Glass Transition of ABS in 3D Printing

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Abstract — In a commercial 3D printer head, plastic ribbon passes through a hot nozzle of an extruder to dispense liquid plastic droplets to construct the model. In this paper a 2D axisymmetric model of a 3D head is considered to study the secondary transition change from below the glass temperature to above the glass-transition temperature of ABS (Acrylonitrile Butadiene Styrene) using COMSOL Multiphysics Software. To achieve accurate results, the melt flow fields in combination with the heat transfer and change in tensile modulus are considered. The model includes the secondary transition, both in terms of latent heat and in terms of other thermodynamic and physical variables. The simulation is based on the assumption that there is no volume change during solidification of ABS. It is also assumed that the velocity of the melted ABS is constant and uniform throughout the modeling domain. The transition from the glassy to the molten state of ABS is modeled using the heat capacity model. A narrow secondary transition is observed during the glass-transition temperature.

Index Terms**—**ABS (Acrylonitrile Butadiene Styrene), Computer Aided Design (CAD), Computer-Aided Manufacturing (CAM), Computer Numeric Control (CNC), Fused Deposition Modeling (FDM), Polylactic Acid (PLA), Selective Laser Sintering (SLS), Stereolithography (SLA), Thermoplastic Polyurethane (TPU).

I. INTRODUCTION

NOT all 3D printers make use of the extruder head for dispensing melted plastic. There are several other 3D printing techniques that are available, differing mainly in the way the layers are built to create the final object. Selective laser sintering (SLS) and fused deposition modeling (FDM) are the most common technologies that make use of melting or softening of material to construct the layers. In a stereolithography (SLA) technique a photo-reactive resin is cured one layer at a time with a UV laser. Fused deposition modeling (FDM), a method of rapid prototyping, makes use of a nozzle ejecting molten thermoplastic and is used to model the object with a controlled movable vertical platform. The FDM technology works using a thermoplastic filament or metal wire which is unwound from a coil and supplying material to an extrusion nozzle which can turn the flow on and off. The nozzle is heated to melt the material and can be moved in both the horizontal and vertical directions by a numerically controlled mechanism similar to conventional Computer Numeric Control (CNC) machine directly controlled by a computer-aided manufacturing (CAM) software package. The model is produced by extruding melted material to form layers as the material hardens immediately after extrusion from the nozzle. This technology makes use of two thermoplastic materials namely: ABS and PLA (Polylactic acid). Other thermoplastic materials that can also be extruded are high-impact polystyrene (HIPS), thermoplastic polyurethane (TPU), aliphatic polyamides (nylon) and recently also PEEK. Paste-like materials such as ceramics and chocolate can also be extruded using the fused filament process and a paste extruder.

Hard plastics like ABS, PMMA (Polymethyl methacrylate) have end use applications well below their glass transition temperatures that is in their glassy state. Their T_g values are well above room temperature, both at around 105 °C (221 °F) [1]. Rubber elastomers like polyisoprene and polyisobutylene are used above their T_g, that is, in the rubbery state, where they are soft and flexible [2].

In polymers the glass transition temperature, T_g, is often expressed as the temperature at which the Gibbs free energy is such that the activation energy allows the cooperative movement of molecular chain segments to slide past each other when a force is applied. When the glass temperature has been reached, the stiffness stays the same until the temperature exceeds T_g, and the material turns rubbery. This region is called the rubber plateau.

II. 3D PRINTER EXTRUDER HEAD

In a conventional extruder a high-volume thermoplastic plastic is melted and forced out through a nozzle to cool into various shapes and profiles such as pipes, tubes, ribbons, films, coatings, wire insulation, or sheet depending on the various kinds of die as shown in Fig. 1. During the extrusion process, plastic material (pellets, granules, flakes or powders) are fed from a hopper into the heated barrel of the extruder. The plastic pellets or powders are gradually plasticated by the heated barrel and pushed through the nozzle by the turning screws and by heaters. The molten polymer is then forced into a die, which shapes the polymer into a desired shape that hardens during cooling. Fig. 1 [3] shows a schematic diagram of an extruder with a feeding hopper through which the plastic pellets or resins enter into a plasticating screw in which pellets get turned into a viscous liquid which is dragged forward by the rotating screw. The melt reaches the end of the cylinder where it is forced through a screen pack and the die to form the desired shape.

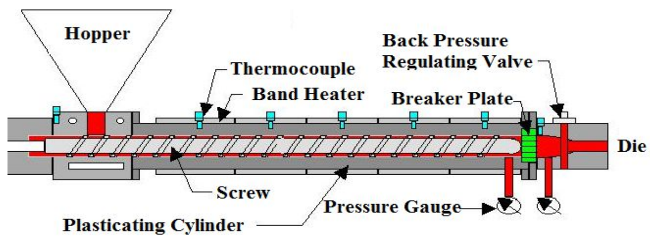

Fig. 1 Schematic diagram of a conventional extruder [3].

The technology of a conventional extruder has been adapted to a commercial 3D printer as shown in Fig. 2 [4]. In Fig. 2, instead of a hopper, a 3D printer uses a continuous plastic filament which is fed from a large spool or reel and pushed through a set of gears to the heated extruder barrel. Molten plastic is forced through the nozzle and is deposited on the working table. The 3D extruder head moves, under computer control, to define the printed shape. Similar to a CNC machine, the 3D printer head is controlled by a computer along with electronic controllers, stepper or servo motors to move and manipulate the mechanical axes of the 3D printer. Usually the head moves in layers, moving in two dimensions to deposit one horizontal plane at a time, before moving slightly upwards to begin a new slice.

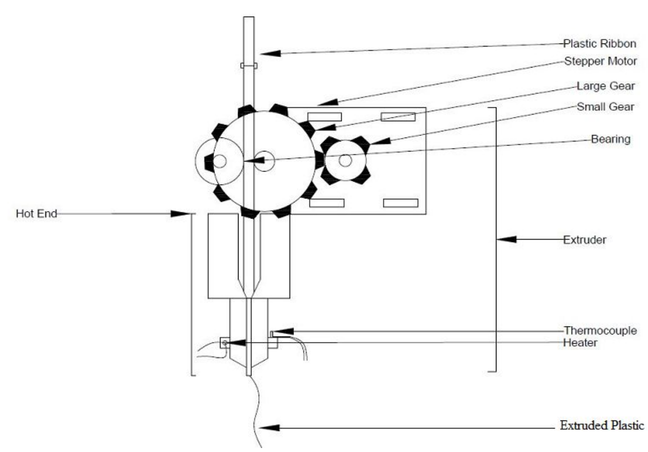

Fig. 2 Schematic diagram showing how plastic ribbon is fed from a large coil through a set of moving gears to a heated barrel of an extruder of a 3D printer head [4].

III. NUMERICAL MODELING

A 2D axisymmetric heat transfer model is considered in the numerical modeling of the 3D printer head. In this simulation molten ABS flows continuously through a narrow nozzle. Also, to optimize the casting process in terms of casting rate and cooling, the thermal and fluid dynamic aspects of the process are also considered. To obtain accurate results, the melt flow fields in combination with the heat transfer and glass (secondary) transition are considered. The model includes the transition from glassy solid to rubbery melt, both in terms of sensible heat along with other physical properties.

The model assumes a steady state and continuous process. The heat transport is described by the equation:

$$\rho C_P \mathbf{u}.\nabla T + \nabla.(-k\nabla T) = Q \tag{1}$$

where k, Cp and Q denote thermal conductivity, specific heat, and heating power per unit volume (heat source term), respectively. The velocity, **u**, is the fixed pulling speed of the plastic ribbon in both the rubbery liquid and the glassy states. As the melt cools down in the air, it becomes a glassy rigid liquid. During the glass transition, a significant amount of heat is released. The total amount of heat released per unit mass during the glass transition is given by the change in enthalpy, ΔH. The heat capacity, Cp, changes considerably during the glass transition. The difference in specific heat before and after the transition can be approximated by

$$\Delta C_P = \frac{\Delta H}{T}. \tag{2}$$

As opposed to neat polymer, a polymer with fillers or reinforcements generally undergoes a broad temperature transition zone, over several degrees Kelvin in which a mixture of both solid and molten polymer co-exist in a "mushy" zone. To account for the sensible heat related to the glass transition, the apparent heat capacity method is used through the Heat Transfer with a Phase Change domain condition. The objective of the analysis is to make ΔT, the half-width of the transition interval small, such that the solidification front location is well defined.

Furthermore, models considered the laminar flow by describing the fluid velocity, **u**, and the pressure, p, according to the equations

$$\rho\frac{\partial u}{\partial t} + \rho\mathbf{u}.\nabla\mathbf{u} =$$
$$\nabla.\left[-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T - \left(\frac{2\mu}{3} - \kappa\right)(\nabla.\mathbf{u})\mathbf{I}\right] + \mathbf{F} \tag{3}$$

$$\frac{\partial\rho}{\partial t} + \nabla.(\rho\mathbf{u}) = 0 \tag{4}$$

where ρ is the density (in this case constant), μ is the viscosity, and κ is the dilatational viscosity (here assumed to be zero). Here, the role of the source term, **F**, is to dampen the velocity at the modulus-change interface so that it becomes that of the rigid phase after the transition from the rubbery. The source term has been taken from equation [5]

$$\mathbf{F} = \frac{(1-\alpha)^2}{\alpha^3 + \varepsilon} A_{mush}(\mathbf{u} - \mathbf{u}_{cast}) \tag{5}$$

where α can be seen as the volume fraction of the liquid phase; A_{mush} and ε represent arbitrary constants (A_{mush} should be large and ε small to produce a proper damping); and $\mathbf{u}_{cast}$ is the velocity of the extruded plastic.

IV. Material Properties of Commonly Used Thermoplastics

The properties of plastics and processes are influenced by the thermal characteristics such as melt temperature (T_m), glass transition temperature (T_g), thermal conductivity (k), and heat capacity (C_P). Table I [6] shows thermal properties of some of the commonly used thermoplastics along with steel. The T_m occurs at a relatively sharp point for crystalline materials. Amorphous materials basically do not have a T_m; they are in a melt state but the viscosity is too high for flow. As the glassy rigid fluid is heated its viscosity decreases exponentially to enable flow. In reality there is no single flow temperature, but rather a range, which is often taken as the peak of a differential scanning calorimetry (DSC) curve. The glass-transition temperature (T_g) is the point below which plastics behaves as glass – it is very strong and rigid, but brittle. Above this temperature it is neither as strong or rigid as glass, but neither is it brittle. The amorphous TPs have a more defined T_g.

TABLE I Thermal Properties of TPs [4]

Plastics	Density $\rho(kg/m^3)$	Melt Temp., T_m (K)	Thermal Conductivity $k(W/(m.K))$	Heat Capacity $C_P(J/(kg.K))$
PP (C)	900	441	0.1-0.22	1700-1900
HDPE (C)	960	407	0.45-0.52	1900
PTFE (C)	2200	603	0.25	1000
PA (C)	1130	533	0.24-0.28	1700
PET (C)	1350	523	0.15-0.4	1200-1350
ABS (A)	1050	378	0.17	1080-1400
PS (A)	1050	373	0.1-0.13	1200
PMMA (A)	1200	368	0.17-0.19	1400-1500
PC (A)	1200	539	0.19-0.22	1200
PVC (A)	1350	472	0.12-0.25	1000-1500
Steel	7900	3023	43	466

V. COMSOL Simulation Parameters

The simulation of a 3D extruder head is a highly nonlinear problem. As a result an iterative approach is taken for finding the solution. The location of the transition between the molten rubbery and the glassy state is a strong function of the casting velocity and the cooling rate in the air. A fine mesh is considered across the rubbery to glassy front to resolve the change in material properties. However, it is difficult to know where this solidification front is located. By starting with a gradual transition between rubbery and glassy, it is possible to find a solution even on a relatively coarse mesh. This solution can be used as the starting point for the next step in the solution procedure, which uses a sharper transition from the rubbery liquid to the glassy solid. This is done using the continuation method. Given a monotonic list of values to solve for, the continuation method uses the solution of the last case as the starting condition for the next. Once a solution is found for the smallest desired ΔT, the adaptive mesh refinement algorithm is used to refine the mesh to put more elements around the transition region. This finer mesh is then used to find a solution with an even sharper transition. This can be repeated as needed to get better and better resolution of the location of the solidification front. In this paper, the parameter ΔT is first ramped down from 300 K to 100 K, then the adaptive mesh refinement is used such that a finer mesh is used around the solidification front. The resultant solution and mesh are then used as starting points for a second study, where the parameter ΔT is further ramped down from 20 K to 17 K. The double-dogleg solver is used to find the solution to this highly nonlinear problem. Although it takes more time, this solver converges better in cases when material properties vary strongly with respect to the solution. ABS parameters that are used in the COMSOL simulation are given in Table-II, and Table-III.

TABLE-II Thermal parameters of ABS used in the COMSOL simulation.

Description	Data Used
Processing temperature	378[K]
Temperature transition zone half width	75[K]
Heat of glass transition	207[kJ/kg]
Heat capacity at constant pressure, glassy state	1200 [J/(kg.K]
Heat capacity at constant pressure, rubbery state	1797.6
Ambient temperature	300 [K]
Melt inlet temperature	378 [K]
Casting speed	1.0 [mm/s]
Heat transfer coefficient, ABS	2000 [W/(m^2.K]
Heat transfer coefficient, air	10 [W/(m^2.K)]
Surface emissivity	0.95

Table-III Thermal parameters of ABS used in the COMSOL simulation.

Glassy ABS	Value	Unit
Thermal conductivity	0.3	W/(m.K)
Density	1050	kg/m^3
Ratio of specific heats	1	1
Rubbery ABS	**Value**	**Unit**
Thermal conductivity	0.2	W/(m.K)
Density	1050	kg/m^3
Ratio of specific heats	1	1

VI. Results and Analysis

The plot in Fig. 3 shows the streamlines close to the nozzle resulting in a vortex. This eddy flow could create problems with a non-uniform surface quality in a real process. Process engineers can thus use the model to avoid these problems and find an optimal nozzle design. To help determine how to optimize process cooling, Fig. 4 plots the conductive heat flux. It shows that the conductive heat flux is very large in the nozzle area. This is a consequence of the heat released during the secondary phase transition, which is cooled by air. An interesting phenomenon of the process is the occurrence of the peak of the conductive heat flux appearing in the center of the flow at the transition zone. Furthermore, by plotting the conductive heat flux at the outer boundary for the process as in the lower plot in Fig. 4, one can see that a majority of the cooling process occurs just outside the nozzle. More interestingly, the heat flux varies along the nozzle wall length. This information can help in optimizing the cooling of the model (that is, the cooling rate and choice of cooling method). One can solve the model using a built-in adaptive meshing technique. This is necessary because the transition zone—that is, the region where the glass transition change occurs—requires a fine mesh size. Fig. 5 is a 3D plot of the velocity magnitude obtained by a revolution of the 2D axisymmetric data set. In Fig. 5, molten ABS passes through the narrow hot nozzle and solidifies as an extruded ABS. Fig. 6 shows the surface temperature distribution with the heat flux direction as indicated by arrows. Fig. 7 shown the fraction of liquid rubbery state along the centerline for all values of ΔT. For smaller values of ΔT, the transition is steeper. Fig. 8 shows the sensible heat as a function of arc length for various values of ΔT. As ΔT gets smaller, in particular ΔT = 10 K, is not entirely smooth. As a result, to model with reduced ΔT increments one requires to increase the mesh resolution.

VII. CONCLUSION

Modeling and simulation of 3D printer head using COMSOL software tools may predict the die design that gives the best properties for the 3D model. Die design may control the heat flux to give the fastest cure rate to make the model strong in least amount of time. The effects of fillers and their influence on cure rate and end use properties can be predicted.

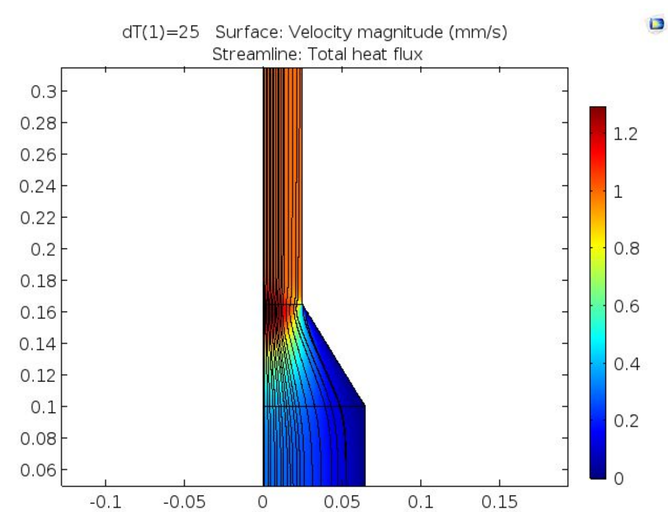

Fig. 3 2D surface velocity magnitude (mm/s) as streamlines of total heat flux.

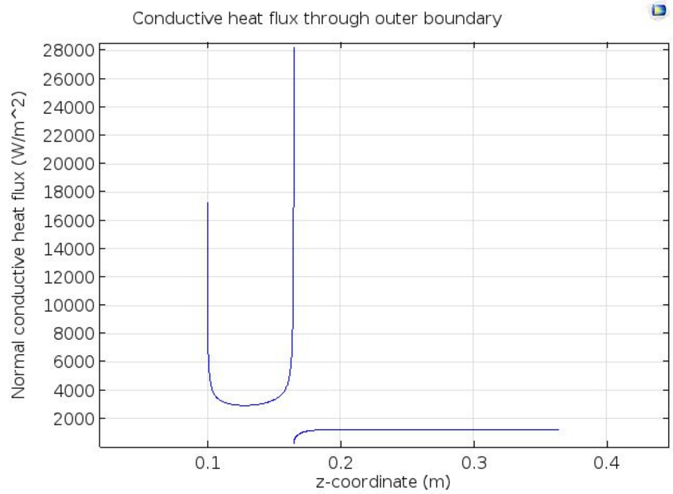

Fig. 4 The cooling as conductive heat flux (top), and through the outer boundary (the cooling zones) after the melt comes out of the hot nozzle.

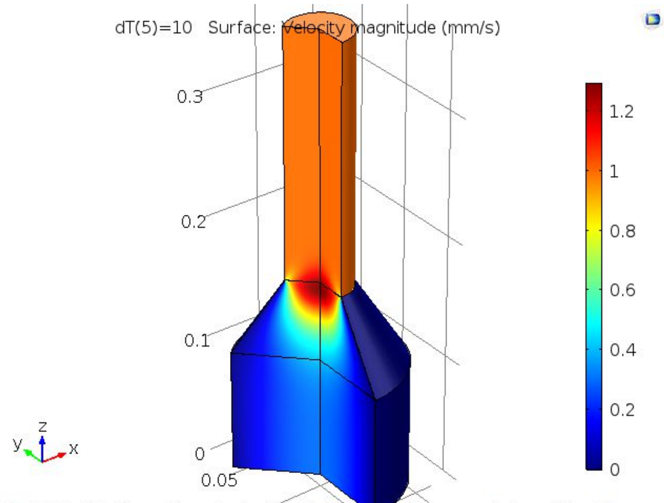

Fig. 5 3D plot shows the velocity magnitude obtained by a revolution of the 2D axisymmetric data set.

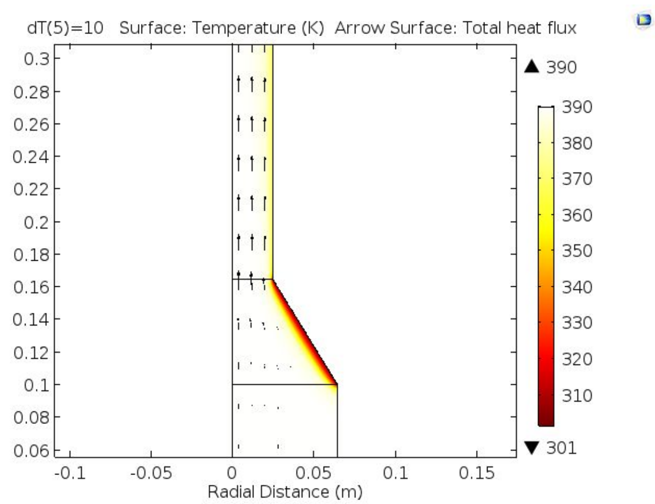

Fig. 6 Surface temperature distribution showing heat flux direction as indicated by arrows.

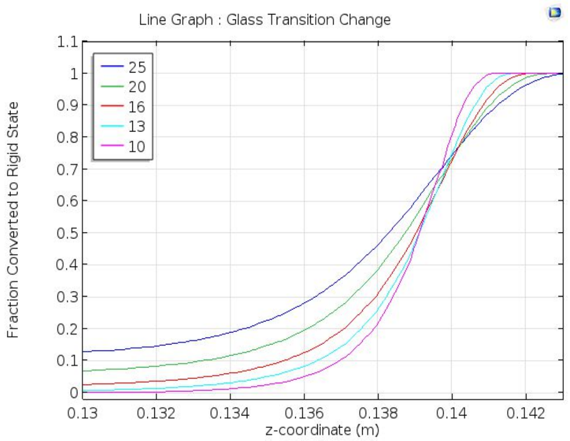

Fig. 7 The fraction of liquid rubbery state along the centerline for all values of ΔT. For smaller values of ΔT, the glass transition is steeper.

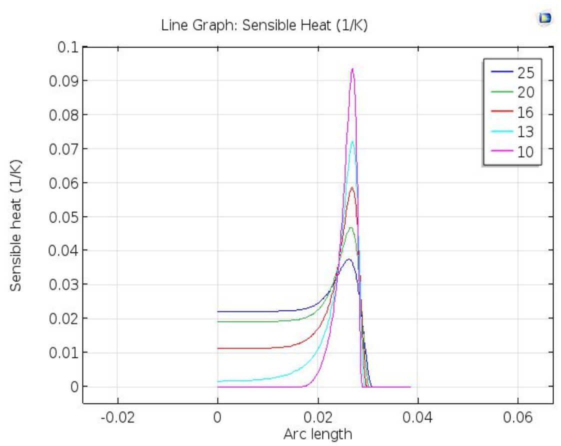

Fig. 8 As ΔT gets smaller, in particular $\Delta T = 10$ K, the curve is not entirely smooth. As a result, to model with reduced ΔT increments one must to increase the mesh resolution.

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