes o valor de Rb , que é a resolução da balança de precisão (Vuolo, 1996).

$$\Delta M_i = \overline{\Delta M}_i + \Delta Rb + \Delta ICb \quad (9)$$

$$u_c^2(\Delta M_i) = \left(\frac{\partial \Delta M_i}{\partial \overline{\Delta M}_i}\right)^2 \cdot u^2(\overline{\Delta M}_i) + \left(\frac{\partial \Delta M_i}{\partial \Delta Rb}\right)^2 \cdot u^2(\Delta Rb) + \left(\frac{\partial \Delta M_i}{\partial \Delta ICb}\right)^2 \cdot u^2(\Delta ICb) \quad (10)$$

$$c_{\Delta M} = \frac{\partial \Delta M_i}{\partial \Delta M_i} = 1; \quad c_{\Delta R_b} = \frac{\partial \Delta M_i}{\partial \Delta R_b} = 1; \quad c_{\Delta I C b} = \frac{\partial \Delta M_i}{\partial \Delta I C b} = 1; \quad (11)$$

5. RESULTADOS

A Tabela 1 demonstra os resultados obtidos em um ambiente controlado onde foram realizadas as medições de massa no sistema projetado, além de uma sexta medição que foi utilizada como parâmetro para identificar a incerteza dentro de uma medição qualquer no sistema. Cada medição teve duração de 90 segundos com aquisição de 10 Hz. Os cálculos de incerteza foram realizados conforme a Tabela 2, segundo os tipos de estimação das incertezas e suas distribuições. Para variáveis com estimação do tipo A os graus de liberdade dependem do número n de dados amostrais utilizados nos cálculos. Já para variáveis com estimação do tipo B as avaliações dependem da distribuição atribuída para cada variável. Em GUM (INMETRO, JCGM, 2008) é determinado como e quando devem ser feitas as estimativas matemáticas tanto do tipo A, quanto do tipo B.

Tabela 1. Média, desvio padrão, incerteza calculada e expandida para as variáveis.

	Balança (g)					Célula de Carga (g)					
	M_1	M_2	M_3	M_4	M_5	M_1	M_2	M_3	M_4	M_5	M
Média	99,69	416,67	363,40	1024,57	1562,18	97,38	408,04	356,29	1004,88	1533,62	30,12
Desv. pad	0,07	0,009	0,004	0,008	0,008	0,95	0,39	0,72	0,31	0,44	0,13
n	3					965	961	959	956	949	985
ν	1					11	1	5	1	2	2
u_c	0,02					0,036	0,022	0,023	0,022	0,024	0,027
K	13,97					2,25	13,97	2,65	13,97	4,53	4,53
U	0,2794					0,082	0,321	0,081	0,316	0,112	0,124

Tabela 2. Valores e cálculo dos componentes de incerteza para todas as variáveis.

Variável	Tipo da variável	Distribuição de probabilidade	Graus de liberdade	$u(x_i)$	$u(x_i)$ (g)	Contribuição. (%) [Eq.] (i)	K
ΔM	B	Normal	2	resultado da Eq.7	0,027		4,53
$\overline{\Delta M}$	A	Normal	985	$=\frac{s_{\Delta M}}{\sqrt{n}}$, onde $s_{\Delta M}$ é o desvio padrão em relação a $\overline{\Delta M}$	0,004	2,28 [7]	
ΔR	B	retangular	INF	$=\frac{R}{2\sqrt{3}}$, onde R é a resolução da célula de carga	0,014	27,63 [7]	
ΔI_{Cac}	B	Normal	1	O maior entre os ΔM_i das 5 cargas	0,023	70,10 [7]	13,97
ΔM_1	B	Normal	11	Resultado da Eq.8 com $i = 1$.	0,037		2,25
ΔM_2	B	Normal	1	Resultado da Eq.8 com $i = 2$.	0,023		13,97
ΔM_3	B	Normal	5	Resultado da Eq.8 com $i = 3$.	0,031		2,65
ΔM_4	B	Normal	1	Resultado da Eq.8 com $i = 4$.	0,023		13,97
ΔM_5	B	Normal	2	Resultado da Eq.8 com $i = 5$.	0,025		4,53
$\overline{\Delta M}_1$	A	Normal	965	$=\frac{s_{\Delta M}}{\sqrt{n}}$, onde $s_{\Delta M}$ é o desvio padrão relativo a $\overline{\Delta M}$ com $i=1$.	0,031	69,61 [10]	
$\overline{\Delta M}_2$	A	Normal	961	$=\frac{s_{\Delta M}}{\sqrt{n}}$, onde $s_{\Delta M}$ é o desvio padrão relativo a $\overline{\Delta M}$ com $i=2$.	0,011	22,76 [10]	
$\overline{\Delta M}_3$	A	Normal	959	$=\frac{s_{\Delta M}}{\sqrt{n}}$, onde $s_{\Delta M}$ é o desvio padrão relativo a $\overline{\Delta M}$ com $i=3$.	0,023	56,97 [10]	
$\overline{\Delta M}_4$	A	Normal	956	$=\frac{s_{\Delta M}}{\sqrt{n}}$, onde $s_{\Delta M}$ é o desvio padrão	0,010	20,57 [10]	

				relativo a $\overline{\Delta M}$ com $i=4$.			
ΔM_5	A	Normal	949	$=\frac{s_{\Delta M}}{\sqrt{n}}$, onde $s_{\Delta M}$ é o desvio padrão relativo a $\overline{\Delta M}$ com $i=5$.	0,014	33,32 [10]	
ΔRb	B	Retangular	∞	$=\frac{Rb}{2\sqrt{3}}$, onde Rb é a resolução da balança de precisão.	0,003	0,62 [10], (i=1) 1,58 [10], (i=2) 0,88 [10], (i=3) 1,62 [10], (i=4) 1,36 [10], (i=5)	
ΔICb	B	t-student	1	$2 \cdot Rb$, onde Rb é a resolução da balança digital.	0,020	29,77 [10], (i=1) 75,67 [10], (i=2) 42,15 [10], (i=3) 77,80 [10], (i=4) 65,32 [10], (i=5)	

Na Figura 2 é demonstrada como as diferentes parcelas da Eq. (7) influenciam no resultado das incertezas do sistema, e fica visível que a menor parcela se encontra na incerteza das médias do sistema. Esse valor baixo é devido ao número grande amostral n que impacta diretamente no cálculo do erro das médias explicitada na Tab. 2. Outro fator contribuinte é o baixo desvio padrão que em geral fica menor que 0,1 g, valor que superou as expectativas já que se apresentou com uma redução de 98% em relação à precisão da célula de carga no datasheet do fabricante. Portanto o sistema se demonstra capaz de ser aplicado em situações em que resoluções pequenas com grande confiabilidade são requeridas. E considerando o valor conservador adotado para a estimativa da incerteza de calibração da balança digital, pode-se considerar que os resultados poderiam ser ainda mais refinados, caso fosse feito o cálculo exato da incerteza de calibração da balança digital com massas padrão.



Figura 2. Contribuição percentual dos termos para a incerteza calculada.

Uma análise realizada para determinar o erro das medições em diferentes faixas de medição foi feita conforme a Fig. 3. O par ordenado representa o erro absoluto, dado pela diferença entre o valor real e o valor da medição obtida do sistema célula de carga e Arduino. Pelo que podemos observar em medições com valores de até 20% da carga nominal do sensor, obtemos erros de valor absoluto menores quando comparados aos demais, com ênfase na faixa de 1,5 kg onde é notável que o valor do erro passa da casa dos centésimos para décimos. Entretanto é notável que em aplicações até a faixa de 1 kg é possível realizar medidas com resultados dentro da resolução esperada para aplicações de menor escala. O motivo da medição 5 possuir um erro maior que os demais é explicado pela Fig. 2, que aponta um comportamento

comum em relação a ΔIcb , ao adotar o valor conservativo de 2 vezes o valor de Rb . A porcentagem que a incerteza desse termo ocupa na soma dos termos é extremamente alta, o que em $\Delta M5$ resulta no valor elevado da 5ª medição. Já nas leituras de M_1 e M_3 , é possível observar um valor maior de $\overline{\Delta M}$, essa particularidade é devida à instabilidade na aquisição das amostras 1 e 3, que produziram um desvio padrão maior que os demais, mesmo estando muito abaixo da resolução da célula de carga adotada. Já os que possuem uma medição mais precisa com menor desvio padrão tiveram uma margem de segurança elevada em decorrência do valor inflado de ΔIcb .

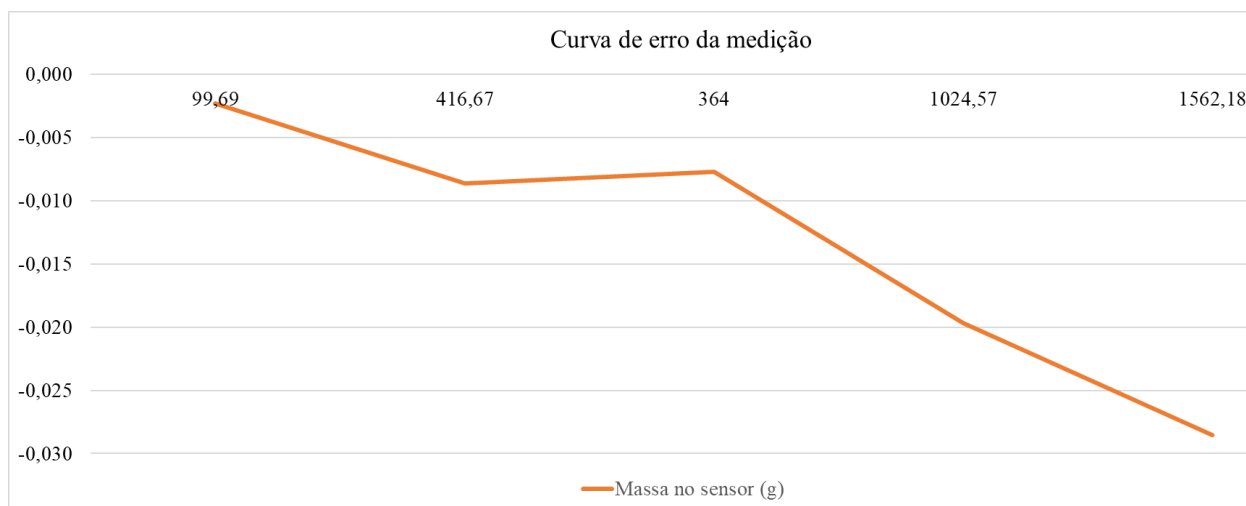


Figura 3. Gráfico da curva de erro nas medições da célula de carga

Para aplicações mais precisas é recomendado coeficientes menores ao calcular a incerteza de calibração do equipamento de referência. Valores entre 0,5 e 1 podem acomodar de forma mais precisa aplicações industriais e laboratoriais como a aquisição de dados em equipamentos que realizam a medição de forças axiais em um sistema, a exemplo de equipamentos como tribômetro e microesclerômetro. Por fim, é importante ressaltar que o resultado de medição pode ser expresso na Eq. (12) em acordo com as normas NBR ISO/IEC 17025:2017 (ABNT, ISO/IEC, 2017), onde é dada de forma clara toda informação referente às medições realizada no sistema assim como sua precisão e confiabilidade. Como mencionado anteriormente tal intervalo de confiança e resolução são suficientes para sua utilização em projetos de menor custo que permitam uma tolerância menos restritiva.

$$M = 0,03012 \pm 0,00012 \text{ Kg com } K = 4,53 \text{ e intervalo de confiança de } 95\% \quad (12)$$

6. CONCLUSÃO

O campo de pesquisa das incertezas possui metodologias e características complexas, o que torna os cálculos extremamente densos e os bancos de dados extensos. Entretanto é possível perceber que após definida um caminho para modelar e interpretar os casos em que o

conhecimento de incerteza se faz necessário, a replicabilidade de fórmulas em um ambiente computacional permite a expansão desses modelos para componentes simples que antes não tinham suas características estatísticas estudadas.

Promover a descoberta de componentes de baixo custo com propriedades de medição que podem atender a maioria dos casos tanto gerais quanto específicos, possibilita o desenvolvimento de equipamentos com características customizáveis a cada aplicação e manutenção facilitada. Que por sua vez colaboram com o desenvolvimento de projetos pequenos com recursos escassos que necessitam de maquinário competente e de boa confiabilidade pelo melhor preço.

Os modelos matemáticos descritos no artigo podem ser replicados para qualquer componente de medição com as mais diversas características, de forma a garantir a veracidade do método pela simplicidade da aplicação nos mais variados sistemas. O resultado de variação de medição menor que 0,0001 Kg para uma massa de média 0,03012 Kg representa um erro de menos de 0,1% em um sistema capaz de rodar nas mais diversas máquinas assim como gerar resultados melhores para aplicações de precisão maior, sinalizando a importância da divulgação de estudos nessa área, de forma a consolidar a padronização desses testes para todos os componentes de medição, sejam em aplicações industriais ou acadêmicas, com equipamentos de alto ou baixo custo.

7. AGRADECIMENTOS

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8. RESPONSABILIDADE PELAS INFORMAÇÕES

Os autores são os únicos responsáveis por todo material escrito nesse artigo.

CAPÍTULO 7

7. ARTIGO 4

Campos, F.A.R., Barbosa, L.M.Q., Almeida, K.F., Oliveira, P.H.V., Santos, T.O., da Silva, L.R.R., Machado, A.R. (2023). COMPARISON OF IMPACT RESISTANCE OF ANNEALED 3D PRINTED PLA ACCORDING TO DIFFERENT PROCESS PARAMETESRS AND IZOD ASTM STANDARDS. In Proceedings of the XXVII International Congress of Mechanical Engineering-COBEM2023. Florianópolis. doi://10.26678/ABCM.COBEM2023.COB2023-0505

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Comparison of impact resistance of annealed 3D printed PLA according to different process parameters and Izod ASTM standards

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Abstract. *The additive manufacture through the Fused Filament Fabrication (FFF) process is one of the most utilized techniques of 3D printing nowadays, which consists of the extrusion of a thermoplastic filament, provided. continuously from a spool, through a nozzle extruder heated for the material deposition in layers. In this process, the deposited polymer cools rapidly for the layer solidification, and then it is reheated with the deposition of the upper layers, making important the study of the thermoplastic properties in accordance to the piece's thermal history, especially in relation to the glass transition temperature (T_g) and the crystallization temperature (T_c). The first indicates the temperature from which the polymeric chains gain mobility and relates with the adhesion between the deposited layers. The second marks the organization tendency of the macromolecules in crystals, that normally make the material more resistant, though less ductile. Due to this phenomenon, the FFF printed part's mechanical properties become dependent on parameters such as nozzle and table temperatures, and layer height, in addition to post-processing operations like annealing. In this sense, this research aimed to evaluate the influence of the printing parameters mentioned and annealing on the impact resistance of FFF fabricated polylactic acid (PLA) parts. It utilized a complete factorial type experimental planning with 2 levels and 4 variables (2^4), for 2 different types of specimens, that allowed use of variance analysis (ANOVA) to identify which are the most significant factors for the impact resistance evaluated according to the standards ASTM D4508 and ASTM D256. The annealing process was identified as the most influential parameter, since only 20 minutes of reheating was enough to increase the piece's average resistance by more than 300% on average. The crystallinity change was discussed according to the change in the translucency of samples. The results demonstrated notable efficacy of the reheating process on improving the mechanical properties, pointing to a great cost-benefit strategy for the industrial segments and for professional consumers to improve their FFF printed parts.*

Keywords *Additive manufacture, Annealing, Impact resistance, Crystallinity*

INTRODUCTION

Currently, with the increased accessibility of modeling software and 3D printers, extrusion-based additive manufacturing has become increasingly popular in research. This is primarily due to its relatively low cost, quick production time, and high geometric accuracy of the produced parts. This technology is called Fused Filament Fabrication (FFF), a process that occurs when a thermoplastic filament is extruded through a nozzle and heated to the point of melting the polymer, which deposits the material in layers and shapes as indicated by a three-dimensional model digital, until reaching the desired result (Sood et al, 2010). There are several polymers that can be used for the realization of such printings, the most common being ABS and PLA.

Despite the advantages of the process, one of the main negative aspects of additive manufacturing by FFF is related to the porosity of the final solid, because as the part is manufactured by layers of filaments. The deposition process leaves a considerable amount of

unfilled regions, and this factor contributes to a lower resistance of the final product. This phenomenon can be seen in Figure 1, where it is also evident the lack of contact between the layers deposited, preventing intertwining between polymeric chains, which is the main mechanism of interfacial adhesion in printed pieces (Sun et al, 2008).

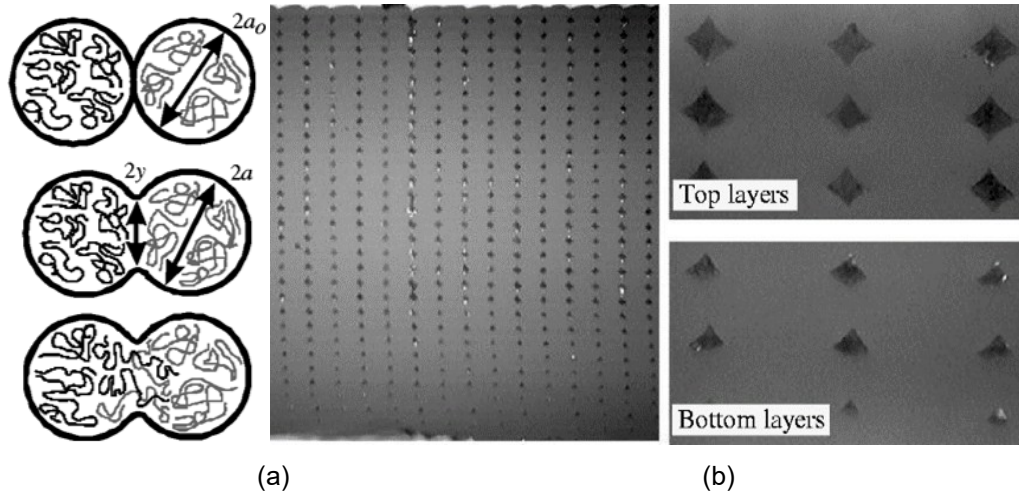


Figure 1. (a) Mechanism of sintering and molecular diffusion. (b) analysis of the interstices between the rows and layers, revealing greater adhesion at the bottom of the piece that spent more time above the vitreous transition temperature. Adapted from Sun et al (2008).

The resistance of the piece produced by FFF also depends directly on its thermal properties. After the material is extruded, it suffers a fast loss of thermal energy due to the contact with the other layers and the external air. During this period in which the material remains above its glass transition temperature (T_g), polymer chains have high rotational mobility and can either intertwine with the chains of adjacent layers (increasing adhesion) or crystallize, depending on the type of polymer (Hart et al, 2020). In the case of PLA, usually printed at around 200 °C and with a T_g close to 50 °C according to Vaes and Puyvelde (2021), the chains are initially disordered after exiting the nozzle, characterizing the amorphous state, and tend to crystallize as the temperature decreases. The rate of crystallization depends on the cooling rate and/or the time in which the polymer remains above its T_g , being influenced, therefore, by printing parameters such as table temperature, nozzle temperature and fan cooling power (Torres et al, 2016). That becomes important for the final characteristics because the level of crystallinity relates to the mechanical properties, chemical and thermal resistance, and the translucency of printed parts (Gao et al, 2021).

Considering this deficit in relation to the resistance of the samples, several studies seek to evaluate which parameters contribute more to improve this property. Many studies demonstrate that infill and wall thickness are beneficial for mechanical strength (Aliheidari et al, 2017). However, such printing criteria raise material and time costs significantly, so the cost of a part with these conditions would be less viable. At the same time, several works have also explored possibilities of optimization of thermal parameters to improve the resistance of the part, including the use of post-treatment by annealing (Bhandari et al, 2019). In these cases, researchers employ

intricate analytical and computational models, together with fracture toughness analysis in high-cost equipment to explain the material behavior changes.

This work sought to address how thermal phenomena alter the properties of printed parts subject to high shear rate typical of impact loads, by performing simpler and faster experiments. Thus, using an experimental design of the full factorial type, the four variables nozzle temperature, table temperature, type of impact testing and the annealing process were evaluated in two levels to see how they alter the impact strength and translucency of the samples, with the last being used as a way of measuring the material crystallinity change due to annealing. For this, the Izod-type test was applied in the PLA samples, analyzing the energy absorbed in the fracture and the opacity of the samples. The statistical analysis of the data by ANOVA allowed the determination of which parameters are statistically significant for changes in the properties and provided an interesting alternative to study the behavior of printed materials.

METODOLOGY

Preparations of the samples

The parts used in the impact tests were printed from natural polylactic acid (PLA) filaments, diameter 1.75 mm of 3DFila brand. Test samples were produced by additive manufacturing using the method Fused Filament Fabrication (FFF) through a 3D printer Creality Ender 3 for different impact test methods, varying also the printing parameters (table temperature, T_{table} , and nozzle temperature, T_{nozzle}) and with or without annealing. This resulted in an experimental design of the complete factorial type in 2 levels and 3 variables (2^3), with sample parameters A to H, as shown in Table 1, being used for both Izod standards ASTM D256 (2018) and ASTM D4508 (2006). It should be noted that during printing, all other parameters remained constant, such as layer height (0.2 mm), printing speed (50 mm/s), nozzle size (0.4 mm), among others. The choice of printing parameters considered the most suitable limits recommended by the filament manufacturer and previous results from other works (Almeida et al., 2023).

Table 1. Complete factorial experimental design 2^3 .

Test condition	T_{table} (°C)	T_{nozzle} (°C)	Annealing
A	85	215	without
B	85	200	without
C	50	200	without
D	50	215	without
E	85	215	with
F	85	200	with
G	50	200	with
H	50	215	with

Annealing

The influence of post-treatment by annealing was studied by subjecting the parts to controlled heating in an electric oven. Half of the printed pieces were annealed in a 10 L electric furnace, Britânia brand, with 1050 W power and a timer that allows automatic shutdown. The samples were placed inside the equipment before its activation and annealed for 20 minutes in a temperature range of around 100 °C to 120 °C, as exemplified in the graph of Figure 2. The oven's internal temperature was measured using 4 thermocouples type K associated with MAX31855 modules connected to an Arduino Uno microcontroller with ATmega processor 328. The data was obtained using the Arduino as a signal acquisition board connected to a notebook, with data recording by CoolTerm 2.0 software. After completing the annealing process and turning off the oven, the parts were kept inside for 20 minutes for cooling before manipulation.

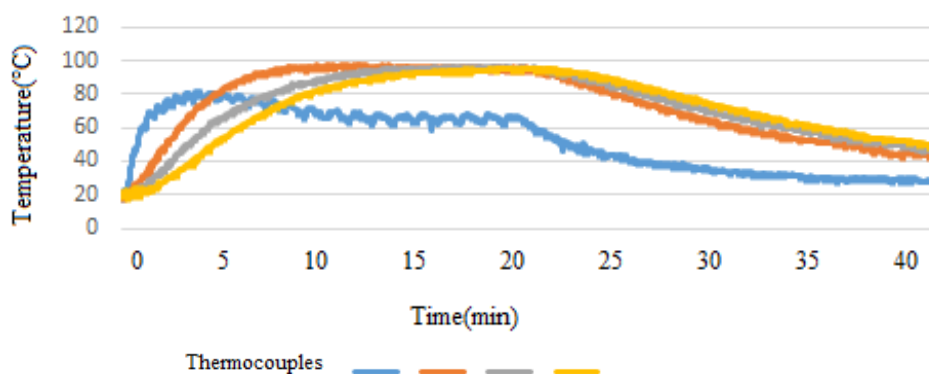


Figure 2. Graphic of the annealing and cooling temperature of the D256 samples by time

Impact test

The Izod-type impact tests were performed according to the ASTM D4508 and ASTM D256 standard in order to obtain the energy absorbed by the samples during its fracture, so as to evaluate the influence of thermal parameters on the resistance of parts at dynamic loads and compare them with one another. The pendulum used has a length of 0.778 m (distance from the pendulum tip to the center of rotation), with total mass of 0.992 kg and center of mass 0.378 m from the center of rotation. The pendulum was raised at a 90° inclination before release, being parallel to the horizontal base of the impact testing machine, resulting in a total energy of 3.68 J and an impact velocity of 5.6 m/s when hitting the sample. All tests followed these standards, and in the final calculation of the energy absorbed by the test specimens, it was discounted the portion of pendulum energy converted into kinetic energy of the fractured part of the sample, thrown after the impact of the pendulum, as recommended by the standards.

Using a pachymeter, measurements of the D256 samples were made, its width, lengths and thickness were taken three times on each specimen, this was then used to verify if the annealing process would cause any geometric changes in the samples, once this phenomenon

is known to take place due to crystallization process (Lluch-Cerezo et al., 2022). Figure 3 shows the ideal dimensions of the specimens according to ASTM D256 and D4508 respectively.

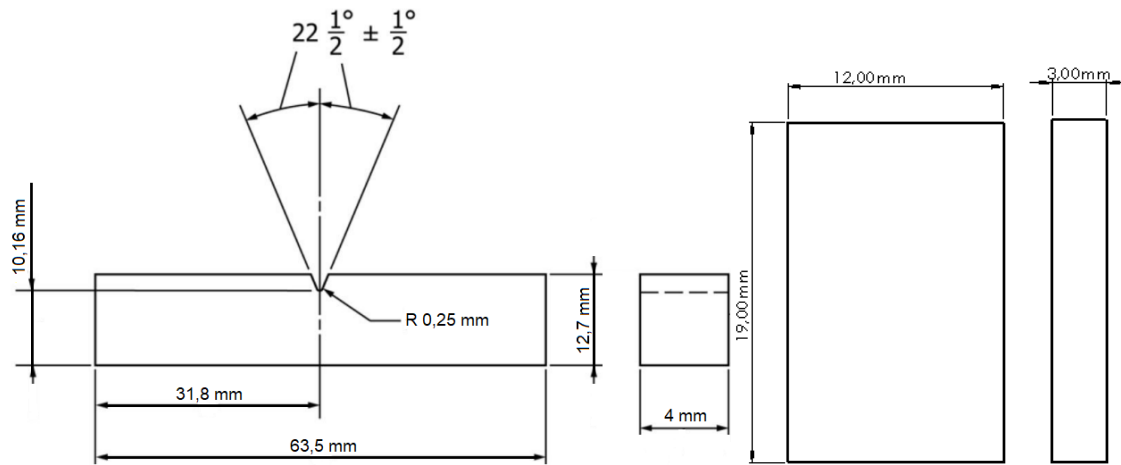


Figure 3. Example of specimens for Izod type test according to ASTM D256 (left) and D4508 (right).

The pendulum calibration was carried out by using a smartphone in the video recording function in slow motion mode, which can record 240 frames per second, analyzing the distance traveled by the tip of the pendulum between one frame and the other, with a rule behind the pendulum. Thus, it was possible to find the impact velocity of the pendulum in the sample, and the energy was calculated according to its dimensions, considering its rotational moment of inertia. The friction was also accounted by releasing the pendulum with no sample and checking how much energy was absorbed by air and bearing friction.

To capture data on the energy absorption of the pendulum by the sample, an encoder type sensor was used, to measure the maximum inclination reached by the pendulum. The encoder consists of a disk of diameter approximate 220 mm with 360 holes 1 mm wide and equally spaced by 1 mm at the edge of the disc, associated with an optical module in a manner similar to that shown in Figure 4a. The LM393 module used can be seen in Figure 4b, while assembly of the machine was done as exemplified in Figure 4c, with the encoder disk replacing the pointer scale. The sensor signal was also checked on an Arduino-type microcontroller, which was connected via USB cable to a mobile phone. The programming used informed the operator the angle displaced by the pendulum with a precision of 0.5°, making it possible to calculate the maximum height reached by the pendulum in comparison with the initial height in the moment of release.

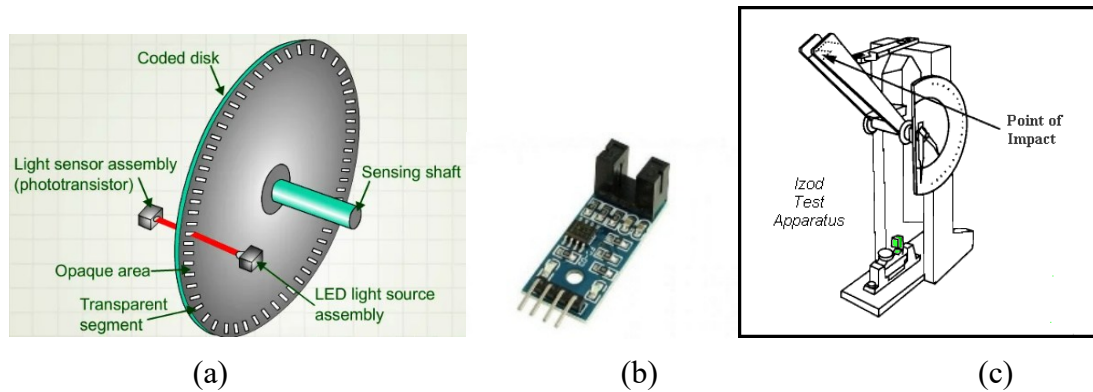


Figure 4. (a) Representative encoder-type sensor schematic (adapted from Instrumentation Tools, 2022). (b) Sensor LM393 optical compatible with Arduino used in the encoder. (c) Example of mounting the encoder on the test machine Izod-type impact (adapted from MatWeb, 2022).

Samples's opacity

The encoder's optical sensor was also used to measure the opacity of the evaluated samples, introducing the fractured piece manually between the LED and the photoreceptor. The passage of the light beam through the material changes the electronic signal provided by the module according to the sample's translucency. In the case of semicrystalline polymers such as PLA, the formation of crystals would generate more compact structures, which do not allow the passage of light between the polymeric chains. In this sense, this method can be used as a tool for estimating crystallinity, although the correct calculation of this property must be done through more reliable tests (Piorkowska and Rutledge, 2013), such as differential scanning calorimetry (also known as DSC, from Differential Scanning Calorimetry) and Dynamic Mechanical Analysis (DMA).

RESULTS AND ANALYSIS

The samples impact strength can be seen in Figure 5, in which the letters A to H indicate the printing and post-treatment conditions that the parts were subjected to, as previously explained in Table 1. It is noticeable that the specimens submitted to the annealing process absorbed a much higher energy when compared to the other non-annealed specimens, with an increase of around 300%. This is also confirmed in the Pareto chart of effects of Figure 6, resultant from analysis of variance. This result may be associated with the fact that during annealing, which maintains the parts at a temperature above the T_g of the polymer, the greater mobility of the macromolecules allows for better intertwining of the polymer chains, improving adhesion between the deposited filaments (Seppala et al, 2017). Another possibility is the change suffered in the empty spaces' configuration, which can coalesce and form structures of lower stress concentration, or even facilitate contact between the layers, as observed by Hart et al (2017). Another possibility of increasing the mechanical properties comes from the crystallization process

itself, since the crystals act as barriers to the stretching of the amorphous chains, which is the initial mechanism of the elastoplastic deformation observed in thermoplastic polymers (Callister, 2006). It is also noticeable that the samples from D4508 had a slightly increased energy absorption when compared with D256, as shown in Figure 5 and confirmed in Figure 6, which may be due to the fact that the D256 samples had a chip that facilitates its fracture, while D4508 didn't have it.

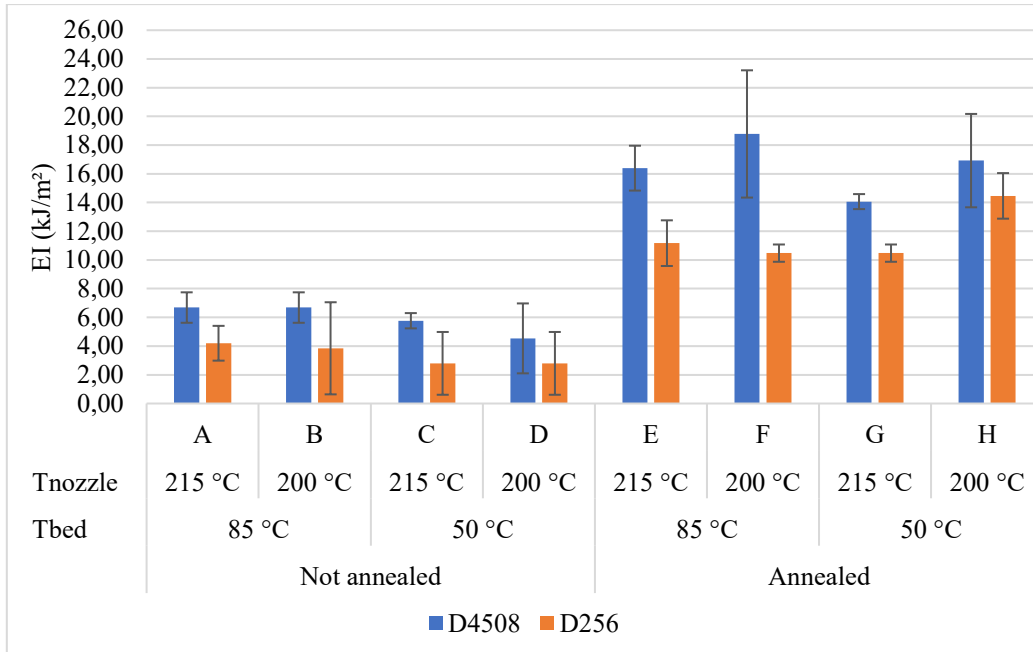


Figure 5. Graphic of the energy absorption by the samples of different standards.

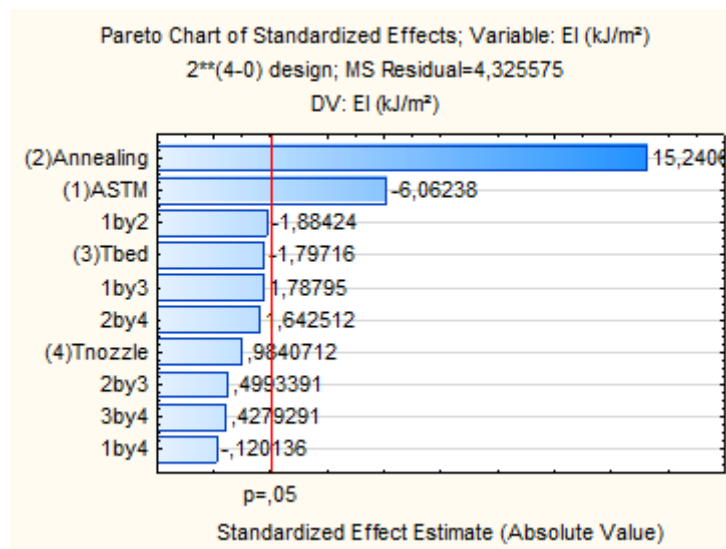


Figure 6. Pareto chart showing the most significant variables that affect the impact resistance of PLA printed parts.

The translucency of both the D256 and D4508 samples were also analyzed. Considering the standard deviations of the results, there wasn't much difference due to the sample geometries

of different standards, but there was a slight increase in the average translucency of the annealed specimens, as seen in Figure 7. However, no variable was statistically significant in ANOVA. It is possible that all samples were too thin to cause a significant alteration of translucency, or that the time and temperature chosen for annealing did not affect the crystallization of the polymer so much.

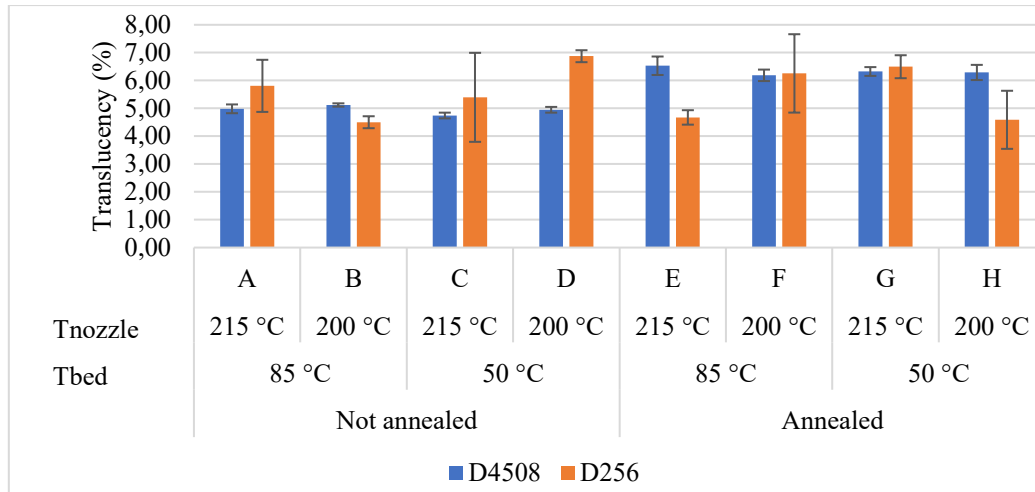


Figure 7. Graphic of the translucency for all samples.

Figure 8 shows the variations of length, width, and thickness of ASTM D256 samples. Although the results for the same sample production parameters vary greatly, as indicated by the large standard deviations, in average, there were some consistent variations. For instance, the table temperature of 85 °C and nozzle temperature of 200 °C of samples B and F caused samples to increase in length and thickness after annealing, while all other printing conditions caused the samples to shrink after annealed. It is important to highlight that the printing parameters can change the geometry of voids in the parts and affect crystal growth orientation. Although there is not a readily visible pattern to explain while only B samples increased in geometry after annealing, it could be associated with less voids between deposited filaments in this conditions, which could be a combination of better layer adhesion and more consistent filament deposition.

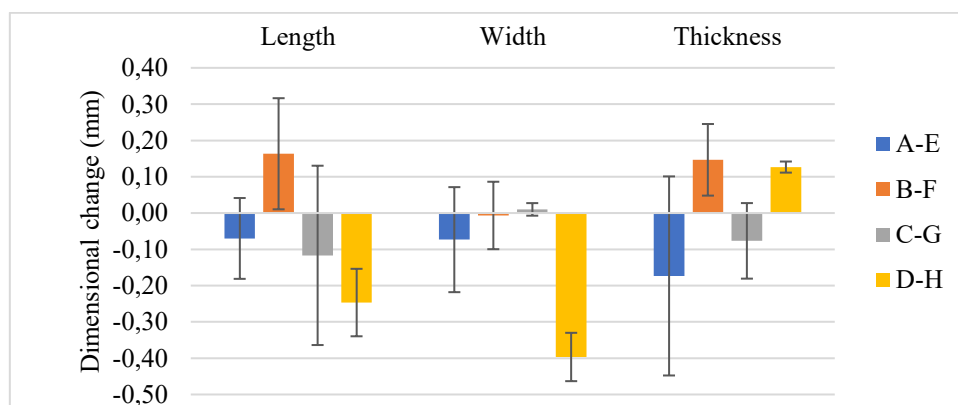


Figure 8. Graphic of the dimensional variation of the samples from ASTM D256.

CONCLUSION

With the greater accessibility to Fused Filament Fabrication processes, its use in research and applications in the industry becomes more common, making it important to evaluate simple and low-cost conditions that improve the resistance of the final parts. In this case, an average improvement of 300% on the Izod impact resistance was found when annealing the parts, both for ASTM D256 and D4508 standards. Although this could be explained both by change in the crystallinity of the parts and by better filament adhesion, it is likely that only the second has taken place, since there was no statistically significant change in the translucency of the samples with any of the variables, considering this factor is intimately correlated with polymer crystallinity. Overall, these results demonstrate a good efficiency of the annealing technique, and by enabling the fine tuning of the printing parameters they constitute a simple and cheap way to improve the mechanical properties of the parts. It is important to highlight that although this kind of experiments allow optimization of the printing conditions, this was not carried in this work.

It is interesting to notice that the type of standard used was a significant parameter in the impact resistance. It is likely that the fact that the D256 samples had a chip on its side was the only cause for difference, since due to this all these samples will need less energy for the fracture to nucleate and propagate along the polymeric material. Another interesting point was the verification of geometric deviations due to the annealing process. This phenomenon is well reported in the literature and may occur due to filling of the voids left between deposited strands in printed parts, or due to crystallization which also changes the material density and specific volume. Since the translucency was not greatly affected as commented before, it is likely that only the first factor explains the overall trend of reducing the parts dimensions. Intriguingly, for one of the printing conditions, with higher table temperature and lower nozzle temperature, samples increased in length and thickness after annealing, on average, which could be related to smaller void volume during printing at these conditions.

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RESPONSIBILITY NOTICE

The author(s) is (are) the only responsible for the printed material included in this paper.

CAPÍTULO 8

8. ARTIGO 5

Campos, F.A.R., Barbosa, L.M.Q., Almeida, K.F., Oliveira, P.H.V., Andrzejewski, G.C., de Sousa Filho, P.V., Machado, A.R. (2023). INFLUENCE OF ANNEALING ON PLA MECHANICAL AND THERMAL RESISTANCE. In Proceedings of the XXVII International Congress of Mechanical Engineering-COBEM2023. Florianópolis. doi://10.26678/ABCM.COBEM2023.COB2023-0503

COB-2023-0350

INFLUENCE OF ANNEALING ON PLA MECHANICAL AND THERMAL RESISTANCE

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Abstract. *Fused Filament Fabrication (FFF) is a widely used additive manufacturing process. It involves extruding a polymer filament through a heated nozzle, which moves in three axes and deposits the material in layers on a flat bed. As the plastic cools and solidifies in each layer, it receives some thermal energy from subsequent depositions. Understanding the thermoplastic properties, particularly the glass transition temperature (when molecules become more mobile and adherent) and the crystallization temperature (when molecules organize into crystals, providing more strength and less ductility), is essential for this process. The objective of this work was to evaluate the impact of annealing on specimens, allowing the materials to crystallize and also improve layer contact and adhesion. Tensile and flexural tests were conducted according to ASTM D638 and ASTM D6272 standards to verify changes in mechanical properties, while heat deflection temperature (ASTM D648) tests and geometric deviation measurement evaluated the thermal resistance and warping, respectively. The methodology involved a complete factorial experimental design with 2 levels and 3 factors (2³), for each of the tests. A universal testing machine was used for both tensile and flexural tests while the heat deflection tests were conducted in an Arduino automatically controlled electric oven to ensure a steady temperature increase rate of 2 °C per minute. Results have shown small changes in the material resistance due to printing, and little dimensional changes as well, with greater effects from printing parameters, which could happen due to sensibility of the material to humidity, since it is contrary to what expected. However, the thermal resistance of the polymer improved greatly, showing an interesting feature of the annealing process for PLA and its wide range of uses in the industry and consumer end applications within additive manufacturing.*

Keywords *Additive manufacture, Annealing, Impact resistance, Crystallinity*

INTRODUCTION

Additive manufacturing (AM) by the Fused Filament Fabrication (FFF) process has shown excellent ability to print parts with complex geometry at lower costs than other AM techniques. This process basically consists of an extrusion system with a movable nozzle, which deposits molten material, layer by layer. The technique has gained space in automotive, biomedical, artistic and educational applications, mainly due to the greater application of plastics and polymeric composites in several fields. Thermoplastic polymers are predominantly used, which have good fluidity close to their melting temperatures, typically in the range of 180 to 300 °C, but with good mechanical strength at room temperature.

A common problem in parts manufactured by FFF is the lower resistance at the interface between the printed layers. This phenomenon causes failure under a variety of test conditions, including tension (Cole et al, 2016; Sood et al, 2010; Fernandez-Vicente et al, 2016), bending (Sun et al, 2008), torsion (Rodríguez and t al, 2000) and compression (Percoco et al, 2012), for which the loading can be static or impact. In the latter case in particular, the lack of adhesion between layers facilitates the nucleation and propagation of cracks between layers (Sharafi et al,

2021). Therefore, the interlaminar bond strength of additively manufactured parts is still one of the main obstacles to the design and use of parts. Figure 1 illustrates this phenomenon, where the lack of contact between the deposited layers hinders proper intertwining of polymeric chains, the crucial mechanism for achieving interfacial adhesion in printed objects (Sun et al, 2008). Addressing this issue is vital for further enhancing the quality and durability of FFF-manufactured items.

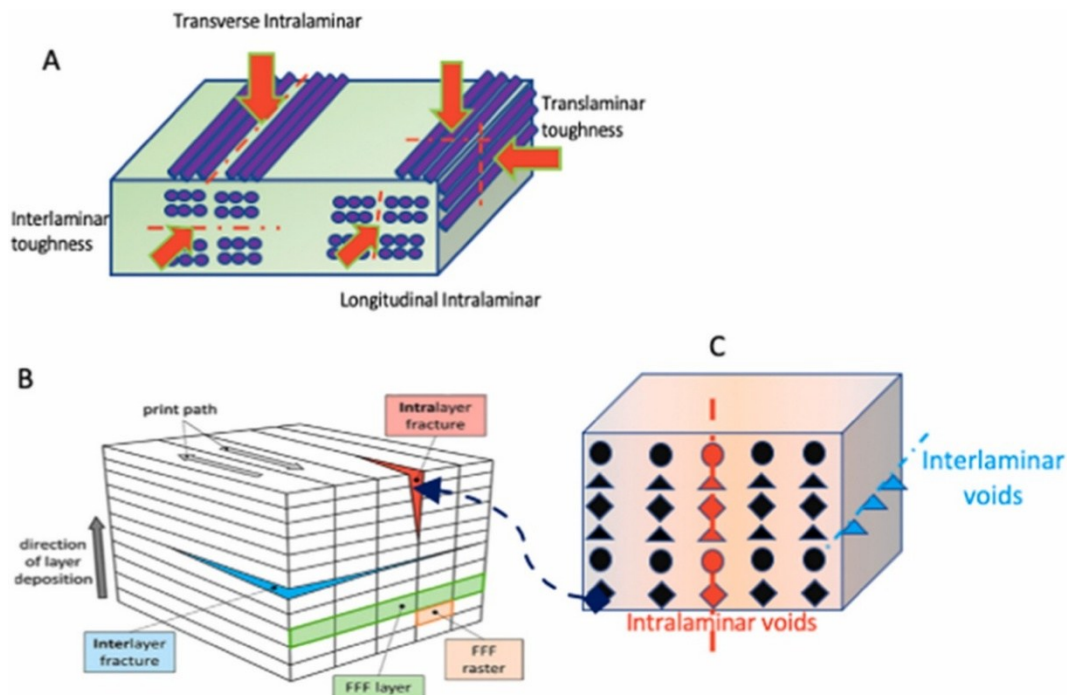


Figure 1. (a) Possible failure modes in parts printed by FFF on composite fiber filaments or (b) purely polymeric filaments with (c) voids between the deposited layers. Adapted from Sharafi et al (2021).

A variety of methods have been employed to improve this adhesion, including optimization of printing parameters, such as scanning speed, printing bed temperature, nozzle temperature, deposition rate, among others (Aliheidari et al, 2017; Johanson, 2016). Other alternatives include using adaptive layer height algorithms (Allen and Trask, 2015), adding plasticizers (Wang et al, 2014) to the filament, using microwave irradiation (Sweeney et al, 2017), or post-processing such as annealing (Hart et al, 2018; Bhandari et al, 2019). While improvements in mechanical performance have been observed using these techniques, these properties rarely approach the mechanical strength and toughness of similarly shaped materials made by more traditional means such as injection molding.

The mechanisms linked to this phenomenon of adhesion between polymers have been described for cases of joining and welding of polymers, so that they can explain the influence of the numerous variables of additive manufacturing on the resistance of parts produced by FFF. In general, the adhesion process is related to the molecular diffusion of the polymer chains from one layer to the other, and therefore, it strongly depends on factors such as the fluidity and surface

tension of the molten polymer, the interface temperature in relation to the glass transition temperature of the polymer (called T_g , being determinant for the mobility of the chains), the time and pressure at the interface of the layers, and phenomena related to possible crystallization in some polymers. During deposition, the polymer is heated to a temperature $T > T_g$ and then extruded over the previously deposited layer, which in many cases has already cooled below the T_g , leading to a rapid and repeated variation of the interface temperature, above and below the T_g (Sun et al, 2008; Seppala et al, 2017). This heat transfer process is very sensitive to printing conditions because they decisively influence the flow and distribution of heat in the part over time (Mackay et al, 2017; Seppala et al, 2017). The complexity of thermal history thus represents another determining factor for good adhesion and interlaminar tenacity. Another point of interest is the phenomenon of crystallization. Depending on the molecular structure of the chains, it is possible for them to group together in an organized and packaged structure, occurring more easily in polymers with shorter, more rigid, unbranched chains and without side groups (Canevarolo Junior, 2006). As the deformation of polymers depends a lot on the movement and stretching of the polymeric chains, the tensile strength, yield strength, modulus of elasticity and behavior under impact strongly depend on the crystallinity content in the volume of the material (Matyjaszewski and Möller, 2000). This content varies according to the cooling conditions of the thermoplastic from its viscous state, as it occurs with the slow organization of the chains in its crystalline configuration, which has lower free energy (Ebewele, 2000).

Many works focused on improving the resistance of parts produced by FFF have already addressed the effects of parameters that modify the geometry and moment of inertia of the part, such as wall thickness, percentage and type of infill. In this regard, this work aimed to verify now the influence of annealing and printing parameters that affect thermal history on the mechanical and thermal properties of PLA. The samples were printed by FFF process and evaluated by tensile tests, flexural tests, geometric deviation, and heat deflection test. The discussions made contribute to a better understanding of these phenomena by students, researchers, and hobbyists.

METODOLOGY

Preparation of the samples

All samples used in this study were printed from natural polylactic acid (PLA) filaments of diameter 1.75 mm, from 3DFila manufacturer. Test samples were produced by additive manufacturing using the method Fused Filament Fabrication (FFF) using a 3D printer Creality Ender 3 to print different geometries for each test standards, varying the printing parameters and annealing as shown in Table 1. A complete factorial experimental design was used for each type of test, in 2 levels and 3 variables (2^3), with sample parameters A to H, being used for tensile test according to ASTM D638 (2014), four point bending flexural test by ASTM D6272 (2017) and heat deflection temperature by ASTM D648 (2018), which measures the polymer resistance to heat

under small mechanical stresses. It should be noted that during printing, all other parameters remained constant, such as layer height (0.2 mm), printing speed (50 mm/s) and nozzle size (0.4 mm).

Table 4. Complete factorial experimental design 2³.

Test condition	Tbed	Tnozzle	Annealling
A	85	215	without
B	85	200	without
C	50	200	without
D	50	215	without
E	85	215	with
F	85	200	with
G	50	200	with
H	50	215	with

Annealing and heat deflection tests

The impact of post-treatment through annealing was investigated by subjecting the printed components to controlled heating in an electric oven. For this purpose, half of the printed samples in each test were annealed using a 10 L electric oven from Britânia, featuring 1050 W. The annealing process involved placing the samples inside the oven before activating it and heating them for 20 minutes within a temperature range of approximately 100°C to 120°C as can be seen in the left side curves of Figure 2, in which the oven's internal temperature was measured by four type K thermocouples connected to MAX31855 Arduino compatible modules. An Arduino Uno microcontroller with an ATmega processor 328 was used as signal acquisition board to record data on the computer with the CoolTerm 2.0 software. After the annealing process was completed, the oven was turned off, and the parts were allowed to cool inside for 20 minutes.

The heat deflection tests, on the other side, were carried by heating the oven in an automatically controlled manner to make the temperature rise in a constant rate of 2 °C/min as required by the ASTM D648 standard. For this, the oven was turned on and off constantly by an electronic relay connected to Arduino also, that switched off the power if the real temperature were above the ideal value at any given time and did the opposite if the real temperature was lower, creating a closed loop control system. The heating curve is also shown at Figure 2, showing good precision of the system. However, a stress of 1.2 MPa was applied to the samples instead of the traditional values recommended by ASTM.

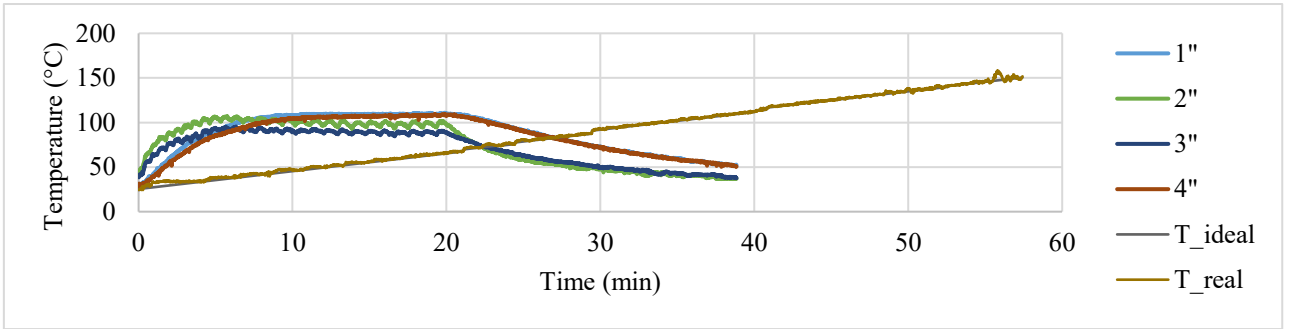


Figure 2. Temperature in the oven measured by thermocouples connected to Arduino, during annealing and during heat deflection tests.

Tensile and flexural tests

The tensile tests were carried with the type 5 specimen of ASTM D638, shown in Figure 3, where the main dimensions are $L = 9.5$ mm, $W = 3.2$ mm, $W_0 = 9.5$ mm, $T = 3$ mm and $LO = 63.5$ mm. The flexural tests were carried with rectangular section beams of dimensions 127 mm x 12.7 mm x 3 mm.

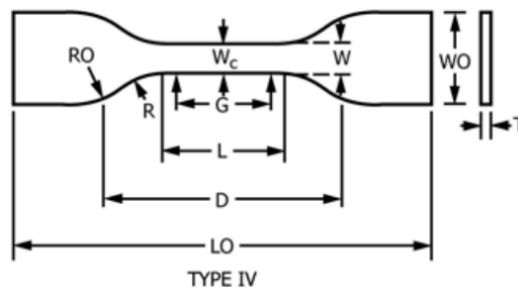


Figure 3. Type 5 test specimen according to ASTM D638 (2014).

Both tests were carried in a custom-built universal testing machine similar to other well established models (Hoffman Tactical, 2023). The equipment was equipped with 4 load cells in parallel, each with max capacity of 50 kg and resolution 0.05 g, with precision of 5 g according to manufacturer. The whole setup was connected to an Arduino for data acquisition in the same manner explained for the annealing tests, however, with HX711 modules. An electric DC motor with reduction gear was used to generate 3 kgf.m of torque, which resulted in a max tensioning force of approximately 150 kg. Instead of the typical 0.01 or 0.1 shear rates recommended by the standard, an intermediary value of 0.04 was used due to limitations in the equipment. The load and displacement were acquired simultaneously and later the results were analyzed in Microsoft Office Excel 2016, calculating the tension and deformation as required by the standards, with examples of the curves shown in Figure 4. Displacement was measured at the machine axle by an encoder, recording the rotation of the main tensioning screw. The maximum stress, deformation at breaking and elastic modulus were calculated for comparison of the mechanical properties.

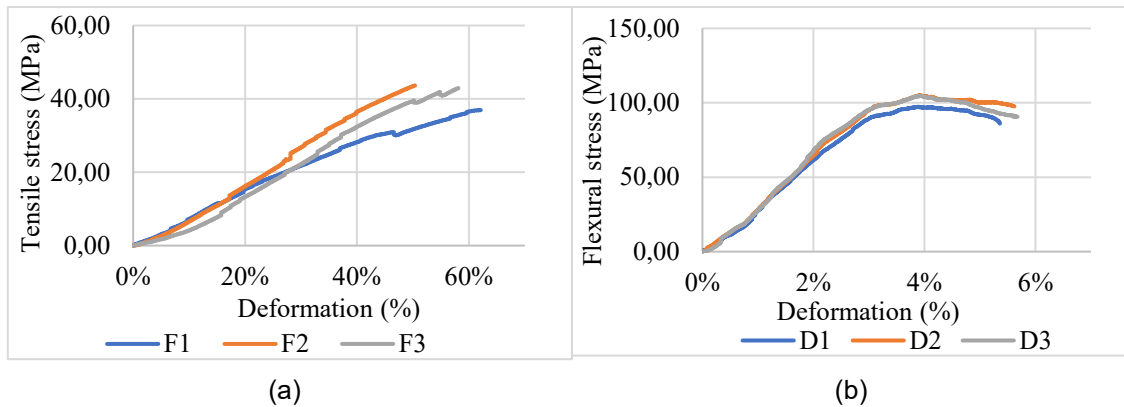


Figure 4. (a) Tensile test curve and (b) flexural test curve showing stress and deformation of samples.

Geometric deviation

The flexural test samples were measured before and after annealing to verify any impact of the process on the dimensions of the printed parts. The thickness, width and length were measured with a caliper with 0.01 mm resolution and 150 mm nominal capacity, The average and standard deviations of the changes were recorded.

RESULTS AND ANALYSIS

The flexural resistance of the samples can be seen in Figure 5, which shows a trend of increasing resistance and elasticity module towards the less severe printing conditions with lower temperatures for table and nozzle. The ductility of the material, however, takes the contrary effect, diminishing in this case. Surprisingly, the annealing process did not seem to affect the mechanical properties of the material. Although it has been shown that the annealing process does alter the material mechanic characteristics, it has also been shown that this effect may be hindered if the samples are affected by moisture (de Almeida et al., 2023), which might have happened in this case. This is confirmed by the Pareto charts of Figure 6, which show that nozzle and bed temperature were statistically significant for the maximum resistance, ductility and elasticity module.

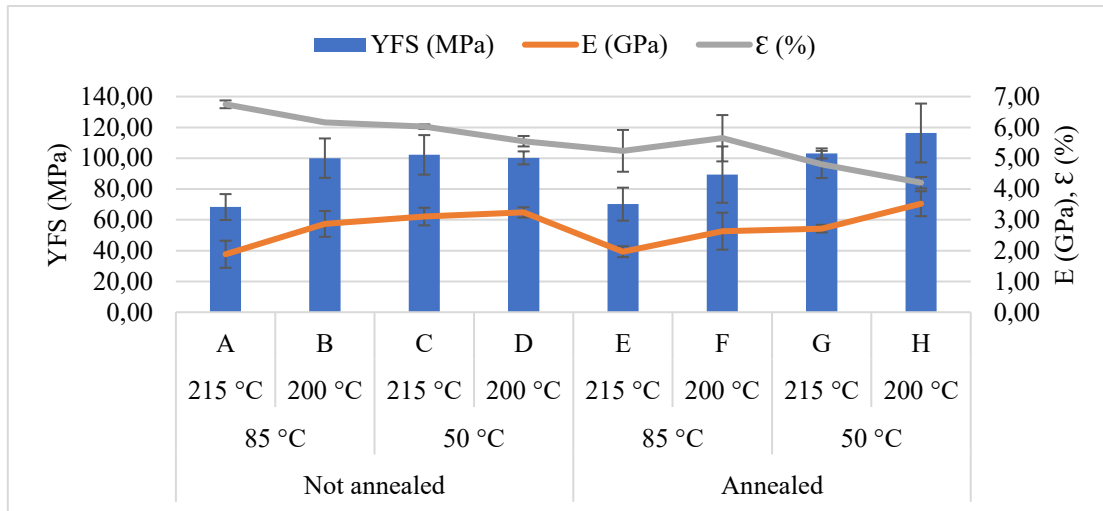


Figure 5. Maximum flexural resistance, maximum deformation, and elastic modulus of bending for all types of samples.

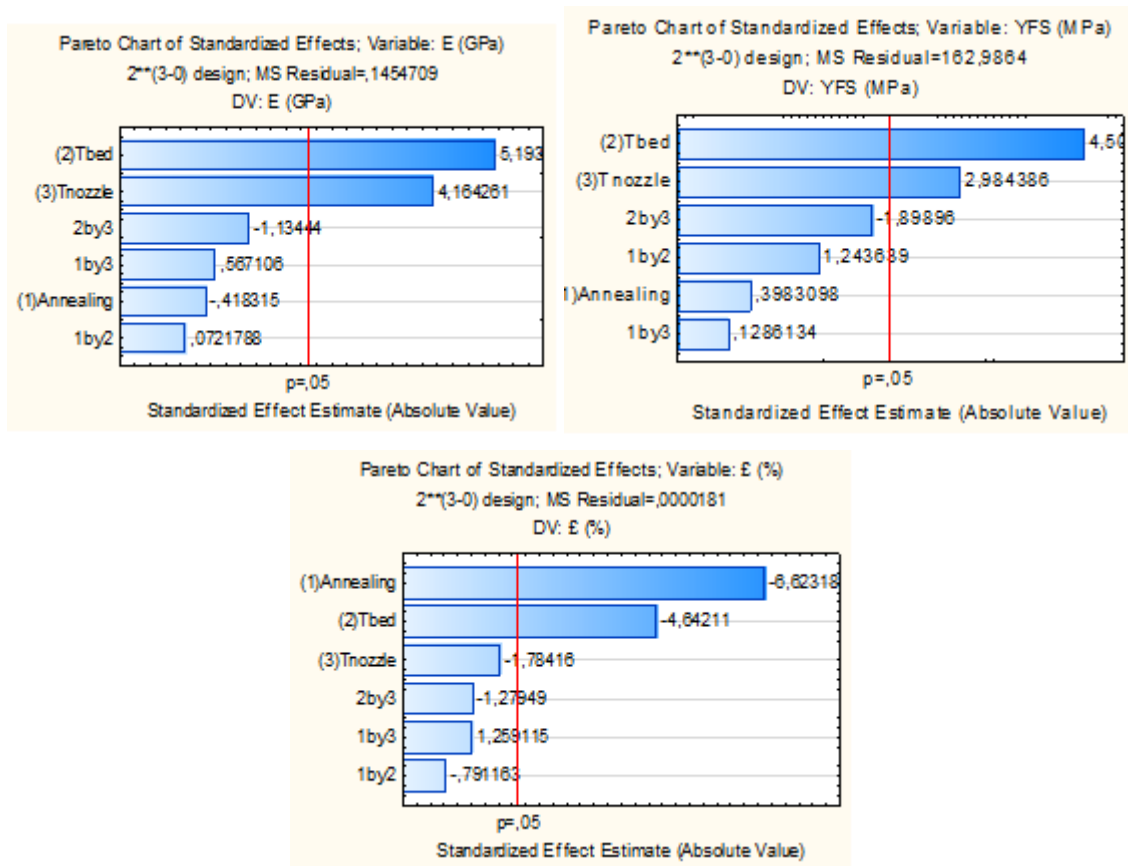


Figure 6. Pareto charts with the most influential variables for the mechanical properties evaluated in the flexural tests.

The tensile resistance of the samples can be seen in Figure 7, which shows again no distinguishable difference between the annealed and printed parts, considering maximum resistance, ductility, and elasticity module. This is confirmed by the Pareto chart at Figure 8, which shows, however, that the nozzle temperature was a statistically significant factor for the elastic

modulus alone. This means that the lower nozzle temperature was beneficial for the material rigidity, which could be associated with chemical damage in the polymer in this harsher printing condition.

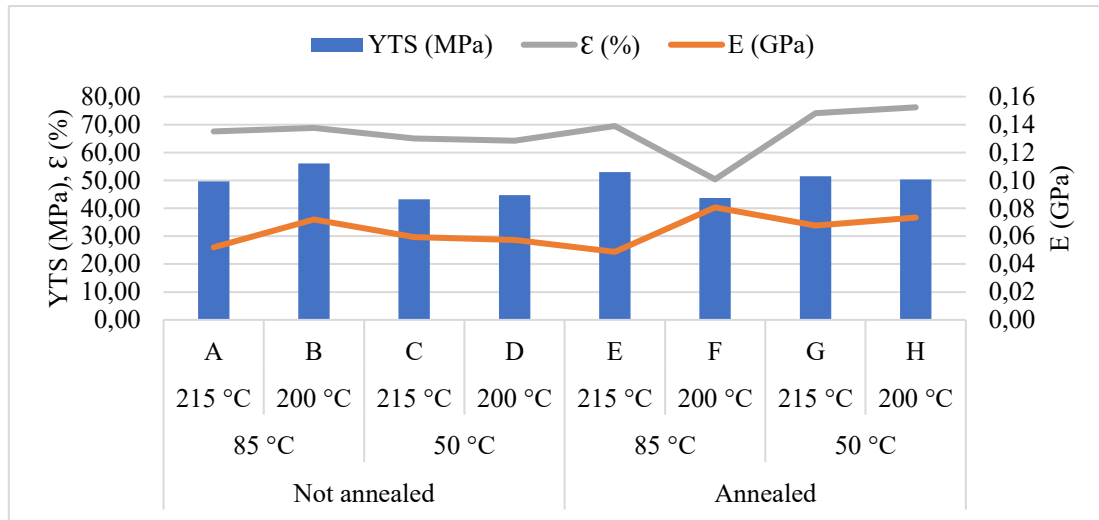


Figure 7. Maximum tensile resistance, maximum deformation and elastic modulus for all types of samples.

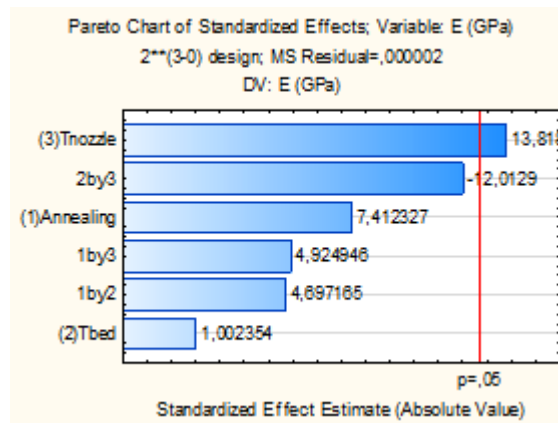


Figure 8. Pareto charts with the most influential variables for the mechanical properties evaluated in the tensile tests.

The material deformation can be seen in Figure 9, which compares the annealed flexural samples with the printed ones. In all cases, it was observed an increase in thickness and decrease in length, which is a common phenomenon that takes place due to crystallization process (Lluch-Cerezo et al., 2022) and due to reorganization of voids (Hart et al., 2018) inherent to the printing process. Surprisingly, condition B had a large increase in width, different from all other printing conditions. It is possible that the lower nozzle temperature and higher bed heating could have resulted in a less voids between deposited filaments, due to better layer adhesion and/or more consistent filament deposition.

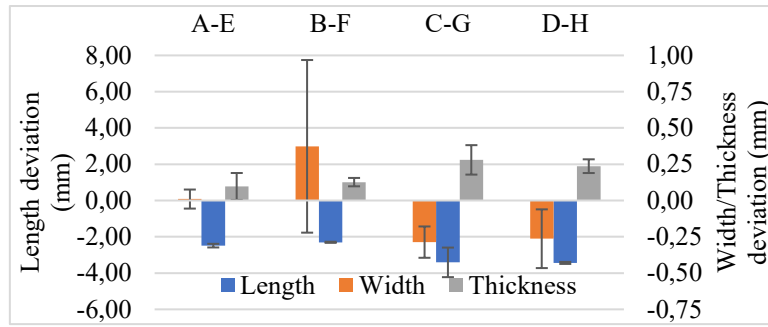


Figure 9. Dimensional change in samples due to annealing.

The thermal resistance of the samples as per ASTM D648 can be seen in Figure 10 showing now that there was a massive increase in the maximum temperature supported by the samples when annealed. Figure 11 shows that bed temperature was also statistically significant, although twenty times less than annealing. It is likely that this change was due to higher crystallinity of the material, since it has already been shown (Piorkowska and Rutledge, 2013) that more crystals require more heat before the material melts. Also, when the material has a great proportion of amorphous phase, this part of the material quickly becomes soft after the material heats above the T_g (Callister, 2006). This way, even though the mechanical properties might not have improved with annealing in this case, the material heat resistance improved enormously, from about 70 °C to more than 140 °C. For instance, this allows for a wide range of new applications for PLA, especially in medical devices, since it would mean that the annealed parts could now be sterilized in dry air or humid vapor, which is typically carried at 120 °C (Vaes and Van Puyvelde, 2021)).

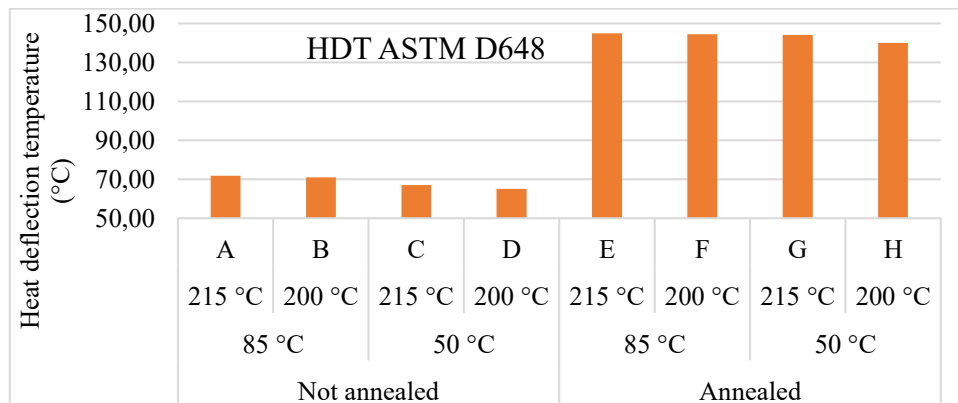


Figure 10. Heat deflection temperature measured according to ASTM D648, indicating PLA thermal resistance depending on printing conditions and annealing.

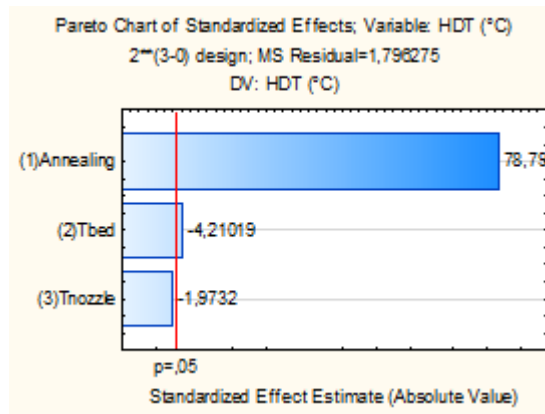


Figure 11. Pareto charts with the most influential variables for the thermal resistance of the samples.

CONCLUSION

The influence of annealing on 3D printing samples mechanical properties and thermal resistance were investigated in this work for PLA, performing tensile tests, flexural tests, geometric deviation verifications, and heat deflection temperature test which indicates material thermal resistance.

The results have shown small changes in the material resistance due to printing, and little dimensional changes as well, with greater effects from printing parameters, which could happen due to sensibility of the material to humidity, since it is contrary to what expected. However, the thermal resistance of the polymer improved greatly, showing an interesting feature of the annealing process for PLA and its wide range of uses in the industry and consumer end applications within additive manufacturing.

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CAPÍTULO 9

9. ARTIGO 6

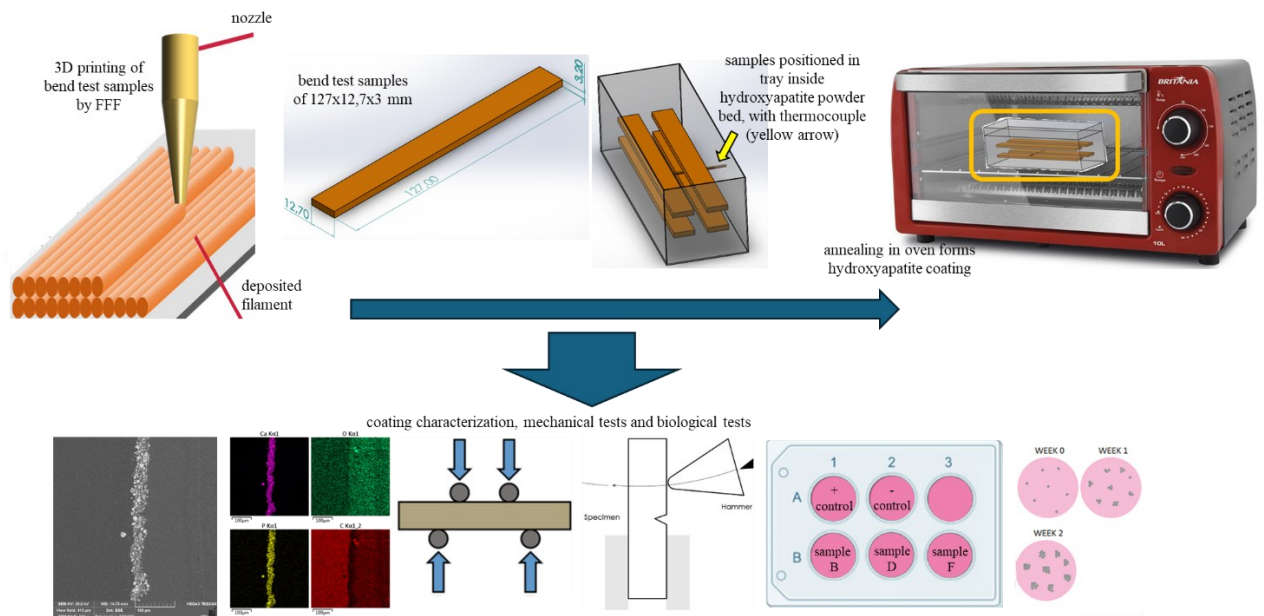
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Production of hydroxyapatite coating on 3D printed PLA parts by powder bed annealing

Abstract

The development of effective and biocompatible coatings for polymeric implants is crucial for advancing orthopedic solutions. This study investigates the feasibility of employing powder bed annealing to deposit hydroxyapatite (HA) coatings on 3D-printed polylactic acid (PLA) parts. The proposed method provides a cost-effective and scalable alternative to conventional coating techniques. The experimental process involved immersing PLA parts in a submicrometric ceramic powder bed followed by thermal treatment to induce adhesion and diffusion of HA particles into the polymer surface. The results demonstrated that the powder bed annealing process successfully generated a uniform HA particulate coating, significantly enhancing the surface roughness, wettability, and hydrophilicity of the PLA substrate. Mechanical characterization revealed an increase in flexural strength and surface microhardness, while maintaining impact resistance. However, a slight reduction in ductility was observed. Biocompatibility tests confirmed that the coated samples supported cell adhesion and proliferation, suggesting their potential for promoting osseointegration in biomedical applications. Compared to existing methods, powder bed annealing allows for the direct integration of bioactive coatings onto polymeric implants without requiring complex post-processing. Additionally, the combination of PLA's biodegradability with HA's osteoinductive properties suggests promising applications for resorbable implants in bone regeneration. This study contributes to the ongoing innovation in bioactive coatings, offering a practical pathway to accessible and personalized orthopedic implants.

Graphical Abstract



Keywords: Hydroxyapatite coating, Powder bed annealing, 3D printing, Polylactic acid (PLA), Orthopedic implants

INTRODUCTION

With the development of technology and medicine, together with the increase in the quality of life of the population in several countries, there has been a growing increase in the life expectancy of its inhabitants [1], which has resulted in an aging of the world population [2]. This creates new challenges related to old age, obesity and a sedentary lifestyle, such as osteoarthritis, which is characterized as a degeneration of the articular cartilage and simultaneous proliferation of bone tissue, cartilage and connective tissue [4], and causes progressive symptoms of pain, limitations of joint movement, stiffness and muscle weakness [5].

This situation has been accompanied by an increasing number of orthopedic problems and a greater demand for the use of implants. Therefore, it is extremely important to conduct research to develop technologies that enable the manufacturing of implants in a more financially accessible way and that use more practical manufacturing methods that offer greater capacity for customization according to the patient's characteristics. In this sense, many studies have been carried out on the feasibility of using polymers [3, 6], such as the successful implantation of a rib implant made of biocompatible Nylon produced by additive manufacturing [7]. Among the benefits of using biocompatible polymers, in addition to their much more affordable price than titanium, the most common material used in implants, it is also worth mentioning that some have satisfactory mechanical properties [8] and an elasticity modulus closer to that of bone tissue, which prevents the effect of bone density loss due to an uneven distribution of load between the implant and bone, known as *stress shielding* [9]. Another major difference of some polymers, such as polylactic acid (PLA), is their resorbable characteristic, with their degradation occurring through hydrolysis and enzymatic activities [10], which can be very useful for the production of small

implants that can break down over time and be absorbed by the body while the bone tissue around them regenerates and takes their place.

Even though there is already a good variety of polymers with good biocompatibility, such as PLA, PCL and Nylon 12, there are studies showing that the compatibility presented by polymers can still be improved using methods for surface modification of the part, since the roughness of the implant has an influence on bone differentiation [11], and that the use of calcium compounds and titanium dioxide in the form of a coating stimulates the regeneration of bone tissue [12, 13].

With this interest in the use of polymers in the manufacture of implants, a manufacturing process that ended up benefiting and standing out was additive manufacturing, such as the *Fused Filament Fabrication* (FFF), which allows the rapid manufacture of polymeric parts with a high level of customization. However, this technology has as its main limitation its high anisotropy, due to layer-by-layer deposition, resulting in mechanical properties dependent on adhesion between layers in the direction perpendicular to the plane of the deposited layers. Thus, a possible method to solve this problem is to perform an annealing process, to coalesce the layers or even fuse them, making the part more homogeneous and reducing anisotropy. Another possible benefit of annealing is the change in the organizational state of the molecules in semicrystalline polymers, such as PLA. In these cases, their permanence at temperatures above the glass transition temperature favors an increase in crystallinity, which can improve their mechanical properties [14].

Many works have attempted to improve 3D printed parts mechanical properties by annealing [15–18], and although the results were very promising with increases in mechanical properties up to 100%, the process could deform the geometry of the parts [66]. However, it has been found that immersing the parts in powder and compacting it could form a mold that would maintain the geometry during annealing and/or remelting [19]. As explained in other works [20], the remelting might cause particles from the powder to adhere in the surface, but they could be easily cleaned after by sanding. With this phenomenon in mind, it was hypothesized in this work that this particle adherence could be used to generate a coating in an innovative, simple and inexpensive way, by immersing the 3D printed PLA part in a powder bed and conducting the annealing and/or remelting process. This could in theory be used not only as a new method for depositing calcium phosphate and titanium dioxide compounds in the surface of PLA, but also as a method to improve the 3D printed parts mechanical properties, potentially setting up a new way to manufacture orthopedic implants.

Thus, this work aimed to use the powder bed annealing process to generate a ceramic particulate coating on PLA parts manufactured by the FFF process. The project consisted of heating and remelting the part immersed in a tray of submicrometric ceramic particulates and then analyzing the influence of the thermal process parameters in the mechanical resistance of the parts and in the formation of the calcium phosphate and titanium dioxide coating, both materials with recognized capabilities of inducing osseointegration in orthopedic implants [64, 65] and widely used for coating commercial implants. The innovative nature of the research stands out,

because although annealing in particulate matrix has already been reported in the literature for improving surface roughness and mechanical properties, the possibility of generating a biocompatible coating had not yet been explored. These studies hereby presented may result in reduced manufacturing costs for customized parts for orthopedic implants, contributing to the general health of the population.

MATERIALS & METHODS

PRODUCTION AND PREPARATION OF TEST SPECIMENS

Several pre-tests were performed to verify the possibilities and suitable conditions for generating a coating through the powder bed annealing process, in which a significant change in the physical and mechanical appearance of the samples was observed, through visual inspection and flexural tests. For instance, it was found that annealing below 170 °C yielded no visible coating, while above 190 °C the sample would suffer significant geometrical deformation after annealing. Besides, as both calcium phosphate and titanium dioxide coatings favor osteointegration of implants as mentioned above, it would be desirable to verify in cytologic tests if there was a better component for the proposed coating method. However, it was also verified that annealing in pure titanium dioxide powder led to severe porosity in the samples, while there was no such disadvantage when using calcium phosphate. For this reason, titanium dioxide could only be tested when mixed with calcium phosphate in these pre-tests.

Thus, as defined in preliminary studies, test samples were prepared in accordance with ASTM D6272 [21], since it was desired to compare the behavior of the test specimens in four-point bending, impact, water contact angle, surface roughness, microhardness and layer thickness tests. As the sample geometry could be used for all tests, it facilitated production and guaranteed that there were always extra test specimens available. In addition, the main advantage of choosing the same geometry was to ensure that during the annealing process there would be no major differences in temperature distribution and heating rate.

All samples were produced one at a time on a Creality Ender 3 v1®, to guarantee that the thermal history of each sample would be the same prior to annealing. The test specimens were produced with a nozzle temperature of 210 °C, table temperature of 60 °C, 100% infill, printing speed of 50 mm/s, layer height of 0.32 mm and diameter nozzle of 1 mm. The adopted test specimen had a parallelepiped shape of 127 mm in length, 12.7 mm in width and 3.2 mm in thickness, as shown in Figure 9, and they were printed with the largest surface in contact with the printing table.

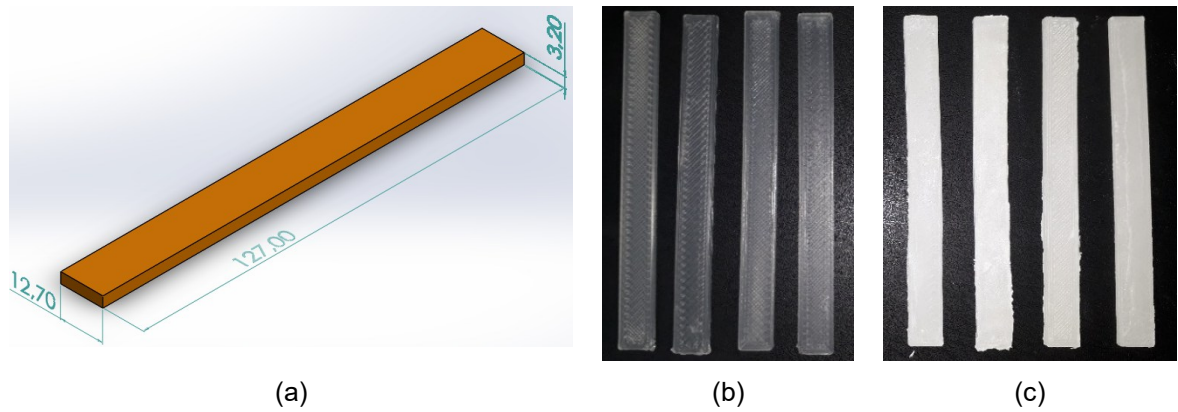


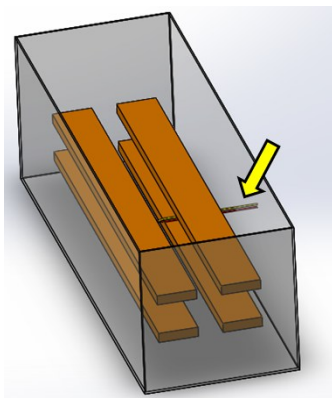
Figure 9. (a) sample geometry. (b) Samples as printed. (c) Coated samples.

The powder bed annealing process was performed using a Britania BFE10V electric oven and the particulate used was pure calcium phosphate (CaPO) and a mixture of 50% calcium phosphate with 50% titanium dioxide (CaPO +TiO₂). Eight test specimens were produced for each condition according to the design of experiment presented in Table 1. Four test specimens were annealed at a time, all of which were positioned inside a single tray and placed at the furnace, as shown in Figure 10. This procedure was adopted because if two trays were used at once, there could be differences in the heat and temperature distribution on the samples. The annealing temperature was controlled by a thermocouple perforating the tray, with its tip positioned between the samples.

For the annealing process, the oven was turned on and regulated on its analogic thermostat to a temperature 10°C above the maximum temperature of the condition being tested. Then the tray was inserted and the temperature inside the tray was monitored as it increased slowly towards the maximum temperature of the condition. It took about 30 minutes to reach 170 °C and 40 minutes to reach 190 °C, because it takes time for the heat to penetrate the tray and disseminate through the powder by thermal conduction. When the temperature indicated by thermocouple reached the maximum temperature of the experiment, the oven was either turned off and opened immediately for the conditions with 0 minutes at maximum temperature, or the oven was regulated on its thermostat to the maximum temperature of the experiment (170 °C or 190 °C) and kept turned on for 5 minutes and then turned off and opened. In both cases, the tray was taken off the oven and allowed to cool down naturally until it decreased to 40 °C, in a room with temperature of 25 °C, which took about 50 minutes. Then the tray was opened, and the samples were retrieved from below the powder and washed smoothly in water, dried in compressed air and stored in plastic containers filled with silica to prevent moisture, until they would be used for the subsequent mechanical and biological experiments. The procedure is patent pending, with code BR 10 2025 000986-2 registered in Brazilian National Institute of Intellectual Protection (INPI).

Table 5. Experimental design of the full factorial type 2³ for powder bed annealing tests.

Condition	Composition	Time at maximum temperature (min)	Maximum temperature (°C)
A	CaPO	5	190
B	CaPO	5	170
C	CaPO	0	190
D	CaPO	0	170
E	CaPO +TiO ₂	5	190
F	CaPO +TiO ₂	5	170
G	CaPO +TiO ₂	0	190
H	CaPO +TiO ₂	0	170



(a)



(b)

Figure 10. (a) Representation of PLA samples positioned in the metallic tray (thermocouple indicated by yellow arrow). (b) Representation of tray with samples positioned in the electric oven. Although the powder is not shown in this representation, it is filling the tray to the top, where a plate covers the tray.

After the test specimens were manufactured, four of each condition were separated for the contact angle measurement, roughness and flexural tests, while the other four of each condition were sectioned in smaller samples for impact tests, layer thickness analysis, microhardness and in-vitro biocompatibility evaluation. First the nondestructive tests such as water contact angle measurements were conducted in the first four samples, and then these same specimens were used for four-point flexural essays, with surface roughness measurements being carried in the fractured parts from the later essay. For the impact tests, layer thickness analysis and microhardness, the other four test specimens were sectioned using an angle grinder equipped with cutting disc. The parts that would be taken to SEM for analysis of layer thickness and chemical composition were embedded in resin, sanded to a 2000-mesh sandpaper, polished and received a 10 nm gold coating on a Leica EM SCD050 metallizer. These samples prepared for analysis in the SEM were the same ones used in the microhardness tests, with all analyses being carried out on the cross section of the sectioned samples. The samples for biocompatibility

tests were cut by a hole saw into small disks of approximately 9.5 mm diameter to be fit in a culture plate.

MATERIALS

All the samples were 3D printed with natural PLA by Filamentos 3D Brasil, and its characteristics are provided in Table 2 according to the manufacturer website (F3D, 2024). PLA is a material with recognized effectiveness in composite materials for orthopedic applications [22], being the most used polymer in composite interference screws [23, 24] and in research with resorbable osseointegrated implants [25]. Neijhoft et al. [26] found that if there is sufficient contact time between filament and nozzle, which can be achieved through small layer heights, the FFF method presents inherent sterility for PLA. Besides, in accordance with other studies [27, 28], it has been shown that autoclaving, the preferred method for sterilizing surgical materials in hospitals, is also able to sterilize 3D printed PLA efficiently and with low distortion for higher size parts [29]. These characteristics further highlights the adequacy of PLA as a material for implants and tissue engineering.

Table 6. Physical and mechanical properties of Premium Natural PLA from Filamentos 3D Brasil [30].

Physical Properties	Value	Unit	ASTM Standard
	1.24	+/-	
Density	0.05	g/cm ³	D792
Fluidity	7 – 9	g/10 min - (190°C - 2.16 Kg)	D1238
Relative Viscosity	4	g/dL Chloroform 30°	D5225
Melting point	165 - 180	°C	D3418
Glass Transition Temperature	55 - 60	°C	D3418
Mechanical Properties	Value	Unit	ASTM Standard
Tensile Strength	51	MPa	D638
Elongation at Break	3,3	%	D882
Impact Resistance (IZOD)	118	J/m	D256
Heat Deflection Temperature	55 - 60	°C (0.45 MPa)	E2092

The calcium phosphate was obtained from a food additive supplier, since this material is widely used as anti-humectant, while the titanium dioxide was obtained from online stores, since it is the world's most used pigment load for white paints. These powders, both of which resemble white fine particulates as thin as wheat flour, were analyzed by X-ray diffraction (XRD) to verify

which were their crystalline structures, on a Shimadzu XRD6000 diffractometer, with 2°/min scanning, 0.02° resolution and 2θ angle of 5 to 60° for calcium phosphate and 20 to 70° for titanium dioxide. The particles were also investigated by SEM (Scanning Electron Microscopy) and EDS (Energy Dispersive Spectroscopy) on a Tescan VEGA 3 and Zeiss EVO MA10 microscopes equipped with Oxford INCAx-act probe, to measure the size of particles and their chemical composition in weight, respectively.

WATER CONTACT ANGLE MEASUREMENT

The water contact angle tests were performed using a 5 μL chromatographic syringe with a fixed needle and a support that ensured the slow and controlled approach of the drop to the surface of the specimen. The drops were 5 μL and three drops were deposited in different positions on the specimens while the procedure was filmed so that it would be possible to later measure the contact angle. This procedure was performed according to Han et al. [31], following the general guidelines of ASTM D7334 [32]. The angles were measured using ImageJ software, and the images were taken from the filming approximately 10 seconds after the drop was deposited. The angles were observed as exemplified in Figure 11, for the two internal angles at the left and right edges, registering the average for each contact angle measurement. Four measurements were carried out in a sample of each condition, for calculation of average and standard deviation.

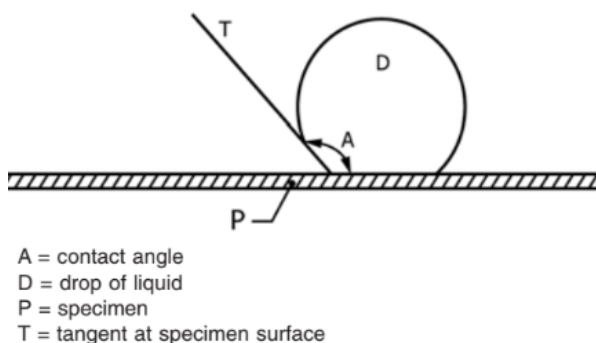


Figure 11. Measurement of contact angle in accordance with ASTM D7334 [32].

ROUGHNESS TEST

For roughness measurements the parameters Ra, Rq and Rz were observed using a portable digital Mitutoyo SJ 201-roughness meter with resolutions of 0.4 μm, 0.1 μm, 0.05 μm and 0.01 μm for a measurement range of 350 μm, 100 μm, 50 μm and 10 μm, respectively. Three specimens were tested per condition following the general recommendations of ISO 4287 [33] and ISO 4288 [34] standards, with three measurements being performed in different positions for each specimen. In addition, a cutoff of 2.5 mm was used, since according to the standard, this value is the most suitable for surfaces with Ra from 2 to 10 μm, resulting in an evaluation length of 12.5 mm.

FLEXURAL TEST

For the bending tests, four specimens of each condition were evaluated using an equipment developed at the Laboratory of Education and Research in Machining (LEPU) in previous works, which follows the requirements of ASTM D6272 (ASTM) standard. The flexural testing machine had 4 parallel load cells with a resolution of 0.05 g and a capacity of 50 kg each, totaling a maximum load of 200 kg. The load cells, with an accuracy of $\pm 0.1\%$ of the maximum load according to the manufacturer (resulting in ± 200 g for this equipment), were connected to HX711 modules linked to an Arduino Uno for amplification and signal conversion. With the results of the bending tests, data on maximum flexural strength (MFS), modulus of elasticity (E) and flexural elongation (ϵ) were obtained. To calculate the modulus of elasticity, which has different possibilities according to the standard, the method used considers the origin at 0 and the maximum load point, as can be seen in the example in Figure 12, which shows the graphs for specimens of conditions B and G, with the points used to calculate the elongation being those highlighted by black dots.

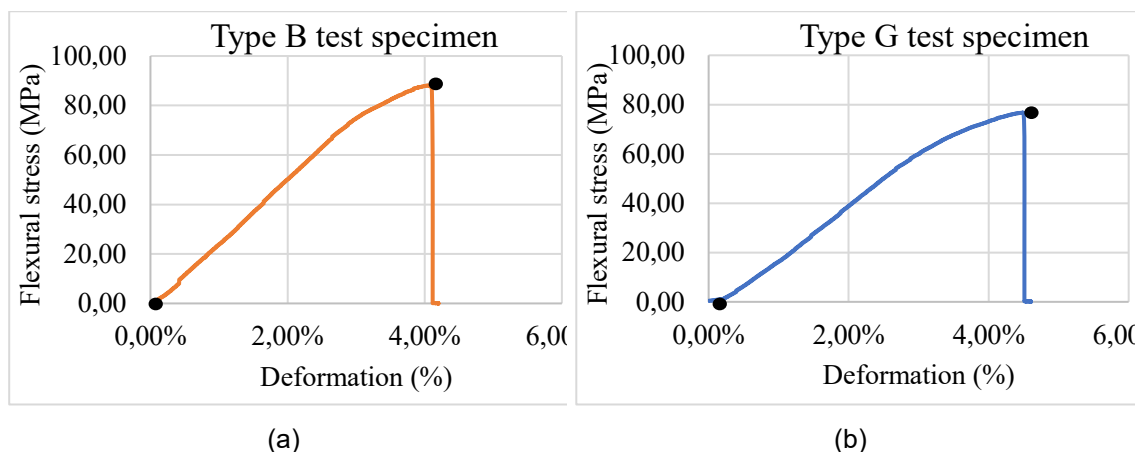


Figure 12. Stress-strain curve with points used for calculating the modulus of elasticity highlighted.

IMPACT TEST

The Izod impact tests were performed according to ASTM D4508 (ASTM) to observe the difference in energy absorbed by the samples. The specimens used were sectioned pieces with length, height and width of 19 mm, 12.7 mm and 3.2 mm respectively. In this test, four specimens were tested per condition, and the pendulum was released at an angle of 0° in relation to the horizontal, reaching a speed of 5.6 m/s when hitting the sample with an energy of 3.8 J. The pendulum used had a length of 0.778 m (distance from the tip to the center of rotation), with a total mass of 0.963 kg and a center of mass at 0.159 m from the center of rotation. The impact testing machine used was adapted from the work of Tsuruta [63], and the measurement of the energy absorption by the sample was performed by an encoder-type sensor fixed to the pendulum

shaft, which measured the maximum angle reached by the pendulum. The encoder consisted of a 220 mm disk with 360 holes 1 mm wide and spaced 1 mm apart, positioned on the edge of the disk together with an LM393 module, fixed to the pendulum support, which was responsible for reading the movement.

COATING LAYER THICKNESS AND CHEMICAL ANALYSIS

For layer thickness analysis, four samples of each condition were embedded in a disk resin, sanded up to 2000 grit sandpaper, polished with 10 µm chromium oxide particles, metallized with a 10 nm gold coating and taken to the same SEM microscopes for BSE (backscattered electron imaging) and EDS analysis. One photo of each of the four samples in the same disk was taken in BSE mode to analyze the cross-section of the original specimen, making possible to measure the layer thickness using the ImageJ software as shown in Figure , and calculating the average of the layer thickness in 3 different regions of each image.

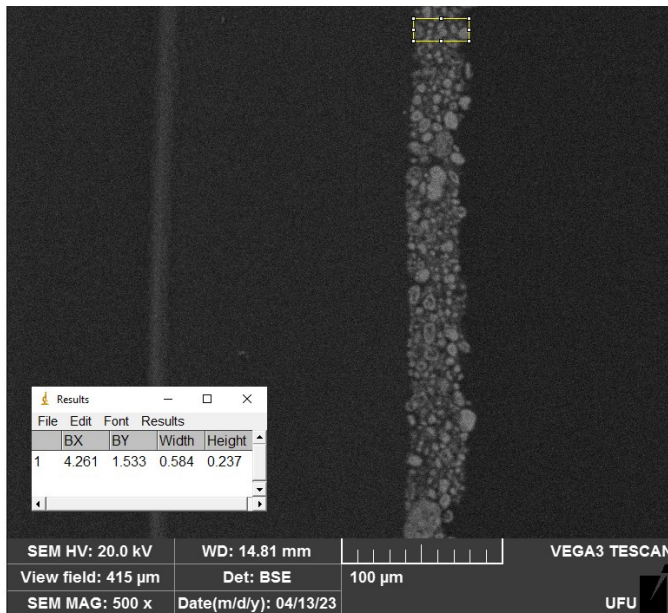


Figure 13. Image illustrating the procedure for measuring the thickness of the layer formed by the adhesion of particulate matter to a type A sample.

MICROHARDNESS ANALYSIS

After examination in the SEM, the samples underwent microhardness testing. To prevent interference, microhardness tests were conducted away from SEM-analyzed areas, as prolonged exposure to the electron beam can degrade the surface. The tests followed ASTM E384 standards, utilizing an HV0.2 scale (1.961 N load), with a 15-second load application and 10x magnification.

Measurements were taken across the sample's cross-section, starting at the surface and extending toward the center, with approximately 300 µm spacing between indentations. Each

major face of two samples from every annealing condition (A to H) was tested, resulting in four measurements per condition. This approach aimed to assess hardness variations from the coating to the substrate's inner regions.

BIOCOMPATIBILITY TESTS AND SEM ANALYSIS

Biocompatibility of the disks cut from samples was evaluated by cytotoxicity assay, using the Alamar blue assay, in which MC3T3-E1 cells, (ECACC 99072810), which are pre-osteoblast derived from mouse calvaria, were cultured in α -MEM 10% FBS medium, after reaching 80% confluence, were plated at a seeding density of 1×10^4 cells on the surface of each disk placed on the bottom of 48 well plate. The plates were incubated overnight at 37 °C in a humidified atmosphere with 5% CO₂ to allow the cells to adhere to the disks. As a positive control, cells attached to the bottom of the plate, without disks and as negative control, cells were cultivated with medium containing DMSO 5%. After 24 hour, 7 days or 14 days, 20 μ L of PBS containing resazurin (7-Hydroxy-3H-phenoxazin-3-one-10-oxide sodium salt) (Sigma-Aldrich, São Paulo, Brazil) at a concentration of 0.3 μ M was added to each well. The plate was incubated for 4 hours protected from light and then the supernatant was transferred to an appropriate plate for fluorescence Reading, which was measured using a VICTOR Nivo™ Plate Reader, at 560 nm excitation and 600 nm emission. For analysis, the absorbance of the samples containing only α -MEM 10% FBS medium (no cells) were subtracted from the samples. The statistical analysis was carried by two-way ANOVA with Tukey's post-test (for multiple comparisons) considering a 95% confidence interval for proliferation analysis with the individual viability after 1, 7 and 14 days.

After 14 days, the wells were washed 3 times in Phosphate Buffered Saline (PBS) 1X and then fixed in 3.2% formaldehyde for 1 hour at room temperature. They were rinsed once more in PBS 1X and gradually dehydrated from ethyl alcohol diluted in distilled water, in concentrations rising from 50% to 100% in 10% increments, for 10 minutes in each, and finally stored in absolute alcohol at 4°C for 1 day. Then they were dried in vacuum for 12 hours and metallized with a 10 nm gold coating to be analyzed by SEM.

RESULTS

POWDER MATERIAL CHARACTERIZATION

The XRD spectrum of calcium phosphate can be seen in Figure 14, in which the peaks at 25.9°; 31.74°; 32.16°; and 32.88° are indicative of the hydroxyapatite (HA) crystal structure according to Hu et al. (2020), differentiating it from other structures such as TCP (tri-calcium phosphate) and BCP (bi-calcium phosphate), commonly obtained in calcium phosphate synthesis reactions. In calcium phosphate with the HA structure, with molecular formula $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, the OH groups appear trapped in the crystal structure, and several authors (Zhang, 2013; Sossa et al., 2018; de Melo Costa et al., 2009) have already shown that its lower solubility and greater

stability in the body make it the preferred structure for implant coating. Regarding TiO_2 , as shown by El-Sherbiny et al. [35] and Ijadpanah-Saravy et al. [36], the peaks at 27.44° ; 36.1° ; 41.28° ; and 56.66° are typical of the rutile structure and differentiate it from anatase and brookite, the other possible crystalline forms. Rutile is in fact the most stable in crystals larger than 35 nm [37] and is the most commonly obtained structure in the industrial production processes of titanium dioxide, with its biological activity being better than that of the amorphous form obtained in some electrochemical processes [38]. The narrow bands indicate high crystallinity of the material used, in addition to uniformity of crystal size.

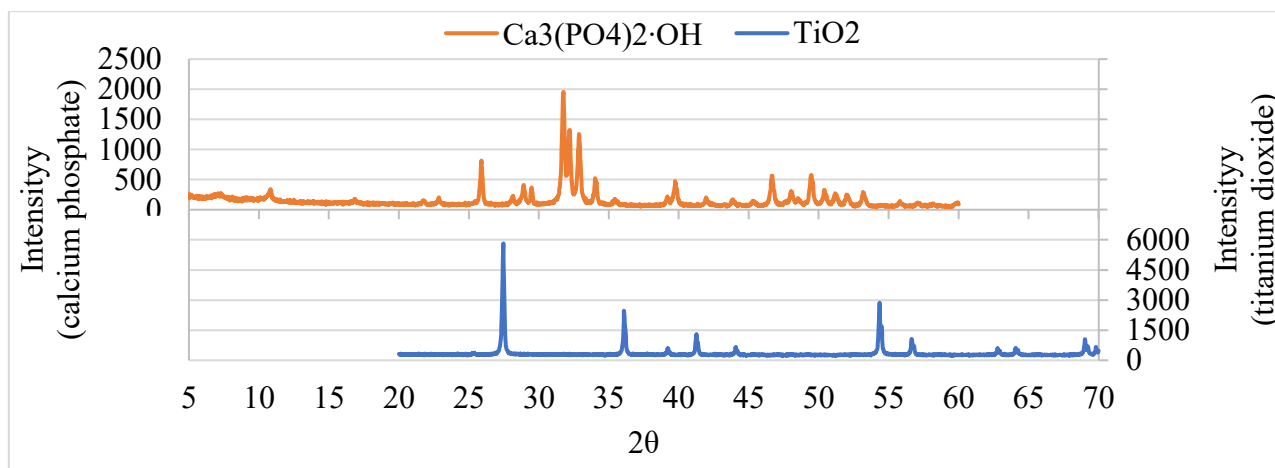
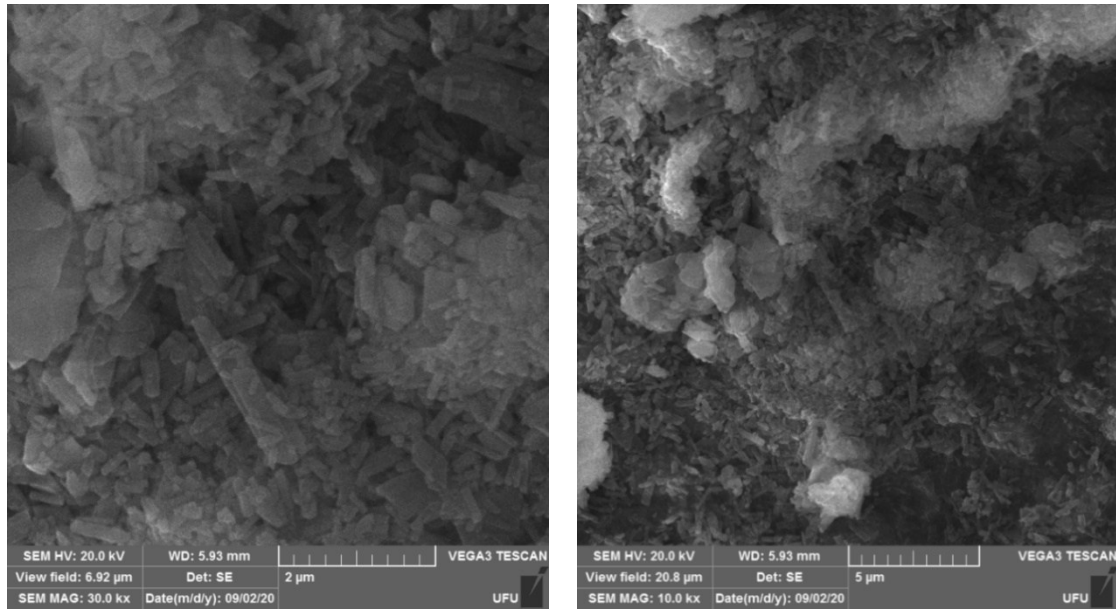


Figure 14. X-ray diffraction for calcium phosphate and titanium dioxide with angle 2θ from 5 to 70° .

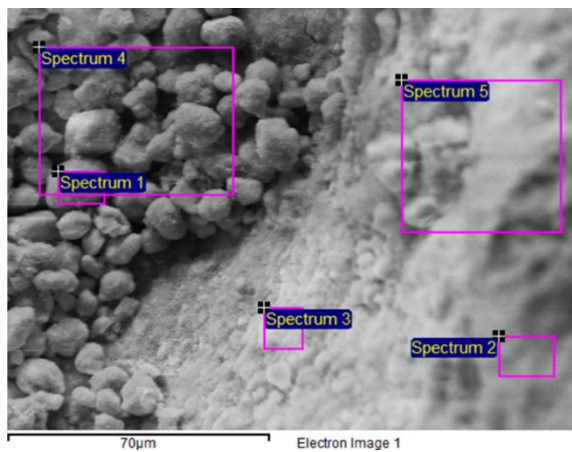
The shape and size of the $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ particles can be seen in Figure 15. The crystals are predominantly rod-shaped with a thickness of around 200 nm. Despite the high surface area, the calcium phosphate powder appears to be less adherent than titanium dioxide, being easier to handle and to clean, so it is possible that the formation of large agglomerates reduces the surface energy of this material. The chemical composition of this calcium phosphate deposited on carbon tape and coated in gold is shown in Figure 16, which also shows a mass content of Ca of around 10% and around 29% of C. This is because the C content and part of the O content comes from the carbon tape substrate, since the EDS rays comes from regions up to 2 μm deep in the sample, and for this analysis the powder was thinly spread on the tape. For the same reason, although the $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ from hydroxyapatite structure leads to an expected mass percentage in the proportion of 40% : 19% : 41% for Ca : P : O, the lower mass of Ca and P in comparison with O comes from the oxygen present in the polymeric carbon tape.



(a)

(b)

Figure 15. Shape and size of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ particles at (a) 30,000x and (b) 10,000x magnifications.



(a)

Elements	% mass spectrum				
Region	1	2	3	4	5
C	28.9	30.78	36.19	26.05	32.4
O	54.67	55.76	55.72	58.45	57.67
P	5.73	4.83	2.98	5.1	3.56
Ca	10.73	8.59	5.11	10.37	6.31

(b)

Figure 16. Chemical composition of calcium phosphate particles deposited on carbon tape and coated with Au.

The size and shape of the TiO_2 particulates can be seen in Figure 17. It is noticeable the approximately spherical or ellipsoidal shape of these particulates, which agglomerate to form larger grains, as also observed by Hu et al. (2014). Due to the submicrometric scale (with particulates of about 400 nm), the material has a high surface/volume ratio, and therefore adheres easily to the substrate, even when not annealed. Their chemical composition can be seen in Figure 18, where a variation in the mass percentages of the elements, including carbon, can be noted. In this case, the C content comes from the polymeric substrate and may be higher or lower depending on the thickness of the TiO_2 layer at each point.

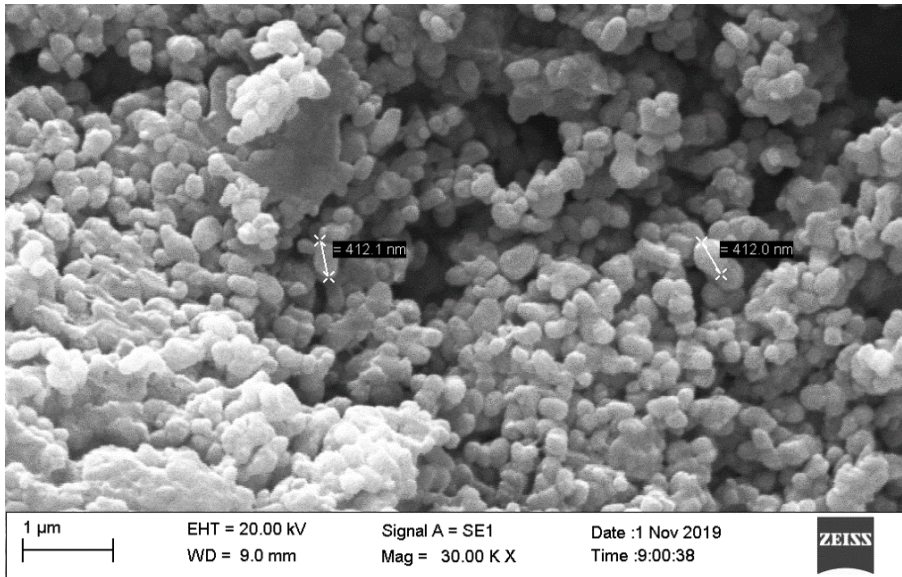
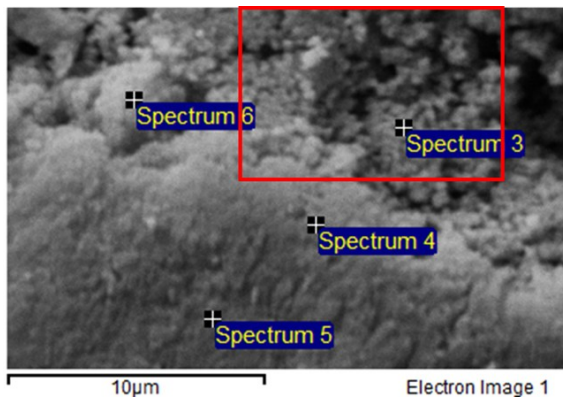


Figure 17. Shape and size of TiO₂ crystals that cluster into larger structures.



Element	% mass spectrum			
Region	3	4	5	6
C	5.19	8.35	9.31	11.71
O	26.37	17.55	21.35	26.74
Ti	39.88	41.38	40.47	31.34
Au	27.87	31.8	27.95	29.32

(a)

(b)

Figure 18. Chemical composition at different points of the TiO₂ coating on polyamide substrate (Campos et al., 2021), with region highlighted for magnification in Fig. 9.

WATER CONTACT ANGLE

The water contact angle is shown in Figure 19 for each annealing condition, for non-annealed samples and for the coated surfaces of the femoral and acetabular components of a commercial hip implant, demonstrated in Figure 20. In all cases, except for specimens E and F, the contact angles were smaller than the non-annealed state and much smaller than 90°, which indicates an improvement in surface hydrophilicity [39]. In fact, together with a high roughness, the contact angles of less than 30° obtained can lead to a superwetting surface as defined by [40], which is a good predictor for the biocompatibility of the material [41]. Also, there were annealing conditions in which the wettability of the 3D printed PLA samples was even better than that obtained for the commercial hip implant, highlighting the potential of this new biomaterial as an inductor for cell adhesion and differentiation [42, 43].

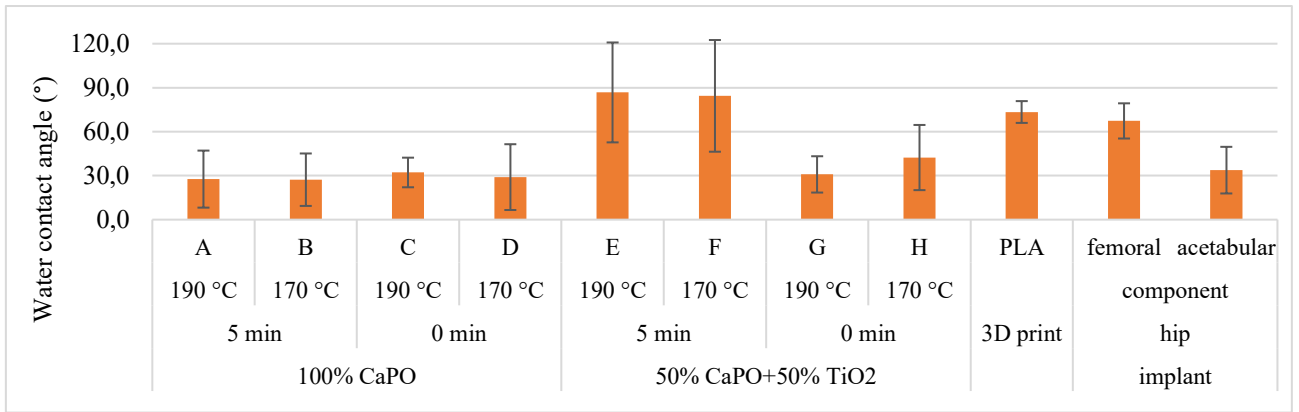
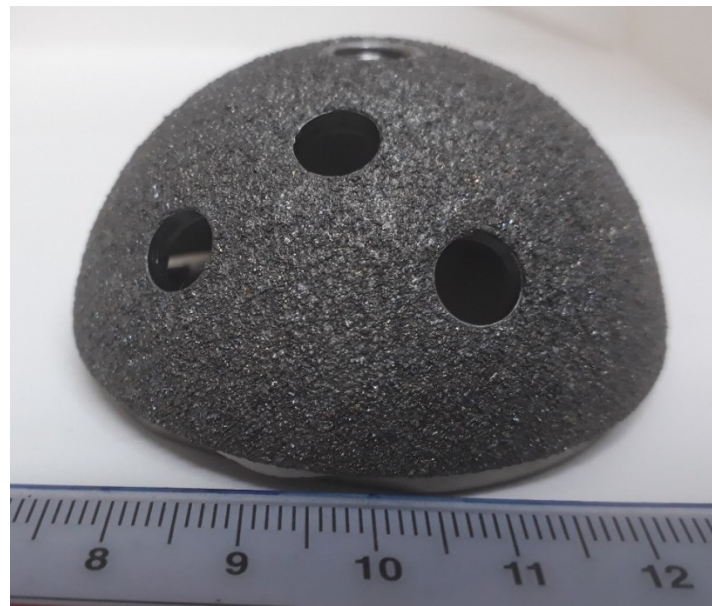


Figure 19. Wetting angles for each condition and comparison to surface of commercial hip implant.



(a)



(b)

Figure 20. Coated surfaces of (a) femoral and (b) acetabular components of commercial hip implant.

Analysis of variance (ANOVA) was performed to assess how the annealing conditions affect the water contact angle, from which the most significant parameters were composition ($p=0,000000$), time in maximum temperature ($p=0,000009$) and the combination of them ($p=0,000001$). Calcium phosphate is a common anti-humectant in the food industry due to its affinity with water, preventing the food from absorbing moisture. Therefore, it is possibly for this reason that it presents greater hydrophilicity. Titanium dioxide covered the surface irregularly, leading to smaller wetting angles on average and greater variability in the results, as in conditions E and F. Regarding temperature, it may not have been significant because at both 170 °C and 190 °C the polymer assumes a similar level of viscosity. The time at maximum temperature may

have been more significant because it provided more time for the diffusion of particulates on the surface, whereas in the case of titanium dioxide, this led to a more irregular surface observed visually and by SEM (Figure 21a and Figure 21b). In these figures, the white/gray lines to the left of each layer are just flaws resulted from the embedding, sanding and polishing processes.

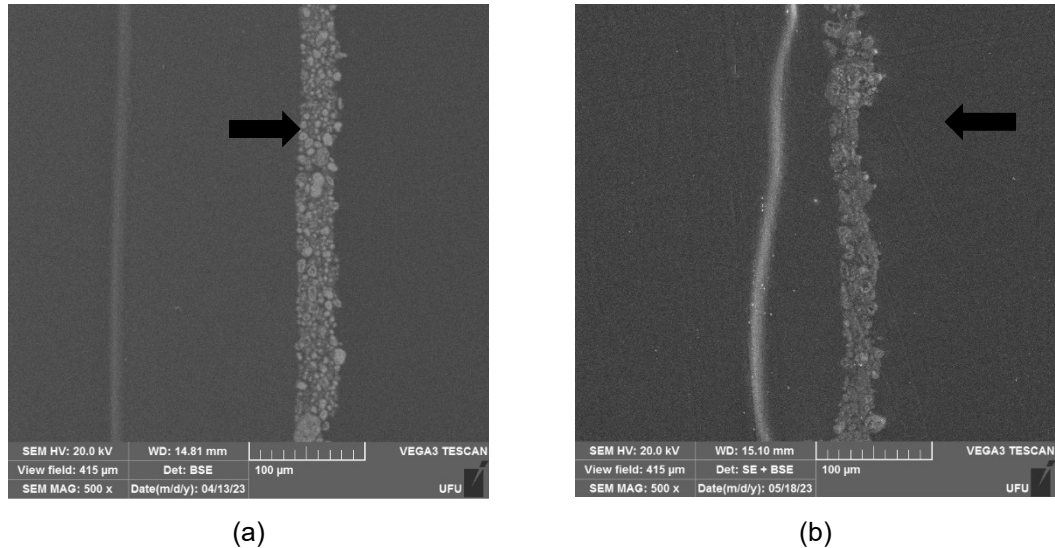


Figure 21. Image obtained by SEM of the coating layer of a test specimen annealed in a) calcium phosphate and b) in a mixture of calcium phosphate and titanium dioxide.

ROUGHNESS TEST

The roughness parameters Ra, Rz and Rq were measured and are shown in Figure 22, from which there is notable difference between the values when changing the chemical composition of the powder bed. According to ANOVA, the chemical composition was in fact significant for a confidence level of 95% for Ra ($p=0,000000$), Rq ($p=0,000446$) and Rz ($p=0,000000$). This greater roughness can also be visually perceived in the test specimens annealed in the mixture of titanium dioxide and calcium phosphate, with the surface of the test specimen having a very rough finish as if the molten PLA was being absorbed by the powder bed. Figure 23 shows two samples annealed in calcium phosphate (type C and D) and two in titanium dioxide with calcium phosphate (type E and H), illustrating the observed results. Comparatively, the roughness values for conditions A to D are close to those observed for the femoral component of the same commercial hip implant of Figure 20a, measured in another previous work [44] with Ra ranging from 4.7 μm to 5.8 μm and Rq from 6 μm to 7.6 μm . This indicates that the surface of the annealed 3D printed PLA parts bear similarity with that of biomaterials already validated for commercial use, which is also a good indicator of the potential of the obtained surfaces.

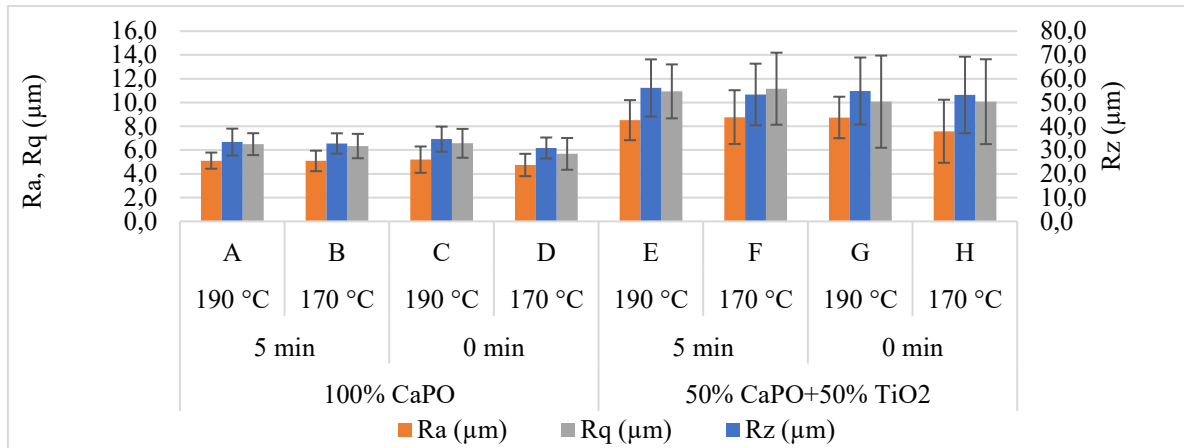


Figure 22. Surface roughness for all the conditions analyzed.

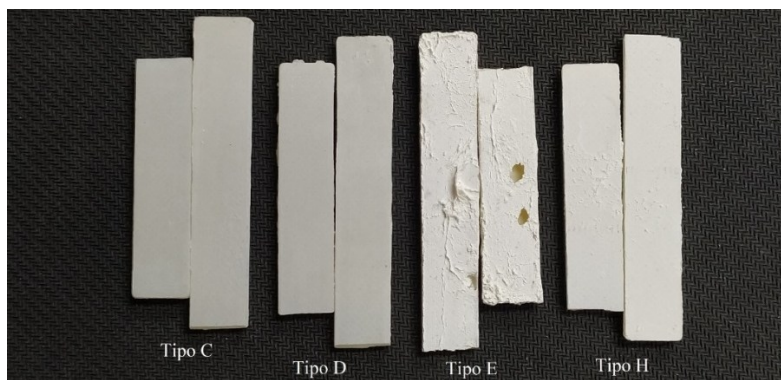


Figure 23. Photograph of the surface of test specimens used in roughness tests (fractured pieces of the bending test). Two bubbles can be seen in right sample of type E.

FLEXURAL TESTS

The results of maximum flexural strength (MFS), modulus of elasticity (E) and flexural elongation (ϵ) are shown in Figure 24. It shows that powder bed annealing resulted in a decrease in elongation as well as an increase in flexural strength and modulus of elasticity. Considering that the coating is very thin in comparison to the bulk material, the mechanical properties will depend almost entirely on the characteristics of the bulk PLA. As the process reaches temperatures above 160 °C for which PLA already starts to melt, the changes observed in MFS, E and ϵ could come from an alteration in the PLA chemical composition, or in its porosity, or in its crystallinity, as explained in other works [67]. Although neither of these properties were measured in this work, previous works have shown that the most important factors that justify increases in mechanical resistance are the modification of pores geometry [69] and polymer crystallization [68]. For elongation and maximum flexural strength, the influence of composition ($p=0,011332$ and $p=0,002948$, respectively) and time at maximum temperature ($p=0,001278$ and $p=0,015807$, respectively) were significant with a 95% confidence level. This can be explained because more crystalline parts tend to be more rigid and have greater mechanical resistance, if they have not become brittle [45]. This occurs because in the amorphous state the

macromolecules are randomly entangled, with a greater possibility of movement when subjected to stresses, while in the crystalline state the macromolecules are rigidly packed, with a lower capacity to stretch and deform [46]. Above the glass transition (T_g), thermal energy generates the vibration of the macromolecules, which have greater freedom to rotate and move, with a natural tendency to crystallize if there is enough time, given that the crystalline state is the state with the lowest free energy [46]. Thus, the thermal history of printing and annealing influences the final mechanical properties of the test specimens, explaining the observed variations. Moreover, the particulate alters the regularity and presence of surface pores, which affect the nucleation and propagation of cracks, as in the case of Figure 23. Thus, due to the stress concentration, composition was also a preponderant factor for the fracture of the samples.

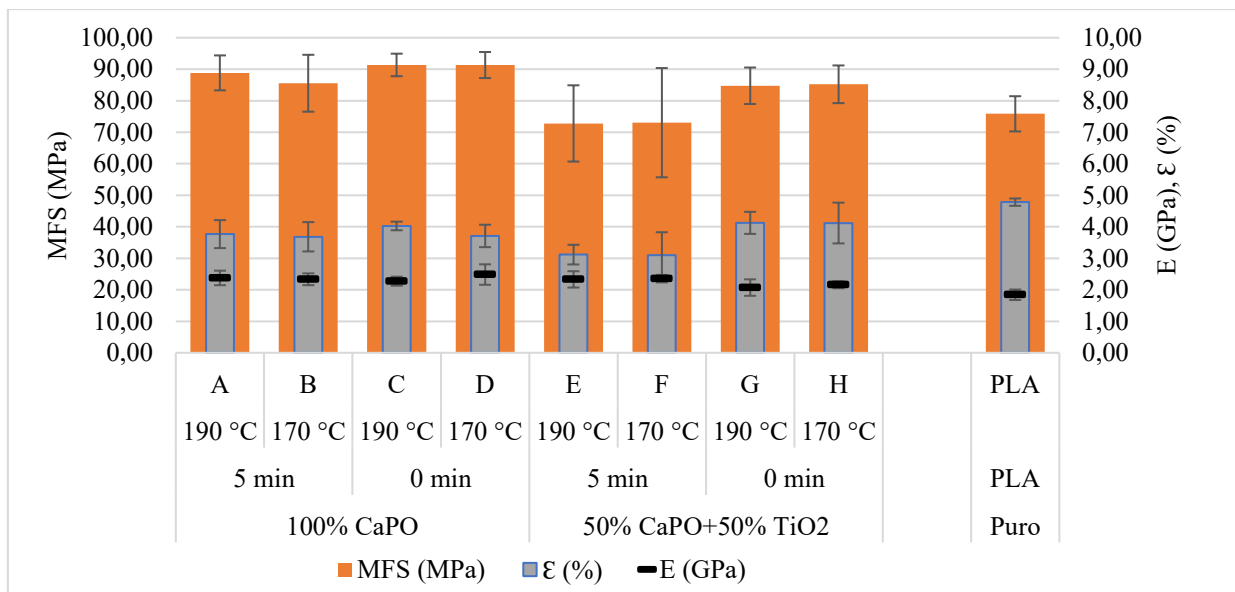


Figure 24. Results of flexural elongation (ϵ), maximum flexural strength (MFS) and modulus of elasticity (E).

These results show that the powder bed annealing process was able not only to create the coating on the PLA surface, but also to improve its resistance, both in comparison to the non-annealed PLA and to PLA flexural resistance values from the literature, which vary from about 60 MPa to 100 MPa [47, 48]. This further supports the attractiveness of this new manufacturing process for PLA coatings, because besides it being simpler and cheaper in comparison to cold gas shooting, plasma spray and other coating processes [49, 50], it can even improve the substrate mechanical properties. It is also important to highlight that as can be seen from Figure 23, even after the fracture of the samples during the bending tests, there was no delamination of the coating from the bulk material. Although no direct measurement of the adhesion of the coating was carried out, this aspect serves as an indirect evaluation of coating integrity as exemplified in ASTM B571 [70], since there was no visible failure in any of the specimens.

IMPACT TESTS

For the impact tests, the graph from Figure 25 shows that there is no explicit trend in the results as a function of the input parameters, which is reinforced by no significance from any factors in ANOVA. Comparing the results obtained with values from other studies [51], which presented results close to 50 J/m for parts produced from PLA by 3D printing, it is observed that powder bed annealing did not impair the impact resistance of the substrate. Again, given the relatively thin coating, the results of the impact test might be influenced primarily by the bulk properties of the PLA, leading to similar impact energy values across all specimens. This indicates that the material conserves its toughness after the surface modification process, enabling it for use in the production of biomaterials.

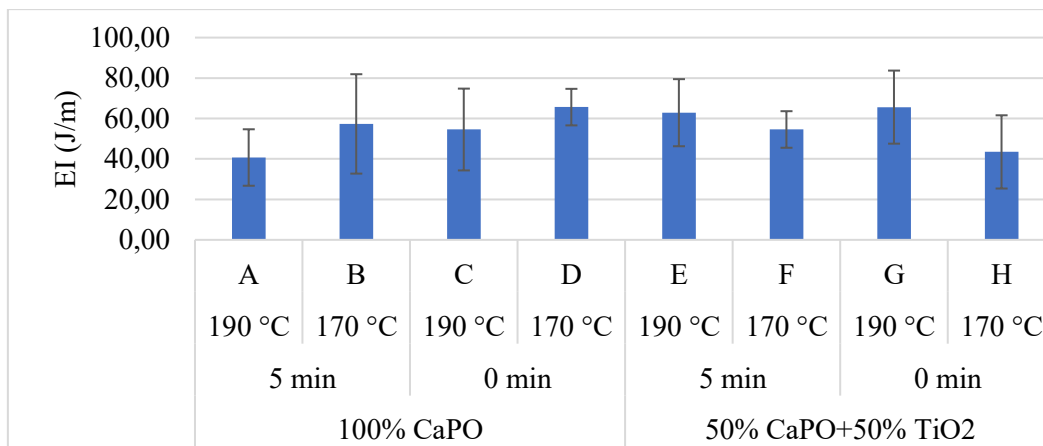


Figure 25. Absorbed energy data for all the conditions analyzed.

COATING LAYER THICKNESS AND CHEMICAL ANALYSIS

The results of the coating layer thickness measured in the SEM are presented in Figure 26 and it shows that pure calcium phosphate composition ($p=0,000019$) and a longer time at maximum temperature ($p=0,000000$) ensured better layer thickness results, whereas both parameters together with the combination ($p=0,023406$) of time in maximum temperature and maximum temperature were significant for a 95% of confidence level. A possible explanation for the influence of the particulate is the fact that, although it cannot be perceived from the images, for calcium phosphate the particulate is visually less adhered when handled, which may make it easier for the particulate to diffuse into the molten polymer more homogeneously, forming a new composite material from the mixture of the particulate and PLA. Likewise, a longer time at maximum temperature allows more diffusion to occur. It is recommended that the coating layer formed should not be too small, since it can be absorbed by the bone tissue very quickly in the first few weeks after implantation, but it should also not be too thick that could make the surface fragile. Thus, an ideal thickness is considered by some authors [52] to be between 30 μm and 80 μm , while others have found it to be between 70 μm to 90 μm [53]. Therefore, it can be

observed that the results obtained in this study could be satisfactory for biomaterial fabrication, since most of the results are between 30 μm and 50 μm .

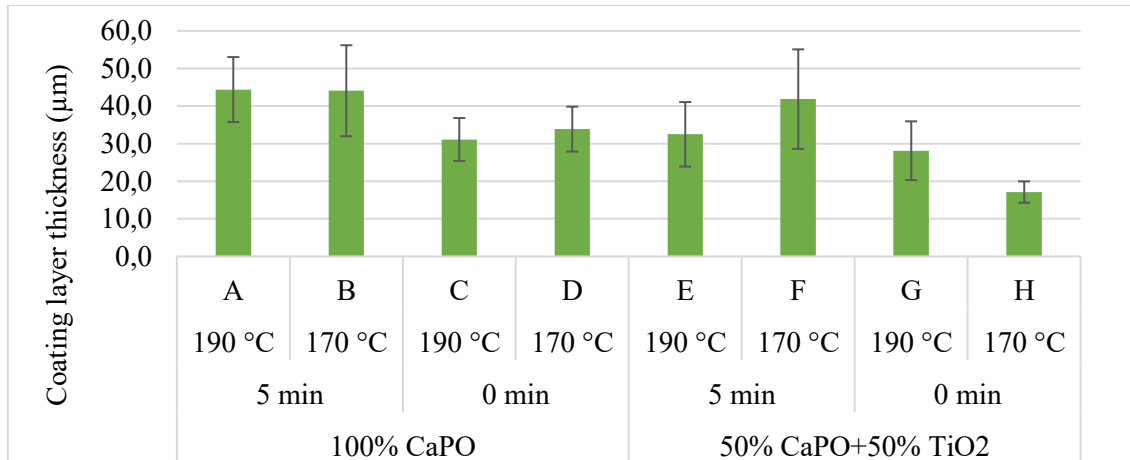
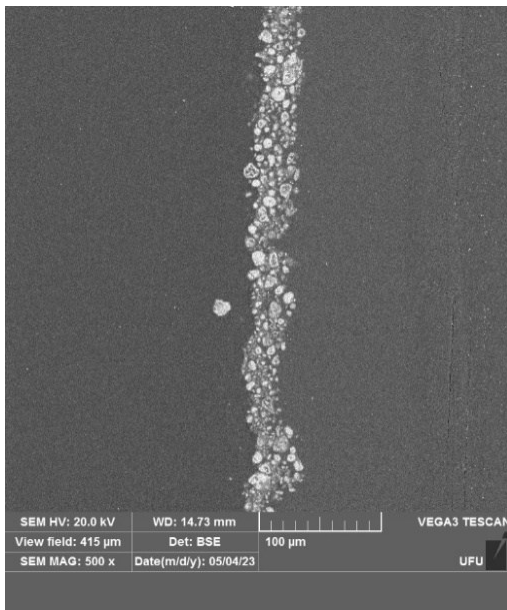
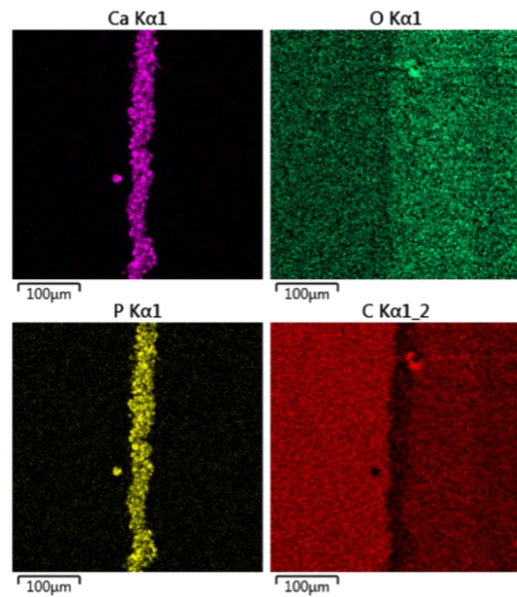


Figure 26. Layer thickness of particulate coatings measured in the SEM, for all the annealing condition.

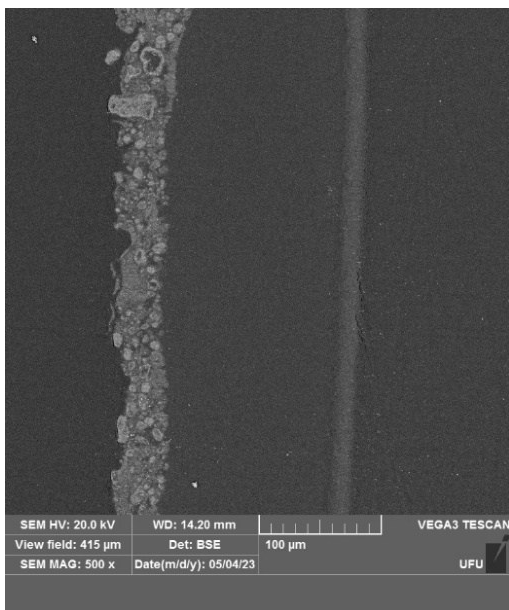
Regarding the chemical composition, it can be inferred that the coating is a composite of calcium phosphate grains interspersed with PLA for samples A to D. In Figure 27a the BSE image shows that the aligned denser white grains have infiltrated the gray PLA substrate (to the right) during annealing, and the composition maps of Figure 27b show that there is a well-defined region where the calcium phosphate was deposited, and in this region, there is also carbon from the PLA substrate. The same is true for samples E to H, for which the coating is a composite of calcium phosphate and titanium dioxide grains interspersed with PLA, as shown in Figure 27c and Figure 27d. Regarding the applicability to implants, it is expected that the composite coating might have an even better behavior than only pure calcium phosphate coating or pure PLA because, as explained in the work of Bernardo et al. [22], the PLA component may offer structural support for cell attachment and growth, while the HA phase releases calcium and phosphate ions that both promote osteoinduction and increase the low pH created by PLA degradation in lactic acid. Besides, the use of composite parts of PLA and calcium phosphate [54, 55] and PLA and titanium dioxide [56] have already shown biocompatibility characteristics, validating this new coating method by power bed annealing as an interesting manufacturing method for biomaterials, especially in the case of interference screws, for which this composite mix has been shown to have good results *in vitro* [57, 58] and *in vivo* [59] and is now widely used in commercial products [25].



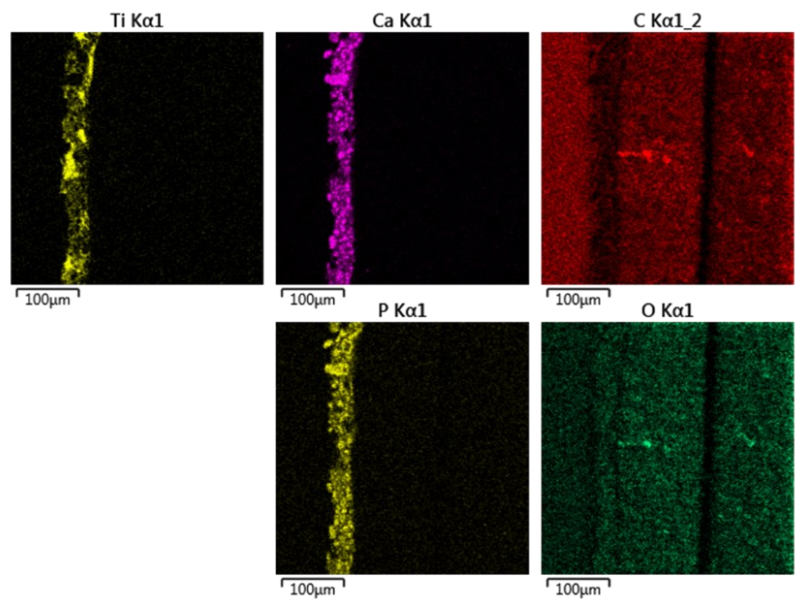
(a)



(b)



(c)



(d)

Figure 27. SEM images for sample D in BSE mode (a) and EDS composition map (b), and for sample E in BSE mode (c) and EDS composition map (d).

MICROHARDNESS ANALYSIS

The microhardness was measured in the cross section of the samples, starting on the coating and moving towards the bulk, with each indentation spaced about 300 μm from the other. As can be seen from the plots in Figure 28, there is not much difference of the microhardness on the sample section, with major differences only being observed very close the surface. The significance analysis showed that the input parameters had no influence on the microhardness in

the cross section. Regarding the large variation in hardness observed in the coating region, the most likely explanation for it is the fact that it borders the embedding resin, which is against the recommendations from ASTM E384 [60]. Therefore, it can be inferred that there is no significant change of the mechanical properties of the substrate at microscale, indicating that this coating process does not damage the substrate's resistance.

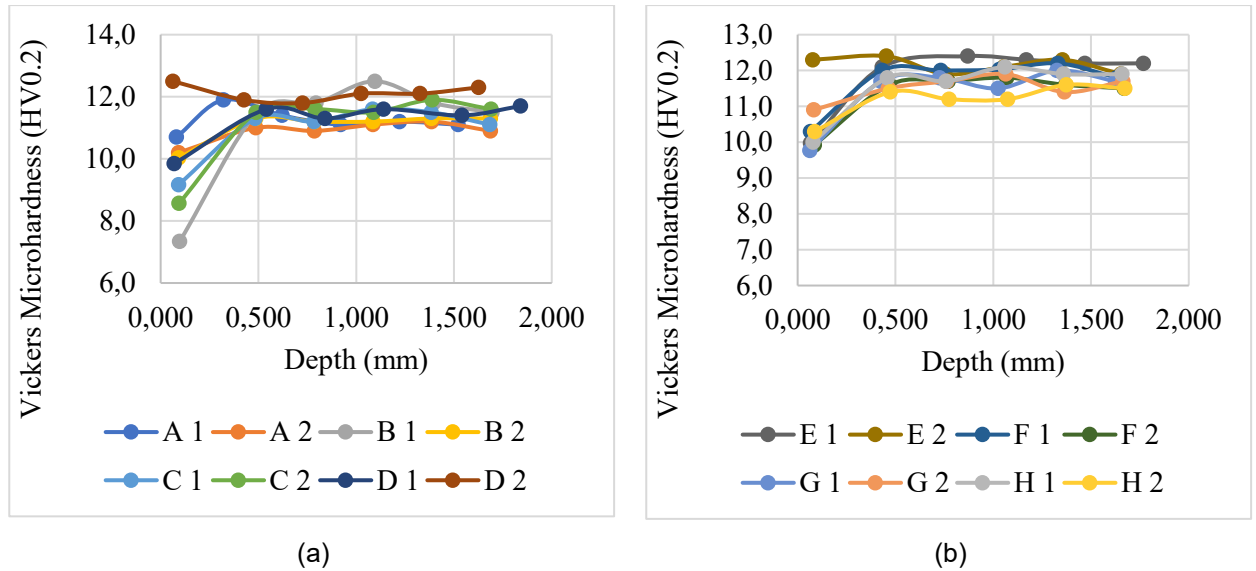


Figure 28. Microhardness variation in the cross section of the sample for conditions (a) A to D and (b) E to H.

BIOCOMPATIBILITY TEST AND SEM ANALYSIS

Cytotoxicity tests were performed only in 3 of the 8 production conditions of the coated samples, also comparing them with pure PLA and negative and positive control materials, as shown in Figure 29. Although in the first day the samples showed worse cell viability, after 14 days all discs showed greater cell growth than in the positive control, with the calcium phosphate and titanium dioxide coating of sample H performing better. Still, not even for the first day the material can be considered cytotoxic, since the cell viability was above the limit of 70% [61]. This indicates that the material, in addition to being non-toxic to cells, inducing possible adhesion and proliferation on the surface of the samples, which is an excellent indication that these biomaterials could become an option for new models of orthopedic implants in the future.

Interestingly, in Figure 30a the MC3T3 cell can be seen well attached on the calcium phosphate grains, with its cell process spreading on the surface of sample B. Similarly, other cells can also be seen in the surface of sample B in Figure 30b, which has a very different aspect from pure PLA surface, for which an isolated cell can be seen in Figure 30c. In this case, even after 14 days, although the cell attached to the surface, its ovoid morphology suggests it did not differentiate into a mature cell [62] with the typical spreading process, exactly because this sample lacked the calcium phosphate and/or titanium dioxide that promote the osteogenic stimuli. In

contrast, Figure 30d shows even more osteocytes spread over the surface from sample H, which presented the best cell viability after 14 days.

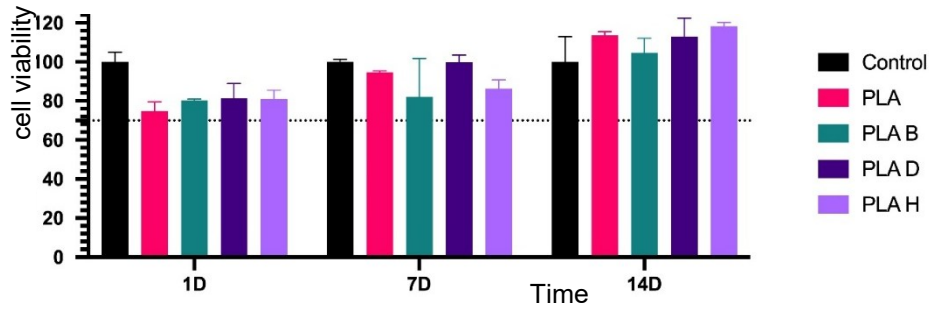
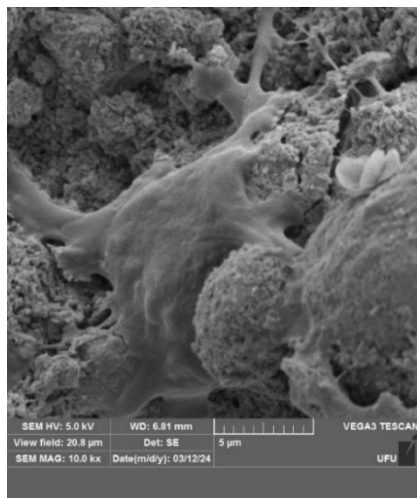
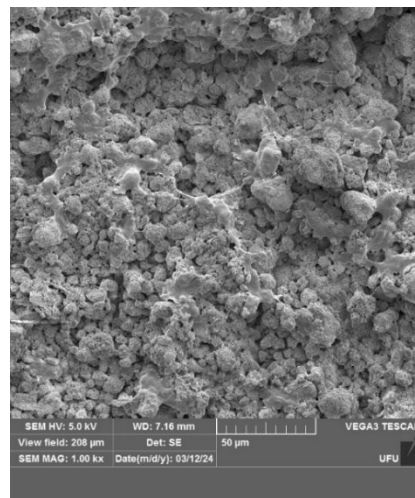


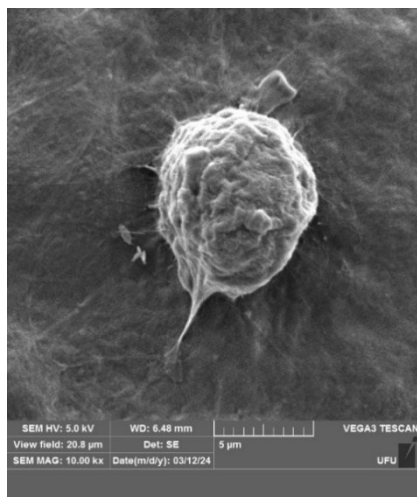
Figure 29. Cell viability after 1, 7 and 14 days for different samples.



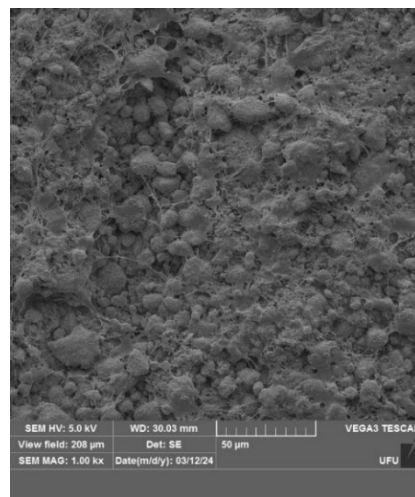
(a)



(b)



(c)



(d)

Figure 30. SEM images of cell adhered in sample B (a), cells spread in the calcium phosphate grains of surface from sample B (b), adhered and not differentiated cell in pure PLA sample (c) and cells spread in the calcium phosphate grains of surface from sample D (d).

COMPARISON AGAINST OTHER COATING TECHNOLOGIES FOR POLYMERIC IMPLANTS

As discussed, the integration of PLA and HA into implants is well established in the literature [71, 73, 88], given the resorbable nature of the former and the osseointegration properties of the later. Therefore, the proposed coating method should be compared to other technologies capable of combining these components for the same goal. This could be achieved either by methods that create a HA coating on PLA or that mix HA into PLA matrix. Considering the first, there have been studies with plasma spray for coating polymers such as PEEK (poly-ether-ether-ketone) [72]. However, considering the high temperatures reached in the plasma arc of about 10^4 K [76], it would most probably not be suitable for coating PLA, which has a melting point of about 160 °C compared to about 340 °C for PEEK. Besides, other works [74] have shown that plasma spray deposited HA may present low adhesion with polymer, with failure of the coating under load before the failure of the substrate. Additionally, plasma spray high temperatures might cause HA to transform into α or β tricalcium phosphate, calcium oxide and/or tetracalcium phosphate, impairing not only the crystallinity [77] and chemical composition of the coating, but also its effectiveness for osseointegration [75]. Flame spray process is a variation that also could potentially deposit ceramic coatings [78] but would suffer from the same drawbacks as plasma spray for PLA as the substrate material. Interestingly, some authors have already been able to deposit titanium dioxide onto low melting temperature polymers such as UHMWPE [79] using vacuum plasma spray, but no other work was found with such feature for PLA. Also, all plasma spray techniques require expensive tooling such as a plasma torch, powder feeder and power supplies with capacity of 25 to 150 kW [76], besides also requiring expensive materials sometimes [80], such as pure nitrogen, argon or helium that act as carrier gases and stabilize the plasma arc.

Although not less expensive due to the necessary costly equipment [81], a potential alternative would be the use of CGS (cold gas shooting), in which micrometric particles accelerated to supersonic speeds in a high-speed gas stream impact and adhere to a substrate, creating a distinct coating [75]. However, almost 90 % of the kinetic energy of the particles is converted into heat, and although there have not been found works with CGS onto polymers, it is likely that it would face the same problems related to excessive heat damaging the substrate. Moreover, it is important to highlight that CGS and all thermal spray are line of sight techniques, and coating the totality of a complex geometry would be more time consuming, even with a robotic arm. In comparison, the powder bed annealing method hereby proposed can create a uniform coating around all the part, even for more complex geometries. Also, it is a much more inexpensive and scalable method, because it only requires an electrical oven (about US\$30) and a metallic tray as tooling (about US\$5), and only about 100 g of HA powder (bought as additive for food industry for about US\$4/kg) and 16 g of PLA (natural PLA bought at US\$20/kg) to produce four samples at each condition. This make the proposed technology especially relevant for developing countries where access to expensive biomedical products is still a health issue. The only drawback of the powder bed annealing process is that it is not able to generate a pure HA

and/or HA+TiO₂ coating in comparison to other techniques. However, the biocompatibility tests showed that phenomenon does not pose a problem, since the coating is still not cytotoxic and leads to cell differentiation. Regarding other coating techniques, as explained in other works [82, 83], despite the lower temperature of sputtering process, it does not create coatings of more than 3 μm, while sol-gel would be limited to 10 μm and may also require deleterious heating of the part to solidify the coating [84]. The powder bed annealing, besides producing coatings of up to 50 μm in thickness, applies heat with the part immersed in powder, which avoids heat deflection and maintains the geometry. Electrodeposition methods [85], on the other hand, cannot be applied to polymers, which are natural electrical insulators.

Finally, in relation to process the mix HA into the PLA matrix, two main processes can be highlighted. The first is injection molding, which has been used successfully to incorporate HA into PLA uniformly [86]. Similarly, these authors also found that annealing the part could enhance the impact resistance as happened for most samples produced by powder bed annealing. However, mixing even small quantities of HA into the whole substrate has been found to decrease the impact [87] and tensile resistance [92] in comparison to pure PLA. Here lies another advantage of powder bed annealing, since except for conditions A and H, all others yield samples with average impact resistance above that of natural PLA used in the tests. The second process to incorporate HA into PLA is additive manufacturing, with several examples of composite filaments being produced for later use in FFF process. However, it has been found that concentrations as low as 10% of HA dispersed into PLA could be prejudicial to its mechanical properties, with its tensile resistance dropping from 50 MPa to 30 MPa [90]. This phenomenon was not observed in the flexural tests carried out with powder bed annealed parts, where the resistance was the same or higher than for natural PLA, while also achieving very low values of water contact angle (mostly less than 30°). This level of hydrophilicity did not happen in other works [91] that used PLA filament with 12% of HA for which water contact angles stayed at 66°, indicating once more the advantage of the powder bed annealing process as it conserves the toughness and resistance of the PLA substrate while presenting the improved biocompatible properties of HA at the surface. Furthermore, incorporating HA to PLA filaments in a uniform dispersion is still a challenge [93] since simple mechanical stirring or high-shear mixing may not suffice, while for other additive manufacturing methods such as SLS, that is also not easy due to a small sintering window and flowability of the heterogeneous powder [94]. It is also important to highlight that conserving a PLA core would be advantageous over creating pure HA parts, due to the inherent low fracture toughness of pure HA manufactured by SLS [89].

CONCLUSIONS

This study demonstrated the viability of using powder bed annealing as an innovative method for producing hydroxyapatite coatings on 3D-printed PLA parts. The process successfully generated a ceramic particulate layer with favorable characteristics for biomedical applications, particularly in orthopedic implants. The results showed that the coating exhibited good thickness

control, improved surface roughness, and enhanced hydrophilicity, which are crucial factors for promoting osseointegration.

Mechanical tests indicated that powder bed annealing enhanced the flexural strength of the PLA parts while maintaining impact resistance and microhardness in the substrate. Although ductility decreased, the mechanical improvements suggest that this method can contribute to stronger and more reliable implant materials. Additionally, biocompatibility tests confirmed that the hydroxyapatite-coated surfaces supported cell adhesion and proliferation, further validating the potential of this technique for biomedical applications.

Compared to conventional coating methods like plasma spraying or chemical deposition, powder bed annealing could offer a cost-effective and scalable alternative. The ability to integrate hydroxyapatite coatings directly onto polymeric implants without complex post-processing steps highlights the practicality of this approach. Furthermore, the combination of PLA's biodegradability with hydroxyapatite's osteoinductive properties suggests promising applications in resorbable implants.

Overall, this research contributes to the ongoing development of personalized, bioactive implants by optimizing a simple yet effective coating technique. Future work should explore long-term *in vivo* performance, refine processing parameters for improved adhesion and uniformity, and investigate alternative bioceramic compositions for tailored implant applications. The findings suggest that powder bed annealing could play a crucial role in advancing polymer-based implant technologies, offering a practical pathway to more accessible and efficient orthopedic solutions.

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CAPÍTULO 10

10. ARTIGO 7

Campos, F.A.R., da Silva, L.R.R., Castro Filice, L.S., Machado, A.R. (2023). Desenvolvimento de um sistema de jateamento para deposição de particulados cerâmicos bioativos na superfície de polímeros termoplásticos. Ainda não publicado.

RESUMO

A crescente demanda por implantes ortopédicos personalizados e de baixo custo tem impulsionado o uso de polímeros biocompatíveis como o ácido polilático (PLA), associado à manufatura aditiva pelo processo Fused Filament Fabrication (FFF). No entanto, o PLA sozinho apresenta baixa bioatividade, exigindo modificações superficiais para induzir osseointegração. Este trabalho investigou a viabilidade de um método inovador de jateamento térmico intermitente para gerar revestimentos de hidroxiapatita (HA) em substratos de PLA impressos em 3D. O processo consiste na aplicação de fluxo de ar quente contínuo, combinado com jatos de ar comprimido contendo particulados cerâmicos, com o objetivo de amolecer a superfície do polímero e favorecer a incorporação das partículas. As amostras foram fabricadas em PLA com 100% de preenchimento e submetidas ao jateamento em quatro condições experimentais variando temperatura, velocidade de deslocamento e tempo de exposição. Apesar da complexidade do sistema, que incluiu sensores, atuadores e controle automatizado via Arduino, os resultados indicaram desafios significativos para o controle térmico e geométrico das peças. Em todas as condições testadas, observou-se grande deformação plástica das amostras, prejudicando a leitura de temperatura interna e a estabilidade do processo. A análise visual revelou alterações na opacidade das superfícies, mas sem formação clara de um revestimento contínuo. Exames complementares por Microscopia Eletrônica de Varredura (MEV) e Espectroscopia por Dispersão de Energia (EDS) confirmaram a deposição de uma camada rica em cálcio e fósforo em regiões localizadas, com espessura média de aproximadamente 4 μm . Entretanto, o recobrimento apresentou baixa uniformidade e adesão heterogênea. As limitações observadas foram atribuídas principalmente ao aporte térmico excessivo e à necessidade de otimização do sistema de alimentação de particulados e controle de fluxo de ar. Os resultados obtidos sugerem que, embora o método de jateamento térmico intermitente tenha potencial para funcionalização superficial de PLA com HA, melhorias substanciais na configuração experimental são necessárias. Estratégias como contenção geométrica das peças e melhor distribuição térmica poderão ampliar a aplicabilidade do processo.

Palavras-chave: hidroxiapatita, PLA, impressão 3D, jateamento térmico, implantes ortopédicos, revestimento bioativo.

INTRODUÇÃO

A crescente demanda por implantes ortopédicos personalizados e de baixo custo tem impulsionado o desenvolvimento de novas tecnologias de fabricação e funcionalização de biomateriais. Entre os diversos materiais empregados, os polímeros termoplásticos, como o ácido polilático (PLA), vêm ganhando destaque devido à sua biodegradabilidade, biocompatibilidade e módulo de elasticidade mais próximo ao do osso humano, reduzindo os efeitos de *stress shielding* (Al-Tamimi et al., 2024; Avval et al., 2015). A possibilidade de sua fabricação por manufatura aditiva, especialmente pelo processo Fused Filament Fabrication (FFF), proporciona ainda maior liberdade geométrica e customização, características desejáveis em aplicações clínicas.

No entanto, o PLA, assim como outros polímeros biocompatíveis, apresenta limitações no que diz respeito à sua bioatividade. Estudos demonstram que a simples presença do polímero não é suficiente para promover osseointegração eficiente (Bernardo et al., 2022). Como alternativa, diversos métodos de modificação superficial têm sido propostos, sendo os revestimentos com compostos cerâmicos, como a hidroxiapatita (HA), uma das estratégias mais promissoras. A presença de HA na superfície do implante atua como indutor da regeneração óssea e melhora a adesão celular, aumentando a eficiência clínica do dispositivo (Hunt et al., 2008).

Os métodos convencionais de deposição de HA, como deposição eletroquímica (Gorejová et al., 2023), revestimento por imersão (Chen et al., 2024) e técnicas de spray térmico a plasma (Singh et al., 2022), muitas vezes apresentam limitações no caso de substratos poliméricos. Isso se deve, principalmente, à necessidade de condução elétrica ou ao elevado aporte térmico desses processos, o que pode comprometer a integridade física e mecânica dos termoplásticos (Guanhong et al., 2011). Técnicas de menor temperatura, como *cold gas dynamic spray* (Gardon et al., 2013), também têm sido investigadas com bons resultados, mas requerem infraestrutura complexa e custos relativamente elevados.

Neste cenário, emerge como alternativa viável o método de jateamento com ar comprimido intermitente e fluxo de ar quente contínuo, que poderia permitir a deposição de particulados cerâmicos sobre superfícies poliméricas com controle térmico eficiente. Ao manter a superfície do PLA acima da temperatura de fusão, mas sem ultrapassar limites que comprometam a geometria da peça, esse processo pode facilitar a incorporação superficial dos particulados, formando camadas cerâmicas aderidas com potencial bioativo. A simplicidade do sistema (baseado em soprador térmico, válvula solenóide e controle automatizado por Arduino) também representa uma vantagem significativa em termos de escalabilidade e acessibilidade tecnológica.

Estudos anteriores demonstraram a viabilidade do processo para polímeros como policarbonato e poliamida (Campos, 2021), além de evidenciar que o calor gerado durante o jateamento poderia promover efeitos secundários benéficos, como aumento da cristalinidade e resistência mecânica das peças (de Almeida et al., 2023). No entanto, ainda são escassos os

trabalhos que avaliam sistematicamente a aplicação desta técnica especificamente para revestimento de PLA com hidroxiapatita, especialmente considerando variáveis como espessura da camada, grau de recobrimento e regularidade da deposição.

Dessa forma, o presente estudo tem como objetivo investigar a aplicação do processo de jateamento térmico intermitente na geração de revestimentos cerâmicos à base de hidroxiapatita em substratos de PLA obtidos por impressão 3D. Serão analisadas as características morfológicas, químicas e físicas das camadas obtidas, com especial atenção à uniformidade do recobrimento e à espessura da camada formada. Os resultados obtidos visam contribuir para a consolidação de um método alternativo, de baixo custo e elevado potencial para a fabricação de implantes ortopédicos bioativos, customizados e tecnologicamente acessíveis.

METODOLOGIA

Polímeros

As amostras para todos os testes de jateamento e recozimento foram fabricadas por manufatura aditiva pelo processo FFF, utilizando-se PLA da F3D Brasil na forma de filamentos de diâmetro 1,75 mm, na cor natural (transparente), para a qual não há inserção de cargas pigmentadoras que podem prejudicar o desempenho mecânico e bioquímico do polímero. O PLA é um material com reconhecida eficácia na utilização em materiais compósitos para aplicações ortopédicas (Bernardo et al, 2022), sendo o polímero mais utilizado em parafusos de interferência compósitos (Ramos et al., 2020; de Oliveira et al., 2023; Esmaeilzadeh et al., 2019) e nas pesquisas com implantes osseointegráveis absorvíveis (Park et al., 2018; Veizi et al., 2022; Dong et al., 2021).

Os corpos de prova foram produzidos com temperatura do bico de 210 °C, temperatura da mesa de 60 °C, 100% de preenchimento, velocidade de impressão de 50 mm/s, altura da camada de 0,32 mm e diâmetro do bico de 1 mm. O corpo de prova adotado tinha formato paralelepípedo, com 127 mm de comprimento, 12,7 mm de largura e 3,2 mm de espessura, conforme mostrado na Figura 1, e foi impresso com a maior superfície em contato com a mesa de impressão.

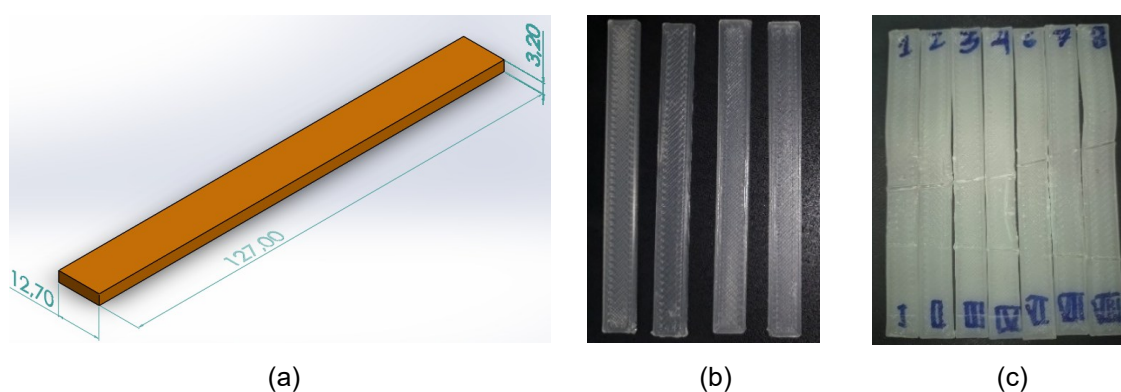


Figura 1. (a) geometria da amostra. (b) Amostras impressas. (c) Amostras jateadas.

Particulados

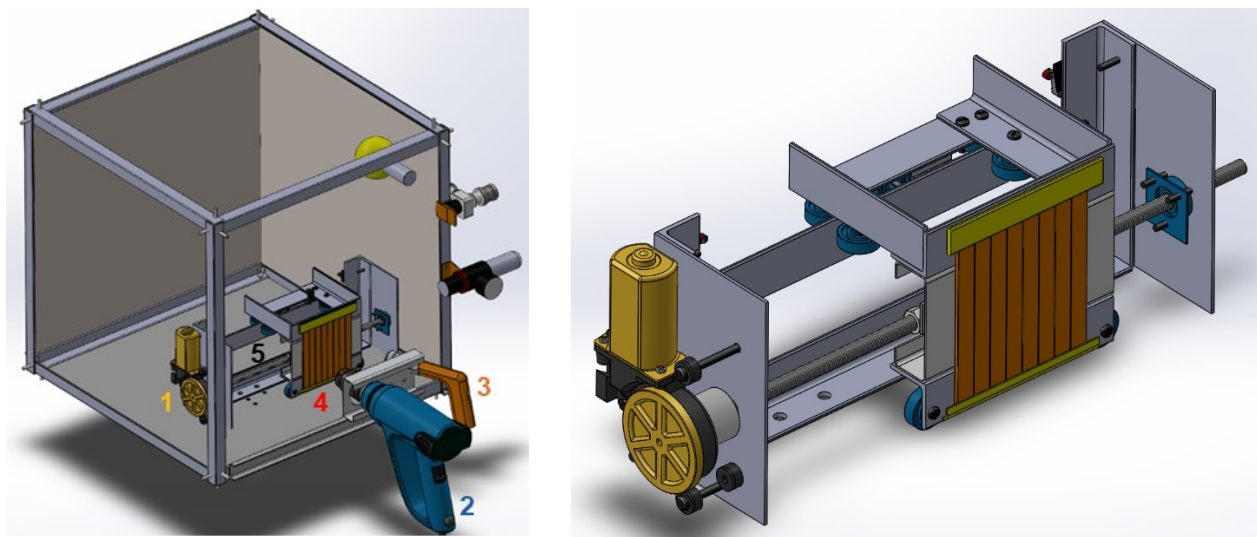
Foram utilizados os particulados de fosfato de cálcio, com estrutura cristalina de hidroxiapatita (HA), já muito comuns no revestimento ou composição estrutural de implantes poliméricos, metálicos, cerâmicos e compósitos. O fosfato de cálcio foi obtido de um fornecedor de aditivos alimentares, uma vez que este material é amplamente utilizado como anti-umectante. Esse pó, o qual se assemelha a partículas brancas tão finas quanto farinha de trigo, foi caracterizado por difração de raios X (XRD) e Microscopia Eletrônica de Varredura (MEV) num trabalho anterior (Campos et al., 2025).

Processo de revestimento por jateamento

O processo de jateamento é governado pelos parâmetros de entrada dispostos na Tabela 1. Juntamente, são apresentados os sensores e atuadores para controle de cada variável de processo, a fim de permitir ajustes. O processo de revestimento foi realizado de maneira muito semelhante ao idealizado em trabalho anterior (Campos, 2021). Foi empregada uma cabine de jateamento (Figura 2a) dentro da qual havia um novo sistema de controle e movimentação das amostras (Figura 2b), para melhoria da regularidade do processo, e para diminuir o tempo de realização dos experimentos. Foi montado um sistema de alimentação dos particulados, através de dosador helicoidal (Figura 3), regulado a 1,5g de particulado por segundo, o qual se acumulava na frente do bico da pistola de jateamento antes de cada jato de ar comprimido. Em relação a aquisição dos dados, foram usados os módulos compatíveis com Arduino (Figura 4), para leitura dos dados dos termopares, sensor de pressão e corrente, para controle do processo.

Tabela 1. Variáveis de entrada, método de controle, sensores e atuadores vinculados.

Variável de entrada	Controle	Sensores	Atuadores	Símbolo
Pressão ar comprimido	regulagem do manômetro	transdutor pressão	válvula solenoide	Par
Intermitência ar comprimido	regulagem do tempo de abertura do ar comprimido	transdutor pressão	válvula solenoide	Intermit
Tempo de jateamento	ligar e desligar dispositivos	contagem no Arduino	botões, circuito elétrico	Tempo
Veloc. deslocam. amostra	Velocidade do motor de passo	--	Motor de passo Nema 17	Veloc/rps
DBCP	ajuste posição suporte			DBCP
Temperatura ar quente soprador	ajuste manual do potenciômetro nos testes	transdutor corrente, termopar	botões, potenciômetro	Tar.q



(a)

(b)

Figura 2. a) Desenho CAD da cabine de jateamento e alguns dos dispositivos auxiliares: motor elétrico em amarelo, à esquerda (1); soprador térmico em azul, à direita (2); pistola de jateamento em laranja, à direita (3); 8 corpos de prova impressos 3D para jateamento, em cor laranja, um ao lado do outro (4), no dispositivo de movimentação das amostras, de cor cinza, no centro (5). b) Desenho CAD do sistema de movimentação das amostras, destacadas em laranja.

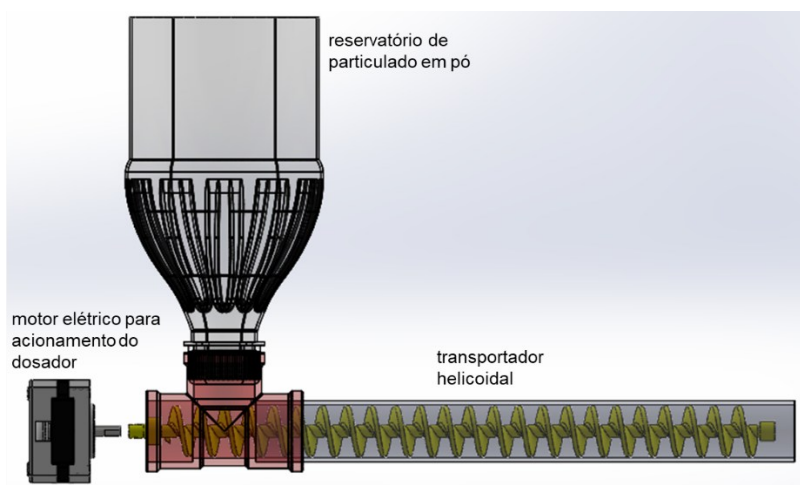


Figura 3. Sistema de dosagem de particulados baseado em transportador helicoidal.



Figura 4. Arduino e periféricos para interface com sensores e atuadores.

Inicialmente foi feito um planejamento experimental com variação linear de cada parâmetro de entrada conforme os níveis -2 a 2 da Tabela 2. No entanto, devido a problemas com os experimentos, foram realizados apenas as 4 condições apresentadas na Tabela 3.

Tabela 2. Parâmetros de jateamento planejados inicialmente, conforme níveis -2 a 2.

		NÍVEIS E VALORES				
		-- QUENTE			++ QUENTE	
VARIÁVEL	UNIDADE	-2	-1	0	1	2
Par	bar	5	4	3	2	1
Intermit	1s jato/Xs ar quente	2	3	4	5	7
Tempo	min	1,2	2,3	3,5	4,6	5,7
Veloc	mm/s	6,0	5,0	3,0	2,0	1,0
rps	Hz	4,00	3,33	2,00	1,33	0,67
DBCP	mm	125	105	85	65	45
Tar q	°C	300	360	420	480	540

Tabela 3. Parâmetros de jateamento para as 4 condições testadas.

		1C	8A	8B	8C
Par	(bar)	3	3	3	3
Intermit	(s)	4	4	5	5
Tempo	(min)	3,5	5,7	5,7	5,7
Veloc	(mm/s)	3	3	2	1
DBCP	(mm)	85	85	85	85
Tar quente	(°C)	420	480	480	540

RESULTADOS

Os experimentos realizados tiveram apenas sucesso parcial, o que se justifica por três fatores principais: dificuldade de controle adequado do processo de jateamento; baixa qualidade dos revestimentos constatadas visualmente após cada processamento; grande deformação plástica das amostras. Em relação ao primeiro fator, destaca-se que devido a quantidade de subsistemas que compõe o sistema de jateamento (dispositivo de movimentação da amostra, sensores de temperatura, controle da intermitência do jato de ar, dispositivo dosador de particulados por transportador helicoidal), foi difícil realizar os testes sem que algum dos subsistemas falhassem. Embora tenha ocorrido casos em que houve bom controle e regularidade do processo, como mostram as curvas de temperatura e pressão do ar comprimido da Figura 5, todas as condições testadas tiveram problema na leitura da temperatura interna dos polímeros. Como pode ser visto na Figura 6a, em trabalhos prévios (Campos, 2021) conseguiu-se posicionar os termopares 1 mm abaixo da superfície do polímero, obtendo uma curva de temperatura que refletia bem o aporte térmico na amostra. No presente trabalho, embora os termopares tenham sido posicionados da mesma maneira, o calor do processo fez as amostras

deformarem tal como mostrado na Figura 6b, com os termopares internos perdendo o contato com o material e levando a gráficos que não refletem o aporte térmico no material, como as curvas dos termopares q1, q2 e q3 na Figura 5. Além disso, em algum momento, algum subsistema falhava antes do tempo total de processo, levando a necessidade de interromper o ensaio. Exemplos de falhas incluem mau funcionamento dos sensores fim de curso que invertem o movimento do suporte das amostras, falha de leitura dos termopares por rompimento dos fios na ponta quente soldada, irregularidade do transporte de particulado pelo transportador helicoidal, entre outros.

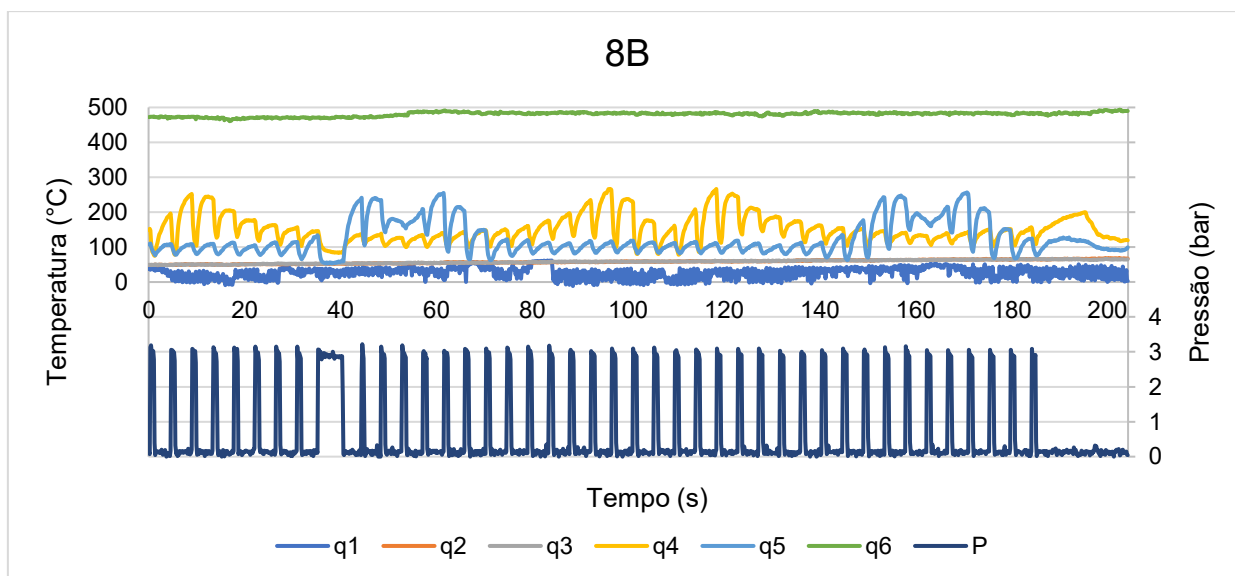


Figura 5. Curvas de variação de grandezas monitoradas durante o processo de jateamento. Os termopares q1, q2 e q3 foram posicionados internamente as amostras, conforme esquema da Figura 6a, ao passo que os termopares q4 e q5 foram posicionados externamente, sendo sensíveis aos fluxos de ar quente e ar comprimido. O termopar q5 mede a temperatura do ar quente na saída do soprador térmico e a curva P indica os jatos intermitentes de ar comprimido.

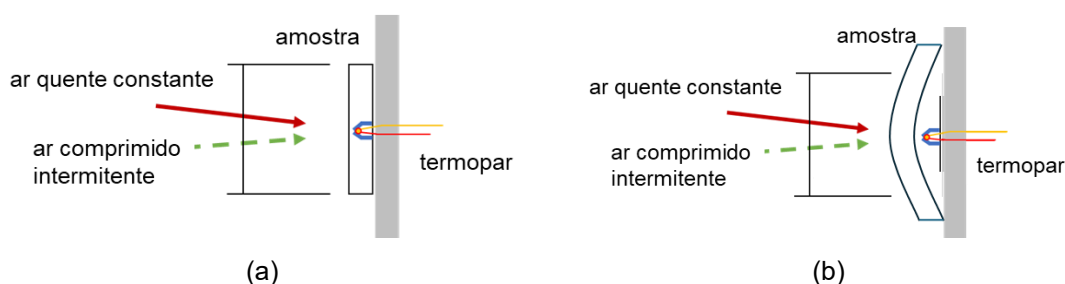


Figura 6. a) Posicionamento dos termopares internos e externos a amostra, para medição da temperatura do ar que impacta a superfície, e da subsuperfície. b) Fenômeno de deformação das amostras de PLA nos experimentos atuais, fazendo perder o contato dos termopares internos.

Em relação ao segundo fator, qualidade do revestimento, pode-se verificar na Figura 7a que embora o aspecto das amostras tenha mudado em relação a aparência inicial (Figura 1b), as amostras ficaram apenas mais opacas, sem uma clara formação de revestimento tal como visto no processo de recozimento discutido em outros trabalhos (Campos et al., 2025). Em relação a deformação das amostras, embora tenha sido utilizado um arame como anteparo para evitar grande deformação das amostras indicada na Figura 6b, ainda houve uma grande distorção como pode ser visto na Figura 7b. Desde a condição 1A até a 8C, aumentou-se progressivamente a temperatura geral de processamento, passando-se de uma situação de nenhuma adesão do particulado a uma adesão ligeiramente superior do particulado as custas de grandes deformações geométricas. Por isso, considerou-se que o processo não teria sucesso mesmo em outras condições e interrompeu-se o planejamento experimental inicial.

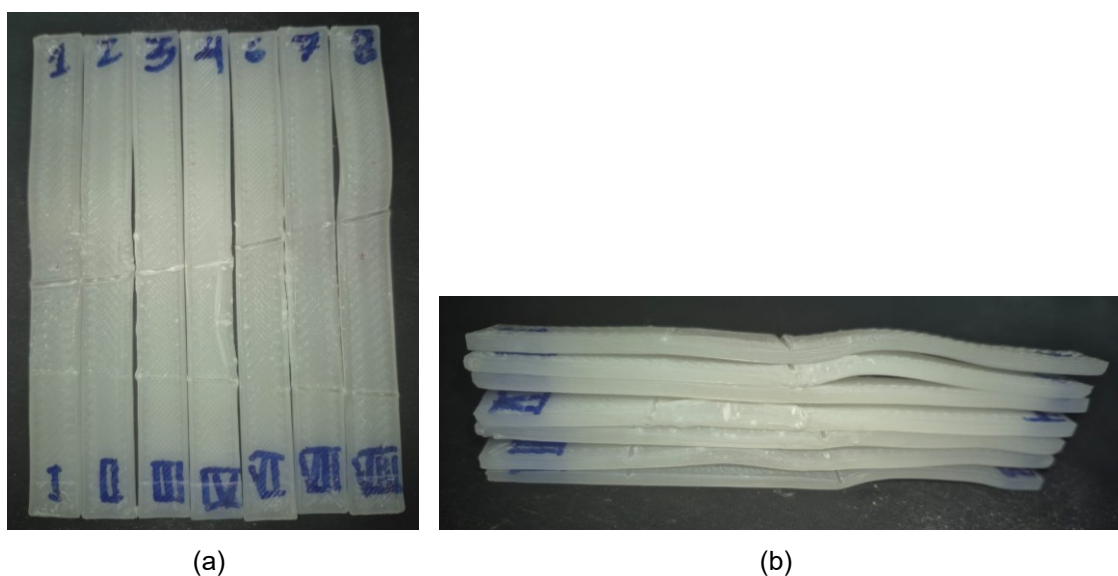
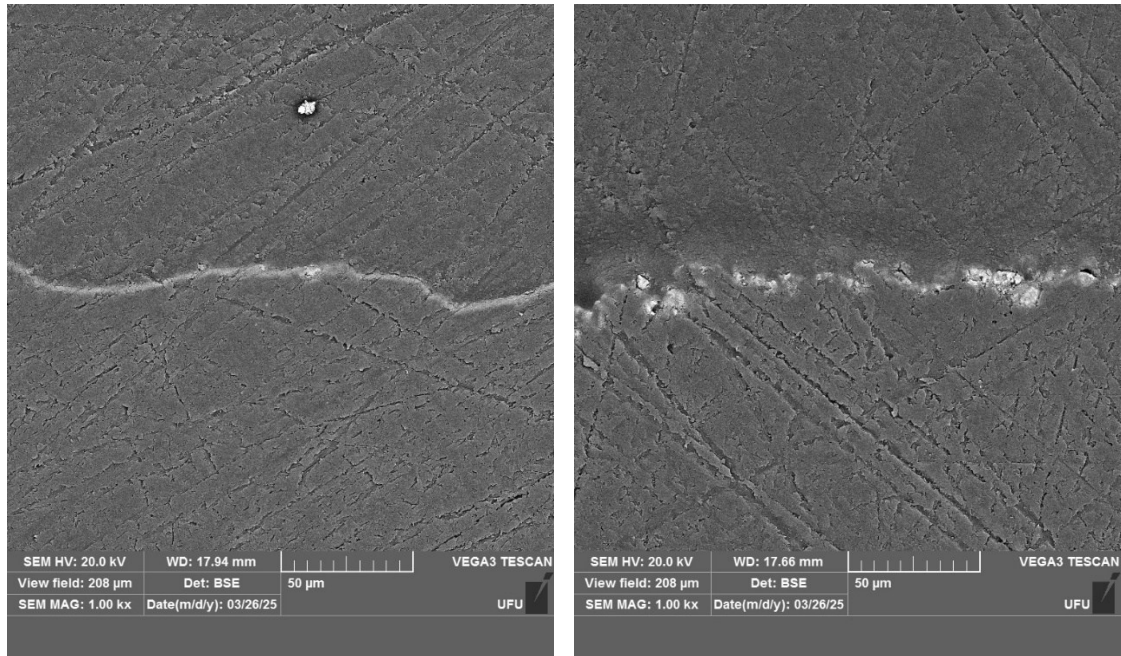


Figura 7. Aspecto deformado das amostras jateadas na condição 8C.

O aspecto visual das amostras geradas nas condições 1C, 8A, 8B e 8C indicou pouca ou nenhuma adesão de particulado na superfície na constatação visual, e por isso não foram feitas análises da composição química da superfície jateada, exceto para uma das amostras da condição 8C. Esta foi seccionada, com um pedaço sendo embutido em resina poliéster, e posteriormente lixado até grão 2000 para realizar análise da seção transversal e verificar se houve adesão de particulados através de MEV e XRD. Como pode ser verificado na Figura 8, houve deposição de particulados de forma irregular, com recobrimento total da superfície em algumas regiões (Figura 8a) e deposição parcial em outras (Figura 8b). Pelos mapas de composição química da Figura 9 e pelos espectros de EDS da linha da Figura 10, percebe-se que o revestimento é rico em cálcio e tem uma espessura aproximada de 4 μm . Segundo a Tabela 4, o revestimento é composto também por carbono do substrato, em alta proporção, indicando a formação de um revestimento compósito. É provável que ao amolecer o substrato com o ar quente, as partículas misturadas ao ar comprimido e jateadas impactaram a superfície do polímero e penetraram nos primeiros micrometros da peça. Embora essa espessura de

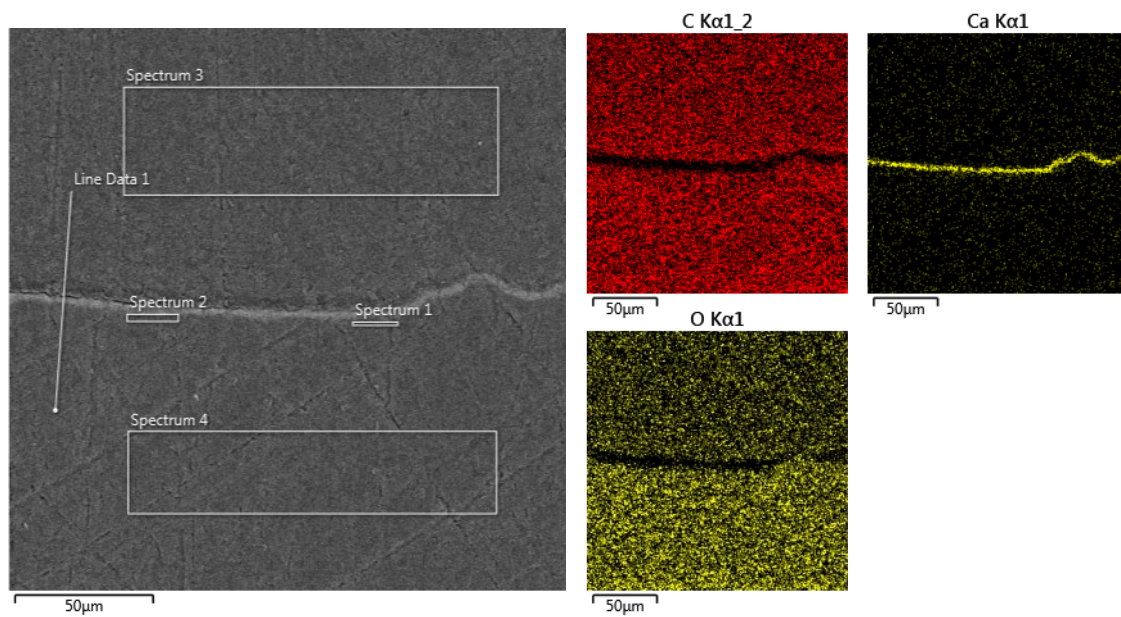
revestimento seja inferior ao revestimento gerado por outras tecnologias, como discutido em outros trabalhos (Campos et al., 2025), o processo de jateamento tem potencial para gerar revestimentos finos de hidroxiapatita em PLA, desde que a deformação geométrica devido ao calor não seja um problema para as peças.



(a)

(b)

Figura 8. Imagens de MEV da seção transversal das amostras produzidas na condição 8C, mostrando o revestimento gerado na superfície.



(a)

(b)

Figura 9. a) Imagem BSE (backscattered electrons) mostrando o revestimento na superfície gerado na condição 8C e as regiões de aquisição do espectro de EDS (retângulos e linha). b) Mapas de composição química.

Tabela 4. Composição química das regiões marcadas na Figura 9a.

Wt%				
Spectrum	1	2	3	4
C	65,63	61,04	65,87	67,37
O	11,14	12,69	34,13	32,63
P	7,34	8,29	0	0
Ca	15,89	17,98	0	0

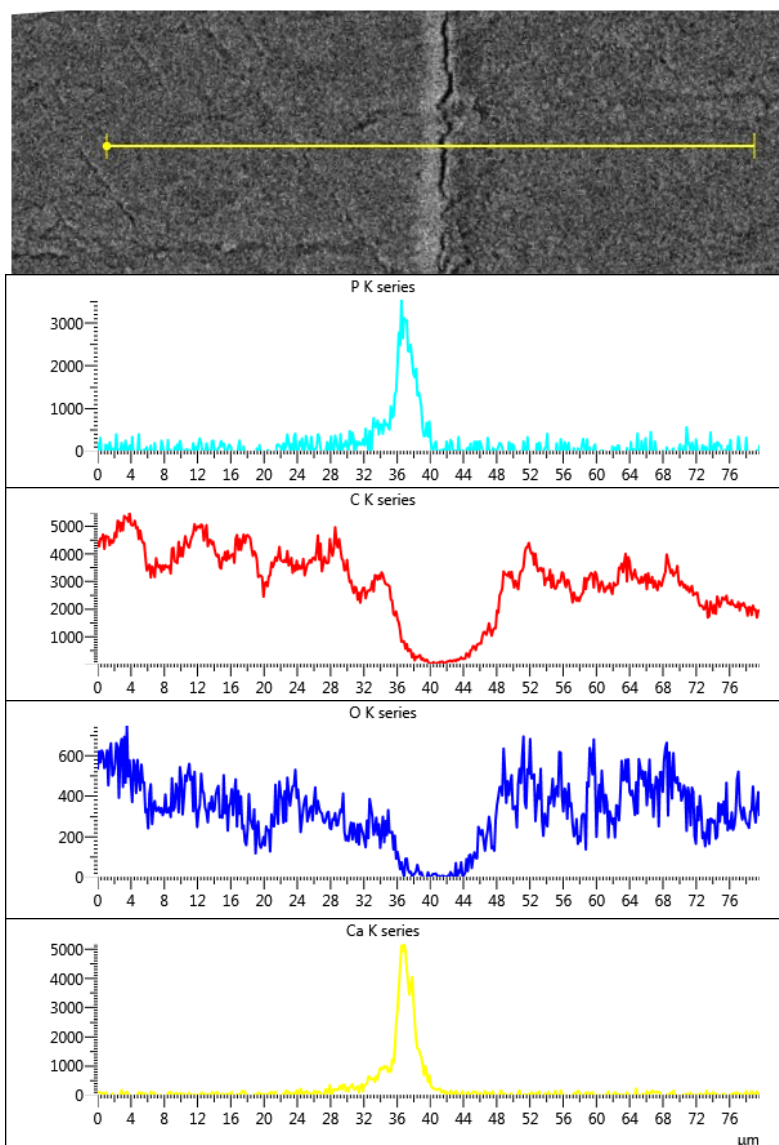


Figura 10. Espectro EDS da linha (Line Data 1) da Figura 9a.

CONCLUSÕES

O presente estudo avaliou a viabilidade da aplicação do processo de jateamento térmico intermitente para a geração de revestimentos cerâmicos à base de hidroxiapatita (HA) em substratos de PLA obtidos por impressão 3D. Embora o método tenha se mostrado promissor em trabalhos anteriores com outros polímeros, os resultados obtidos neste estudo indicam desafios significativos para sua aplicação em PLA, especialmente relacionados ao controle térmico e à integridade geométrica das peças durante o processamento.

Os experimentos demonstraram que, apesar da dificuldade em manter um controle preciso dos parâmetros e da ocorrência de deformações plásticas nas amostras, foi possível obter adesão parcial de particulados cerâmicos à superfície polimérica. As análises de MEV e EDS confirmaram a presença de uma camada superficial rica em cálcio e fósforo, com espessura média de aproximadamente 4 µm em regiões localizadas. Contudo, a irregularidade do recobrimento e a grande deformação das peças destacam a necessidade de otimização do processo.

Para que o método possa ser consolidado como uma alternativa viável para a funcionalização de implantes ortopédicos em PLA, recomenda-se a investigação de estratégias para minimizar o aporte térmico excessivo, como a implementação de fluxos de ar mais bem distribuídos ou o uso de anteparos para contenção geométrica. Além disso, melhorias na automação e robustez do sistema de controle podem reduzir a ocorrência de falhas nos subsistemas durante o jateamento.

Em síntese, o processo de jateamento térmico intermitente apresenta potencial para gerar revestimentos bioativos finos em substratos poliméricos, mas demanda ajustes técnicos significativos para alcançar a uniformidade e qualidade necessárias em aplicações clínicas. Estudos futuros focados na otimização de parâmetros e na avaliação do comportamento biológico dos revestimentos obtidos serão essenciais para a evolução desta tecnologia.

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CAPÍTULO 11

11. ARTIGO 8

Campos, F.A.R., da Silva, L.R.R., Castro Filice, L.S., Machado, A.R. (2023). Optimization of mechanical and surface properties of hydroxyapatite-coated PLA parts by powder bed annealing. Ainda não publicado.

ABSTRACT

The functionalization of thermoplastic polymer implants with bioactive coatings is essential to improve osseointegration and long-term clinical performance. In this work, hydroxyapatite (HA) coatings were applied to 3D printed polylactic acid (PLA) specimens via powder bed annealing, and the effects of annealing temperature and annealing time on mechanical and surface properties were systematically investigated. A full-factorial 2^3 design of experiments was conducted, followed by response surface methodology (RSM) to identify processing conditions that optimize flexural strength, impact resistance, coating thickness, and surface wettability. PLA specimens were fabricated in accordance with ASTM D6272 and subjected to annealing at peak temperatures of 170–190 °C for times between 0–10 min. Mechanical properties were assessed by four-point bending and impact tests, while coating thickness was evaluated by SEM cross-section imaging, and wettability by water contact angle measurements. Results showed that higher annealing temperatures and times significantly increased coating thickness ($p < 0.000001$) due to enhanced surface diffusion, with greater deposition at specimen edges compared to the midsection. Surface wettability improved markedly for most conditions, achieving water contact angles as low as 18.1°, indicating potential for enhanced bone integration. However, prolonged annealing often reduced impact energy and flexural elongation, suggesting a trade-off between bioactivity and mechanical resilience. RSM identified processing regions capable of achieving favorable combinations of coating adhesion and mechanical performance, although deviations between predicted and experimental results—especially for the condition optimized for flexural strength—highlighted the need for improved process control. Overall, powder bed annealing proved to be a low-cost, polymer-compatible approach for integrating bioactive HA coatings into additively manufactured PLA implants. Further work should address process repeatability and evaluate biological performance *in vitro* and *in vivo* to validate clinical applicability.

Keywords: Polylactic acid, Hydroxyapatite coating, Powder bed annealing, Additive manufacturing, Surface wettability, Mechanical properties

INTRODUCTION

The growing demand for patient-specific, cost-effective orthopedic implants has driven the development of new manufacturing technologies and functionalization methods for biomaterials. Among these, thermoplastic polymers such as polylactic acid (PLA) have attracted considerable attention due to their biodegradability, biocompatibility, and mechanical properties that are closer to those of natural bone, thereby reducing stress shielding effects in load-bearing applications (Al-Tamimi et al., 2024). Furthermore, PLA's processability by additive manufacturing allows the creation of complex, customized geometries, enabling personalized implant solutions with reduced production costs and lead times (da Silva et al., 2021).

For orthopedic and dental implants, surface modification plays a critical role in improving osseointegration and long-term performance. Hydroxyapatite (HA), a bioactive calcium phosphate ceramic with chemical similarity to the mineral component of bone, is well known for its osteoconductive and bioactive properties (Hunt et al., 2008). Its incorporation onto polymeric substrates has been shown to enhance surface wettability, promote cell adhesion, and accelerate bone tissue integration (Bernardo et al., 2022). However, conventional HA coating methods such as plasma spraying (Ortega-Bautista et al., 2024), electrophoretic deposition (Gorejová et al., 2023), and sol-gel processing (Jaafar et al., 2020) often require high processing temperatures or electrically conductive substrates, limiting their applicability for thermally sensitive polymers like PLA.

Powder bed annealing has recently emerged as a promising low-cost and scalable approach to functionalize polymeric implants with bioactive ceramic coatings (Campos et al., 2025). In this method, polymer parts are embedded in a powder medium containing HA particles and heated to a temperature near the polymer's melting point. At these temperatures, partial surface softening allows ceramic particles to adhere via a diffusion-driven process without causing structural degradation. Beyond enabling coating deposition, annealing can also modify the crystallinity of PLA, potentially influencing its mechanical performance, thermal stability, and degradation rate (Ma et al., 2021).

Optimization of such processes requires balancing multiple, and often competing, performance parameters. For instance, higher annealing temperatures and times may enhance coating thickness and adhesion but could also induce brittleness or reduce impact resistance (Campos et al., 2023). Similarly, modifications that improve hydrophilicity (a key factor for bone integration) may come at the expense of reduced flexural strength. Therefore, a systematic investigation using design of experiments (DOE) and response surface methodology (RSM) is essential to identify process conditions that maximize overall implant performance.

In this work, the optimization of mechanical and surface properties of hydroxyapatite-coated PLA specimens produced by powder bed annealing was determined. Using a full-factorial 2³ DOE, the effects of annealing temperature and heating time on flexural strength, modulus of elasticity, impact resistance, coating thickness, and water contact angle were analyzed. The results provide insights into the trade-offs inherent in this functionalization process and highlight the potential of powder bed annealing as a practical route for producing customized, bioactive polymeric implants.

METHODOLOGY

All specimens were fabricated using natural PLA filament supplied by Filamentos 3D Brasil, with its properties reported on the manufacturer's website (F3D, 2024). The calcium phosphate used in this study was sourced from a food additive supplier, as this compound is commonly employed as an anti-caking agent. The test specimens were fabricated following the ASTM D6272 standard (ASTM, 2017). This approach was chosen to enable direct comparison of the samples' performance in four-point bending, impact resistance, water contact angle and coating thickness evaluations. The selected geometry was suitable for all these tests, simplifying manufacturing and ensuring the availability of spare specimens. Moreover, using identical dimensions offered the advantage of minimizing variations in temperature distribution and heating rate during the annealing process.

All specimens were manufactured individually on a Creality Ender 3 v1® printer to ensure uniform thermal history prior to annealing. Printing parameters included a nozzle temperature of 210 °C, a bed temperature of 60 °C, 100% infill, a printing speed of 50 mm/s, a layer height of 0.32 mm, and a nozzle diameter of 1 mm. The adopted geometry consisted of a parallelepiped measuring 127 mm in length, 12.7 mm in width, and 3.2 mm in thickness, printed with the largest face in direct contact with the build plate. The powder bed annealing process was carried out in the same manner as explained in previous works (Campos et al., 2025), with four samples inside the tray. However, for this work, a 2³ design of experiments was used, with the levels shown in Table 1, which would allow the use of surface response methodology.

Table 1. 2³ design of experiments for powder bed annealing process.

Condition	Tmax (°C)	Time in Tmax (min)
A	170	0
B	170	5
C	170	10
D	180	0
E	180	5
F	180	10
G	190	0
H	190	5
I	190	10

The process was controlled by thermocouples inserted near the samples (inside the tray) and inside the oven, as explained previously (Campos et al., 2025). The heating curves from Figure 1 and Figure 2 show the powder bed annealing curves for conditions A and B, respectively. It takes about 20 to 25min for the temperature of the samples to reach near 170 °C. The time (Time in Tmax) was counted from the moment it reached 2 °C below the maximum temperature

(Tmax) and then the oven was turned off, opened and the tray with the samples was taken out and allowed to cool down at room temperature down to about 60 °C. The samples were retrieved from the powder bed, washed smoothly in water, dried in compressed air and stored in recipients filled with silica gel.

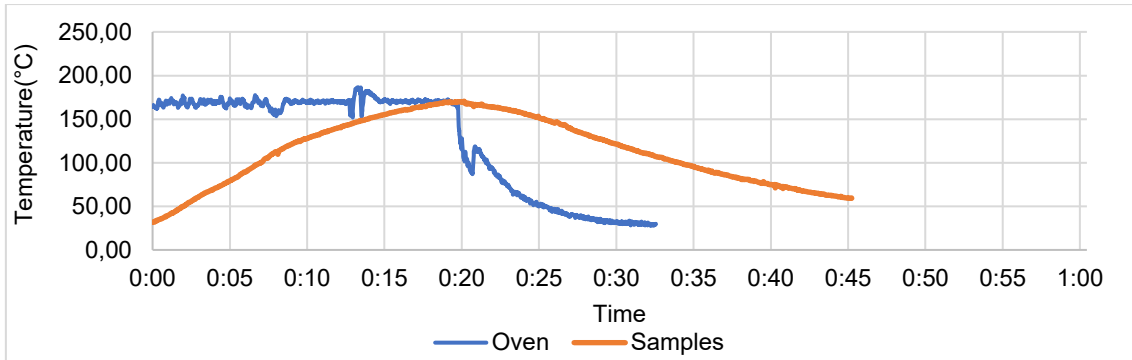


Figure 1. Heating curve for condition A.

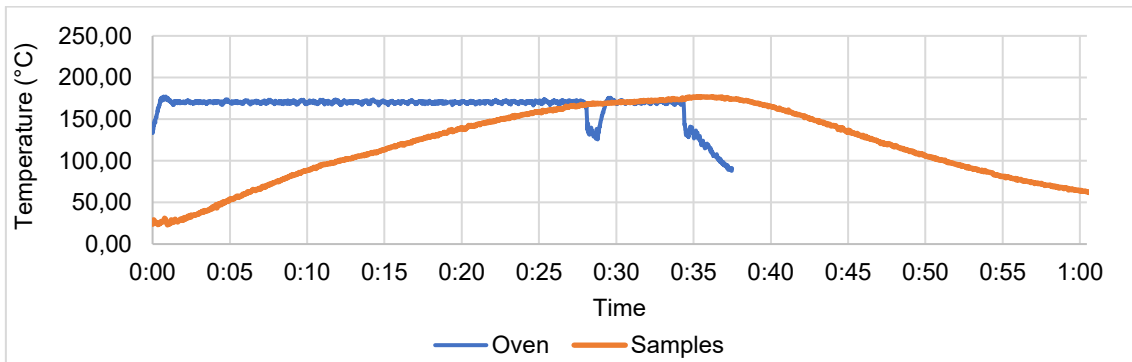


Figure 2. Heating curve for condition B.

After the samples were produced, three samples of each condition were subjected to 4 point bending tests according to ASTM D6272 (ASTM, 2017), in a universal testing machine with a load cell of 100 kg maximum capacity, resolution of 0.01 g and precision of 100 g. The results were used to calculate the maximum flexural strength (MFS), modulus of elasticity (E) and flexural elongation (ϵ). The remaining sample was first used in water contact angle measurement as per ASTM D7334 (ASTM, 2022). Three drops of 5 μ L were photographed separately and then the angle was measured in ImageJ software, as shown in Figure 3. Afterwards, this same sample was sectioned in smaller pieces 19 mm long for impact tests, which were executed according to ASTM D4508 (ASTM, 2006) for three pieces from each condition, using equipment adapted from the work of Tsuruta (2008). The pendulum was released at an angle of 0° in relation to the horizontal, reaching a speed of 5.6 m/s when hitting the piece with an energy of 3.8 J. The pendulum used had a length of 0.778 m (distance from the tip to the center of rotation), with a total mass of 0.963 kg and a center of mass at 0.159 m from the center of rotation. Additionally, two pieces were sectioned for coating thickness analysis in the cross section, with one being removed from the middle part of the sample and the other removed from the sample's end side.

They were both embedded in resin, sanded up to 1200 grit sandpaper, metallized with a 10 nm gold coating and taken to SEM microscope for BSE (backscattered electron imaging) analysis. Three photos of each piece were taken to analyze the cross-section of the original sample, making it possible to measure the HA layer thickness using the ImageJ software as shown in Figure 4.

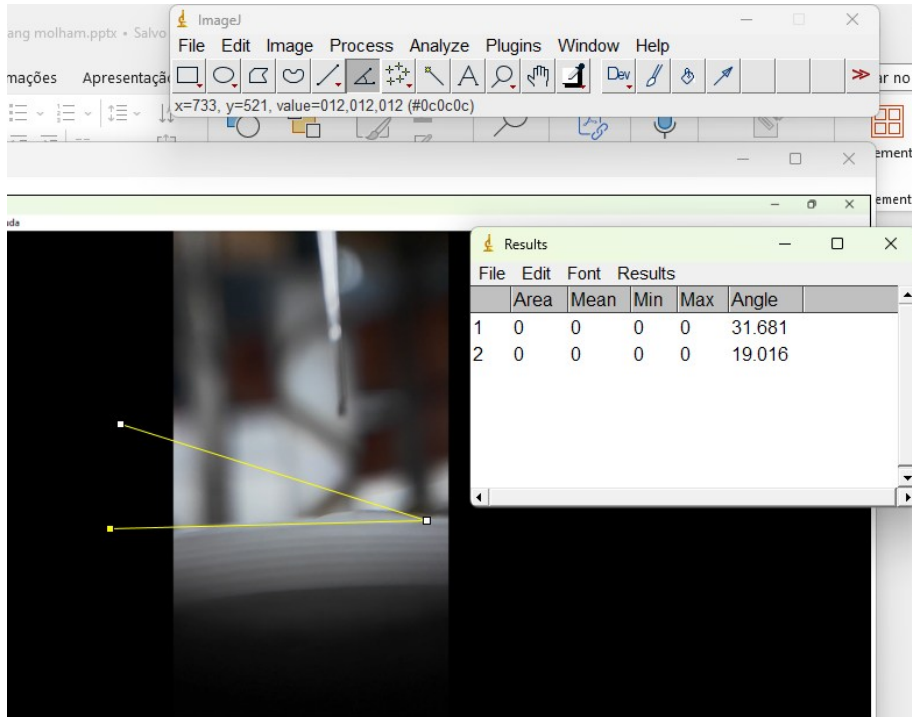


Figure 3. Measurement of contact angle at the edge of the photographed droplet, using ImageJ.

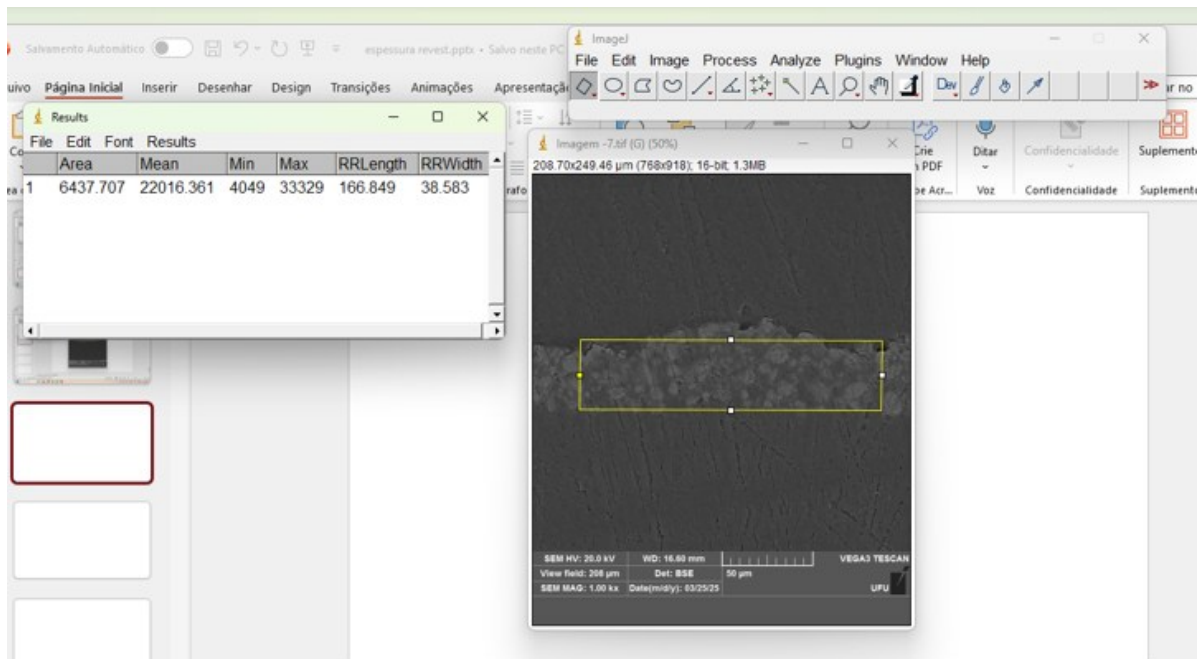


Figure 4. Example of coating thickness measurement at the cross section of the sample, using ImageJ software.

Finally, after the experiments, surface response methodology was applied using Statistica 12 software, to yield the resulting equations that modelled each output variable according to the input parameters. The outputs were then calculated for each value of Tmax and Time in Tmax in Tmax in the range of 170 °C to 190 °C (in 1 °C increments) and 0 min to 10 min (in 0.5 min increments). This allowed to obtain the optimal points O1, O2 and O3, for the highest MFS, lowest water contact angle, and highest impact resistance, respectively. Then the powder bed annealing process was repeated to generate new samples at these conditions, which were employed in the same mechanical and surface characterization tests to validate the method.

RESULTS

The results of the 4 point bending tests together with the response surface are shown in Figures 5 to 7, while in Figure 8 the results for the optimal points are also shown. It can be seen there is a significant difference between MFS and ϵ for pure PLA and for annealed samples, with the powder bed annealing process reducing both properties for most conditions. Tmax was a significant variable for MFS and E, considering a reliability index of 95 %, with $p=0.021424$ and $p=0.028739$ respectively, and this is probably due to the types of PLA crystals formed at each temperature (Ma et al., 2021), with more stable crystals yielding better flexural resistance. However, for some reason the optimal point O1, which should present better MFS in accordance with the response surface, actually yielded a result worse than the other optimal points and many other annealing conditions. This indicates that either there were experimental errors in the results from the 2^3 design of experiments or there were execution errors in the powder bed annealing of the optimal points.

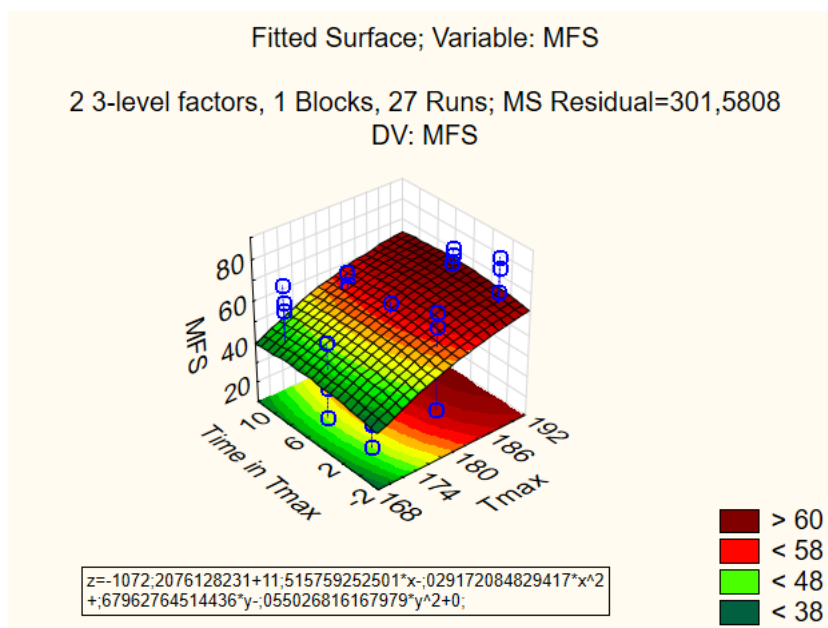


Figure 5. Fitted response surface for MFS (MPa) according to Time in Tmax (min) and Tmax (°C).

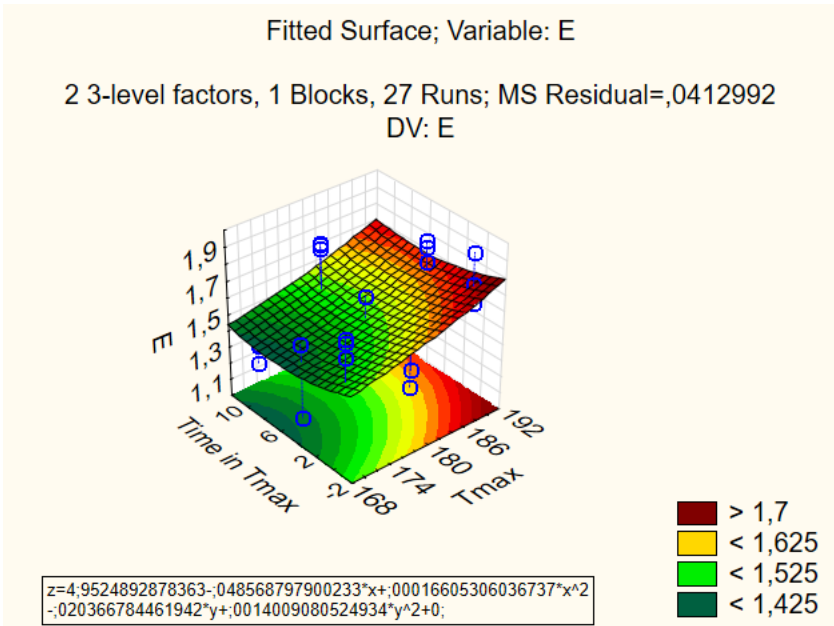


Figure 6. Fitted response surface for E (GPa) according to Time in Tmax (min) and Tmax (°C).

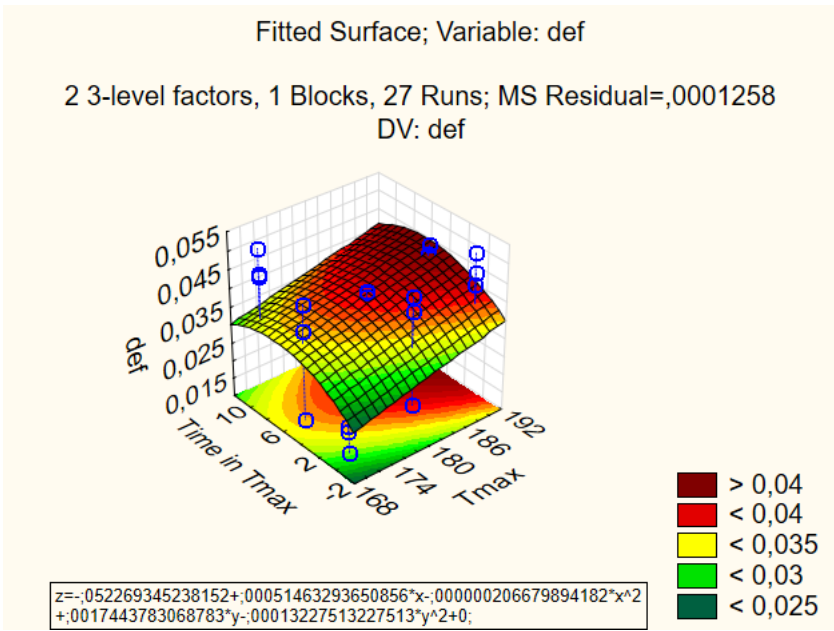


Figure 7. Fitted response surface for ε (%) according to Time in Tmax (min) and Tmax (°C).

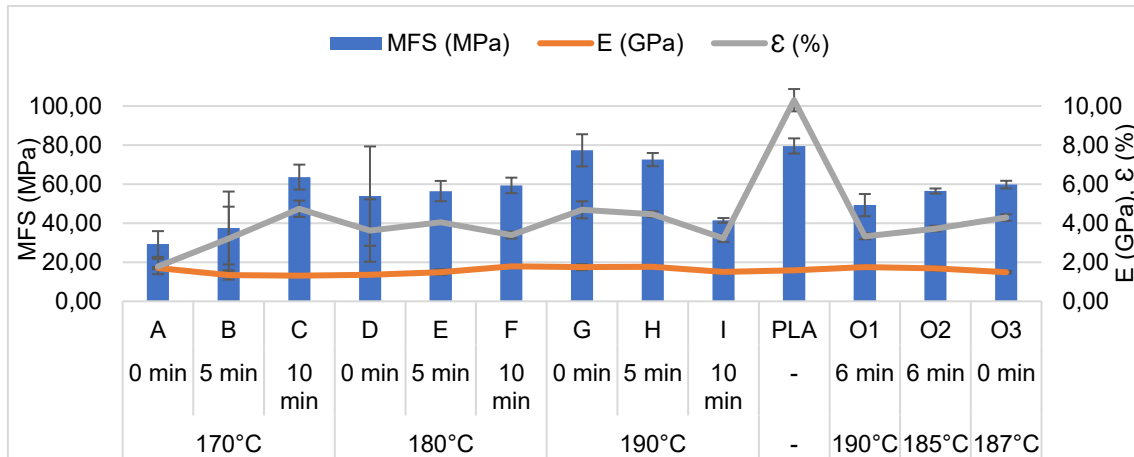


Figure 8. MFS, E and ε for each annealing condition.

Regarding coating thickness, the response surfaces are shown in Figure 9 to 11, while the coating thickness for all conditions is presented in Figure 12. Higher values for T_{max} and Time in T_{max} increase the coating thickness, with these two variables being significant with $p=0.000000$, considering a reliability index of 95 %, for both input variables at all measurements (middle, side end and both together). This is in accordance with the hypothesis that the adhesion of particulates on the surface of PLA occurs through a diffusion process, generating a composite layer with infiltrated particles as can be seen from Figure 4. The optimal point for this variable would be condition I, which presents the highest time and temperature, both of which facilitate diffusion by placing PLA in a more viscous state. It is also interesting to notice that thickness in the side end was always higher than in the middle, which is in accordance with the expected heat distribution in the samples. Since the metallic tray and the samples have a parallelepiped shape, when placed in the oven, the side ends heat faster than the middle region, justifying these results.

However, for the optimal points from the other variables, higher differences between them were expected, especially for condition O1. This suggests that indeed that the execution of the powder bed annealing process at these conditions was not ideal and might be the reason why the optimal points calculated by the empirical equations did not yield a true optimized result.

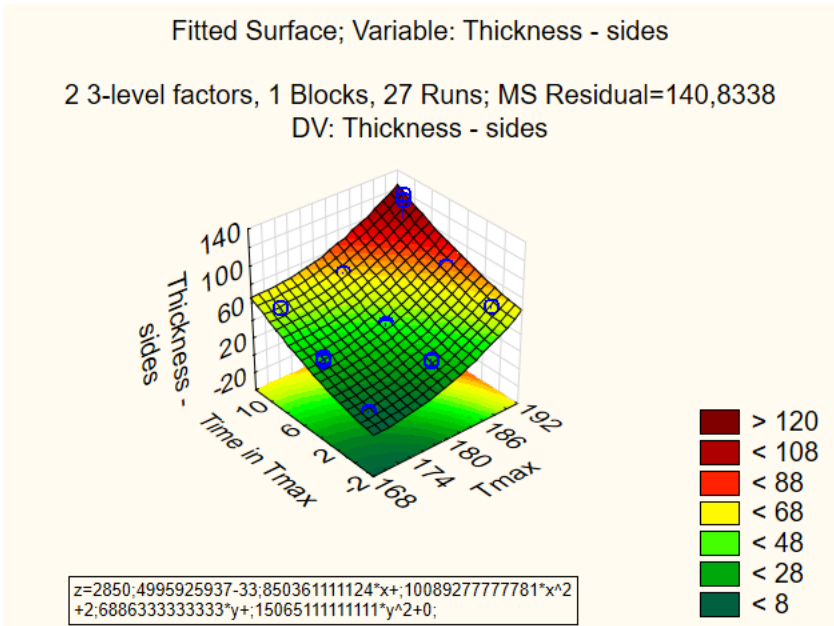


Figure 9. Fitted response surface for coating thickness at the end side of samples (μm) according to Time in Tmax (min) and Tmax ($^{\circ}\text{C}$).

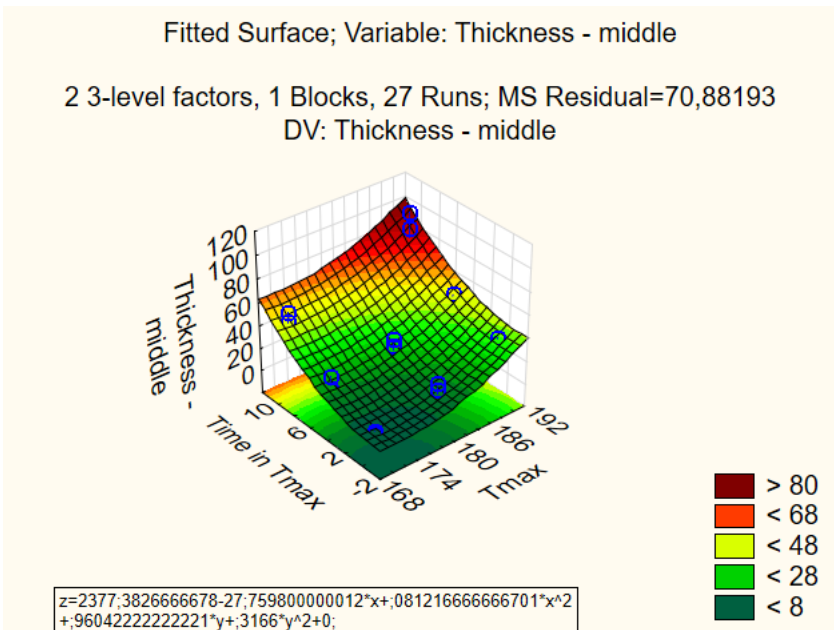


Figure 10. Fitted response surface for coating thickness at the middle of samples (μm) according to Time in Tmax (min) and Tmax ($^{\circ}\text{C}$).

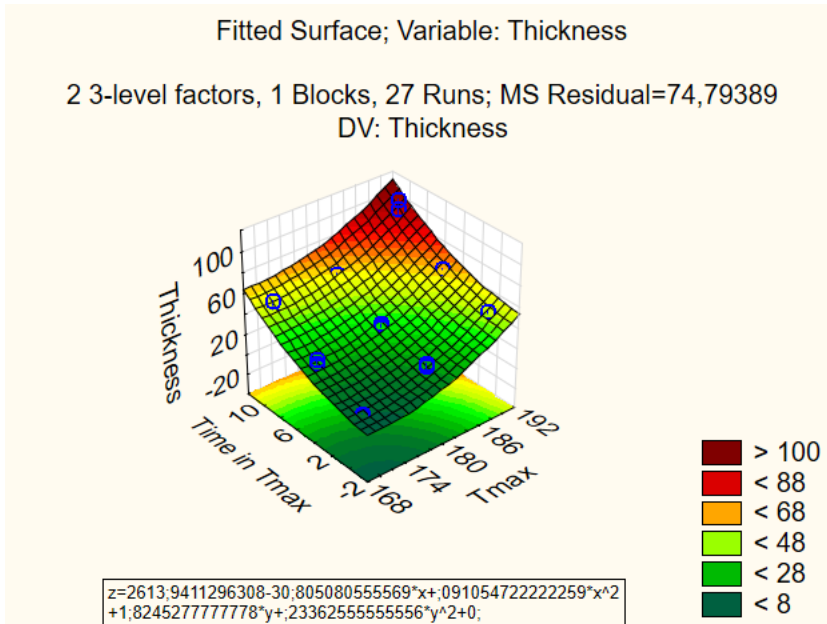


Figure 11. Fitted response surface for coating thickness, considering end and middle together (μm), according to Time in Tmax (min) and Tmax ($^{\circ}\text{C}$).

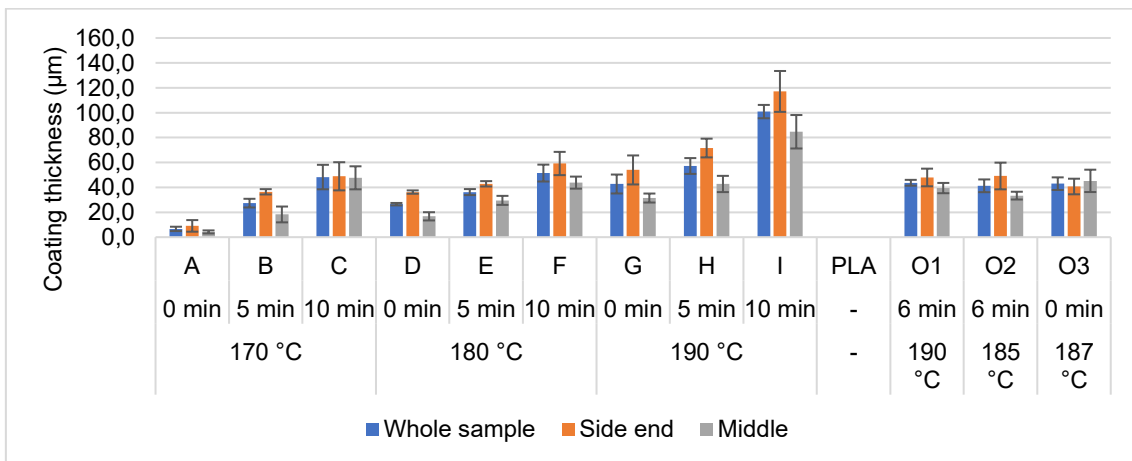


Figure 12. Coating thickness for each annealing condition.

For water contact angle, the surface response is shown in Figure 13 while the measurements for all conditions are shown in Figure 14. It is evident that except for condition A, all the others were successful in improving hydrophilicity of the surface of the samples, which is a good predicment of the adequability of this new coating for osseous implants (Sartoretto et al., 2015). The response surface methodology gave the optimal point O2 at 185°C and 6 min, for which the water contact angle was measured at $19,6^{\circ}$. Although there were lower values than this for conditions F and H (at $18,8^{\circ}$ and $18,1^{\circ}$), point O2 was close to the expected values. However, the high water contact angles for condition O1 suggest again that there were some type of experimental problem at least in this optimized point, for which contact angle is in disagreement with the expected values.

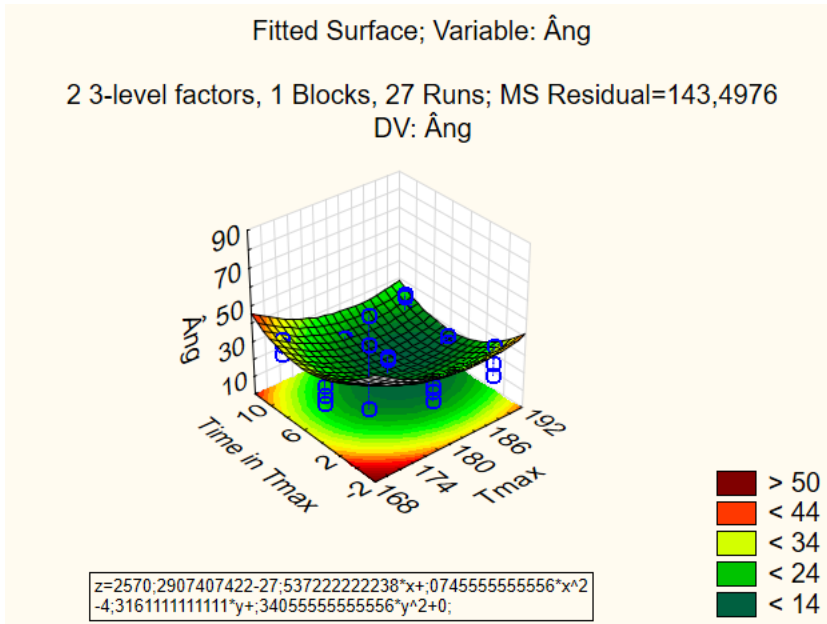


Figure 13. Fitted response surface for water contact angle ($^{\circ}$) according to Time in Tmax (min) and Tmax ($^{\circ}$ C).

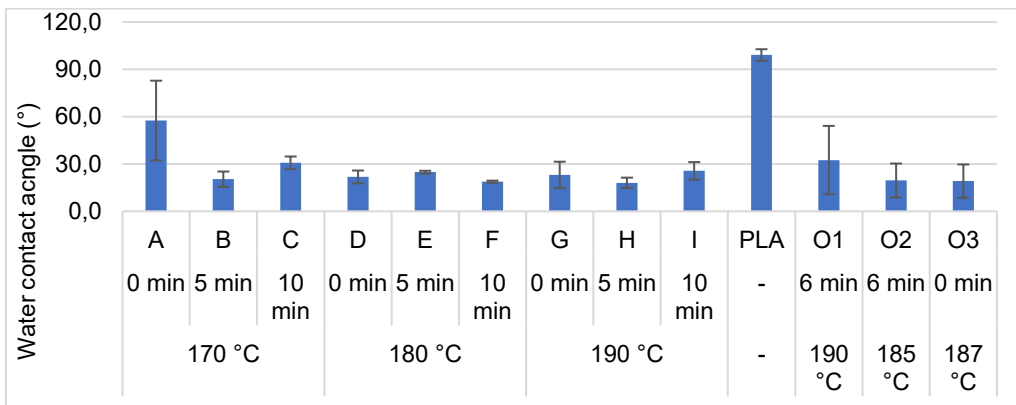


Figure 14. Water contact angle measurement for each annealing condition.

Finally, the response surface for impact energy is shown in Figure 15 and the results for all conditions are shown in Figure 16. Only Time in Tmax was significant, considering a reliability index of 95 %, with $p=0.040631$, and although there was no clear trend in the results, a higher time always seemed to worsen the impact energy of the samples. This might be caused by hot crystallization of the samples, which favors formation of big crystallites instead of interspersed ones, as explained by Ma et al. (2021). Nevertheless, except for conditions C, I and O1, all others reached impact energy values compatible with that of pure PLA, indicating that the powder bed annealing process maintains the impact resistance of the samples in most cases. Regarding the optimal points, although O3 was calculated according to the experimental equation to give the best impact energy, its result was still lower than for conditions D, F, G and H. Still, from the optimal points, it reached the highest value, as expected.

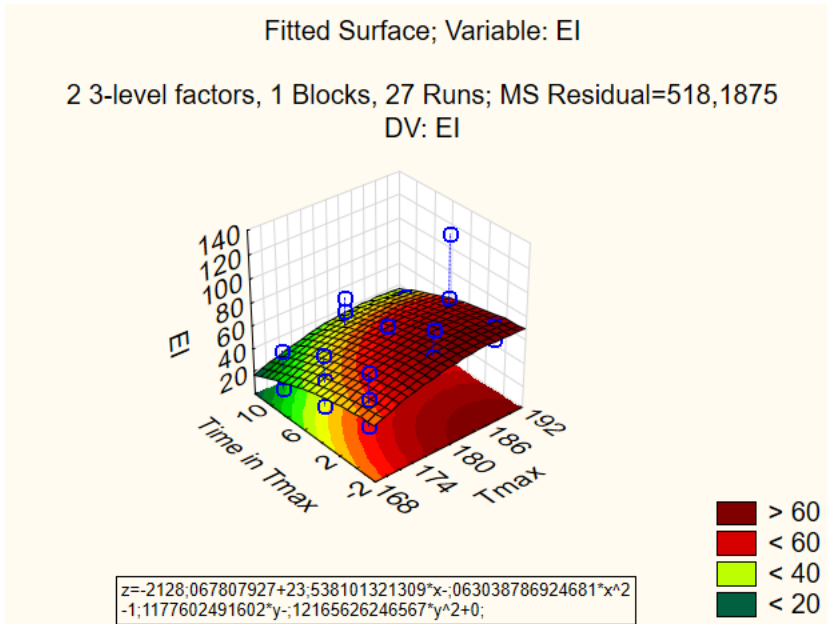


Figure 15. Fitted response surface for impact energy (J/m) according to Time in Tmax (min) and Tmax (°C).

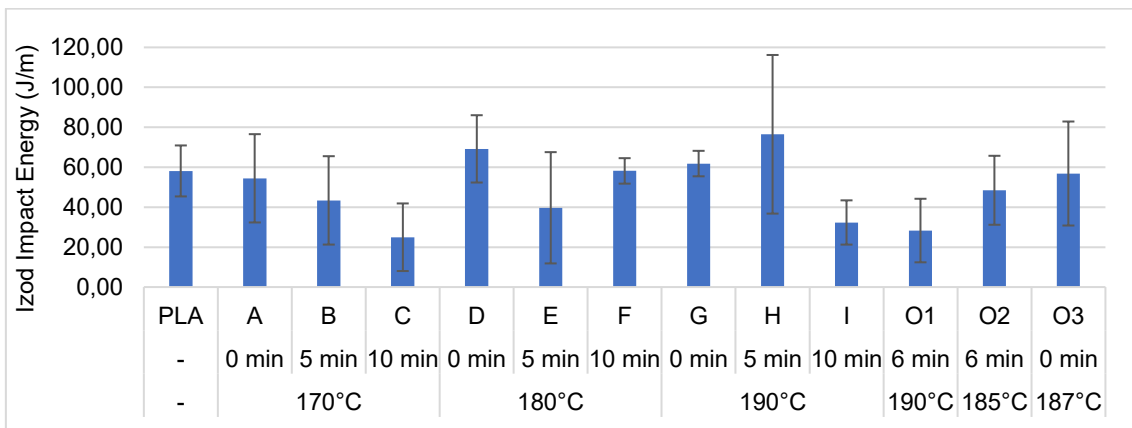


Figure 16. Impact energy for each annealing condition.

CONCLUSIONS

This study demonstrated that powder bed annealing is a viable and scalable method for producing hydroxyapatite-coated PLA components with improved surface bioactivity, as evidenced by the significant reduction in water contact angle across most processing conditions. The results confirmed that both annealing temperature and dwell time at peak temperature critically influence coating thickness, flexural performance, and wettability. Higher temperatures and longer dwell times promoted greater coating deposition due to enhanced surface diffusion, although they also tended to reduce impact resistance and flexural elongation.

Response surface methodology proved effective in identifying processing regions that balance coating performance and mechanical integrity, even though deviations between predicted and experimental values—particularly for the O1 condition—suggest that process

control and repeatability require further refinement. Notably, sufficient HA layer thickness was attained and hydrophilicity was substantially enhanced without severely compromising mechanical properties in several intermediate processing conditions, such as conditions F, G, H and O3, supporting the feasibility of tailoring the annealing parameters for specific implant requirements.

Finally, the findings reinforce the potential of powder bed annealing as a low-cost, polymer-compatible alternative for functionalizing additively manufactured implants with bioactive ceramic coatings. Future work should focus on refining thermal uniformity within the powder bed, validating process reproducibility, and extending the investigation to *in vitro* and *in vivo* evaluations to confirm the clinical relevance of the optimized parameters.

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CAPÍTULO 12

12. ARTIGO 9

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ABSTRACT

The development of low-cost and patient-specific implants with bioactive surfaces remains a challenge in orthopedic biomaterials, particularly for resorbable polymers such as polylactic acid (PLA), which have limited temperature resistance and coating adhesion. This study evaluates a novel powder bed annealing process that simultaneously enhances the mechanical and thermal properties of 3D-printed PLA parts while generating a hydroxyapatite (HA) and titanium dioxide (TiO₂) based bioactive coating. PLA specimens produced via fused filament fabrication were annealed in powder beds containing HA or HA/TiO₂ mixtures at 170–190 °C, with varied dwell times, followed by autoclave sterilization cycles under different drying conditions. Two-factorial experimental designs were applied to assess coating thickness, chemical composition, flexural and impact resistance, Heat Deflection Temperature (HDT), and coating adhesion (by progressive load scratch testing). Annealing temperature emerged as the dominant factor for performance enhancement. Samples treated at 180 °C exhibited the highest maximum flexural strength (up to 37 MPa) and modulus of elasticity, with autoclaving, especially with drying, maintaining or improving these values. Impact resistance increased by more than 100 % after autoclaving for some conditions, likely due to favorable crystallographic transitions. Coating thickness ranged from 20–50 µm, with higher stability after sterilization at 180 °C. HA content derived from EDS analysis confirmed deep particulate diffusion into the polymer matrix. Thermal stability was significantly improved, with HDT increasing from ~65 °C for as-printed PLA to ≥150 °C after powder bed annealing, enabling deformation-free autoclave sterilization. Coating adhesion strengths of 83–139 MPa exceeded those of many polymer–ceramic and metal–ceramic coatings reported in the literature. The process maintained coating integrity under bending stresses of up to 91 MPa, with failure resistance influenced by coating thickness, HA content, and homogeneity. The findings demonstrate that powder bed annealing can integrate mechanical reinforcement, temperature resistance improvement, and osseointegrative surface formation in a single, scalable step using standard Fused Filament Fabrication (FFF) printers and basic laboratory ovens. This approach eliminates the need for complex deposition methods such as plasma spraying or sputtering, offering a practical manufacturing route for customized, sterilization-resistant, bioactive PLA implants. The results position this innovative process as a promising technology for the clinical translation of resorbable polymer implants, warranting further *in vivo* evaluation to validate long-term osseointegration and degradation behavior.

Keywords: powder bed annealing, resorbable polymers, hydroxyapatite coating, progressive load scratch test, autoclave sterilization.

INTRODUCTION

The increasing number of orthopedic procedures globally (Brumat et al., 2022; Madrid, 2022) has been driving demand for implants and prosthetic devices. However, conventional implant materials, particularly metallic biomaterials such as titanium, pose significant challenges due to their high manufacturing cost (Davis et al., 2022) and mechanical incompatibility with native bone (Kim et al., 2019; Swalsky et al., 2024). One of the most common problems associated with metallic implants is the stress shielding effect, caused by the mismatch in elastic modulus between the implant and bone tissue, leading to bone resorption and implant loosening over time (Tavakkoli Avval et al., 2015).

In this context, biocompatible polymers, especially those that are biodegradable and customizable, have emerged as viable alternatives. Among them, polylactic acid (PLA) stands out for its widespread use in biomedical applications, due to its ease of processing, biocompatibility, bioresorbability, and mechanical properties suitable for moderate-load-bearing applications (Szymczyk-Ziółkowska et al., 2020; Benatti et al., 2019). PLA-based materials have been successfully used in the production of bone fixation devices (Al-Tamimi et al., 2024), interference screws (Hunt et al., 2008; Jamari et al., 2023; Veizi et al., 2022), and tissue engineering scaffolds (Alonso-Fernández, 2023). PLA can also be tailored through structural modification (Haneef et al., 2022), copolymerization (Mohamed Haneef et al., 2019), and surface treatments to enhance its performance (Saniei and Mousavi, 2020).

A particularly relevant advancement in the fabrication of polymer-based implants is additive manufacturing (AM), specifically the Fused Filament Fabrication (FFF) method. It allows for the rapid prototyping of highly customized parts with geometries that are difficult or impossible to achieve using traditional subtractive manufacturing. This enables the production of patient-specific implants at lower costs, reducing waste and lead time (da Silva et al., 2021; Agarwal et al., 2022). However, FFF-printed polymers, particularly PLA, often suffer from anisotropic mechanical properties due to layer-by-layer deposition and poor interlayer adhesion (Pratama et al., 2021; Arifvianto et al., 2021).

To overcome these limitations, post-processing methods such as thermal annealing have been proposed to improve crystallinity and reduce anisotropy. Annealing above the glass transition temperature of PLA (~60–65 °C) enables molecular rearrangement and formation of crystalline domains, enhancing thermal stability, stiffness, and sometimes even impact resistance (Kishore et al., 2020; Valvez et al., 2022; Yu et al., 2023; Valvez et al., 2023; Hart et al., 2018; Hart et al., 2020). Nonetheless, traditional annealing processes may lead to dimensional distortion of the printed parts, which limits their application when geometric precision is crucial (Pratama et al., 2021).

To address this, recent studies have proposed annealing PLA parts while immersed in a powder bed to support the geometry during heating, preventing deformation and facilitating even heat distribution (Szust et al., 2022; Hernández-Castellano et al., 2022). While this method has primarily been explored as a dimensional stabilization technique, it opens the potential for an innovative dual-function approach: not only improving the polymer's internal structure but also modifying its surface. This novel approach, termed powder bed annealing, was explored in our previous study (Campos et al., 2025) with functional particulates. It was observed that hydroxyapatite (HA) and titanium dioxide (TiO₂) particles, when present in the powder bed during annealing, adhered to the softened surface of PLA, forming a uniform coating layer. The process resulted in a hybrid composite coating with a significant content of bioactive ceramics integrated into the polymeric surface, creating a potential osseointegrative layer for orthopedic applications.

Hydroxyapatite, the main inorganic constituent of natural bone, is widely regarded for its osteoconductive and bioactive properties, supporting bone in-growth and implant integration (Bernardo et al., 2022; da Silva et al., 2024; Sossa et al., 2018). Additionally, titanium dioxide, particularly in its rutile phase, has been shown to improve cell adhesion and promote osteoblast activity, while also offering antimicrobial benefits (Fei Yin et al., 2013; Jouanny et al., 2010; Duarte et al., 2020). The possibility of forming a HA/TiO₂ composite coating using the powder bed annealing process offers an appealing route for generating bioactive surfaces on PLA implants without the need for complex and costly equipment like plasma spraying, sputtering, or electrodeposition (Rafiei et al., 2025; Ortega-Bautista et al., 2024).

An additional benefit of powder bed annealing could be the concurrent improvement in the temperature resistance of the printed parts. As demonstrated in prior research, annealing of semicrystalline polymers like PLA can significantly increase their Heat Deflection Temperature (HDT) (Péter et al., 2021), enabling the parts to withstand more rigorous sterilization methods such as autoclaving (Gofman et al., 2013; Abeydeera and de Silva, 2023), which is a critical step for clinical translation. While PLA is traditionally considered unsuitable for high-temperature sterilization due to its low T_g and high distortion (Told et al., 2022; Neijhoft et al., 2023; Ferràs-Tarragó et al., 2022; Moreau et al., 2024), studies have reported that certain annealing treatments can elevate its HDT above 120 °C (Campos et al., 2023) and that would increase PLA suitability as an implant material.

Given these insights, the present study aims to advance this innovative approach by systematically evaluating the mechanical and thermal behavior, as well as the surface coating characteristics of PLA parts subjected to powder bed annealing and coated with HA and TiO₂ particles. This work builds upon earlier findings to explore the interplay between annealing parameters (temperature, time at peak temperature) and the nature of the particulate bed in influencing coating thickness, adhesion, and composition. Additionally, the impact of autoclave sterilization on the coated parts was investigated to assess their viability for surgical use, addressing both functional performance and practical constraints. Furthermore, this study seeks to evaluate the extent to which submicron particles diffuse and anchor into the softened PLA

matrix during annealing, to verify if there is robust adhesion and long-term mechanical integration, which are critical for in-vivo performance.

The innovative nature of this study lies in its proposition of a low-cost, simple, and scalable surface modification process that simultaneously enhances mechanical performance, creates bioactive coatings, and improves sterilization resistance. This approach circumvents the limitations of traditional coating methods that require complex infrastructure or high-cost inputs, offering a practical route to producing custom-fit implants using standard desktop 3D printers and basic lab ovens. Finally, this work incorporates rigorous quantitative assessment protocols, including flexural and impact testing (ASTM D6272 and D4508), progressive load scratch testing for coating adhesion (ASTM D7027), SEM/EDS for surface characterization, and HDT evaluation (ASTM D648), to provide a comprehensive evaluation of the resulting materials. By integrating these testing methodologies with two-factorial experimental designs, the influence of each process parameter can be statistically evaluated, offering reliable guidance for optimizing future manufacturing strategies. In summary, this research addresses a critical need in the biomedical field: the development of accessible, customizable, and sterilization-resistant polymeric implants with bioactive coatings. By leveraging the synergistic effects of additive manufacturing, powder bed annealing, and ceramic surface functionalization, this study contributes to the ongoing transformation of implant manufacturing, aligning cost-effective fabrication with clinical efficacy and regulatory compliance.

METHODOLOGY

Materials

All the samples were 3D printed in natural PLA from Filamentos 3D Brasil (F3D, 2025), supplied in 1 kg spools of filament with 1.75 mm diameter. The calcium phosphate was obtained from Adicel (Adicel, 2025), a food additive supplier, according to which the tricalcium phosphate can be used in food industry as anti-humectant, stabilizer, pH regulator, clouding agent, and concentrated source of calcium. This white mineral compound in a fine, crystalline powder is obtained by the reaction between food-grade phosphoric acid and hydrated lime. Titanium dioxide was purchased from online stores, since it is the world's most used pigment load for white paints, and it also presents as a fine white crystalline powder.

Chemical characterization by X-ray diffraction (XRD) and SEM (Scanning Electron Microscopy) and EDS (Energy Dispersive Spectroscopy) of both particulates was conducted in previous work (Campos et al., 2025). It has been revealed that the calcium phosphate is of hydroxyapatite (HA) crystalline structure, which is the preferred structure for implant coating due to its lower solubility and greater stability in the human body (Hu et al., 2020; Sossa et al., 2018; de Melo Costa et al., 2009), while the titanium dioxide is of the rutile crystalline structure, which presents adequate biological activity as well (Duarte et al., 2020). The HA and the TiO₂ present in

the form of small crystals with thickness of about 200 nm to 500 nm which agglomerate into larger particles of about 2 μm to 10 μm .

Production and preparation of test specimens

As explained in previous works (Campos et al., 2025), test samples were prepared in accordance with ASTM D6272 (ASTM, 2002) because with this geometry it was also possible to generate samples to perform impact tests, microhardness measurements, layer thickness and chemical composition analysis, investigate heat deflection temperature and adhesion of coating by scratch tests. Besides facilitating production, it guaranteed an equal heat input and thermal history during the annealing process. Samples were printed one by one on a Creality Ender 3 v1® 3D printer with a nozzle temperature of 210 °C, table temperature of 60 °C, 100% infill, printing speed of 50 mm/s, layer height of 0.32 mm and diameter nozzle of 1 mm.

After printing, samples were coated by the powder bed annealing process for which a detailed explanation can be found in the work of Campos et al. (2025). The procedure is patent pending, with code BR 10 2025 000986-2 registered in Brazilian National Institute of Intellectual Protection (INPI). Their geometry, dimensions and printing orientation are shown in Figure 1a. In Figure 1b and Figure 1c it is possible to see the aspect of samples as printed and after coating generation, respectively.

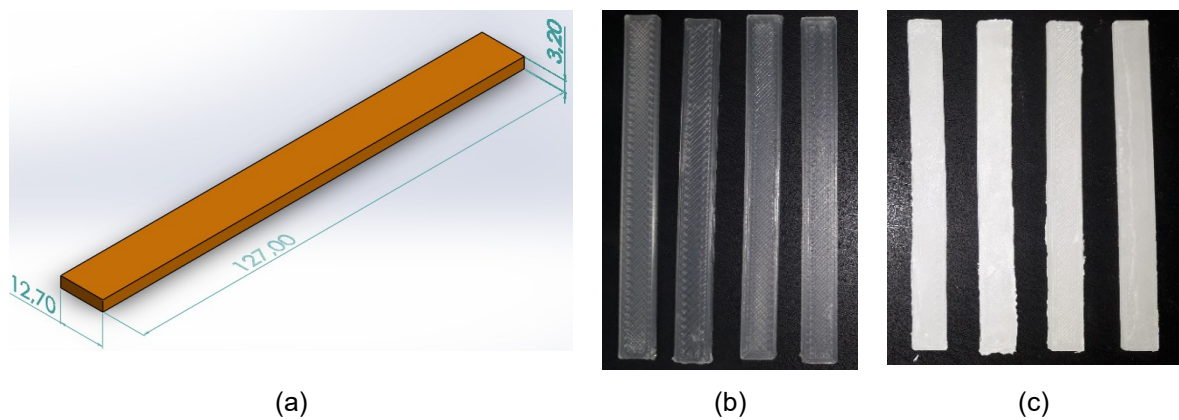


Figure 31. (a) Sample geometry. (b) Specimens as printed and (c) after coating generation.

For the current work, samples were first divided into two designs of experiments (DoE) as shown in Figure 2, both of them of 2^3 factorial type. In the first one, carried out as per Table 1, the coating thickness and chemical composition, together with flexural and impact properties were investigated according to annealing and autoclaving parameters. The second design was used to study the influence of powder bed annealing conditions on coating adhesion and part's temperature resistance, as shown in Table 2.

Table 1. 2³ design of experiments to investigate the influence of annealing temperature and autoclaving sterilization parameters on samples flexural resistance, impact resistance, coating layer thickness and coating chemical composition.

Condition	Annealing temperature (°C)	Cycles	Drying
A	180	1	No
B	180	1	Yes
C	180	2	No
D	180	2	Yes
E	170	1	No
F	170	1	Yes
G	170	2	No
H	170	2	Yes

Table 2. 2³ design of experiments to investigate the influence of powder bed annealing parameters on samples thermal resistance and coating adhesion.

Condition	Particulate	Time at Tmax (min)	Tmax (°C)
A	100 % CaPO	5	190
B	100 % CaPO	5	170
C	100 % CaPO	0	190
D	100 % CaPO	0	170
E	50 % CaPO + 50 % TiO ₂	5	190
F	50 % CaPO + 50 % TiO ₂	5	170
G	50 % CaPO + 50 % TiO ₂	0	190
H	50 % CaPO + 50 % TiO ₂	0	170

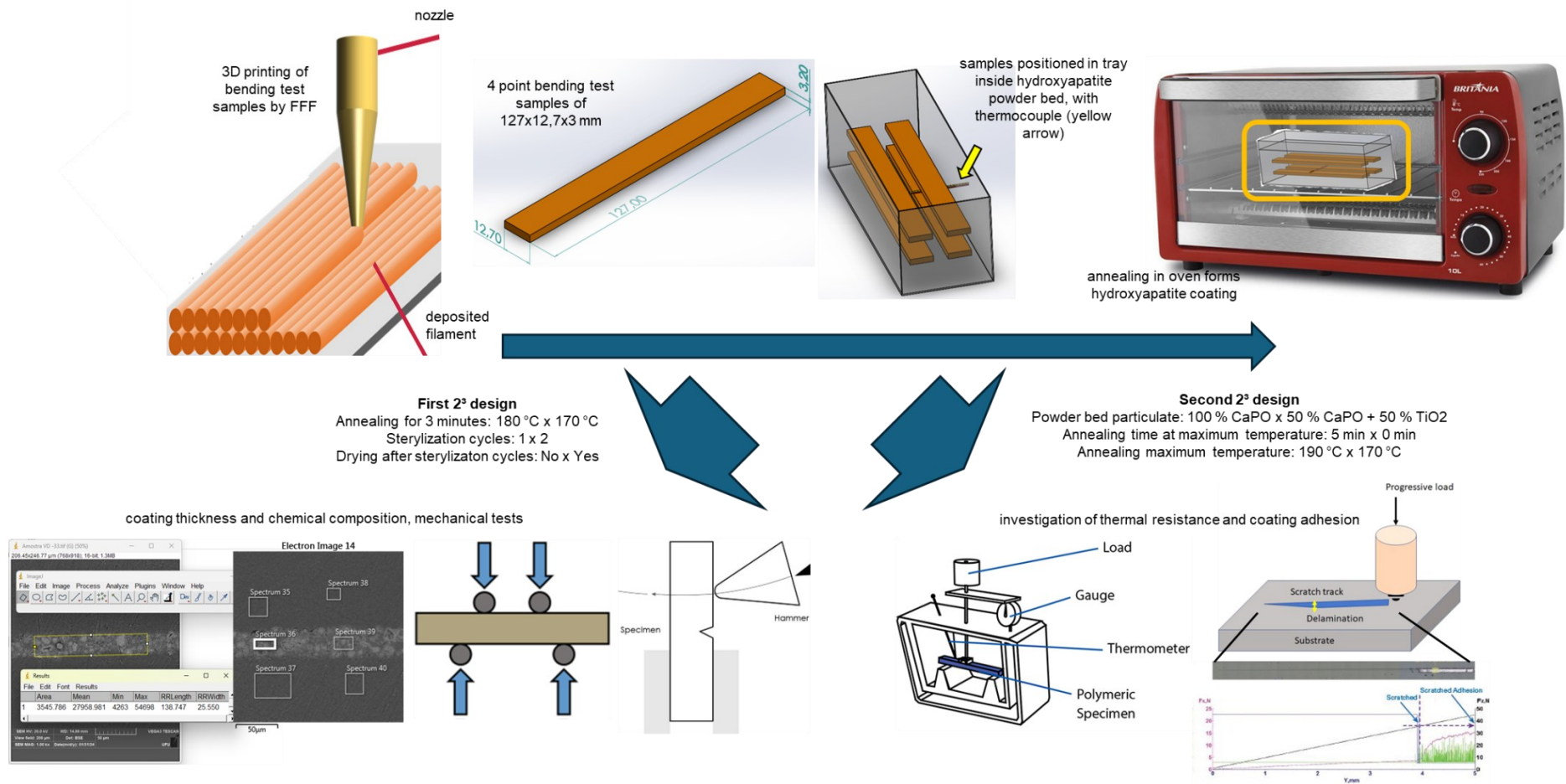


Figure 2. Schematic of the general experimental methodology. After 3D printing, samples were coated by powder bed annealing process in different conditions according to two 2³ designs of experiments. The first was used to investigate coating thickness, chemical composition and mechanical properties according to annealing and sterilization conditions. The second was used to investigate thermal resistance and coating adhesion in regard to the annealing parameters.

For the first DoE, powder bed annealing was carried using only calcium phosphate particulate because it was found on previous works that this condition yielded better mechanical properties. Four samples were produced at each condition, with 3 being used for bending tests and the last one being cut into 3 impact tests samples and 2 pieces for analysis of coating thickness and chemical composition. Powder bed annealing was conducted by heating samples immersed in a powder bed inside a metallic tray. The 4 samples were placed in the tray, which was taken into an electric oven with thermocouples inserted into the powder bed near the samples, monitoring the temperature as exemplified in Figure 3. When the maximum temperature (T_{max}) was reached, the tray was kept for 3 minutes in the oven and then taken off and allowed to cool naturally in air at a room temperature of 25 °C. Then the samples were retrieved from below the powder bed, washed smoothly in water, dried in compressed air and stored in plastic containers filled with silica to prevent moisture, until they were used for the subsequent experiments. The autoclave sterilizations were carried in a Cirstófoli Vitale 21L water vapor autoclave with sterilization temperature kept between 126°C to 130°C, which corresponds to a pressure of 1.5 kgf/cm² to 1.9 kgf/cm². After placing 250 ml of distilled water in the equipment, together with the samples, each cycle was comprised of about 20 minutes for the equipment to heat and another 20 minutes for the sterilization to occur. When drying was enabled, it took 20 minutes at 120 °C.

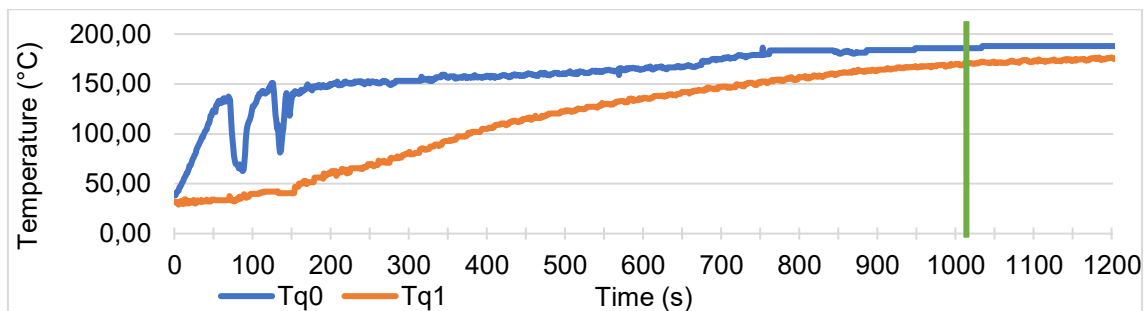


Figure 3. Temperature monitoring of the powder bed annealing process, with thermocouple Tq0 measuring temperature inside the electrical oven and thermocouple Tq1 measuring temperature inside the powder bed near the samples. The green line marks the moment when the temperature of 170 °C was reached, from which 3 minutes were counted before taking the tray out of the oven.

For the second DoE, it was desirable to verify if there were advantages regarding coating adhesion when using calcium phosphate together with titanium dioxide (50 % CaPO + 50 % TiO₂) instead of only the first (100 % CaPO). Also, as a sequence of the investigation initiated in previous work (Campos et al., 2025), the powder bed annealing temperatures (T_{max}) of 170 °C and 190 °C were used, together with the times at maximum temperatures (Time at T_{max}) of 0 and 5 minutes. Aside from these differences in input parameters, the powder bed annealing happened in the same methodology as for the first DoE, producing instead 8 samples for each condition (4 at each annealing operation), 3 of which were subjected to thermal resistance tests and 2 of each subject to adhesion investigation.

Flexural tests

Four point bending tests were conducted for three specimens of each condition of the first DoE in a universal testing machine with 200 kg capacity, ± 200 g accuracy and following the requirements of ASTM D6272 (ASTM, 2002) standard. The data on maximum flexural strength (MFS), modulus of elasticity (E) and flexural elongation (ϵ) were obtained. To calculate the modulus of elasticity it was measured the tangent of the straight segment formed between the origin at 0 and the stress at 0.5 % deformation as can be seen in the example given in Figure 4, which shows the graph for specimens of condition B.

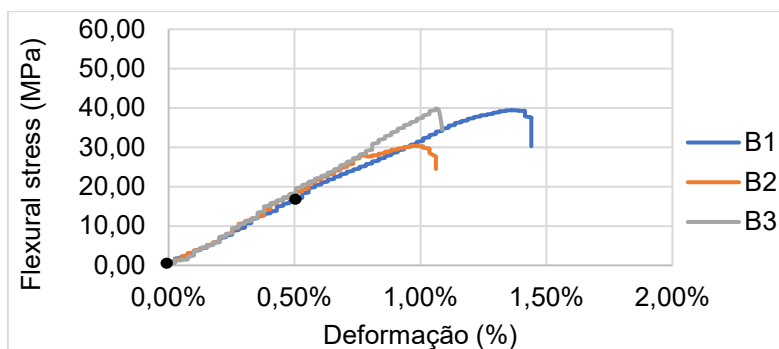


Figure 4. Stress-strain curve with points used for calculating the modulus of elasticity highlighted for B1 curve.

Impact tests

The Izod impact tests were performed according to ASTM D4508 (ASTM, 2006) to observe the influence of autoclave sterilization on the energy absorbed by the samples, which were 19 mm in length, 12.7 mm in width and 3.2 mm in thickness. Three specimens were tested per condition of the first DoE with a pendulum of 778 mm in length, 0.963 kg in mass and center of mass at 159 mm from the rotation center released from a horizontal position and reaching a speed of 5.6 m/s when hitting the sample with an energy of 3.8 J. The impact testing apparatus employed in this study was a modified version based on the design by Tsuruta (2008). The energy absorbed by the specimen during impact was measured using an encoder-type sensor attached to the pendulum's shaft, which recorded the pendulum's peak angular displacement. This encoder featured a 220 mm diameter disk with 360 holes, each 1 mm in width and spaced 1 mm apart, arranged along the disk's outer edge. An LM393 module, mounted on the pendulum support, was used to detect and convert the disk's movement into digital signals analyzed by an Arduino Uno.

Coating layer thickness and chemical analysis

Coating layer thickness and chemical analysis were carried in the cross section of 2 segments from a sample of each condition of the first DoE. The first segment was cut from the

extremity of the parallelepiped shaped flexural sample, while the second segment was cut from the middle, both of which were then embedded in resin, sanded to a 2000-mesh sandpaper, polished and received a 10 nm gold coating on a Leica EM SCD050 metallizer. They were later taken to SEM microscopy for BSE (backscattered electron imaging) and EDS analysis, with three images of each segment being used to measure the layer thickness. One photo of each of the four samples in the same disk was taken in BSE mode to analyze the cross-section of the original specimen, making possible to measure the layer thickness using the ImageJ software as shown in Figure 5a and to verify the coating chemical composition as shown in Figure 5b. The proportion of HA in the coating was calculated as the division of the Ca content in the coating (weight percentage measured by EDS) by the Ca content of pure calcium phosphate powder analyzed in EDS.

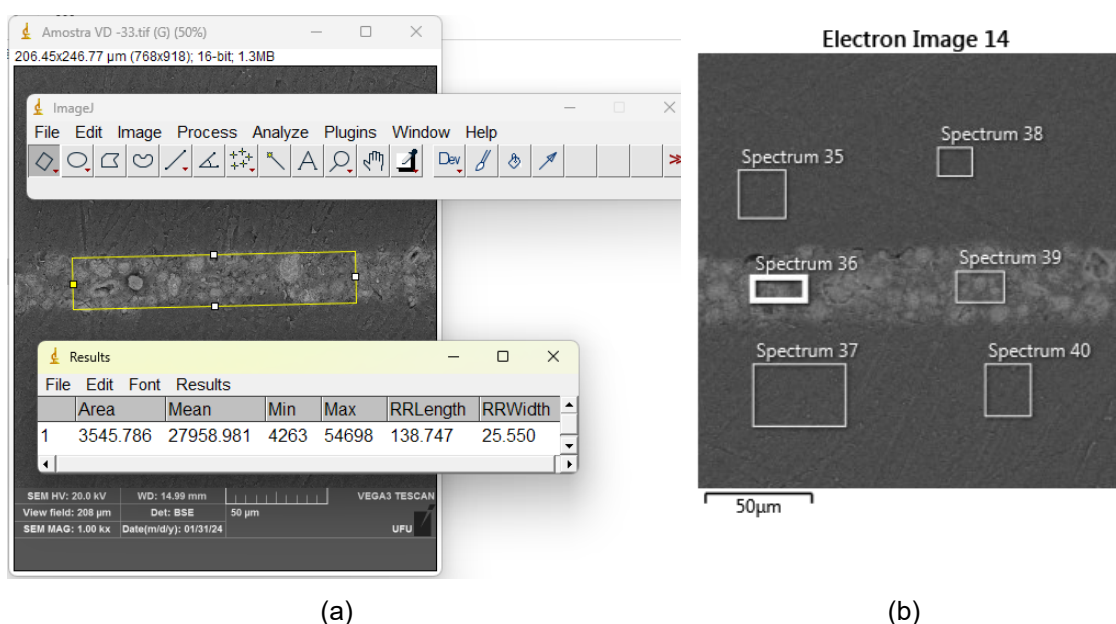


Figure 5. (a) Image illustrating the procedure for measuring the thickness of the layer formed by the adhesion of particulates to a type D sample, measuring 25.550 µm in this case (RRWidth). (b) Different regions of coating (spectrums 36 and 39), embedding resin (spectrums 35 and 38) and substrate (spectrum 37 and 40) chosen for EDS analysis.

Temperature resistance by Heat Deflection Temperature

Heat deflection temperature is defined as the temperature at which a standard test bar deflects a specified distance under a standardized load. It is used to determine heat resistance, as per ASTM D648 (2018), and distinguishes between materials that are capable of sustaining light loads at high temperatures. Since the glass transition temperature and the crystallinity of semicrystalline polymers correlate with the maximum temperature the material can withstand, this type of test can be used to compare the T_g and crystallinity of materials produced under different heating and/or cooling conditions. An electronically controlled oven for ramp heating was built by instrumenting a 10L Britania electric oven (Figure 6a) with a power of 1050 W. The internal oven

temperature was measured by a K-type thermocouple connected to Arduino MAX31855-compatible module. An Arduino Uno microcontroller with an ATmega 328 processor was used as a signal acquisition board for data logging to the computer with CoolTerm 2.0 software. Temperature deflection tests were performed with the samples on specific supports (Figure 6b), heating the oven in an automatically controlled manner at a constant rate of 2 °C/min as required by ASTM D648. To achieve this, the oven was constantly switched on and off by an electronic relay also connected to the Arduino (as shown in Figure 6c), which turned off the power if the actual temperature was above the ideal value at a given time and did the opposite if the actual temperature was lower, creating a closed-loop control system. The heating ramp is also shown in Figure 6d, demonstrating the system's good accuracy. However, a stress of 1.2 MPa was applied to the samples instead of the traditional values recommended by ASTM.

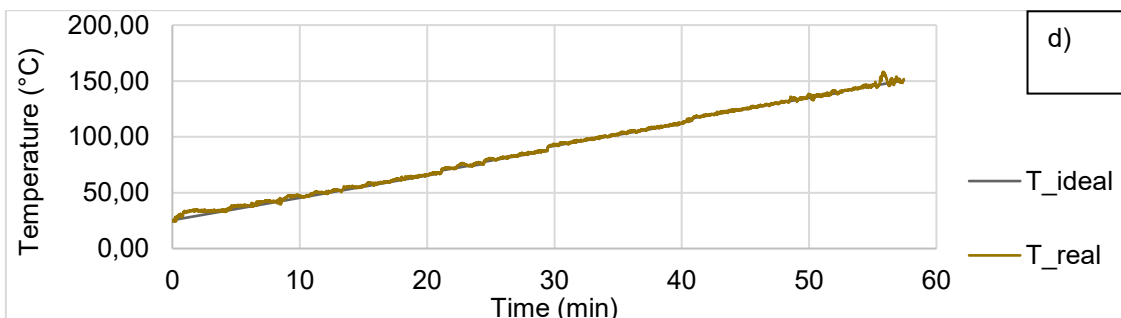
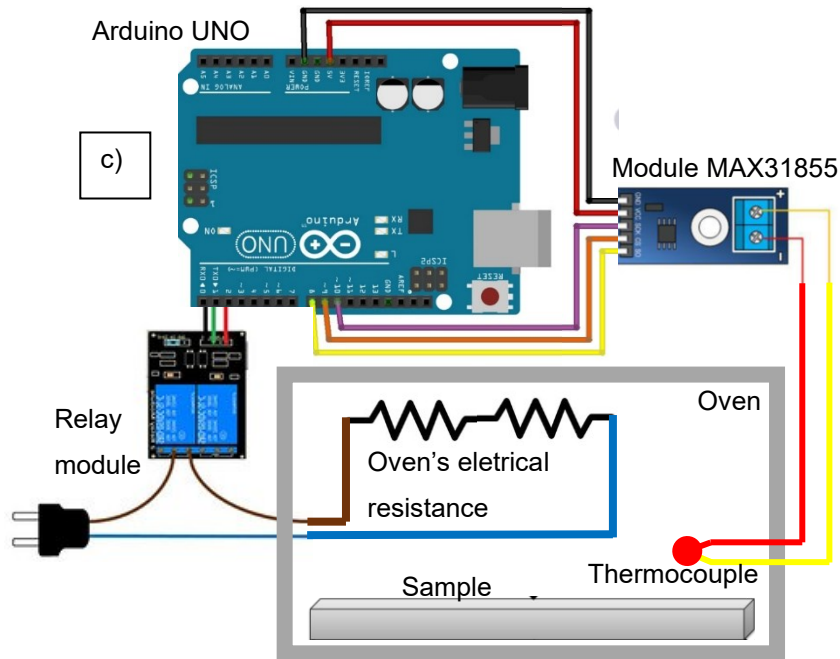
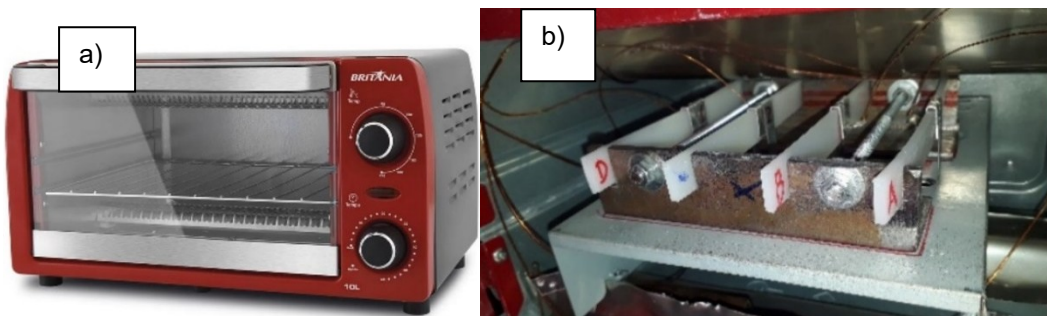


Figure 6. (a) Britania 10 L electric oven. (b) Samples on a support for the heat deflection test. (c) Schematic of the ramp temperature control system, consisting of an Arduino Uno, MAX31855 module with a type K thermocouple, and relay to turn the furnace on/off. (d) Temperature in the furnace measured by thermocouples connected to the Arduino, during the heat deflection tests.

Quantitative coating adhesion

For these tests, 2 samples of each condition of the second DoE were coated in gold for later SEM inspection, and 4 progressive load scratch tests were conducted in each sample. Coating adhesion was quantified following the general requirements of ASTM D7027 (ASTM, 2020) and using an automated microsclerometer adapted from a 3-axis mini CNC machine. For this, 2 load cells were arranged to measure contact forces in the normal (F_n) and tangential (F_t) directions, with a maximum load of 1 kg and 10 kg, resolution of 0.01 g and 0.1 g, and precision of 1 g and 10 g, respectively, according to the manufacturer. Calibration of the load cells and uncertainty measurement was carried in a previous work (da Silva et al., 2023). The system, represented in Figure 7, operates at a maximum acquisition rate of 12 Hz and can generate the force vs. displacement graphs shown in Figure 8a. For the tests, the load was generated when the indenter was forced to advance against the sample 25 mm in X and 0.2 mm in Z directions, simultaneously, with speed of 1 mm/s, following G-code commands input in Candle 1.1.7 software. It is worth noting that although the mini CNC is only capable of controlling the movement of the coordinate axes, for small loads it was observed that there is a linear relationship between normal force and movement of the Z-axis spindle. Thus, when the scratches were made with linearly increasing depth, F_n presented a similar behavior, as can be seen in Figure 8a, with normal loads varying from 10 gf to approximately 180 gf (1,77 N).

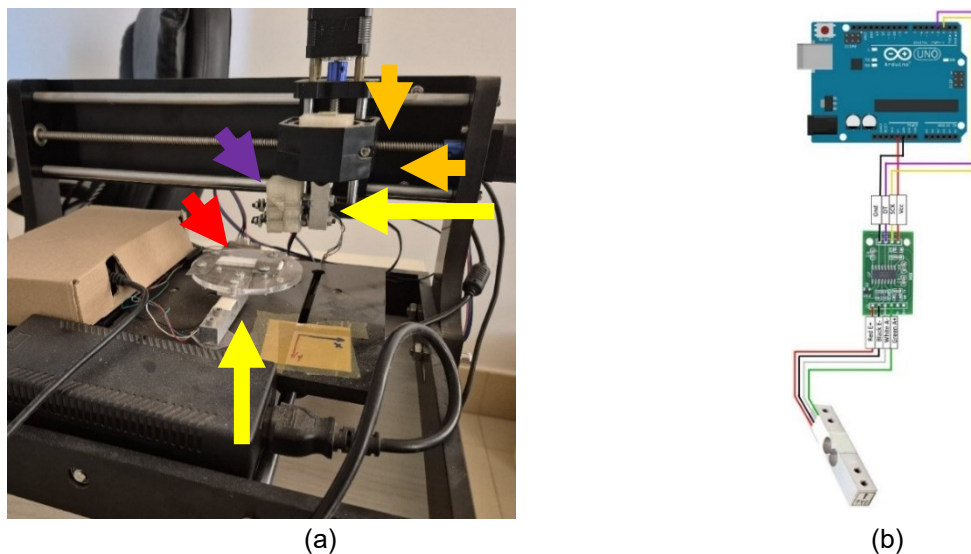


Figure 7. (a) Mini CNC apparatus used for scratch testing, with yellow arrow indicating the load cells for measuring normal and tangential force, orange arrows indicating the X and Z axes, purple arrow indicating indenter holder and red arrow indicating sample (white parallelepiped clamped

to acrylic round plate). (b) Contact force measurement system, with load cell, HX711 module and Arduino.

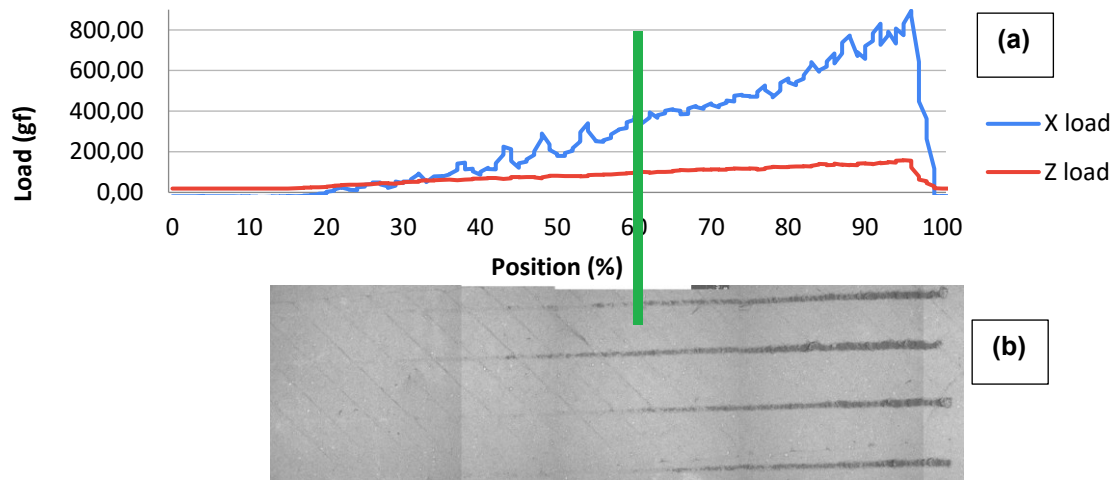


Figure 8. (a) Graph of load x displacement generated by the advance of the indenter against the sample (condition C from second DoE) in X and Z direction simultaneously, for the first scratch. (b) BSE composed image of the 4 scratches made in sample 1 from condition C, with green bar marking the initial failure of the coating and correspondent critical load for the first scratch.

The critical load, defined as the load at which failure of the coating occurs, is determined by verifying the point in the graph that corresponds to the initial failure region indicated by a contrast at the composed SEM images of the scratch, exemplified in Figure 8b. This image was obtained by aligning several BSE images using the SE image as a guide, as demonstrated in Figure 9. The contrast in BSE image means that there are two regions with different chemical composition, and the darker region that appears as the scratch progresses is due to exposure of the polymeric substrate. For this work, the failure of coating was defined not only by the change of contrast but also by a minimum width of 0.1 mm for each scratch and, as recommended by ASTM D7027, a continuous length of at least twice the size of the stylus, as exemplified in Figure 10a. Regarding the indenter, which can be seen in Figure 10b, a small dressing tool with diamond tip was used instead of the 1 mm steel sphere recommended by the standard, to achieve coating failure within loads lower than the capacity of the loadcells. The diamond tip was measured in the SEM to be a square based pyramid with 2.7 mm x 2.7 mm base by 1.12 mm height and edge radius of 125 μm approximately. Based on this, the critical stress for the critical load in Z direction was calculated as the load divided by the square area of 0.1 mm width and 0.1 mm length.

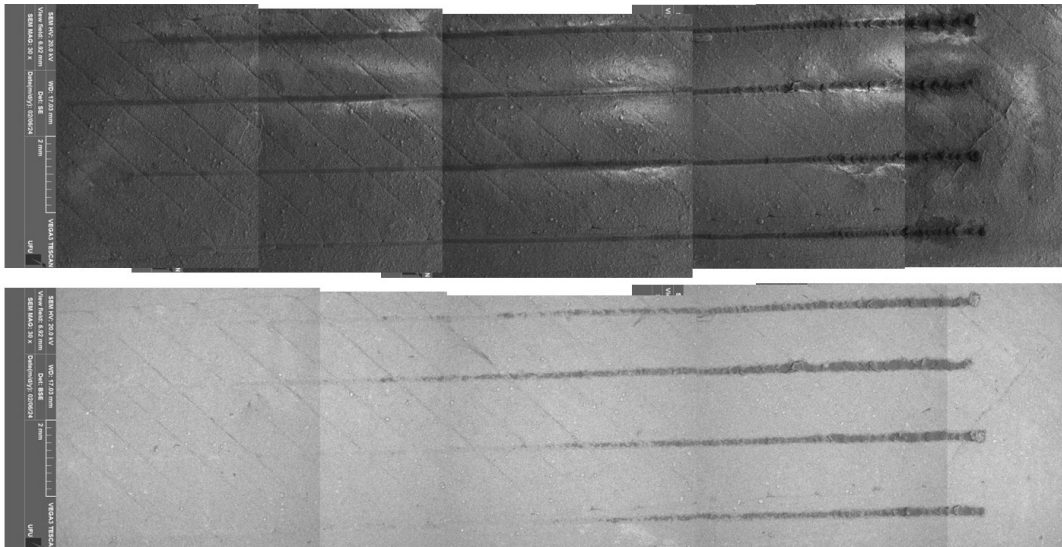


Figure 9. Example of how BSE images were composed for each sample, with alignment guided by SE images. Printing deposition lines can be seen in diagonal direction.

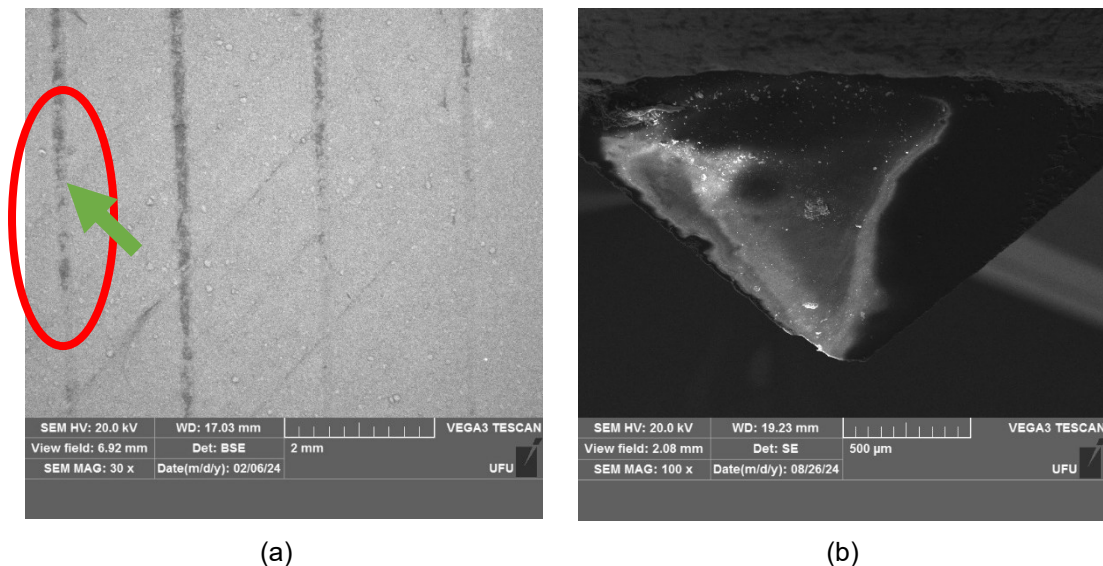


Figure 10. (a) BSE image from condition C (second DoE) with green arrow showing onset of coating failure, defined not only by the change of contrast but also by a minimum width of 0.1 mm for each scratch and, as recommended by ASTM D7027, a continuous length of at least twice the size of the stylus. (b) Indenter tip analyzed in SEM.

Statistical analysis

All experiments regarding mechanical properties (4 point bending, impact and heat deflection temperature tests) and surface characterization (coating layer thickness, coating chemical composition, coating adhesion) were subject to statistical significance analysis by ANOVA using Statistica 11 software, with level of significance of 5 % and 95 % reliability index. The p-values of significant effects were reported, and additionally the standard deviations were shown in the graphs.

RESULTS

Flexural tests

The maximum flexural strength (MFS), modulus of elasticity (E) and flexural elongation (ϵ) results are presented in Figure 11. It is verified that there is a clear difference between samples annealed at 170 ° and 180 °C, with the latter presenting higher MFS and E. Indeed, the powder bed annealing temperature was found to be the most significant factor in ANOVA with $p = 0.000012$ for MFS and $p = 0.000011$ for E. Also, for all conditions, drying after autoclaving improved resistance, with this being the second most significant factor with $p = 0.000249$ for MFS and $p = 0.018770$ for E. Finally, the number of autoclaving cycles was also significant for MFS with $p = 0.018721$ and an increase in maximum stress with 2 cycles instead of 1. Regarding ϵ , the only significant factor was drying process with $p = 0,043066$, which on average increased elongation when carried out after autoclaving.

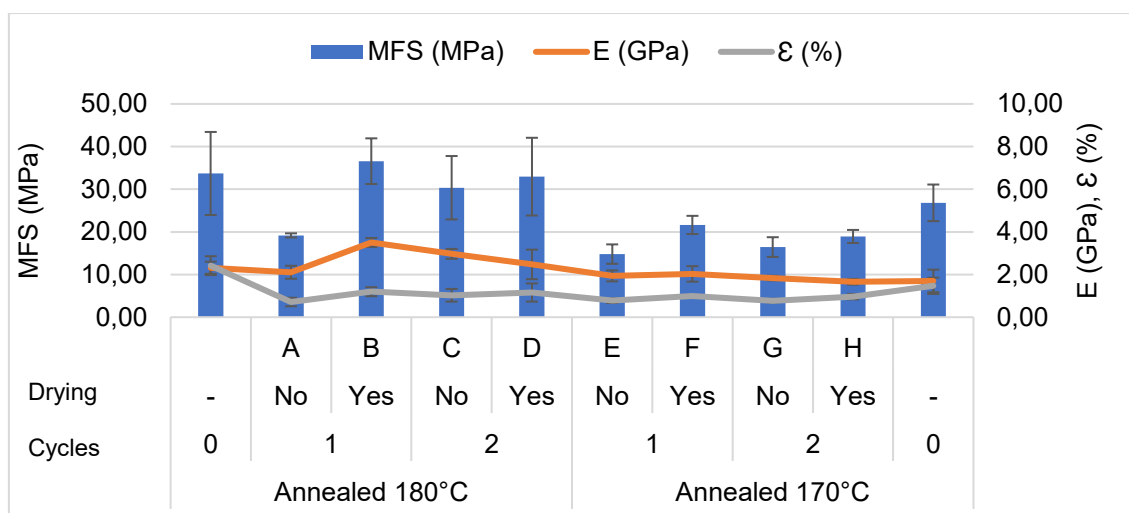


Figure 11. Maximum flexural strength (MFS), flexural modulus of elasticity (E) and maximum deformation (ϵ) for samples before (0) and after (1 or 2) autoclaving cycles.

Although the initial flexural properties before autoclaving (0 cycles) might be the reason for these behaviors, it is likely that changes in PLA chemical composition, sample porosity and/or crystallinity are more preponderant, as explained by Arifvianto et al. (2021), Hart et al. (2018) and Hart et al. (2020), respectively. Considering the temperatures to which PLA was subjected to during annealing (170 °C to 180 °C), autoclave cycles (126 °C to 130 °C) and drying (120 °C), it is conceivable that increases and decreases in mechanical properties come from the types of crystalline structures that are favored with the thermal history of each condition. As explained by Ma et al. (2021), the crystals α and δ are formed between 100 °C to 120 °C, with the former being favored above 120 °C and the latter, considered an unorganized crystal type, favored below 100 °C. Also, β crystals and γ crystals have been created at around 170 °C and 140 °C,

respectively. Therefore, the overall better properties reached on conditions A to D might be due to a higher content of α crystal, while the worse properties from condition E to H might be related to unorganized crystalline forms of PLA. Additionally, this same phenomenon might explain why MFS and E changed with the autoclaving cycles and drying operations, since they all work as some sort of heat treatment for the polymer and cause changes in crystallinity, even though they are meant as a sterilization technique. It is important to highlight that in comparison to the literature for PLA (Mitrović et al., 2024; Mazur et al., 2022) and previous works with the powder bed annealing process (Campos et al., 2025), the values found for MFS at the present work were significantly lower (19 MPa to 37 MPa against about 50 MPa to 100 MPa). This is probably due to humidity in the filament before the powder bed annealing, which hinders the improvements in mechanical properties that usually accompany the annealing process (de Almeida et al., 2023). However, even in this case, the resistance values might still be enough for application in polymeric implants, since the maximum stresses on can be significantly reduced to less than 25 MPa in customized 3D printed designs (Anitha et al., 2015; Al-Tamimi, 2024). This supports the use of powder bed annealing as a manufacturing process that yields parts capable of supporting autoclaving, which is the preferred sterilization method for orthopaedical implants.

Izod impact tests

The results of Izod impact energy are shown in Figure 12, from which is clear that parts annealed at 180 °C again had an advantage, with this factor being the most significant with $p = 0.000001$. The second most significant was the autoclaving cycles, with $p = 0,022622$, and a reduction in impact energy when 2 cycles are used instead of 1. Interestingly, the non-autoclaved samples presented values consistent with the literature (de Almeida et al., 2015), which indicates the thermal input from the powder bed annealing process did not improve the impact resistance of the samples. However, after autoclave cycles, the impact energy increased more than 100 % for some conditions, which means the thermal input was effective in this case.

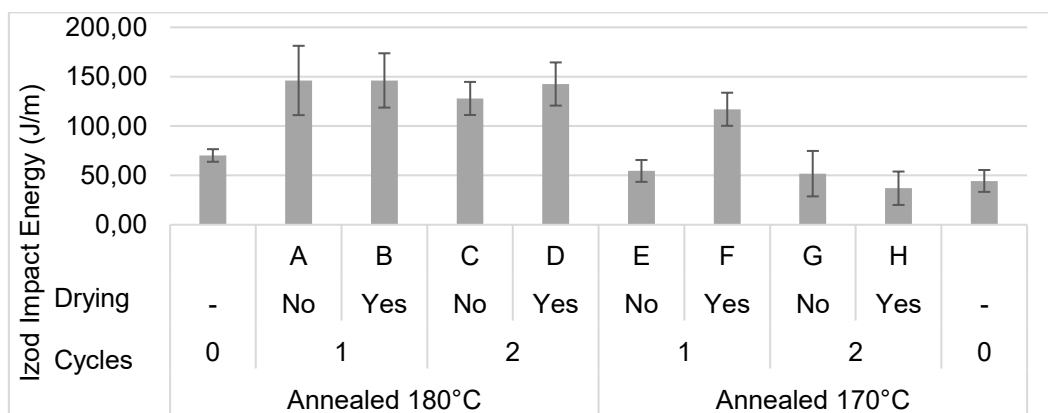


Figure 12. Izod impact energy for samples before (0) and after (1 or 2) autoclaving cycles.

Since the coating is very thin, this can only be explained by the bulk properties of the PLA substrate. Again, as explained by Ma et al. (2021), the unorganized δ crystal structure and a more dispersed amorphous phase are both favored in temperatures close to 120 °C which happens during autoclaving but not during annealing. It is likely that the unorganized form of the crystal together with the highly dispersed amorphous phase both favor impact toughness, which would explain the great improvements in impact energy after autoclaving. Again, this behavior was not so well observed for samples annealed at 170 °C, which further suggests that these samples were tainted by humidity before powder bed annealing, which somehow prevents the beneficial effects of autoclaving into impact resistance. Furthermore, it is important to state that even for these samples, impact values were still enough for most applications of PLA as implant material, since they were leveled with those from injection molding (Wang et al., 2017), which is the standard manufacturing process for current PLA commercial implants. This reinforces the adequateness of autoclaving as a sterilization method for PLA implants with HA coating from the powder bed annealing process, indicating that this manufacturing method is suitable for implant production, once they can be sterilized by the most common technique used for surgical material.

Coating layer thickness and chemical analysis

The hydroxyapatite coating thickness for each condition of the first DoE is presented at Figure 13, from which it is possible to see again a better result from samples annealed at 180 °C, with this being the most significant factor in ANOVA with $p = 0,000000$. Also, the number of cycles ($p = 0,000054$), combination of these two factors ($p = 0,000000$) and combination of number of cycles and drying ($p = 0,000002$) were significant too, for a 95 % confidence interval. Considering that the powder bed annealing produced similar coating thickness in comparison to previous works (Campos et al., 2025), of 28 μm against 33 μm for 170 °C annealing with pure calcium phosphate, these results indicate a poor performance of coatings from this condition when autoclaved, with coating thickness diminishing with cycles. This did not happen for samples produced at 180 °C, which probably means that the later condition yields coatings with better stability that do not peel, degrade or diminish when subjected to autoclaving. Still, although most autoclaving conditions achieved coating thickness that fall short of the desired minimum of 50 μm recommended by Nuswantoro et al. (2024), the values below 30 μm might be beneficial for avoiding coating delamination while maintaining enhanced osseointegration properties (Jaafar et al., 2020). This also contributes to the suitability of powder bed annealing and autoclaving sterilization as methods capable of producing and sterilizing HA coated customized PLA implants.

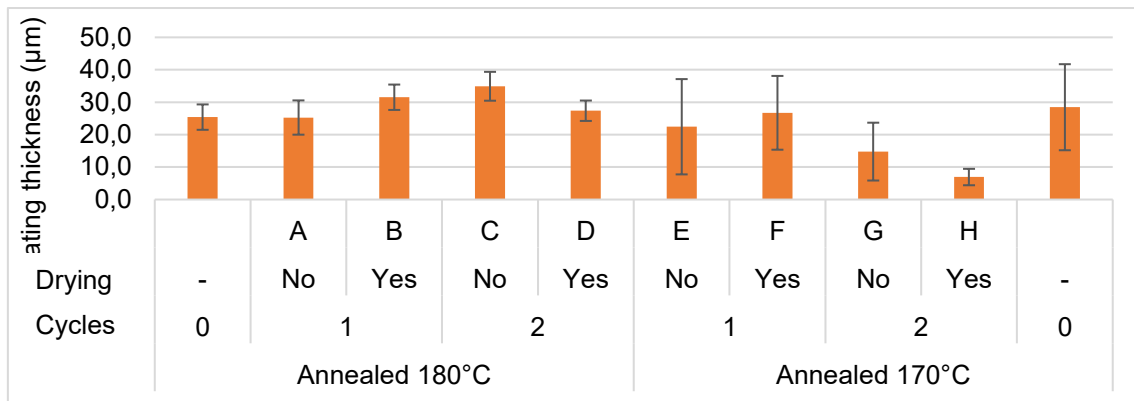


Figure 13. Coating thickness measured for samples before (0) and after (1 or 2) autoclave cycles.

Regarding coating chemical composition, the HA proportion was calculated as the division of Ca element content in each condition divided by the Ca element content in pure HA powder, which was measured to be 31.39 %. The results shown in Figure 14 clearly indicate that the coating is a composite formed by an intertwined mix of hydroxyapatite and PLA from the substrate. This supports the claim that this innovative coating is created from the diffusion of HA submicrometric particles into the viscous PLA substrate during powder bed annealing (Campos et al., 2025), for only such mechanism would be capable of reaching such high HA content into a coating of about 20 µm to 50 µm in depth.

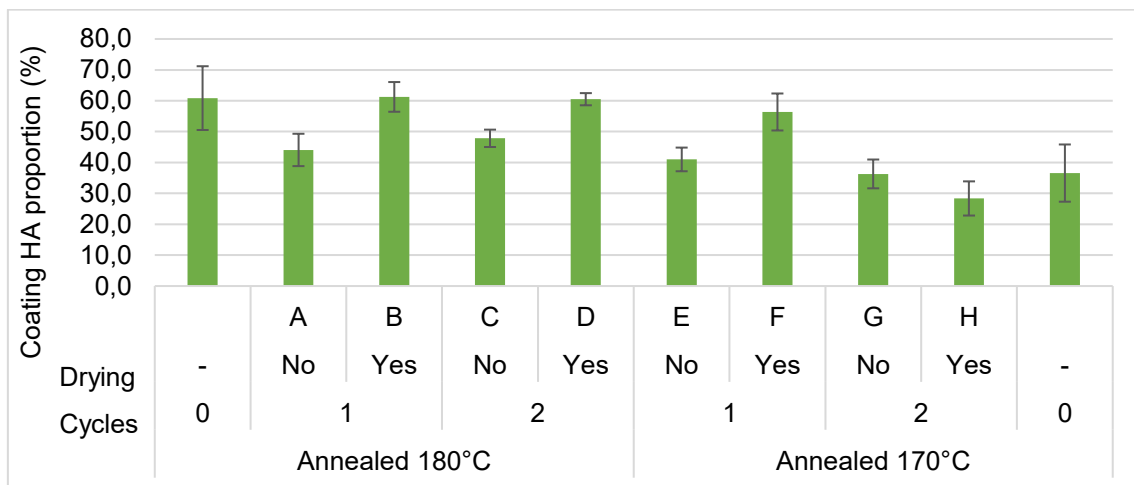


Figure 14. Coating HA proportion measured for samples before (0) and after (1 or 2) autoclaving cycles.

ANOVA reveals that the annealing temperature was again significant ($p = 0.000032$) with a better performance of samples produced at 180 °C, which confirms the suitability of this condition for producing HA coated PLA implants. Drying was the second most significant factor ($p = 0.001319$), improving coating HA proportion. This could signify that autoclaving sterilization is somehow diluting the calcium content in the coating, with the HA proportion returning to the previous levels after drying. Since the water absorption to PLA is very low (Banjo et al., 2022), this behavior might be explained by HA water absorption, which occurs at high levels according

to the water absorption curves reported by Santos et al. (2002) and Sultana and Khan (2013). Therefore, it is likely that during autoclaving the water vapor is also diffused into the PLA coating, reducing the HA proportion in the coating, but returning to the previous levels after drying takes out the water content. SEM images shown in Figure 15 support this phenomenon, where for condition A, with no drying, the coating presents less contrast, which suggests a smaller content of Ca elements that appear brighter in the non-autoclaved sample.

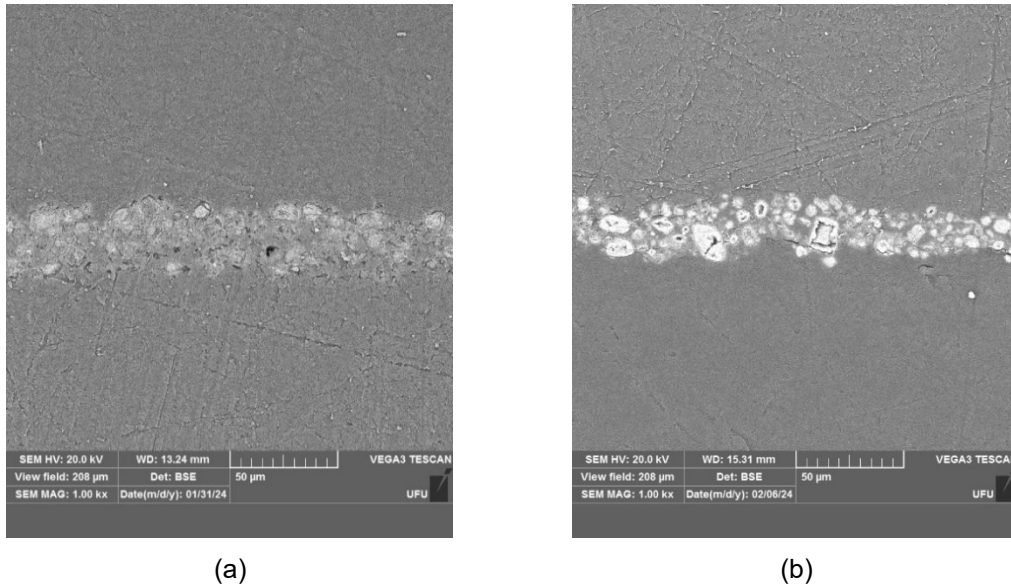


Figure 15. (a) Autoclaved sample from condition A, with no drying, showing less contrast for the coating, suggesting less Ca content. (b) Non-autoclaved sample produced at 180 °C annealing.

Temperature resistance by Heat Deflection Temperature

The Heat Deflection Temperature of samples produced according to the second DoE is shown in Figure 16, from which it becomes evident that for all powder bed annealing conditions there is a significant increase in thermal resistance, from 65 °C for 3D printed pure PLA to at least 150 °C on all conditions. It is likely that this change was due to higher crystallinity of the material, since it has already been shown (Piorkowska and Rutledge, 2013) that more crystals require more heat before the material melts. Interestingly, there seems to be a better performance of samples annealed at 170 °C, which suggest a better stability of the crystals formed at this temperature. Regardless, both levels allow the powder bed annealed PLA parts to withstand autoclaving sterilization conditions, which is crucial for application of this new manufacturing method towards medical devices (Pérez Davila et al., 2021). And this is in accordance with T_{max} being the only significant effect ($p = 0.000000$), once a higher temperature facilitates crystallization (Vaes and Van Puyvelde, 2021). Again, this subsidizes the proposed powder bed annealing not only as a coating manufacturing method, but also as a heat treatment capable of simultaneously improving the substrate mechanical and thermal properties.

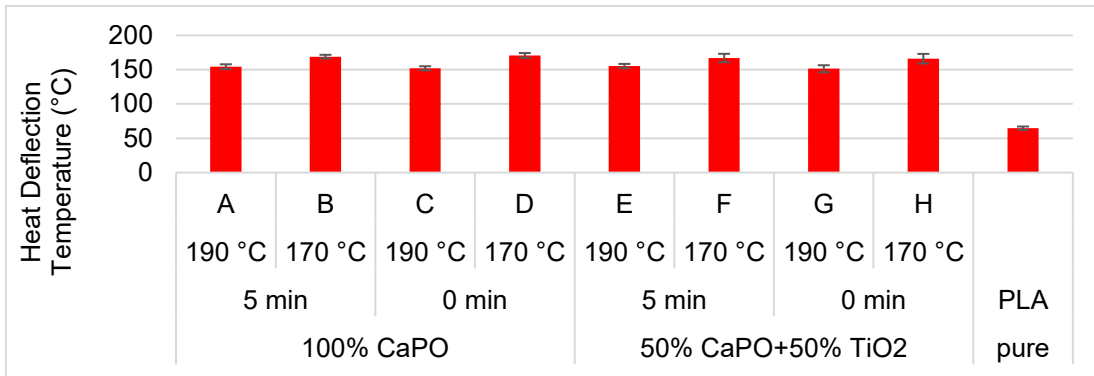


Figure 16. Heat deflection temperature for powder bed annealed samples, showing increase in thermal resistance for all conditions.

Quantitative coating adhesion

Coating adhesion was mensurated as the critical stress in Z direction that caused the indenter to perforate the coating and expose the PLA substrate during the progressive load scratch test, with results presented in Figure 17. ANOVA has shown that the most significant factors were Time at Tmax ($p = 0,000010$), Tmax ($p = 0,000429$), the combination of these factors ($p = 0,000005$) and the combination of particulate and Tmax ($p = 0,000099$). Overall, the higher times and temperatures yielded more resistant coatings for most conditions, which is in line with the higher coating thickness achieved in these conditions on previous works (Campos et al., 2025). Therefore, the most likely factor that affects resistance would be the depth attained by HA particulates through diffusion during annealing. However, the linear correlation between these two variables (thickness and adhesion) is only 0.35, which suggests that there are other factors that affect coating adhesion.

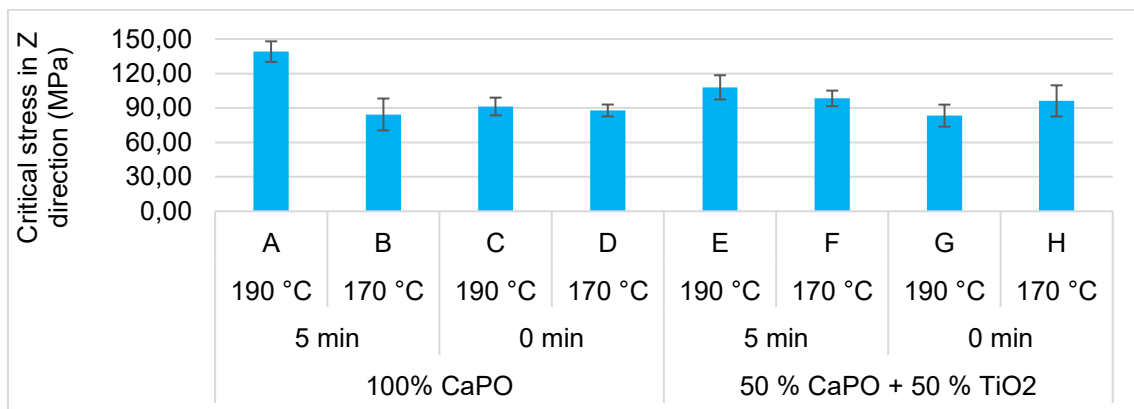
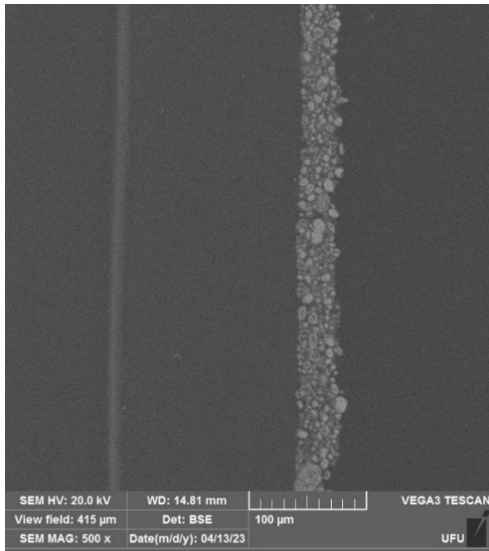


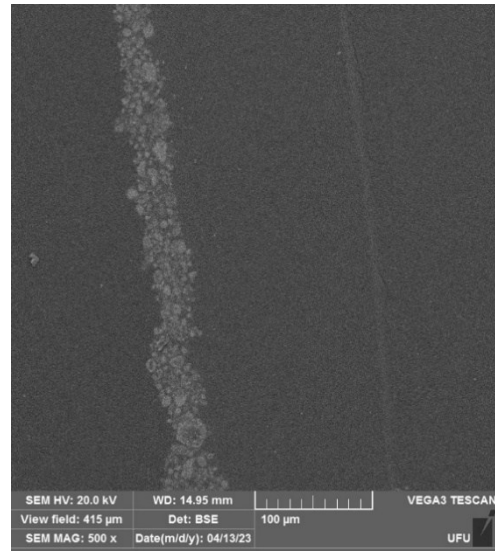
Figure 17. Adhesion resistance of coating in progressive load scratch test performed in samples from the second DoE.

As can be seen in Figure 18, although coatings generated in different conditions might present the same thickness, there can be differences in HA content and coating regularity that might further justify the better performance of some conditions over others. For instance, the HA

coating of condition A, that presented the best adhesion result, shows higher homogeneity (Figure 18a) and higher Ca content (Figure 18c) than the coating of condition C, which seems more irregular (Figure 18b) and has less Ca content (Figure 18d). Therefore, it is probable that coating adhesion depends on coating thickness, HA content and coating regularity altogether. Also, even though a more conservative method was used to calculate critical stress, the results in between 83 MPa to 139 MPa were even higher than those from other works (Sharifi et al., 2018) that ranged from 56 MPa to 99 MPa for PEEK/HA composite coating, and much higher than the 8 MPa to 13 MPa found for electrodeposited HA coating on titanium alloy (Khlifi et al., 2021) and the 11 MPa to 25 MPa found for HA coating on polycarbonate-polyurethane substrate (Barnes et al., 2012). This is in line with the finding that no coating delamination happened during bending stresses of up to 91 MPa on previous samples produced by the powder bed annealing process (Campos et al., 2025). Considering that coating adhesion is equally as important as osseointegration for implant performance (Duan et al., 2012), these results confirm this technique as an interesting coating method for orthopaedical resorbable implants.

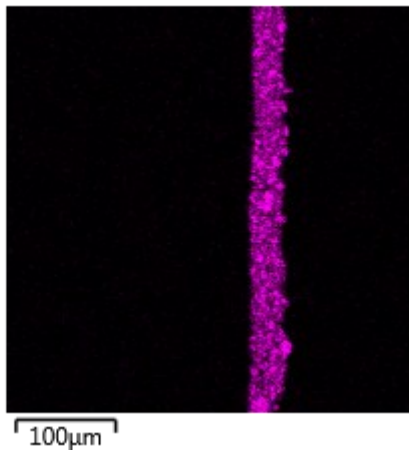


(a)



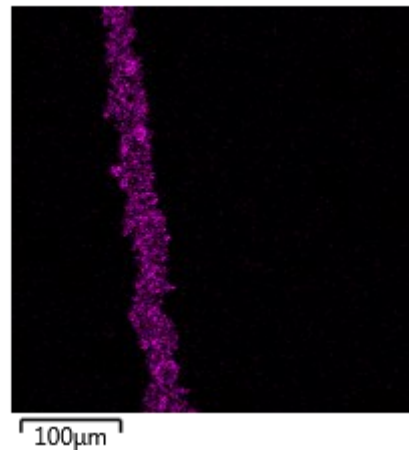
(b)

Ca K α 1



(c)

Ca K α 1



(d)

Figure 18. BSE images from the cross section of samples from (a) condition A and (b) condition C, which appear to present very close coating thickness. EDS maps of calcium content for the same images of (c) condition A and (d) condition C, with the former showing a brighter coating which comes from a higher Ca content.

CONCLUSIONS

This study demonstrated that powder bed annealing is a versatile post-processing route for simultaneously enhancing the thermal resistance, mechanical performance, and surface bioactivity of 3D-printed PLA parts. By embedding hydroxyapatite (HA) and titanium dioxide (TiO₂) particles into the polymer surface during annealing, a uniform composite coating was achieved without resorting to complex or high-cost deposition technologies.

Annealing temperature proved to be the dominant parameter influencing performance. Samples treated at 180 °C exhibited the highest maximum flexural strength (MFS) and modulus of elasticity (E), with statistical significance. MFS ranged from 19 MPa to 37 MPa, which, despite being lower than the 50–100 MPa typically reported for PLA after annealing, remains suitable for many implant geometries designed to operate under stresses below 25 MPa. Drying after autoclaving further improved MFS and E, while two autoclave cycles increased MFS compared to one cycle. In impact resistance, parts annealed at 180 °C again outperformed those processed at 170 °C. Although annealing alone did not enhance Izod impact strength, autoclaving increased it by over 100 % in some conditions, likely due to microstructural rearrangements favoring δ crystal formation and a more dispersed amorphous phase.

Surface coating analysis revealed that annealing at 180 °C yielded thicker and more stable HA layers, with average thicknesses near 28 μ m for 170 °C and higher values at 180 °C. Autoclaving at lower annealing temperatures led to coating loss, whereas coatings from the 180 °C condition retained integrity even after sterilization. Although most coatings were below the 50 μ m target suggested for optimal osseointegration, thinner layers may reduce delamination risks while preserving bioactivity. The HA proportion in coatings reached levels consistent with deep particulate diffusion into the PLA matrix, confirming strong interfacial integration.

Thermal resistance improvements were particularly notable. Heat Deflection Temperature (HDT) increased from ~65 °C in as-printed PLA to \geq 150 °C for all annealed conditions, enabling survival under autoclave sterilization (126–130 °C) without significant distortion. This enhancement is attributed to increased crystallinity induced by annealing. Coating adhesion strength, measured via progressive load scratch testing, reached 83–139 MPa, exceeding values reported for PEEK/HA composites (56–99 MPa) and far surpassing those of electrodeposited HA on titanium alloys (8–13 MPa). The best adhesion occurred at higher T_{max} and longer hold times, correlating with higher HA content and improved coating uniformity.

Overall, the results confirm that powder bed annealing can be tailored to produce custom 3D-printed PLA implants with robust HA-based coatings, autoclave sterilization compatibility, and mechanical properties appropriate for moderate-load-bearing biomedical applications. The

process is low-cost, scalable, and compatible with standard desktop FFF printers and basic laboratory ovens, offering a practical route for decentralized, patient-specific implant manufacturing. Future work should focus on optimizing coating thickness for long-term osseointegration, investigating *in vivo* performance, and expanding the approach to other bioresorbable polymer–ceramic systems.

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CAPÍTULO 13

13. CONCLUSÕES

Os resultados desta tese evidenciam a interdependência entre os parâmetros de impressão 3D, recozimento e revestimento por jateamento na determinação do desempenho mecânico, químico e biológico de substratos poliméricos destinados a implantes ortopédicos. As análises demonstraram que a modificação controlada do histórico térmico e das condições de fabricação do revestimento é capaz de alterar significativamente a integridade estrutural das peças e o potencial de osseointegração, confirmando a hipótese central do trabalho.

No processo de manufatura aditiva por FFF (Fused Filament Fabrication), verificou-se que a espessura de casca é um parâmetro mais importante do que o infill para a resistência da peça, sendo que o aumento do último pode inclusive prejudicar a resistência em alguns casos. A temperatura do bocal e a temperatura da mesa de impressão também exercem influência direta na adesão interlaminar, densidade aparente e grau de cristalinidade do polímero, com melhores resultados mecânicos para condições de impressões mais quentes em peças maciças, e pior resistência para condições mais quentes em peças ocas. No caso da altura de camada, embora camadas mais espessas tendam a deixar maiores vazios, elas aceleraram o processo e diminuem o aporte térmico, o que mostrou-se um benefício para a resistência mecânica.

Após a impressão, o recozimento revelou-se uma etapa estratégica para a melhoria das propriedades estruturais. O aumento controlado da temperatura até valores acima da transição vítrea (T_g) promoveu reorganização molecular e aumento da cristalinidade do PLA. Em temperaturas brandas de 100 °C a 120 °C, o recozimento simples (sem leito de pó) triplicou a resistência ao impacto de 6 kJ/m² para 18 kJ/m², e elevou a temperatura de deflexão térmica de 70 °C para aproximadamente 140 °C. Já no recozimento em leito de pó, em temperaturas de 170 °C a 190 °C, houve elevação da máxima resistência a flexão de em torno de 75 MPa (PLA impresso 3D) para até mais de 90 MPa (amostras recozidas), concomitante a um aumento do módulo de elasticidade (1,84 GPa para até 2,48 GPa) e redução do alongamento (de 4,7 % reduziu para até 3,1 %). Já nesse caso a resistência à deflexão térmica chegou a valores próximos de 170 °C. Supõe-se que a aplicação do recozimento nessas diferentes faixas levou a uma redistribuição das fases amorfas e cristalinas, explicando as variações observadas. Contudo, os resultados não se repetiram em alguns experimentos, sendo as causas mais prováveis a umidade presente nas amostras antes do recozimento e dificuldades com o controle da temperatura e grau de compactação do particulado nos recozimentos.

A integridade estrutural pós-revestimento foi confirmada por microscopia eletrônica de varredura (MEV), na qual observou-se a formação de uma camada compósita homogênea, formada por particulados cerâmicos entremeado por PLA, com espessuras variando de aproximadamente 10 µm a 120 µm, dependendo dos parâmetros de recozimento (tempo e temperatura). O teor de hidroxiapatita variou de 40 % a 60 % em massa, nas regiões do

revestimento analisadas por EDS, a rugosidade superficial teve um Ra de 5 a 8 μm , e o ângulo de molhamento chegou a valores próximos de 20° para algumas condições analisadas, indicando adequabilidade dos revestimentos para aplicação em implantes. Isso foi confirmado em testes de citotoxicidade *in-vitro*, nos quais as amostras revestidas tiveram crescimento celular acima do material controle, após 14 dias, juntamente com indícios de diferenciação celular verificado nas imagens de MEV. O revestimento se mostrou bem aderido ao substrato também, destacando-se do substrato apenas para tensões de contato da ordem de 80 a 140 MPa.

No que se refere ao processo de jateamento intermitente com ar quente e ar comprimido misturado aos particulados cerâmicos, apesar das adaptações realizadas, não houve geração efetiva de um revestimento biocompatível. Embora uma das condições testadas tenha revelado a deposição de uma camada compósita de PLA com HA, de aproximadamente 3 μm , a camada não foi homogênea em toda a peça. Além disso, apesar de em condições mais frias não haver deposição visível de revestimento na superfície, nas condições mais quentes, que poderiam favorecer essa deposição, houve deformação geométrica devido ao calor excessivo. Ainda que processo possa se tornar viável em estudos futuros, há também um problema de complexidade inerente ao controle dos vários parâmetros de jateamento, que requer um sistema mais robusto do que o que foi construído até o momento.

A sinergia e custo-benefício da impressão 3D de polímeros reabsorvíveis e recozimento para deposição de um revestimento bioativo revelou-se um dos principais avanços desta pesquisa. O uso de insumos de baixo custo, a personalização proporcionada pela impressão 3D, e a escalabilidade e biocompatibilidade do revestimento por recozimento são aspectos que reforçam o potencial dessas tecnologias inovadoras para o uso clínico em implantes personalizados.

Em síntese, a tese demonstrou que a otimização conjunta dos parâmetros térmicos e superficiais é o caminho para o desenvolvimento de implantes poliméricos de alto desempenho. A abordagem experimental e analítica adotada permitiu não apenas correlacionar as variáveis de processo com as propriedades finais das peças, mas também propor modelos empíricos de previsão de desempenho baseados em técnicas de otimização multidimensional. Os resultados reforçam a viabilidade de utilizar polímeros como substratos funcionais em substituição parcial a metais em determinadas aplicações ortopédicas, desde que revestidos adequadamente com materiais bioativos.

13.1 CONSIDERAÇÕES FINAIS E TRABALHOS FUTUROS

Os resultados obtidos ao longo desta pesquisa consolidam uma metodologia inovadora de revestimento e modificação térmica de polímeros termoplásticos, abrindo novas perspectivas para a manufatura de implantes ortopédicos personalizados. O conceito de integração entre impressão 3D e recozimento em leito de pó mostrou-se tecnicamente viável e cientificamente promissor, unindo aspectos de engenharia térmica, ciência dos materiais e bioengenharia.

Como principais avanços, destaca-se a comprovação de que a combinação de tratamento térmico e revestimento cerâmico pode simultaneamente melhorar a resistência mecânica do PLA e promover uma superfície bioativa capaz de favorecer a osseointegração. O controle da temperatura e do tempo de recozimento permite ajustar o grau de cristalinidade, reduzindo anisotropias e aumentando a estabilidade dimensional. Paralelamente, o jateamento adaptado introduz uma microtextura compatível com adesão celular, sem causar danos térmicos severos ao substrato.

Entretanto, os resultados também apontam oportunidades de aprimoramento. O primeiro ponto diz respeito ao melhor controle dos parâmetros de recozimento, uma vez que percebeu-se em um dos grupos de experimentos que o ajuste dos parâmetros de entrada para condições otimizadas não elevou as propriedades mecânicas tal como esperado. Sugere-se o uso de um tubo cerâmico para isolar termicamente o trecho do termopar que passa dentro do forno e chega a bandeja, para evitar erros de medição da temperatura do processo, que é um importante parâmetro de controle. Outra necessidade é a de uniformizar a pressão aplicada no leito de pó. Isso deve ser feito combinando uma colocação mais precisa do leito particulado e das amostras, associada a uma pressão mais uniforme na tampa da bandeja (colocando um peso morto, por exemplo).

Outro fator de interesse é o aprofundamento dos ensaios biológicos. Até o momento, os testes foram focados em análises físico-químicas e biocompatibilidade *in vitro*. Recomenda-se a realização de testes com linhagens osteoblásticas (MC3T3-E1, hFOB) e modelos tridimensionais de cultura celular, permitindo avaliar não apenas a viabilidade, mas também a diferenciação e mineralização. Ensaios *in vivo* em modelos animais poderão consolidar a aplicabilidade clínica dos implantes, analisando a taxa de regeneração óssea e a estabilidade mecânica ao longo do tempo.

No campo da modelagem computacional, há grande potencial para ampliar a aplicação de técnicas de otimização multidimensional. A utilização de métodos evolutivos, redes neurais e algoritmos de superfície de resposta pode permitir a previsão de desempenho mecânico e biológico a partir de combinações de parâmetros de impressão e revestimento, reduzindo o número de experimentos necessários e acelerando o desenvolvimento de novos materiais.

Outra perspectiva relevante é a expansão do método para outros polímeros termoplásticos de maior resistência térmica, como PEEK e PEKK, que possuem histórico consolidado em aplicações biomédicas. O mesmo processo de recozimento e jateamento poderá ser adaptado para esses substratos, buscando combinações de camadas híbridas com HA, TiO₂ ou β -TCP. Essa diversificação aumentaria o alcance industrial da metodologia, possibilitando a produção de próteses craniofaciais, intervertebrais ou odontológicas personalizadas.

Finalmente, sugere-se o desenvolvimento de ensaios de durabilidade (como testes de fadiga e tribológicos) à esterilização, fundamentais para a certificação de dispositivos médicos. A avaliação da estabilidade dos revestimentos após exposição a ciclos repetidos de autoclavagem, radiação gama ou óxido de etileno poderá confirmar a robustez dos materiais

frente às exigências clínicas. Em síntese, o conjunto de resultados obtidos oferece uma base sólida para continuidade do trabalho em três frentes principais:

1. Aperfeiçoamento do processo, com maior controle térmico e deposição homogênea;
2. Validação biológica, com ampliação dos testes *in vitro* e *in vivo*;
3. Expansão tecnológica, aplicando os conceitos a novos polímeros e sistemas híbridos.

Essas direções não apenas fortalecem a relevância científica da pesquisa, mas também aproximam o desenvolvimento de biomateriais poliméricos funcionalizados das demandas reais da engenharia clínica, consolidando a integração entre manufatura avançada e biotecnologia aplicada à saúde.