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# Progress on Roll-to-Roll Coating of High-Performance 2D Polymer Films: Part III

by David C. McLeod, Emil J. Sandoz-Rosado, Eric D. Wetzel,  
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## **Progress on Roll-to-Roll Coating of High-Performance 2D Polymer Films: Part III**

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| <b>14. ABSTRACT</b><br>This report provides an update on research conducted January–May 2022 at the Rochester Institute of Technology (RIT) and on a pilot scale coating line at Kodak on roll-to-roll two-dimensional polymer (2DP) coatings and films. Highlights include the following: detailed studies on how the rheology of 2DP and dummy solutions change with water content, evaluation of doctor-bladed 2DP coating laydown and drying at varying water content, production of Ossila slot-extrusion die coatings of 2DP at varying relative humidity, the results of a large-scale coating trial using a pilot scale line where coating windows were established using dummy solutions and 2DP film sections as long as 30 ft and 9.5 inches wide were produced, and the evaluation of 2DP coatings made on various roll-to-roll support materials commonly used in industry. |                                    |                                          |                                         |                                                                 |                                               |
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## 1. Introduction

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The goal of this research is to produce high-quality two-dimensional polymer (2DP) films using a roll-to-roll coating process at an industrial scale facility, such as the RC5 pilot production line at Kodak. When the project started in Fall 2020, it was determined that roll-to-roll coatings of the chemical formulations developed at the U.S. Army Combat Capabilities Development Command (DEVCOM) Army Research Laboratory (ARL) were achievable using a slot-die coating process at the Battery Prototype Center (BPC) at the Rochester Institute of Technology (RIT). In anticipation of additional coating experiments on this coating machine, a 5-inch-wide slot-extrusion die was refinished and dedicated to this research.

In Spring/Summer 2021, it was established that the BPC roll-to-roll coatings could be delaminated and neutralized to produce stand-alone films that exhibit desirable properties comparable to those obtained at ARL. During that time, it was also found with benchtop doctor blade coatings that the humidity conditions used to dry the coated films had a significant effect on the properties and performance of the coatings and the neutralized films. It was also demonstrated that for some substrates such as copper, uncontrolled spontaneous delamination could occur under certain drying conditions following the coating process. Although delamination of the coated 2DP film is necessary for the proper use of this film after the coatings are generated, uncontrolled delamination during the drying process would be undesirable. Furthermore, it was observed during the slot-die roll-to-roll coating process that some leakage under the slot-extrusion die occurred at the higher flow rates required to produce thicker coatings with a wet thickness above 200  $\mu\text{m}$ . This leakage, which interferes with the wet thickness control of the coatings, was determined to be mainly due to the super-spreading property of the 2DP coating solution formulation described in more detail below.

To solve the leakage problem, in Fall 2021 contact angle and wetting experiments on materials with varying surface energies and edge geometries were carried out. It was demonstrated that the contact line of the coating solution could be pinned at the bottom edge of the extrusion die, depending on the design geometry of the slot-die lip. It was also found that this result could be achieved even with a stainless-steel slot die, which is the most common material used for slot dies at Kodak. However, because of the high surface energy of stainless steel, which would normally promote surface wetting of low surface tension solvents such as the one exhibited by the solvent of the 2DP formulation, it was also decided that a coating trial at Kodak would be needed to verify this conclusion and provide us with a coating map that would be used in future coatings of this and other modified formulations. Therefore, a coating trial was scheduled on the RC5 coating machine

at Kodak for April 6, 2022. This machine was selected because it is capable of coating organic solvent formulations, and it has drying capabilities suitable for the drying times needed for the proper drying of the 2DP coatings. Although the decision to carry out this trial was made at the end of Fall 2021, scheduling was somewhat delayed due to the limited availability of the formulation solvent.

In anticipation of this Kodak trial the research work during Spring 2022, which is summarized in this report, focused on preparing for this trial. The first goal was finding a “dummy” solution for obtaining the coating window to preserve the stock of the 2DP monomers used in the formulation and to minimize cost. This goal consisted of identifying a polymer to be used in preparing these solutions using the same solvent and then characterizing the rheology of these solutions and comparing with the monomer solutions to match the rheology of the “dummy” solutions to that of the monomer solutions. The second goal of this work was to carry out experiments simulating the coating and drying conditions of the RC5 machine so that any potential problems are identified, mitigated, and prevented. To facilitate this work, a benchtop scale coating device that was previously purchased from Ossila by ARL was loaned to the RIT team. One significant advantage of this device over the blade coater that has been used by the RIT team is that the Ossila coater is capable of making pre-metered coatings so that the coating thickness can be independently controlled, unlike the blade coating process. The results from the Ossila experiments and from the coating trial on the RC5 Kodak machine are summarized in this report.

The formulations used in the Kodak trial were similar to the previous formulations with two variations in the water content. In general, the solution used thus far comprises two monomers: 1,3,5 tris[4-aminophenyl]benzene (TAPB) and phenyl-1,4-dialdehyde (PDA). These two monomers are dissolved in a mixture of trifluoroacetic acid (TFA) and water. In addition to being a solvent, the TFA also acts as a catalyst in the polymerization reaction. As a result, when the two monomers are dissolved in TFA, a reaction takes place that produces a TAPB-PDA imine polymer and water. The extent of the polymerization in the solution is not complete, and additional polymerization continues during the coating and drying process. The solids loading used for the Kodak trial was 200 mg of total monomers per milliliter (mL) of total solvent. The water content variations were 3% and 5% water in the TFA/water solvent mixture. These water content levels include the amount of water produced during the condensation-type polymerization reaction.

As mentioned above, when the TAPB/PDA/TFA/water mixture is coated onto a support, the polymerization continues and accelerates as TFA, and water evaporate and the concentration of the monomers in the coating increases. During the coating and drying processes, a 2D structure of the resulting polymer is also formed to

produce the final 2DP films. The details of the extent of the polymerization, structure, and cross-linking produced during the coating and drying processes are not yet fully understood and additional research is required in this area to optimize the final chemical and physical properties of the 2DP films. After casting and drying these coatings, the 2DP films are delaminated from the support substrate and neutralized to eliminate excess TFA so that a stable stand-alone 2DP film is produced. As with the coating and drying processes, the effect of the delamination and neutralization procedures on the final product properties is not completely understood. Although there has been much progress surrounding this project, additional research is needed to establish how the 2DP films can be produced industrially (roll-to-roll) via reproducible and reliable pre-metered process, to develop methods to characterize the quality of the final 2DP films, and to determine how to optimize the quality of these films. In addition, future experiments will include the replacement of TAPB with 1,3,6,8-tetrakis[4-aminophenyl]pyrene (TAPPy) to evaluate this new chemistry as well.

## **2. Experimental Methods, Results, and Discussion**

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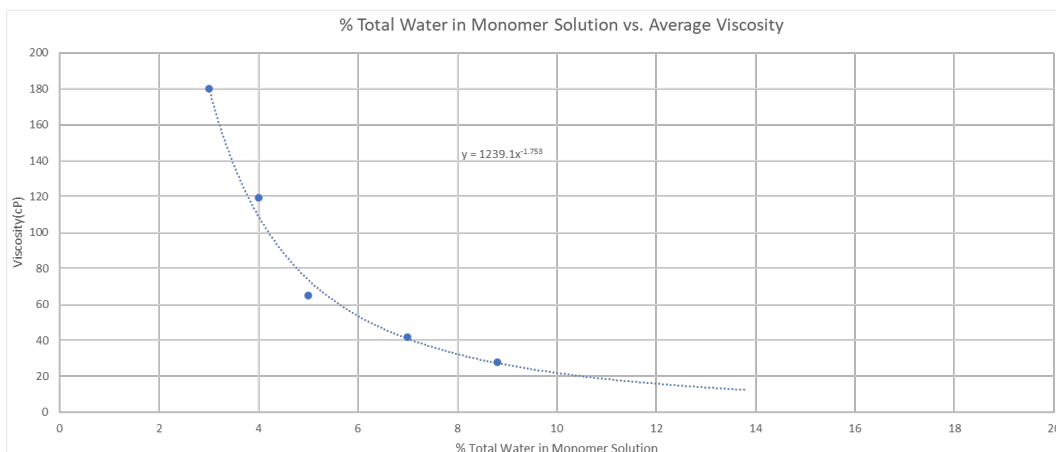
### **2.1 Rheology of 2DP Solutions**

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In the preparation of the TAPB/PDA/TFA/water solution there are two variables that have been explored. One is the total monomer solids loading with the TAPB/PDA ratio remaining constant based on the stoichiometry of the polymerization reaction, and the other is the water/TFA ratio. The solids concentration is specified by the total mass of the monomers per solvent volume (in mg/mL) and the water/TFA ratio is specified by the total water fraction (in vol % abbreviated by simply %) in the solvent, which includes the water deriving from the polymerization reaction. Both variables affect the viscosity of the final solution. Since the viscosity of the coating solution is a key variable affecting the coating window in the slot-die coating process, the viscosity of the formulations being considered for the coating trial at Kodak was thoroughly characterized.

For each solution made with varying water content, viscosity measurements were recorded with a capillary viscometer and plotted to examine the effect of the water content on the final monomer solution viscosity. All viscosity measurements were made with the same capillary viscometer. A plot of the viscosity of a 200-mg/mL monomer solution as a function of the total water content is shown in Figure 1. As seen in the Figure 1 plot, the viscosity decreases considerably as the water content increases. This is most likely because the polymerization reaction is reversible and the addition of water pushes the reaction equilibrium toward the

monomers/oligomers rather than toward the high molecular weight polymer, which will naturally have a higher viscosity as molecular weights increase.

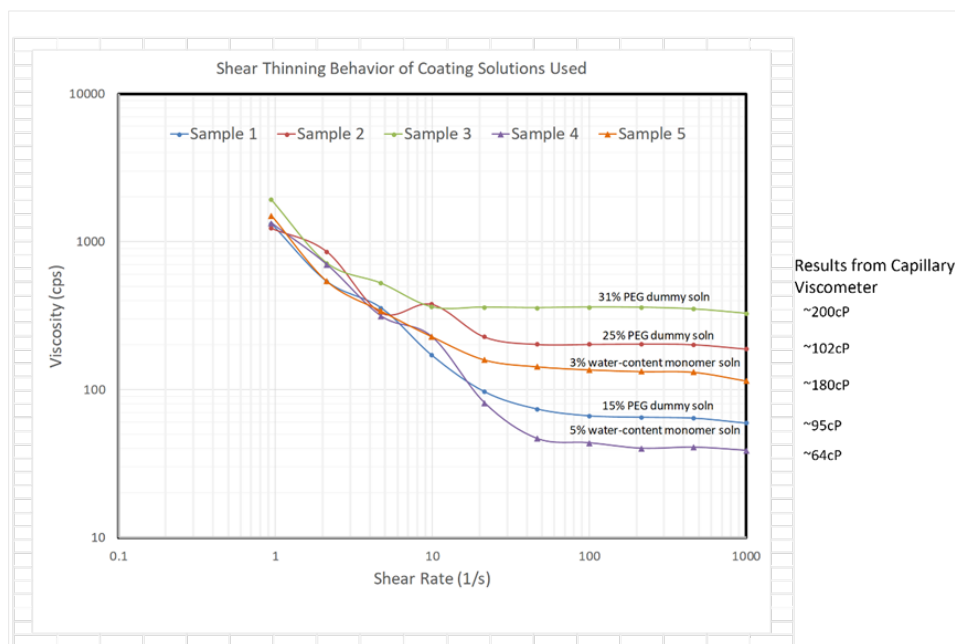


**Figure 1.** A power curve fitted over data points reflecting the viscosity for a given percentage of water present in monomer solutions. All monomer solutions created have an inherent 2% total water in the solution; thus, this graph is plotted in total % water in solution.

The viscometer used was a size 200 CANNON-Fenske capillary viscometer with a 20–100 cS range of viscosities and a constant of 0.0954 cS/s. For solutions with an approximate density of 1.5 g/mL the viscosity range becomes 45–150 cP. A capillary-type viscometer was selected because with this viscosity measurement method the solution has very little exposure to air during the measurement. This feature minimizes the TFA evaporation, which would tend to vary the solids concentration and hence the viscosity during the measurement. In addition, TFA is hygroscopic, and the viscosity of the monomer solutions is known to vary with water content. Viscosity is determined by multiplying the time taken for the solution to flow between two pre-marked lines on a capillary tube by the viscometer constant to obtain the viscosity in centistokes and then multiplying by the density of the solution to obtain the viscosity in centipoise. The 200-size rating was chosen based on the anticipated viscosity values of the monomer solutions used.

While at Kodak for the trial coating on the RC5 equipment, rheology measurements were also made on a cone and plate viscometer, which measures the solution viscosity under increasing shear rates. The viscosity measurements made at Kodak were in good agreement with the RIT results at the shear rates produced in the capillary viscometer. This conclusion is made considering that the volatility and hygroscopic nature of the solutions would introduce some variability in the cone and plate measurements at Kodak as well as the capillary viscometer measurements. This conclusion also holds true for the dummy solutions that were used, as discussed in Section 2.2. The results are shown in Figure 2; the viscosity of the dummy solutions is included as an overall comparison between the viscosity

of the monomer solutions and the dummy solutions as well as the comparison of the capillary viscometer measurements with those of the cone and plate viscometer. All formulations were found to be shear thinning.



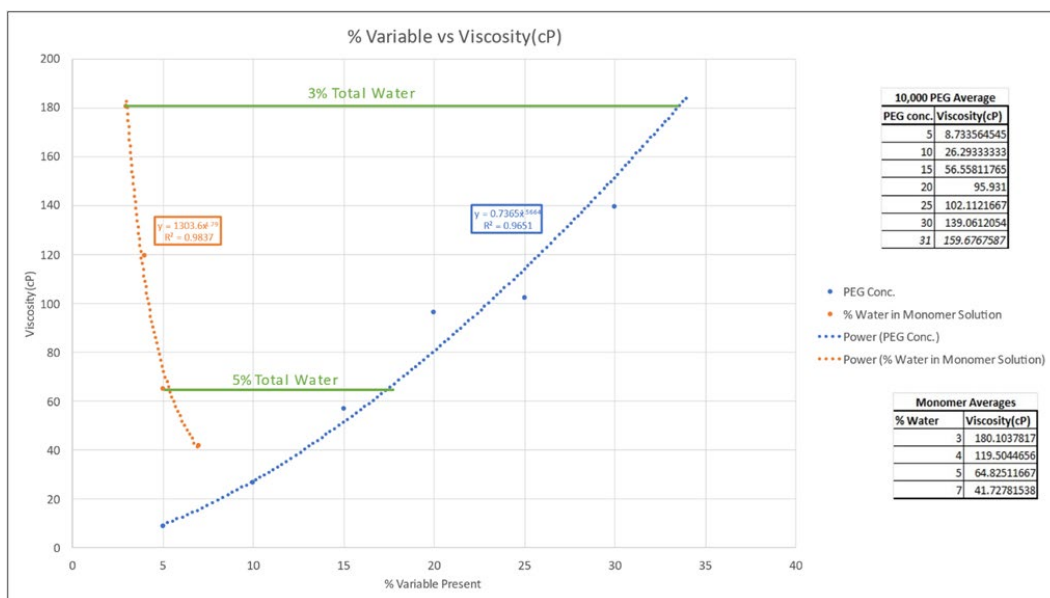
**Figure 2.** Shear thinning behavior of dummy and monomer solutions as measured with a cone and plate viscometer at Kodak and comparison of these measurements with the capillary viscometer measurements shown on the right of the graph.

## 2.2 Rheology of Dummy Solutions

In preparation for the Kodak coating trials dummy solutions were also prepared to mitigate cost and the availability of monomer. By creating dummy solutions possessing similar physical properties to the monomer solutions, it is possible to establish a good coating window prior to the introduction of the monomer solutions; thus, facilitating good-quality coatings without wasting the valuable monomer solutions. To ensure that the dummy solutions have very similar surface tension and spreading properties as the monomer solutions, the same solvent mix of 5/95 water/TFA was used to prepare the dummy solutions. This solvent mix was the standard water content used in most of the monomer solutions used in our previous experiments.

The polymer selected to adjust and control the viscosity of the dummy solutions was polyethylene glycol (PEG). This polymer was chosen for its low cost and availability in a wide variety of different molecular weights. It was found that PEG with a molecular weight of 10,000 Daltons was most suitable for creating solutions comparable in viscosity to the monomer solutions at nominal solids loadings. To establish which concentrations would best match the monomer solutions used, a

variety of solutions with different concentrations of PEG in a water/TFA solvent with 5% water content were prepared and their viscosity was measured with the same capillary viscometer. For convenience, the concentration of the PEG in the dummy solutions was determined in the same way as the concentration of the monomer solution, which is weight of solids per volume of solvent, given as simply “% PEG.” Hence, a 10% PEG solution refers to a dummy solution with 10 g of PEG in 100 mL of water/TFA solvent with 5% water content, as defined above. This approach enabled us to present and compare the viscosity of the monomer solutions at different water contents with the viscosity of the dummy solutions with PEG solutions at different concentrations as shown in Figure 3.



**Figure 3. Viscosity of dummy solutions with a given weight percentage and monomer solutions with a given water content percentage. Comparison of these two curves led to the decision of which solutions would be used for the Kodak trial.**

Prior to the Kodak trial it was decided that in addition to the 5% water content monomer solution, which has been the standard used in our experiments, a 3% water content solution would also be used during the Kodak trial. This was decided because the viscosity of these two solutions (Figure 1) was in the range of 50 to 200 cP, which would be ideal for handling and determining a general coating window. The 3% water content monomer solution was also found to give good results in terms of the final properties of the 2DP films. Based on this decision, it was determined that three dummy solutions would be used to simulate the coating behavior of the monomer solutions and establish the coating window during the Kodak trial. The three selected concentrations were 15%, 25%, and 31% polymer, with the intention of simulating monomer solutions in the range of 3% and 5%

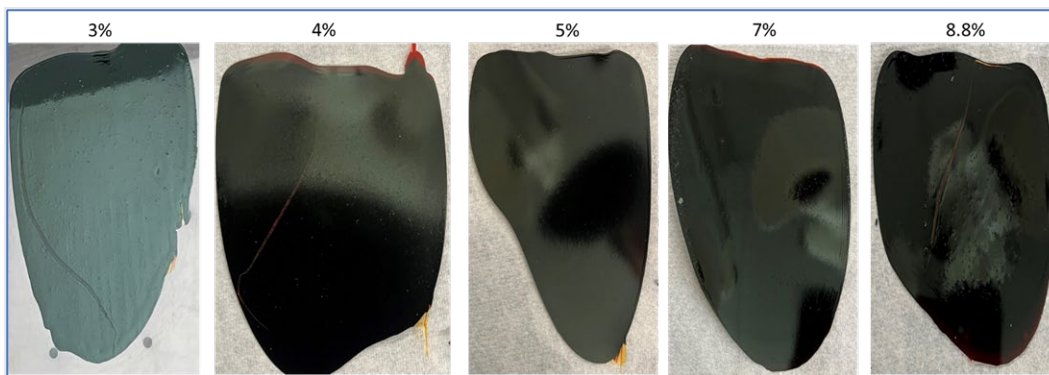
water. The correlation between the viscosity of all these solutions in the ranges mentioned are shown in Figure 3.

### **2.3 Blade Coatings to Evaluate Conditions on the RC5**

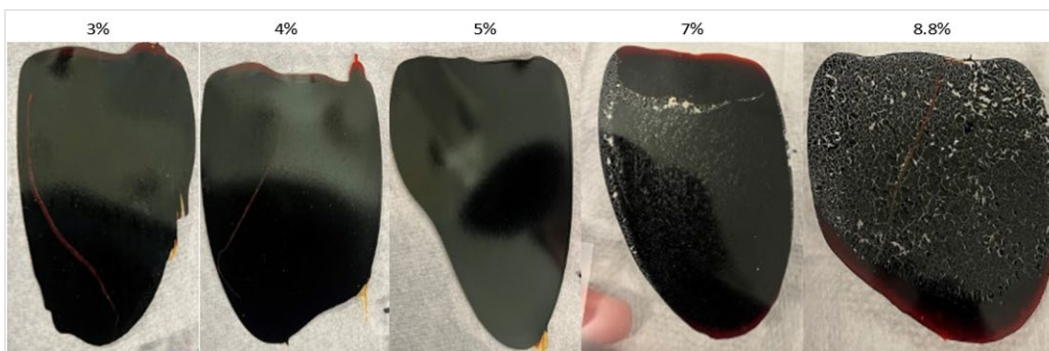
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Given that 2DP coatings had not yet been evaluated at RIT using monomer solutions with different total water content other than the standard 5%, some experimental coatings were made with water content variations prior to the Kodak trial to evaluate the stability and quality of such coatings at drying conditions comparable to those anticipated at Kodak. Therefore, coatings were cast, dried, and evaluated from monomer solutions comprising 3%, 4%, 5%, 7%, and 8.8% total water content. These water contents include the amount of water deriving from the polymerization reaction as discussed above. Each of these coatings were cast on polyethylene terephthalate (PET) film using the blade coating process with an 8-mil (200- $\mu$ m) blade gap on an automatic draw-down machine (ADM) coater under similar conditions with as much control of the drying conditions as possible. Therefore, in these experiments the ambient humidity was an uncontrolled variable and the relative humidity (RH) during casting and drying varied slightly in each coating in the 40%–50% range. The PET selection as the support was made because it has been observed that the 2DP will bind to PET, avoiding the spontaneous delamination that has been observed with some other supports.

To further simulate conditions expected on the RC5, each coating underwent an accelerated drying period under a heat gun to mimic the dryers available in the RC5 coating machine. It was found that under accelerated drying conditions each coating remained uniform and was dry (i.e., dry to the touch or not tacky) in 3–5 min. Lower water percentage coatings appeared to remain stable longer than their higher percentage counterparts, with the lower coatings exhibiting some stress tearing as the coating dried and the higher percentage coatings exhibited cracking and flaking, as observed with earlier coatings. All coatings were left to sit overnight at ambient conditions to further observe stability with time. After a hold time of 16 h, it was observed that 3%–5% water content coatings had remained largely unchanged with some stress tearing observed early in the drying time; however, the 7% and 8.8% coatings were severely damaged with most of the coating experiencing cracking and delamination. Figure 4 images show the coatings after the initial drying and Figure 5 images show the coatings after a 16-h hold.



**Figure 4.** 2DP coatings of varying water content immediately after they have been dried at an accelerated rate and temperature using a hair dryer. All coatings were produced with the ADM coater on PET support with 200- $\mu$ m gap.



**Figure 5.** The condition of the polymer coatings shown in Figure 4 after ~16 h of exposure to ambient room conditions.

## 2.4 Ossila Coatings to Evaluate Conditions on the RC5

The viscosity of the monomer solutions and the dummy solutions was characterized (Sections 1 and 2). After the rheology characterization and by the middle of March 2022, a procedure was developed for making coatings on the Ossila coater. This procedure is detailed in the appendix. Using this procedure the following experiments were carried out.

The monomer solution used in these initial Ossila coatings was at a total monomer concentration of 200 mg/mL and a water content of 7%. This water content was used in many of the previous experiments before the standard was changed to 5% and then more recently to 3%. Additionally, this was the water content that was indicated by the blade coatings discussed in the previous section to show a transition to cracking and delamination. The coatings were made on glass to avoid the spontaneous delamination that was observed with copper and aluminum supports. The wet thickness was 150  $\mu$ m, which is in the range of what is anticipated at the Kodak trial. The speed used was 2 ft/min (10 mm/s for the Ossila setting) and the solution flow rate was 4.57 mL/min (76.2  $\mu$ L/s for the Ossila setting). The

coating was made with a 5-mil gap between the die and the glass support. The results at the end of the coating and during the different steps of the neutralization process in ethanol and triethylamine (TEA) are shown in Figure 6.



**Figure 6.** Images from left to right show the progression of monomer coating ID 20220328-A as it goes through the different stages related to its neutralization. Note: “Fingerprinting” seems to appear in regions where flow is inconsistent and fluid has flowed over an already coated region.

This experiment was repeated, and the corresponding results are shown in Figure 7. The initial coatings and the resulting 2DP delaminated and neutralized films were of good quality with relatively uniform thickness, with the exception that the end of each coating (shown at the top of each image) was thicker due to the remaining solution flowing out of the die at the end of the coating process. This nonuniformity was corrected in subsequent coatings. As observed earlier with blade coatings, the drying environment and drying conditions have a significant effect on the quality of the coatings obtained after they are dry. Under high humidity conditions the coatings and the subsequent delaminated and neutralized films exhibit a surface texture that is dimpled and may be characterized as an orange peel surface texture. Similar effects on PET support and spontaneous delamination on copper and aluminum supports have been observed in previous experiments. In addition, spontaneous delamination from copper support during drying was also confirmed at the April 6, 2022, Kodak trial and has been attributed to uncontrolled and relatively high humidity during drying. Since the humidity of the ambient environment in the RIT lab is not controlled, it was decided that an Ossila coater enclosure with RH control was needed to enable us to carry out experiments under controlled RH conditions.



**Figure 7.** Images from left to right show the progression of monomer coating ID 20220330-A as it goes through the different stages related to its neutralization. This coating was a replicate of the ID 20220328-A coating.

A prototype “dry box” enclosure was constructed from a large plastic rectangular container that was big enough to enclose the whole Ossila coater. After the Ossila was placed in this enclosure, a steady flow of argon was introduced to replace the humid air and reduce the humidity in the enclosure. Within a few minutes a low humidity of 3% RH was achieved, and a coating was made with a die gap of 5 mil, while a gentle flow of argon kept the humidity in the enclosure between 2% and 10% RH at an ambient temperature of 21 °C. The water content in the monomer solution used for the coating was 3% and the substrate was glass. The coating speed was 5 mm/s (1 ft/min) and the monomer flow rate was 25  $\mu\text{L/s}$  (1.5 mL/min). At the 50-mm coating width the resulting wet thickness is 100  $\mu\text{m}$ .

Except for the slightly wider coating at the start (due to lead solution being dispensed to ensure the lip was fully wet) the width of the coating was constant, indicating uniform thickness as well. After the coating was completed, it was kept in the enclosure unperturbed for about 40 min with no significant degradation nor any of the surface texture formation discussed above. After this time, the coating on the glass substrate was removed from the enclosure and neutralized using the standard 10 min per bath neutralization in ethanol and TEA/ethanol wherein the delamination and normal color changes were observed without issues. After neutralization, the delaminated film was found to slightly deteriorate similarly to other 2DP films in their final drying stage. The final dry thickness was measured as 30  $\mu\text{m}$ , which is about 30% of the initial wet thickness. Figure 8 shows images of the sequential stages after coating and until the final delaminated and neutralized film was obtained.

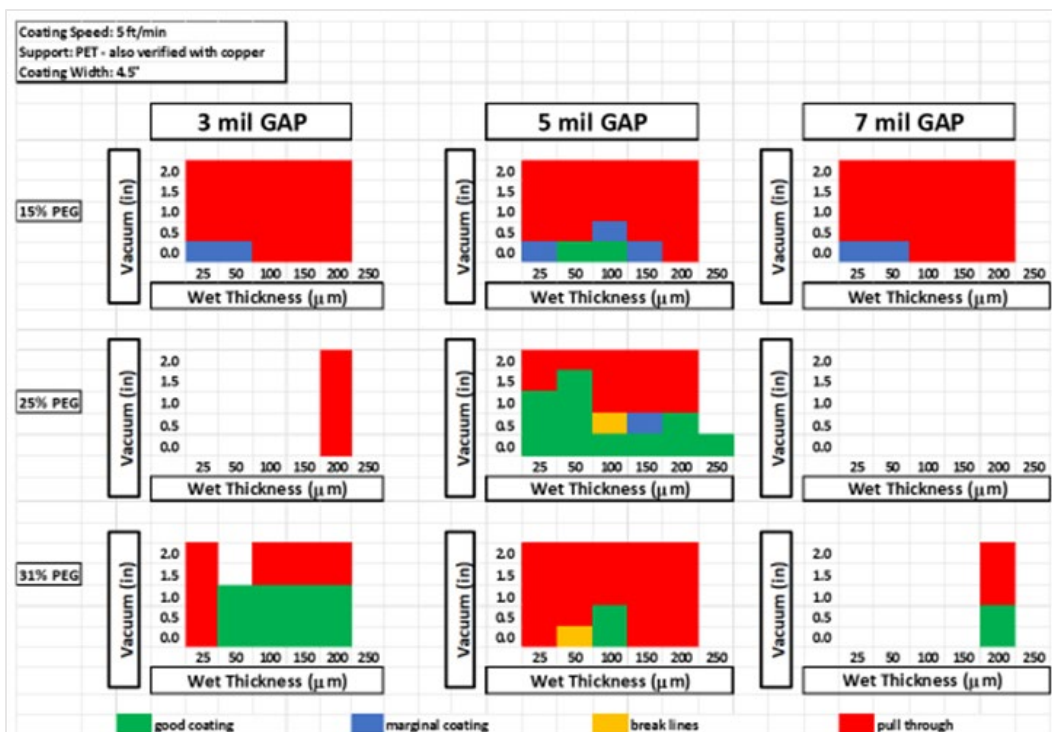


**Figure 8.** Images from left to right show the progression of monomer coating ID 20220407-A as it goes through the different stages related to its neutralization. Note: This coating remained as seen in the leftmost image for over 40 min under low RH conditions without any of the issues observed with similar coatings held at ambient conditions with higher RH.

Because of the success of this experiment, a second-generation enclosure was fabricated to improve on this prototype and eliminate some limitations of the original enclosure—i.e., some leveling parts of the Ossila instrument had to be removed for the coater to fit under the plastic box and to enable access to the control panel of the Ossila, which was covered and not easily accessible in the prototype design. Results from this new enclosure design will be reported in the next progress report.

## 2.5 Kodak RC5 Experimental Results

The highest priority goal during the RC5 coating experiment was establishing a coating window for the two monomer solutions that were prepared for the trial. As stated earlier, three dummy solutions composed of PEG dissolved in a water/TFA solvent mixture were used to outline the low, middle, and high points in the viscosity range of interest. To obtain the coating window, selected variables were methodically altered under controlled conditions using a 4.5-inch-wide die and the quality of the coating was observed and recorded. The variables of most interest were the solution used, the gap between the support and the die lip measured (in mil), the wet thickness coated (in  $\mu\text{m}$ ), and the vacuum applied to the coating in inches of water. By adjusting one variable at a time and observing the quality of the resulting coating, the maps shown in Figure 9 were constructed. For each coating solution and die gap the wet thickness was varied and the vacuum required to produce a good coating was sought. The criterion for good coating was a uniform coating with the absence of fundamental coating failures such as break lines, pull through, and poor edge control. For a given coating solution once the acceptable vacuum range for a set of wet thicknesses was established at a specified die gap, the gap was changed and the procedure was repeated.



**Figure 9.** Coating window map of the conditions required to establish quality laydown of a coating at varying viscosities and die-gap distances. This map is not complete and can be built upon in the future to establish a more complete coating map.

When the vacuum is varied, the indicators of a poor coating are pull through, break lines, and poor edge control. Pull through occurs when there is too much vacuum on the coating bead, causing liquid to be pulled over the bottom lip of the die and resulting in coating solution leakage and, consequently, uncontrolled wet thickness. This coating failure was confirmed with a fiber-optic borescope camera, which provided viewing of the bottom of the die lip. The borescope used was a Vividia ME-630. In the most severe case, pull through is exhibited by all the solution being pulled down and away from the die, resulting in no actual lay-down of material. Break lines are observed when the die-gap distance is too large and the lip and support are too far apart. Therefore, break lines can be resolved by reducing the die-gap spacing. Poor edge control is a key indicator that the thickness of the coating may not be what is intended, since thickness is determined by the width of the coating and the flow rate of the solution. Loss of edge control is usually caused by a lack of pinning the edges of the coating to the end of the slot and may be resolved by increasing the vacuum.

After the coating windows were established for each of the dummy solutions the 4.5-inch-wide die that was used for the coating window was cleaned and prepared for the two monomer solutions. The first round of coatings was made with the monomer solution containing 5% water. This was done because normally the

lowest viscosity coating solution is used first. By starting with the lower viscosity solution, the delivery system can be subsequently purged with the higher viscosity solutions. Accordingly, the 5% water content solution was purged with the more viscous 3% water solution when the 5% coatings were complete. The initial coatings were made with a wet thickness of 100  $\mu\text{m}$  with the 4.5-inch-wide die on copper support. To minimize solution waste, the coating conditions were selected based on the coating map for the 25% PEG dummy solution as prior data indicated that they were similar in viscosity. After the coating window was confirmed with selected coating conditions, the die was switched to a 9.5-inch-wide die and coating samples with lengths of about 30 ft were obtained on copper support. Images of the quality of typical coatings right after the coating point are shown in Figure 10.



**Figure 10.** Examples of visually good coatings at the slot die. They are coated onto copper support and display no break lines or pull through with good edge control, indicating that the coating thickness is as expected and there is no lost material.

For the 9.5-inch-wide samples mentioned above, the temperature of the drier sections of the RC5 was initially set to 140 °F so that the film would be dry by the time it was wound up. It was observed that on the copper support the coating began to lift off the support beginning at the edges. At this location the drying may be occurring faster due to the higher airflow on the coating. The spontaneous delamination proved problematic as tears began to appear in the drying coating and very quickly large sections of the coating were completely delaminated and shredded. Examples of the spontaneous delamination and shredding in the RC5 dryers are shown in Figure 11. The exact reason for this outcome is not clear but it is most likely a combined result of uncontrolled high humidity along with the hot airflow from the blowers in the dryer. Previous results with blade coatings and on the Ossila coater produced similar results of spontaneous delamination and film shredding on copper and aluminum support, in agreement with the results on the RC5 coater.



**Figure 11.** Result of the coating (shown in Figure 10) moving through the dryer section of the RC5. The coating rapidly delaminated and shredded itself. This may have resulted from high RH, high dryer temperature, issues with poor support adhesion, or any combination of these causes.

Subsequent coatings were made at room temperature and still exhibited delamination and tearing but not nearly as rapidly or aggressively as the first coating. Toward the end of this experimental coating trial, the 5% water content solution was replaced with the 3% solution and additional coatings were generated with the lower temperature drying. Using the coating window map of Figure 9, conditions were determined for the 3% solution based on the coating map of the 31% PEG dummy solution. Initial coatings at 100- $\mu\text{m}$  wet thickness on copper support appeared significantly more stable than earlier coatings with less severe deterioration. However, the observed cracking, delamination, and shredding obtained were still unacceptable. Attempts were made to increase the wet thickness to 200  $\mu\text{m}$  but were largely unsuccessful as edge control was lost with higher flow rates.

In the interest of investigating whether the copper support was contributing to the issue of the aforementioned drying problems some coatings were coated on PET for comparison with the same coating conditions. The coatings on PET exhibited some stress tears from the drying process but overall appeared to adhere better than coatings on copper support, as expected, and no significant delamination or deterioration was observed even at higher temperatures.

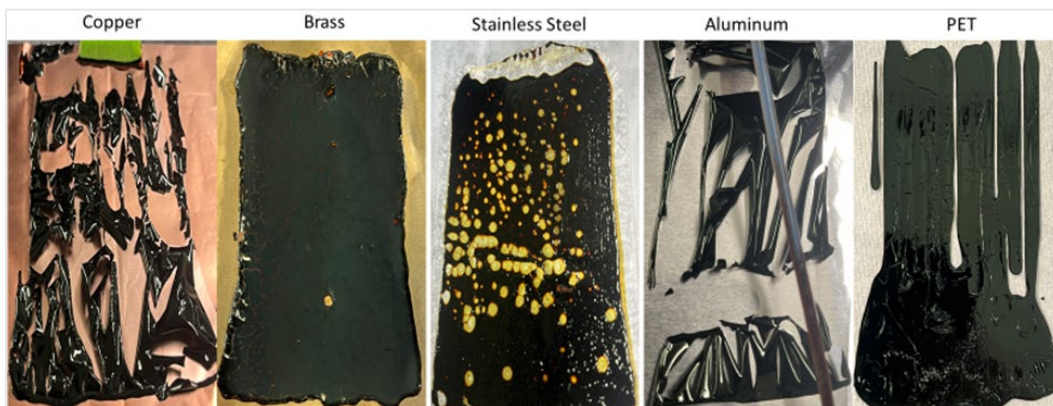
## **2.6 Support Evaluations**

As a result of the spontaneous delamination observed during the Kodak trial a study into other possible supports was initiated. Good humidity control for the coating experiments at RIT was still largely unavailable at this time but given that during the experiments at Kodak the humidity was also not well controlled and uncertain, a preliminary support-screening study at ambient humidity conditions was deemed worthwhile.

The supports examined were copper, brass, stainless steel, aluminum, and PET, with glass as a control. Glass was used as a control because of the more extensive use of this solid support before the use of the flexible supports. In addition, the die gapping can be more readily controlled with this solid support so that a realistic gap can be established for the other supports as a valid comparison. Each coating was made under identical conditions except for humidity, which varied from 30% to 50%. The results are shown in Figures 12 and 13, where images of the initial coatings are shown and images were taken after a hold time, respectively.



**Figure 12.** The initial coating images for the support study intended to give data on whether the shredding/spontaneous delamination was affected by the support.



**Figure 13.** Images were taken at the point in time each coating from Figure 12 experienced the maximum amount of damage in ambient conditions. Each image was taken no later than 30 min after the initial coating with the copper and aluminum images being taken at roughly 10 min.

As seen from Figures 12 and 13, copper and aluminum coatings behaved as expected and as seen previously, in that they resulted in delamination, tearing, and deterioration in roughly 10 min. Thus, in these cases if the initial coatings are not subjected to the neutralization baths quickly, they rapidly deteriorate. The coating on stainless steel appeared to be a better-quality coating until repellencies began to appear throughout, and the edges began to recede roughly 5 min after laydown. The

brass coating appeared to remain stable significantly longer than the other coatings with some minor cracking appearing at the edges around 30 min after the initial coating and then spreading throughout the coating. The final coating on PET developed cracking and texturing around 10 min after initial coating, which grew worse over time. In summary, the coatings experienced the most damage in the shortest amount of time in the following order (from least to most): brass, PET, aluminum, stainless steel, and copper. However, because these experiments were carried out without any ambient humidity control, they are considered preliminary results and need to be repeated with better humidity control.

### **3. Conclusions and Future Directions**

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Prior to this work it was concluded that after all the experimental research with blade coatings and Ossila pre-metered coatings, as well as the three trial coatings at the BPC, the team was ready to conduct a coating trial on one of the pilot/production coating machines at Kodak. The RC5 machine was selected. This is a nonaqueous solvent machine with long dryer sections capable of accommodating dry times of up to 25 min, which may be necessary for ideal drying for the 2DP coatings. Such a trial provided coating window maps for the monomer solutions that are currently of interest and confirm what we have learned thus far from our benchtop experiments with benchtop coatings and from results on the BPC. In addition, this experiment established and documented coating feasibility on an industrial roll-to-roll coating machine capable of producing large samples of 2DP film. Accordingly, this project report summarizes the work completed prior to this trial, and the results obtained from this trial, which was carried out on April 6, 2022.

In preparation for this coating trial, the viscosity of monomer solutions with different water content was characterized, providing information necessary for the selection of the monomer solutions that were used. Furthermore, lower-cost dummy solutions simulating the viscosity and surface properties of the monomer solutions were also prepared and their relevant properties characterized to minimize the waste of the more-expensive monomer solutions during the determination of the coating windows needed for this and subsequent pilot/production trials. Blade coatings and pre-metered coatings on the Ossila coater were also executed in preparation of the Kodak trial.

During the Kodak trial the following achievements were made:

- 1) Solution preparation methods were established for making 1–2 L quantities of TAPB/PDA/TFA/water solutions and PEG/TFA/water dummy solutions.

- 2) Robust coating windows for the dummy solutions were obtained and documented. Coatings with no vacuum were also demonstrated, opening up the future use of the BPC without any expensive modifications to the current setup for mounting the 5-inch-wide ARL-dedicated die, which does not currently have vacuum capability. The utility of the dummy solutions to obtain coating windows that can be used with the monomer solutions was validated. The higher viscosity solutions produced a significantly more open coating window.
- 3) The use of the fiber-optic camera was successfully demonstrated, in that the bottom of the die lip could be viewed and recorded so that any leakage of monomer solution could be ascertained and documented.
- 4) After the coating windows were discovered, the narrow width die was replaced by one that was 9.5 inches wide, and 30+ continuous feet of monomer solution were coated on copper support. Based on the established coating windows, wet thicknesses were realized that were higher than had been previously achieved with good control (up to 150  $\mu\text{m}$ ). The resulting dry thickness of these coatings was approximately 30% or higher than the wet thickness, which is a very desirable 2DP film feature.
- 5) Both low- and high-viscosity solutions with 5% and 3% water content, respectively, were successfully coated with good control.
- 6) A new cleaning procedure between the two monomer solutions was successfully implemented.

The most significant result from this trial was the confirmation that under uncontrolled humidity conditions during drying the coatings exhibit undesirable behavior. Namely, on copper and aluminum spontaneous delamination with eventual tearing and shredding of the delaminated film is observed. This result indicates that additional research work is required to develop methods for controlling the delamination so that it can be achieved on demand rather than prematurely, randomly, or uncontrolled. Consequently, experiments will be designed and planned to reach this goal using the Ossila coater with a surrounding enclosure wherein the humidity can be controlled. As part of this research, the specific mechanism causing the spontaneous delamination during the drying process will be investigated, along with the screening of different flexible supports and their contribution due to their adhesion properties, as well as the examination of the effect of different monomer formulation chemistries. In summary, these research topics may be separated into two major groups: a process research piece and a formulation research piece. As this work progresses, and more results become available, additional coating trials using the RIT BPC and the Kodak RC5 coating equipment will be scheduled.

## **4. References**

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1. McLeod DM et al. Progress on roll-to-roll coating of high-performance 2D polymer films: part I. DEVCOM Army Research Laboratory (US); 2023 Apr. Report No.: ARL-TR-9667.
2. McLeod DM et al. Progress on roll-to-roll coating of high-performance 2D polymer films: part II. DEVCOM Army Research Laboratory (US); 2023 Apr. Report No.: ARL-TR-9668.

## **Appendix. Operation of the Ossila Slot-Die Coater**

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In this appendix a step-by-step process is described for the standard operation of the Ossila slot-die coater, with specific instructions for use with trifluoroacetic acid (TFA) as a solvent for two-dimensional polymer (2DP) coating. This appendix provides a preliminary version of this procedure. Several important modifications are still being made, including the use of an enclosure to control the relative humidity of the environment during the coating process. Accordingly, a modified procedure containing all the improvements will be included in the next progress report.

## A.1 Ossila Operation

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- 1) **Physically level the Ossila** via the “feet” located at each corner. Different surfaces may not be exactly level so each time the Ossila is moved this should be verified.
- 2) **Physically level the coating stage** via the screw knobs located at the front two corners and at the center of the back. The front two screws control leveling left to right; whereas, the back screw controls the front-to-back leveling. To verify the stage is leveled, turn on the height gauges and with the manual setting bring the stage forward and backward; if the gauges remain within 50 microns of each other the stage can be considered level.
- 3) **Assemble the die head** and attach to the mounting plate above the stage.  
**Note:** When attaching the threaded Luer lock adapter it is best to also use the two white rubber washers.
- 4) **Secure the chosen support** to the stage roughly 1 cm from the front-most edge of the stage as that is where the die head will sit when in the starting position.
  - a) If the support is a glass wafer or some other rigid support a small amount of tape may be used at the front and back of the support to secure it.
  - b) If the support is flexible and or tends to buckle when unsecured, dispense a small amount of water onto the stage prior to placing the support. The surface tension of the water should assist in flattening the support. To ensure the support is secured, tape should also be placed at the corners and edges of the support where buckling/wrinkles are expected.
- 5) **Gap the die head** at the appropriate height from the support. Gap height is controlled by the micrometers located at the top of the Ossila. The central positioning of the micrometers does not allow for very fine control so die positioning should be closely observed. The right micrometer is responsible

for the majority of die movement. All gapping should be verified with pre-measured shims.

- a) If the die head seems to be consistently uneven, the screws located on the back of the plate that hold the die may be loosened and retightened. These screws hold the springs that control die height in place (these springs appear to be rusted and may need future replacement).
- 6) **Fill the syringe** by first attaching the clean tubing to a fresh syringe. The female end of the tubing should then be placed into a vial of the desired solution and a minimum of 3 mL should be drawn into the syringe. **Note:** The Ossila syringe pump has a minimum volume of 2 mL so anything less will not dispense. The syringe should then be inverted with the end of the tubing still in solution and with gentle pressure push in the plunger until the air bubble is out of the system. Carefully dry off the female end of the tubing with a clean paper towel.
- 7) **Attach the syringe** to the Luer lock previously screwed into the die head. Using the manual setting on the Ossila marked by the button “M” walk in the syringe pump until the syringe fits snug between the two holding positions. Once the syringe fits in place the wing nuts at the front and back of the syringe pump should be tightened to secure the syringe in place. The barrel clamp should also be affixed to hold in the syringe at this time.
- 8) **To ensure no runoff** a small piece of paper towel should be secured to the stage from the end of the support to the final position of the die head. A small amount of TFA water mix should be placed below the final position of the die so that there is no drying or precipitation in the die at the end of the coating. **Note:** TFA under the die is necessary if the die will not be immediately removed after coating.
- 9) **With the manual controls** walk in the syringe slowly until solution is observed evenly at the lip of the die head.
- 10) **Run the preset program** by pressing the play button when in program mode.
- 11) **Carefully remove the die head and syringe from the Ossila.** This step can be held for later if the coating is conducted in a dry box.
- 12) **To clean the die head, do the following:**
  - a) Remove the tubing from the Luer lock and purge the remaining solution back into the container it was drawn from.
  - b) Fill the syringe with TFA/water mix and reattach the tubing to the die head. With the die head held above a waste beaker purge the syringe. This step should be repeated at least twice.

- c) Disassemble the die head and carefully clean each piece with TFA and paper towels. **Note:** The contents of the waste beaker contain enough TFA to effectively clean the die pieces.
- d) To ensure all TFA and polymer have been removed each piece may be washed in ethanol or have some applied via disposable pipette. Ethanol causes the monomer to precipitate so it should be apparent if any remains. **Note:** In absence of ethanol, methanol may be used but **only** inside the fume hood with respective hand and eye protection.

## A.2 Ossila Program Usage

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The Ossila interface is user friendly and can be broken down very simply.

- 1) **Manual Mode** marked with the button “M” is the screen from which the user can manually control both the stage position and syringe pump positioning. The up and down arrows in this screen control which variable the user is changing—either the stage position or the syringe pump position. The right and left arrows control the physical positioning with right meaning “forward” and left being “backward.” By pressing OK on either of the two options the user can control the rate at which each variable moves. **Note:** The rates in manual mode are preset.
- 2) **Program Mode** marked with the button “P” is the screen from which the user can preset coating programs. In this mode to change any given value the user must first select it by pressing the OK button, at which point they can change the values with the arrow keys. To know which values to use for a given coating refer to the Microsoft Excel spreadsheet labeled “Ossila Coating Calculation.” **Note:** If the value is too precise for the Ossila it will autocorrect it to the closest value it can guarantee.
- 3) **Settings Mode** marked with the button “S” is the screen from which the user can adjust Ossila conditions. To change a given setting it must first be selected by pressing the OK button and then by making the adjustments with the arrow buttons. **Note:** Ensure the correct syringe size is selected as this can affect the built-in flow rate function in the Ossila.
- 4) **Return, Start, and Stop** buttons can be found to the right of the Ossila screen. The return button reorients the stage to the preset starting position (which can be changed in the settings screen). The start button begins the selected preset program, but only when on the program page. The stop button halts the coating program if there is an issue.

## List of Symbols, Abbreviations, and Acronyms

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|        |                                                   |
|--------|---------------------------------------------------|
| 2D     | Two-Dimensional                                   |
| 2DP    | Two-Dimensional Polymer                           |
| ADM    | Automatic Draw-Down Machine                       |
| ARL    | Army Research Laboratory                          |
| BPC    | Battery Prototype Center                          |
| DEVCOM | U.S. Army Combat Capabilities Development Command |
| ID     | Identification                                    |
| PDA    | Phenyl-1,4-Dialdehyde                             |
| PEG    | Polyethylene Glycol                               |
| PET    | Polyethylene Terephthalate                        |
| RH     | Relative Humidity                                 |
| RIT    | Rochester Institute of Technology                 |
| TAPB   | 1,3,5-Tris(4-Aminophenyl)Benzene                  |
| TAPPy  | 1,3,6,8-Tetrakis(4-Aminophenyl)Pyrene             |
| TEA    | Triethylamine                                     |
| TFA    | Trifluoroacetic Acid                              |

1 DEFENSE TECHNICAL  
(PDF) INFORMATION CTR  
DTIC OCA

1 DEVCOM ARL  
(PDF) FCDD RLB CB  
TECH LIB