STUDY ON INCORPORATING SUPPORT MATERIAL IN RAPID FREEZE PROTOTYPING

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ABSTRACT

Rapid Freeze Prototyping (RFP) is a rapid prototyping method that uses water freezing into ice to make three-dimensional parts. Each layer of a geometry is deposited and allowed to freeze before the next layer is added. Using a support material in RFP is a relatively new addition to the process. Validating the successful use of a support material in conjunction with the main build material of water is presented in this paper. The support material selected for use is a eutectic sugar solution. The selection criteria, properties, and characteristics of the support material are discussed. Of particular interest is the diffusion between the support and main build material, which must be minimized to an acceptable level for producing good quality, reproducible, complex parts.

1. Introduction

Solid freeform fabrication (SFF) methods were originated in the early 1980's. Several of these methods have been well developed and are now commercially available. These methods include Stereolithography (SLA), Fused Deposition Modeling (FDM), Selective Laser Sintering (SLS), Laminated Object Manufacturing (LOM), Three-dimensional printing (3D-P), and Direct Metal Deposition (DMD). The build materials used in these various types of SFF methods vary with each type, but range from metal to paper to polymers. Each of these methods begins with a CAD model and utilizes a slicing program to find the geometry of very thin slices. The slice geometry is then used to build the three-dimensional part in a layer-by-layer manner following the slice geometry. Some methods use the main build material for support when building complex parts, such as SLA, SLS, LOM, and 3D-P. However, other methods use a different material as the support material, such as FDM and DMD [14].

Rapid Freeze Prototyping (RFP) is a relatively new SFF technique that is currently being investigated. RFP is a method that uses water freezing into ice as its medium to create three-dimensional parts. Compared with other SFF processes, RFP has many potential advantages, including less expensive equipment and material, cleaner material and process, less energy consumption, better surface finish, and ease of building multi-color parts [10]. The RFP building process is conducted in a freezer. A drop-on-demand nozzle moves in a prescribed manner and deposits water or support material layer-by-layer on desired locations according to the cross-sections of a three-dimensional CAD model. The setup also consists of a pressurized containment unit, an X-Y table to control the substrate to obtain the correct part geometry, a Z-axis elevator to raise the nozzles for the successive layers, and circuit driven nozzles. A local cooling system was recently installed in the RFP setup. The local cooling system consists of a liquid nitrogen supply, a solenoid valve which opens on demand and vacuum jacketed transfer hose. The local cooling is controlled by the software that controls the nozzle opening and x-y positioning system. The liquid nitrogen provides a temperature of –195° C when the liquid is dispensed from the tank into the surrounding region around the nozzle. The nozzle has a heater, which keeps the liquid warm until it is deposited. Figure 1 shows a schematic of the setup.

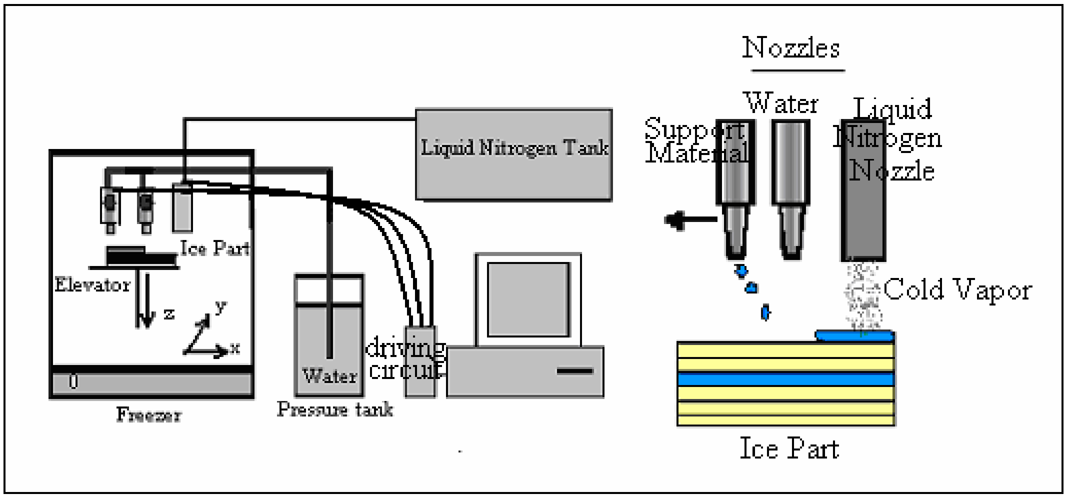


Figure 1: Principle of Rapid Freeze Prototyping

An experimental setup has been constructed and used to create many types of three dimensional ice parts. A photo of some ice parts, with the freezer, x-y table, and water depositing workhead of the experimental setup in the background, is shown in Figure 2 [1]. These ice parts have been made without the use of support material since their geometries are such that the walls are no more than 45° from the vertical. The need for a support material is very real in RFP, since complex parts cannot be built without it. Finding a suitable support material for use with RFP is imperative.

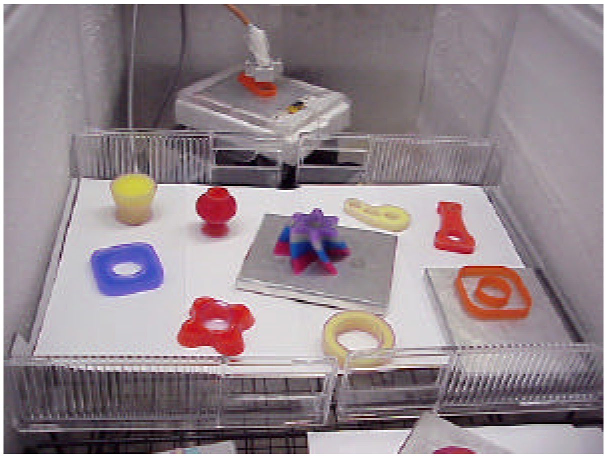


Figure 2: Experimental setup and example ice parts

The objective of this paper is to explore using a support material in RFP. The presentation of this paper is as follows. In section 2, the support material suited for RFP is identified and discussed. Section 3 discusses the analysis needed to understand the interaction between the ice and support material. Section 4 presents the experimental results of building ice parts in conjunction with a support material. Section 5 concludes the paper.

2. Identification of the Support Material

The search for a suitable support material to be used in RFP was a challenging process. The support material preferably has all of these qualities: not soluble in water, a similar contact angle to water, non-toxic and environmentally benign, easily obtainable, and easily removable from the ice in a method that will not affect the remaining structure. There were many substances considered, including a number of different types of oil. The oil had a contact angle that was not compatible with water/ice, so this was eventually eliminated as an option. After many considerations and testing, it was determined that a support material fitting all of the prescribed criteria could not be identified. However, by removing one criterion, the condition of not soluble in water, a couple of materials that could be used as a support material were identified. A possible solution at the top of the list for a support material was a eutectic salt solution, and the second choice was a eutectic sugar solution. Figure 3 shows the phase diagram for the salt and sugar solutions. Table 1 lists some material properties for both solutions.

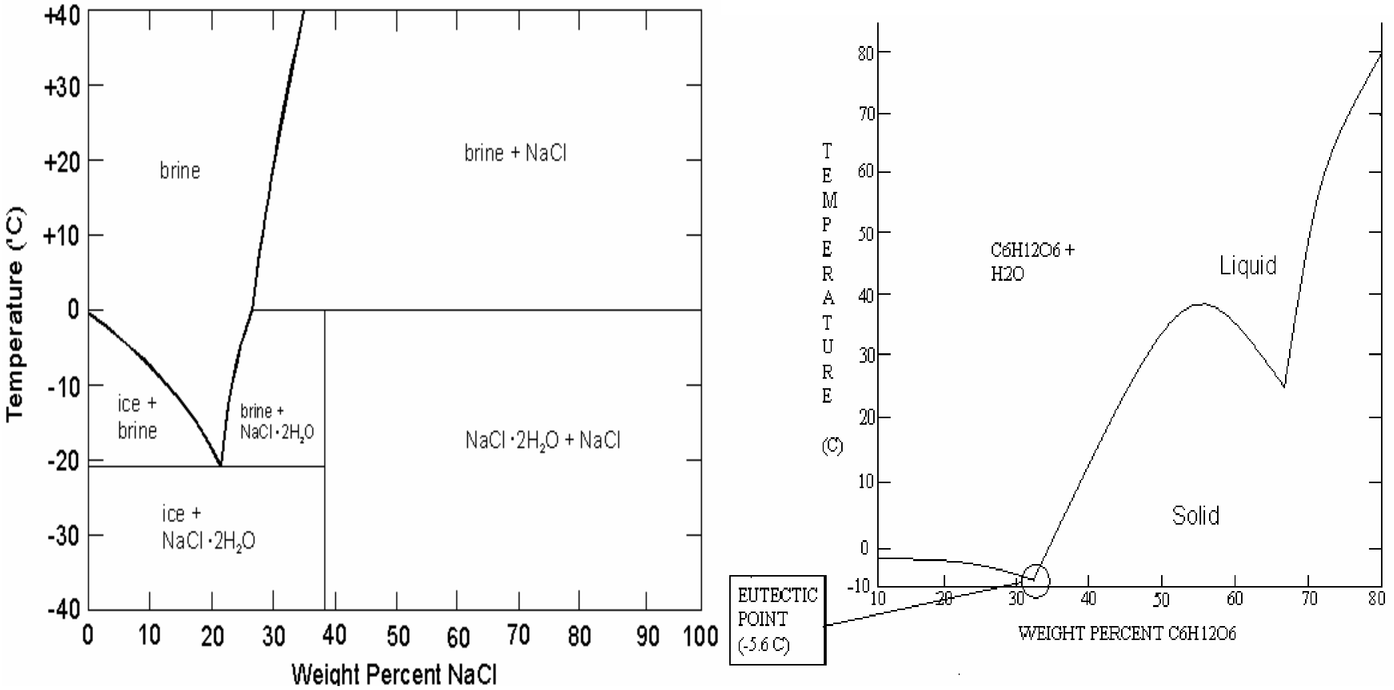


Figure 3: Phase diagrams for salt solution(a) and sugar solution(b)

Table 1: Properties of Support Material [13]

Solution	Concentration (by weight)	Melting Point
$NaCl – H_20$	23.5 % NaCl	-21.3 ° C
$C_6H_{12}O_6 – H_2O$	33 % $C_6H_{12}O_6$	-5.6 ° C

The building of the ice part needs to be done in a freezer colder than the melting point of the support material. Then the built part is placed in a freezer between 0° C and the melting point of the support material to melt the support material. From the control stand point, the larger temperature difference was preferred. By looking at the difference in melting point between water and the two materials, the salt solution became the first choice due to the larger range in which can remove the support material and leave the ice as was originally deposited.

In order to check the interaction of the two solutions with ice during the removal process, some qualitative experiments were done. A known amount of water was frozen completely, then a known amount of the support material was placed on top of the ice in the container and allowed to freeze. This was done in a –60° C freezer to ensure that both materials were completely frozen. The results of these experiments showed that the salt solution would not be an acceptable choice because it degraded the ice part too much. The frozen salt solution interacted with the ice in the container much like placing salt pellets on a frozen sidewalk in the winter melts the ice on the sidewalk. The level of interaction between the sugar solution and the ice, however, was acceptable. The difference in the mass of the ice from the end of the experiment to the initial amount of water was less than 2.4% each time for the sugar solution, but the difference was up to 40% for the salt solution. Thus the sugar solution was deemed a suitable choice for the support material. Table 2 gives the quantitative values of the experiments outlined here, while Table 3 summarizes the properties of water/ice and the sugar solution.

Table 2: Amount of ice loss when support material is removed

Solution	*Init. H_2O wt. (g)*	*Init. Sup. Mat. Wt. (g)*	*Final ice weight (g)*	*% diff. of ice to initial wt.*
1 Sugar	*12.08*	*10.25*	*12.04*	*-0.33*
2 Sugar	*9.97*	*10.25*	*9.81*	*-1.6*
3 Sugar	*11.34*	*10.89*	*11.18*	*-1.41*
4 Sugar	*9.66*	*10.77*	*9.5*	*-1.66*
5 Sugar	*10.13*	*10.36*	*9.89*	*-2.37*
6 Sugar	*10.66*	*10.98*	*10.43*	*-2.16*
7 Sugar	*15.33*	*11.37*	*14.94*	*-2.54*
8 Sugar	*13.02*	*10.64*	*12.88*	*-1.07*
1 Salt	*9.71*	*11.41*	*6.36*	*-34.5*
2 Salt	*10.03*	*11.57*	*6.6*	*-34.2*
3 Salt	*9.81*	*10.13*	*6.26*	*-36.2*
4 Salt	*9.74*	*11.56*	*5.81*	*-40.3*
5 Salt	*9.67*	*11.24*	*7.01*	*-27.5*
6 Salt	*9.76*	*11.18*	*7.29*	*-25.3*
7 Salt	*9.81*	*11.33*	*7.46*	*-24*
8 Salt	*9.72*	*11.2*	*7.35*	*-24.4*

The properties listed in Table 3 for the eutectic sugar solution were calculated using various methods. The thermal diffusivity, thermal conductivity and heat transfer coefficient were assumed to be very close to the value for water, since the addition of sugar most likely won't change these properties significantly. The density of the solid state for the sugar solution was estimated to be the corresponding percentages of each material combined. The specific heat was estimated by taking the value of the specific heat of sugar as it comes out of a saturated solution and combining that with the corresponding amount of water that comprises the solution.

Table 3: Properties of water/ice versus the sugar solution support material

	H_2O	$C_6H_{12}O_6$(33%) – H_2O
Density p_{solid} p_{liquid}	 917 kg/m^3 1000 kg/m^3	 917 kg/m^3 1140 kg/m^3
Specific Heat Cs (solid) Cl (liquid)	 2094 J/kg-°C 4174 J/kg-°C	 1404 J/kg-°C 2800 J/kg-°C
Thermal diffusivity(α)	1.146 X 10-6 m^2/s	1.146 X 10-6 m^2/s
Thermal conductivity(*l*)	2.2 W/m-°C	~ 2.2 W/m-°C
Latent heat of fusion(L)	335000 J/kg	234000 J/kg
Heat transfer coefficient (h)	8.66 W/m^2-°C	~8.66 W/m^2-°C

Since the condition of non-solubility in water was eliminated from the list of criteria, the possibility of diffusion is always present. Diffusion will occur to some extent when both materials are in contact, so this must be taken into account. Predicting and measuring the diffusion when the materials are in a liquid state at the interface is discussed in the next section.

3. Interface between ice and support material

Sui and Leu [1] studied the ice line in RFP extensively and have shown that the water droplets ejected from the nozzle unite together before freezing and form a continuous water line. They showed that the deposited line height and width can be represented by the following equations [15]:

$$\Delta z = \sqrt{\frac{f \cdot \sin(a/2)}{n}} \tag{1}$$

$$w = \sqrt{\frac{f}{v \cdot \sin(a/2)}} \tag{2}$$

where *f* is the volumetric feed rate, v is the scan speed, and α is the contact angle, which has been determined to be 20° for water when used in the experimental –20° C freezer [6]. The contact angle, α, was determined by measuring the layer thickness and line width in various ice parts. Equations (1) and (2) were then used to find the contact angle. As far as applying Equations (1) and (2) to a support material, these equations still apply and the contact angle for a support material can be found in a similar method as was used for finding the contact angle for water. Since the contact angle is a function of ambient temperature, the contact angle should be determined experimentally depending on the ambient temperature of the freezer. The contact angle that was found for the ice and support material in the conditions of this paper is discussed in the next section on experimental results. The volumetric feed rate, *f*, can be found by using the following equation:

$$f = \frac{p}{4} d^2 N \sqrt{2g\Delta h} \qquad (3)$$

where d is the nozzle opening diameter, N is the duty cycle of the nozzle, g is the gravitation constant, and Δh is the height difference between the nozzle and the liquid supply. [3]

The calculation of the minimum wait time, which is the time for a layer to completely freeze, is an important aspect in any type of rapid prototyping, since it will determine how fast a part can be made. In RFP, it has been shown that the minimum wait time can be found with the following equation:

$$t_{\min} = \frac{E\Delta z}{l \cdot \Delta T \sqrt{m}} \sqrt{1 + \frac{l \cdot \Delta T}{E\mathrm{A}}} \qquad (4)$$

where E is the enthalpy of the system and $E = p_l(L + c_l \Delta t)$, p_l is the density of the liquid, L is the latent heat of the material, c_l is the liquid specific heat, Δt is the temperature difference between the initial temperature and the freezing temperature, Δz is the layer height, *l* is the thermal conductivity, ΔT is the temperature difference between the freezing temperature of the material and the build ambient temperature, m = 2h/ *l* w, h is the heat transfer coefficient, w is the layer width and A is the thermal diffusivity. If the layer height and width are assumed to be equal for both water and the support material and are set to typical dimensions of 0.1 mm and 1 mm respectively, the properties of water and the support material can be found in Table 2, and Equation (4) can be used to find the predicted minimum wait time between each layer for both water and the support material. By allowing this amount of time for each layer, each layer will have had a sufficient amount of time to completely solidify. This predicted wait time is shown in Figure 4 as a function of ambient temperature.

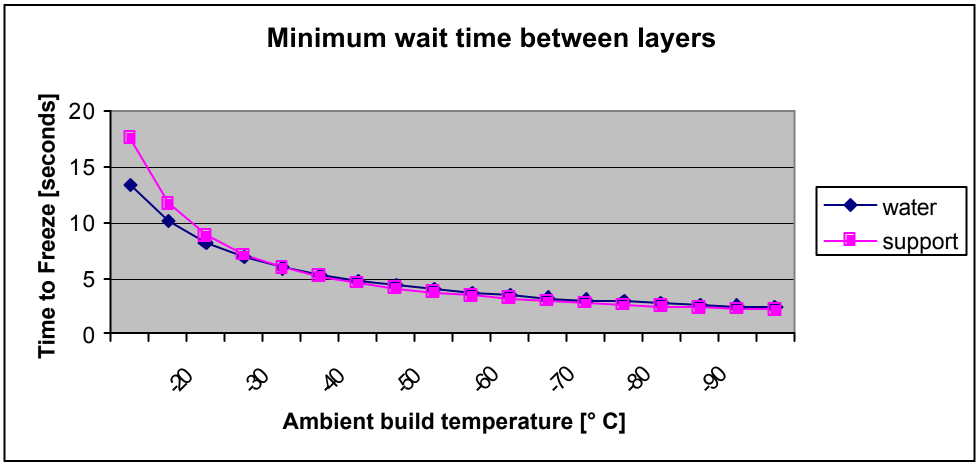


Figure 4: Minimum wait time between deposition of layers

Since diffusion will always occur to some extent when a liquid is in contact with another liquid of higher or lower concentration, it is important to minimize the diffusion rate as much as possible. Diffusion is of particular concern when water is deposited on top of a layer of support material, since the water will melt the support material due to the higher specific heat of the water. When support material is deposited on an already frozen layer of ice, melting does not occur, so diffusion is negligible.

Diffusion can be quantified by using Fick's law. Fick's law states that the mass flux of a solute, J, into an area of less concentration can be calculated by a diffusion coefficient, D, multiplied by the differential of the concentration over the distance traveled. The equation is represented below:

$$J = -D\frac{\partial c(x,t)}{\partial x} \tag{5}$$

The mass flux has units of mass per area time. The diffusion coefficient is found experimentally and ranges in values for gases, liquids and solids. By using the mass flux and the wait time for the layer deposition in RFP, the total mass flux can be calculated. Obviously, the lesser the amount of time that the layer needs to freeze, the lesser amount of mass diffusion will occur.

4. Experimental Results

In order to build with water and support material together, the height of the deposited lines must be calculated beforehand in order to allow the correct number of layers to be deposited to create the correct height. Since local cooling has been implemented into the RFP system, the contact angles of both the water and the support material were measured so that the layer height could be found. In order to check for the contact angle, lines of water and support material were deposited while using local cooling and measured upon completion. By knowing the measured height and width of the walls, Eqs. (1) and (2) were used to find the contact angle. It turns out that using local cooling affects the contact angle of water, which was 20° in a –20° C freezer. The contact angle comes out to be about 12° when the ambient temperature around the area being built is locally cooled. The support material has a contact angle of about 14° when using the local cooling, so the scan speed and/or volumetric feed rate need to be changed accordingly so that the two materials may be built and have the same line height. For example, if the scan speed is set to 50 mm/s and the volumetric feed rate is 17.85 mm^3/s, the line width and line height for ice can be found by Eqs. (1) and (2) to be 0.194 mm and 1.85 mm respectively and for support material the line width and line height can also be found with Eqs. (1) and (2) to be 0.209 mm and 1.71 mm. Since the line heights need to be the same as each other, the support material line height is set equal to that of ice, which is 0.194 mm, and then the scan speed is recalculated using Eq. (1) for the support material. The recalculated scan speed is 58.12 mm/s. Using two scan speeds in the construction of one ice part will result in uniform heights by the different materials used.

To check the interactions of the ice and support material in the RFP process, a simple cylinder part with a middle section removed was built. This part was built in the original –20° C freezer. The support material used here is the sugar solution. Figure 5 shows the ice part with the ice sections and the support material section (in the middle) before and after the support material was removed.

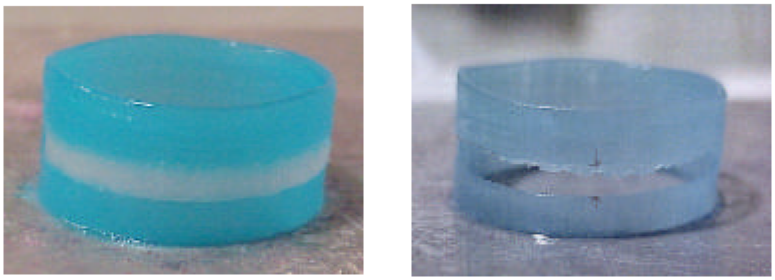


Figure 5: Ice part before (left) and after (right) support material is removed

It can be seen in the right hand side of Figure 5 that there is quite a lot of interaction occurring at the interface between the ice and the support material, when the support material is being built upon by the water/ice. The edge of the ice after the support material removed is very uneven. The boundary where ice is the lower material and the support material is deposited on top does not have this uneven boundary. Water has a higher specific heat than the support material, as shown in Table 3. Consequently, when the support material is the lower surface and water is being deposited on top, the not-yet-frozen water melts the support material. This is followed by diffusion between the support material and water and a re-freezing process afterwards. In order to minimize this melting, diffusion and re-freezing process, the water needs to freeze very quickly on top of the frozen support material in order to minimize the diffusion from occurring. Diffusion occurs substantially only during the liquid phase, so shortening the time of the liquid phase as much as possible is required.

Figure 6 shows a cylindrical ice part similar to the part shown in Figure 5.This part was built with the additional local cooling system. It can be seen that the interface between the support material layer and the ice layer above is now very smooth and there is no indication of substantial diffusion.

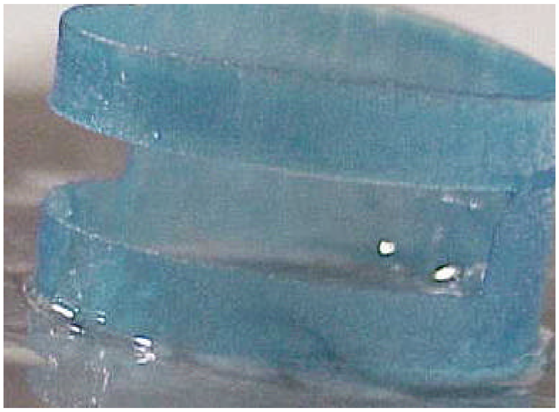


Figure 6: Ice part built with local cooling during interface layers

Quantitative experiments were conducted to find out the effect of temperature on diffusion. Since it is very difficult to measure the actual diffusion rate, wall heights were measured instead. Ice walls were built in different ambient temperature environments. Twenty-five layers of water were deposited onto a frozen wall of support material. The heights were predicted for no diffusion and the ice walls were measured for height after the support material was removed. If diffusion does occur, then the wall height will be less than predicted. The support material in this case was melted off at -1° C. Figure 7 shows the measured wall heights at different ambient temperatures compared with the predicted wall height without diffusion. Table 4 gives the values used in Figure 7. The deviation is also shown that represents the difference between the wall height with no diffusion and the measured wall height average for each ambient temperature.

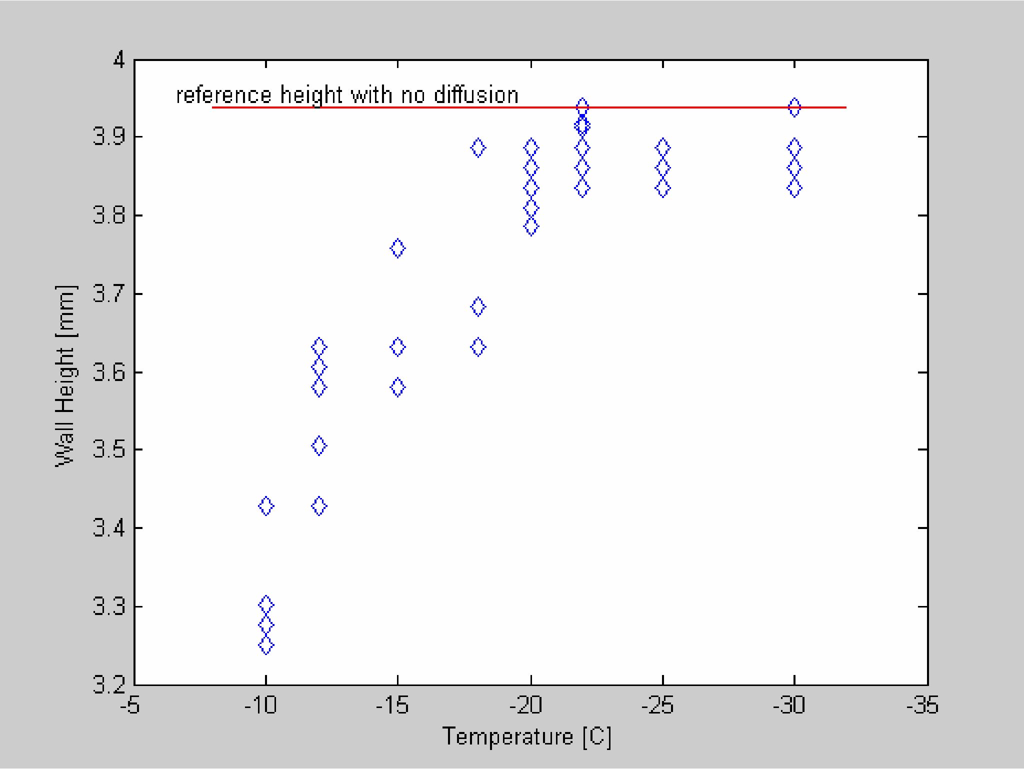
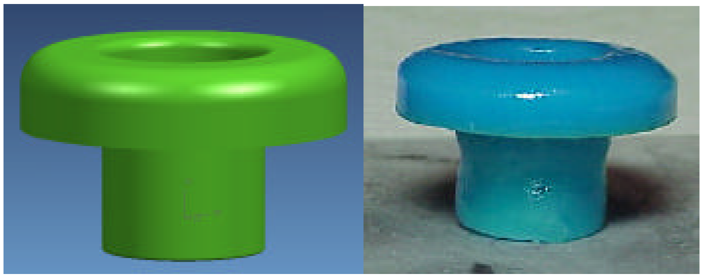


Figure 7: Measured height data for ice walls built in varying ambient temperatures

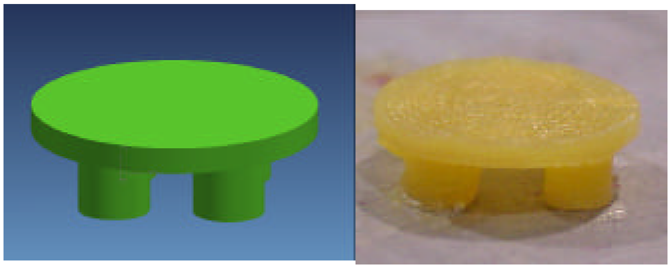
Table 4: Diffusion quantitative experiments

Freezer Amb. Temp.	Predicted wall height [mm] w/o diffusion	Measured wall heights[mm]	Deviation
-10	3.938	3.315	0.623
-12	3.938	3.562	0.376
-15	3.938	3.683	0.255
-18	3.938	3.734	0.204
-20	3.938	3.835	0.103
-22	3.938	3.891	0.047
-25	3.938	3.861	0.077
-30	3.938	3.880	0.058

Since a support material has been found that can be used with RFP, and also utilizing the local cooling system, many complex and also solid parts may be built now. Solid parts can be modeled as a two-dimensional system, which is much more complex than the one-dimensional case taken into account in this paper. However, the same logic of local cooling can be applied to solid parts. It can be shown experimentally that using local cooling and a support material, complex and solid parts can be made, as shown in Figure 8.



Part A: CAD model(left) and actual RFP ice part (right)



Part B: CAD model (left) and actual RFP ice part (right)

Part C: Ice part with support material (left), after removal (center) and during build (right)

Part D: CAD model (left) and actual RFP ice part (right)
Figure 8: Complex ice parts built with RFP experimental setup

These ice parts have been built using various techniques of process planning. Part A was built in a concentric circle fashion, starting from the outer diameter circle and working inward to create a solid cylinder. The support material was deposited in a similar fashion around the lower cylinder to a diameter large enough to support the upper section of the ice part. Part B was built in a similar fashion, but the 'legs' were each built separately and deposited in concentric circles with support material deposited in the lower section of the building process. Part C was built with a true raster motion. Both the water and support material were deposited in this manner for each layer. Part D was built very similar to part A with concentric circles being deposited, except this part was built from the inner circle to the outer. Each of these parts were placed in a -5° C kerosene bath upon completion and allowed to sit in the bath overnight to remove the support material from the ice structure.

5. Conclusions

A suitable support material has been identified and tested for use in the Rapid Freeze Prototyping process. The support material identified is a eutectic sugar solution. It is water soluble so diffusion does occur when the support material and main material of water are both in liquid states. To control the diffusion rate as much as possible, a local cooling sub-system has been installed into the RFP system that creates a very cold environment around the deposition region and causes both water and liquid support material to freeze much faster. Ice parts have been made utilizing local cooling and show a marked difference at the interface. It has been shown through experiments that the rate of diffusion decrease as the ambient temperature decreases and the change in the ice wall height due to the diffusion becomes negligible when the temperature around the ice part being built is lower than -20 ° C.

Acknowledgement:

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6. References:

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