Additive Manufacturing and Mechanical Characterisation of COC/TiO_2/CNT Composite Filaments for 3D-Printed Static Mixers

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Abstract

Cyclic olefin copolymer (COC)-based composite filaments containing TiO_2 and carbon nanotubes (CNTs) were developed for fused filament fabrication (FFF) of functional static mixer structures. The influence of filler composition (1.5–3 wt% TiO_2 and 0–0.5 wt% CNTs) on filament processability, mechanical performance, and printability was systematically evaluated. Composite filaments were produced via twin-screw melt compounding and extruded to a diameter of 1.75 mm, followed by FFF of tensile specimens and static mixers. Mechanical properties of the printed specimens were determined according to ISO 527-2:2025. Additionally, tensile work to fracture was obtained from the tensile testing software as a supplementary metric representing the mechanical work recorded up to specimen fracture. TiO_2 addition had minimal impact on tensile strength and printability, whereas CNT incorporation progressively reduced tensile strength (by up to 68 % relative to the corresponding TiO_2-only formulation), elongation, and tensile work to fracture. All formulations exhibited stable extrusion, uniform filament formation, and defect-free printing without warping or clogging. Young's modulus ranged from 450 to 870 MPa. The study demonstrates that COC/TiO_2/CNT hybrid systems can be successfully processed under the selected conditions for the FFF fabrication of geometrically complex flow components, enabling direct fabrication of static mixers for process intensification applications.

Keywords

Additive manufacturing, composite filaments, static mixers, titanium dioxide, cyclic olefin copolymer, carbon nanotubes

1 Introduction

Additive manufacturing (AM), and in particular fused filament fabrication (FFF), has emerged as a versatile approach for the production of complex three-dimensional structures, with applications ranging from rapid prototyping to functional engineering components.[1,2] Beyond its geometric freedom, FFF enables the fabrication of customised flow structures such as static mixers, lattices, and reactor inserts, which can be tailored to enhance transport phenomena, including mixing, heat transfer, and mass transfer.[3–5] However, the development of functional composite feedstocks suitable for FFF remains challenging, as the incorporation of particulate fillers into thermoplastic matrices often leads to competing requirements between functional performance and processability. In particular, maintaining stable extrusion, filament integrity, and reliable layer deposition becomes increasingly difficult with increasing filler loading.[6–8]

Polymeric matrices such as cyclic olefin copolymer (COC) are of interest for advanced manufacturing applications due to their favourable combination of thermal stability and chemical resistance. These properties make COC a suitable candidate for the fabrication of structured components where dimensional stability and process reliability are essential.[9–11] The incorporation of functional fillers into such matrices enables further tailoring of material properties; however, careful control of filler dispersion and loading is required to preserve printability.[12] Titanium dioxide (TiO_2) is widely used as a functional inorganic filler due to its stability and broad applicability in advanced material systems, while carbon nanotubes (CNTs) may additionally contribute to mechanical reinforcement. In composite systems, CNTs may also influence interfacial interactions and the microstructure of the polymer matrix, thereby affecting rheological behaviour during processing.[13–15] Nevertheless, increasing filler content can introduce challenges such as agglomeration, increased melt viscosity, and reduced mechanical performance of printed parts.[12]

In recent years, FFF has increasingly been explored for the fabrication of structured functional components, including flow reactors and static mixers. These geometries are of particular interest because they enable controlled flow

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distribution and enhanced internal mixing compared with conventional packed-bed systems.[16,17] The ability to directly manufacture such structures from composite filaments offers a pathway towards integrated reactor components, where geometry and material composition are simultaneously engineered. However, the relationship between composite formulation and manufacturability remains insufficiently understood, particularly in systems containing multiple functional fillers. A systematic evaluation of how filler content affects both filament processability and final part performance is therefore essential for the rational design of printable functional materials.[18–20]

Within this context, photocatalytically active materials represent one possible application area for structured polymer composites. Titanium dioxide is frequently employed in functional systems due to its stability and ability to interact with ultraviolet light, while structured reactor geometries can improve exposure and transport conditions.[21–23] However, in many previously reported systems, functional activity is introduced through post-processing steps such as surface coating or impregnation of printed structures, which can introduce additional processing complexity and potential variability in performance. This highlights the importance of developing material systems in which functional components are directly integrated into printable feedstock.[24–27]

In this study, COC-based composite filaments containing varying amounts of TiO_2 and CNTs were developed for FFF processing and the fabrication of static mixer structures. The primary objective was to evaluate the influence of filler content on filament processability, extrusion ability, mechanical properties, and 3D printability. The resulting composite structures were investigated as printable flow elements with potential for future reactor applications. Photocatalytic functionality is considered as a potential application of the TiO_2/CNT-containing structures, while the present study is limited to establishing the relationship between composite formulation, processability, mechanical properties, morphology, and FFF printability. Evaluation of photocatalytic and continuous-flow reactor performance is beyond the scope of the present work.

2 Materials and methods

2.1 Materials

Cyclic olefin copolymer (CAS No. 26007-43-2, TOPAS Advanced Polymers GmbH, Oberhausen, Germany) was selected as the polymer matrix due to its chemical resistance and thermal stability. Titanium dioxide (TiO_2, trade name: AEROXIDE TiO_2 P25, Evonik Industries, Essen, Germany) was used as a photocatalyst. Multi-walled carbon nanotubes (MWCNTs) (Sigma-Aldrich, Burlington, MA, USA) were incorporated as a conductive secondary phase. Although CNTs do not exhibit intrinsic photocatalytic activity, they can facilitate electron transport in TiO_2-based systems, promoting charge separation and potentially enhancing photocatalytic efficiency.

2.2 Sample preparation

COC was supplied in granule form and used directly for composite preparation. The granules were dry blended with varying amounts of TiO_2 and CNTs for 2 min to obtain homogeneous powder mixtures (Table 1). The filler contents were varied according to the compositions listed in Table 1 to investigate the influence of TiO_2 and CNT loading on filament processability. The sample names indicate the filler contents, where "T" refers to the weight percent of TiO_2 and "C" refers to the weight percent of CNTs. The prepared mixtures were melt-compounded using a Rondol 21 mm LAB TWIN (Rondol Industrie, Nancy, France) twin-screw extruder operating at 50 rpm, with temperature settings for the individual heating zones from feed to nozzle, set to: 230 °C, 230 °C, 230 °C, 235 °C, and 235 °C. The resulting composite filaments were cooled in a distilled water bath and subsequently pelletized again using the granulator. During processing, no significant difficulties, such as polymer degradation or nozzle clogging, were observed.

Table 1 – Composition of COC/TiO_2/CNT composites used for filament preparation

Tablica 1 – Sastav COC/TiO_2/CNT kompozita upotrijebljenih za pripremu filamenata

Sample	w(COC)/%	w(TiO_2)/%	w(CNT)/%
COC	100.00	0.00	0.00
COC 1.5T 0C	98.50	1.50	0.00
COC 1.5T 0.25C	98.25	1.50	0.25
COC 1.5T 0.5C	98.00	1.50	0.50
COC 3T 0C	97.00	3.00	0.00
COC 3T 0.25C	96.75	3.00	0.25
COC 3T 0.5C	96.50	3.00	0.50

The composite granules were processed using a Noztek Pro single-screw extruder (Noztek, Shoreham-by-Sea, West Sussex, UK) to produce filaments suitable for 3D printing. The extruded filament diameter was maintained at 1.75 mm ± 5 %, as required for compatibility with the 3D printer. Filament extrusion was carried out at 225 °C, and the material was cooled by air using the extruder's integrated ventilation system. As the extruder operates at a fixed rotation speed, no adjustment of screw speed was possible. The resulting functional filaments were subsequently used for the fabrication of static mixers by 3D printing. For mechanical characterisation, tensile test specimens were fabricated using a Zortrax M200 3D printer (Zortrax, Olsztyn, Poland) according to the ISO 527-2:2025 standard.[28] The printer uses fused filament fabrication additive manufacturing technology. The fabrication process began with the computer-aided design of the tensile specimens using Autodesk Fusion software. After completing the design, the model was exported as an .stl file, a standard format used for additive manufacturing. The .stl file was subsequently imported into Z-Suite slicing software, where the printing parameters were defined. The slicing software converts the 3D model into machine-readable instructions that guide the layer-by-layer fabrication process on the 3D printer. During the 3D printing, conditions for the COC composites were as follows: nozzle temperature range of 235 to 238 °C, platform temperature of 85 °C, and an infill density of 60 %. The same procedure was applied for the fabrication of the static mixers.

2.3 Characterisation

The mechanical properties of the prepared specimens were evaluated by tensile testing using a Zwick Röell AG UTM 1445 (ZwickRoell GmbH & Co. KG, Ulm, Germany) universal testing machine in accordance with ISO 527-2:2025.[28] The tests were performed at a crosshead speed of 10 mm min^{-1} and an initial gauge length of 45 mm. Three specimens (n = 3) were tested for each formulation, and the results are reported as the mean ± standard deviation. Young's modulus, tensile strength, and elongation were determined from the tensile tests. In addition to the standardised tensile properties, tensile work to fracture was obtained directly from the Zwick testing software as the mechanical work recorded during the tensile test up to specimen fracture. The instrument reported this quantity in N·m, equivalent to J. Tensile work to fracture is reported here as a supplementary, non-standard metric and is not a material property defined by ISO 527-2:2025.

The fractured surfaces of the 3D-printed tensile test specimens were analysed using scanning electron microscopy (SEM) to investigate the microstructural features, fracture behaviour, and dispersion of the CNT and TiO_2 fillers within the polymer matrix. Micrographs were acquired using a Tescan Vega 3 (TESCAN, Brno, Czech Republic) scanning electron microscope operated at an accelerating voltage of 20 kV and equipped with a secondary electron detector. Prior to imaging, the samples were mounted on aluminium stubs and sputter-coated with a conductive gold/platinum layer in argon plasma for 60 s to improve surface conductivity and enhance image quality.

3 Results and discussion

3.1 Mechanical properties

The mechanical behaviour of the COC/TiO_2/CNT composites (Fig. 1) was evaluated through tensile testing of the 3D-printed specimens. The parameters measured included Young's modulus (E), tensile strength (maximum stress, σ_m), stress at break (σ_b), elongation at maximum stress (ε_m), elongation at break (ε_b), and tensile work to fracture (W), as reported by the testing software. These metrics were used to assess the influence of filler content on the intrinsic material properties and the structural performance of printed parts (Table 2).

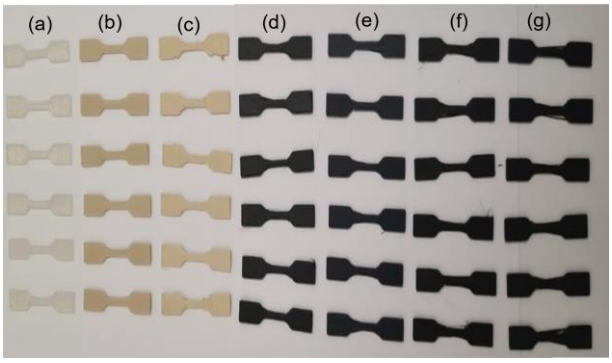


Fig. 1 – 3D-printed tensile test specimens: (a) COC; (b) COC 1.5T 0C; (c) COC 1.5T 0.25C; (d) COC 1.5T 0.5C; (e) COC 3T 0C; (f) COC 3T 0.25C; and (g) COC 3T 0.5C

Slika 1 – 3D-ispisani uzorci za vlačno ispitivanje: (a) COC; (b) COC 1.5T 0C; (c) COC 1.5T 0.25C; (d) COC 1.5T 0.5C; (e) COC 3T 0C; (f) COC 3T 0.25C; i (g) COC 3T 0.5C

The pure COC exhibited moderate stiffness (E = 874 ± 144 MPa), tensile strength of 37.5 ± 2.0 MPa, elongation at break of 3.08 ± 0.34 % and low work to fracture (0.57 ± 0.10 J), providing a baseline for comparison. Incorporation of small amounts of TiO_2 and CNTs (1.5T 0.25C) led to a pronounced reduction in maximum stress and break stress (13.2 ± 1.0 MPa and 12.2 ± 1.7 MPa), while E decreased to 503 ± 63 MPa. This indicates that the combined addition of TiO_2 and CNTs at this composition adversely affected the tensile

Table 2 – Mechanical properties of the prepared composites
Tablica 2 – Mehanička svojstva pripremljenih kompozita

Sample	σ_m/MPa	ε_m/%	σ_b/MPa	ε_b/%	E/MPa	W/J
COC	37.5 ± 2.0	3.04 ± 0.27	37.2 ± 2.2	3.08 ± 0.34	874 ± 144	0.57 ± 0.10
COC 1.5T 0C	29.1 ± 1.8	3.03 ± 0.02	28.9 ± 2.0	3.05 ± 0.22	630 ± 40	0.42 ± 0.03
COC 1.5T 0.25C	13.2 ± 1.0	2.03 ± 0.25	12.2 ± 1.7	2.10 ± 0.25	503 ± 63	0.13 ± 0.02
COC 1.5T 0.5C	9.3 ± 0.9	0.20 ± 0.04	9.3 ± 0.9	0.20 ± 0.04	452 ± 54	0.01 ± 0.00
COC 3T 0C	37.7 ± 1.8	3.30 ± 0.25	37.0 ± 2.6	3.30 ± 0.25	825 ± 83	0.57 ± 0.07
COC 3T 0.25C	24.6 ± 2.1	2.85 ± 0.32	24.5 ± 1.9	2.87 ± 0.33	565 ± 41	0.34 ± 0.07
COC 3T 0.5C	14.6 ± 2.0	2.40 ± 0.14	14.5 ± 2.0	2.45 ± 0.18	454 ± 31	0.17 ± 0.03

response of the printed material, potentially due to changes in filler matrix interactions or local variations in filler dispersion. At higher TiO_2 loadings (3T 0C), the material preserved its tensile strength (37.7 ± 1.8 MPa) and exhibited comparable stiffness (E = 825 ± 83 MPa), indicating that the addition of TiO_2 had no adverse effect on the mechanical properties. To isolate the effect of CNT incorporation, CNT-containing formulations were compared with the corresponding TiO_2-only composites. For the 1.5 wt% TiO_2 series, the addition of 0.25 wt% CNT reduced the maximum tensile stress from 29.1 ± 1.8 MPa to 13.2 ± 1.0 MPa, elongation at break from 3.05 ± 0.22 % to 2.10 ± 0.25 %, Young's modulus from 630 ± 40 MPa to 503 ± 63 MPa, and tensile work to fracture from 0.42 ± 0.03 J to 0.13 ± 0.02 J. At 0.5 wt% CNT, these values further decreased to 9.3 ± 0.9 MPa, 0.20 ± 0.04 %, 452 ± 54 MPa, and 0.01 ± 0.00 J, respectively. Overall, increasing the CNT content from 0 to 0.5 wt% resulted in a 68 % reduction in maximum tensile stress relative to the corresponding TiO_2-only formulation.

A similar trend was observed for the 3 wt% TiO_2 series. The addition of 0.25 wt% CNT reduced the maximum tensile stress from 37.7 ± 1.8 MPa to 24.6 ± 2.1 MPa, elongation at break from 3.30 ± 0.25 % to 2.87 ± 0.33 %, Young's modulus from 825 ± 83 MPa to 565 ± 41 MPa, and tensile work to fracture from 0.57 ± 0.07 J to 0.34 ± 0.07 J. At 0.5 wt% CNT, these values further decreased to 14.6 ± 2.0 MPa, 2.45 ± 0.18 %, 454 ± 31 MPa, and 0.17 ± 0.03 J, respectively. Overall, increasing the CNT content from 0 to 0.5 wt% resulted in a 61 % reduction in maximum tensile stress. These results demonstrate a consistent deterioration in tensile properties with increasing CNT content relative to the corresponding TiO_2-only formulations. (Figs. 2, 3, and 4). This behaviour may be associated with CNT-induced stress concentrations and/or local dispersion heterogeneity within the COC matrix. The mechanical property comparisons presented here are descriptive and based on the measured mean values and standard deviations.

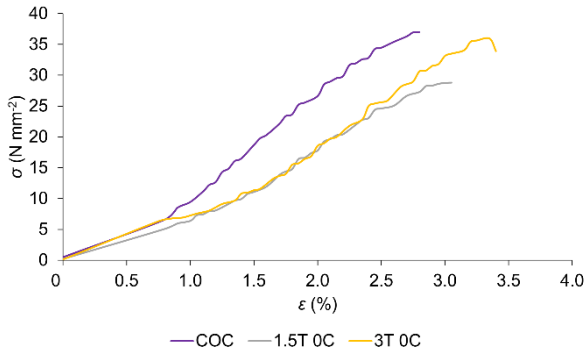


Fig. 2 – Representative stress–strain curves of pure COC and COC/TiO_2 nanocomposites with increasing TiO_2 content
Slika 2 – Reprezentativne krivulje naprezanje-istezanje čisti COC i COC/TiO_2 nanokompozita s povećanjem udjela TiO_2

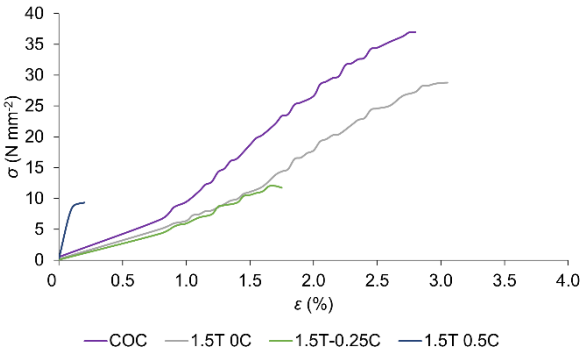


Fig. 3 – Representative stress–strain curves of pure COC and COC/TiO_2/CNT nanocomposites for 1.5 % TiO_2 and increasing CNT content
Slika 3 – Reprezentativne krivulje naprezanje-istezanje čisti COC i COC/TiO_2/CNT nanokompozita pri 1,5 % TiO_2 i povećanjem udjela CNT-a

As no inferential statistical analysis was performed, the differences between formulations are discussed descriptively based on the measured mean values and standard deviations. Accordingly, these trends should be interpreted within the variability of the experimental data.

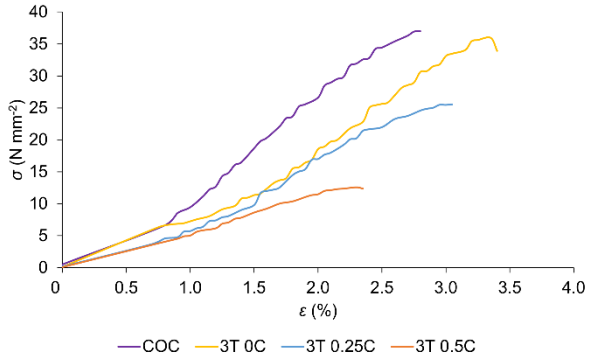


Fig. 4 – Representative stress–strain curves of pure COC and COC/TiO_2/CNT nanocomposites for 3 % TiO_2 and increasing CNT content

Slika 4 – Reprezentativne krivulje naprezanje-istezanje čisti COC i COC/TiO_2/CNT nanokompozita pri 3 % TiO_2 i povećanjem udjela CNT-a

3.2 3D printing

All prepared composites were suitable for fabrication using 3D printing. Representative examples of the printed static mixers are shown in Fig. 5.

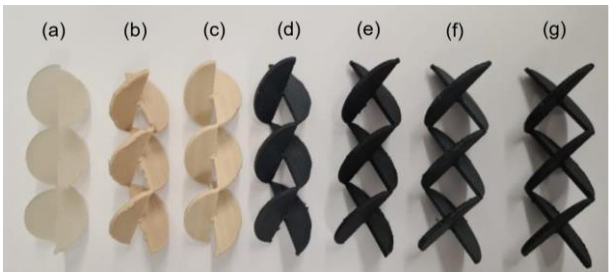


Fig. 5 – 3D-printed composite static mixers: (a) COC; (b) COC 1.5T 0C; (c) COC 3T 0C; (d) COC 1.5T 0.25C; (e) COC 1.5T 0.5C; (f) COC 3T 0.25C; and (g) COC 3T 0.5C

Slika 5 – 3D-ispisane kompozitne statičke miješalice: (a) COC; (b) COC 1.5T 0C; (c) COC 3T 0C; (d) COC 1.5T 0.25C; (e) COC 1.5T 0.5C; (f) COC 3T 0.25C; and (g) COC 3T 0.5C

The static mixers were successfully printed using the same processing parameters, resulting in defect-free structures with good layer adhesion. The printed parts showed high dimensional accuracy, closely matching the designed geometries. No cracking, warping, or deformation was observed during or after fabrication, indicating stable processing and reliable structural integrity of printed components.

3.3 SEM

SEM analysis of the fractured surfaces further confirmed the quality of the fabricated composites. The micrographs (Fig. 6) revealed a relatively homogeneous dispersion of TiO_2 particles throughout the polymer matrix, with no significant agglomeration observed in the examined regions. The fillers appeared to be well embedded within the matrix, indicating good interfacial adhesion between the TiO_2 particles and the surrounding material. The fracture surfaces exhibited limited particle pull-out and an absence of large interfacial voids, suggesting effective stress transfer across the filler-matrix interface. In addition, the fracture morphology showed continuous filament bonding and compact layer fusion, supporting the observations of strong interlayer adhesion obtained from the macroscopic inspection of the printed parts. These observations indicate relatively uniform TiO_2 distribution and good interfacial contact within the examined regions of the selected COC 3T 0.25C formulation. The analysed sample, containing 3 wt% TiO_2 and 0.25 wt% CNT, was selected because it represented one of the formulations with a relatively higher filler content, making it suitable for evaluating the overall fracture morphology and filler distribution under more demanding conditions. However, the presented SEM micrographs do not provide CNT-specific evidence of agglomeration; therefore, the possible contribution of CNT agglomeration or local dispersion heterogeneity to the observed mechanical behaviour remains an inferred mechanism rather than a direct experimental observation.

The results obtained in this study can be contextualised with respect to previous work on filler-containing thermoplastics for fused filament fabrication. *Wu et al.* investigated CNT-containing materials produced by FFF, addressing the influence of filler incorporation on the mechanical performance of printed parts.[29] Similarly, the present results demonstrate that increasing CNT content strongly affected the mechanical response of the COC/TiO_2/CNT composites. In both TiO_2 series investigated here, increasing CNT content resulted in reductions in tensile strength, elongation, Young's modulus, and tensile work to fracture. These changes may reflect CNT-induced stress concentrations, local variations in filler dispersion, and/or filler-matrix interactions. However, these mechanisms were not directly resolved by the present SEM analysis. Importantly, the deterioration in mechanical properties did not result in a corresponding loss of processability. All investigated COC/TiO_2/CNT formulations were successfully extruded into dimensionally stable filaments (1.75 mm ± 5 %) and subsequently processed by FFF without nozzle clogging, warping, or process interruption. The results therefore indicate that, within the investigated composition range, mechanical performance was more sensitive to CNT incorporation

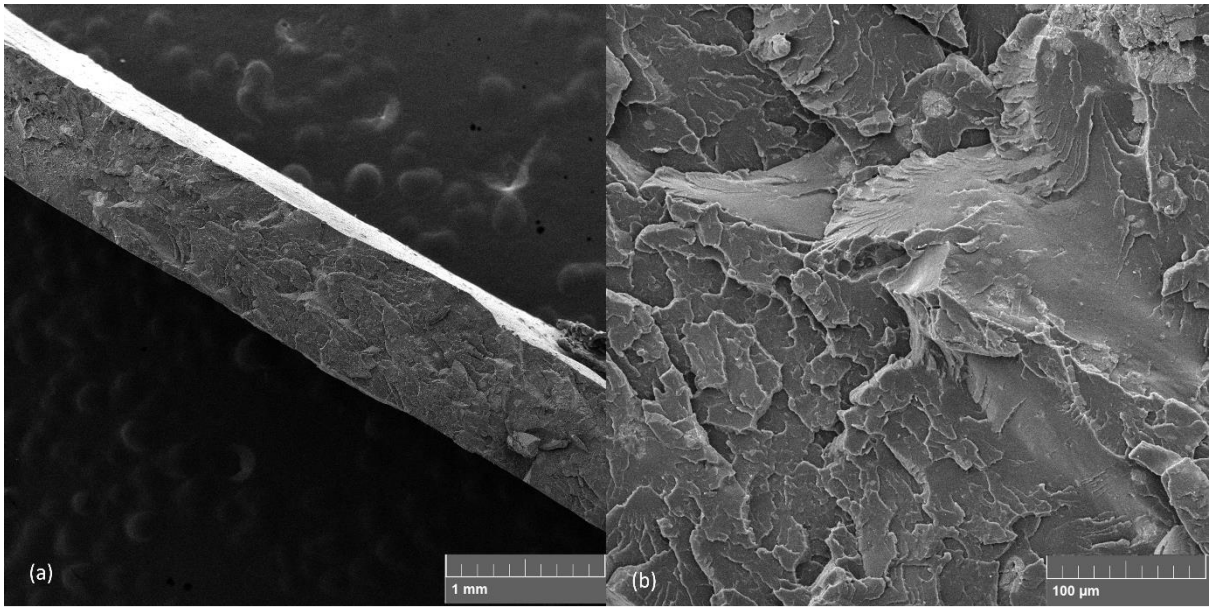


Fig. 6 – SEM micrographs of the fracture surface for the COC 3T 0.25C sample at (a) 50×, and (b) 500× magnification
Slika 6 – SEM mikrografije lomne površine uzorka COC 3T 0.25C pri povećanju (a) 50× i (b) 500×

than the overall ability of the composites to undergo filament extrusion and FFF processing. The present approach can also be contrasted with that of *Kundra et al.*, who produced 3D-printed nickel catalytic static mixers using a post-print corrosive chemical treatment for continuous-flow hydrogenation.[30] In the present study, TiO_2 and CNTs were instead incorporated directly into the COC matrix during composite preparation, allowing static mixer structures containing the functional fillers to be fabricated directly by FFF without subsequent chemical treatment. Although photocatalytic or catalytic performance was not evaluated in the present work, this direct incorporation approach simplifies the fabrication route and provides a basis for the future development of functional structured flow components.

This comparison is particularly relevant in the context of application-oriented flow structures. All investigated COC/TiO_2/CNT formulations could be used to fabricate static mixers while maintaining continuous material deposition and the intended overall geometry. Although CNT incorporation progressively reduced the measured tensile properties, this did not prevent the fabrication of geometrically complex structures under the selected FFF conditions. These findings highlight that mechanical performance and manufacturing processability should be considered as related but distinct aspects when developing composite feedstocks for FFF. In this respect, direct incorporation of TiO_2 and CNTs into the COC matrix provides a straightforward route for fabricating structured flow components with potential applications in process intensification.

4 Conclusion

In this study, COC/TiO_2/CNT composite filaments were successfully developed and processed by fused filament fabrication for the production of tensile specimens and static mixer structures. The results showed that TiO_2 incorporation had a limited effect on the mechanical performance or printability of the COC matrix, while increasing CNT content reduced tensile strength, elongation, and tensile work to fracture, potentially reflecting CNT-induced stress concentrations and local variations in filler dispersion or filler-matrix interactions. Despite these reductions, all investigated formulations retained sufficient structural integrity for successful 3D printing. SEM analysis of the selected COC 3T 0.25C formulation indicated relatively homogeneous TiO_2 distribution, good interfacial contact, and strong interlayer bonding within the examined regions. All composites exhibited stable melt processing, filament extrusion, and defect-free deposition without nozzle clogging, warping, or dimensional instability. The successful fabrication of static mixer geometries demonstrates that the developed hybrid composites can be successfully processed under the selected conditions for the fabrication of complex flow structures by FFF. The present work demonstrates that multi-filler COC-based composites can maintain stable printability under the investigated conditions while enabling the fabrication of structured flow components. The developed composites therefore represent promising feedstocks for the additive manufacturing of structured flow components, while their photocatalytic and reactor performance require further experimental evaluation. The present findings reflect the processing conditions

established and applied in this study, including tensile specimens printed at 60 % infill using the selected FFF parameters. Under these conditions, all investigated formulations were successfully processed into filaments and printed into tensile specimens and static mixer geometries. Static mixer fabrication was assessed based on successful printing and visual integrity, while detailed SEM characterisation was performed on the selected COC 3T 0.25C formulation. Further investigation across a wider range of printing conditions, composite formulations, and application-specific performance tests would provide additional insight into the capabilities of these materials.

Author Contributions

M. P. M.: Formal analysis, Methodology, Supervision, Validation, Visualisation, Writing-review and editing. E. F.: Conceptualisation, Data curation, Formal analysis, Investigation, Visualisation, Writing-original draft, Writing-review and editing. D. V.: Conceptualisation, Formal analysis, Funding acquisition, Methodology, Supervision, Validation, Visualisation, Writing-review and editing. All authors have read and agreed to the published version of the manuscript.

Institutional Review Board Statement

Not applicable.

Informed Consent Statement

Not applicable.

Data Availability Statement

The raw data supporting the conclusions of this article will be made available by the authors on request.

Conflicts of Interest

The authors declare no conflicts of interest.

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References
Literatura

1. *A. A. Rashid*, *M. Koç*, Fused Filament Fabrication Process: A Review of Numerical Simulation Techniques, Polymers **13** (20) (2021) 3534, doi: https://doi.org/10.3390/polym13203534.
2. *L. Zhou, J. Miller, J. Vezza, M. Mayster, M. Raffay, Q. Justice, Z. Al Tamimi, G. Hansotte, L.D. Sunkara, J. Bernat*, Additive Manufacturing: A Comprehensive Review, Sensors **24** (9) (2024) 2668, doi: https://doi.org/10.3390/s24092668A.
3. *A. Dey, M. Ramoni, N. Yodo*, A Survey on Fused Filament Fabrication to Produce Functionally Gradient Materials, Materials **17** (15) (2024) 3675, doi: https://doi.org/10.3390/ma17153675.
4. *R. Guerra Silva, M. J. Torres, J. Z. Viñuela, A. González Zamora*, Manufacturing and Characterization of 3D Miniature Polymer Lattice Structures Using Fused Filament Fabrication, Polymers **13** (4) (2021) 635, doi: https://doi.org/10.3390/polym13040635.
5. *F. L. Rashid, K. A. Hammoodi, N. M. L. Al Maimuri, M. K. Abdalrahem, H. I. Mohammed, A. Ameen, E. B. Agyekum, A. Bouabidi,* Triply Periodic Minimal Surface Heat Exchanger: Innovations, Mathematical Modelling, and Performance Enhancement – A State-of-the-Art Review, Int. Commun. Heat Mass Transf. **175** (2026) 111120, doi: https://doi.org/10.1016/j.icheatmasstransfer.2026.111120.
6. *P. M. Angelopoulos, M. Samouhos, M. Taxiarchou*, Functional Fillers in Composite Filaments for Fused Filament Fabrication; A Review, Mater. Today: Proc. **37** (2021) 4031–4043, doi: https://doi.org/10.1016/j.matpr.2020.07.069.
7. *J. Leśniowski, A. Stawiarski, M. Barski,* Enhancing the Performance of FFF-Printed Parts: A Review of Reinforcement and Modification Strategies for Thermoplastic Polymers, Materials **18** (2025) 5185, doi: https://doi.org/10.3390/ma18225185.
8. *V. Monfared, H. R. Bakhsheshi-Rad, S. Ramakrishna, M. Razzaghi, F. Berto,* A Brief Review on Additive Manufacturing of Polymeric Composites and Nanocomposites, Micromachines **12** (2021) 704, doi: https://doi.org/10.3390/mi12060704.
9. *A. Agha, W. Waheed, N. Alamoodi, B. Mathew, F. Alnaimat, E. Abu-Nada, A. Abderrahmane, A. Alazzam,* A Review of Cyclic Olefin Copolymer Applications in Microfluidics and Microdevices, Macromol. Mater. Eng. **307** (8) (2022) 2200053, doi: https://doi.org/10.1002/mame.202200053.
10. *E. Forjan, M.-P. Marković, K. Šulek, D. Vrsaljko,* Processing and Characterization of Copper Reinforced Cyclic Olefin Copolymer Filaments for 3D Printing, J. Appl. Polym. Sci. **143** (2025) e58163, doi: https://doi.org/10.1002/app.58163.
11. *M. Cesaria, M. Calcagnile, V. Arima, M. Bianco, P. Alifano, R. Cataldo,* Cyclic Olefin Copolymer (COC) as a Promising Biomaterial for Affecting Bacterial Colonization: Investigation on *Vibrio campbellii*, Int. J. Biol. Macromol. **271** (2024) 132550, doi: https://doi.org/10.1016/j.ijbiomac.2024.132550.
12. *J. Chen, R. An, W. S. Tey, Q. Zeng, L. Zhao, K. Zhou,* In Situ Filler Addition for Homogeneous Dispersion of Carbon Nanotubes in Multi Jet Fusion–Printed Elastomer Composites, Adv. Sci. **10** (2023) 2300593, doi: https://doi.org/10.1002/advs.202300593.
13. *L. Wan, C. Deng, Z.-Y. Zhao, H.-B. Zhao, Y.-Z. Wang,* A Titanium Dioxide–Carbon Nanotube Hybrid to Simultaneously Achieve the Mechanical Enhancement of Natural Rubber and Its Stability under Extreme Frictional Conditions, Mater. Adv. **2** (2021) 2408–2418, doi: https://doi.org/10.1039/D0MA00823K.
14. *E. Morokov, P. Shershak, M. Burkov, A. Eremin, E. Popkova, N. Yakovlev, I. Zhiltsova,* Influence of CNT Filler in Polymer

Matrix on Impact Damage Propagation in the Volume of Carbon Fiber Laminates, Polymers **17** (2025) 891, doi: https://doi.org/10.3390/polym17070891.

15. *V. P. Prasadam, A. M. Huerta Flores, N. Bahlawane,* CNT–TiO_2 Core–Shell Structure: Synthesis and Photoelectrochemical Characterization, RSC Adv. **11** (2021) 33169–33178, doi: https://doi.org/10.1039/D1RA05723E.
16. *M. Zeraatkar, M. D. de Tullio, G. Percoco,* Fused Filament Fabrication (FFF) for Manufacturing of Microfluidic Micromixers: An Experimental Study on the Effect of Process Variables in Printed Microfluidic Micromixers, Micromachines **12** (2021) 858, doi: https://doi.org/10.3390/mi12080858.
17. *V. Muñoz-Perales, M. van der Heijden, P. A. García-Salaberri, M. Vera, A. Forner-Cuenca,* Engineering Lung-Inspired Flow Field Geometries for Electrochemical Flow Cells with Stereolithography 3D Printing, ACS Sustain. Chem. Eng. **11** (2023) 12243–12255, doi: https://doi.org/10.1021/acssuschemeng.3c00848.
18. *V. N. Sukumaar, S. M. Rangappa, Y. Liu, S. Siengchin,* A Comprehensive Review on the Influence of Fused Deposition Modelling Process Parameters upon Thermoplastic Composite Materials, Adv. Ind. Eng. Polym. Res. **9** (2026) 281–303, doi: https://doi.org/10.1016/j.aiepr.2025.11.006.
19. *L. Nyman, P. Lehto, K. Kukko, A. Kestilä, E. Kallio,* Strength and Poisson's Ratio of Fused Filament Fabrication Parts Made from Carbon Filler Enhanced PEEK Compounds at Elevated Temperatures, Sci. Rep. **14** (2024) 31628, doi: https://doi.org/10.1038/s41598-024-80470-7.
20. *V. Dananjaya, M. Yang, Y. Zheng, C. Abeykoon,* Effect of Filler Characteristics and Processing Route on Bamboo Powder-Reinforced PLA Composites, J. Clean Prod. **537** (2025) 147193, doi: https://doi.org/10.1016/j.jclepro.2025.147193.
21. *A. Enesca, C. Cazan,* Polymer Composite-Based Materials with Photocatalytic Applications in Wastewater Organic Pollutant Removal: A Mini Review, Polymers **14** (2022) 3291, doi: https://doi.org/10.3390/polym14163291.
22. *M. Hirota, Y. Sugita, M. Ishijima, T. Ikeda, J. Saruta, H. Maeda, T. Ogawa,* UV Photocatalytic Activity of Titanium Dioxide (TiO_2) Surface Contaminated with Bacterial Biofilm: Implications for Photo-Restoration of Osteoconductivity, Mater. Today Adv. **12** (2021) 100182, doi: https://doi.org/10.1016/j.mtadv.2021.100182.
23. *I. S. O. Barbosa, Y. A. Manrique, D. Paiva, J. L. Faria, R. J. Santos, C. G. Silva,* Efficient Photocatalytic Reactors via 3D Printing: SLA Fabrication and TiO_2 Hybrid Materials, RSC Adv. **15** (2025) 2275–2286, doi: https://doi.org/10.1039/D4RA07121B.
24. *C.-H. Chen, S.-C. Wang, H.-W. Chen, T.-Y. Chou, C.-S. Chang,* High-Efficiency Photocatalytic Reactors Fabricated *via* Rapid DLP 3D Printing: Enhanced Dye Photodegradation with Optimized TiO_2 Loading and Structural Design, ACS ES&T Wat. **4** (2024) 1883–1893, doi: https://doi.org/10.1021/acsestwater.4c00002.
25. *M. A. Marchenkova, J. K. Gadzhiev, A. A. Guda, A. V. Soldatov, S. V. Chapek,* Three-Dimensionally Printed Catalytic Structures, J. Manuf. Mater. Process. **9** (2025) 372, doi: https://doi.org/10.3390/jmmp9110372.
26. *J.-R. Chen, W.-H. Tsai, C.-K. Su,* TiO_2 Nanoparticle–Coated 3D-Printed Porous Monoliths Enabling Highly Sensitive Speciation of Inorganic Cr, As, and Se, Anal. Chim. Acta **1271** (2023) 341489, doi: https://doi.org/10.1016/j.aca.2023.341489.
27. *N. Li, K. Tong, L. Yang, X. Du,* Review of 3D Printing in Photocatalytic Substrates and Catalysts, Mater. Today Energy **29** (2022) 101100, doi: https://doi.org/10.1016/j.mtener.2022.101100.
28. International Organization for Standardization. ISO 527-2:2025, Plastics – Determination of Tensile Properties – Part 2: Test Conditions for Moulding and Extrusion Plastics, 3rd ed.; ISO: Geneva, Switzerland, 2025.
29. *Y. Wu, V. Neto, R. Valente, D. K. K. Cavalcanti, T. Gomes,* Mechanical characterization of CNT/PLA parts via FFF additive manufacturing, Polym. Eng. Sci. **66** (2026) 2726–2738, doi: https://doi.org/10.1002/pen.70384.
30. *M. Kundra, Y. Zhu, X. Nguyen, D. Fraser, C.H. Hornung, J. Tsanaktsidis,* 3D printed nickel catalytic static mixers made by corrosive chemical treatment for use in continuous flow hydrogenation, React. Chem. Eng. **7** (2022) 284–296, doi: https://doi.org/10.1039/D1RE00456E.

SAŽETAK

Aditivna proizvodnja i mehanička svojstva kompozitnih filamenata COC/TiO_2/CNT za 3D-ispis statičkih miješalica

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Kompozitni filamenti na bazi cikličkog olefinskog kopolimera (COC), koji sadrže titanijev dioksid (TiO_2) i ugljikove nanocijevi (CNT), razvijeni su za izradu funkcionalnih statičkih miješalica postupkom 3D-ispisa, proizvodnja rastaljenim filamentom (FFF). Sustavno je ispitan utjecaj sastava punila (1,5 – 3 mas. % TiO_2 i 0 – 0,5 mas. % CNT-a) na preradljivost filamenata, mehanička svojstva i mogućnost 3D-ispisa. Kompozitni filamenti proizvedeni su miješanjem u taljevini u dvopužnom ekstruderu te ekstrudirani do promjera od 1,75 mm. Nakon toga postupkom FFF izrađeni su uzorci za vlačno ispitivanje i statičke miješalice. Mehanička svojstva ispisanih uzoraka određena su u skladu s normom ISO 527-2:2025. Osim toga, iz programske podrške uređaja za vlačno ispitivanje dobiven je rad loma kao dodatni pokazatelj koji predstavlja mehanički rad zabilježen do loma uzorka. Dodatak TiO_2 imao je neznatan utjecaj na vlačnu čvrstoću i mogućnost ispisa, dok je dodatak CNT-a postupno smanjivao vlačnu čvrstoću (do 68 % u odnosu na odgovarajući sastav koji sadržava samo TiO_2), istezanje i rad do loma. Sve su formulacije pokazale stabilnu ekstruziju, ujednačeno oblikovanje filamenta i ispis bez nedostataka, deformiranja uslijed izvijanja ili začepljenja mlaznice. Youngov modul iznosio je od 450 do 870 MPa. Rezultati istraživanja pokazuju da se hibridni sustavi COC/TiO_2/CNT u odabranim uvjetima mogu uspješno prerađivati postupkom FFF za izradu geometrijski složenih protočnih elemenata, čime se omogućuje izravna izrada statičkih miješala za primjenu u intenzifikaciji procesa.

Ključne riječi

Aditivna proizvodnja, kompozitni filamenti, statičke miješalice, titanijev dioksid, cikloolefinski kopolimer, ugljikove nanocijevi

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