COMSOL simulation of CNT assembly in an epoxy matrix under static magnetic fields for polymer nanocomposite applications

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Organization of carbon nanotubes (CNTs) within epoxy matrices can be effectively achieved using magnetic field application. In our previous experimental work, multi-walled CNTs were magnetized, diazotized, and magnetically aligned to form aligned CNT-epoxy composites. While effective toughness improvement was experimentally observed with small CNT addition, more understanding about magnetic assembly of CNTs is desired, to effectively complete CNT assembly before the epoxy cures and also to avoid re-agglomeration of CNTs. In this work, assembly behaviors of ellipsoid particles, that simulate CNT bundles, in a fluid domain, that simulates the epoxy matrix, under the static magnetic field are being studied. Higher ellipsoid aspect ratio was observed to be effective to decrease the magnetic assembly time, while some ellipsoid lower aspect ratio and larger original ellipsoid separate distance combination prevented their magnetic assembly. When assembly is achieved, the assembly time was observed to be much smaller (<0.1 second) than the currently dedicated assembly time in our experiments (~10s of minutes). Further studies with more ellipsoids, varying ellipsoid positions, and increasing magnetic field strength are planned in future.

I. Introduction

Nanoparticle reinforcement of polymer matrices has been of interests to the aerospace community due to their potential multi-functional applications. Among various nanoparticles, carbon nanotubes (CNTs) has been especially studied intensively due to their light weight, and their exceptional mechanical, electrical, thermal, and even smart functions: ~1000 GPa stiffness, >10 GPa strength [1], ~<1 mΩ.cm electrical resistivity [2], and ~6600 W/(m.K) thermal conductivity [3]. Meanwhile, effective integration of CNT into epoxies and elastomers is still a challenge. CNTs tend to agglomerate due to their small size; surface functionalization has been effective to disperse and suspend CNTs within matrices, providing effective mechanical property reinforcement [4, 5].

After effective mixing of CNTs within matrices, CNT organization is still sought after for anisotropic reinforcement; aligned CNTs are expected to be more effective, for example in fracture toughness reinforcement by crack bridging [6] and also in anisotropic electrical and thermal conduction. So far, mechanical shearing and field application (acoustic, electrical, and magnetic [2, 7-10]) have been attempted to align CNTs. In our laboratory, we employ magnetic fields to align CNTs as this method enables non-contact CNT organization with three-dimensional tailorability with the moderate strength (~100s of G, slightly higher than the fridge magnet) in a short assembly time [11, 12]. In addition, unlike acoustic and electric field applications, magnetic field will not be affected by damping and insulation from viscous matrices. Yet, magnetic assembly of CNTs within polymer matrices need to be studied further in order to achieve the desired CNT morphology.

In this work, multi-physics simulation was conducted using COMSOL software to understand the effect of various parameters on CNT assembly. In experimental work, fracture toughness improvement of 71.66% was achieved by adding 0.5 vol.% of CNTs aligned with the magnetic field of 180 G [13]. Magnetic assembly of CNTs is conducted at the working temperature to reduce the viscosity, and CNT assembly needs to be completed before the polymer cures and the viscosity increases. In addition, higher magnetic field application (300 G) resulted in smaller fracture toughness improvement: 20.49% improvement with 0.5 vol% CNTs aligned with 300 G. This trend can be attributed to CNT re-agglomeration by magnetic assembly. The aspect ratio of CNTs is expected to help to provide higher magnetic moment, and also to experience higher viscous moment to resist movement. Below, ellipsoids that simulate CNT bundles will be applied with the magnetic field, and the effect of original CNT distribution (inter-ellipsoid distance and relative orientation) on the time required to complete assembly will be evaluated.

II. Materials and Methods

A. Setting the CNT bundle size and shape from our experimental studies

First, to identify the ellipsoid particle size to be simulated, CNT agglomerate size and shape were inspected. In our experimental work, multi-walled CNTs (~200 μm length as grown) are coated with thin nickel layer (~80 nm) to make them magnetically responsive, and then functionalize their surface using diazotization [14] to disperse them in a selected epoxy system (EPON 862 resin and EPIKURE W hardener). These processed CNTs were dispersed with DMF solution, and were inspected under optical microscope. The CNTs were looser but still agglomerated as bundles, and the CNT bundle length and width were measured as 14 ± 4 μm and averaged as 3 ± 1 μm when averaged over 108 measurements (see **Figure 1**); the aspect ratio can thus be calculated as 9 ± 2. In the COMSOL simulation, such CNT bundles were simulated as an ellipsoid with this measured aspect ratio, because the analytical solutions exist for viscous forces and torques about ellipsoids [15].

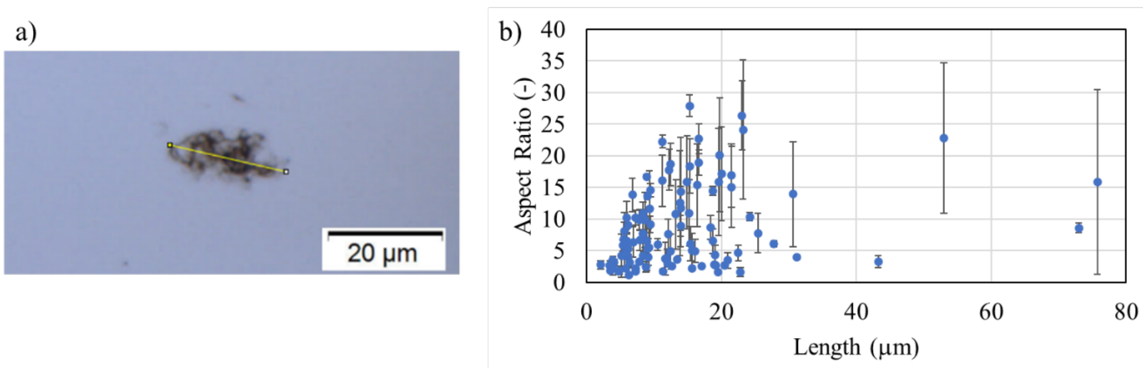

Fig. 1 Measurement of the processed CNT bundles: a) optical microscopy image, and b) measured aspect ratio.

B. Setting the COMSOL simulation

A two-dimensional square plane was set up (80 μm side length), and ellipsoid particles were placed with varying aspect ratio, relative orientation (0 deg - 90 deg), and inter-particle distance (5 μm - 20 μm), while keeping the volume of the particles (62.8 μm^3), as shown in **Figure 2**. The ellipsoid particles were assigned with nickel material (density: 8900 kg/m^3, relative permeability: 600), and the rest that surround the particles was assigned as the fluid with the viscosity (70 cP) of the EPON862/EPIKURE W resin system at its working temperature (70 ^oC) and with the density of 998 kg/m^3. After the first meshing, the model was applied with the static magnetic field (180 G). The magnetic module of COMSOL was used to calculate the magnetic force and forces and torques. The solid mechanics module and the fluid mechanics module of COMSOL were coupled to calculate the particle movement as a response to the applied magnetic field at a time interval of 10^{-4} s. After this time step, the domain was re-meshed, and the calculation was repeated until the particles were aligned along the applied magnetic field. Overall, two sets of COMSOL simulation studies have been conducted to understand the effects of 1) magnetic particle interactions and 2) original relative particle positions (inter-particle distances and relative alignment).

As for the first study, the time required to complete magnetic assembly was studied with two different configurations. Time required to complete particle alignment along the magnetic field was calculated and compared about the one vs. two particles (20 μm original separation distance, aspect ratio of 7.5). The initial angle was set as 89.9 degrees. Magnetic and viscous forces (translation), and magnetic and viscous torques (rotation) were simulated (see **Figure 2a**). In addition, time required to complete assembly was also calculated about the two particles (5, 10, and 20 μm original separation distance) with varying aspect ratio. The initial angle was set as 0 degrees. Only magnetic and viscous forces (translation) were simulated (see **Figure 2b**).

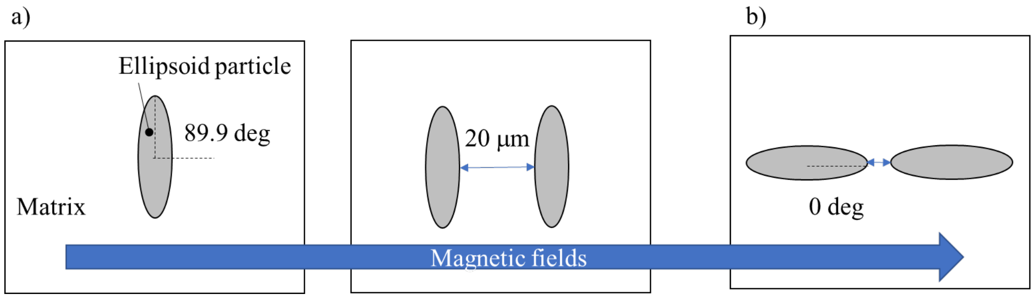

Fig. 2 Schematics of the COMSOL domain to study the effect of particle interactions: a) comparison of rotation time between one vs. two particles, and b) comparison of assembly time with varying aspect ratio.

As for the second study, the time required to complete assembly between the two particles were studied with varying aspect ratio where both translation and rotation are considered. I started with the case where magnetic assembly takes the longest time: the initial angle of the two ellipsoids was set as 89.9 degrees (see **Figure 3a**). The original separation distance was set as 20 μm, and the aspect ratio was varied (5, 7.5, and 10). To understand more about the effect of original particle positions, various relative particle angles (0, 30, 60, 90 degrees for one side of the particles) were set (see **Figure 3b**).

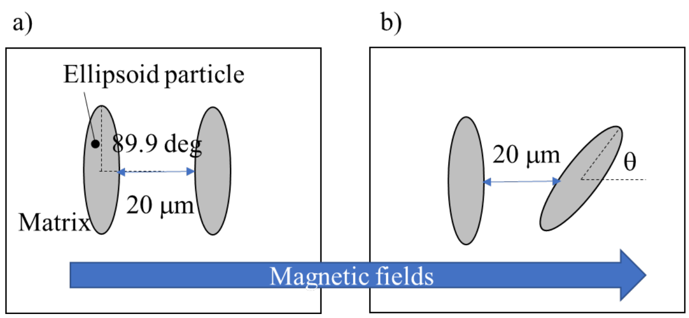

Fig. 3 Schematics of the COMSOL domain to study the effect of the original particle positions: a) comparison of assembly time of the two vertical particles with varying aspect ratio, and b) comparison of assembly behaviors with varying relative particle angles.

III. Results

A. Effect of particle interaction

The particle interaction promoted their alignment along the applied magnetic field, according to results of the simulation illustrated in **Figure 2a**. As shown in **Figure 4**, the time required to complete alignment is smaller with two particles than with one particle, indicating that particle interaction helps to accelerate rotation.

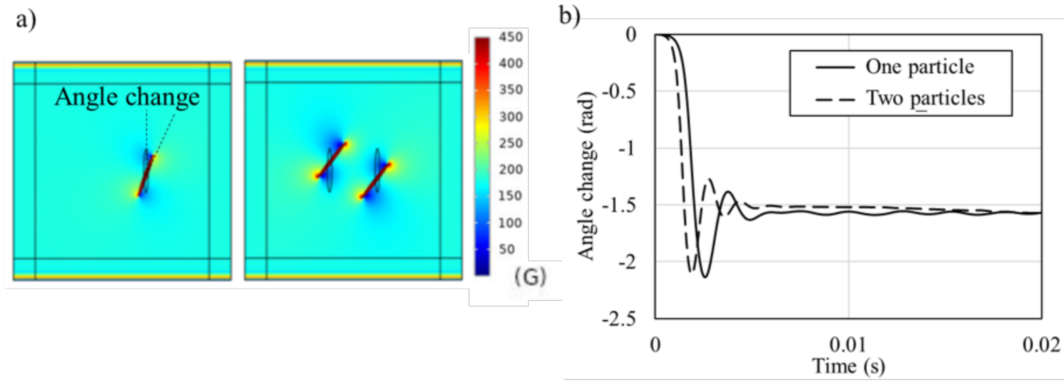

Fig. 4 Comparison between the cases with one particle vs. two particles (20 µm original separation distance, 7.5 aspect ratio): a) COMSOL simulation results, and b) time required to complete particle alignment along the applied magnetic field.

The particle interaction became stronger with increasing aspect ratio, according to results of the simulation illustrated in **Figure 2b**; the results are summarized in **Figures 5a** and **5b**. This trend can be attributed that the magnetic field flux strength around the particles increases with increasing aspect ratio (see **Figure 5c**); with increasing aspect ratio, demagnetization decreases and the magnetic lines are condensed at sharper ellipsoid's edges. The simulation results shown in **Figure 5** are about the cases with the initial separation distance of 5 µm. As the initial separation distance increases, the particles with smaller aspect ratio were observed not to assemble; for example, the particles with the aspect ratio of 1 did not assemble with the separation distance of 10 µm, and the particles with the aspect ratio of 5 did not assemble with the separation distance of 20 µm.

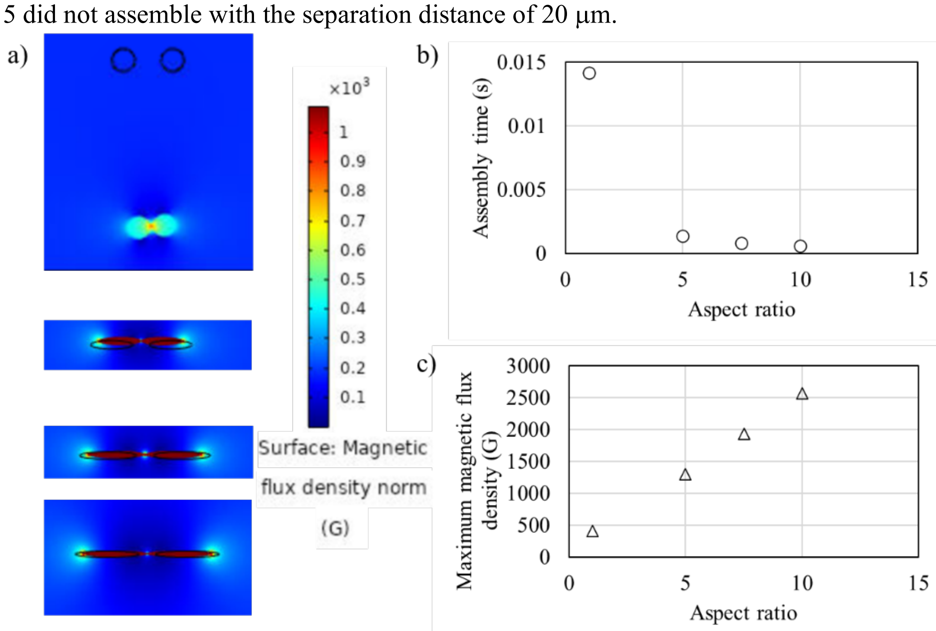

Fig. 5 Comparison of magnetic assembly with varying aspect ratio (5 µm original separation distance): a) COMSOL simulation results, b) time required to complete particle assembly, and b) the maximum magnetic field strength.

B. Effect of original particle positions

The effectiveness of higher aspect ratio was also confirmed when two vertical particles are assembled (the original particle angle of 89.9 degrees). As summarized in **Table 1**, the time required to complete the assembly decreased with increasing aspect ratio; the two particles with the smallest aspect ratio (5) did not complete assembly (see **Figure 6**). In **Figure 7**, the time required to complete assembly is compared with varying relative particle angles. When one particle angle is set as 0 degree, the assembly time increases with the initial angle of the other particle.

Table. 1 Time required to complete assembly between the two vertical particles (89.9 degrees particle angle, and 20 μm original separation distance) with increasing aspect ratio.

Aspect Ratio	5	7.5	10
Assembly time (s)	Did not assemble	0.0313	0.0189

a) Aspect ratio 5 b) Aspect ratio 7.5 c) Aspect ratio 10

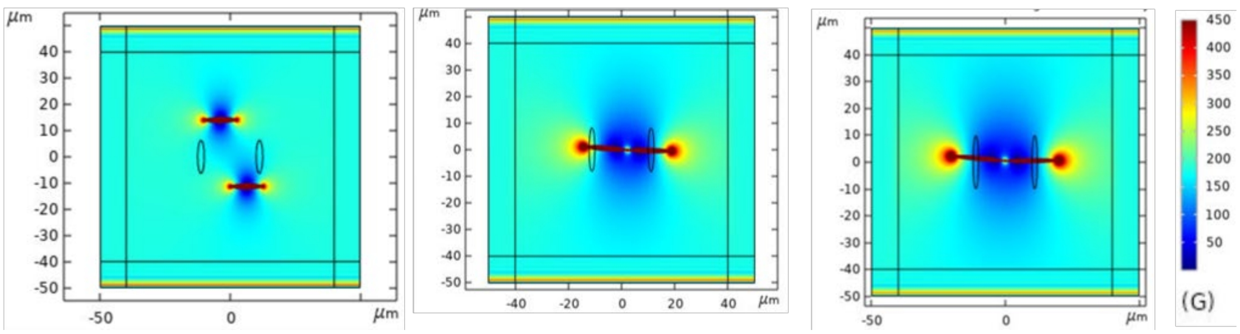

Fig. 6 Comparison of COMSOL simulation results with varying aspect ratio: a) aspect ratio of 5, b) 7.5, and c) 10.

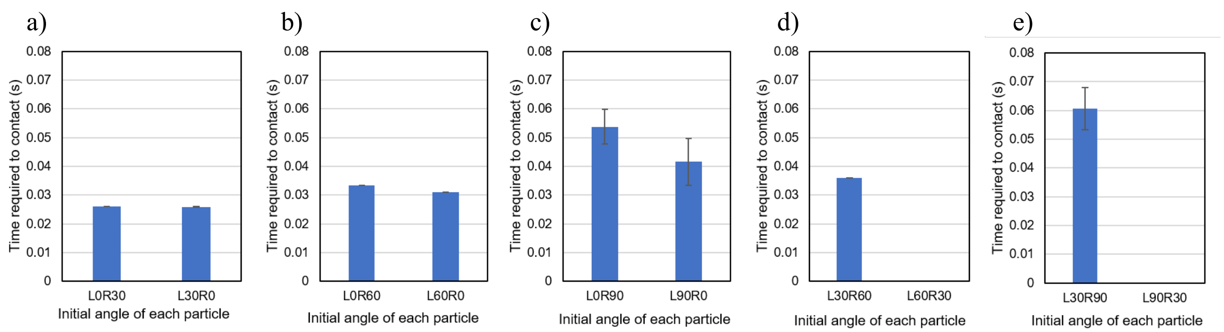

Fig. 7 Time required to complete assembly between the two particles (20 μm original separation distance) with varying initial angles of a) left 0 deg and right 30 deg, b) left 0 deg and right 60 deg, c) left 0 deg and right 89.9deg, d) left 30 deg and right 60 deg, and e) left 30 deg and right 89.9 deg.

IV. Conclusion

In this work, assembly behaviors of ellipsoid particles under the static magnetic field are being studied, in order to understand magnetic assembly behaviors of CNTs within an epoxy and to ensure their effective alignment during the limited working time. Higher aspect ratio of the CNTs was observed to be effective to decrease the alignment and assembly time, while some lower aspect ratio and larger original CNT separate distance combination prevented CNT assembly. Higher initial angles between CNTs caused more time for assembly or even prevented the assembly. When CNT assembly can be enabled, the assembly time was observed to be very small (<0.1 second), indicating that the current assembly time in our experimental work (~10s of minutes) can be shortened [13]. Further studies are necessary about the effect of the original CNT positions and also study assembly behaviors of more than just two particles. In addition, in our experimental studies also indicated that the higher magnetic strength resulted in CNT agglomeration [13]; studies of multiple particles with increasing field strength will be of our interest.

Acknowledgments

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