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# MICROMECHANICAL ELASTOPLASTIC MODELING AND CHARACTERIZATION OF 3D PRINTABLE BIOPOLYMER NANOCOMPOSITES

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## ABSTRACT

This research centers on computationally predicting the elastoplastic micromechanical behavior of a novel biopolymer nanocomposite material system comprising nanohydroxyapatite (nHA) particles in a biopolymer matrix. Realistic Representative Volume Elements (RVEs) were generated to replicate the actual microstructure of the nanocomposite, accounting for factors like nHA particle dispersion, inclusion aspect ratio, and nHA length distribution. The Drucker-Prager constitutive model used to model the 3D-printed functionalized biopolymer matrix was calibrated using tensile and compression test data and verified with shear test data. The developed computational tool was subsequently utilized to investigate the impact of nanoparticle dispersion and arrangement on the elastoplastic properties of the nanocomposite. These findings offer valuable insights for designing mechanically robust 3D printable nanocomposite materials.

## 1 INTRODUCTION

Polymer nanocomposites are a class of materials that consist of a polymer matrix reinforced with nanoscale particles. The addition of nanoparticles to a polymer matrix aims to significantly enhance the mechanical, thermal, and electrical properties of the resulting composite material [1], including stiffness, strength, and thermal stability. This versatility has led to widespread applications across industries such as aerospace, automotive, electronics, and biomedical engineering [2]–[4]. Biobased polymer matrices are a class of polymers derived from renewable biological resources, such as plants, animals, or microorganisms. These matrices form the fundamental structure in biocomposites offering an alternative to traditional petroleum-based polymers. Inconsistent nanoparticle characteristics, such as shape, size, orientation, and agglomeration, hinder precise local dispersion control. The complex nature of these materials, including the heterogeneous distribution of nanoparticles within the polymer matrix, poses challenges for accurate prediction of their mechanical performance [5]. Conducting nanoscale experiments is expensive, and establishing correlations between process, microstructure, and properties for early design of these materials is challenging. Formulating analytical models is complex, with limitations in accurately describing nanocomposite microstructures and capturing nonlinear material behavior, making them less effective in assessing local failures within these systems [6], [7].

Finite element method (FEM)-based micromechanical modelling is a useful tool for studying the behavior of polymer nanocomposites at different length scales. These models can provide insight into the mechanical and thermal properties of nanocomposites, as well as their electronic and optical properties, which can be used to optimize the design of nanocomposites for specific applications. An appropriately sized representative volume element (RVE) must capture the key characteristics of the material microstructure, including the complex geometrical

characteristics of the particulate phase [8]. While micromechanical RVE methods are applied to predict nanocomposite mechanical properties, particularly CNT-based nanocomposites, the complex microstructure and inconsistent inclusion features have led to reliance on simplifying assumptions. Consequently, limited attention has been given to elastoplastic micromechanical modelling of polymer nanocomposites using realistic RVEs based on the actual microstructure of nanocomposite systems [9].
The aim of this study was to develop a robust computational tool to predict the elastoplastic micromechanical behaviour of a novel biopolymer nanocomposite material.

# 2 Materials and Methods

In this study, the nHA inclusions were modelled as elastic isotropic [10] and the biopolymer matrix was modelled using the Drucker-Prager elastoplastic constitutive model. For this purpose, realistic RVEs were generated using MSC Digimat software according to the actual microstructure of the novel nanocomposite, considering nHA particle dispersion through the biopolymer matrix, inclusion aspect ratio, and nHA length distribution. To capture the elastoplastic constitutive response of the 3D-printed functionalized biopolymer matrix, the Drucker-Prager constitutive model was calibrated and verified using data from performed tensile and compression tests and validated with data from performed shear tests as an independent test [9].

***Biopolymer Characterization Tests***

For the tensile tests, dogbone-shaped test specimens (Overall length: 30 mm; Gauge length: 10 mm long, 2.5 mm wide, and 2 mm thick; according to the ASTM D3039, 2017) were 3D printed using a Phrozen Sonic XL 4 K mSLA-type 3D printer (Phrozen Technology, Taiwan). 3D stereolithographic (.stl) files were sliced using the Phrozen slicer software. Tensile testing employed a Psylotech µTS system with a 1.6 kN load cell (Psylotech Inc., Evanston, IL, USA) [9].

According to ASTM-D695, a right cylinder or prism specimen with a length, twice the major width or diameter is recommended for compression tests. After some trial designs, the right cylinder specimen with 2.5 mm in diameter and 5 mm in length was selected. The cylindrical samples were printed on the mSLA printer without any fixtures and right on the bed of the 3D printer. The quasi-static compression tests were performed on a Psylotech TS mechanical testing system using compression platens fixtures [9].

There are no uniaxial testing standards for characterizing the shear properties of plastics. Consequently, the uniaxial shear specimen geometry was adapted from a unique specimen geometry initially proposed for shear testing of metallic alloys under static and dynamic stress [11]. Although the mini-shear sample geometry had some complications related to fabrication, it has the advantage of enabling the shear test using a uniaxial test frame. Mini-shear samples were printed accordingly [9] and tested following the same test set up for the uniaxial test.

Using the obtained experimental data (Table 1) the Drucker-Prager material properties were obtained for the biopolymer matrix [9]. Single-element uniaxial tension, compression and shear tests (Fig.1) were performed to verify the suitability of the Drucker Prager model to capture the experimentally measured response of the matrix material at quasi-static strain rates.

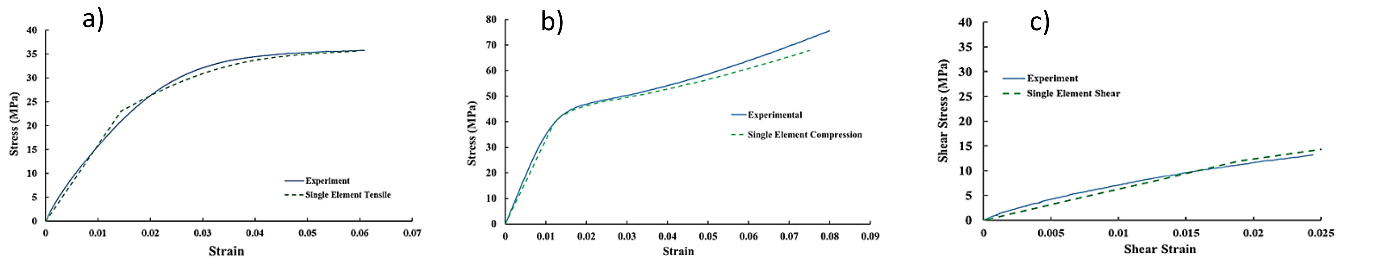


Figure 1. Experimental and single-element quasi-static verification test results for the biopolymer matrix tested in a) Tensile, b) compression c) Shear.

Table 1. The assumed elastic properties of nHA [12] and measured biopolymer matrix properties.

| | Young Modulus (MPa) *E* | Poisson Ratio (*v*) | Tensile Yield Strength (MPa) | Compression Yield Strength (MPa) |
|---|---|---|---|---|
| **Nanohydroxyapetite** | 114000 | 0.29 | - | - |
| **Biopolymer matrix** | 1690 | 0.39 | 21 | 35 |

# 3 Results and Discussion

Five configurations of RVEs were generated [9] to replicate the microstructure of the nanocomposite system under study. The first class consists of unidirectionally aligned nHA particles with a constant length, the second class comprises aligned high aspect ratio nHA particles, the third class includes aligned varied length distribution based on experimentally obtained real microstructure data [9], the fourth class involves applying orientation tensors to individual nanoparticles for random orientation while varying the particle length, and the fifth class consists of randomly dispersed, randomly oriented, and varied length distribution RVEs with microscale agglomerations derived from the real microstructure. These RVEs (assuming an average length of inclusion of 120 nm, aspect ratio of 4 and average number of inclusions of 185) were developed to assess the effect of nanoparticle dispersion, orientation and length distribution on the orthotropic elastoplastic properties of the studied nanocomposite and to validate the elastoplastic response of realistic RVE against the studied nanocomposite system to use this RVE for further local failure initiation within the material system.

***Elastoplastic properties of generated RVEs***

The response of the generated class of RVEs was further examined for predicting the elastoplastic behavior of the model nanocomposite system. By incorporating the elastoplastic properties of the biopolymer matrix and the elastic properties of the nHA inclusions, as outlined in Table 1, and implementing the periodic boundary condition, the predicted homogenized elastoplastic stress-strain response was obtained for the five representative classes of RVEs, as shown in Fig.2. The stress-strain curves demonstrate that RVEs with a constant volume fraction initially exhibit slight disparities in their elastic response, but noticeable differences emerge post-yield, highlighting the impact of particle dispersion and distribution on elastoplastic properties.

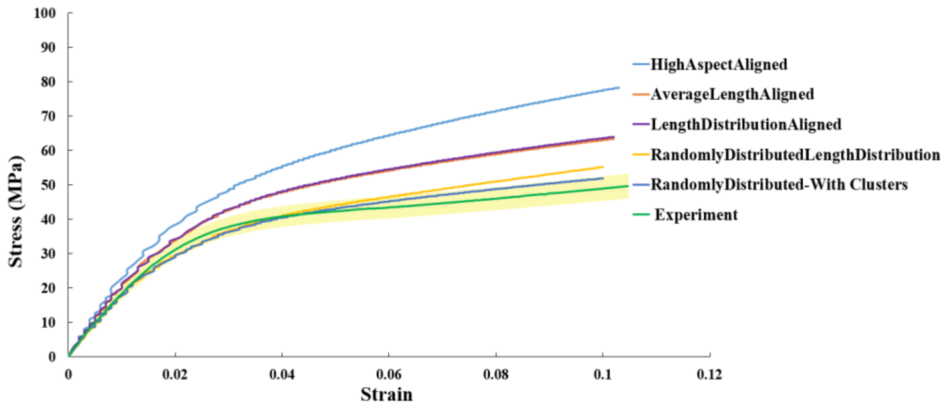


Figure 2. Elasto-plastic stress-strain response of five classes of generated RVEs compared with the average experimental stress-strain response of the nanocomposite [9].

Notably, more pronounced deviations are observed in the stress-strain curves of aligned RVE classes compared to randomly oriented RVEs and experimental data after yielding. Emphasizing that optimizing volume fraction alone is insufficient, the study underscores the need to investigate nanoparticle distribution within the matrix for improved elastoplastic mechanical properties. Stress-strain curves from randomly oriented, length-distributed RVEs with nanoscale clusters align well with average experimental stress-strain curves of functionalized nanocomposites, emphasizing the importance of realistic microstructures in RVE generation for accurate elastoplastic predictions. Stress contour maps in RVEs (Fig.3) reveal distinctive shear lag responses in the matrix, especially pronounced in aligned RVEs, underscoring the significance of microstructure features and inclusion dispersion in predicting nanocomposite elastoplastic properties accurately.

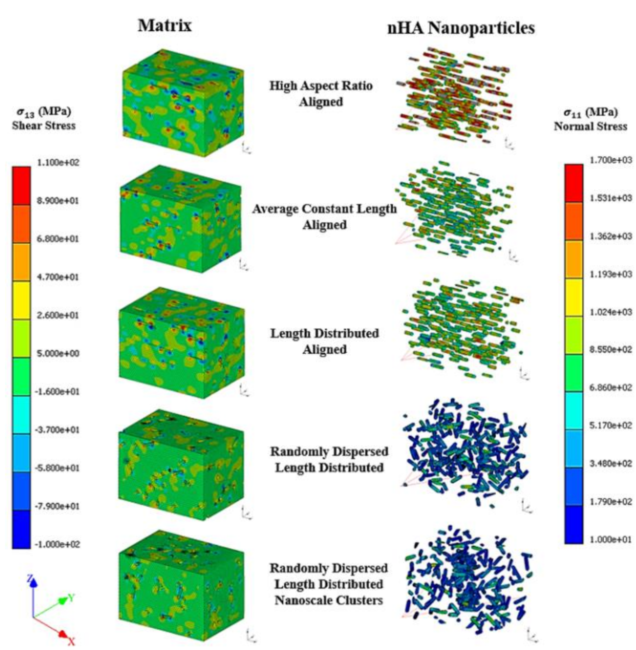


Figure 3. Shear stress ($\sigma_{13}$) in the matrix and normal stress ($\sigma_1$) contours in the inclusion of five classes of generated RVEs.

Under consistent loading, elastoplastic stress contours vary significantly among RVE classes, illustrating the influence of inclusion shape and volume fraction. Normal stress contours in inclusions highlight improved load-bearing capabilities with aligned inclusions and hindered load transfer in the presence of agglomerations, impacting nanocomposite mechanical properties.

To further investigate the effect of agglomerations on the local deformation of the matrix in the studied nanocomposite systems, planes were cut through the location of agglomerations. As seen in the contour plots (Fig.4), the agglomerations can act as stress concentrations within the nanocomposite material. The stress tends to concentrate around the agglomerations, putting excessive stress on the surrounding matrix material. This concentrated stress can exceed the material's yield strength, leading to local plastic deformation of the matrix material. Moreover, the matrix around agglomerations is more confined and can restrict the deformation of the surrounding matrix material. This confinement effect can hinder the plastic deformation and flow of the matrix around the agglomerates and the material may exhibit reduced ductility in these regions, which could lead to cavitation failure [13].

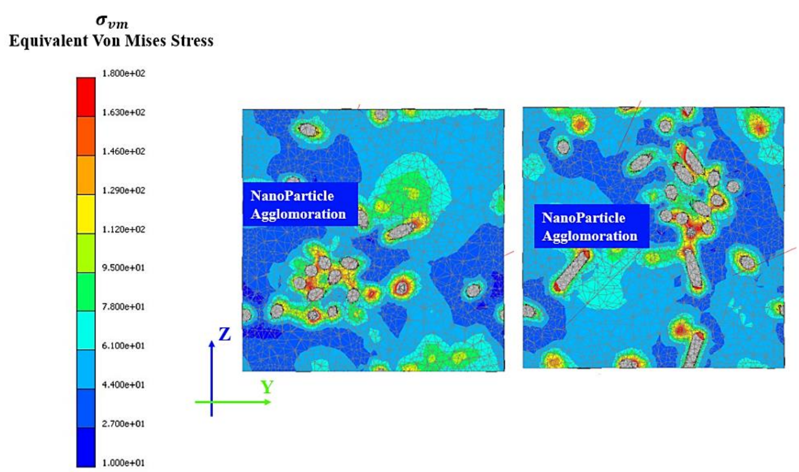


Figure 4. Von mises stress contour in the regions of agglomerations; the matrix demonstrates higher stress levels and may act as stress concentration regions for the onset of local failure.

# 4 Conclusion

This paper introduces a computational tool for predicting the elastoplastic micromechanical properties of biopolymer nanocomposite systems. Realistic RVEs, based on the studied nanocomposite's microstructure, were generated to investigate the influence of nHA nanorod alignment, dispersion, length distribution, and aspect ratio on elastoplastic properties. The findings emphasize that optimizing volume fraction alone is insufficient for designing mechanically competent 3D printable nanocomposites, urging more focus on nanoparticle distribution and alignment. While increasing inclusion volume fraction faces limitations due to viscosity challenges, enhancing aspect ratio and alignment within a constant volume fraction proves effective for enhancing mechanical properties. The findings in this study can be used as design guidelines for developing mechanically competent 3D printable nanocomposite materials.

# 5 REFERENCES

[1] S. Fu, Z. Sun, P. Huang, Y. Li, and N. Hu, "Some basic aspects of polymer nanocomposites: A critical review," *Nano Mater. Sci.*, vol. 1, no. 1, pp. 2–30, 2019, doi: 10.1016/j.nanoms.2019.02.006.

[2] J. Mehta *et al.*, "Effect of nanofillers and nanotoxicity on the performance of composites: Influencing factors, future scope, challenges and applications," *Polymer Composites*, vol. 43, no. 6. John Wiley and Sons Inc, pp. 3335–3349, Jun. 01, 2022. doi: 10.1002/pc.26635.

[3] M. Naffakh, A. M. Díez-Pascual, C. Marco, G. J. Ellis, and M. A. Gómez-Fatou, "Opportunities and challenges in the use of inorganic fullerene-like nanoparticles to produce advanced polymer nanocomposites," *Progress in Polymer Science*, vol. 38, no. 8. pp. 1163–1231, 2013. doi: 10.1016/j.progpolymsci.2013.04.001.

[4] A. Kausar, I. Rafique, and B. Muhammad, "Aerospace Application of Polymer Nanocomposite with Carbon Nanotube, Graphite, Graphene Oxide, and Nanoclay," *Polymer - Plastics Technology and Engineering*, vol. 56, no. 13. Taylor and Francis Inc., pp. 1438–1456, Sep. 02, 2017. doi: 10.1080/03602559.2016.1276594.

[5] S. Y. Fu, X. Q. Feng, B. Lauke, and Y. W. Mai, "Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate-polymer composites," *Compos. Part B Eng.*, vol. 39, no. 6, pp. 933–961, 2008, doi: 10.1016/j.compositesb.2008.01.002.

[6] M. Chwał and A. Muc, "Design of reinforcement in nanoand microcomposites," *Materials (Basel).*, vol. 12, no. 9, 2019, doi: 10.3390/ma12091474.

[7] P. Jojibabu, Y. X. Zhang, and B. G. Prusty, "A review of research advances in epoxy-based nanocomposites as adhesive materials," *Int. J. Adhes. Adhes.*, vol. 96, 2020, doi: 10.1016/j.ijadhadh.2019.102454.

[8] K. Baek, W. Lee, H. Shin, and M. Cho, "Multiscale study on determining representative volume elements size for mechanical behaviours of complex polymer nanocomposites with nanoparticulate agglomerations," *Compos. Struct.*, vol. 253, 2020, doi: 10.1016/j.compstruct.2020.112796.

[9] S. S. Hashemi, "Experimental and Computational Micromechanical Investigations for Developing Mechanically Competent 3D Printable Nanocomposite Biomaterials," 2023, Accessed: Dec. 21, 2023. [Online]. Available: https://uwspace.uwaterloo.ca/handle/10012/19887

[10] J. L. Katz, P. Spencer, Y. Wang, A. Misra, O. Marangos, and L. Friis, "On the anisotropic elastic properties of woods," *J. Mater. Sci.*, vol. 43, no. 1, pp. 139–145, 2008, doi: 10.1007/s10853-007-2121-9.

[11] A. Abedini, C. Butcher, and M. J. Worswick, "Fracture Characterization of Rolled Sheet Alloys in Shear Loading: Studies of Specimen Geometry, Anisotropy, and Rate Sensitivity," *Exp. Mech.*, vol. 57, no. 1, pp. 75–88, Jan. 2017, doi: 10.1007/s11340-016-0211-9.

[12] A. Fritsch, L. Dormieux, C. Hellmich, and J. Sanahuja, "Mechanical behavior of hydroxyapatite biomaterials: An experimentally validated micromechanical model for elasticity and strength," *J. Biomed. Mater. Res. - Part A*, vol. 88, no. 1, pp. 149–161, Jan. 2009, doi: 10.1002/jbm.a.31727.

[13] F. Sharifpour, J. Montesano, and R. Talreja, "Assessing the effects of ply constraints on local stress states in cross-ply laminates containing manufacturing induced defects," *Compos. Part B Eng.*, vol. 199, 2020, doi: 10.1016/j.compositesb.2020.108227.