

## Biomaterials' Surface Functionalization by High Frequency Micropatterning Embossing on PEEK Samples

Marco Magro<sup>1,a\*</sup>, Luigino Filice<sup>1,b</sup>, Michele Perrelli<sup>1,c</sup>, Domenico Mundo<sup>1,d</sup>,  
Francesco Moscato<sup>2,e</sup>, Francesco Gagliardi<sup>1,f</sup>

<sup>1</sup>Department of Mechanical, Energetic and Management Engineering, cube 45 C, Ponte P.Bucci, University of Calabria, Rende (CS) 87036 Italy

<sup>2</sup>Center for Medical Physics and Biomedical Engineering, AKH Vienna, Leitsstelle 4L, Währinger Gürtel 18-20, Medical University of Vienna, 1090 Vienna, Austria

<sup>a\*</sup>marco.magro1@gmail.com, <sup>b</sup>luigino.filice@unical.it, <sup>c</sup>michele.perrelli@unical.it

<sup>d</sup>domenico.mundo@unical.it, <sup>e</sup>francesco.moscato@meduniwien.ac.at,

<sup>f</sup>francesco.gagliardi@unical.it,

**Keywords:** PEEK, biocompatibility, surface treatment, embossing, contact angle test, surface free energy.

**Abstract.** PEEK is a thermoplastic polymer widely employed in the orthopedic field for the fabrication of prosthetic devices, owing to a Young's modulus comparable to that of human cortical bone. Surface functionalization through biomaterial micropatterning represents an effective strategy to enhance osteointegration. To this end, an innovative vibration-assisted surface embossing process was applied to PEEK samples. The surface patterning was performed using a square punch with a side length of 0.5 mm, fabricated via CNC milling. The process is enabled by a linear actuator capable of generating controlled vibrations to induce localized heating of the polymer surface. After that, the application of a post-load is required for the embossing stage. This system allows frequency tuning in the range of 1–4 kHz. Finally, the patterned surfaces were sonicated through an ultrasound cleaner and characterized through contact angle measurements and white-light interferometry, confirming the feasibility of the process and demonstrating an increase in both the polar component of the surface free energy and the hydrophilicity compared with merely polished specimens. Enhancing the polar component of surface free energy is an effective and low-cost strategy to improve biomaterial biocompatibility, confirming the relevance of the proposed surface modifications. Slightly hydrophilic surfaces promote preferential osteoblast adhesion and stable cytoskeletal organization, demonstrating the complementary roles of surface topography in shaping cellular responses.

### Introduction

Over the past decades, polymeric biomaterials have gained increasing relevance in bioengineering, tissue engineering, and implantable medical devices due to their tunable chemical composition, adaptable mechanical properties, and processing versatility. Their structural flexibility enables modulation of elasticity, rigidity, degradation rate, porosity, and surface chemistry, making them suitable for a broad range of biomedical applications [1].

Both natural and synthetic polymers are widely employed for scaffolds, membranes, coatings, and implantable devices because of their adaptability and compatibility with surface modification strategies. However, the implantation of any biomaterial inevitably triggers an inflammatory and immunological response, and the long-term clinical performance strongly depends on the nature of the biomaterial–tissue interface [2]. Suboptimal surface–tissue interactions may lead to fibrous encapsulation, functional isolation of the implant, and eventual clinical failure, sometimes requiring revision surgery to prevent acute inflammatory reactions or tissue necrosis [3].

Since the first biological events occur at the biomaterial surface, surface properties play a decisive role in determining host response. Immediately after implantation, rapid adsorption of water molecules and proteins leads to the formation of a conditioning layer that mediates subsequent cellular interactions and immune recognition [4]. Therefore, even subtle changes in surface chemistry or

morphology can significantly affect protein adsorption, cell adhesion, proliferation, and differentiation. Biocompatibility thus extends beyond the absence of cytotoxicity and includes the ability to positively interact with cells and biological fluids while ensuring long-term mechanical and functional stability [5].

Surface integrity, chemical composition, hydrophilicity, and topography are critical parameters influencing cellular behavior. Surface characteristics regulate protein adsorption and integrin-mediated signaling pathways, thereby affecting cytoskeletal organization and intercellular communication [6]. For this reason, surface engineering has become a central strategy in the development of next-generation biomedical materials.

Among the approaches proposed to tailor biomaterial surfaces, chemical functionalization, bioactive coatings, and micro-/nano-topographical modification are widely investigated [7]. Surface micropatterning has attracted considerable interest because it enables control over cell morphology, alignment, and adhesion through purely physical cues. Micro- and nano-patterns can influence extracellular organization, cytoskeletal tension, and lineage-specific responses without altering the bulk properties of the material [8].

Within this context, polyetheretherketone (PEEK) represents a highly attractive polymer for orthopedic and dental applications due to its excellent mechanical performance and a Young's modulus (8.3 GPa) close to that of human cortical bone (10–20 GPa) [9]. Despite its favorable mechanical and thermal properties, PEEK exhibits an intrinsically bioinert and hydrophobic surface, which limits protein adsorption and cell adhesion. Consequently, surface modification—either chemical or mechanical—is required to enhance immune and tissue interactions [10,11]. In the absence of surface functionalization, PEEK may demonstrate limited capacity to promote cell adhesion and ingrowth [12].

In this framework, vibration-assisted and thermomechanical surface modification techniques offer promising alternatives to conventional chemical treatments. The methodological approach considered here is based on a vibration-assisted surface micropatterning process aimed at generating controlled micrometric features while preserving the bulk structural integrity of PEEK. The process relies on localized heating induced by high-frequency vibrations applied perpendicularly to the polymer surface (1–4 kHz) through a microstructured mold connected to a linear actuator. The oscillating matrix promotes thermomechanical softening at the interface, enabling the imprinting of well-defined surface patterns without extensive thermal exposure of the entire component [13,14].

Other advanced techniques, such as two-photon lithography, have demonstrated the capability to fabricate highly precise microstructured PEEK surfaces with improved cell culture outcomes [15]. However, despite their high resolution, these methods are often limited by low processing rates, high equipment costs, and scalability constraints, which restrict their broader industrial adoption. These limitations highlight the need for cost-effective, scalable, and mechanically simple approaches for controlled surface pattern generation.

Surface wettability plays a complementary role in regulating protein adsorption and cell adhesion [16]. Surface topography directly affects wetting behavior, influencing how bone cells interact with microstructured textures. Slightly hydrophilic surfaces have been shown to favor adhesion and spreading of human mesenchymal stem cells (hMSCs), promoting stable focal adhesions and organized cytoskeletal structures [17].

Enhancing the polar contribution to surface free energy facilitates favorable protein conformations and modulates ligand–receptor interactions involved in osteogenic differentiation pathways [18]. Cells exposed to highly polar surfaces exhibit improved adhesion and spreading compared to those on apolar substrates, leading to enhanced osteogenic responses [19]. Consequently, increasing surface polarity represents an effective strategy for improving the biocompatibility of polymeric biomaterials.

Considering the current state of the art, the present study introduces an innovative vibration-assisted thermomechanical micropatterning process for PEEK surface optimization. Unlike conventional chemical functionalization or high-cost lithographic techniques, the proposed method employs perpendicular high-frequency oscillations (1–4 kHz) transmitted through a patterned matrix to induce localized interfacial softening and imprint controlled surface geometries. The primary

objective is to generate reproducible micro-patterns capable of enhancing cell adhesion and proliferation while preserving the bulk mechanical properties of PEEK. The process is designed to be cost-effective, mechanically simple, and potentially scalable, thus addressing current limitations in PEEK surface functionalization technologies and positioning vibration-assisted embossing as a promising alternative for next-generation biomedical implants.

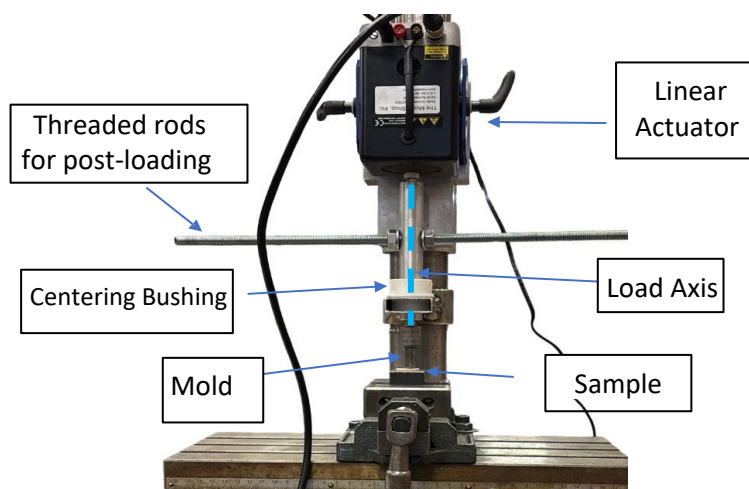
## Materials and Method

PEEK specimens were cut from a 1 m long bar with a diameter of 15 mm, resulting in samples with a height of 5 [mm]. Subsequently, the specimens were polished using an automatic lapping machine (Struers Tegramin 25) following a customized procedure adapted from a protocol reported in the literature [20]. Specifically, the polishing sequence, detailed in Table 1, involved the use of SiC abrasive papers and Struers diamond polishing cloths. Using this approach, a surface roughness Ra of 0.2  $\mu\text{m}$  was achieved, as measured by a profilometer.

**Table 1.** Polishing parameters.

| Polishing Cloth | Lubricant                        | Polishing Time [min] | Applied Load [N] |
|-----------------|----------------------------------|----------------------|------------------|
| SiC foil – P500 | Water                            | 0:15                 | 20               |
| SiC foil – P800 | Water                            | 0:30                 | 20               |
| MD - Largo      | DiaPro Largo 9 [ $\mu\text{m}$ ] | 1:10                 | 15               |

The experimental setup was assembled on a supporting structure composed of a cylindrical frame and an X-axis vise, enabling micrometric positioning of the sample and precise alignment of the patterned mold at the desired location. A linear actuator (SmartShaker model K2007E01, The Modal Shop) was mounted onto the frame, and an aluminum shaft rigidly connected to the linear actuator oscillates along the load axis, transmitting vibrations to the sample through the mold fixed at its end. To improve patterning accuracy and prevent lateral misalignment, a custom-made centering bushing was designed to constrain the system to a single degree of freedom, namely translation along the load axis, thereby ensuring perpendicular contact between the mold and the PEEK sample surface. A function generator supplied a harmonic input signal to the linear actuator, allowing precise control of the excitation frequency within the 1–4 kHz range. After the vibration-assisted phase, a static post-load was applied along the same load axis to complete the embossing stage and ensure full replication of the mold geometry onto the PEEK sample surface, with calibrated masses positioned on threaded rods to generate the required forging load. The complete setup is shown in Fig. 1.



**Fig. 1.** Experimental setup for vibration-assisted surface embossing, including the linear actuator, patterned mold, and post-loading system. The actuator applies a harmonic oscillating load driven by a function generator, and the mold, thread-connected to it, transfers the vibration to imprint the micro-pattern onto the PEEK surface. The loading axis is indicated by the blue dashed line. After the vibration phase, a threaded rod is used to apply calibrated weights for the final forging step.

To obtain the desired surface pattern with a depth of a few micrometers, it was necessary to scale the processes adopted in those studies [13,14]. This requirement arises from the fact that conventional embossing equipment was not employed; instead, relatively low applied loads on the order of several tens of newtons and excitation frequencies well below the typical 28 kHz were used. Consequently, the overall cost of the experimental setup is significantly lower than that of the systems reported in the literature, at the expense of requiring the design and fabrication of a customized mold to maximize process effectiveness. Specifically, tests were performed by varying the frequency in the range of 1–4 kHz and the applied mass during the post-loading phase in the range of 2–6 kg. The configurations tested are described in Table 2.

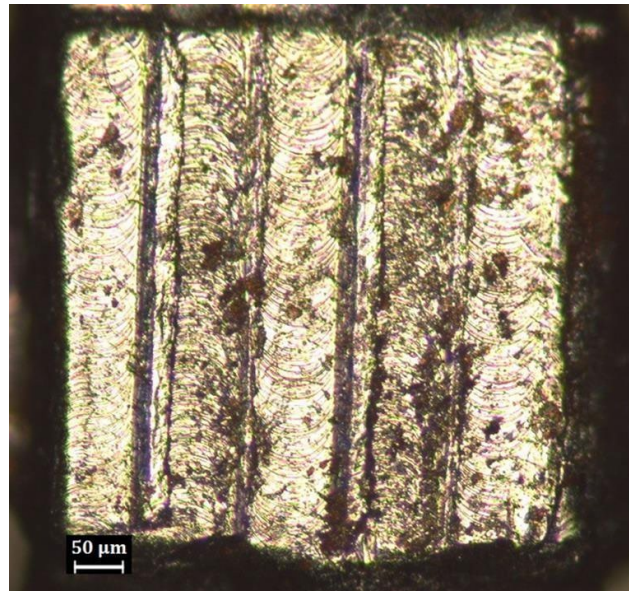
**Table 2.** Process parameters adopted for the two tested configurations.

| Configurations | Frequency [Hz] | Post-load [kg] |
|----------------|----------------|----------------|
| a              | 1000           | 2              |
| b              | 4000           | 2              |
| c              | 1000           | 6              |
| d              | 4000           | 6              |

Steel was selected as the material for mold fabrication, as it provides an optimal combination of machinability and mechanical strength, along with good thermal conductivity. Furthermore, steel exhibits the hardness required to effectively imprint and scratch the surface of the PEEK substrate.

The fabrication of the square mold with a side length of 0.5 mm was carried out using a conical engraving milling tool with a diameter of 0.05 mm, supplied by Meusburger (model VHZ 15136). The machining operation was performed on a CNC milling machine (Mazak Vertical Center NEXUS 420A), starting from a high-strength steel bar with a diameter of 15 mm.

At the end of the machining process, the mold was analyzed using an optical microscope (LEICA DM 4000), which confirmed that the desired geometry had been successfully achieved. Each rectangular protrusion intended to imprint its shape onto the PEEK surface exhibits a length of 0.5 mm and a width of 0.05 mm, resulting in a total contact area of 0.125 mm<sup>2</sup>. The mold can be observed in Fig. 2.



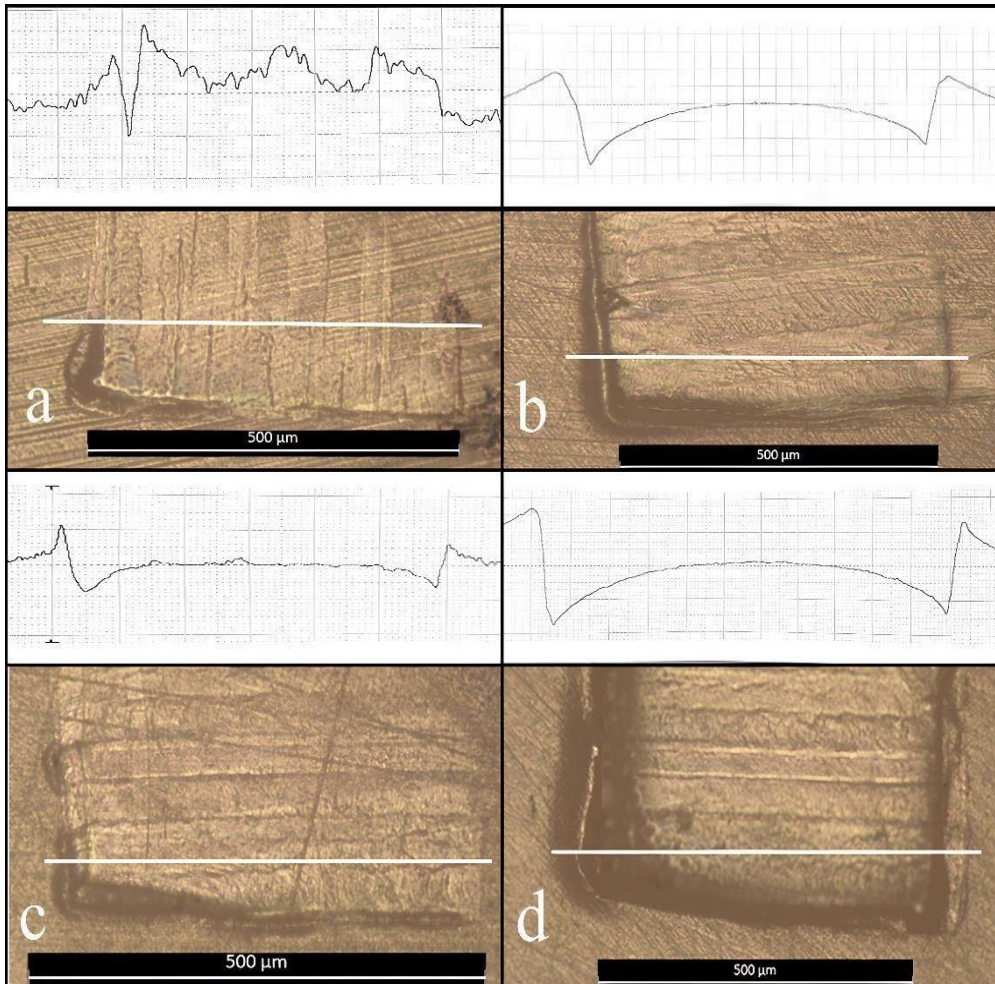
**Fig. 2.** Optical microscopy image of the fabricated mold.

The measurements of contact angle were carried out using a KRÜSS Drop Shape Analyzer and deionized water was the reference liquid. The sessile drop method was used. The surface pattern employed for contact angle testing was produced under a process configuration with an excitation frequency of 4000 Hz and an applied mass of 6 kg.

## Results

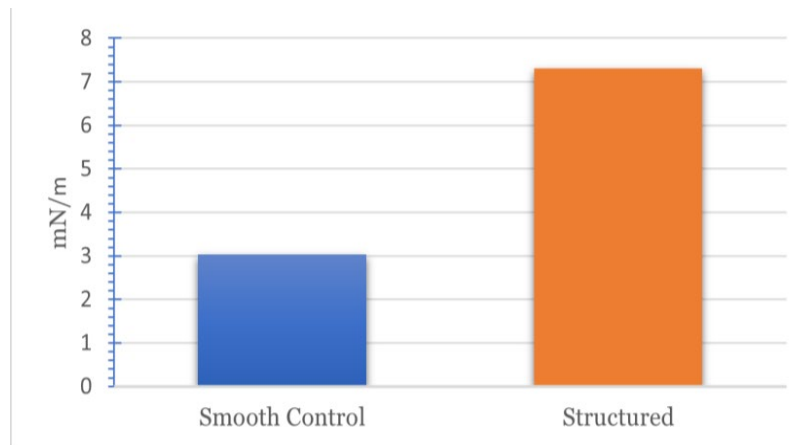
The feasibility of the process was confirmed through the analysis performed on the samples after the surface micropatterning operation. Fig. 3 displays the patterns resulting from the different excitation frequency (i.e., 1 and 4 kHz) and the applied mass during the post-loading phase (i.e., 2 and 6 kg). Subsequently, the surface of each patterned specimen was characterized by contact angle measurements and compared with those of polished control samples. The results indicate that patterned surfaces exhibit a lower contact angle compared with the polished control surfaces. Specifically, the optimized patterned surface shows a contact angle of  $67.3^\circ (\pm 2.60^\circ)$ , whereas the polished control group presents a higher value of  $78.76^\circ (\pm 3.20^\circ)$ . This demonstrates that the optimized surface is more hydrophilic. These values are reported as the grand means of contact angles, calculated from five measurements per specimen across five specimens for each surface condition (polished and patterned). The total surface free energy was found to be comparable between the patterned specimens and the polished control samples, indicating that the applied surface modification did not significantly alter the overall energetic balance of the material.

However, a marked difference was observed in the polar component of the surface free energy. In particular, the patterned surfaces exhibited a polar component more than twice that of the control group, with values of  $7.3 (\pm 1.19)$  mN/m compared to  $3.03 (\pm 1.25)$  mN/m for the polished specimens.



**Fig. 3.** Optical microscopy images of micropatterned PEEK surfaces and corresponding profilometer (Mitutoyo SJ-410) scans along the white line. Pattern definition increases with actuator frequency (a–b), while imprint depth increases with post-loading mass (c–d). The maximum imprint depth, expressed as  $Ry,max$ , was  $2.755 \mu\text{m}$  (a),  $5.57 \mu\text{m}$  (b),  $8.64 \mu\text{m}$  (c), and  $25.39 \mu\text{m}$  (d). Letters correspond to the process configurations in Table.

In Fig. 4 the graph of the polar component of SFE is shown. The process parameters used are 4000 Hz and 6 kg of post-load.



**Fig. 4.** Polar component of the Surface Free Energy of structured PEEK samples, patterned with 4000 Hz and 6 kg of post-load (configuration d in Table 2), compared to the control group.

### Discussion

The results obtained verified both the feasibility and the effectiveness of the proposed vibration-assisted micropatterning process for surface optimization of PEEK substrates. The process enabled the generation of highly accurate micrometric surface structuring while minimizing thermal effects on the polymer material. This represents a significant advantage over conventional thermal or laser-based surface structuring techniques, particularly for materials such as PEEK, which exhibit reduced chemical stability at elevated temperatures. Importantly, the achieved imprint depths ranged from a minimum of 2.755  $\mu\text{m}$  to a maximum of 25.32  $\mu\text{m}$ . This increased depth capability is considered beneficial, as it demonstrates that by properly tuning the process parameters, a wide range of surface pattern depths can be deliberately achieved.

The results of the surface wettability analyses revealed a clear reduction in the value of the contact angle due to the influence of the topography introduced in the form of micropatterns on the polished control samples. This effect indicates a certain increase in the hydrophilicity of the surface. The increase in hydrophilicity has a biological significance mainly due to the known possibility of greater cell affinity [16]. The increase in hydrophilicity implies that the proposed surface treatment might influence the surface to become more biocompatible. Despite having comparable overall surface free energy between the patterned and polished groups, there was a marked increase in the polar component of the surface free energy for micropatterned samples, reflecting values greater than twice of the control. This observation points to an elevated surface affinity for the adsorption of polar biomolecules, including proteins and ligands, playing an intrinsic mediator or facilitating role in relating to immune cells post-implantation based on interaction with implanted materials. These protein interactions have been well recognized for playing critical early-stage roles in modulating biologically-active responses [18].

It is also significant to note that the range of attained values for the contact angle, close to  $60^\circ$ , is reported in the literature as the optimal range for hMSCs [21]. In fact, it is reported to be associated with improved cell adhesion, spreading, and osteogenic differentiation. This implies that the proposed method for vibration-assisted micropatterning could also be useful in the improvement of osteointegration and osteoblastic differentiation properties on PEEK surfaces. In general, the results indicate that vibration-assisted surface micropatterning could be considered a promising method with low impact for the modulation of the bioactive properties of PEEK-based devices without interfering with the material properties.

## Conclusion

This work successfully demonstrates that vibration-assisted micropatterning is an effective and low-impact technique for enhancing the surface properties of PEEK, a key orthopedic biomaterial. The process precisely imprints micro-scale patterns, significantly increasing surface hydrophilicity, and, most importantly, the polar component of surface free energy. These modifications create a more bioactive interface, optimized for the preferential adsorption of proteins and enhanced adhesion, spreading, and creates surface conditions known to promote differentiation.

By improving these critical early-stage biological interactions without altering the bulk material's properties, this scalable and cost-effective surface functionalization strategy presents a highly promising way for boosting the osteointegration and long-term clinical success of PEEK-based implants.

## References

- [1] O. Mozgova, O. Chernyayeva, A. Sroka-Bartnicka, P. Pieta, R. Nowakowski, S. Pieta, Physicochemical characterization of biodegradable polymers for biomedical applications: Insights from XPS, DRIFT, and AFM techniques, *J. Polym. Environ.* 33 (2025) 3477–3511.
- [2] M. Drobot, S. Ursache, M. Aflori, Surface functionalities of polymers for biomaterial applications, *Polymers* 14 (2022) 2307.
- [3] N. Kalashnikov, J. Barralet, J. Vorstenbosch, Implantable medical devices, biomaterials, and the foreign body response: a surgical perspective, *J. Biomed. Mater. Res. A* 113 (2025) e37983.
- [4] C.J. Wilson, R.E. Clegg, D.I. Leavesley, M.J. Percy, Mediation of biomaterial–cell interactions by adsorbed proteins: a review, *Tissue Eng.* 11 (2005) 1–18.
- [5] M. Rahmati, E.A. Silva, J.E. Reseland, C.A. Heyward, H.J. Haugen, Biological responses to physicochemical properties of biomaterial surfaces, *Chem. Soc. Rev.* 49 (2020) 5178–5224.
- [6] J. Wei, T. Igarashi, N. Okumori, T. Maetani, B. Liu, et al., Influence of surface wettability on competitive protein adsorption and initial attachment of osteoblasts, *Biomed. Mater.* 4 (2009) 045002.
- [7] F. Rossi, M. Van Griensven, Polymer functionalization as a powerful tool to improve scaffold performances, *Tissue Eng. Part A* 20 (2014) 2043–2051.
- [8] Y. Ito, Surface micropatterning to regulate cell functions, *Biomaterials* 20 (1999) 2333–2342.
- [9] R. Ma, T. Tang, Current strategies to improve the bioactivity of PEEK, *Int. J. Mol. Sci.* 15 (2014) 5426–5445.
- [10] B. Pidhatika, V.T. Widyaya, P.C. Nalam, Y.A. Swasono, R. Ardhani, Surface modifications of high-performance polymer polyetheretherketone (PEEK) to improve its biological performance in dentistry, *Polymers* 14 (2022) 5526.
- [11] W. Zheng, D. Wu, Y. Zhang, Y. Luo, L. Yang, X. Xu, et al., Multifunctional modifications of polyetheretherketone implants for bone repair: a comprehensive review, *Biomater. Adv.* 154 (2023) 213607.
- [12] Y. Chen, Z. Chen, K. Lei, J. Ding, L. Yu, Surface modification of polyetheretherketone for boosted osseointegration: a review, *Biomater. Adv.* (2023).
- [13] H.J. Lee, K. Park, Development of composite micro-patterns on polymer film using repetitive ultrasonic imprinting, *Int. J. Precis. Eng. Manuf. Green Technol.* 1 (2014) 341–345.
- [14] J. Kosloh, J. Sackmann, W.K. Schomburg, Ultrasonic fabrication of microfluidic channels from polyether ether ketone (PEEK), *Microsyst. Technol.* 23 (2017) 5505–5513.

- 
- [15] M. Vostatek, E. Verin, M. Tamm, M. Rothbauer, S. Toegel, F. Moscato, Bone-mimetic osteon microtopographies on poly- $\epsilon$ -caprolactone enhance the osteogenic potential of human mesenchymal stem cells, *Macromol. Biosci.* 25 (2025) 2400311.
- [16] R.A. Gittens, L. Scheideler, F. Rupp, S.L. Hyzy, J. Geis-Gerstorfer, Z. Schwartz, et al., A review on the wettability of dental implant surfaces II: biological and clinical aspects, *Acta Biomater.* 10 (2014) 2907–2918.
- [17] A.B. Faia-Torres, S. Guimond-Lischer, M. Rottmar, M. Charnley, T. Goren, K. Maniura-Weber, et al., Differential regulation of osteogenic differentiation of stem cells on surface roughness gradients, *Biomaterials* 35 (2014) 9023–9032.
- [18] V.M. Villapun Puzas, L.N. Carter, C. Schröder, P.E. Colavita, D.A. Hoey, M.A. Webber, et al., Surface free energy dominates the biological interactions of postprocessed additively manufactured Ti-6Al-4V, *ACS Biomater. Sci. Eng.* 8 (2022) 4311–4326.
- [19] F. Awaja, E. Carletti, W. Bonani, G. Speranza, Vinculin focal adhesion of osteoblast-like cells on PEEK coated with ultra-thin polymer nanofilms, *J. Appl. Polym. Sci.* 132 (2015) 42181.
- [20] S. Cinel Şahin, H.L. Sağesen, Effects of polishing protocols on the surface roughness and color stability of polyetheretherketone (PEEK), *Eur. Oral Res.* (2023).
- [21] L. Hao, H. Yang, C. Du, X. Fu, N. Zhao, S. Xu, et al., Directing the fate of human and mouse mesenchymal stem cells by hydroxyl–methyl mixed self-assembled monolayers with varying wettability, *J. Mater. Chem. B* 2 (2014) 4794–4801.