Characterization and Modeling of Carbon Black/Ultra-High-Molecular-Weight-Polyethylene Nanocomposites Manufactured with Equal Channel Angular Extrusion

Kateryna Miroshnichenko[1, a)], Stanislav Buklovskyi[1, b)], Kostiantyn Vasylevskyi[2, c)], Igor Tsukrov[1, d)], Hannah J. Favreau[3, e)], Rebecca J. Thomson[3, f)], Peder C. Solberg[3, g)], Douglas W. Van Citters[3, h)]

[1]*University of New Hampshire, Durham, NH 03824 USA*
[2]*Callentis Consulting Group, Austin, TX 78704 USA*
[3] *Dartmouth College, Hanover, NH 03755 USA*

[a)] Kateryna.Wells@unh.edu
[b)] S.Buklovskyi@unh.edu
[c)] kostia@callentis.io
[d)] Corresponding author: Igor.Tsukrov@unh.edu
[e)] hannah.j.favreau.th@dartmouth.edu
[f)] Rebecca.J.Thomson.TH@dartmouth.edu
[g)] Peder.Solberg.TH@dartmouth.edu
[h)] Douglas.W.Van.Citters@dartmouth.edu

Abstract. Ultra-High Molecular Weight Polyethylene (UHMWPE) is widely used as a bearing surface in total and partial joint arthroplasty. In addition to medical applications, this polymer is utilized in the fields of ballistic protection, sports, and industrial tribology. The addition of carbon allotropes, such as nanographite or carbon black powders, to UHMWPE offers potential benefits including added conductivity, increased wear resistance, and introduction of micro-tracers for understanding microstructural behavior and monitoring damage [1]. The mechanical properties of these Carbon/UHWPE nanocomposites can be enhanced by subjecting them to equal channel angular extrusion (ECAE) as a way to introduce large shear strains to achieve higher molecular entanglement of UHMWPE and better distribution of carbon nanoparticles [2, 3].

In this paper, micro-computed tomography (μCT) is used to characterize carbon black (CB) and nanographite (N27SG) reinforced UHMWPE polymers. It is shown that the procedure described in [1] results in almost uniform distribution of carbon inclusions around UHMWPE particles with both compression molding (CM), and ECAE processes. Multiscale numerical models of the composite are developed based on the μCT images, including mesoscale finite element (FE) models of representative volume element (RVE) on the mesoscale, and micromechanical predictions for carbon-rich interphase layers on the microscale.

INTRODUCTION

Using carbon reinforcement with UHMWPE polymers provides additional functional opportunities associated with increased electrical conductivity, improved wear resistance, and potential improvements in electromagnetic interference shielding. Nanocomposites with CB and N27SG inclusions can be manufactured by a well-developed CM technique. Recently, ECAE process has been considered as a way to improve the overall properties of UHMWPEs and Carbon/UHMWPE composites. It involves extrusion of the material to impose significant shear strains to achieve higher molecular entanglement and better distribution of carbon inclusions. The resulting microstructure of the composites and their mechanical and electrical properties have been described in [7] and references therein, mostly focusing on N27SG inclusions.

This paper focuses on the UHMWPE reinforced with CB, but the results for N27SG are also included for comparison. It is shown that the μCT data can be used to develop numerical models of the composite.

The paper is organized as follows. First, we present the results of μCT studies of the composites. Then, development of mesoscale (on the order of UHMWPE particles) models of the material is discussed. After that, the manufacturing information is combined with μCT data to extract CB volume fraction in carbon-rich interphase layers between UHMWPE particles. Finally, Eshelby tensor-based Mori-Tanaka scheme is used for micromechanical modeling of these interphase layers.

PROCESSING OF μCT

The microstructure of ECAE and CM processed Carbon/UHMWPE composites was determined by μCT. Specimens containing 0.5 wt%, 1.0 wt.%, 1.5 wt.%, 5 wt.%, and 10 wt.% of CB were analyzed. In addition, for comparison, composites with the same N27SG load were considered. A set of the samples also underwent the remelting process to check if it affects the microstructure of the composites. A total of 20 samples were scanned. The μCT scans were performed using ZEISS Xradia 610 Versa microscope.

Figure 1 shows examples of microstructures for 1.5 wt.% CB and N27SG specimens produced with ECAE and CM processing techniques. The scanned region was 9.35 x 107 μm^3. Gray corresponds to UHMWPE resin particles; areas containing carbon inclusions are seen as white. Dark gray circles on the top of the specimens are artifacts caused by the cone beam-based x-ray system.

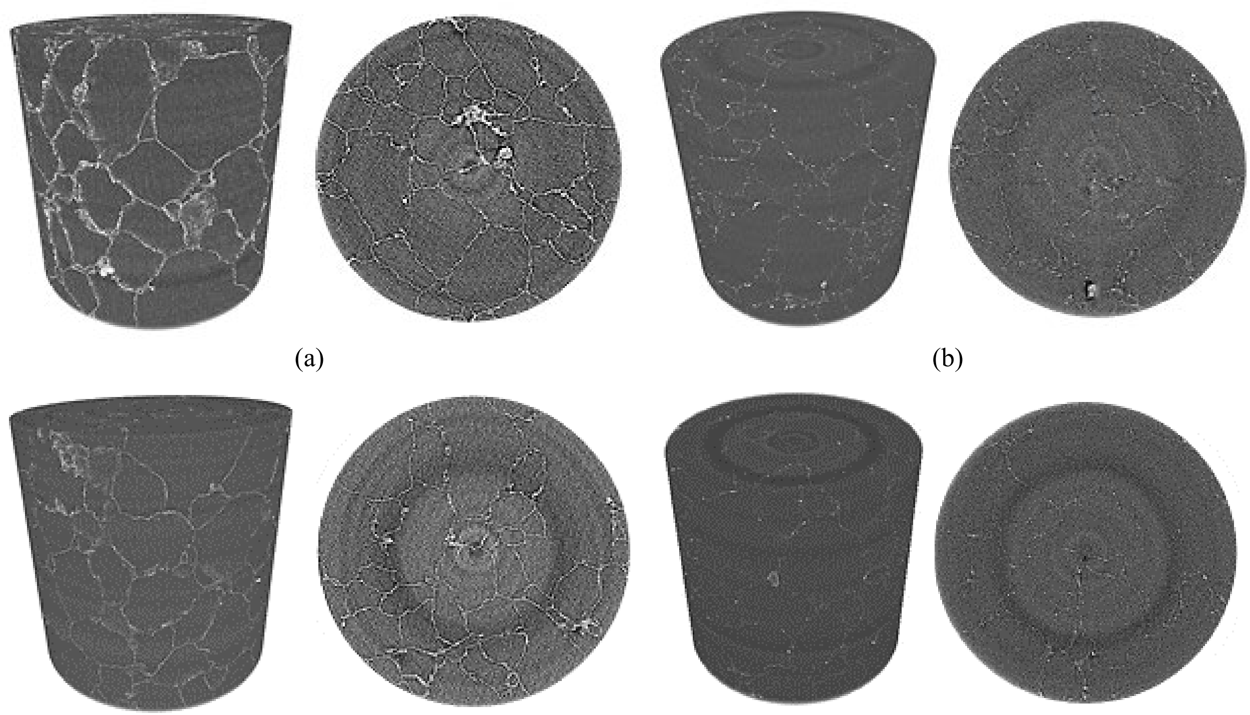


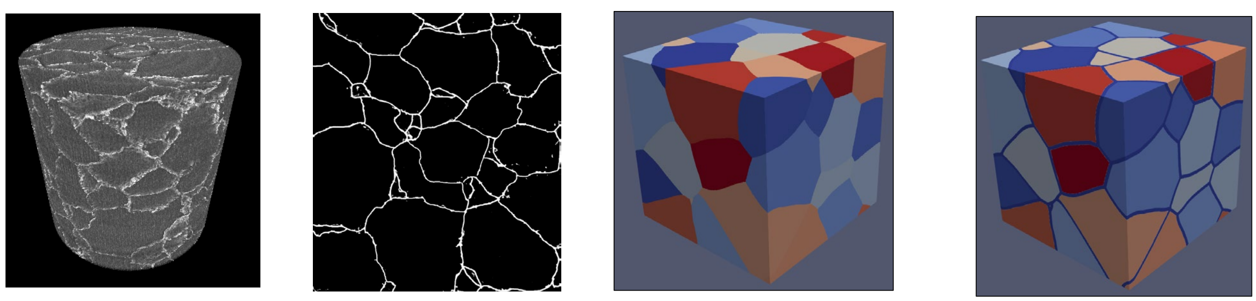
FIGURE 1. Samples with 1.5% weight load of carbon: (a) CB/UHMWPE produced by CM, (b) N27SG/UHMWPE produced by CM, (c) CB/UHMWPE produced by ECAE, (d) N27SG/UHMWPE produced by ECAE

It was observed that CB particles for all weight fractions form a more uniform boundary layer as compared to nano-graphite particles which agglomerate into clusters. It was also observed that the ECAE process leads to thinning of the carbon-rich boundary layer between the polymer grains. This effect can be attributed to the friction between the grains during angular extrusion leading to smearing of the boundary. For large volume fractions (5%, 10%) of carbon there were some voids, mostly located in agglomerations of carbon inclusions. However, ECAE process appeared to make agglomerations and voids smaller and less noticeable. Finally, it was observed that remelting process does not affect the microstructure of the composite.

Analysis of the image shows that carbon inclusions are distributed around UHMWPE particles forming a carbon-rich layer with high volume fraction of the inclusions. This layer was explicitly incorporated in the mesoscale numerical models of Carbon/UHMWPE composites.

MESOSCALE MODEL OF CB/UHMWPE COMPOSITES

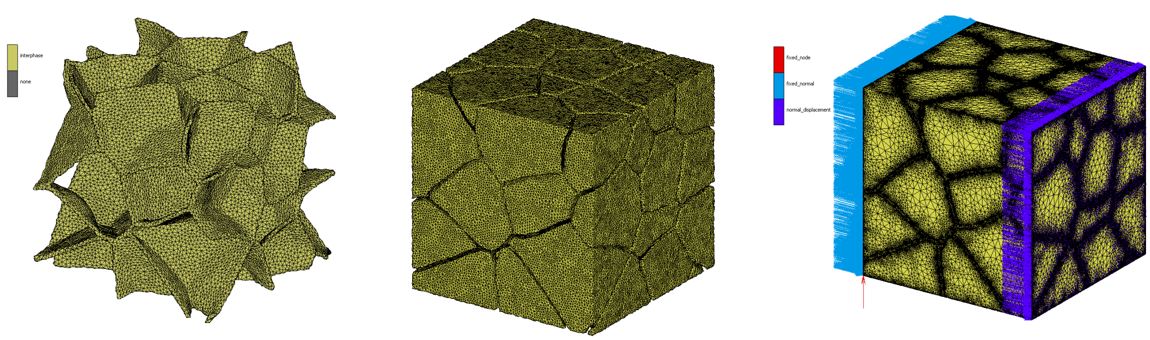
The μCT images were used to develop mesoscale numerical models of the considered CB/UHMWPE composites. Finite element models of representative volume element (RVE) were developed. The statistics on size, shape, and orientation distribution of UHMWPE particles and spatial distribution of carbon inclusions were extracted. This statistics was used to create synthetic microstructures in *Dream3D* open-source software [http://dream3d.bluequartz.net/]. The data from *Dream3D* was exported as a file in VTK format where each feature (particle) had its own label (number). This file was used to obtain representation of the RVE as a labeled 3D matrix of integer numbers. Each number in the matrix represents a voxel that belongs to the feature of the corresponding number. The carbon-rich interphase layer, observed in μCT, was introduced separately by a custom *MATLAB* image processing script. The script involves finding a perimeter layer of each feature and relabeling that layer. Faces of the RVE required a special treatment. The algorithm can be repeated, the number of repetitions is determined by the desired thickness of the interphase layer. Figure 2 illustrates the algorithm of the RVE developed process.



(a) (b) (c) (d)

FIGURE 2. Synthetic microstructure reconstruction framework: (a) Raw μCT scan of Carbon/UHMWPE composite, (b) Images processed via Dragonfly and MATLAB, (c) Synthetic microstructure of the composite, (d) Synthetic microstructure of the composite with additional interphase layer

The generated RVEs were converted to FE meshes utilizing *Iso2Mesh* open source [http://iso2mesh.sourceforge.net/] package as shown on Fig. 3.



(a) (b) (c)

FIGURE 3. FEA mesh of Carbon /UHMWPE RVE: (a) Carbon-rich interphase, (b) UHMWPE particles, (c) Boundary conditions for "prescribed strain" FEA simulations

Initially, RVEs are stored in a form of volumetric matrix, where each feature has its own unique integer label. To generate FE mesh all UHMWPE particles were labeled as phase "1" and the interphase layer was labeled as phase "2" of the composite. This process results in 3D volume matrix with two labels which can be meshed into labeled volumetric tetrahedral elements using *Iso2mesh.* This mesh can be exported into *MSC Marc* using a custom *MATLAB* formatting script.

The resulting finite element models of RVEs can be used to determine the effective mechanical and thermal properties of Carbon/UHMWPE composites with various volume fractions and levels of dispersion of CB inclusions. Numerical simulations for the composites' effective properties based on these FEA meshes are underway.

ANALYSIS OF μCT IMAGES FOR NUMERICAL MODELING

White layers surrounding each UHMWPE particle in μCT images (as shown in Fig. 1) contain high concentration of carbon inclusions, as schematically represented in Fig. 4.

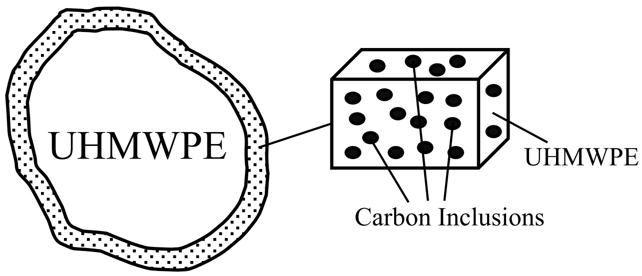


FIGURE 4. Schematics of UHMWPE particle surrounded by carbon-rich layer.

In this paper we consider micromechanical modeling of UHMWPE with CB inclusions. The volume fraction ($f_{c/L}$) of the inclusions in the layer can be evaluated as a ratio of the volume fraction of inclusions in the overall composite (f_v) and the volume fraction of white-colored regions in the μCT images, as evaluated by *Dragonfly* software [https://www.theobjects.com/index.html]:

$$f_{c/L} = \frac{f_v}{f_L}, \tag{1}$$

where

$$f_v = \frac{f_w}{f_w + \left(1 - f_w\right)\dfrac{\rho_c}{\rho_m}}, \tag{2}$$

f_w is the weight fraction of the inclusions in the composite, ρ_c = 1.9 g/cm^3 is the density of CB inclusions, and ρ_m = 0.93 g/cm^3 is the density of UHMWPE. The results are summarized in Table 1.

TABLE 1. Percent volume fractions of CB-containing phase observed by μCT.

f_w	f_v	f_L	$f_{c/L}$
0.5	0.25	0.4	0.61
1	0.49	1.5	0.33
1.5	0.74	2.3	0.32
5	2.5	5.5	0.46
10	5.16	9.0	0.57

MICROMECHANICAL MODELING OF CARBON-RICH LAYER

The effective elastic properties of the carbon-rich layer were defined by utilizing Mori-Tanaka micromechanical scheme [4,5]. CB inclusions were modeled as spherical inhomogeneities with the corresponding Eshelby tensor. In the case of elastic properties, the micromechanical prediction of the overall stiffness tensor is

$$\underline{C} = \left(f_m \underline{C}_m + f_{c/L} \underline{C}_i : \underline{A}\right) : \left(f_m \underline{I} + f_{c/L} \underline{A}\right)^{-1} \quad (3)$$

where $\underline{I}$ is the 4[th] order identity tensor, subscripts m and i denote matrix and inclusions; $\underline{C}_m$ and $\underline{C}_i$ denote the tensors of elastic moduli of the corresponding phases, $f_{c/L}$ and $f_m = 1 - f_{c/L}$ are the volume fractions of matrix and inclusions, respectively, $\underline{A}$ is the 4[th] order strain concentration tensor $\underline{A} = \left[\underline{I} + \underline{S} : \left(\underline{C}_m\right)^{-1} : \left(\underline{C}_i - \underline{C}_m\right)\right]^{-1}$, and $\underline{S}$ is the Eshelby tensor for spherical inclusion.

For stiff carbon black particles (assumed perfectly rigid as compared to UHMWPE having E=670 MPa [6], G=260 MPa), the required values of the Young's and shear moduli with volume fraction $f_{c/L}$ are given in Table 2. These predictions are used as material properties of the carbon-rich interphase in the meso-scale FEA models.

TABLE 2. Effective properties of UHMWPE composite reinforced with CB inclusions

$f_{c/L}$	E/E_{UH}	G/G_{UH}
0	1	1
0.32	1.95	1.98
0.33	1.99	2.03
0.46	2.73	2.79
0.57	3.68	3.78
0.61	4.16	4.28

DISCUSSION AND CONCLUSIONS

The presence of carbon particles (CB or N27SG) in UHMWPE can provide additional functionality such as increased stiffness, electric conductivity, and wear resistance. Analysis of μCT images shows that for the considered manufacturing processes (CM and ECAE), it is possible to achieve almost uniform distribution of carbon inclusions around UHMWPE particles with minimum porosity. CB inclusions disperse better while N27SG inclusions form more clusters. However, ECAE process facilitates better dispersion of the inclusions and reduction in porosity. Also, remelting doesn't change the overall microstructure of the composite. Note that these μCT observations are also supported by optical and SEM microscopy, and infrared spectrometry [1, 7].

Numerical modeling of Carbon/UHMWPE composites can be performed on two length scales. First, microscale modeling of carbon-rich layer surrounding each UHMWPE particle is conducted using Mori-Tanaka micromechanical scheme. Contributions of CB and N27SG inclusions are evaluated with the Eshelby tensor for spherical or oblate spheroidal shapes. Secondly, a FE model of RVE is considered. The model has two phases, UHMWPE particles and the carbon-rich interfacial layer with the properties previously determined by micromechanical modeling. Applying the prescribed strain or the prescribed temperature boundary conditions, the overall mechanical and thermal properties of the composite can be obtained.

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