

**Direct Write Printed Capacitors Utilizing the Polymer PMMA and Silver Nanoparticles**

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**Abstract**

From its birth in the military of the late 1900's, to the tantalizing possibilities of healthier citizens, and happier consumers through modern electronics, direct write technology has, and will continue, to come a long way (9). Direct write technology allows one to spray thin films onto substrates (a basic supporting material such as a glass slide) utilizing inks made up of solutes and particles such as polymers and nanoparticles (11). This is done in much the same way as an aerosol printer, the ink forms a spray which is deposited on the substrate below. Using this technology, as well as a mixture of poly (methyl methacrylate), abbreviates PMMA, silver nanoparticles, and solvents methyl benzoate and toluene, this research aims to design a capacitor. Stepping stones to this goal include measuring the glass transition temperature (Tg) of PMMA, recording and measuring the changes in dielectric constant that ensue from this, and developing a conductive silver layer bellow the melting temperature of PMMA. Conductivity was not achieved when silver slides were sintered at a temperature of 150 degrees C (90 percent of the melting temperature of PMMA) for durations of 1,3,5, and 7 hours(8). The Tg rose to an average of 112 degrees C, seven degree from that of bulk PMMA ( 105 degrees C.), and was higher for samples with a higher flow rate (higher concentration of PMMA per unit of area)(2). No feasible method was discovered for measuring the dielectric constant of a thin film of PMMA on a glass substrate (5).

**Introduction**

 Direct write technology has existed in myriad forms since its inception for military purposes in the early 1990's; one of its applications, especially of late, consists of the creation of flexible and more cost effective electronics from simple transistors to complete circuits (8). This study aims to investigate whether printed silver nanoparticles and the polar polymer poly (methyl methacrylate), or PMMA, can form an efficient direct-write synthesized capacitor.

 The silver nanoparticles used were capped in decanoic acid and are 4-7 nm in diameter (courtesy of Tyler Blumenthal and Krishnamraju Ankired). Toluene and methyl benzoate were used as solvents for the nanoparticles and PMMA; their role is to solvate the particles in order to facilitate printing. The methyl benzoate was used to help evenly distribute the polymer during evaporation. (Deegan et. al.)

 In its simplest form, a capacitor consists of two metal plates separated by a dielectric medium with the purpose of storing charge (5). A dielectric medium is a material that is easily polarized by the application of an electric field. This concept may be illustrated by the flash on a camera; the capacitor stores charge until the button is pressed at which point capacitor discharges, causing the light bulb to flash. In order to maximize capacitance (the ratio of charge over the plates to voltage between them), one may decrease the distance between the plates, increase the dielectric constant of the material (a measure of how well the material polarizes) as well as increasing the area of the plates.(5) .

 In order to manufacture a direct write capacitor, several events must ensue, including measuring the glass transition temperature (Tg) of PMMA. A glass transition occurs when a material transitions from glassy to rubbery behavior; the temperature at which this occurs can be measured by a thermo-mechanical analyzer (TMA). The material should then be heated above Tg and changes in the dielectric constant recorded. Progressing to the attempted creation of a conductive silver layer, weight percentage of silver nanoparticles used and the temperature to which the layers are heated can be varied. Finally, using the results from the prior experiments, constructing a capacitor will be attempted (4).

**Broader Impact**

Capacitors became important in the age of the telephone and their necessity has increased to the point that they are found in everything from cameras to cars and computers (5). The fact is, without these small, seemingly insignificant components, the majority of electrical gadgets and machines would cease to function, including those of an urgent medical nature. Direct write technology has the potential to make capacitors more affordable, flexible, and lighter (4).

**Procedure**

**Part one:**  Discerning the glass transition temperature of a 2-D layer of PMMA

 **A:** Mixing a solution of PMMA, toluene, and methyl benzoate

 **Materials:**

 ***Table 1. Materials Used (PMMA Solution)***

|  |  |  |
| --- | --- | --- |
| **Name of Chemical**  | **Density** | **Amount used** |
| PMMA (Scientific Polymer Products INC.) | 1.19 g/ml | 0.1426 g (1.5 wt. %) |
| Methyl Benzoate (Acros Organics) | 1.904 g/ml | 2 ml |
| Toluene (Aldrich)  | 0.9 g/ml | 18 ml |

Other materials used:

 10 ml Syringe (2) Automatic stirrer (VWR stirrer/hotplate)

 50 ml Flask with lid Mass balance (Precia 125A)

 Weighing paper Gloves

 **Procedure:**

1. Weigh 0.1426 g of PMMA on weighing paper

 2. Put on gloves

 3. Measure 18 ml of toluene and 2 ml of methyl benzoate

 4. Add toluene, methyl benzoate and PMMA to the flask (cap the flask or most will evaporate)

 5. Mix with an automatic stirrer at 400 RPM overnight

**B:** Using a direct-write machine to lay a seven layer film of the above PMMA solution

 **Materials:**

20 ml Syringe SonoTek direct-write printer (S/N 55837)

 Gloves Fischer pre-cleaned glass slides

 Towels The solution from part A

 20 ml Vial with lid

 **Procedure:**

1. Turn off the automatic stirrer and pour solution from part one into the vial and cap it (wear gloves when handling solution).

 2. Turn on the computer and the SonoTek machine by turning the front red dial to the right.

 3. Turn on the air by turning the red switch on the top rear-left of the machine to the right

 4. Turn the door-bypass off then press F1 and follow the procedure on the screen. Press F1 again when finished.

 5. Use blue shop towels to shield the sides and door from being sprayed by the machine. Then put fax paper down on the bottom of the machine and press F7 and then F3 to turn on the vacuum to hold the fax paper down.

 6. Place a glass slide on the fax paper. Move the solution from the vial into a syringe and attach to the machine (Use the Poly only line and wear gloves).

 7. Open the computer program called Generator control. Under run power click 10 Watts.

 8. Set the infuse volume to 1 ml below the amount of solution used (18.00 ml in this case).

 9. Path speed should be 23 ml/min and the line spacing set to three ml.

 10. Using the Pathmaster program and the remote, create a path that includes two dots to the side of the fax paper to clear any excess polymer, one at the beginning and one at the end, and a spiral around the slide in the middle.

 11. Before beginning to print, hit purge while the printer is aimed at the side of the fax paper until you see your solution coming out of the print head.

 12. Hit run, then wet run in the Pathmaster program to start printing a layer. Dry for five minutes after the first layer and for five +2 \* (# of layers-1) minutes after each additional layer. Repeat as desired.

 **C:** Testing the slides from part B for a glass transition temperature using a thermo- mechanical analyzer.

 **Materials:**

Q400 EM Thermo-mechanical analyzer from TA Instruments

 Glass slides from part one-B

 A clean, empty, Fischer slide

 Glass cutter

 **Procedure:**

1. Cut the slides from part one-B in half width- wise.

 2. Cut one of the halves from each slide into six pieces using the glass cutter. Place the other remaining halves aside.

 3. Turn on the computer to the right of the thermo-mechanical analyzer. Click on Q-Series Explorer on the desktop. Click TMA.

 4. Check to see if the expansive probe is in the machine.

 A. If not, remove the probe by first pushing the furnace button on the touch screen at the front of the machine, moving the furnace to the left, and opening the black door on the front of the thermo-mechanical analyzer. Turn the silver knob to the left while gently holding the probe. When it is loose enough gently pull it up and out of the machine.

 B. To install a probe, gently lower it in the machine and tighten it in by moving the silver knob to the right. Close the door.

 5. Press the probe up button twice on the screen on the front of the machine and place one of the small pieces cut from the slides from part one-B on the stage under the probe's tip.

 6. Move the furnace back over the stage and press furnace.

 7. Press measure and record the measurement in mm.

 8. Go to experiment ---> wizard, and then select the expansion probe, standard mode, and the test ramp. Set the final temperature at 150 degrees C. and the ramp rate at five degrees C. per minute. The sample purge flow should be set to 50 ml/min. Set the preload force at .1 N and the applied force at .02 N.

 9. Turn on the rear nitrogen tank to the left of the door when one faces the door to the left. Press the green run button on the computer.

 10. Repeat steps 5-9 for three pieces of each slide. Then using step four for reference switch to the penetrative probe and repeat steps 5-9 for the three remaining pieces of each slide.

 11. Repeat steps 4-9 and test an empty Fischer glass slide twice each using both the penetrative and expansive probes.

**Part two:** Sintering methods to achieve a conductive silver layer

 **A:** Mixing a silver solution

 **Materials:**

 ***Table 2. Materials Used (Ag Solution)***

|  |  |  |
| --- | --- | --- |
| **Name of Chemical**  | **Density** | **Amount used** |
| Silver | 10.5 g/ml | .0253 g (1.5 wt. %) |
| Methyl Benzoate (Acros Organics) | 1.904 g/ml | 2 ml |
| Toluene (Aldrich)  | .9 g/ml | 18 ml |

Other materials used:

 Same as in part 1-A

 **Procedure:**

Same as in part 1-A except Ag and not PMMA added

 **B:** Printing a four layer slide of Ag solution

 **Materials:**

Same as in part 1-B, and the solution referred to is that from part 3-A

 **Procedure:**

Same as in part 1-B, except only four layers sprayed.

 **C:** Sintering the slides from part 3-B

 **Materials:**

Omegalux LMF3550 programmable furnace

 Slides from part 3-B

 **Procedure:**

1. Place on of the slides from part 3-B and place it in the furnace.

 2. Press the red button with a thermometer and up and down arrows on it to the top-right of the screen to ramp the temperature as desired.

 3. Press the button below the top one that has a thermometer on it to set the first temperature (T1) to 150 degrees C. and the second temperature (T2) to 50 degrees C.

 4. Press the button below the middle one that has a clock on it to set the time it is heated at 150 degrees C (here, this was done for times of one , three, five, and seven hours).

 5. Press the green start button.

 6. When finished remove the slide and shut down the machine.

 **D:** Testing the conductivity of the sintered slides from part 3-C

 **Materials:**

Keithly 4-pronged multimeter

 Signatone 1160 series probe station with a tip spacing of 25 microns

 **Procedure:**

This process was done by James Randal at TDL.

**Results**

**Part one:** Glass transition temperature of 2-D PMMA

 The glass transition temperature of Ficher glass slides and PMMA appeared to increase from that of the bulk 3-D value (105 degrees C.); and the average value found was 112 degrees C. (2). This may be in part due to the behavior of the glass substrate (refer to figure one and table three below). The samples with a higher PMMA concentration (a flow rate of .75 vs. .5 ml/min) experienced a slightly higher Tg (around 124 degrees C vs. 100, refer to figure one and table three below).



 ***Figure 1. (above) Graph showing the relations between Tg with a higher amount of PMMA(C1-C2) and those with a lower amount (B-1 and B-2)***

***Table 3. Tg of TMA analyzed slides containing PMMA***

|  |  |  |
| --- | --- | --- |
| **Probe Type**  | **Slide number** | **Tg (PMMA + glass) degrees C.** |
| expansive | B-1 | 93 |
|  | B-3 | 109 |
|  | B-4 | 111 |
|  | C-1 | 119 |
|  | C-2 | 141 |
|  | C-3 | 117 |
| Penetrative | B-1 | 75 |
|  | B-2 | 140 |
|  | B-3 | 70 |
|  | C-1 | 130 |
|  | C-2 | 118 |
|  | C-3 | 120 |

**Part two:** Conductivity vs. sintering time

 Conductivity was not achieved when sintering at 150 degrees C for any length of time tested using a four pronged multi-meter (for additional details in regards to materials or procedure please refer to procedure part 2-D). Please refer to table three below for additional details. This proved true regardless of infuse rate.

***Table 4. Conductivity vs. Sintering Time***

|  |  |  |  |
| --- | --- | --- | --- |
| **Infuse Rate (ml/min)** | **Slide Name** | **Time Sintered (Hours at 150 degrees C.)** | **Conductive?** |
| .5 | A-1 | 1 | not measureable , some activity |
| .5 | A-1 | 5 | not measurable, some activity |
| .75 | A-2 | 3 | no |
| .75 | A-2 | 7 | no |

**Discussion**

The average glass transition temperature of the PMMA samples was 112, around seven degrees higher than the bulk Tg for 3-D samples ([2](http://web.mst.edu/~wlf/Bulk/Andrews.html)). This is consistent with the results of Kabomo et. al. (8).This most likely resulted from a combination of the behavior of the glass substrate and the 2-D vs. 3-D structure, being more planar and organized than that of the 3-D version. This would result in a higher glass transition temperature because it would take more energy to break the resulting stronger dipole -dipole bonds that would result. The glass substrate's stiffness would also interfere with the TMA's measurement of the Tg of the PMMA by itself. The fact that the samples with more PMMA(aka a higher flow rate when sprayed) registered a higher Tg than those with less suggests that the more PMMA per area increases the dipole-dipole bonds and requires more energy to break ( i.e., to transition from a glassy to a rubbery state).

 No measureable conductivity was detected in the slides (A-1 and A-2) when tested with a four pronged multimeter (please refer to table three under results).Slide A-1 had a slightly lower silver concentration than A-2 (A-1 was sprayed at a volume of .5 ml/min) and was heated to 150 degrees C and tested for conductivity after one and five hours. Some conductive activity was apparent, yet not to a useful or measurable degree. Slide A-2 was sprayed at a volume of .75 ml/min (i.e., has a larger silver content) and heated to 150 degrees C and checked for conductivity after three and seven hours. These tests failed to detect any conductivity. This was surprising considering the fact that the slide with longer sintering times and a higher silver concentration was the least conductive (1).

 The purpose of sintering the slides is to burn off the capping agent used (in this case decanoic acid) so that the silver can make connections that are essential to conductivity. It can be pictured thus: before sintering each silver particle is coated in decanoic acid, which can be envisioned as an island surrounded by the sea. There is no way to get to another location (or for electrons to travel, in practical terms) while the barrier is in place (while the particles are capped in decanoic acid). Sintering is the process which allows electrons to travel by removing said barrier, and thus allows for conductivity. This would logically suggest that slides that were heated at a higher temperature (and with a higher silver concentration) would be more conductive; this is why the results mentioned above were a bit surprising. This could be the result of experimental error while spraying the slide A-2, such as scratches and impurities.

 While raising the sintering temperature would be one way to improve conductivity, the ultimate goal is to form a capacitor by direct write printing a solution containing the polymer PMMA and silver nanoparticles, which separate into layers resembling a capacitor during drying. This implies that any sintering that occurs would affect both the silver nanoparticles and the polymer as well. PMMA has a melting point of 160 degrees C (2), thus the sintering temperature would ideally be below this, which is why 150 degrees C. was chosen to sinter the silver particles. Since the temperature of sintering will remain static, to improve conductivity lengthen the sintering time, silver concentration, or use a different capping agent that burns off with a lower temperature.

**Conclusion**

In summation, in attempting to sinter silver nanoparticles caped in decanoic acid at 150 degrees C. ( slightly over 90% of the melting point of PMMA), conductivity was not successfully reached. This occurred because heating at this temperature for one, three, five, and seven hours proved insufficient to burn off the decanoic acid, and possibly due to defects when the slides were sprayed with the 1.5 percent silver mixture (by weight). When using the thermo mechanical analyzer on the glass slides sprayed in a seven layer PMMA pattern, it was discovered that the Tg was raised to an average of 112 degrees C, seven degrees above the Tg of bulk PMMA. Slides with a higher flow rate of PMMA (.75 vs. .5 ml/min) recorded a higher Tg than those with the lower flow rate.

 For future research one would consider attempting to increase conductivity by capping the silver nanoparticles in Elaidic acid, filtering the nanoparticles to reduce the excess capping agent (3), and using smaller, square-shaped particles (7). Curing at a higher temperature might also increase conductivity, but it would result in melting the PMMA, so sintering for a longer time should be considered, as well as adding a larger weight percent of silver nanoparticles and a higher infuse rate (6). Discovering a method to easily measure the dielectric constant of a thin film on a glass slide and forming a working capacitor would be the ultimate reach of this project .Another idea to consider includes increasing the ratio of toluene to methyl benzoate from 9:1 to 9:1.5 to increase the drying time and possibly reduce the amount of nanoparticles in the polymer (Suggested by Tyler Blumenthal) and to see how much this behavior impacts conductivity and the dielectric constant.

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