

3-D Nano-Fiber Manufacturing by Controlled Pulling of Liquid Polymers using Nano-Probes

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Abstract — In-addition to the applications of imaging and characterization, proximal probes are proposed to be used as three-dimensional (3-D) nano-scale manufacturing tools in this paper. Commercially available Atomic Force Microscope (AFM) systems are mainly limited to 1-D or 2-D manipulation tasks, and advanced 3-D nano-manufacturing applications are not possible. Therefore, this paper proposes 3-D nano-scale manipulation of liquid polymer nano-fibers by using precise positioning and temperature control. AFM nano-probe is used to pull or extrude thermoset or thermoplastic polymers precisely to fabricate 3-D polymer nano-fiber structures. A liquid SU-8 polymer structure bridge between the probe tip and a substrate is held when pulling the probe from the surface with controlled speed and position. For thermoset polymer, by heating the substrate and moving the AFM probe tip in a precise 3-D trajectory, the liquid fiber is cured in real-time while a predetermined 3-D shape is constructed. To model the curing of thermoset resins a three dimensional transient heat transfer scheme using Alternate Direction Implicit (ADI) finite volume method has been developed which numerically simulates the kinetics of cure, specifically the exothermic heat given out during the cure reaction of thermosetting resin.

Keywords – Nano-manipulation, ADI Heat Transfer, Nano-manufacturing, Nano-fibers

I. INTRODUCTION

Engineering breakthroughs have opened mindsets to revolutionary engineering. Nanotechnology envisioned over the centuries in the realms of science fiction is now available at our fingertips. Explorations in this new field have impacted in nearly every aspect of our daily living, ranging from medicine to our indispensable electronic gadgets. One of such explorations is a new method of fabricating fibers in the nano meter length scale, which could serve as basic building blocks in diverse applications such as assembly of nano/micrometer systems or for packaging of higher order assemblies, etc.

Use of polymers is not new and they have been studied in detail [1-3]. However there is a thrust to develop and study polymers at the nano-scale [4,5]. Nano-manipulation area is growing fast [6,7], and this paper investigates the ability to fabricate nano-fibers by controlled pulling of liquid polymers. This involves a detailed analysis of the visco-elastic, thermal and crystallization kinetics effects. In this paper we discuss our infant steps towards a not too distant horizon of 3-D nano-manufacturing involving nano-fibers. A detailed thermal study of polymers at the micro/nano-scale has been performed, results of which are discussed in this paper. The choice between using thermoplastics or thermosetting resins was out of convenience. Thermosetting polymers are available in liquid

form at room temperature hence we could devise quick experiments to validate our initial thoughts as outlined in Figure 1. Thermoplastics however can be used easily by heating the tip of AFM, which can be accomplished with passing current through a doped silicon AFM probe.

The following strategy as outlined in Figure 1 is proposed. An AFM tip is brought and dipped in a thermoset resin pool, from where it moves over a heated substrate. It makes contact with the substrate and is retracted, thus forming a nano-fiber. Curing of thermoset resin starts as soon as contact with the heated substrate is formed.

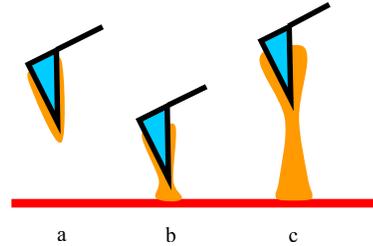


Figure 1. (a) AFM with polymer, (b) AFM+polymer making contact with heated substrate, (c) AFM retracted, forming a nano-fiber and curing of polymer starts

Curing of thermoset polymers is normally accomplished by providing external excitation to the monomers present in the resin. Many methods have been developed for providing this excitation and in our case we use a heated substrate. It is of importance to determine the curing times of such nano-fibres of high aspect ratio. Such data is not available and to our knowledge similar work has not been done elsewhere. A comprehensive transient heat transfer model to model the cure kinetics has been developed and experiments have been conducted with various polymers to verify the proof of concept.

II. HEAT TRANSFER MODEL

Temperature solutions are based upon Fourier's heat conduction equation for three-dimensional, transient anisotropic heat transfer with constant material properties and an internal heat generation source term. In its most simplified form the equation can be written as

$$\rho C \frac{\partial T}{\partial t} = \kappa_x \frac{\partial^2 T}{\partial x^2} + \kappa_y \frac{\partial^2 T}{\partial y^2} + \kappa_z \frac{\partial^2 T}{\partial z^2} + \rho \frac{\partial Q}{\partial t} \quad (1)$$

where ρ is the density (Kg/m³), C the specific heat (J/Kg.K), K_x , K_y , K_z the thermal conductivities in (W/m.K) and Q is the

heat generated by the kinetics of reaction per unit volume. No analytical solution is obtained for this general equation, as the rate of reaction depends on time and temperature. This general problem has thus to be solved by using numerical methods, and following assumptions are made:

- Parallelepiped geometry.
- High aspect ratio geometry (length/width >10).
- Thermal and cure kinetic material parameters are assumed constant, independent of time and temperature.
- No part reduction occurs during the curing process.
- Continuum heat conduction.

Initial and Boundary Conditions:

Neumann or insulated boundary conditions were enforced on the sides and Dirichlet or prescribed temperature boundary condition was enforced on the top surface. The heated substrate can be modeled as a heat flux boundary condition or another Dirichlet temperature boundary condition as shown in Figure 2. The model formulation is flexible enabling arbitrary initial temperature T_i and degree of cure α_i , distributions throughout the domain at the start of the simulation.

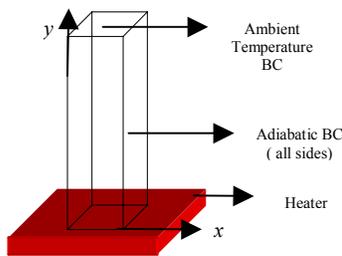


Figure 2. Geometry and Boundary Conditions(BC) for numerical analysis

For our analysis, we set the initial conditions as: α_i to be zero and T_i to be ambient temperature.

Geometry for Numerical Simulations

The choice of parallelepiped geometry (Figure 3) would be a reasonable approximation to a cylindrical fiber for determining the curing time required for different aspect ratio geometries. In addition, initial experiments have shown the formation of a conical fiber shape, terminating at the apex. Hence, in our software, artificial boundary resistance zones which can account for the conical geometry effects are provided. Inclusion of such zones provides the attractive feature of excluding domains with high thermal resistance in our numerical studies. This feature will be utilized in later studies of nano-fiber fabrication and simulation and will be able to accurately model a conical geometry.

Choice of Numerical Scheme

A comprehensive error analysis was performed to determine the best numerical scheme. Comparison was made between finite difference and finite volume methods with Explicit and Alternating Direction Implicit (ADI) methods as shown in Figure 4. Criterion for error analysis was established as

$$Error = \frac{(T_{max} - T_{max(analytical / ANSYS)})}{T_{max@ steady_state}} \tag{2}$$

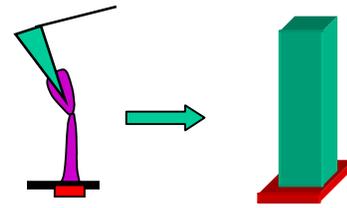


Figure 3. Geometry simplification

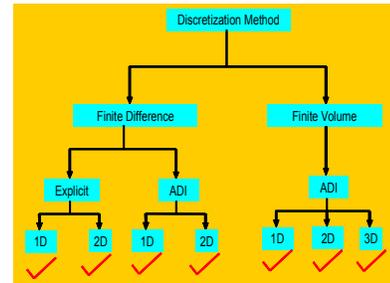


Figure 4. Numerical comparisons/Software Developed

It was found that the finite volume method gives the least error and hence was chosen for subsequent three dimensional development. ADI technique was chosen over Explicit methods as we were able to increase the time step of calculation by a factor of 5-10 times, thus making it faster than Explicit method and yet still not accrue any significant errors.

Modeling of Cure Reaction:

The term $\partial Q / \partial t$ represents the instantaneous heat generation per unit volume of material and is introduced to account for the exothermic chemical reaction associated with the curing process. It is a cure rate dependent term which is evaluated throughout the domain at every time step during the incremental solution. The degree of cure or extent of reaction, at time t is defined by the ratio, $\alpha = Q_t / Q_\infty$, where Q_t is the amount of heat generated up to time t , and Q_∞ is the total amount of heat generated during a complete cure, which is obtained from Differential Scanning Calorimetry (DSC) measurements. The time and temperature dependence of the degree of cure throughout the curing reaction is often represented by the following Arrhenius equation [8]

$$\frac{1}{Q_\infty} \frac{dQ_t}{dt} = \left(1 - \frac{Q_t}{Q_\infty}\right)^n k_0 \exp\left(-\frac{E}{RT}\right) \tag{3}$$

where n is the apparent order of the reaction, E is the energy of activation, k_0 is the pre-exponential factor, R is the ideal gas constant and T is the absolute temperature. The cure $d\alpha / dt$ rate is typically determined empirically with isothermal DSC

measurements. The degree of cure over each time step increment during the simulation is based on the degree of cure at the previous time step and the instantaneous cure rate at the current time step. The degree of cure at node (i,j,k) for time step $t+\Delta t$ is computed from the relationship:

$$\alpha_{i,j,k}^{t+\Delta t} = \alpha_{i,j,k}^t + k_0 \Delta t \exp\left(-\frac{E}{RT}\right) \quad (4)$$

and the heat evolved is given by

$$\Delta Q = Q_\infty (\alpha_{t+\Delta t} - \alpha_t) \quad (5)$$

This value of exothermic heat given out during cure reaction is included in every time step. Temperature and degree of cure distributions throughout the domain are computed at each time step increment as a function of cure cycle temperature history. The exothermic heat given out after a volume has cured completely is set to zero.

Finite Volume Formulation

Figure 5 shows the control volume around a point P . We locate the control-volume faces in relation to the grid points exactly midway between the neighboring grid points. Equation 1., without the exothermic heat generation term can be written in finite volume formulation as [9]:

$$a_p^0 (T_p^1 - T_p^0) = f \left[a_E (T_E^1 - T_p^1) - a_W (T_p^1 - T_W^1) + a_N (T_N^1 - T_p^1) \right. \\ \left. - a_S (T_p^1 - T_S^1) + a_B (T_B^1 - T_p^1) - a_F (T_p^1 - T_F^1) \right] \\ + (1-f) \left[a_E (T_E^0 - T_p^0) - a_W (T_p^0 - T_W^0) + a_N (T_N^0 - T_p^0) \right. \\ \left. - a_S (T_p^0 - T_S^0) + a_B (T_B^0 - T_p^0) - a_F (T_p^0 - T_F^0) \right] \quad (6)$$

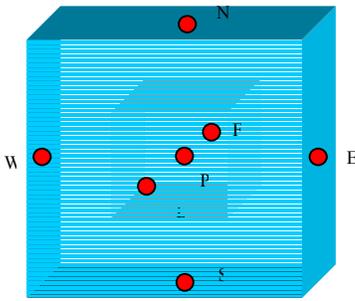


Figure 5. Control volume representation around central point P. E, W, N, S, B and F are East, West, North, South, Back and Front, respectively.

where the subscripts define the points and the superscript '0' signifies the previous time step and '1' stands for current time step. The coefficients a_i are defined as

$$a_p^0 = \frac{3\rho c \Delta x \Delta y \Delta z}{\Delta t}; \quad a_E = \frac{k_e \Delta y \Delta z}{(\delta x)_e}; \quad a_W = \frac{k_w \Delta y \Delta z}{(\delta x)_w} \\ a_N = \frac{k_n \Delta x \Delta z}{(\delta y)_n}; \quad a_S = \frac{k_s \Delta x \Delta z}{(\delta y)_s} \\ a_B = \frac{k_b \Delta y \Delta x}{(\delta z)_b}; \quad a_F = \frac{k_f \Delta y \Delta x}{(\delta z)_f} \quad (7)$$

ADI implementation is carried on by dividing each time into three equal segments. In each sub segment, one direction is

treated implicitly (by taking 'f' to be equal to 1) and the other two directions explicitly (by taking 'f' to be equal to 0). To achieve higher accuracy, we consider one direction to be implicit (following the Crank-Nicholson formulation, taking 'f' to be equal to 0.5) and the other two directions explicitly. This procedure is alternated between all time sub segments in each time step. The exothermic heat as defined in equation (5) is included as a constant term in equation (6) and is calculated at every time step.

III. RESULTS

Numerical Studies of heat transfer and cure reaction

We took a sample polymer EPON 862/N (as curing properties of SU-8 are not available to us at the present time) and performed numerical simulations for different aspect ratio geometries. The properties of this polymer are given in Table 1 [10]. We used the same values of thermal conductivity in all directions thus making our model isotropic. Our model however has the capability of including anisotropic behavior where the thermal conductivities are matched at the interfaces of control volumes.

We ran test cases for aspect ratios of 1:5 in order to reduce computation time. We believe that these results can be straightforwardly extrapolated to higher aspect ratio geometries. However exact aspect ratios obtainable with this approach can only be determined from experiments and visco-elastic models (currently under development). The continuum heat conduction assumption is valid due to high aspect ratios where the length of nano-fibers extends in several hundreds of nanometers.

Property	Name	Value	Units
R	Universal Gas Constant	8.314	J/mol.K
n	Rate constant	1.66	#
Q_∞	Heat of Reaction	2000	KJ/Kg
ρ	Density	1600	Kg/m ³
C	Specific Heat	1000	J/Kg.K
k_x, k_y, k_z	Thermal Conductivity	0.72	W/m.K
E	Activation Energy	53.83	KJ/mol

Table 1. Material properties and values of constants obtained using DSC measurements for Epoxy EPON 862/N

Preliminary results obtained agree with intuition on time required to cure nano-fibers as shown in Figure 6.

The time taken to cure reduces drastically with scaling of nano-fibers and for a $2 \times 2 \times 10 \mu\text{m}^3$ sample, the time taken for the complete cure is of the order of 6.45×10^{-4} seconds, suggesting an instantaneous cure, as observed experimentally. However our model at the present time does not include the ability to identify the state of the cure. This can be achieved by incorporating the kinetics of phase transformations and monomer to polymer polymerization reactions.

Transient state of the cure is shown in Figure 7. The fiber is shown in horizontal direction for best visualization purposes only. Blue represents a nano-fiber at the beginning of cure

reaction where the state of the cure is zero and red indicates a complete cure with the state of cure being one.

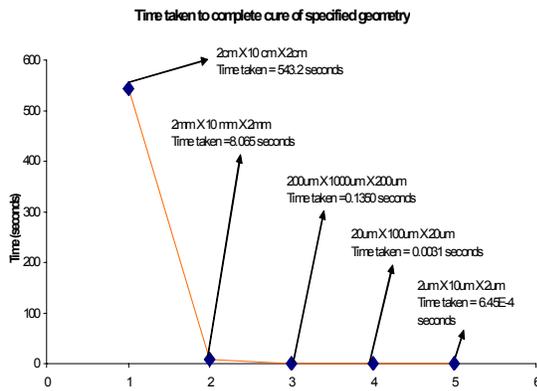


Figure 6. Time taken to cure

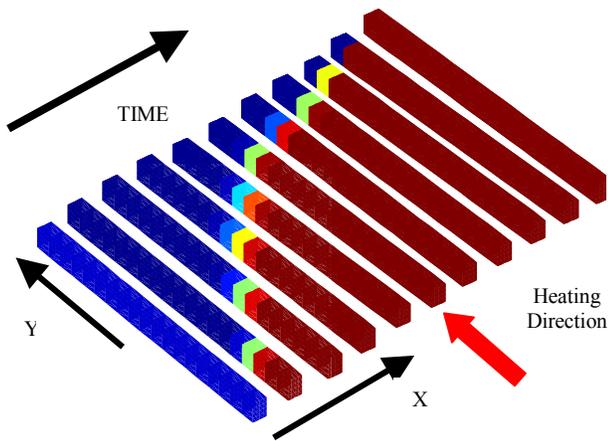


Figure 7. Transient curing of a nano-fiber (Blue=No cure, Red=Complete cure)

Experimental Results

For our pulling experiments, SU-8 2002 (Microchem Inc., MA) thermoset polymer was coated on a glass surface, and a silicon AFM probe was used to pull the polymer in the vertical direction. During the pull, the glass substrate was heated to 90 °C to cure the polymer. Resulting nano-fiber structures obtained are shown in Figure 8. Since the polymer was not coated on the AFM probe tip, the pulled structures look like cones rather than fibers. After a wait time of approximately 30 minutes, the SU-8 structure was observed to cure even without heating during the pulling since the surface area to volume ratio of the pulled polymer is very high and the curing agent evaporates quickly.

IV. CONCLUSIONS

Initial simulated and experimental results of pulled polymer nano-structures using an AFM probe are demonstrated. Transient numerical analysis suggests instantaneous cure of polymer nano-fibers. This presents a possible opportunity of

fabricating nano-fibers in parallel with no wait times and opens new nano-manufacturing directions. Characterizing or maturing this novel approach requires a comprehensive numerical model coupling visco-elastic, thermal, crystallization kinetics analytical models along with experiments. An in-depth search of the best polymer(s) for such applications would be very beneficial. This novel technique would be revolutionary for fabricating 3-D conductive and nonconductive nano-structures for future smart circuits, devices, sensors, materials, and robotic mechanisms. By this method, also, very sharp polymer AFM probe tips could be fabricated. These polymer tips would be very useful for soft biological object or polymer surface AFM imaging.

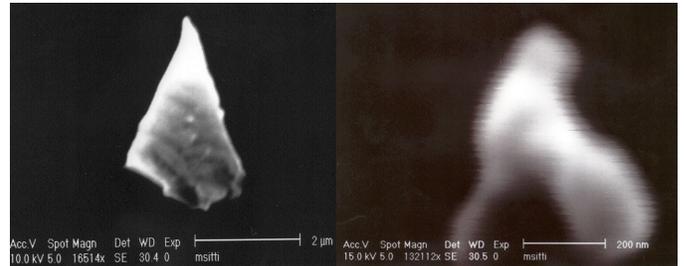


Figure 8. SU-8 thermoset polymer is pulled by a silicon AFM probe, and cured during pulling. Scale bars: 2 μm (left image) and 200 nm (right image).

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