Simulating The Alignment of Carbon Nanotubes Within a Non-Constant Viscosity Fluid Medium

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Abstract :

Steriolithography(SLA) 3D printing has had rather limited use of carbon nanotubes (CNTs) as additives with its historic use for making parts ESD safe. However, it has been demonstrated that CNTs in resin parts increases part strength and aligning the nanotubes within the part increase strength even further. This project aims to compare the effects of aligning CNTs in static viscosity resin to that of dynamic viscosity of curing resin and the determine the feasibility of CNT alignment in SLA 3D printing. Through simulation it can be shown that supposed sweet spot for CNT alignment on a viscosity profile exists however, the gains in time and alignment quality are marginal at best.

1 Introduction

1.1 Prior Works

3D printing often makes use of additives to improve the strength of parts or their functionality. Carbon nanotubes (CNTs) have been used in fused deposition molding (FDM) 3D printers [Acquah et al., 2016], however, they are less frequently used in resin steriolithography (SLA) 3D printing. There is both research and products for CNTs in resins. On the product side, Tethon 3D offers a SLA 3D printing resin containing CNTs allowing the part to be ESD safe as well as stronger. Research has also been conducted in this field. Morais et al., 2019 demonstrated that CNTs can be aligned within resin that can then be cured and additionally, Khan et al., 2013 showed that aligning CNTs within a resin part increases its strength.

1.2 Overview

Both Morais et al., 2019 used a curing agent that was mixed into the resin while being heated instead of using ultraviolet activated agent that is used in SLA printing. While Khan et al., 2013 did use a UV cure resin, the process took approximately 30 minutes to cure which is not suitable for 3D printing where thousands of layers are cured for a single print. Additionally, both these experiments performed their initial calculations assuming a constant viscosity of resin and ran current through the resin with CNTs for the entire duration of the curing process.

To see if CNT alignment in resin can be practically performed for SLA 3D printing, we simulating CNT alignment with a non-constant viscosity as resin cures to find a part of the curing process would result in faster alignment times.

2 Analysis

2.1 Carbon Nanotube Alignment

This analysis of carbon nanotube alignment is based off of Oliva-Avilés et al., 2016 which can be referenced for further detail.

For this analysis, we can look at each carbon nanotube in two dimensions, moving in the x, y plane and rotating at an angle θ. We can first look at rotational motion, which is affected by three forces: dielectrophoresis (DEP), Coulombic forces, and viscosity. Taking all three of these forces into account, we can write the governing equation:

$$I\frac{d^2\theta}{dt^2} + T_{DEP} + T_{fr} + T_{coup} = 0 \tag{1}$$

Where I is the moment of inertia of the CNT and can be calculated from the following:

$$I = m(a^2 + b^2)/5 \tag{2}$$

$$m = d_{cnt}V \tag{3}$$

$$V = \frac{4}{3}\pi ab^2 \tag{4}$$

Where a is the major axis of the CNT and is equal to half of the length of the CNT and b is the minor axis and equal to half of the diameter of the CNT. The torque exerted on the CNT due to the electric field is given by:

$$T_{DEP} = \frac{1}{4}V\epsilon_m E^2 Re[\alpha^*]sin(2\theta) \tag{5}$$

Where E is the magnitude if the electric field, V is the volume of the CNT, and the complex polarization factor, α^* is given by:

$$\alpha^* = \frac{(\epsilon^*_{eq} - \epsilon^*_m)^2}{(\epsilon^*_m + (\epsilon^*_{eq} - \epsilon^*_m)L)(\epsilon^*_{eq} + \epsilon^*_m)} \tag{6}$$

Which indicates the separation of charges within the CNT. L is the longitudinal polarization factor which is given by:

$$L = \frac{ln(2a/b) - 1}{(a/b)^2} \tag{7}$$

In the complex polarization factor, ϵ^*_m is the permittivity of the surrounding fluid and ϵ^*_{eq}, the equivalent permittivity of the CNT and interphase layer is given by:

$$\epsilon^*_{eq} = \epsilon^*_{lay}\left(\frac{\epsilon^*_{CNT} + \frac{\delta}{2a}(\epsilon^*_{CNT} - \epsilon^*_{lay})}{\epsilon^*_{lay} + \frac{\delta}{2a}(\epsilon^*_{CNT} - \epsilon^*_{lay})}\right) \tag{8}$$

Where ϵ^*_{CNT} is the permittivity of the CNT and ϵ^*_{lay} is the permittivity of the interphase layer between the CNT and fluid. Additionally, permittivity is given by:

$$\epsilon^* = \epsilon - j\frac{\sigma}{2\pi f} \tag{9}$$

Where σ is the electrical conductivity and f is the frequency of the electrical field. However, we are only using the real part of the permittivity.

The torque due to viscous friction is given by:

$$T_{fr} = 8\pi\eta(t)r_e^3 K_r \frac{d\theta}{dt} \tag{10}$$

Where $\eta(t)$ is the viscosity of the fluid which is a function of time and will be discussed further in the next section. r_e is the equivalent radius of a sphere of volume equal to that of the CNT and is given by $a^{1/3}b^{2/3}$. The constant, K_r, the rotational friction coefficient is given by:

$$K_r = \frac{4p^2(1-p^2)}{3\left(\frac{2p^{2/3}(2-p^{-2})}{K_t} - 2\right)} \tag{11}$$

Where $p = a/b$ and K_t, the transnational friction coefficient is given by:

$$K_t = \frac{\sqrt{1-p^{-2}}}{p^{-2/3}ln[p(1+\sqrt{1-p^{-2}})]} \tag{12}$$

Since each of the CNTs are polarized, they will have a positive and negative end. We can calculate the torqe exerted on a CNT from the presence of another CNT. The over all force for a positive charge to a negative charge is given by:

$$F_{1+-} = \frac{1}{4\pi\epsilon_m}\frac{|q_{1+}^*||q_{2-}^*|}{|r_1^+ - r_2^-|^2} \tag{13}$$

Where r_1^+ and r_2^- are the distances from the origin to the positive end of the first CNT and the negative end of the second CNT respectively. The charge of the ends of the CNTs are given by:

$$q_i^* = \frac{\epsilon_m V_i E}{2a_i}\frac{\epsilon_{eq,i}^* - \epsilon_m^*}{\epsilon_m^* + (\epsilon_{eq,i}^* - \epsilon_m^*)L_i} \tag{14}$$

Where L_i is the length of CNT i. We can repeat this process to four forces: F_{+-}, F_{++}, F_{-+}, and F_{--}. Each of the forces also have an angle, γ which is the angle between the force and the direction of the CNT i. Allowing us to say that the torque experienced by the CNT i due to the presence of CNT j is given by:

$$T_{i,coup,oppose} = a_i[F_{i,++}sin(\gamma_{i,++}) + F_{i,--}sin(\gamma_{i,--})] \tag{15}$$
$$T_{i,coup,attract} = a_i[F_{i,+-}sin(\gamma_{i,+-}) + F_{i,-+}sin(\gamma_{i,-+})] \tag{16}$$
$$T_{i,coup} = T_{i,coup,oppose} + T_{i,coup,attract} \tag{17}$$

We can now look at the transnational motion of the CNT which is controlled by viscous friction force, Coulombic forces and a short range repulsive force. The governing equations in the x and y directions are given by:

$$m\frac{d^2x}{dt^2} + (F_{fr})_x + (F_{coup})_x + (F_{rep})_x = 0 \tag{18}$$
$$m\frac{d^2y}{dt^2} + (F_{fr})_y + (F_{coup})_y + (F_{rep})_y = 0 \tag{19}$$

Vicious friction is similar to that regarding rotational motion and is given by:

$$(F_{fr})_x = 6\pi\eta(t)r_e K_t \frac{dx}{dt} \tag{20}$$

$$(F_{fr})_y = 6\pi\eta(t)r_e K_t \frac{dy}{dt} \tag{21}$$

Where K_r has been replaced with K_t for transnational motion.

The Coulombic force also remains unchanged and for the x and y directions is given by:

$$(F_{i,coup})_x = (F_{i,+-})_x + (F_{i,++})_x + (F_{i,-+})_x + (F_{i,--})_x \tag{22}$$
$$(F_{i,coup})_y = (F_{i,+-})_y + (F_{i,++})_y + (F_{i,-+})_y + (F_{i,--})_y \tag{23}$$

Finally, we dd a repulsive force for transnational motion that prevents CNTs from overlapping within a radius Δ:

$$F_{i,rep} = (F_{i,coup})\left(e^{-100\left(\frac{|r_2^- - r_1^+|}{\Delta}-1\right)} + e^{-100\left(\frac{|r_2^+ - r_1^-|}{\Delta}-1\right)}\right) \tag{24}$$

2.2 Resin Curing Dynamics

As discussed above, the viscosity of the fluid medium that the CNT is in is not constant and will change as the resin cures. The viscosity of resin as it cures involves three factors, the degree of cure, temperature, and time. Using Muc et al., 2019, we can derive the following. Starting with the viscosity as given by the Castro-Macosko Model as:

$$\eta = Bexp\left(\frac{T_b}{T}\right)\left(\frac{\alpha_g}{\alpha_g - \alpha}\right)^{C_1 + C_2\alpha} \tag{25}$$

Where B is the initial viscosity of the resin and $T_b = E/R$ where E is the activation energy to start curing the resin and R is the ideal gas constant. α_g is the degree of cure which is:

$$\alpha_g = [r(f-1)(g-1)]^{-1/2} \tag{26}$$

Where r is the ratio between resin and hardener and f and g are the number of functional group in the resin and hardener, the sites that react with the hardener in the resin and vise versa. We can apply a reaction kinetics model for the degree of cure of resins given by Sourour et al., 1976 as:

$$\frac{\partial\alpha}{\partial t} = (k_1 + k_2\alpha^m)(1-\alpha)^n \tag{27}$$

Where k_1 and k_2 are defined from the Arrhenius relationship as:

$$k_i = A_i exp\left(\frac{-E_i}{T}\right) \tag{28}$$

Using this relationship, we can solve for viscosity and approximate the equation to be:

$$\eta = Be^{\frac{E}{RT}\alpha} \tag{29}$$

Where B is the initial viscosity of the resin, E is the activation energy, RT is kinetic energy as a function of temperature, and α is the degree of cure.

3 Simulation

The simulation was written in Python and looks at the kinematics of two CNTs in a resin fluid, as shown below. The values used values were used as constants for the CNT and interphase layer are shown in Table 1 below. The values for the constants of the surrounding resin are in Table 2 below. The code can be found at here.

CNT permittivity, ϵ_{CNT}	$1 * 10^5$
CNT conductivity, σ_{CNT}	$1 * 10^4$
Interphase permittivity, ϵ_{lay}	$1 * 10^4$
Interphase conductivity, σ_{lay}	$1 * 10^{-4}$

Table 1
CNT and interphase layer initial values

Resin permittivity, ϵ_m	$1 * 10^4$
Resin conductivity, σ_m	$1 * 10^{-4}$
Initial resin viscosity, η_i	1500 mPa

Table 2
Resin static values

4 Discussion

Starting with constant viscosity, repeating research already done, we can get the following results below. The electric field is oriented vertically. Both CNTs start out horizontally at $\theta = \pi$ and are run for 30000 time steps at a rate of 100 steps a second for a total of 300 seconds.

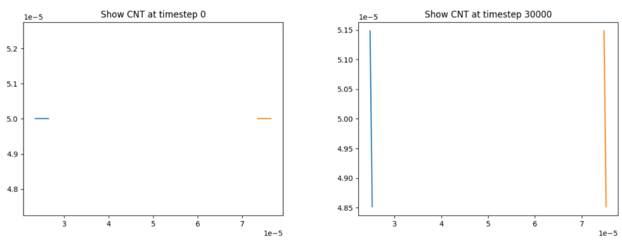

Figure 1. Comparison for timestep 0 and timestep 30000 (300 seconds) at constant viscosity

We can also start the CNTs out at different orientations, getting the same result. This time the CNT on the left was started out at $\theta = \pi/6$ and the other at $\theta = \pi$.

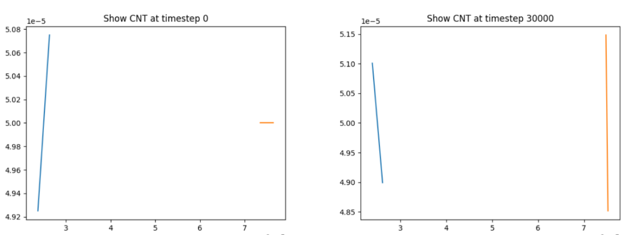

Figure 2. Comparison for timestep 0 and timestep 30000 (300 seconds) at constant viscosity

Or both can be started out at an angle that is not flat. Here both are started out at $\theta = \pi/6$ as seen in Figure 3

Introducing the dynamic viscosity, we can first look at the viscosity profile of the resin. Since this is oriented towards SLA printing, the time it takes to reach over 70 percent of complete cure takes place under 5 seconds. Figure 4 shows the viscosity profile below. We would ideally want to align the CNTs within the two to four second range where the viscosity of the resin is lower than its initial value.

Running our first rest gives the following result in Figure 5. The CNTs were both started at $\theta = \pi$ and run for 30000 timesteps.

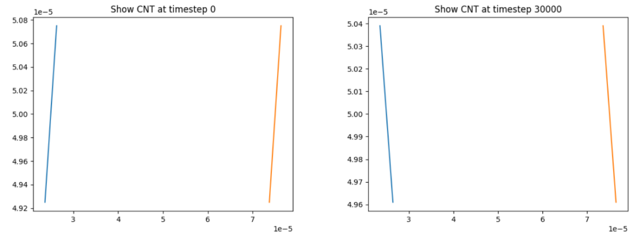

Figure 3. Comparison for timestep 0 and timestep 30000 at different starting angles

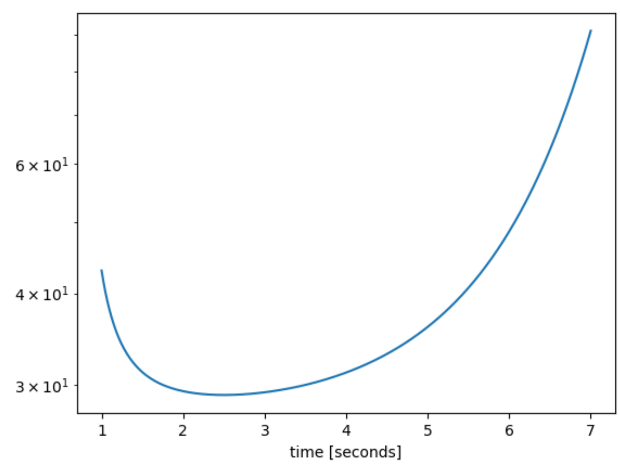

Figure 4. Viscosity profile over 7 seconds

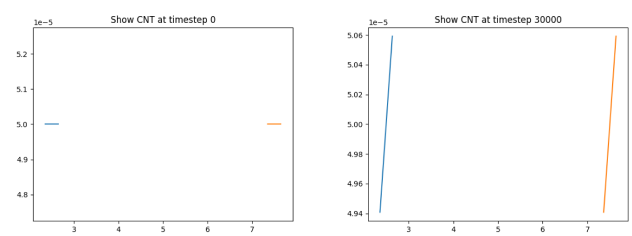

Figure 5. First test with dynamic viscosity

Since it is difficult the see a discernible difference in the graphical read out, we can look at the numerical read out to see the difference. For the test at constant viscosity:

```
0  i: [3.14159265]  j: [3.14159265]
3  i: [-7.75356643e+22]  j: [-7.75356643e+22]
30  i: [-6.19300055e+22]  j: [-6.19300055e+22]
300  i: [-2.66876527e+23]  j: [-2.66876527e+23]
3000  i: [-4.35410152e+24]  j: [-4.35410152e+24]
30000  i: [-9.33663857e+54]  j: [5.74264433e+54]
```

And for the test using dynamic viscosity:

```
0  i: [3.14159265] j: [3.14159265]
3  i: [-35332417.84059966]  j: [-35332417.84059966]
30  i: [-4.52506955e+10]  j: [-4.52506955e+10]
300 i: [-7.95177836e+11]  j: [-7.95177836e+11]
3000 i: [1.64941533e+12]  j: [1.64941533e+12]
30000  i: [3.08086762e+12]  j: [3.08086762e+12]
```

The difference between the two runs are noticeable small and the majority of the alignment happened within the first 30 seconds of running.

5 Conclusion

There is potential in aligning CNTs within SLA printed parts, however, the gains from tuning this system to align CNTs at the proper time on the viscosity profile appear to be marginal. However, different resins with more aggressive profiles that are very reactive and harden quickly would need a tuning process like this one to ensure that CNTs are aligned. Additionally, more work could be done running a simulation on more than two CNTs and analysing the statistical distribution of alignment as a metric for performance.

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