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The Shape and Size Effect of the Diatom Frustule Addition on the Compression Behavior of an Epoxy

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Abstract. The effects of the *Achnanthes Taeniata* and the diatomaceous earth (diatomite) frustules addition on the compressive strength of an epoxy matrix were investigated experimentally. The *Achnanthes Taeniata* frustules having relatively high length/diameter aspect ratio (2-4) were isolated and cultured in laboratory. While the as-received commercial natural diatomite frustules were non-homogenous in shape and size. The filling epoxy matrix with ~6 wt% of commercial natural diatomite increased the compressive strength from 60 MPa to 67 MPa, while the *Achnanthes Taeniata* frustules addition increased to 79 MPa. The increased compressive strength and modulus of the the *Achnanthes Taeniata* frustules filled epoxy was attributed to the higher aspect ratio and relatively strong bonding with the epoxy matrix. The more effective load transfer from the matrix to the *Achnanthes Taeniata* frustules associated with the enhanced interface bonding was also proved microscopically. The frustules were observed to pull-out on the fracture surface of the *Achnanthes Taeniata* frustules filled epoxy.

Introduction

Diatoms are a group of unicellular chlorophyte algae with the size range of 5 μm and 5 mm. The centric type diatoms are radially symmetric and circular in shape and the pennate diatoms are bilaterally symmetric with elongated shapes [1]. The skeleton of diatoms is known as frustule, which is made of amorphous silica, and the surface of the skeleton is coated with an organic surface layer. The frustules have regularly arranged pores on their surfaces with the sizes of 10-200 nm [2]. They are only soluble in strong alkali acids such as hydrogen fluoride. Diatomaceous earth, also known as diatomite or kieselguhr, is a sedimentary siliceous rock formed by the accumulation of the dead diatom cells in the bottom of the oceans or fresh waters [3]. Diatomite is mainly used as filtration material, abrasive, insecticide, soil conditioner and cement additive [4] as well as the filler material in polymers [5]. The three-dimensional structure of diatoms has also potentials to be used in the processing of microelectronic devices [6]. Diatoms, as being biocompatible, have also potentials for the applications in the drug-delivery as they have relatively high surface area (100 m^2/g) associated with the nano-porous structure. The shapes of the frustules can be altered by varying the silicification degree [6,7].

The mechanical properties of the frustules have shown to vary with the location of the measurement, attributed to the varying degree of bio-mineralization [8-12]. The elastic modulus of *Coscinidiscus* ranged 1.5-15.6 GPa and *Navicula pelliclosa* 7-100 GPa, depending on the location of the measurements taken [13]. When frustules are used as filler in polymer matrices, a strong interlocking between the polymer matrix and frustules is expected due to the high surface area and nano-porous surface layer structure of the frustules. In a previous study, the compressive modulus and yield strength of an epoxy matrix were shown to increase with the diatom frustule addition and the stress enhancement of filled epoxy was ascribed to relatively high strength of frustules and strong interlocking between the frustules and the polymer matrix [5,14]. It was also shown that the

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filling the epoxy matrix with the heat-treated frustules at a certain temperature maximized the matrix strengthening of the composite [15]. The present study is a continuation of the previous studies and aims to investigate the effect of diatom frustules' shape and size on the compression stress-strain behavior of a polymer matrix at quasi-static strain rate. For that, pennate type in-house cultured *Achnanthes Taeniata* frustules and commercial diatomaceous earth frustules were used as fillers in an epoxy matrix. The results of the compression tests were used to identify the effect of frustule's shape on the mechanical properties.

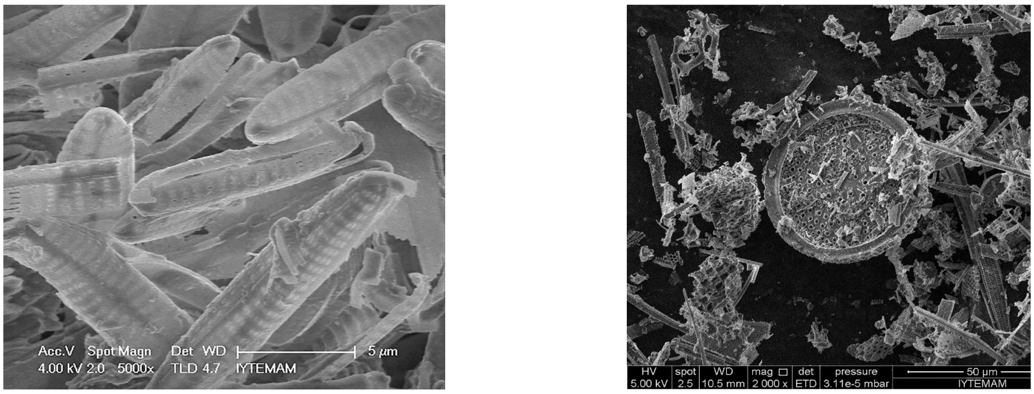
Materials and Method

The isolation of the *Achnanthes Taeniata* frustules and the following diatom culturing processes were given in details elsewhere [16]. In a final processing stage, the cultured diatom solution was subjected to nitric acid digestion to remove the residual salts such as sodium chloride, potassium chloride and calcium chloride and as well as the organic layer on the surface of the diatoms. The natural diatom frustules (Johnson Matthey Co., England) are composed of various types of frustules species, including pennate and centric types. The crystallographic structure of diatom frustules was determined using Philips X'Pert Pro X Ray Diffraction (XRD) device (Cu-Kα radiation, λ=1.54 A° and 40 kV, 5-80^o general scanning). The elemental composition of diatom frustules was determined using Spectro IQ II X Ray Fluorescence (XRF) device. The chemical bonding of frustules was determined with Perkin Elmer FTIR System Spectrum BX Fourier Transform Infrared Spectroscopy (FT-IR) device. FT-IR analysis was performed in a range of 400-4000 cm^{-1} wavenumbers. The morphological properties and surface topography of frustules and frustule filled composite samples were investigated using FEI Quanta 205 FEG and Philips XL-30S FEG Scanning Electron Microscopy (SEM) in secondary electron and back scattered electron modes.

Bispenol A-type epoxy resin was used as the matrix for diatom frustule filling due to its high strength and dimensional stability after thermal curing. Nitric acid treated the *Achnanthes Taeniata* frustules and diatomite frustules were mixed with the epoxy resin using an Ultra-Turrax T 25 IKA digitally controllable mechanical disperser at 20000 rpm. Mixing process was continued until a homogeneous mixture was obtained. The mixture was then subjected to vacuum (-1 Pa) to remove the entrapped gas bubbles. The air bubbles risen to the surface of the mixture was burst after a while as a result of the vacuum environment. Then the hardener (Grandmer VN-111, Süper Selva Şti, İzmir, Turkey) with an amount 25% of epoxy resin was added to the mixture. The mixture was then stirred gently not to create new air bubbles and poured into a silicon mold (4x4x1 cm). The mixture was allowed to stay in the mold at room temperature for 24 h. After the polymerization reaction, the sample was removed from the mold and cured at 110°C for 5 h. The compression test samples were core drilled from the molded composite plates. During core drilling water was used as coolant. The test samples were 9.80 mm in diameter and 12 mm in length with an aspect ratio of 1.22. For comparison neat epoxy samples were also prepared using the same procedure. The compression tests were performed using Shimadzu universal testing machine at a crosshead speed of 5 mm/min corresponding to a strain rate $7x10^{-3}$ s^{-1}. Before each test the compression platens were lubricated using grease. The composite samples for microscopy were prepared by mounting the samples in Buehler epo-wick branded fast curing epoxy. Samples were grinded with Buehler Met-II SiC grinding papers through 800, 1000, 1200, 2000 and 2400 grids. Then, the samples were polished sequentially 9 µm, 6 µm, 3 µm and 1 µm diamond solution.

Results and Discussion

The SEM picture of the cultured *Achnanthes Taeniata* frustules is shown in Fig. 1(a). The *Achnanthes Taeniata* frustules are pennate type and their lengths vary between 6 µm and 12 µm, the width between 3 and 4 µm with the aspect ratios between of 2 and 3. The pore size on the frustule walls ranged 100-200 nm. The as-received diatomaceous earth powder is composed of both centric and pennate diatom frustules as seen in Fig. 1(b). Ninety percent of as-received diatomaceous earth powder frustules were smaller than 54.37 µm and 10% less than 3.964 µm with a mean particle size of 15.09 µm. The crushed frustules seen in the same figure resulted from the milling process applied by the producer.



(a) (b)

Fig. 1 The SEM picture of (a) *Achnanthes Taeniata* frustules after nitric acid treatment and drying and (b) as-received commercial diatomite

The XRD spectra of *Achnanthes Taeniata* frustules are shown in Fig. 2(a). The major phase is amorphous opal-A structure. The *Achnanthes Taeniata* frustules, based on the XRF analysis, are composed of 81 % SiO_2, 1.4 % MgO and 1.1 % Na_2O. The FTIR analysis of *Achnanthes taeniata* diatom frustules is shown in Fig. 2(b). Peaks at 468.11, 548.11, 857.29, 844.86 and 1081.08 cm^{-1} correspond to the Si-O bonding and the peak at 779.45 cm^{-1} to Si-O-Si bonding. The remaining peaks are likely due to the residual organics in the powder. The XRD spectra of as-received commercial diatomaceous earth powder reveal an amorphous opal structure as the major phase and the quartz as the minor phase (Fig. 2(c)). The diatomaceous earth powder consists of 90 % of SiO_2, 5 % of Al_2O_3, 1.5 % of Fe_2O_3, 1 % of MgO, and 0.5 % of CaO. The FTIR spectra of the as-received diatomaceous earth powder is shown in Fig. 2(d). The characteristic Si-O-Si peaks at 470, 790 and 1090 cm^{-1} are seen in the same figure.

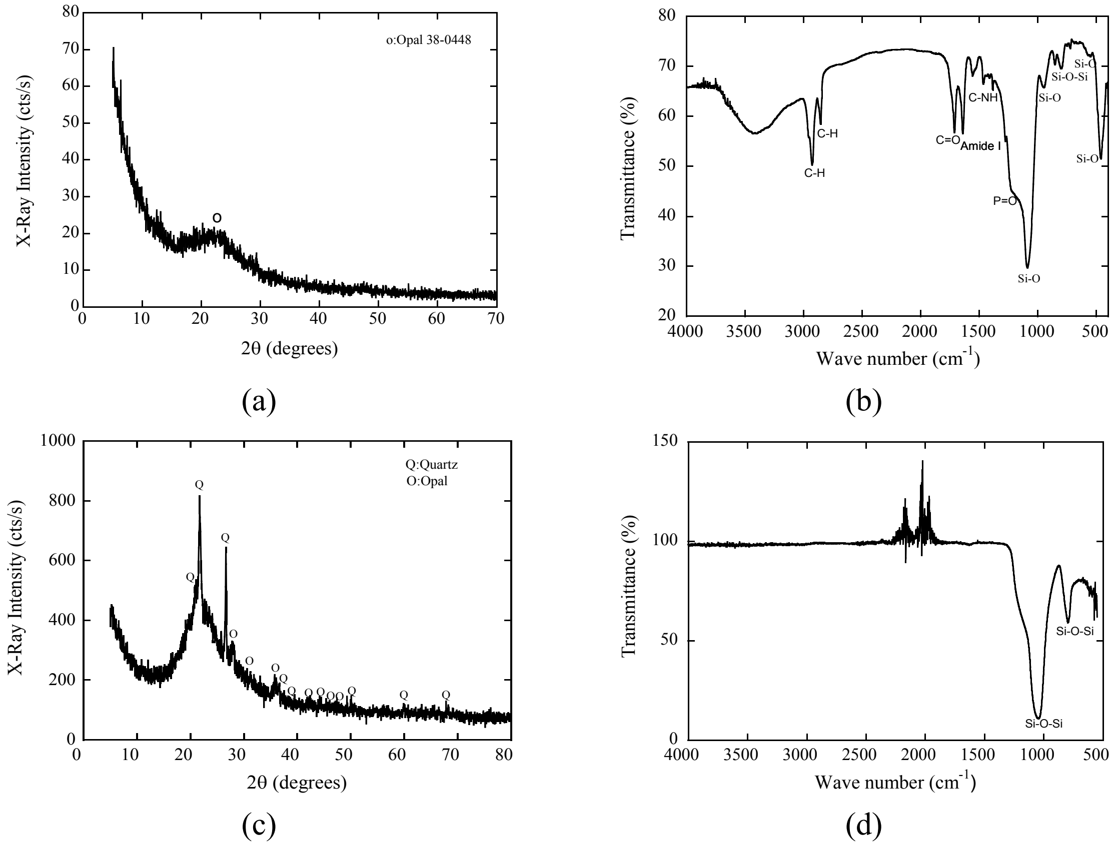
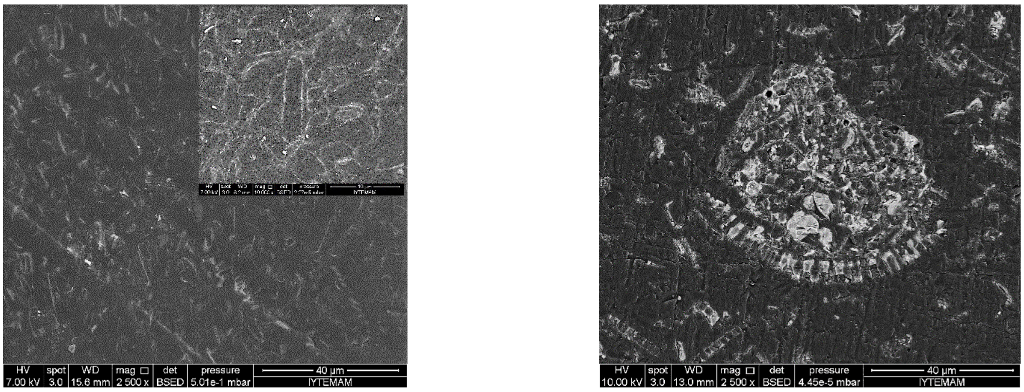


Fig. 2 (a) The XRD spectra and (b) FTIR analysis of *Achnanthes taeniata* diatom frustules after nitric acid digestion and (c) The XRD spectra and (d) FTIR analysis of as-received commercial diatomite

The cross-sectional SEM micrographs of polished surfaces of the mechanical test samples (normal to the compression axis) of the *Achnanthes Taeniata* frustule and diatomite filled epoxy are shown in Fig. 3(a) and (b), respectively. The distribution of the *Achnanthes Taeniata* frustules in the epoxy matrix is relatively homogenous and near planar random as depicted in the inset of Fig. 3(a). Very large and small frustules are seen in the natural diatomite filled epoxy sample in Fig. 3(b). The representative nominal compressive stress-strain curves of neat epoxy, *Achnanthes Taeniata* frustule and diatomite filled epoxy matrices are shown in Fig. 4. The tests were repeated at least three times. The compressive strength is the initial maximum stress as shown in Fig. 4. After the maximum stress, the deformation presumable proceeds inelastically. The compressive strength values of three tests were averaged and reported in present study. Filling epoxy matrix with ~6 wt% of natural commercial diatomite increased the compressive strength from 60 MPa to 67 MPa and *Achnanthes Taeniata* frustule to 79 MPa, respectively. A higher strengthening, ~10 MPa, and increased elastic modulus are found with the *Achnanthes Taeniata* frustule addition. The increased compressive yield strength is attributed to the increased aspect ratio of the *Achnanthes Taeniata* frustules compared to the natural diatomite. The *Achnanthes Taeniata* frustules have homogeneous geometry with almost the same aspect ratio. On the other side, commercial diatomite frustules have non-homogeneous geometry with varying aspect ratios.

The SEM pictures of the fracture surfaces of the *Achnanthes Taeniata* frustules and diatomite filled epoxy samples are shown in Fig. 5(a) and (b), respectively. The fracture surface of the *Achnanthes Taeniata* frustules filled epoxy sample consists of debonded and pull-out frustules. The *Achnanthes Taeniata* frustules remain unfractured on the fracture surface (Fig. 5(a)). While, the large size natural diatomite frustules are seen to be debonded and also fractured on the fracture surface (Fig. 5(b)). The fracture surface SEM images have clearly shown that the stronger bonding between frustules and matrix in the *Achnanthes Taeniata* frustules filled epoxy lead to the efficient loading of the stronger the *Achnanthes Taeniata* frustules and hence increased modulus and compressive strength.



(a) (b)

Fig. 3 The SEM images of polished surfaces of (a) *Achnanthes Taeniata* frustule filled epoxy and (b) diatomite filled epoxy

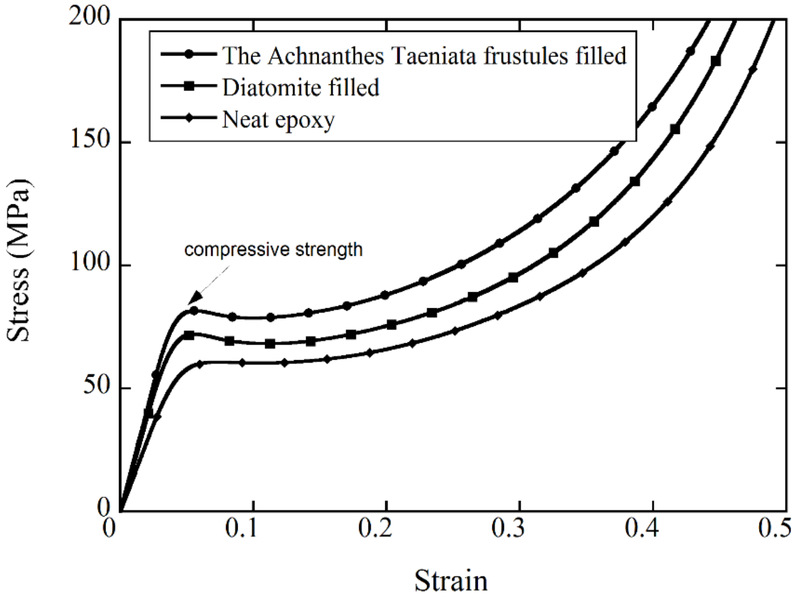
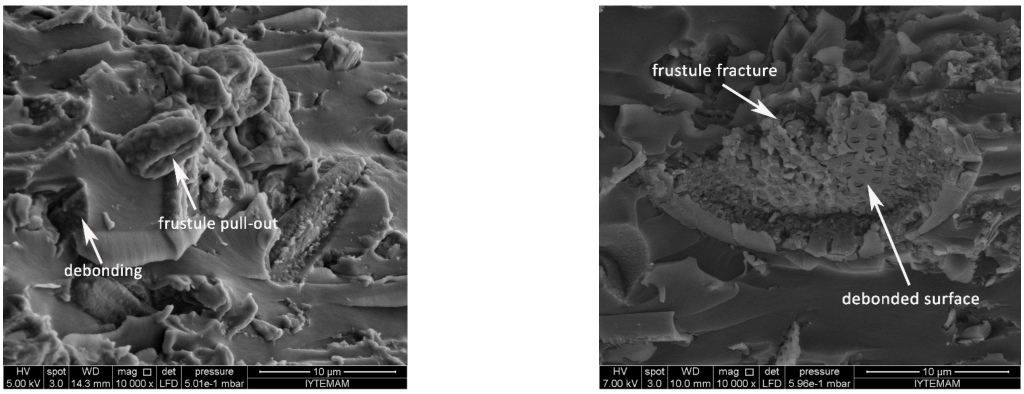


Fig. 4 The compressive stress-strain curves of neat epoxy, *Achnanthes Taeniata* frustule filled epoxy and diatomite filled epoxy



(a) (b)

Fig. 5 The SEM images of fracture surfaces of a) *Achnanthes Taeniata* frustule filled epoxy and (b) diatomaceous earth filled epoxy

Conclusions

The effect of filling of an epoxy matrix with the *Achnanthes Taeniata* frustule homogenous in shape and size and the diatomite frustules non-homogenous in shape and size was experimentally investigated through compression testing. Although, both frustule additions increased the compressive strength of neat epoxy, the effect further increased with the *Achnanthes Taeniata* frustule addition. The increased compressive strength and modulus of the the *Achnanthes Taeniata* frustule filled epoxy was attributed to the increased aspect ratio and relatively strong bonding with the matrix. This was proved with the SEM micrographs of the *Achnanthes Taeniata* frustule filled epoxy fracture surface showing the excessive frustules pull-out.

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