Eliminating Voids in FDM Processed Polyphenylsulfone, Polycarbonate, and ULTEM 9085 by Hot Isostatic Pressing

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Abstract

Objectives

Fused Deposition Materials (FDM) have been used to make moulds and models, but interest has been directed toward making in-use parts by using FDM to process polymers. However, the FDM plastics are not as strong as the parent material from which they are formed because of the voids left between rows of filament. The purpose of this study is to determine if hot isostatic pressing (hipping) effectively eliminates voids in FDM processed polyphenylsulfone, polycarbonate, and ULTEM 9085 polymers to strengthen the material. Also, samples will be cold sprayed for possible canning for hipping. These objectives will be completed by hot pressing samples of FDM polymers to determine if applying heat and pressure increases the density of the material, hot pressing tensile samples to determine if densification leads to strengthening, cold spraying polymer samples, and analyzing the mesostructure of the hot pressed and cold sprayed samples.

Findings

It was found that hot pressing does reduce the volume of voids though it may cause distortions at higher temperatures. Hot pressing can strengthen the material, but a clear trend has not yet been determined. Cold spray copper nanoparticles were successfully deposited, but further study is needed before using as a canner.

1. Introduction

Fused Deposition Materials (FDM) are made by heating a thin polymer filament in a computer controlled head which deposits the material, layer by layer, to form a three-dimensional object. The program uses a computer aided design (CAD) file to guide the head as it layers the materials so that it can create complex geometries to great accuracy [10]. This process is useful for

creating hard to machine designs for working models, moulds, and form and fit verification [1]. FDM polymers can also be used for creating in-use parts. A problem with this is the strength of the material. Although the original polymer may be strong, the FDM polymer will contain voids as a result of the processing which significantly decreases the strength of the material.

Many approaches may be taken to solve this problem. Jose F. Rodriguez et al maximized the strength of fused-deposition ABS plastic parts. He says that the strength depends on the bulk polymer strength, fiber layout, void geometry and extent of fiber bonding, and the fiber-to-fiber bond strength. He concluded that the transverse strength could be increased by optimizing the processing settings and post-fabrication annealing. He also found, however, that annealing caused distortion in the parts. In another study, Jose F. Rodriguez optimized the design of fused deposition acrylonitrile butadiene styrene (ABS) for stiffness and strength using a mathematical model [10]. Prashant Kulkarni and Debasish Dutta investigated the effects of different deposition paths on stiffness. These results were compared to an analytical model created using laminate analysis. They found that the model could be useful in helping designers engineer deposition to meet stiffness requirements [8]. While hipping is generally used for metals and ceramics, some have used it for plastics. Pirkko Jarvela et al studied the hot isostatic pressing of extruded polypropylene for strength improvement. They concluded that hipping with optimal parameters increased the strength of the material [6]. O. R. Hughes et al used powder-assisted hot isostatic pressing to increase the density of cold-compacted PBI powders. Using this technique, they achieved densities of about 99% of the ultimate PBI density [5]. Rizwan M. Gul and Frederick J. McGarry use hot isostatic pressing to eliminate defects in compacted ultra high molecular weight polyethylene resin. They found that hipping could consolidate the material

well if processed at the correct parameters. They discovered that processing temperature affected the microstructure more than any other variable [4].

The purpose of this study is to determine if hot isostatic pressing (hipping) effectively eliminates voids in FDM processed polyphenlysulfone, polycarbonate, and ULTEM 9085 polymers with the goal of strengthening the material. Also, the samples will be cold sprayed for experimentation with strength and possible canning for hipping. These objectives will be completed by hot pressing samples of FDM polymers to determine if applying heat and pressure increases the density of the material, hot pressing tensile samples to determine if densification leads to strengthening, cold spraying polymer samples, and analyzing the mesostructure of the hot pressed and cold sprayed samples.

2. Broader Impact

While increasing the density of FDM polycarbonate, polyphenylsulfone, and UTLEM 9085 for strength is a small development in FDM processing, it is important in the context of rapid manufacturing. According to CSA technical editor Carol Y. Wang, "Several technologies collectively known as Rapid Manufacturing (RM) have been developed to shorten the design and production cycle, and promise to revolutionize many traditional manufacturing procedures" (www.csa.com/discoveryguides/rapidman/overview.php.)

Rapid Manufacturing shortens the design cycle because injection molding or tooling a part from a new design could take weeks. Using rapid prototyping, this may only take one or two days. Rapid Manufacturing shortens the production cycle, because if a part in a manufacturing process breaks, manufacturing must stop until the part is repaired or replaced. A part takes only a day or two to make using rapid prototyping while it may take a week or more to

injection mold or tool the part. By reducing the design and production cycles, companies save time and money. This translates into better products and prices for consumers.

At first glance, this study may seem minor, but when seen in the context of rapid manufacturing, strengthening FDM processed polymers becomes useful to industry and ultimately, the good of people.

3. Procedure

3.1 Materials

FDM processed polyphenylsulfone provided by Boeing

FDM processed polycarbonate and ULTEM 9085 provided by Stratasys

Cold mount material

Copper nanoparticles

Nickel electroless bath

3.2 Equipment

Precision balance

Metallurgical Microscope

Carver® AutoFour Automated 30 Ton Laboratory Press

MTS 858 Mini Bionix II tensile machine

Cold Spray Equipment

3.3 Density Measurements

The bulk density of each sample was determined using a precision balance with a hook on the bottom to use as a suspension balance as shown in Figure 1. The mass was measured in air and in water and the density was calculated using Archimedes principle as follows:

$$\rho_{object} = \rho_{liquid} * m_{object} / (m_{object\ in\ air} - m_{object\ in\ liquid})$$

This density was compared to the theoretical density to find the fraction of porosity:

$$f_{porosity} = 1 - \rho_{bulk} / \rho_{theoretical}$$

The thickness of each sample was also recorded before hot pressing.

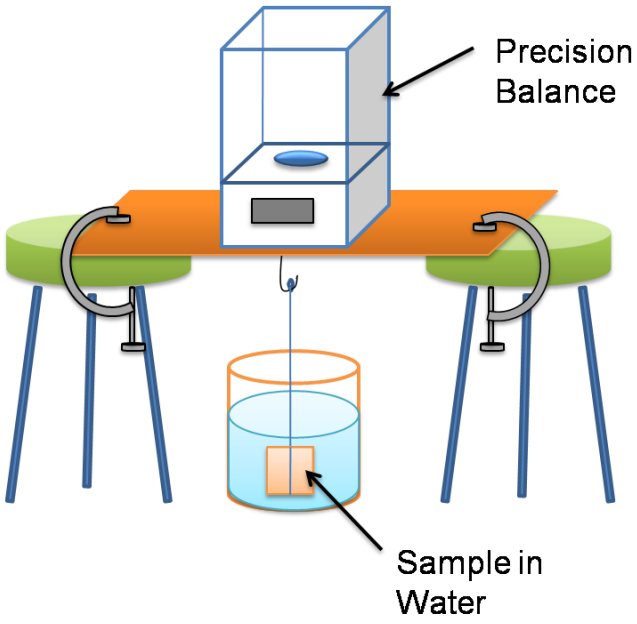


Figure 1: Density Measurement Set Up

3.5 Hot Pressing

The samples were hot pressed at different temperatures and pressures using a Carver AutoFour hot press for one hour each (see Figure 2). The matrixes of planned and actual parameters are shown in Figures 4, 6, and 8. Density and thickness were measured again after hot pressing. The samples were cut and cold mounted and viewed using optical and metallurgical microscopes.

Figure 2: Carver AutoFour Hot Press

3.6 Tensile Testing

The strength of FDM polycarbonate and UTLEM 9085 was measured using an MTS 858 Mini Bionix II tensile machine. The samples were machined according to ASMT D 638 type I. They were first cut into rectangles using a band saw, and then cut into a dog bone shape using a die and router as shown in Figure 3. Five samples for each measurement were tested. The strength was measured along two different layup orientations for both polycarbonate and ULTEM 9085. Samples were laid up with fibers running at 0 and 90 degrees to the testing direction, and positive and negative 45 degrees. Tensile samples that were hot pressed were also tested. The materials were hot pressed before being cut to size as described above. Three tensile samples for each hot press parameter were tested because of time restrictions. The samples that were hot

pressed for making the tensile samples were 3 inches by 6 inches which is significantly larger than the one square inch samples hot pressed before.

Figure 3: Tensile Sample Die

3.7 Cold Spray

Polyphenylsulfone samples were cold sprayed with copper nanoparticles, nickel electroless plated, and cold mounted for analysis.

4. Results

4.1 Density and Hot Pressing

The processing parameters for each sample are shown in Tables 1-3.

Table 1: PPSU Table of Parameters		
Sample #	Temp. (˚F)	Pressure MPa
1	302	60
2	419	60
3	452	60
4	302	100
5	419	80
6	-	-
7	302	140
8	419	104

Table 2: Polycarbonate Table of Parameters		
Sample #	Temp. (˚F)	Pressure MPa
1	280	45.6
2	230	45.6
3	180	45.6
4	205	45.6
5	230	62.2
6	160	100
7	-	-
8	180	73.2
9	180	149

Table 3: ULTEM 9085 Table of Parameters		
Sample #	Temp. (˚F)	Pressure MPa
1	330	44
2	280	44
3	230	44
4	-	-
5	280	83
6	230	69
7	180	44
8	-	-
9	180	90

The density measured before and after hot pressing for each sample is shown in the tables below.

Table 4: Density Before Hot Pressing (g/cm^3)			
Sample #	PPSU	Polycarbonate	ULTEM 9085
1	1.10	1.15	1.19
2	1.08	1.15	1.18
3	1.08	1.15	1.18
4	1.09	1.15	1.19
5	1.09	1.15	1.19
6	1.08	1.15	1.19
7	1.09	1.15	1.19
8	1.08	1.15	1.19
9	1.10	1.15	1.18
10	1.07	-	-
Theoretical	1.29	1.2	1.34

Table 5: Density After Hot Pressing (g/cm^3)			
Sample #	PPSU	Polycarbonate	ULTEM 9085
1	1.25	1.20	1.26
2	1.27	1.16	1.24
3	1.28	1.16	1.20
4	1.26	1.16	-
5	1.27	1.19	1.26
6	-	1.18	1.26
7	1.26	-	1.20
8	1.24	1.17	-
9	-	1.19	1.25
Theoretical	1.29	1.2	1.34

In Figures 4-9 the hot pressing results are shown.

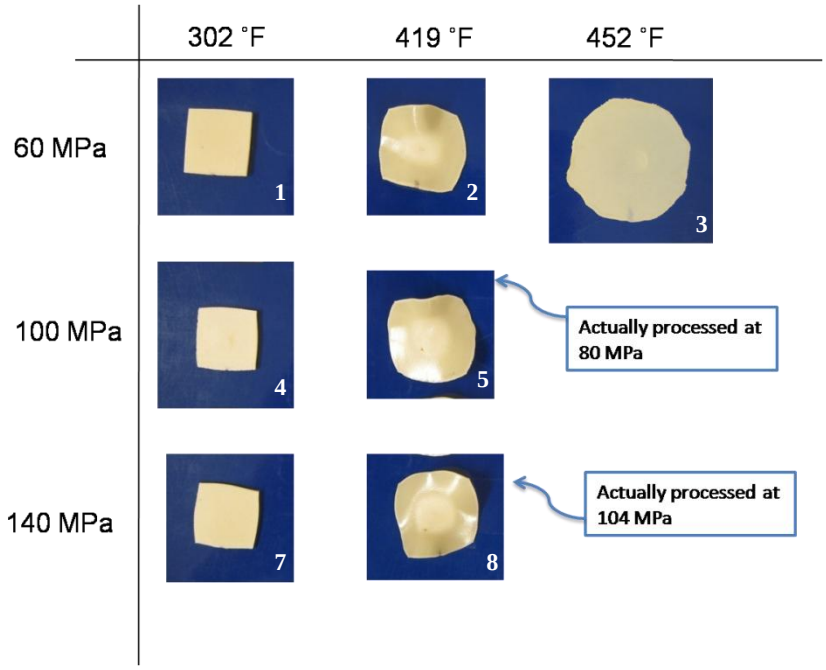


Figure 4: PPSU hot press parameter matrix and results

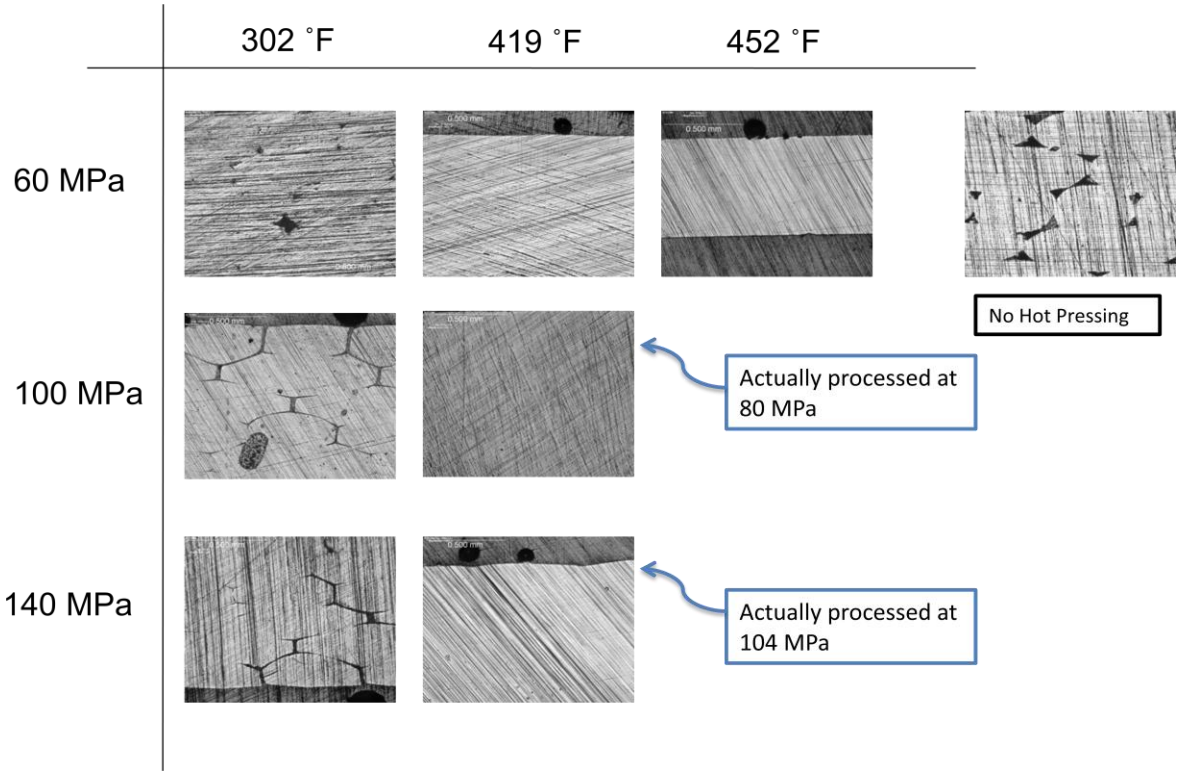


Figure 5: PPSU micrograph matrix

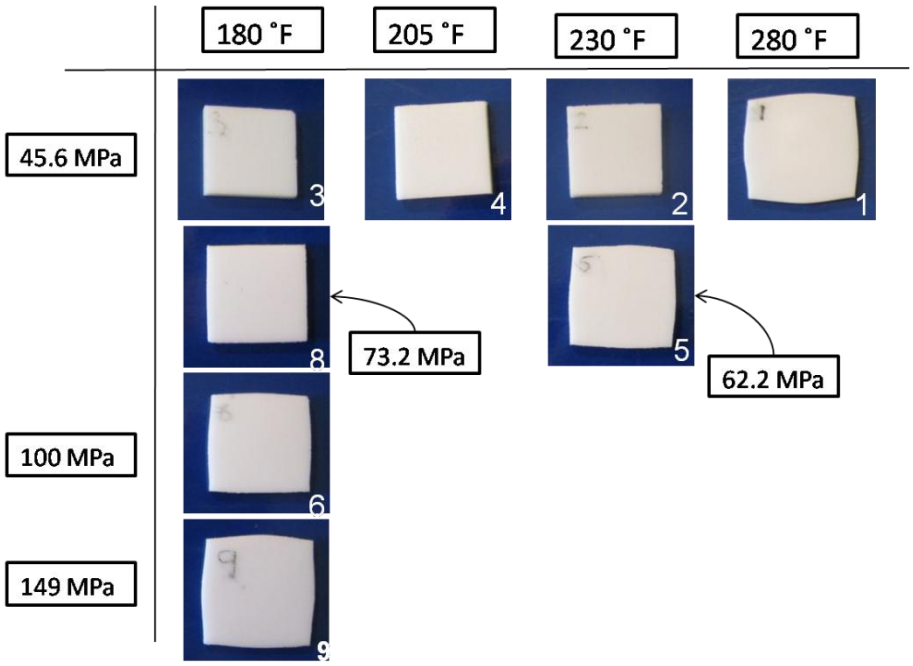


Figure 6: Hot Pressed polycarbonate parameter matrix and results

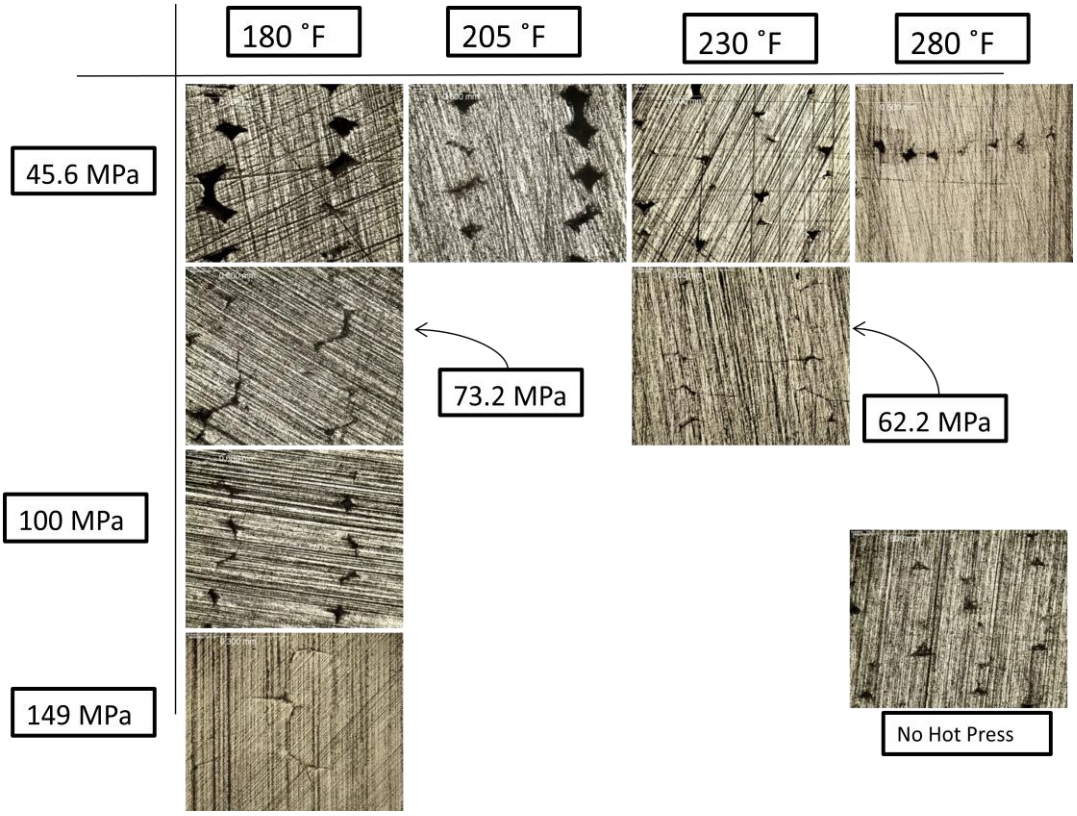


Figure 7: Polycarbonate micrograph matrix results

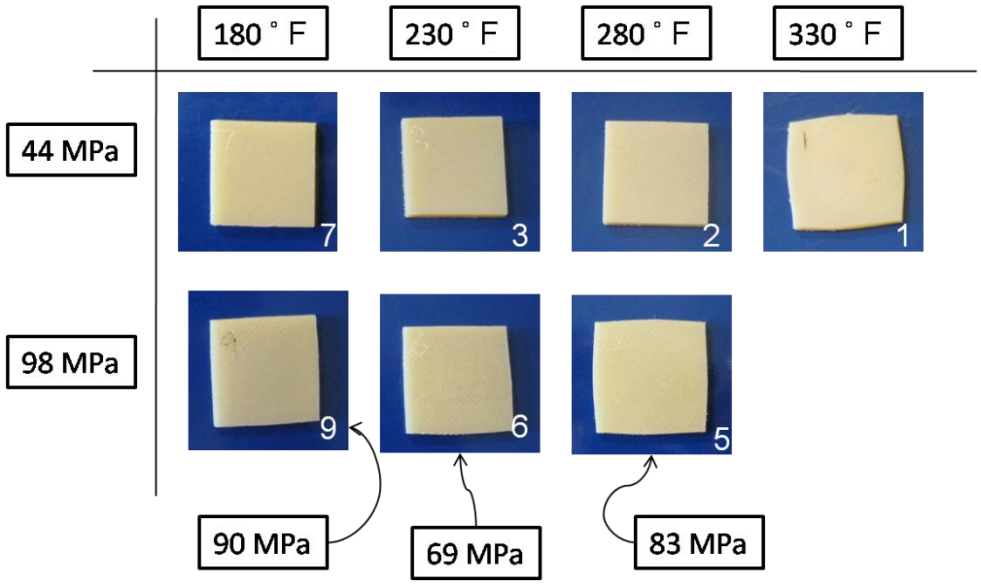


Figure 8: Hot Pressed ULTEM 9085 parameter matrix and results

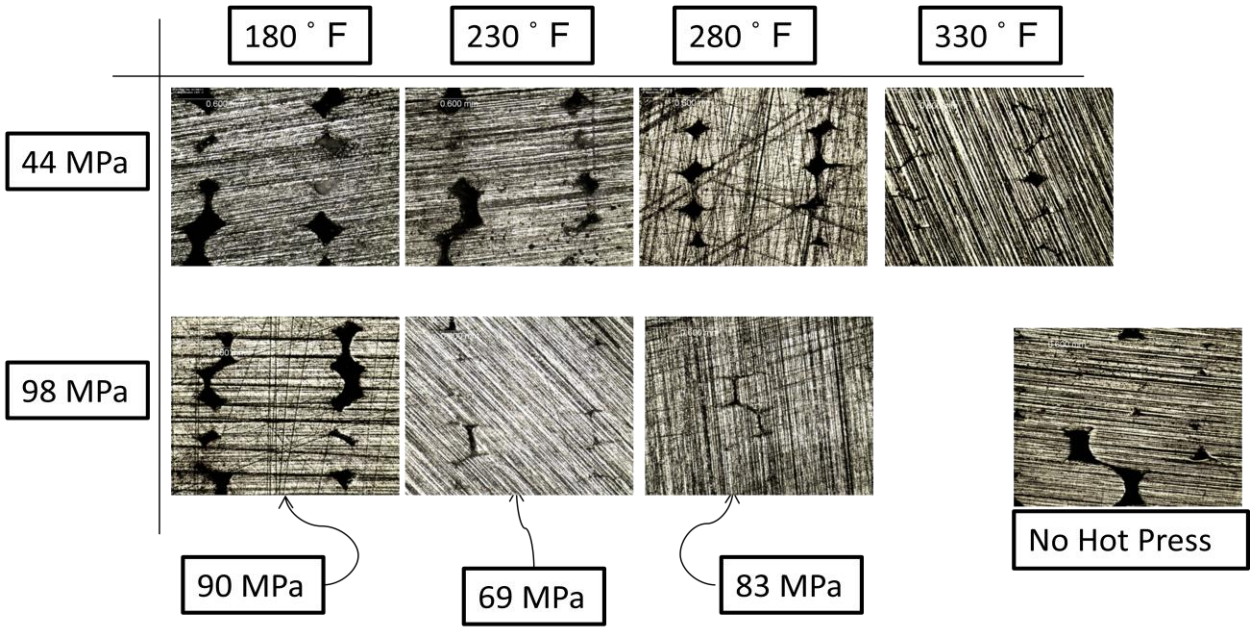


Figure 9: ULTEM 9085 micrograph matrix

The percent reduction in thickness is shown below.

Table 6: % Reduction in Thickness			
Sample #	PPSU	Polycarbonate	ULTEM 9085
1	20.2	35.1	29.8
2	61.6	4.6	11.6
3	80.5	3.1	3.9
4	28.4	3.4	-
5	66.6	21.4	26.4
h6	-	19.8	14.7
7	41.8	-	3.1
8	67.4	12.2	-
9	-	35.1	17.1

The porosity before and after hot pressing is shown in the table below.

Table 7: Fraction of Porosity						
Sample #	PPSU		Polycarbonate		ULTEM 9085	
	Before	After	Before	After	Before	After
1	0.147	0.0313	0.0404	0.0032	0.115	0.057
2	0.162	0.0193	0.0440	0.0374	0.117	0.071
3	0.159	0.0071	0.0394	0.0320	0.119	0.102
4	0.155	0.0210	0.0449	0.0332	0.115	-
5	0.156	0.0132	0.0408	0.0093	0.111	0.057
6	0.164	-	0.0416	0.0125	0.113	0.063
7	0.157	0.0198	0.0450	-	0.115	0.108
8	0.164	0.0418	0.0421	0.0265	0.115	-
9	0.150	-	0.0421	0.0077	0.119	0.069

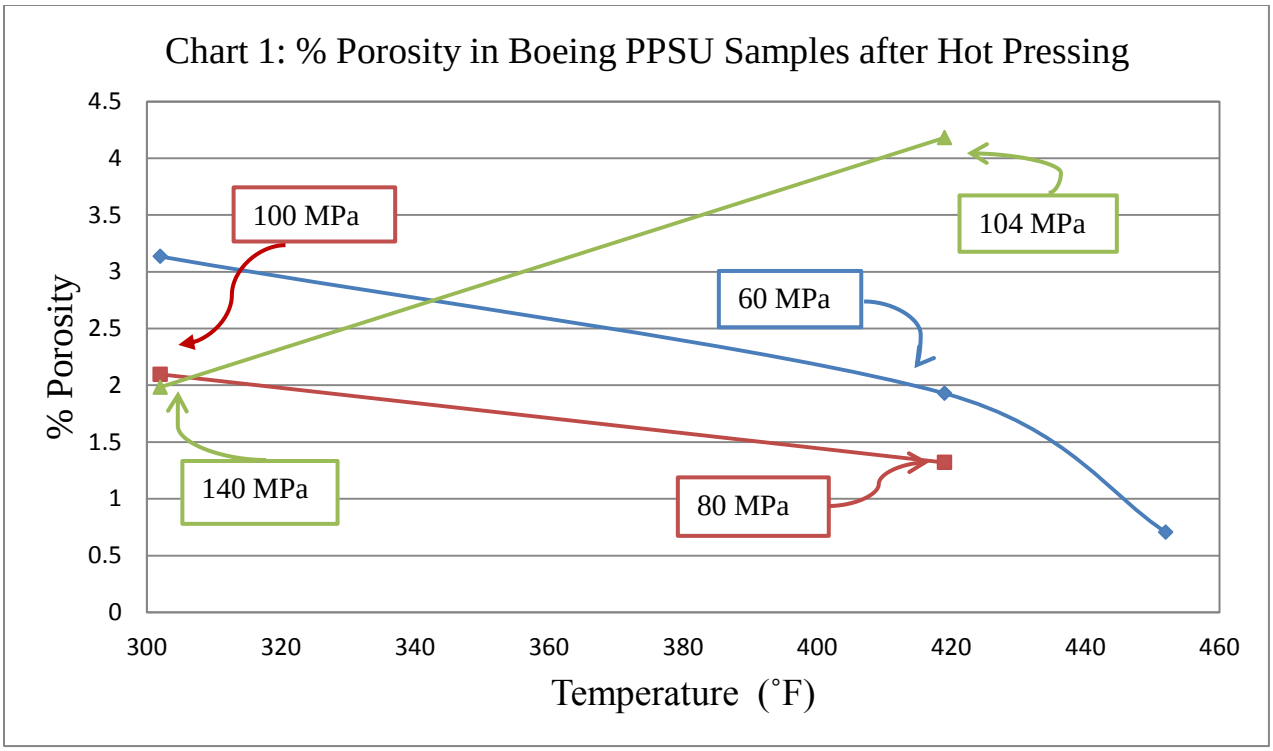


Chart 1: % Porosity in Boeing PPSU Samples after Hot Pressing
% Porosity
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
300
320
340
360
380
400
420
440
460
Temperature (˚F)
100 MPa
104 MPa
60 MPa
140 MPa
80 MPa

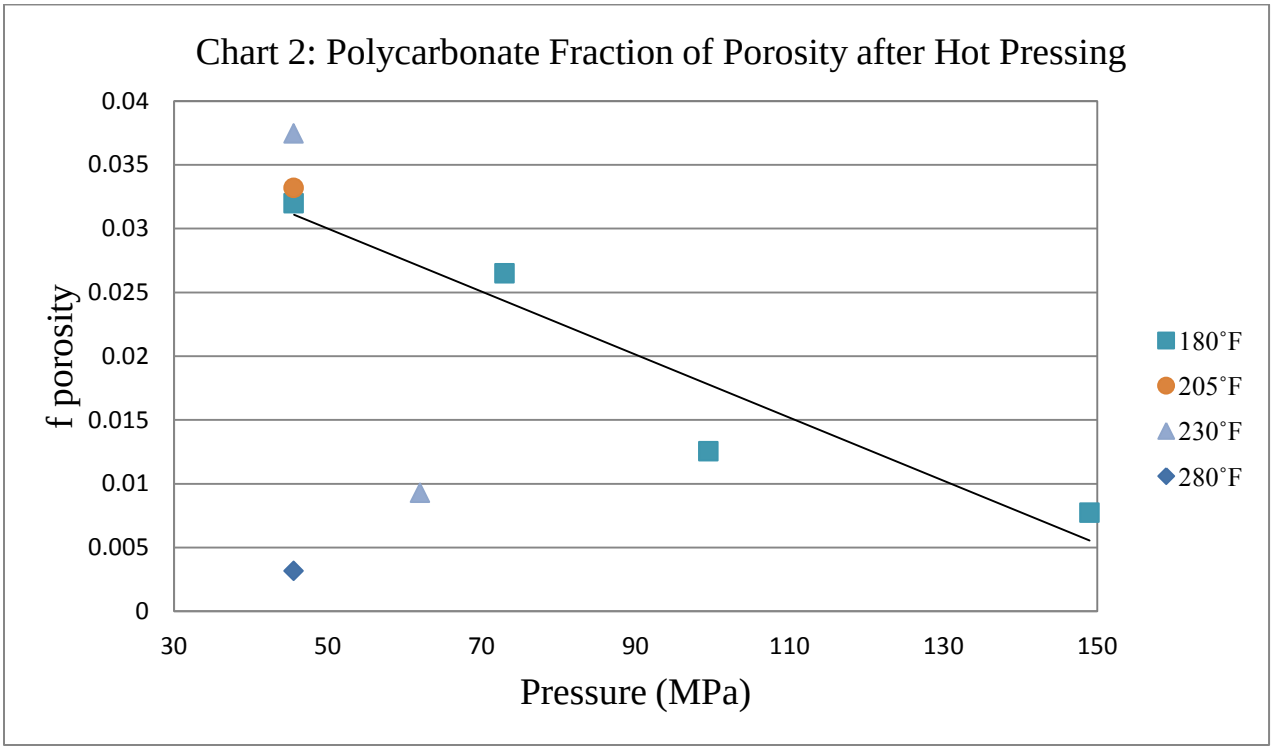


Chart 2: Polycarbonate Fraction of Porosity after Hot Pressing
f porosity
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
30
50
70
90
110
130
150
Pressure (MPa)
180˚F
205˚F
230˚F
280˚F

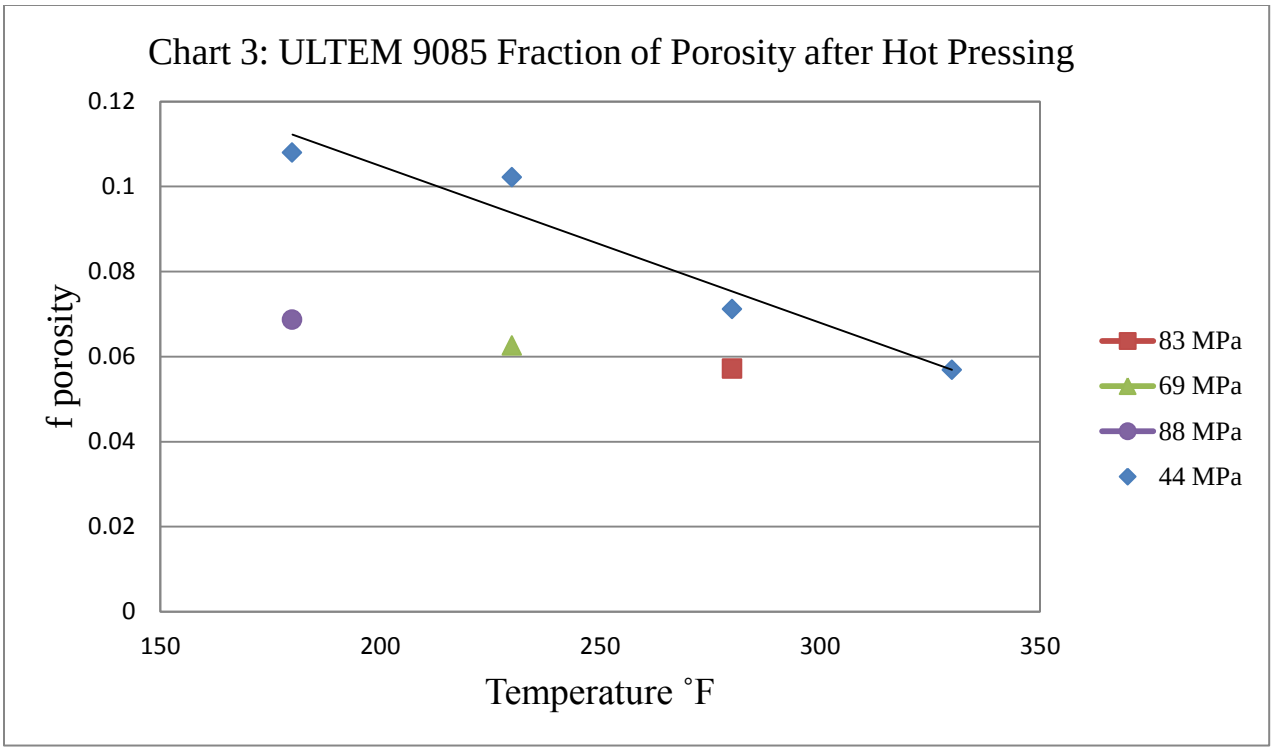


Chart 3: ULTEM 9085 Fraction of Porosity after Hot Pressing
f porosity
0.12
0.1
0.08
0.06
0.04
0.02
0
150
200
250
300
350
Temperature ˚F
83 MPa
69 MPa
88 MPa
44 MPa

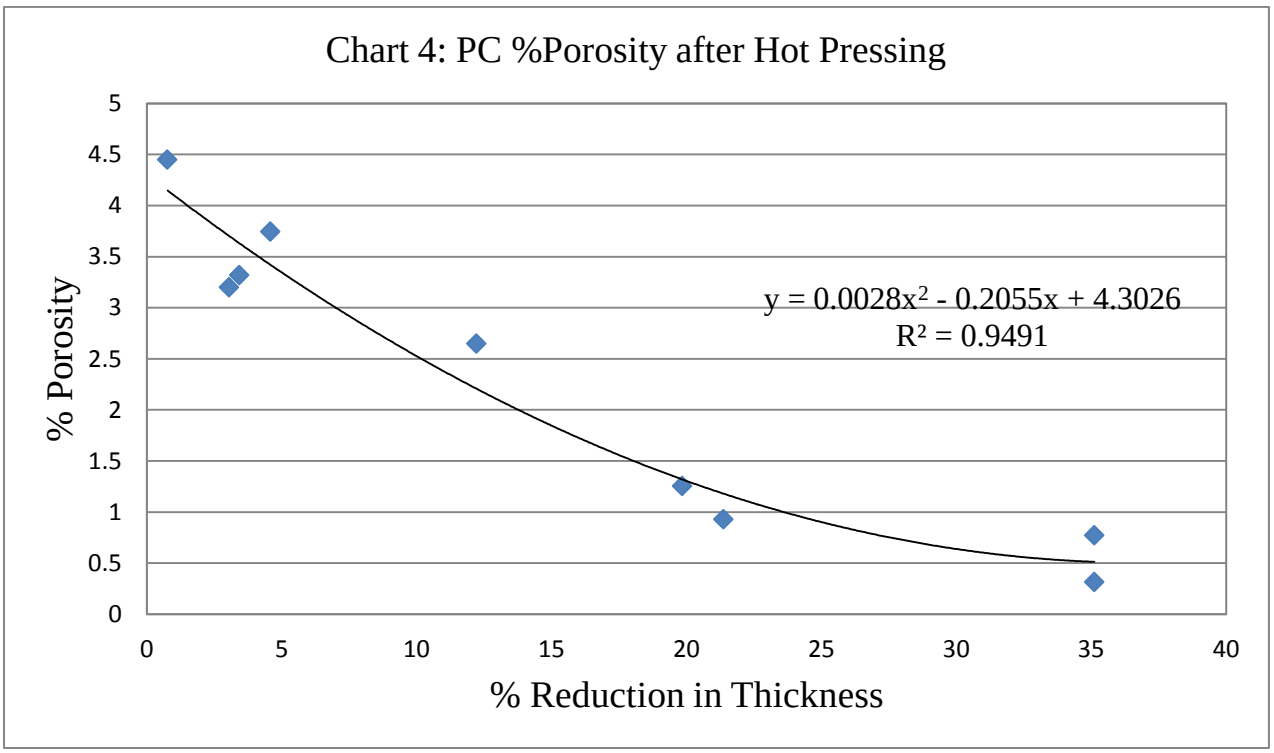
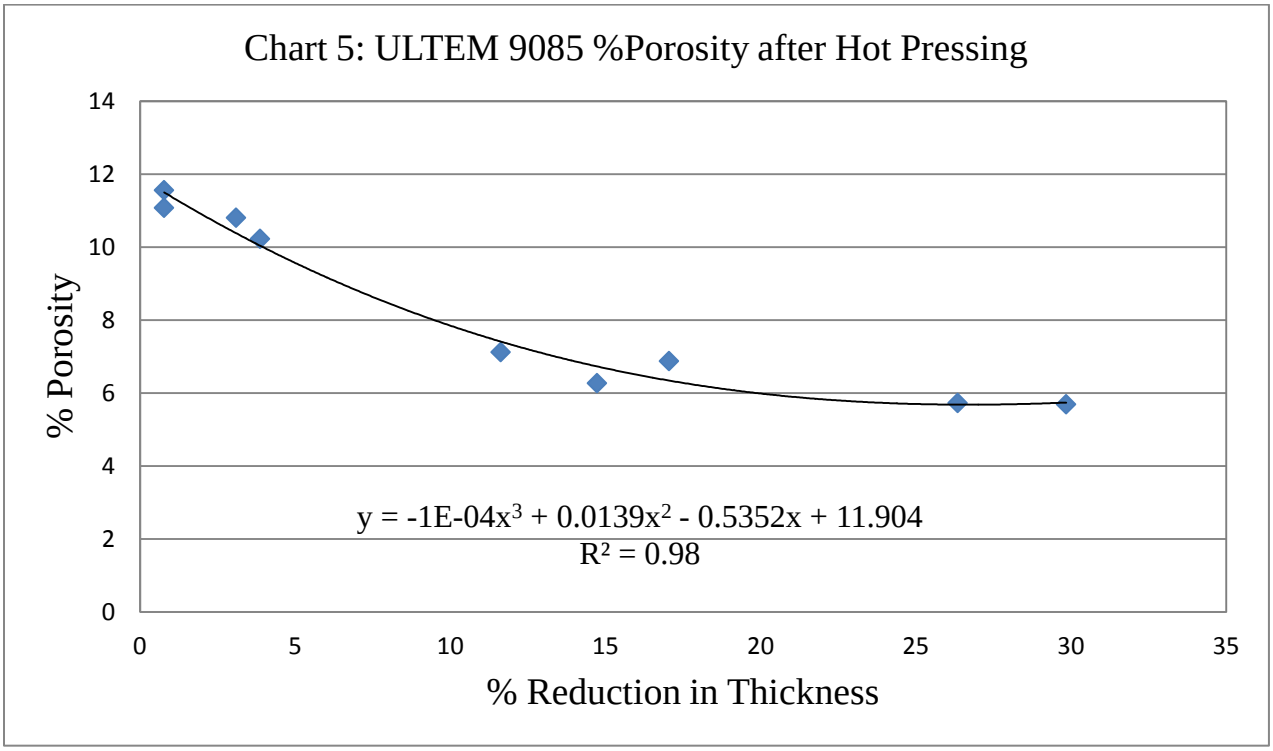


Chart 4: PC %Porosity after Hot Pressing
% Porosity
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
5
10
15
20
25
30
35
40
% Reduction in Thickness
y = 0.0028x² - 0.2055x + 4.3026
R² = 0.9491



4.2 Tensile Tests

Tensile tests were performed on the FDM materials at two different layup orientations – 45/45 ad 0/90. Tensile tests were also performed on the hot pressed FDM materials only at the 45/45 layup pattern.

Table 8: Mechanical Properties pre- Hot Press				
	Polycarbonate		ULTEM 9085	
Average of Quantity	45/45	0/90	45/45	0/90
Modulus of Elasticity (ksi)	271.2	281.3	256.5	288.5
Standard Deviation	0.00426	0.00250	0.00776	0.00375
Tensile Strength at Yeild (psi)	6110.0	6123.6	6073.9	6966.0
Standard Deviation	158.5	232.3	70.8	170.0
Ulimate Strength (psi)	6652.0	6679.6	6624.3	7315.8
Standard Deviation	171	194	167	302
Percent Elongation	2.6	2.6	4.0	0
Standard Deviation	0.569	1.08	2.38	1.45

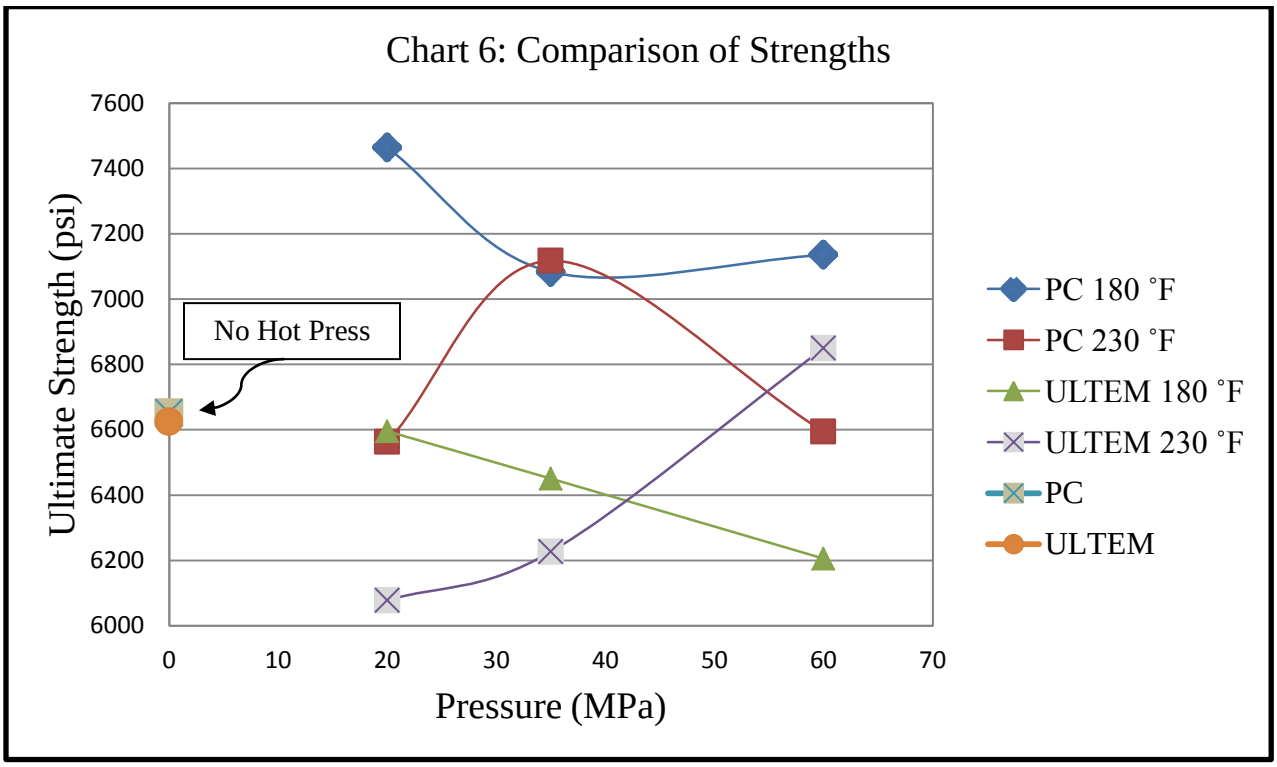


Chart 6: Comparison of Strengths
Ultimate Strength (psi)
7600
7400
7200
7000
6800
6600
6400
6200
6000
0
10
20
30
40
50
60
70
Pressure (MPa)
No Hot Press
PC 180 ˚F
PC 230 ˚F
ULTEM 180 ˚F
ULTEM 230 ˚F
PC
ULTEM

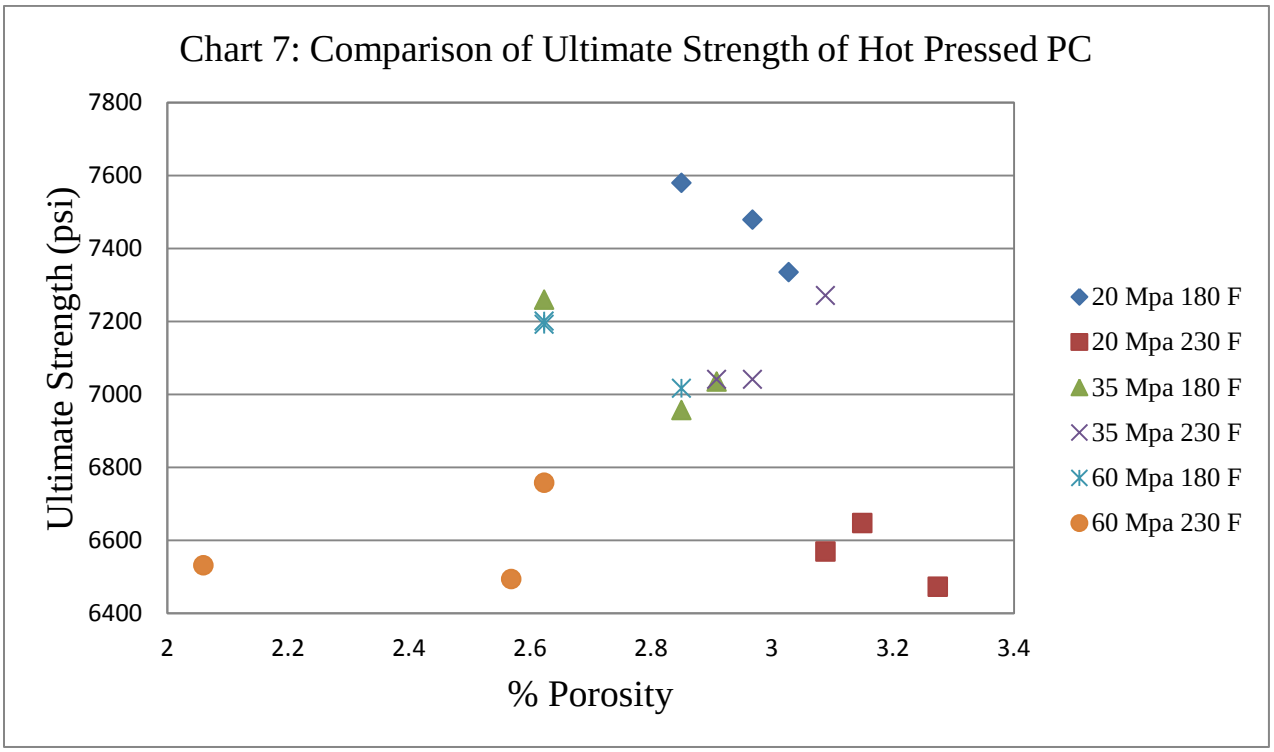
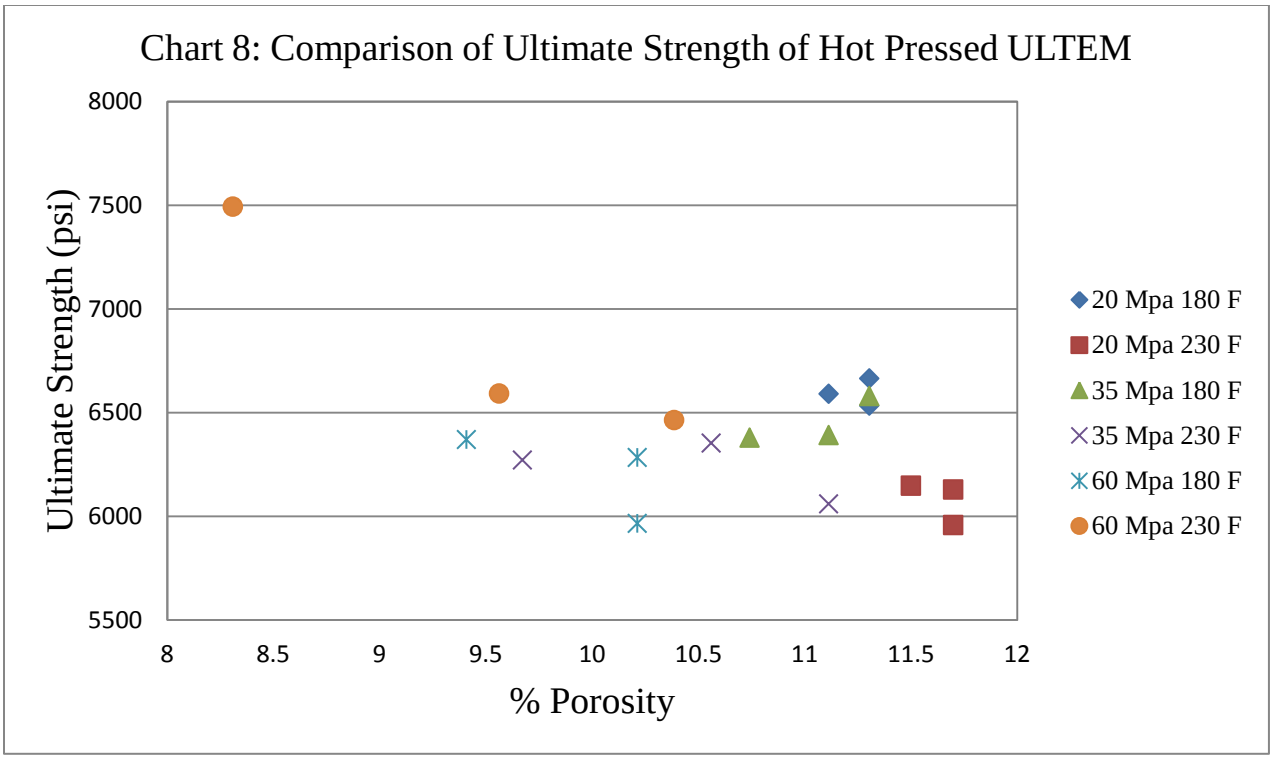


Chart 7: Comparison of Ultimate Strength of Hot Pressed PC
Ultimate Strength (psi)
7800
7600
7400
7200
7000
6800
6600
6400
2
2.2
2.4
2.6
2.8
3
3.2
3.4
% Porosity
20 Mpa 180 F
20 Mpa 230 F
35 Mpa 180 F
35 Mpa 230 F
60 Mpa 180 F
60 Mpa 230 F



4.3 Cold Spray

The cold spray parameters were experimented until a good deposition was achieved as shown in Figure 10. The samples were then nickel electroless plated. This was intended to keep the copper from rolling off the sample during polishing.

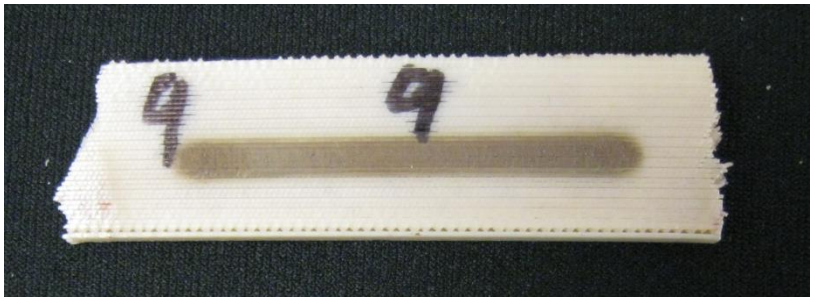


Figure 10: Copper Nanoparticle Cold Spray

The samples were then cold mounted and observed using a metallurgical microscope. A view of this is shown in Figure 11. The rough upper surface is probably from the high impact speed of

the copper onto the polymer. The copper cannot be seen on the surface of the sample where it was deposited, but some can be seen in the center as indicated in Figure 11. This probably rolled over from the surface. Because no copper can be seen on the surface of the sample, the copper deposition was not thick enough. The copper that was there probably rolled over during polishing.

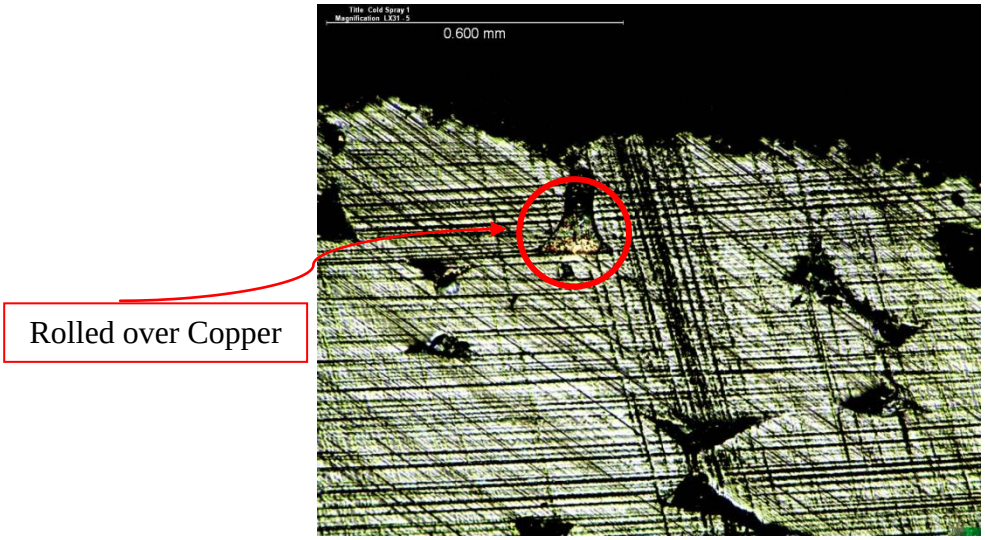


Figure 11: Cold Sprayed Sample at 5x Magnification

5. Discussion

Hot pressing effectively reduced the volume of voids in FDM processed polyphenylsulfone (PPSU), polycarbonate (PC), and ULTEM 9085, but the thickness was reduced significantly (see Table 6) and the material was distorted at the higher temperatures. The polycarbonate samples were processed first to determine the experimental procedure. The temperatures were based on the glass transition temperature (Tg) which was found using dynamic mechanical analysis (DMA). The three temperatures used were at, below, and above the Tg. The pressures used were based on the range given for the hold pressure used in injection molding of PPSU. The temperatures at the Tg caused distortion of the sample into a saddle

shape. This may have to do with the stresses being released as the material is allowed to flow and as the material is undergoing the glass transition.

Above the Tg, the sample completely flattened. The higher pressures caused the square samples to "barrel" by bowing out on the sides as can be seen in Figure 4. This may be because the material heated and flowed better on the edges of the sample than in the middle. In Figure 5, micrographs are shown for each processing parameter and without hot pressing. The sample with no hot pressing has more circular fibers while they are more flat from hot pressing in the other samples. In the samples at higher temperatures, the material was consolidated very well. No voids could be seen in many areas of the material in the PPSU though some voids could be seen near the center portion of such samples. In the samples at the lower temperature and the higher pressures, the voids are consolidated, but dark lines between the fibers can be seen indicating that the fibers are just squished together not bonded. This shows that a sample may have increased in density but the bonding between fibers may not be strengthened. Increasing the strength by increasing the bond area is the real goal of this project, so it is apparent that the microstructure must be examined before conclusions about the effectiveness of increasing the density are made for future samples.

Polycarbonate and ULTEM 9085 provided by Stratasys were also hot pressed. This time, temperatures below their glass transition temperatures were used to avoid the extreme distortion. The results are shown in Figures 5 through 9. Though the saddle shape did not appear in these samples, the barreling did occur at the higher pressures and temperatures. Similar conclusions can be made here as with the PPSU samples that the samples had greater bonding at higher temperatures and more compression at the higher pressures. However, the consolidation in these samples was not as good as in the higher temperature PPSU samples. Because pressure was only

applied in the normal (perpendicular) direction, consolidation in that direction was much greater. However, in hot isostatic pressing, pressure would be applied from each direction equally and consolidation would be even on each side. This may cause greater bonding from side to side than hot pressing did. Knowing this, it may be concluded that the high pressures that achieved good consolidation in this study may not be needed in hot isostatic pressing. Hot pressing the material caused material to squish out on the sides because the pressure was applied only to the top and bottom. This would not happen in hot isostatic pressing, so the applied pressure would be more effective.

Tensile specimens of non-hot pressed samples were pulled to measure strength. This data is presented in Table 8. Data for pos- hot pressing strength is shown in Charts 6-8. This data is non-conclusive because no definite trends can be seen. It can be seen that hot pressed samples were both stronger and weaker than the non hot pressed samples. The processing pressures were lower than were used for the squares because the surface area was much greater for the rectangles used for the tensile samples. The hot presses used could not provide the force needed to apply the same pressure to the bigger samples.

It has not yet been determined if cold spray would be an effective canner for FDM materials for hipping. However, it would likely work if a thick enough deposition could be achieved. A canner is required because of the pores open to the surface of the sample. If air can enter these holes, the pressure applied to the material will push into those holes instead of pushing the surface of the material and consolidating the voids.

6. Conclusions

6.1 Summary

In this study, FDM processed polymers were hot pressed to determine if hot isostatic pressing could effectively eliminate voids to increase strength. It was found that hot pressing does reduce voids in FDM polymers, but it does not necessarily strengthen the material. Some samples were strengthened, but not by a large amount. Hipping has not been performed at this time, but the results of hot pressing show that hipping could be an effective way of strengthening the FDM polymers.

6.2 Future Work

Recommendations for future work are to further optimize the hot isostatic pressing procedure and to further experiment with cold spray as a canner for this process. From the micrographs in Figures 5, 7, and 9, it can be seen that samples at higher temperatures bonded better, but they became distorted. The distortion may be avoided by leaving the sample in the hot press (or in the oven for hipping) until it is cooled. The lower temperatures increased the density of the samples, but did not significantly increase the bonding between fibers. The pressure has an effect on the reduction in density of the samples, but does not necessarily increase the bond area unless it is accompanied with a high enough temperature.

More mechanical testing should be done to determine a trend on the strength changes with hot pressing. Smaller rectangles should be hot pressed instead of a rectangle for three specimens. This way the correct pressures can be reached. However, the samples should still be machined to the dog bone shape after hot pressing so that the change in size during hot pressing does not affect the shape of the dog bone.

Other tests should be done as well. For example, a peel test could be used to determine the strength of the bonds created by hot pressing. This could be done by hot pressing two sheets of FDM polymer together and peeling them apart. Another option would be to hot press two samples end to end and pull the resulting rectangle in a tensile test. If only the temperature effects were being examined, this could be done in an oven with little no pressure applied. Using these tests, a minimum temperature for bonding could be found. Also, accurate theoretical densities should be determined. The densities used in the calculations in this paper were found in literature. More accurate results would be achieved if a theoretical density were calculated for the fibers used to create the FDM polymers.

7. References

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