

Synthesis of Antimicrobial Poly(Vinyl Alcohol) Films  
American University  
Klare Lazor

Results

**1. Cross-linking Techniques**

*1.1 Visual Appearance*

**22,000 MW Films Synthesized to Date**

PVOH (22,000MW): 2/11/13: 1gram of PVOH in 25mL of water. Very flimsy and clear. Not brittle. Control one.

PVOH (22,000MW) + 1 ml Glutaraldehyde: 2/11/13: 1 gram of PVOH in 25mL of water. Clear hard and very brittle. Control 2.

PVOH (22,000MW) + 1ml of Glutaraldehyde+ 0.01% Quaternary Ammonium Salt: 2/28/13: 1 gram of PVOH in 25mL of water. Flimsy and hard feels like paper bag. Least hard out of the quaternary ammonium salt films. Chalky clear color. Significantly shrunk compared to the control 1 and 2.

PVOH (22,000MW) + 1ml of Glutaraldehyde +0.1% Quaternary Ammonium Salt: 2/28/13: 1 gram of PVOH in 25mL of water. Still flimsy and hard with a paper bag texture. However, slightly harder with the increase in quaternary ammonium salt. Chalky clear color. Significantly shrunk compared to the control 1 and 2.

PVOH (22,000MW) + 1ml of Glutaraldehyde +1.0% Quaternary Ammonium Salt: 2/28/13: 1 gram of PVOH in 25mL of water. Starting to lose flimsiness, harder than 0.01% and 0.1%. Chalky clear color. Significantly shrunk compared to the control 1 and 2.

PVOH (22,000MW) + 1ml of glutaraldehyde + 10% Quaternary Ammonium Salt: 2/28/13: 1 gram of PVOH in 25mL of water. Lost all flimsiness, very hard compared to 0.01%, 0.1% and 1%. Chalky clear color. Significantly shrunk compared to the control 1 and 2. Shrunk the most.

PVOH (22,000MW) + 1ml of Glutaraldehyde + 0.01% Phenol: 2/11/13: 1 gram of PVOH in 25mL of water. Hard bendable. Chalky clear color.

PVOH (22,000 MW) + 1ml of Glutaraldehyde + 0.1% Phenol: 2/11/13: 1 gram of PVOH in 25mL of water. Hard and more bendable. Chalky clear color.

PVOH (22,000 MW) + 1ml of Glutaraldehyde + 1% Phenol: 2/11/13: 1 gram of PVOH in 25mL of water. Hard and even more bendable. Chalky clear color.

PVOH (22,000 MW) + 1ml of Glutaraldehyde + 10% Phenol: 2/11/13: 1 gram of PVOH in 25mL of water. Hard and even more bendable. Chalky clear color.

**146,000-186,000MW Films Synthesized to Date**

PVOH(146,000-186,000MW): 2/1/13: 0.5 grams of PVOH in 25mL of water. Bendable not brittle, but solid and firm. Cant tear. Holds it shape. Clear and translucent slightly chalky. But can make folds.

PVOH(146,000MW) + 1ml of glutaraldehyde: 1/21/13: 0.5 grams of PVOH in 25mL of water . More brittle than standard. In some areas hard and then others not. PVOH didn't entirely dissolved so there is a clump in it.

PVOH(146,000-186,000MW) + 1ml of glutaraldehyde + 0.1% of Isopropanol:1/21/13: 0.5 grams of PVOH in 25 ml of water. Even more brittle.

Pretty flimsy but hard in some places. Curled up in one area after cut. Broke apart a bit. Clear.

PVOH(146,000-186,000MW) + 1ml of glutaraldehyde + 1.0% of Isopropanol:1/21/13: 0.5 grams of PVOH. Didn't dissolve very well in certain areas. Very hard in areas that it didn't dissolve. Clear.

PVOH(146,000-186,000MW) + 1ml of glutaraldehyde + 10% of Isopropanol:1/21/13: 0.5 grams of PVOH in 25mL of water. Didn't dissolve very well in certain areas. Has clumps. Very hard in areas that it didn't dissolve. Clear.

PVOH(146,000-186,000MW) + 1ml of glutaraldehyde + 100% of Isopropanol:1/21/13: 0.5 grams of PVOH in 25mL of water. Has little clumps of PVOH spread throughout that are very hard. The rest of film is more solid. Very uneven distribution. Little more sturdy than rest. Didn't dissolve very well in certain areas. Has clumps. Very hard in areas that it didn't dissolve. clear

PVOH(146,000-186,000MW) + 1ml of glutaraldehyde + 0.1% phenol: 2/11/13: 0.5 grams of PVOH in 25mL of water. Small crystalline clumps of PVOH and phenol spread so densely throughout the film that it really never made an even or smooth surface (crystals throughout). Otherwise it is hard, brittle and breaks of in clumps. Clearish.

PVOH(146,000-186,000MW) + 1ml of glutaraldehyde + 1.0% phenol: 2/11/13: 0.5 grams of PVOH in 25mL of water. Mostly a well made film, smooth surface with the exception of small section on the edge that is clump. Bends and breaks. Clear.

PVOH(146,000-186,000MW) + 1ml of glutaraldehyde + 9% phenol: 2/11/13: 0.5 grams of PVOH in 25mL of water. Almost the same as the 0.1%. Clumps of phenol and PVOH spread throughout. Brittle but hard. Little yellow tint/ clear.

#### **146,000-186,000MW Hydrogels Synthesized to Date**

PVOH(146,000-180,000MW) + 1ml of glutaraldehyde + 17.23μL butyne-1-ol: 1 gram PVOH in 25mL of water. Small shrunk a lot from before cross-linking. White milky white. Very hard. Holds its shape from after cross-linking not bendable.

PVOH(146,000-180,000MW) + 1ml of glutaraldehyde + 17.4μL isopropanol: 1 gram PVOH in 25 ml of water. A lot more whiter than the butyne. Small shrunk a lot from before cross-linking. White milky white. Very hard. Holds its shape from after cross-linking not bendable.

## 1.2 Chemical Changes

### 1.2.1 FTIR of Phenol and Glutaraldehyde in PVOH Films

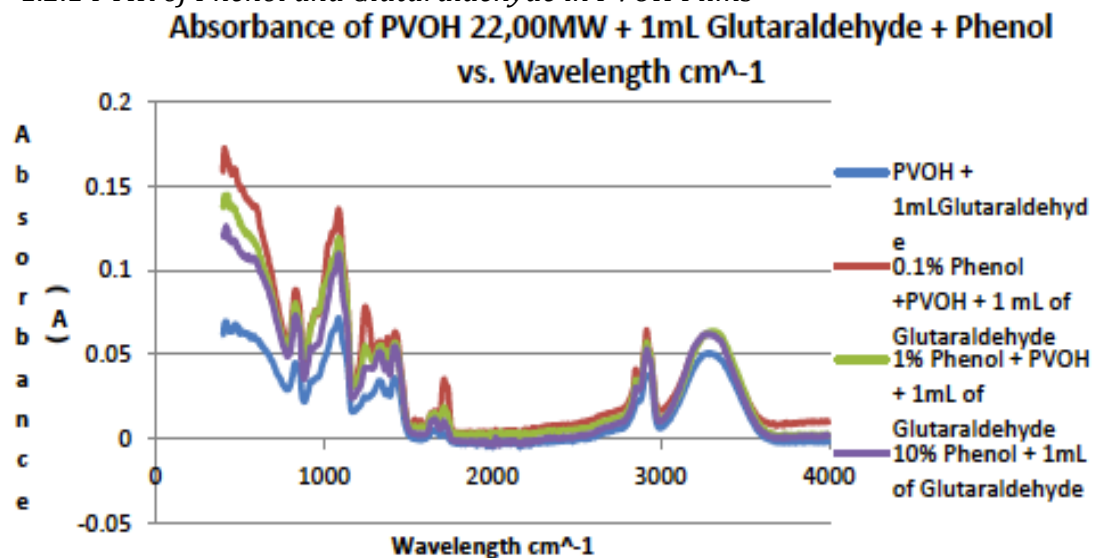


Figure1: FTIR spectra of Phenol in PVOH with 1 mL of glutaraldehyde after crosslinking with different percentages occupied OH groups Phenol.

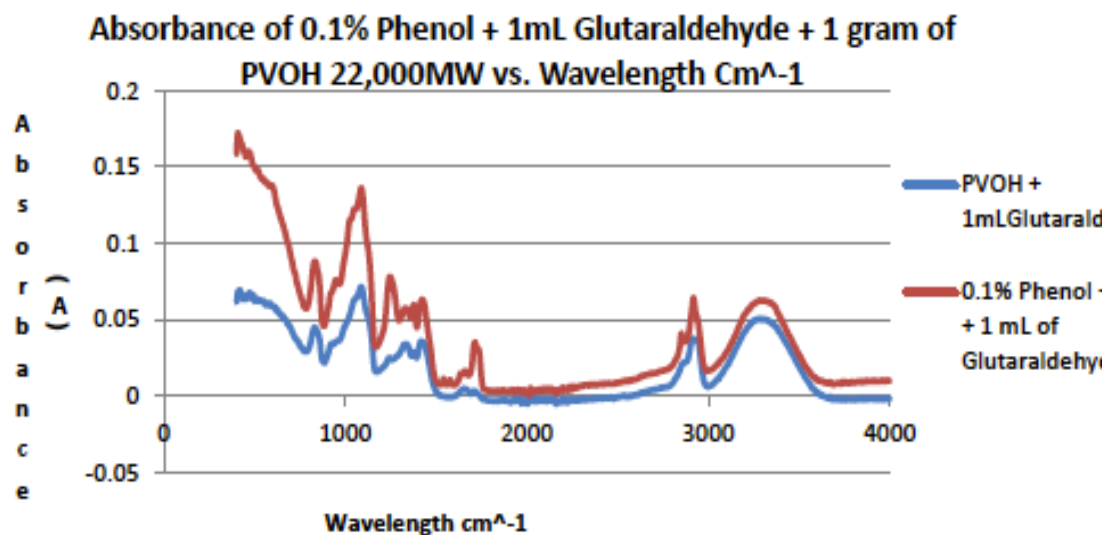


Figure 2: FTIR spectra of Phenol in PVOH with 1 mL of glutaraldehyde after crosslinking with 0.1% of OH groups in PVOH occupied by Phenol.

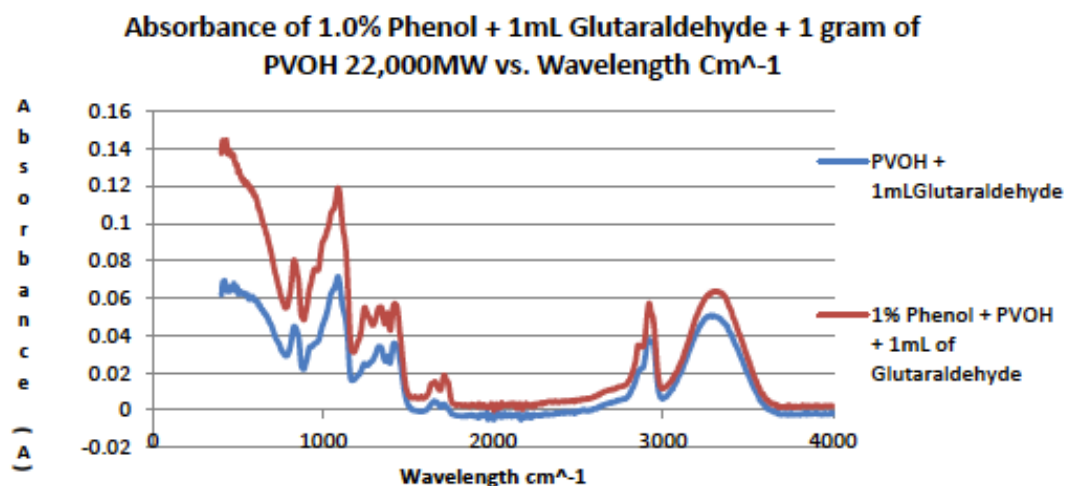


Figure 3: FTIR spectra of Phenol in PVOH with 1 mL of glutaraldehyde after crosslinking with 1.0% of OH groups in PVOH occupied by Phenol.

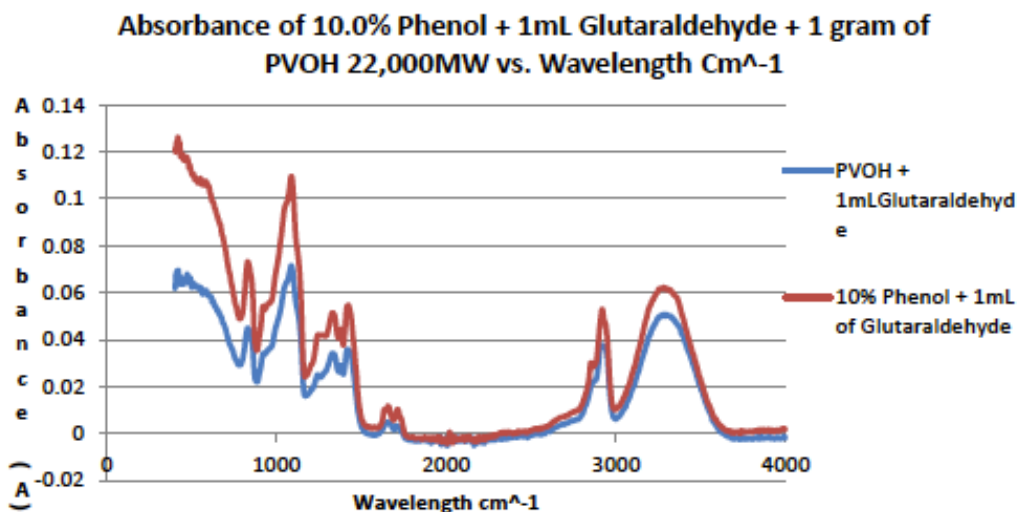


Figure 4: FTIR spectra of Phenol in PVOH with 1 mL of glutaraldehyde after crosslinking with 10.0% of OH groups in PVOH occupied by Phenol.

As you can see in figure 1, the control, PVOH + 1mL of Glutaraldehyde, had predominant maximum absorbance's at  $3295.0684 \text{ cm}^{-1}$  (0.05066 A), two peaks  $2804.3021\text{--}2914.1602 \text{ cm}^{-1}$  (0.02324–0.03772 A),  $1651.0742 \text{ cm}^{-1}$  (0.0049A), and  $1086.084 \text{ cm}^{-1}$  (0.07149A). In addition, from figure 1-3, an increase in absorbance with the addition of phenol is obvious, as well as the additional appearances of peaks between the ranges  $16000\text{--}1500 \text{ cm}^{-1}$  and  $1400\text{--}1200 \text{ cm}^{-1}$ . However, they are very discreet

1.2.2 FTIR of (S)-(-)-(3-Chloro-2-hydroxypropyl)trimethylammonium chloride (Quaternary Ammonium Salt) and Glutaraldehyde in PVOH Film

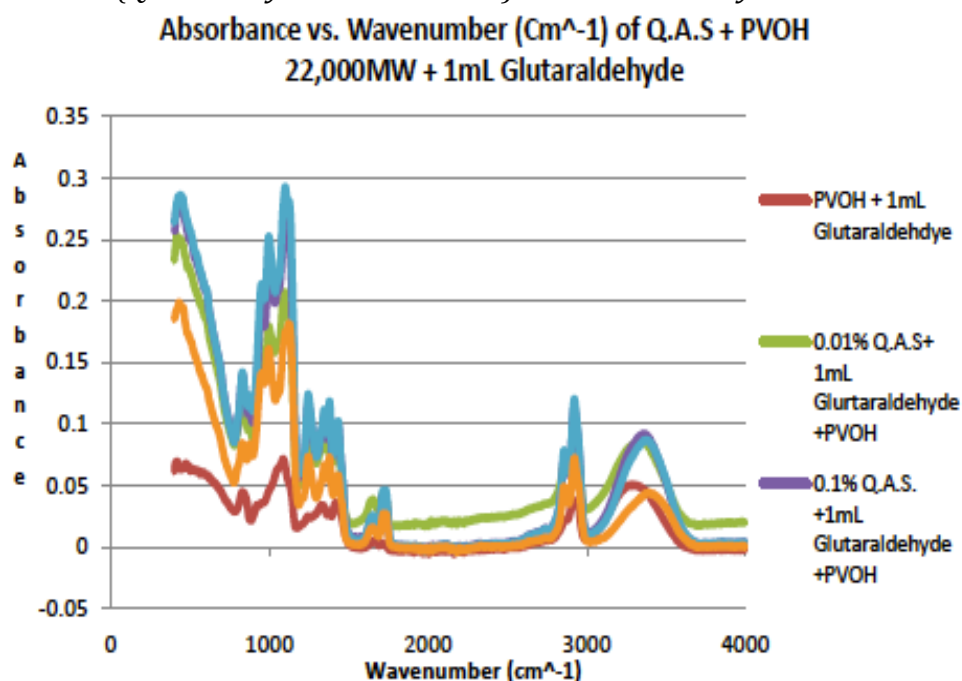


Figure 4: FTIR spectra of Quaternary Ammonium Salt in PVOH with 1 mL of glutaraldehyde after crosslinking with different percentages of occupied OH groups by Quaternary Ammonium Salt.

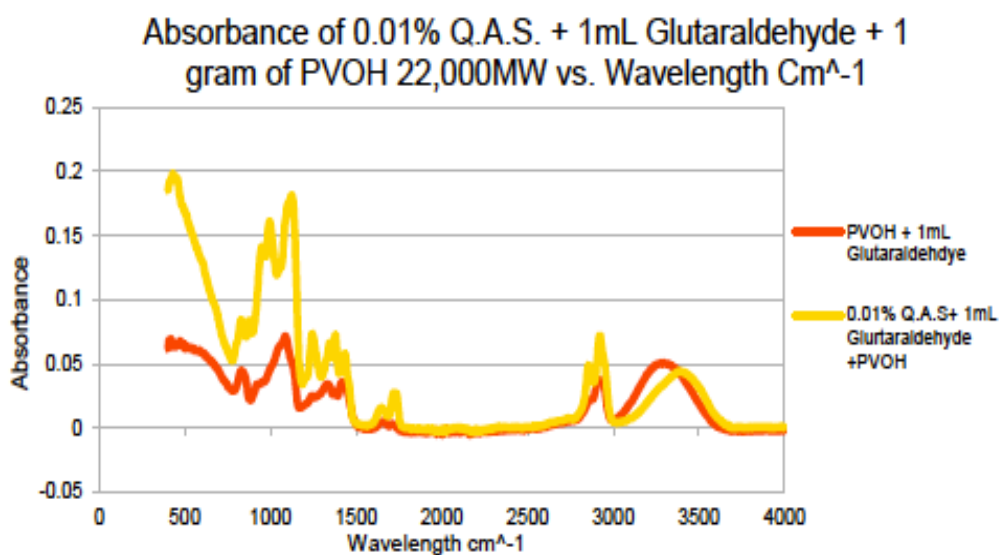


Figure 5: FTIR spectra of Quaternary Ammonium Salt in PVOH with 1 mL of glutaraldehyde after crosslinking with only 0.01% of OH groups occupied with Quaternary Ammonium Salt.

Absorbance of 0.1% Q.A.S. + 1mL Glutaraldehyde + 1 gram of PVOH 22,000 MW vs. Wavelength  $\text{cm}^{-1}$

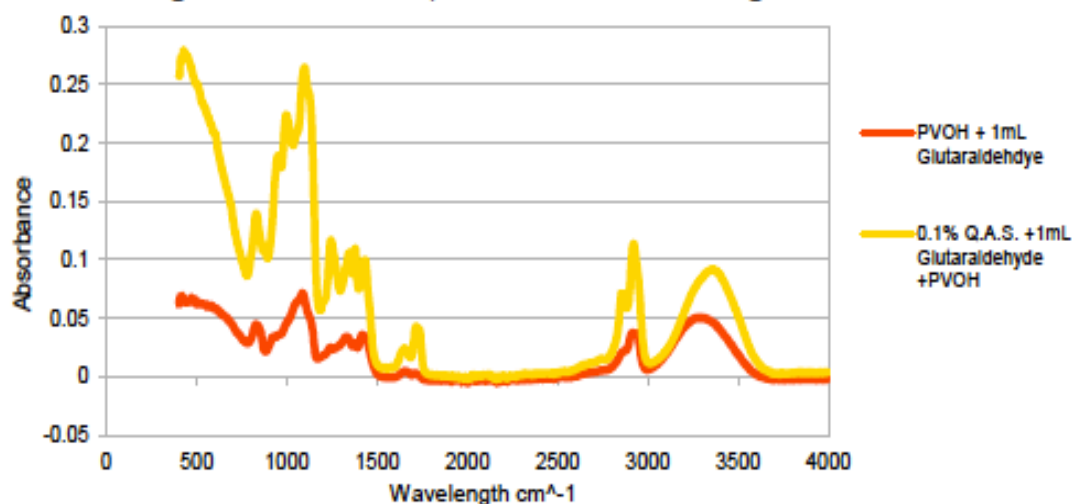


Figure 6: FTIR spectra of Quaternary Ammonium Salt in PVOH with 1mL of glutaraldehyde after crosslinking with only 0.1% of OH groups occupied with Quaternary Ammonium Salt.

Absorbance of 1.0% Q.A.S. + 1mL Glutaraldehyde + 1 gram PVOH 22,000 MW vs. Wavelength  $\text{cm}^{-1}$

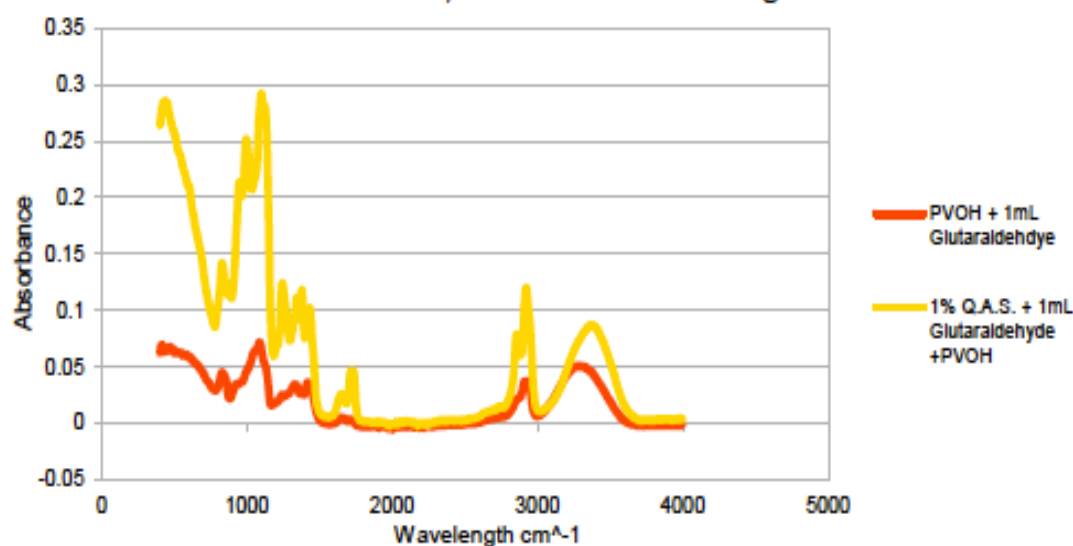


Figure 7: : FTIR spectra of Quaternary Ammonium Salt in PVOH with 1mL of glutaraldehyde after crosslinking with only 1.0% of OH groups occupied with Quaternary Ammonium Salt.

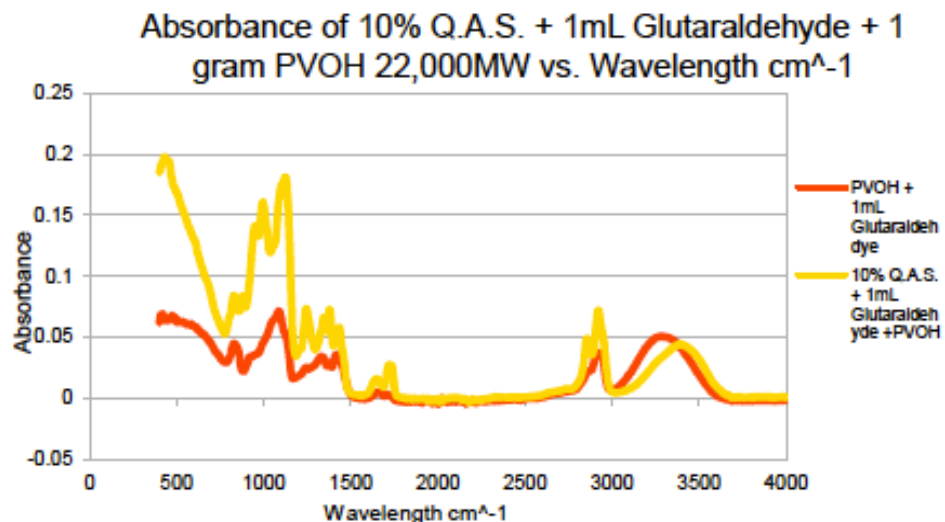


Figure 8: : FTIR spectra of Quaternary Ammonium Salt in PVOH with 1mL of glutaraldehyde after crosslinking with only 10.0% of OH groups occupied with Quaternary Ammonium Salt.

As you can see in figure 4, the control, PVOH + 1mL of Glutaraldehyde, had predominant maximum absorbance's at  $3295.0684 \text{ cm}^{-1}$  (0.05066 A), two peaks  $2804.3021$ - $2914.1602 \text{ cm}^{-1}$  (0.02324-0.03772 A),  $1651.0742 \text{ cm}^{-1}$  (0.0049A), and  $1086.084 \text{ cm}^{-1}$  (0.07149A). In addition, from figure 4-8, an increase in absorbance with the addition of Quaternary Ammonium Salt is obvious, as well as the additional appearances of peaks between the ranges  $1200$ - $800 \text{ cm}^{-1}$  and  $1500$ - $1250 \text{ cm}^{-1}$ . In addition, a distinct shoulder can be seen forming at the wavelength  $2857.5195 \text{ cm}^{-1}$ .

### 1.3 Thermal and Crystalline Properties

#### 1.3.1 DSC Data of All Films to Date

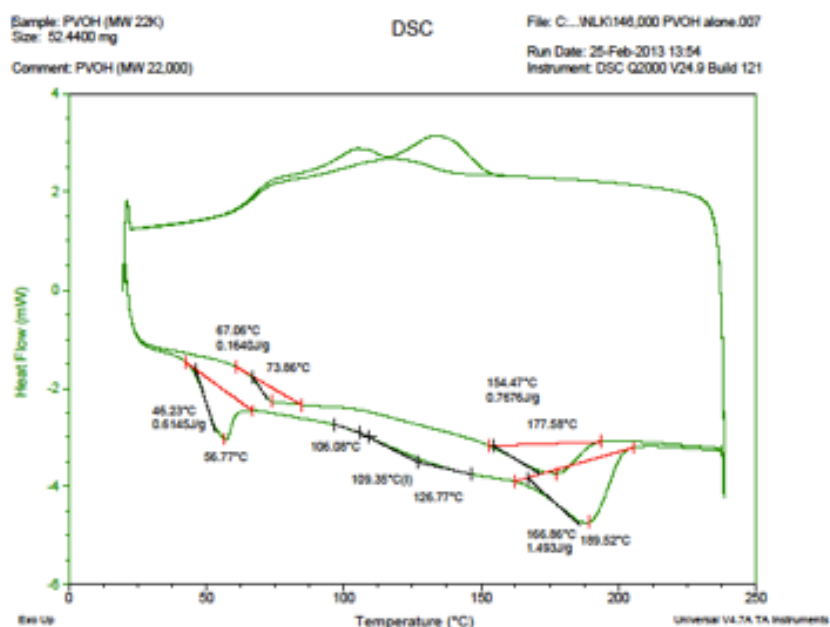


Figure 9: PVOH M.W. 22,000. Film was synthesized with 1 gram of PVOH and 25mL of water, which was melted and poured into a dish to dry over night.

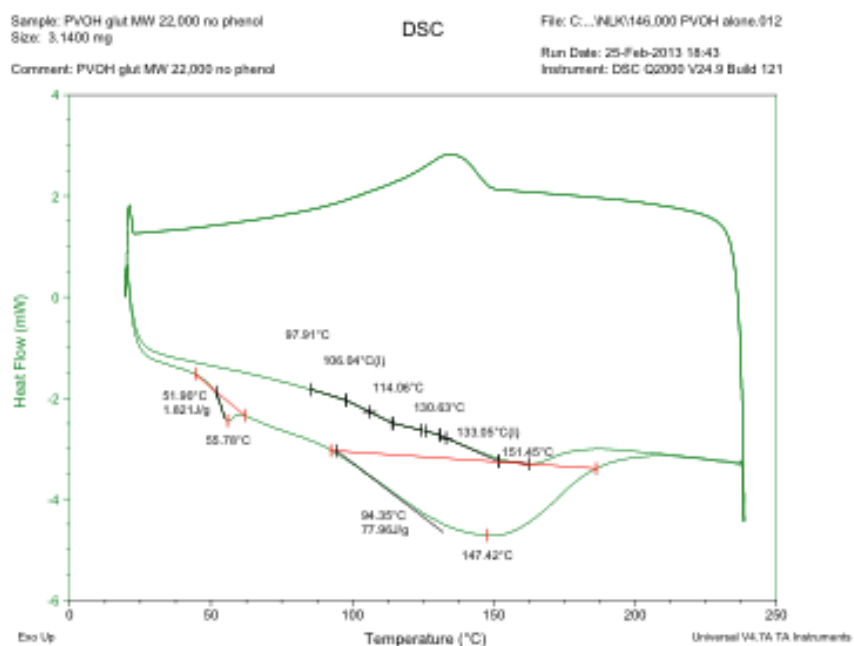


Figure 10: PVOH M.W. 22,000. Film was synthesized with 1 gram of PVOH, 25mL of water, 1ml of glutaraldehyde, which was melted and poured into a dish to dry over night.

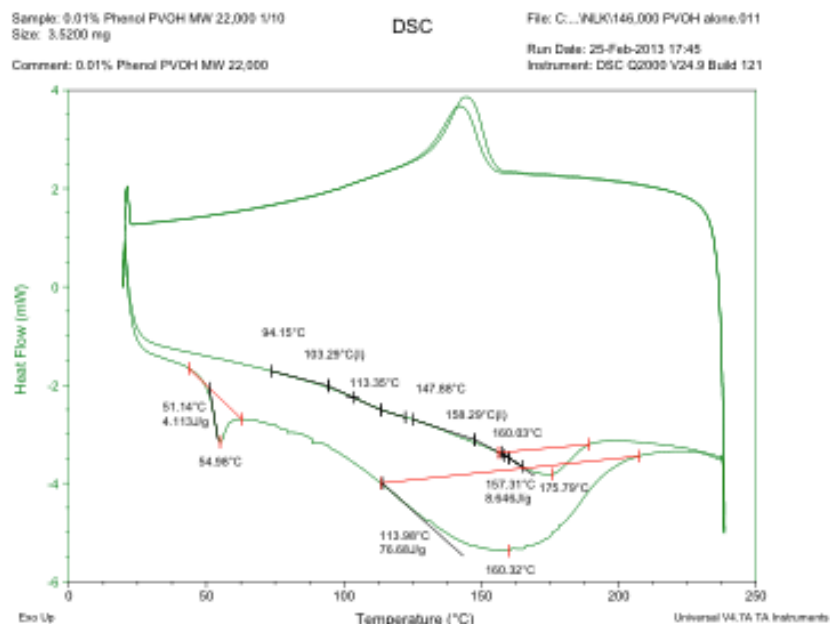


Figure 11: PVOH M.W. 22,000. Film was synthesized with 1 gram of PVOH, 25mL of water, 1ml of glutaraldehyde and phenol. The percentage of OH groups in PVOH occupied by phenol was 0.01%. Reagents were melted and poured into a dish to dry over night

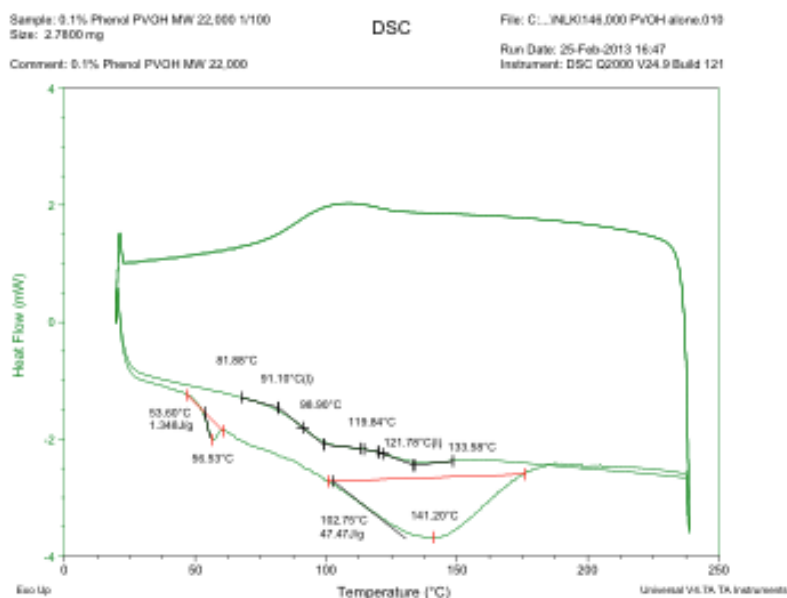


Figure 12: PVOH M.W. 22,000. Film was synthesized with 1 gram of PVOH, 25mL of water, 1ml of glutaraldehyde and phenol. The percentage of OH groups in PVOH occupied by phenol was 0.1%. Reagents were melted and poured into a dish to dry over night.

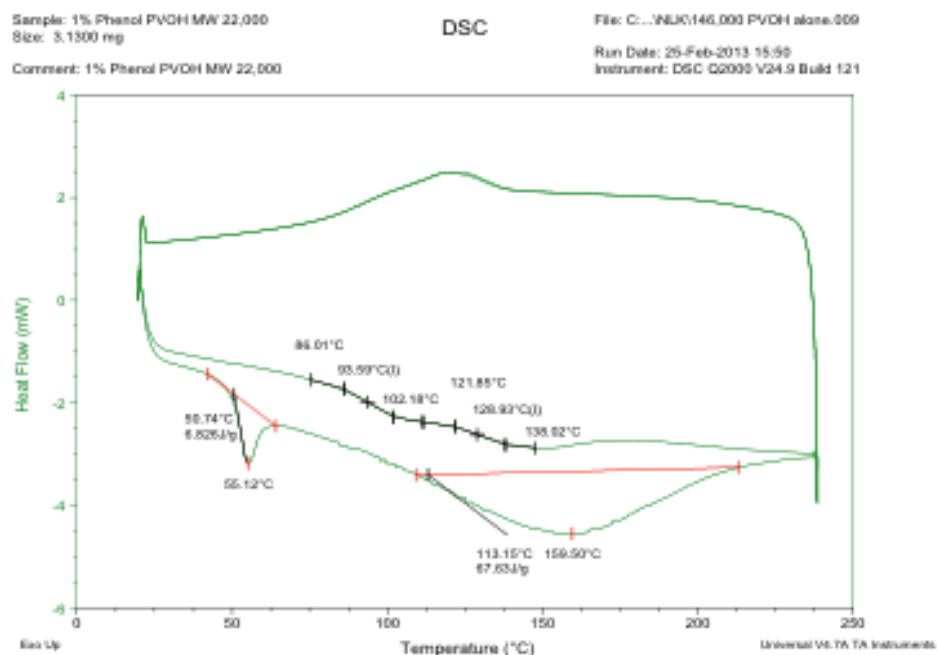


Figure 13: PVOH M.W. 22,000. Film was synthesized with 1 gram of PVOH, 25mL of water, 1ml of glutaraldehyde and phenol. The percentage of OH groups in PVOH occupied by phenol was 1.0%. Reagents were melted and poured into a dish to dry over night.

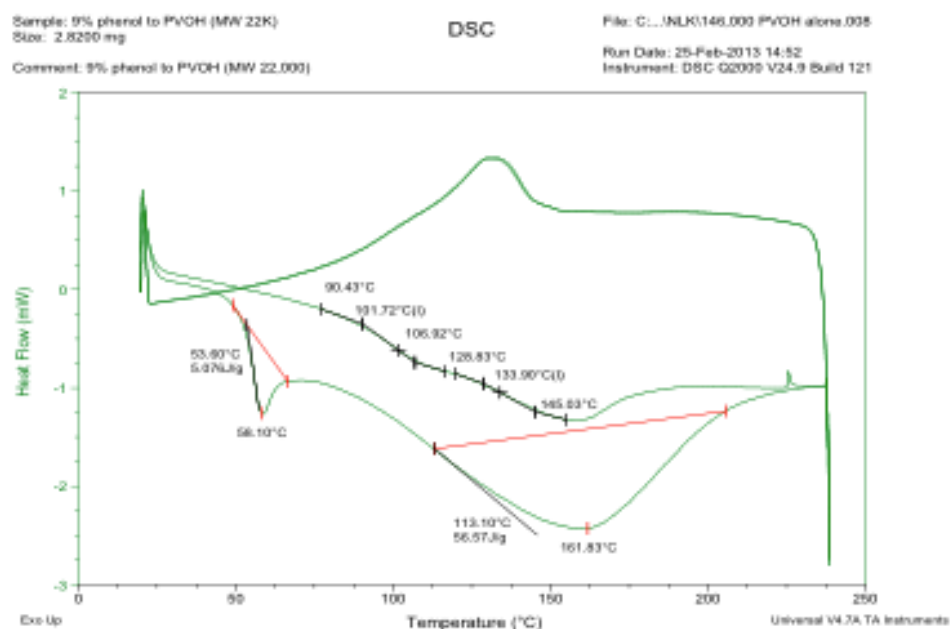


Figure 14: PVOH M.W. 22,000. Film was synthesized with 1 gram of PVOH, 25mL of water, 1ml of glutaraldehyde and phenol. The percentage of OH groups in PVOH occupied by phenol was 10.0%. Reagents were melted and poured into a dish to dry over night.

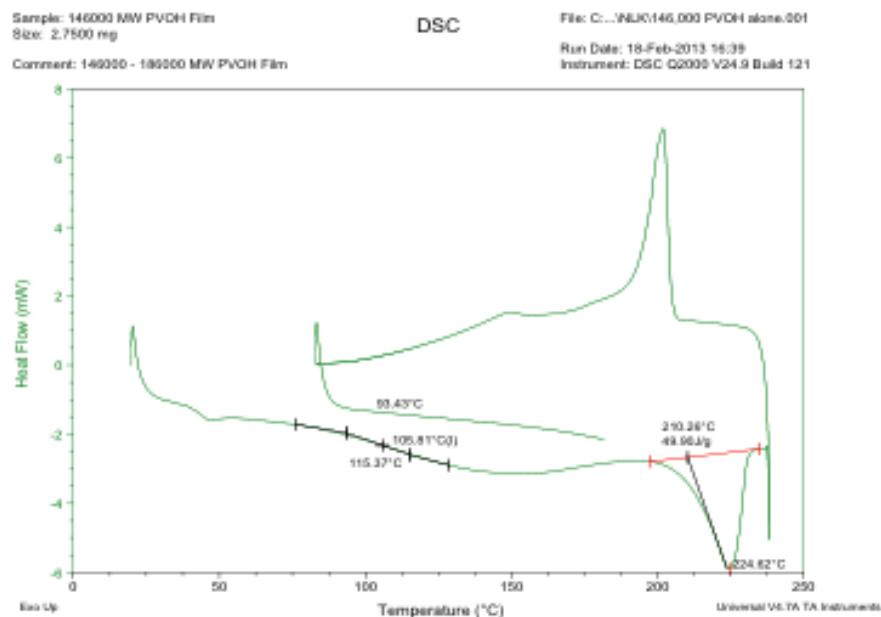


Figure 15: PVOH M.W. 146,000-186,000. Film was synthesized with 1 gram of PVOH and 25mL of water, which was melted and poured into a dish to dry over night. Reagents were melted and poured into a dish to dry over night.

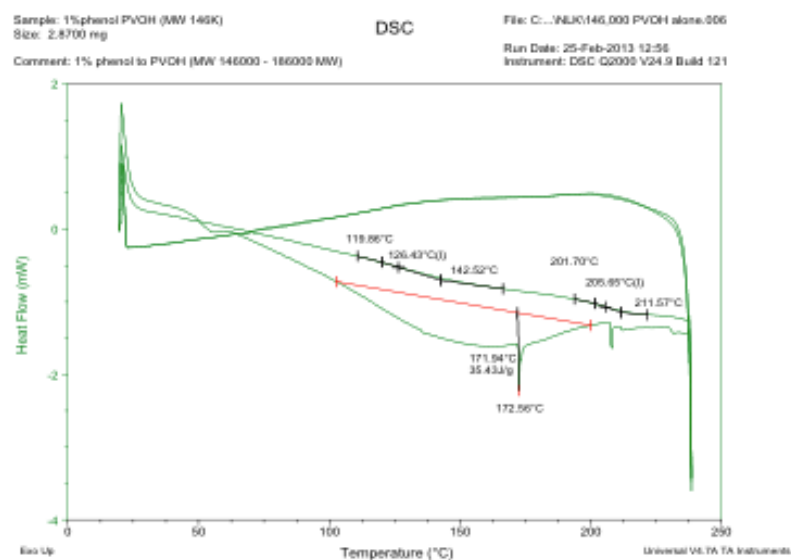


Figure 16: PVOH M.W. 146,000-186,000. Film was synthesized with 1 gram of PVOH, 25mL of water, 1ml of glutaraldehyde and phenol. The percentage of OH groups in PVOH occupied by phenol was 1.0%. Reagents were melted and poured into a dish to dry over night.

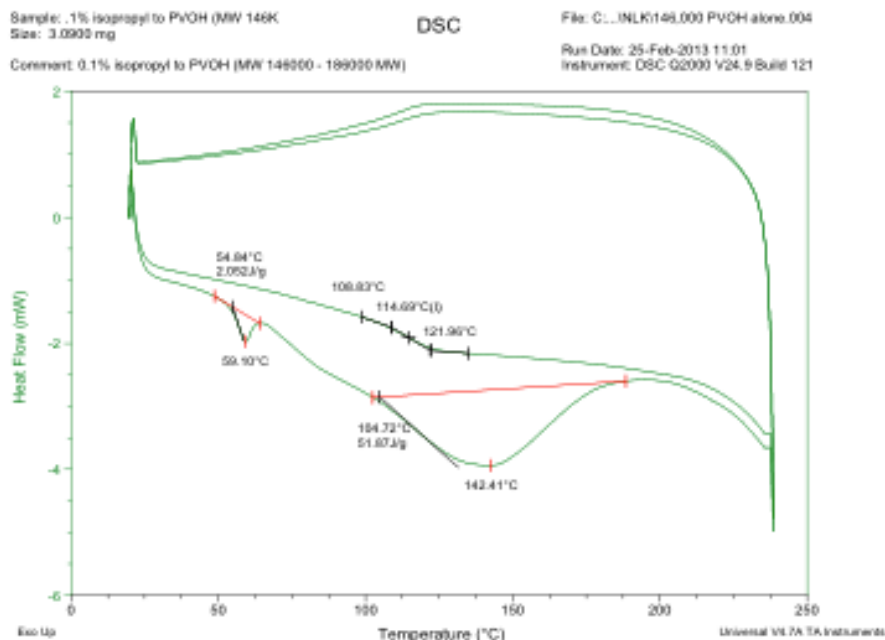


Figure 17: PVOH M.W. 146,000-186,000. Film was synthesized with 1 gram of PVOH, 25mL of water, 1ml of glutaraldehyde and isopropanol. The percentage of OH groups in PVOH occupied by isopropanol was 0.1%. Reagents were melted and poured into a dish to dry over night.

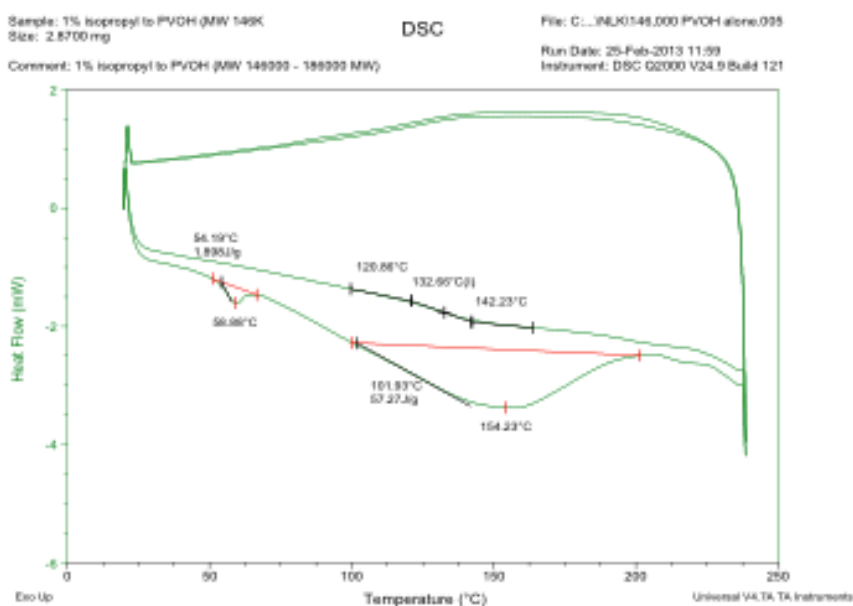


Figure 18: PVOH M.W. 146,000-186,000. Film was synthesized with 1 gram of PVOH, 25mL of water, 1ml of glutaraldehyde and isopropanol. The percentage of OH groups in PVOH occupied by isopropanol was 1.0%. Reagents were melted and poured into a dish to dry over night.

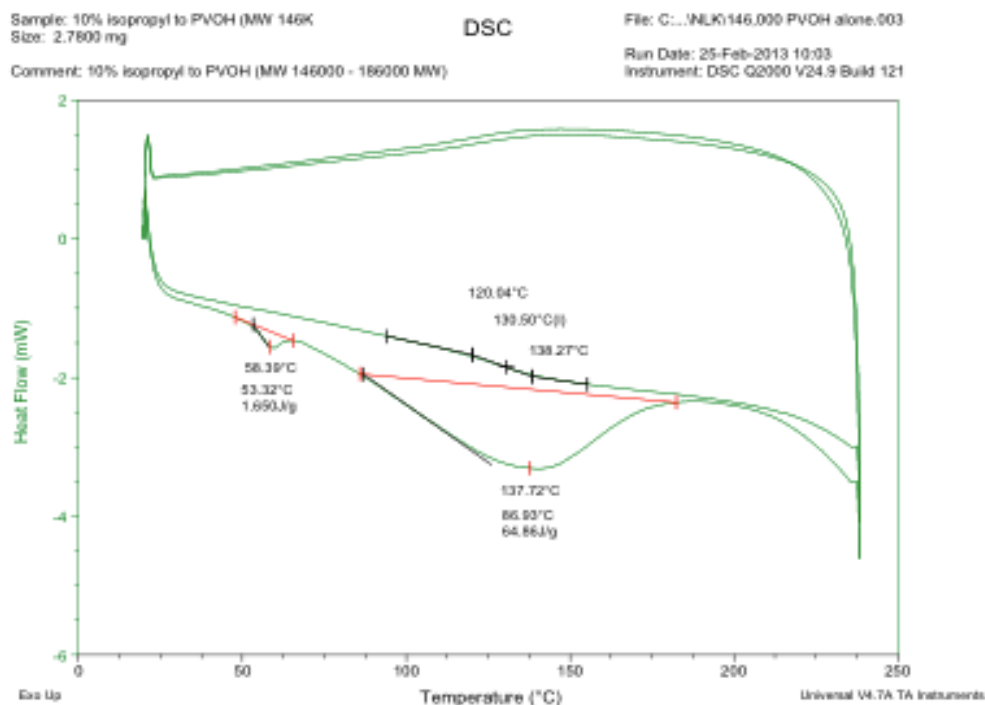


Figure 19: PVOH M.W. 146,000-186,000. Film was synthesized with 1 gram of PVOH, 25mL of water, 1ml of glutaraldehyde and isopropanol. The percentage of OH groups in PVOH occupied by isopropanol was 10.0%. Reagents were melted and poured into a dish to dry over night.

Table 1: DSC Analysis.

| Film                                           | Presence of a Crosslinking Peak | Glass Transition Temperature (°C) | Temperature of Dehydration (°C) | Presence of Recrystallization Peak |
|------------------------------------------------|---------------------------------|-----------------------------------|---------------------------------|------------------------------------|
| PVOH (MW = 22,000)                             | Yes                             | 109.35                            | 177.58, 189.52                  | Yes, small peak                    |
| PVOH + Glut (MW = 22,000)                      | Yes, but small                  | 106.4, 133.05                     | 147.42                          | Yes, small peak                    |
| PVOH + Glut + 0.01% phenol (MW = 22,000)       | Yes                             | 103.29, 158.29                    | 160.32, 175.79                  | Yes, medium peak                   |
| PVOH + Glut + 0.1% phenol                      | Yes, but small                  | 91.10, 121.78                     | 141.20                          | No                                 |
| PVOH + Glut + 1% phenol                        | Yes                             | 93.59, 128.93                     | 159.50                          | No                                 |
| PVOH + Glut + 10% Phenol                       | Yes                             | 101.72, 133.90                    | 145.03, 161.83                  | Yes                                |
| PVOH (MW = 146 - 186,000)                      | Yes                             | 105.81                            | 224.62                          | Yes, very large peak               |
| PVOH + 1% Isopropanol (MW = 146,000 - 186,000) | Yes                             | 114.69                            | 142.41                          | No                                 |
| PVOH + 1% Isopropanol                          | Yes                             | 132.66                            | 154.23                          | No                                 |
| PVOH + 10% Isopropanol                         | Yes                             | 130.50                            | 137.72                          | No                                 |

Table 1 summarizes the key information extracted from the DSC spectra. PVOH (22,000MW) has a cross-linking peak, a glass transition temperature at 109.35C, a dehydration temperature at 177.58C and 189.52 and a very small recrystallization peak. PVOH(22,000MW)+glutaraldehyde has a cross-linking peak, a glass transition at 106.4C and 133.05C, a dehydration temperature at 147.42C, and a small recrystallization peak. PVOH(22,000MW)+glutaraldehyde+0.01%phenol has a cross-linking peak, a glass transition at 103.29C and 158.29C, a dehydration temperature at 160.32C and 175.79C, and a recrystallization peak. PVOH(22,000MW)+glutaraldehyde+0.1%phenol has a cross-linking peak, a glass transition temperature of 91.10C and 121.78C, a dehydration temperature at 141.2C and no recrystallization peak. PVOH(22,000MW)+glutaraldehyde+1%phenol has a cross-linking peak, a glass transition at 93.59C and 128.93C, a dehydration temperature at 159.50C and a no recrystallization peak. PVOH(22,000MW)+glutaraldehyde+10%phenol has a cross-linking peak, a glass transition at 101.72C and 133.90C, a dehydration temperature at 145.03C and 161.83C, and a recrystallization peak. PVOH(146,000-186,000MW) has a cross-linking peak, a glass transition at 105.81C, a dehydration temperature at 224.62C and a recrystallization peak. PVOH(146,000-186,000MW)+glutaraldehyde+0.1%isopropanol has a cross-linking peak, a glass transition at 114.69C, a dehydration temperature at 142.41C, and no recrystallization peak. PVOH(146,000-186,000MW)+glutaraldehyde+1.0%isopropanol has a cross-linking peak, a glass transition at 132.66C, a dehydration temperature at 154.23C and no recrystallization peak. PVOH(146,000-186,000MW)+glutaraldehyde+10%isopropanol has a cross-linking peak, a glass transition at 130.50, a dehydration temperature at 137.72C and no recrystallization peak.

## 2. Bacteria Testing with BL21 E. Coli

### 2.1 Plate Culture with (S)-(-)-(3-Chloro-2-hydroxypropyl)trimethylammonium chloride (Quaternary Ammonium Salt) + PVOH 22,000MW + 1mL Glutaraldehyde Films



Figure 19: Quaternary Ammonium Salt on its own.

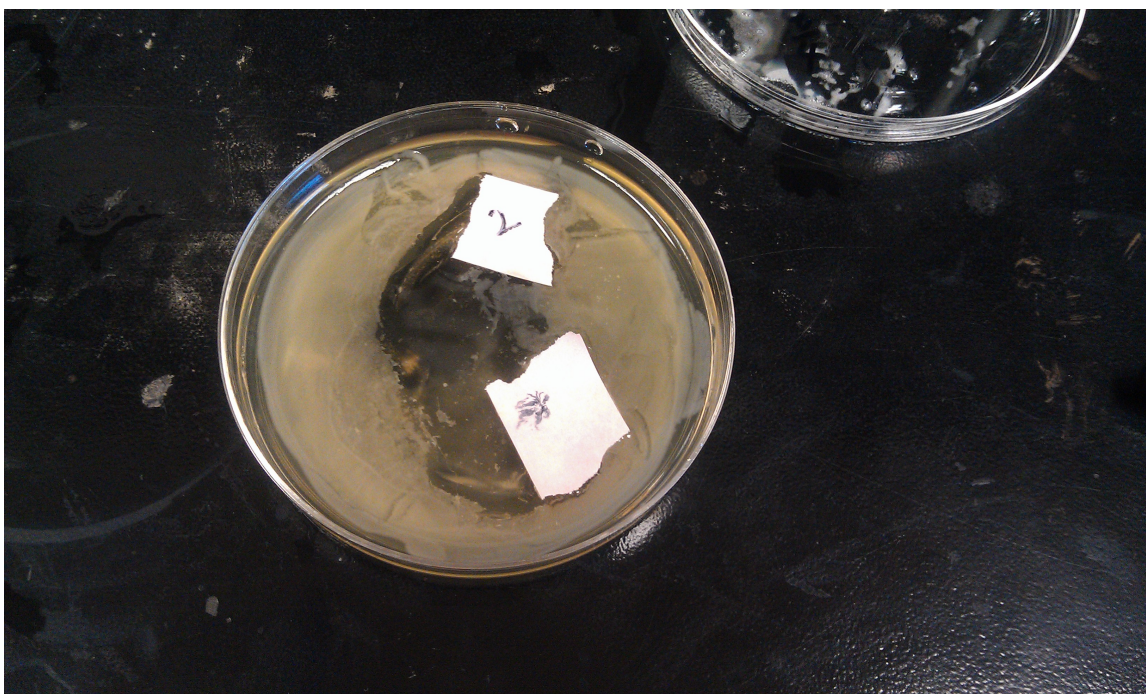


Figure 20: PVOH 22,000 MW Film.

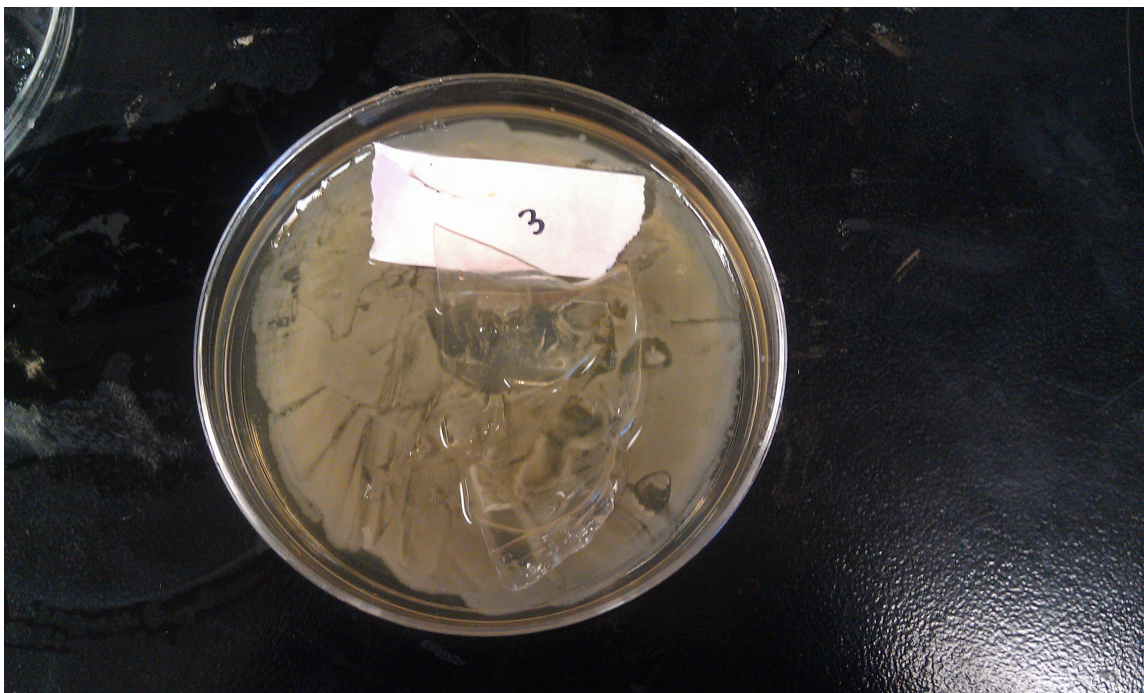


Figure 21: PVOH 22,000 MW + 1mL of glutaraldehyde film.

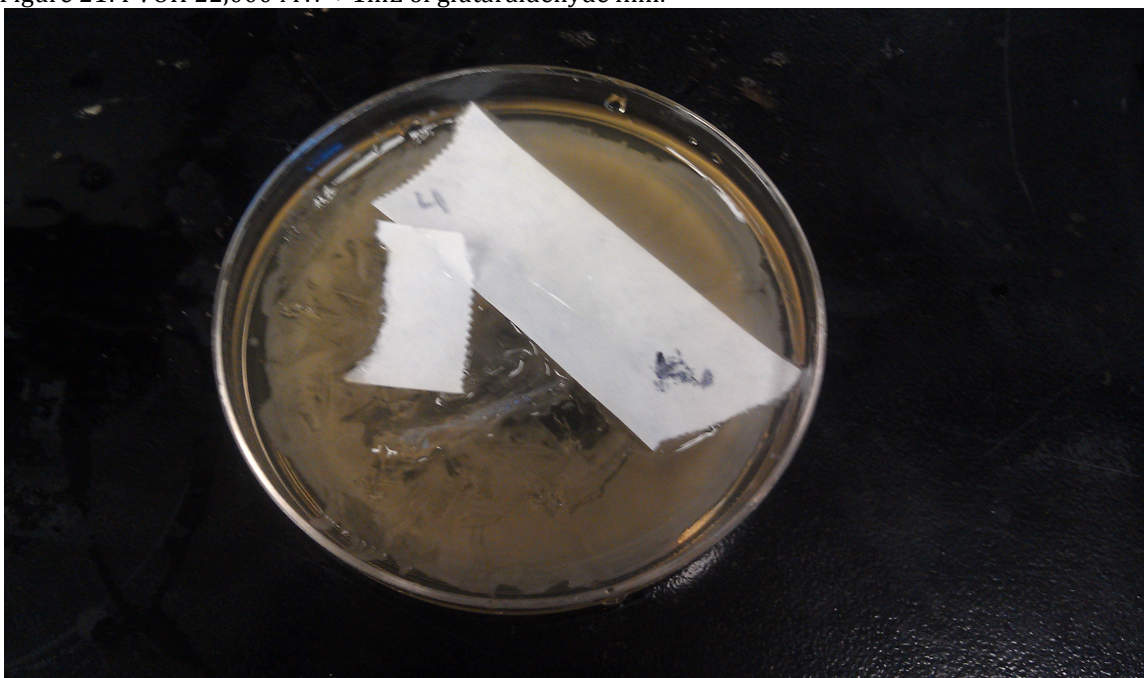


Figure 22: PVOH 22,000MW + 1mL of glutaraldehyde + 0.01% quaternary ammonium salt.

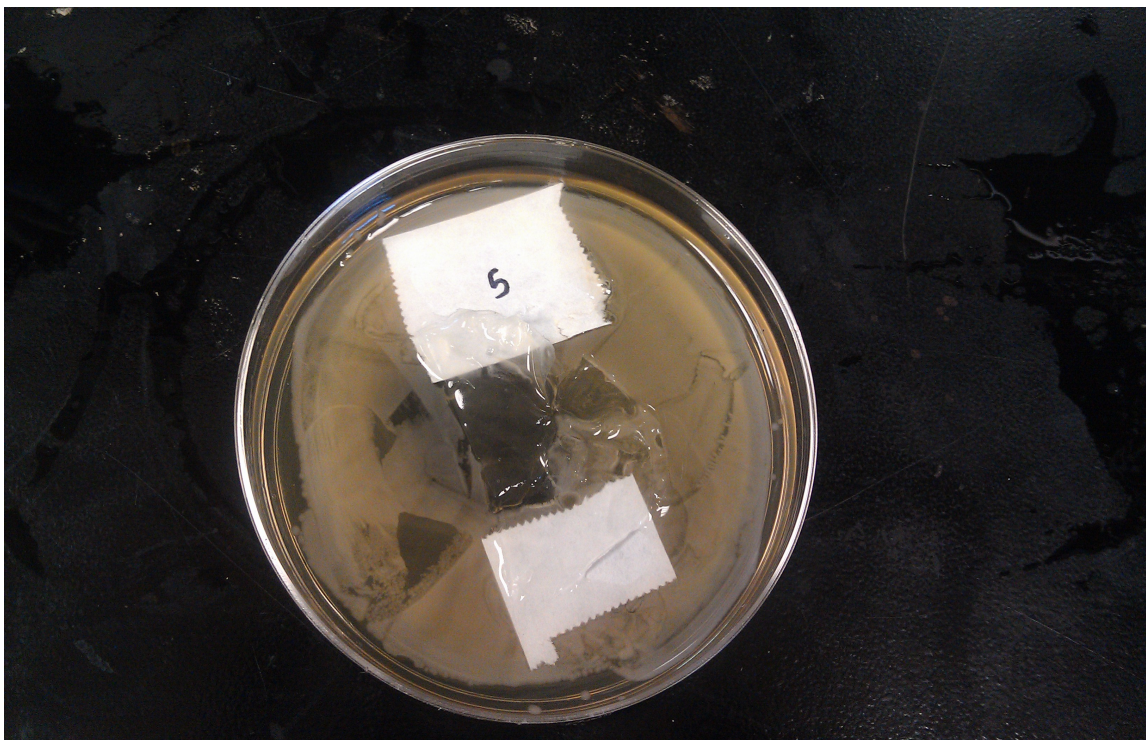


Figure 23: PVOH 22,000MW + 1mL glutaraldehyde + 0.1% Quaternary Ammonium Salt.

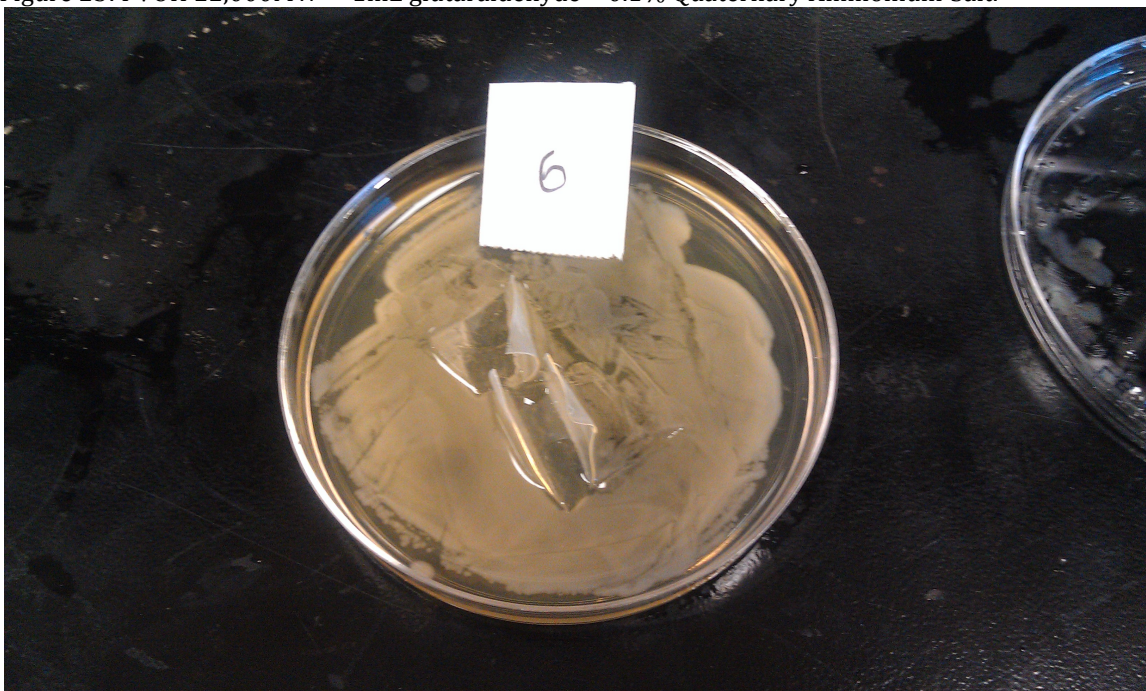


Figure 24: PVOH 22,000MW + 1mL glutaraldehyde + 1% Quaternary Ammonium Salt.

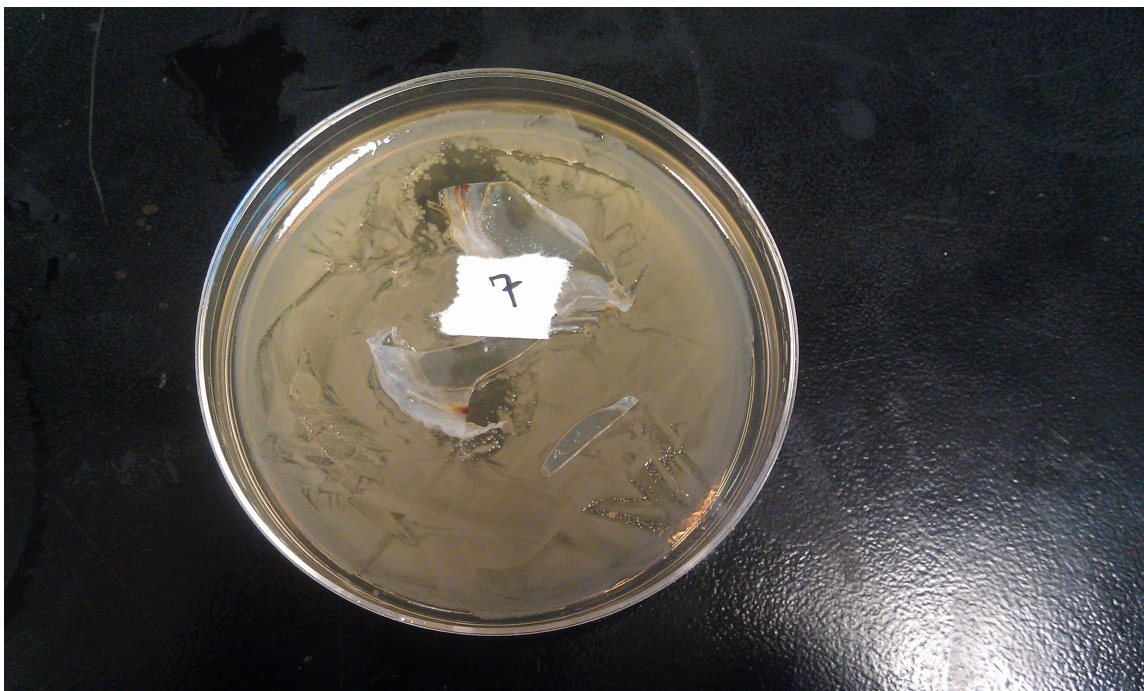


Figure 25: PVOH 22,000MW + 1mL glutaraldehyde + 10% Quaternary Ammonium Salt.



Figure 26: Nothing was the control.

In comparison to the control (Figure 26), the others plates did not vary much in growth of *E. Coli* (Figure 20-25). Except for the one covered with the Quaternary Ammonium Salt on its own (Figure 19). Figure 25 and 24, showed some lack of growth where the films were place, these films contained 0.01% and 0.1% percent Quaternary Ammonium Salt. In addition, most of the films curled overnight during the incubation and were no longer touching the agar.

2.2 Erlenmeyer Flask Culture with (S)-(-)-(3-Chloro-2-hydroxypropyl)trimethylammonium chloride (Quaternary Ammonium Salt) + PVOH 22,000MW + 1mL Glutaraldehyde Films

### Absorbance of Bacteria at 60 Minutes

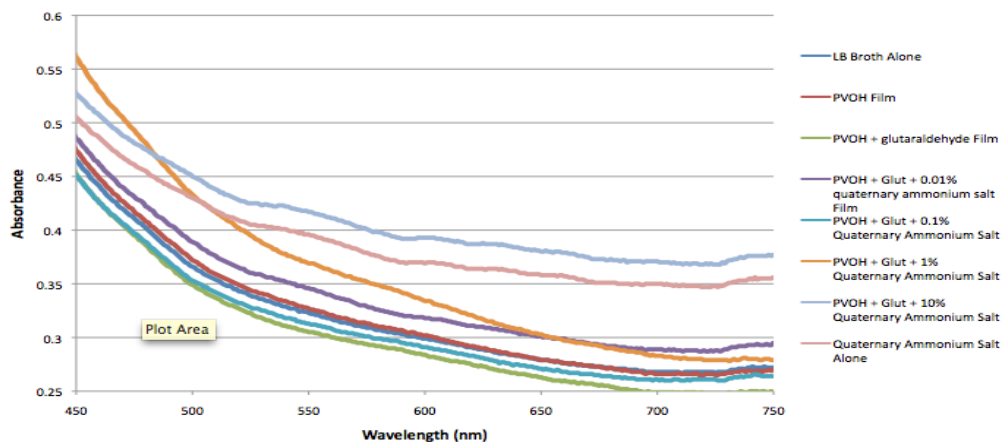


Figure 27: Is a plot of Absorbance of Bacteria vs. wavelength 60 minutes after films were placed in cultures.

### Absorbance of Bacteria at 180 Minutes

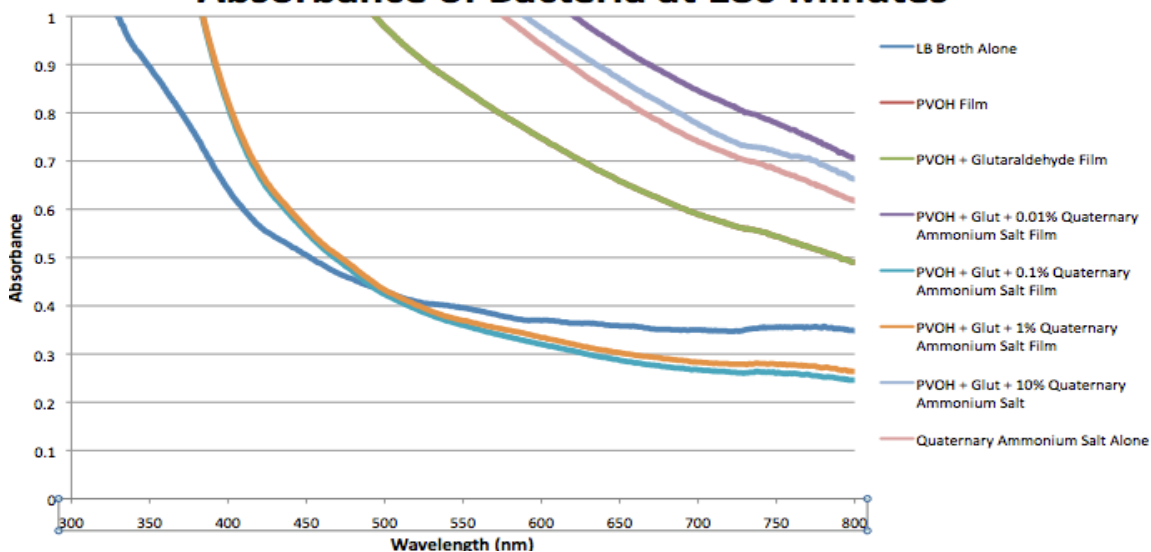


Figure 28: Is a plot of Absorbance of Bacteria vs. wavelength 180 minutes after films were placed in cultures.

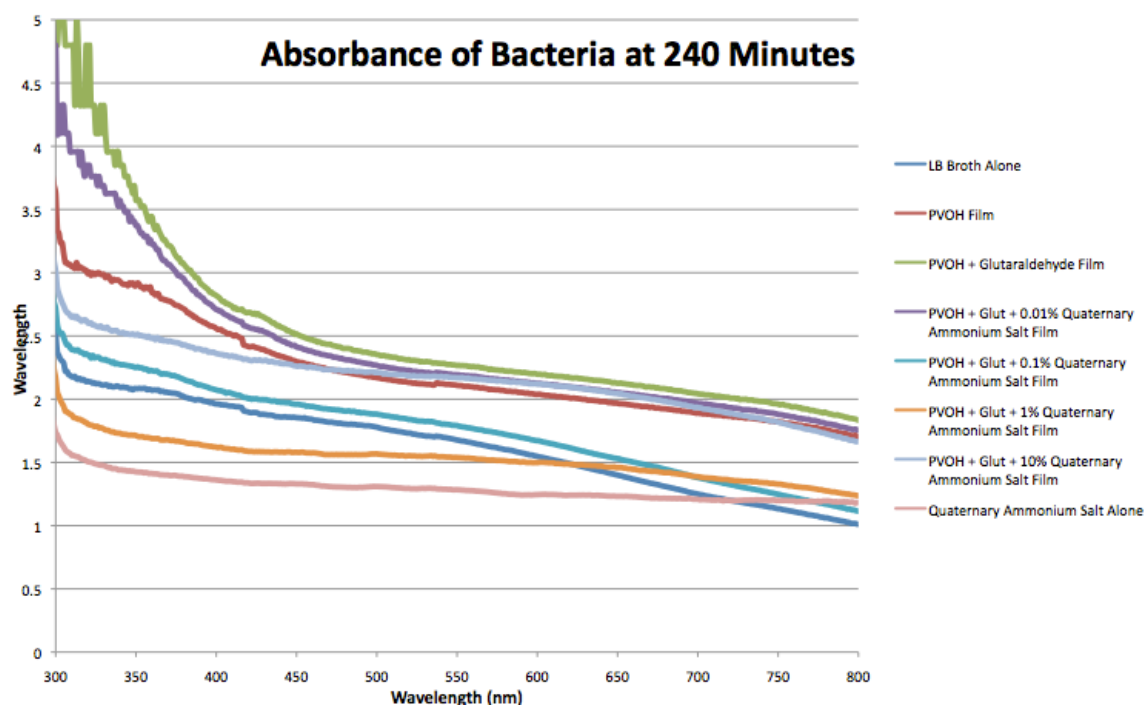


Figure 29: Is a plot of Absorbance of Bacteria vs. wavelength 240 minutes after films were placed in cultures.

Figure 27, after 60 minutes, an increase in absorption occurred in comparison to the LB Broth alone for four films. In order of increasing absorption in comparison to LB Broth was: PVOH + 1mL Glutaraldehyde + 1.0% Quaternary Ammonium Salt, PVOH + 1mL Glutaraldehyde + 0.01% Quaternary Ammonium Salt, Quaternary Ammonium Salt, and PVOH + 1mL Glutaraldehyde + 10% Quaternary Ammonium Salt. The three films with a decreased absorption in comparison to the LB Broth were PVOH Film, PVOH + 1mL Glutaraldehyde + 0.1% Quaternary Ammonium Salt, and PVOH + 1mL of Glutaraldehyde.

Figure 28, after 180 minutes, an increase in absorption occurred in comparison to the LB Broth alone for four films. In order of increasing absorption in comparison to LB Broth was PVOH + 1mL Glutaraldehyde, PVOH Film, PVOH + 1mL of Glutaraldehyde + 10% Quaternary Ammonium Salts, and PVOH + 1mL of Glutaraldehyde + 0.01% Quaternary Ammonium Salts. Two films significantly decreased in absorbance in comparison to the LB Broth alone: PVOH + 1mL Glutaraldehyde + 1.0% Quaternary Ammonium Salt and PVOH + 1mL of Glutaraldehyde + 0.1% Quaternary Ammonium Salt.

Figure 29, after 240 minutes, as increase in absorption occurred in comparison to the LB Broth alone for all the films.

## Discussion

### 1. Cross-linking Techniques

#### 1.1 Visual Appearance

The visual appearance of the films varied depending on the method by which the film was prepared. Films containing polyvinyl alcohol, or PVOH, alone no matter the molecular weight (MW= 22,000 or 146,000-186,000) had a clear color and good flexibility. Upon addition of glutaraldehyde, the films became hard and very brittle, but did not result in a color change. No difference can be seen between 22,000MW and 146,000-186,000MW films with the addition of glutaraldehyde.

Films prepared containing PVOH 22,000MW, (S)-(-)-(3-Chloro-2-hydroxypropyl)trimethylammonium chloride (quaternary ammonium salt) and glutaraldehyde were clear, slightly flimsy, hard and had a texture resembling a paper bag. In addition, after cross-linking, the films shrunk significantly compared to the films containing just PVOH and glutaraldehyde. The shrinking could potentially be due to the positive charge on the quaternary ammonium salt. Last, the films flimsiness increased with the increase of OH groups being occupied by quaternary ammonium salt. This is due to the decrease in cross-linking, as well as bulky size of the quaternary ammonium salt. In addition, during the cross-linking, the films leached a material into the surrounding water. The material is most likely the PVOH attached to the quaternary ammonium salt. The salt is very hydrophilic. Consequently, during the cross-linking process, some of this material dissolved in water before it could react with the glutaraldehyde and cross-link.

Films prepared containing PVOH 22,000MW, phenol, and glutaraldehyde were hard, but bendable. As the percentage of OH groups of phenol occupied increased, the film became more bendable. Once again, this was due to the decrease in cross-linking.

Films prepared containing PVOH 146,000-186,000MW, isopropanol, and glutaraldehyde were very brittle and hard compared to the standard PVOH and glutaraldehyde film. In addition, since the PVOH did not dissolve some films had recrystallized clumps of PVOH. The clumping was determined to be due to a high molecular weight and lack of water for dissolving.

Films prepared containing PVOH 146,000-186,000MW, phenol and glutaraldehyde were bendable and breakable. In addition, clumps of phenol and PVOH are spread throughout each film. Last, the film with the highest percentage of OH groups occupied by phenol had a yellow tint to it, which is most likely due to the phenol present in the film.

Hydrogels prepared containing PVOH 146,000-186,000MW, isopropanol and glutaraldehyde were jelly like after a series of cycles of freezing and thawing. During the additional cross-linking process, the gels formed a blister, which eventually dissipated. After cross-linking, the gels were extremely hard and were a milky white color. In addition, the gels shrunk significantly.

Hydrogels prepared containing PVOH 146,000-186,000MW, butyne-1-ol and glutaraldehyde were also jelly like after a series of cycles of freezing and thawing. During the additional cross-linking process, the gels also formed a blister, which eventually dissipated. After cross-linking, the gels were extremely hard and were a milky white color. In addition, the gels shrunk significantly.

## 1.2 Chemical Changes

### 1.2.1 FTIR of Phenol and Glutaraldehyde in PVOH Films

According to Mansur, PVOH films cross-linked with glutaraldehyde have four distinct regions of vibration modes:  $3550\text{--}3200\text{cm}^{-1}$  for the O-H stretch of the intermolecular and intramolecular hydrogen bonds,  $1750\text{--}1735\text{cm}^{-1}$  for the C=O bonds, and  $1150\text{--}1085\text{cm}^{-1}$  for the C-O-C bonds (1). As you can see in Figure 1, these modes are present in the control. However, upon addition of phenol to the films, no significant change in vibration modes can be seen. A peak should be seen between  $1600\text{--}1580\text{cm}^{-1}$ ,  $1500\text{--}1450\text{cm}^{-1}$  and  $3100\text{--}3000\text{cm}^{-1}$  (2). For 1.0% and 10.0%, little peaks can be seen in these regions, figure 3 and 4. Whereas for 0.1%, the peaks are more prominent, figure 2. Nonetheless, it is hard to tell whether these developing peaks are due to the presence of phenol or not. However, DSC indicated it was attached. Nonetheless, further synthesis and testing of films is needed.

### 1.2.2 FTIR of (S)-(-)-(3-Chloro-2-hydroxypropyl)trimethylammonium chloride (Quaternary Ammonium Salt) and Glutaraldehyde in PVOH Film

As stated previously, PVOH films cross-linked with glutaraldehyde have four distinct regions of vibration modes:  $3550\text{--}3200\text{cm}^{-1}$  for the O-H stretch of the intermolecular and intramolecular hydrogen bonds,  $1750\text{--}1735\text{cm}^{-1}$  for the C=O bonds, and  $1150\text{--}1085\text{cm}^{-1}$  for the C-O-C bonds (1). These modes can be observed in figure 4. Upon addition of the quaternary ammonium salt, an increase in absorbance is obvious, as well as the additional appearances of peaks between the ranges  $1200\text{--}800\text{cm}^{-1}$  and  $1500\text{--}1250\text{cm}^{-1}$ . In addition, a distinct shoulder can be seen forming at the wavelength  $2857.5195\text{cm}^{-1}$ . The addition of the ammonium salt should result in the addition of three vibration modes: two peaks at  $2926\text{cm}^{-1}$  and  $2886\text{cm}^{-1}$ , as well as one at  $1414\text{cm}^{-1}$  and another at  $1482\text{cm}^{-1}$  (2). The  $1482\text{cm}^{-1}$  corresponds to the methyl group of the ammonium and the  $1414\text{cm}^{-1}$  corresponds to the C-N stretching mode (2). The two peaks at  $2926\text{cm}^{-1}$  and  $2886\text{cm}^{-1}$  can be clearly observed in figures 5-8, and were described earlier as the growing peak with the shoulder. In addition,  $1414\text{cm}^{-1}$  and  $1482\text{cm}^{-1}$  can also be observed in the figures as well. Thus, the quaternary ammonium salt is present in the film. However, to officially confirm its attachment further testing will be performed, such as a dye test and DSC.

### 1.3 Thermal and Crystalline Properties

The films with PVOH(22,000MW)+glutaraldehyde+phenol had two glass transitions, which indicates that the phenol was successfully attached. Aromatic groups form more stable pi-pi interactions that result in a 2<sup>nd</sup> glass transition once intermolecular forces are overcome by kinetic motion (3). As the concentration of phenol increased, the two glass transitions became sharper. In addition, as the concentration of phenol increased the glass transition temperature decreased. A decrease in glass transition indicates less cross-linking, which is expected as more phenol is incorporated into the film because less OH groups are available for cross-linking (3).

For PVOH(146,000-186,000MW)+glutaraldehyde+isopropanol films, as the concentration of isopropanol increased, the glass transition temperature increased. Higher glass transition temperature means more cross-linking (3). If isopropanol was attached, the glass transition temperature should have decreased as the

concentration of isopropanol increased. As a result, the isopropanol did not attach. It most likely did not attach because most of it evaporated off before it could be cross-linked.

## **2. Bacteria Testing with BL21 E. Coli**

### **2.1 Plate Culture with (S)-(-)-(3-Chloro-2-hydroxypropyl)trimethylammonium chloride (Quaternary Ammonium Salt) + PVOH 22,000MW + 1mL Glutaraldehyde Films**

Since the quaternary ammonium salt on its own, figure 19, showed lack of growth of E. Coli, it can be concluded that the quaternary ammonium salt had antibacterial properties. Nonetheless, quaternary ammonium salt is toxic in high concentrations regardless. Therefore, a better control needs to be used in further testing that will take into consideration the range of salt present in the film. Figure 5 and 4, showed some lack of growth where the films were placed, these films contained 0.01% and 0.1% percent Quaternary Ammonium Salt. Since, these films showed some lack of growth, we could conclude that the films have antibacterial properties. In addition, most of the films curled overnight during the incubation and were no longer touching the agar. This skewed the results drastically. Future testing needs to ensure that the films touch the plate throughout the 24 hours of incubation. As a result, further testing is needed to obtain better and clearer results.

### **2.2 Erlenmeyer Flask Culture with (S)-(-)-(3-Chloro-2-hydroxypropyl)trimethylammonium chloride (Quaternary Ammonium Salt) + PVOH 22,000MW + 1mL Glutaraldehyde Films**

Figures 27-29, data were extremely difficult to interpret. The data was unpredictable and no pattern was observed. At certain time intervals, the quaternary ammonium salt present in the film did decrease the absorption in comparison to the control indicating a decrease in the amount of living E. coli. However, the variation in data is too extreme to conclude that the quaternary ammonium is definitely affecting the E. coli. The variation is most likely due to unequal distribution of colonies through the solution. Future testing will need to address this issue. Possible solutions include using a syringe to filter larger colonies out, yet this too will skew our results.

## **References**

- (1) Mansur, H., Sadahira, C., Souza, A., and Mansur, A. (2007). "FTIR spectroscopy characterization of poly(vinyl alcohol) hydrogel with different hydrolysis degree and chemically crosslinked with glutaraldehyde". *Material Science and Engineering C* 28 (2008) 539-548.
- (2) Yongbo Song, Yunxia Sun, Xianzheng Zhang, Jinping Zhou, and Lina Zhang (2008). "Homogeneous Quaternization of Cellulose in NaOH/Urea Aqueous Solutions as Gene Carriers". *Biomacromolecules* (2008) 9 (8), 2259-2264.
- (3) Guirguis, O. and Moselhey, M. (2012). "Thermal and structural studies of poly(vinyl alcohol) and hydroxypropyl cellulose blends". *Natural Science*, 4, 57-67. doi: 10.4236/ns.2012.41009.