MULTISCALE APPROACHES TO FORMATION OF THERMOPLASTIC PREPREG SHORT CARBON FIBER

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ABSTRACT

The fabrication of prepreg carbon fiber typically involves continuous fibers or fabrics which cannot be easily translated to discontinuous fibers. Additionally, applying prepreg coatings typically involves resins of relatively high viscosity making facilitating traditional coating methods which are not receptive to short fibers. In this work we demonstrate the application of high performance thermoplastic polyimides to short carbon fibers. We show the development of a variety of coating techniques used to produce prepregs from the solution and melt states. The quality, thickness, and uniformity of these coatings are assessed using fluorescence and scanning electron microscopy. We illustrate the capabilities of these methods to apply coatings subject to interfacial conditions. Furthermore we show the effect of interfacial treatments (oxidation, reduction, sizing, etc.) on coating quality. Through large scale techniques, it is possible to fabricate short fiber prepregs for use in high performance composite materials.

1. INTRODUCTION

There is growing interest in using short carbon fiber for composite manufacturing, however, typical fabrication techniques for continuous fiber composites do not translate to short fibers. In continuous carbon fiber tow processing, the carbon fiber surface is treated by running the tow through a coating bath of polymer solution or neat resin. The coated tow is then weaved into a mat known as a prepreg. Unfortunately, continuous coating of short carbon fiber cannot be done using this technique. For short carbon fiber to compete on the scale of continuous tow, methods for coating and alignment must be realized.

Coating of particles is a highly developed field [1][2]. Application of coatings has been achieved using a variety of methods including spray coating, dry coating, and fluidization. Particles are typically small and uniform geometries, making coating processes relatively straight forward. Short carbon fibers, however, are high aspect ratio particles, meaning coating processes are more difficult to engineer. Applying typical large-scale coating techniques to short carbon fibers has yet to be achieved. Furthermore, the ability to translate solid particle coating methods to high aspect ratio particles remains unaddressed.

In this work we develop multiscale approaches to coating short carbon fibers. We demonstrate the ability to apply quality, reproducible coatings on the carbon fiber surface using both solution based and melt techniques. We use fluorescence and scanning electron microscopy to image the

SAMPE Conference Proceedings. Charlotte, NC, May 20-23, 2019. Society for the Advancement of Material and Process Engineering – North America.

surface after processing. We summarize our findings for the different methods and propose future directions to improve the process.

2. EXPERIMENTATION

2.1 Materials

Ultem 1000 Polyetherimide was obtained from Sabic and used as received. Chloroform, acetone, ethanol, ethyl acetate, and aminopropytriethoxy silane (APES) were obtained from BDH Chemicals and used as received. Short carbon fiber were in the form of Mitsubishi Dialed, with a nominal diameter of 8 mm and length of 5 mm. These fibers are received with sizing, which is removed using multiple washes with multiple solvents (water, acetone, methanol, and toluene) under sonication and dried before use. Example solvent based formulations were prepared using chloroform which is ideal because of its high vapor pressure, compatibility with other volatile solvents, and it high diffusivity and solubility in PEI.

2.2 Experimental Methods

The experimental methods applied in this work are used to replicate several common coating methods available for both large substrate and particulate coating [3].

2.2.1 Dry Coating

Dry coatings were achieved using a mixing chamber contained within a temperature controlled furnace. A diagram is shown in Figure 1. For this technique, short fibers are stirred at temperature (above T_g) in the presence of PEI powder. The coating program can be varied such the time of stirring, time of heating, time at which polymer is added, and relative volumes of fibers and polymer can be varied to tune coating parameters. Further, the temperature, geometry of the container, mixing speed, impeller geometry, and polymer particle size can be used to vary the coating achieved.

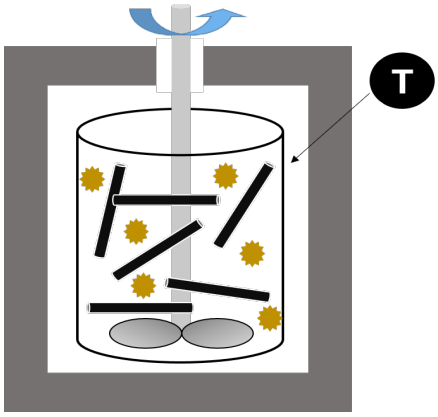
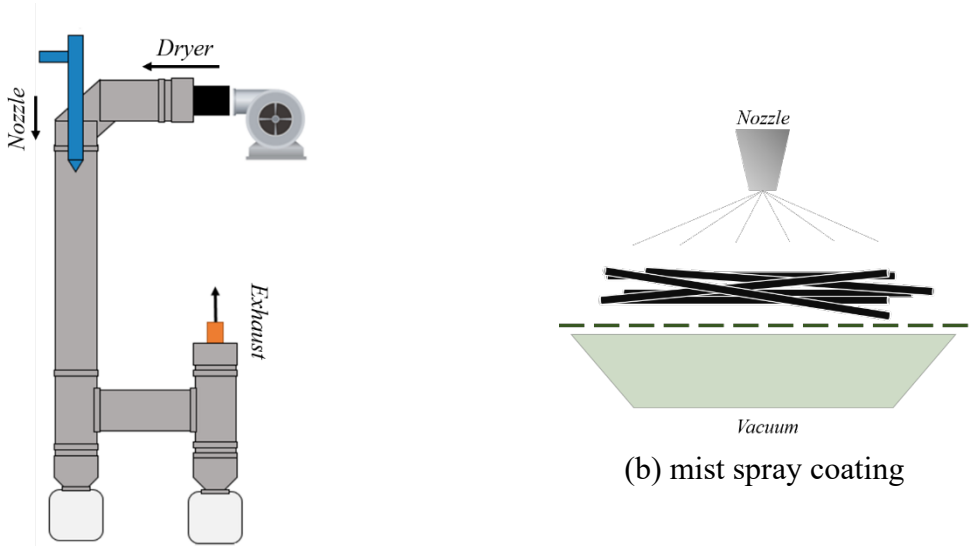


Figure 1. Dry Coating Apparatus.

2.2.2 Spray Coating

Spray drying was achieved using a custom assembled apparatus, shown in Figure 2. The setup is comprised of a long cylindrical body into which a formulation of short fibers, polymer, and solvent is sprayed using an air-driven nozzle. A constant stream of heated air is supplied and coated fibers are collected at the bottom of the main chamber and the auxiliary cyclone. The process parameters available to tune coating properties are the formulation flow rate and nozzle geometry, the drying air flow temperature and flow rate, and the spray chamber dimensions.



(a) spray dryer

(b) mist spray coating

Figure 2. Spray coating apparati.

Mist spray coating was achieved using a spray nozzle positioned over short fibers which were supported on metal mesh. Under the mesh, continuous vacuum is pulled. Droplets either deposit on the fiber surface or are removed by the vacuum. Process parameters available to control coating properties include the nozzle geometry, coating formulation flow rate, nozzle distance from the fibers, vacuum flow rate, and exposure time.

2.2.3 Solution Coating

Dip coating was achieved by manually dipping tufts of short fibers into a solution formulation. This formulation typically contains polymer dissolved in a good solvent, and may include additional components. Alternatively, some coatings were applied wherein short fibers were dispersed into the coating formulation and removed from solution using a metal mesh. From the coating solution fibers were either dried under quiescent air or precipitated in a secondary solution and then dried. The major control parameter for this technique is the coating formulation and the solidification procedure.

Larger scale designs of the dip coating method were as follows. The first is a lab scale version wherein fibers are submerged into a coating formulation and removed using a large mesh (net dipping), which simulates the smaller scale version exactly. The second variety was developed

wherein coating formulation including fibers were dispensed into an anti-solvent bath continuously (liquid extruded coatings). A larger, continuous pilot scale dip coating apparatus was developed wherein fibers in coating formulation are separated using a continuous flow nozzle and a mesh conveyer (conveyer coating). Fibers are either dried or quenched with anti-solvent continuously on the mesh support. A final semi-batch pilot scale version of dip coating was developed wherein coating formulation was sprayed onto dry short fibers using a high flow rate nozzle contained in a large chamber (or packed bed). Diagrams of these techniques are compared in Figure 3.

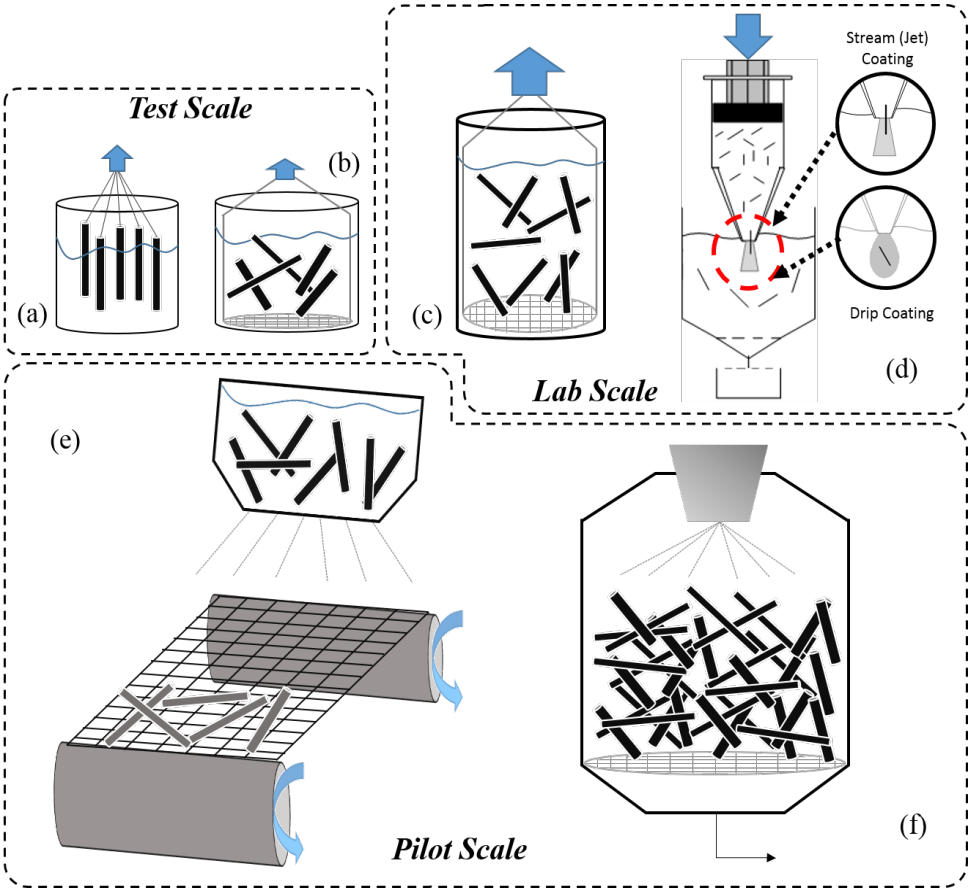


Figure 3. Multi-scale approaches to dip coating short fibers: (a) single fiber dipping, (b) net extraction, (c) net dipping, (d) liquid extruded coatings, (e) conveyer coating, and (f) packed bed coating.

Liquid extruded coatings (Figure 3d) were achieved via a custom setup. The setup consists of a tapered nozzle connected to a syringe pump. Formulation is continuously injected into the bath and fibers are recovered by filtration. The apparatus can be operated in two ways: (i) using low flowrates to drip formulation into the bath and (ii) using higher flow rates to jet the formulation continuously. In drip coating, a single droplet containing one fiber surrounded by coating formulation is quenched. In jet coating, a continuous jet is quenched. The main control

parameters for both extrusion techniques include: the coating formulation and quenchant formulation, the flow rate of formulation (velocity of the stream), and the nozzle dimensions.

In conveyer coating (Figure 3e), surface tension drives coating formulation around individual fibers. When fibers are captured on the mesh conveyer, the coatings are consolidated and solidified using either natural drying or induced solidification (heated drying, forced convection, quenching, etc.). Several control parameters exist, including: the coating formulation composition and flowrate, distance between the belt and nozzle, belt speed, and belt length. Further parameters like the belt geometry (pore size) and nozzle geometry likely contribute to the coating results.

For the packed bed (Figure 3f), large volumes of coating formulation are introduced to a dry fiber packed bed. Surface tension holds formulation around the fibers until solidification occurs via the same techniques as in conveyer coating. The high flow nozzle acts as a distributor to saturate the bed. Using this technique, the coating is applied not by spraying onto the fibers but by flow of fluid through the fiber bed. This technique is more convenient for the case of quenched fiber coatings because anti-solvent can be used to displace the coating formulation and flow through the packed bed. Major control parameters include: the coating formulation composition, the volume of fibers, the dimensions of the packed bed, and the spray procedure. The spray procedure can vary by the volume of formulation flowed, the volume of anti-solvent flowed, the time/flowrate of both flows, and the time between flow of formulation and anti-solvent.

2.2.4 Surface Treatments

In order to determine the role of surface chemistry on the solution coating process, several conventional surface modification approaches were applied on short carbon fibers. Oxidation was achieved by immersing fibers in pure nitric acid at 85 °C under reflux for 1 hr. Fibers are then rinsed in deionized water and dried. Reduction of the surface was achieved by first applying the oxidation procedure followed by immersion of fibers in a solution of tetrahydrofuran (THF) and $LiAlH_4$ at room temperature for 2 hr. Hydrochloric acid is added to remove the metals. Fibers are then rinsed in deionized water and dried. Further detail on these techniques can be found in [4]. Silanization of the reduced carbon fiber surface was achieved using solution application technique. A solution of 2 % aminopropyltriethoxy silane (APES) in ethyl acetate containing short carbon fibers was reacted at 75 °C for 1 hr then rinsed and dried for 12 hr at 100 °C. More detail on this procedure can be found in [5].

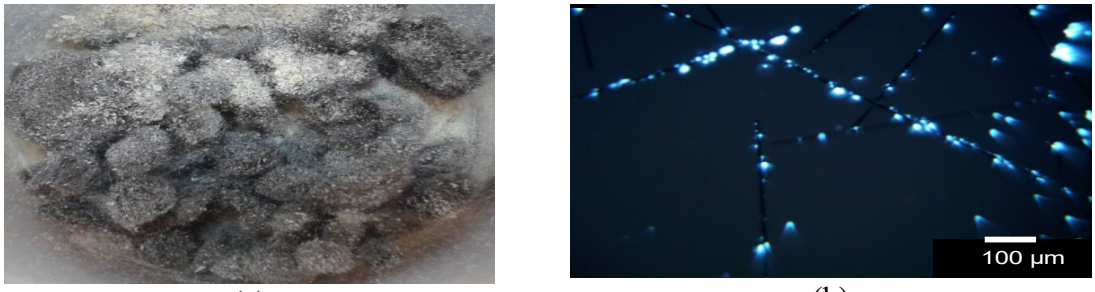
2.3 Coating Characterization

The coated short carbon fibers were analyzed for quality using fluorescence microscopy. Because of its aromatic structure, polyetherimide is natively UV active allowing for direct observation of the polymer coating on the surface of the fiber. For the micrographs shown in this work, blue colored areas (or white, depending on the camera) indicate polymer. Coating quality was qualitatively analyzed for morphology, relative thickness, fractional coverage, and uniformity across a single batch, i.e. percent of uncoated or partially coated fibers. Some additional analysis is made by imaging using scanning electron microscopy (SEM) to observe the local morphology of the coating.

3. RESULTS

3.1 Dry Coating

Dry coating offers a solvent-free technique of coating applicable to a bulk quantity of fibers. We use a melt coating approach utilizing a standard mixing impeller at 240 °C. The results are shown in Figure 4. The coatings show only small particles of polymer adhered to the fiber surface. The main drawback to this method is high fiber attrition. As shown in Figure 4a, typical batches consist of agglomerated fibers, caused by the shear applied, and many fiber fragments surrounded by unattached polymer. This creates major issues in separations and in the final product. As shown by Figure 4b, the coated fibers have only discrete particles of polymer attached, with no continuous films present. Melt coating was deemed an impractical route because high viscosity polymer melts are not easily applied as coatings using this technique. In order to solve this, solvent techniques were investigated.



(a) (b)

Figure 4. Melt coating results: (a) picture of a typical batch and (b) micrograph of individual fibers.

3.2 Spray Coating

Spray methods are often applied to achieve uniform coatings on the substrate. Typical resulting coatings from spray drying and mist spray coating are shown in Figure 5. In spray coating, individual fibers are dried with some amount of coating formulation surrounding. The increased temperature allows the coating to solidify quickly, increasing the throughput over quiescent drying. The fibers shown in Figure 5a and 5b are two examples of spray dried fiber coatings where the formulation differed in PEI concentration between 0.01% and 0.1%, respectively. It is clear that the coating area/quality is controllable by the formulation. Increasing amount of polymer in the formulation increases the mass of polymer attached to the fiber. Interestingly the coating appears to dry into small particles distributed along the surface with some continuous films between. We suspect these particles occur due to partial dewetting of the fiber surface before the solvent has time to evaporate and the kinetic process by which solidification occurs. The increased rate of evaporation increases the quality of the film over that of quiescently dried fibers (see below). The main drawbacks to this method are the resulting waste PEI particles, caused by the dilute concentration of fibers in the feed stream. This is necessary in order to avoid clogging of the nozzle. Separating waste PEI from the coated fibers is prohibitive. Further investigation of spray technologies is required to increase the concentration of fibers allowable and minimize waste.

Figure 5c and 5d show results of mist spray coated fibers. These fibers were coated using the same formulation, comprised of 0.3% PEI, however differ in spray time between 1s and 10s, respectively. For convenience, these fibers are imaged in place on the mesh used for coating. The same result is shown for mist sprayed fibers as with spray dried fibers. With increasing mass applied, by increasing either formulation concentration or spray time, an increased coating thickness is achieved. Because of the random nature of the mist spray, defects created in the coating are removed leaving a full layer of PEI surrounding the fiber. The major drawback to this method is the waste generated. However, this method shows promise for coating high volumes of fibers efficiently. More investigation must be done to optimize the process to achieve discrete fibers that are completely coated at high area fraction of fibers on the mesh.

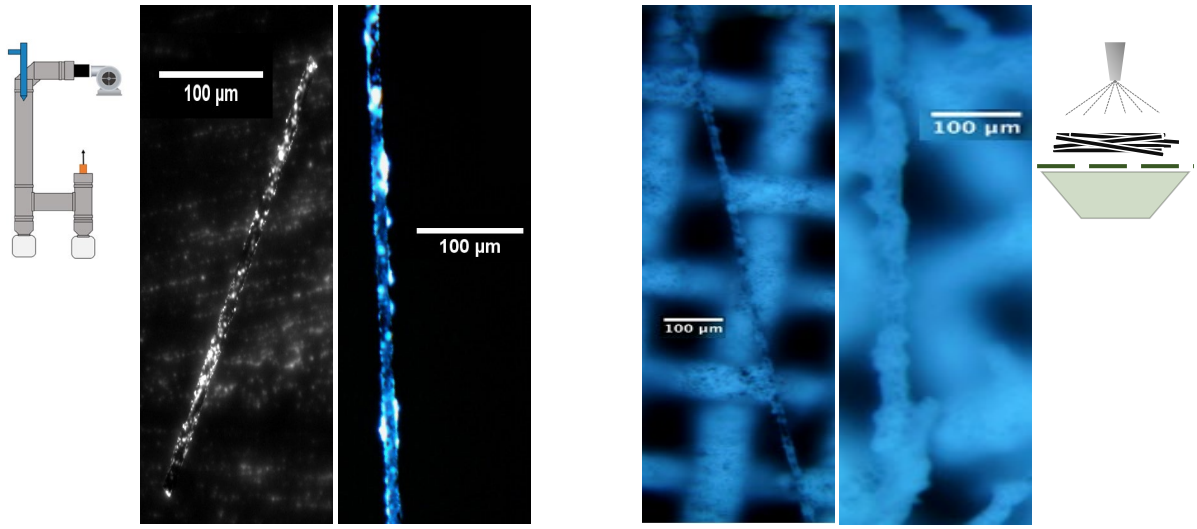


Figure 5. Results of spray coating techniques: (a,b) spray drying and (c,d) mist coating.

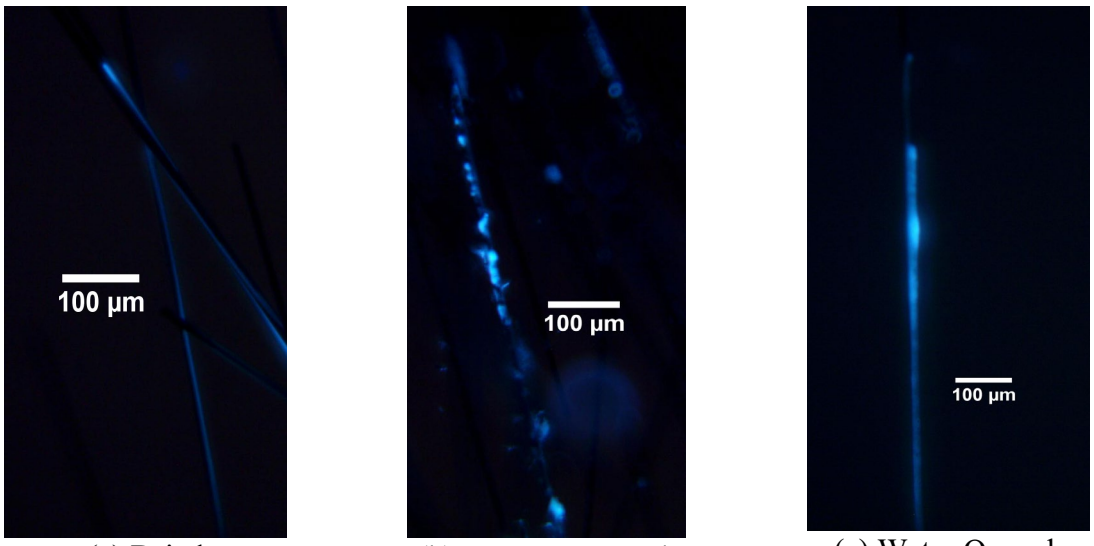
3.3 Solution Coating

To further investigate the effect of coating method on the quality and scalability of coated fibers, we use several techniques to determine the critical coating parameters on a small scale and then attempt to scale these methods to pilot scale operations. Solution based coatings offer more manageable processing with regards to collecting and recycling materials. In this work we use a coating formulation consisting of PEI dissolved in chloroform.

3.3.1 Effect of Solidification Method

There are three approaches to solidifying coatings cast from solution: (i) quiescent evaporation of solvent, (ii) forced evaporation of solvent, and (iii) precipitation from solvent, or quenching. For solution formulations of high vapor pressure, such as the chloroform based formulation used in this work, both quiescent and forced evaporation occurs quickly (less than 1 mL/min) and thus only quiescent is considered here. This process is easily applied, however leads to difficulties in

recycling the formulation solvent and residual polymer. Precipitation of the polymer from its solvent is achieved by exposure to an anti-solvent which drives the polymer out of solution near the surface creating a self-adhering coating of agglomerate particles on the surface. This method creates a mixed waste stream which is easily recovered and can be recycled using typical process equipment.



(a) Dried (b) Acetone Quench (c) Water Quench

Figure 6. The effect of solidification technique on dip coated carbon fibers.

Figure 6 shows the effect of solidification technique on carbon fibers coated using the dip coating method with a formulation of 0.1 % PEI in chloroform. The quiescently dried sample shows only small amounts of coating occurring around the edges of the fiber. This is likely due to partial dewetting and migration of the coating solution away from some parts of the fiber while drying occurs. Because this drying process is slow enough to allow dewetting, several characteristics are created in the coatings: non-uniformity across a single batch, non-uniformity in a single coating, many uncoated fibers, and defects in the coating surface. The sample which is quenched in acetone shows a more pronounced coating, however the surface is covered only in particulates created by the kinetic dissolution of the PEI from chloroform. This differs from the water quenched sample which shows a thin film spread across the surface of the fiber. Because water and chloroform are mostly immiscible, the PEI precipitates at or near the interface, creating a film which, if near the fiber surface, will form a coating. These coatings are more uniform in some cases but far less controllable than for acetone, which is soluble in chloroform and therefore always precipitates polymer near the fiber. For this reason, fiber to fiber variability is the lowest for the acetone quenched case and more coating mass is present.

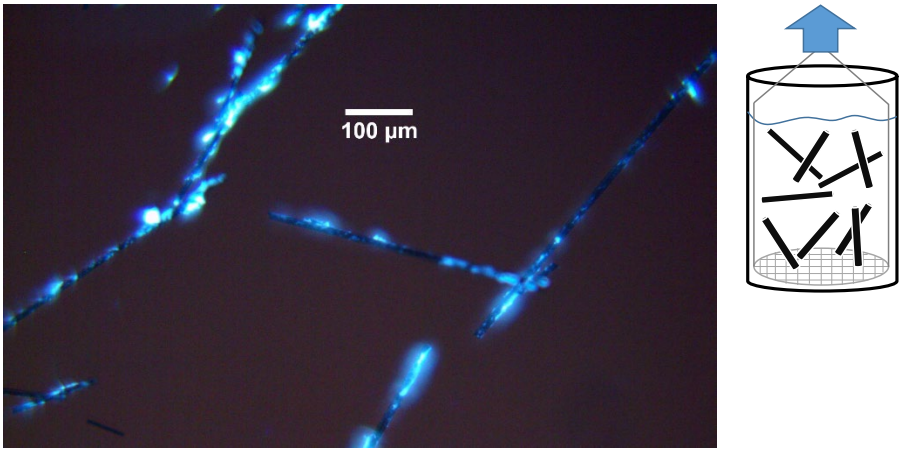
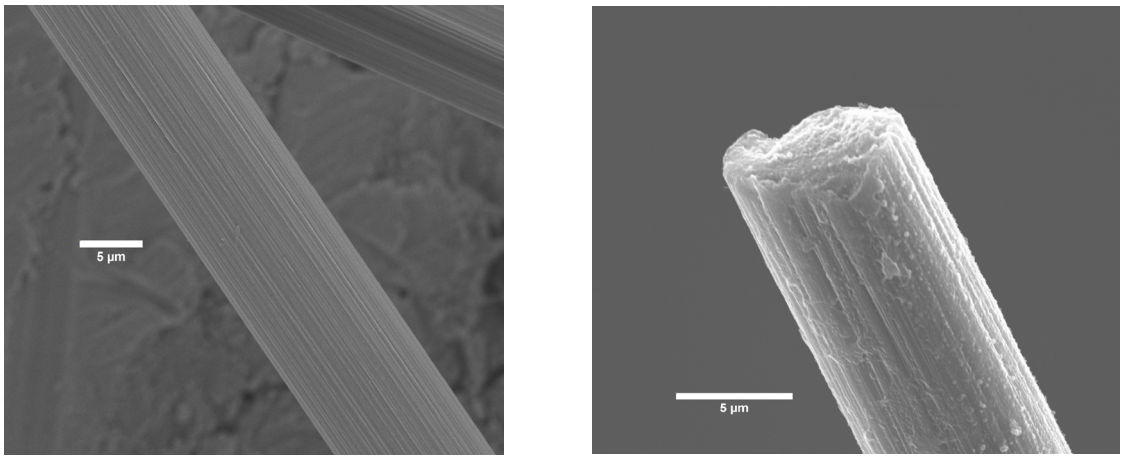


Figure 7. Lab scale dip coated fibers.

These results were repeated using a larger lab scale process (net dipping) to test uniformity. Figure 7 shows a typical batch which is coated using 0.1 % PEI in chloroform and quenched in acetone. These results closely follow those shown in Figure 6b, illustrating repeatability of the technique which is not shown by either drying and water quenched methods. Additionally, the uniformity across multiple fibers in the batch is favorable, with similar coating quality and thickness across fibers within the same batch. This is afforded by the acetone quenching technique. The critical parameter in this process is the time between removal from the coating formulation and quenching because this timescale competes with the timescale of dewetting. The acetone quenching process is more controllable than drying, allowing for solidification of the coating before dewetting occurs and allows for uniform coating formation on all fibers in the batch.



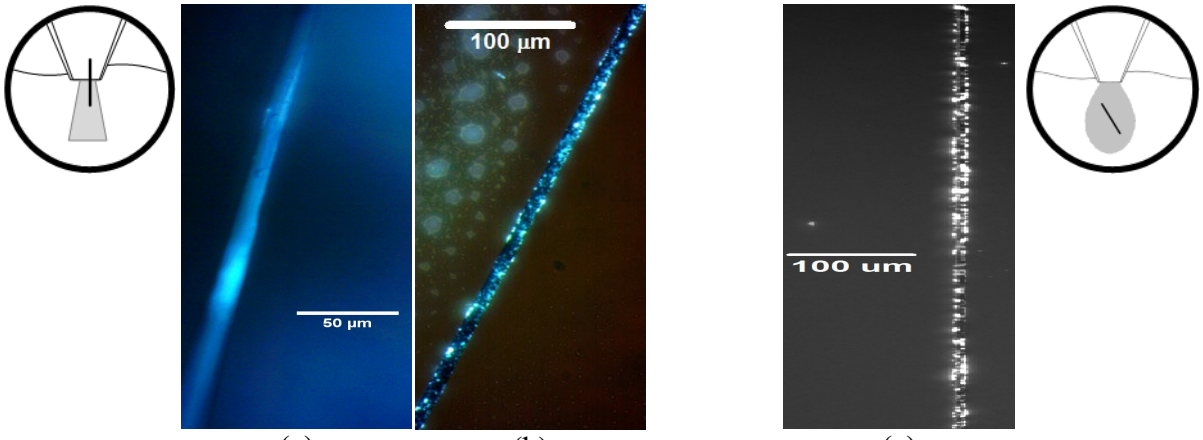
(a) as received (b) coated fibers

Figure 8. SEM micrographs of the representative change at the fiber surface due to coating.

Figure 8 shows SEM micrographs of the untreated fiber surface as compared to an example coated fiber. The typical striated surface features are very noticeable in the as received fiber. After coating, the surface features have been reduced suggesting that the PEI has infiltrated creating high surface area contact directly with the fiber. Additionally there appears to be a semi-continuous coating surrounding the fiber. These observations have positive implications for the final prepreg. During infusion of the resin into the bulk fibers, high viscosity resins often have difficulty forming full contact with the fiber surface leading to lower adhesion and reduced mechanical properties. Forming this layer increases the processability and further adheres the fiber surface to the resin because of the additional matrix material on the surface.

3.3.2 Liquid Extruded Coatings

Another method of solution based coating investigated was continuous liquid extruded coatings. Fibers were continuously processed and quenched using either acetone or water. Example results are shown in Figure 9. For water, a more defined jet or droplet can be formed due to the high interfacial tension suggesting that it is possible to control the position of the interface and thus force a coating on all fibers. For high flow rates (jetting) a smooth continuous film is formed, however fiber to fiber variability remains high, most likely due to the diameter of the nozzle as compared to the fiber. In acetone, particulates are formed because the location of the boundary between chloroform and acetone is not key to the coating. For low flow rates (dripping), particulate coatings are formed likely because of breakup of the film during settling and because the interface is not uniform around the fiber. This method is not highly scalable because it relies on very small fluidic components and only dilute solutions of fibers can be used to avoid fragmentation. There is an inherent trade-off between the optimizing the coating conformity using the nozzle geometry and the ability of fibers to flow freely. Additionally, separating the product requires several stages. Further investigation of the method and techniques to tune the location of the interface is needed to determine the possibility of consistent, conformal films on the fiber surface.

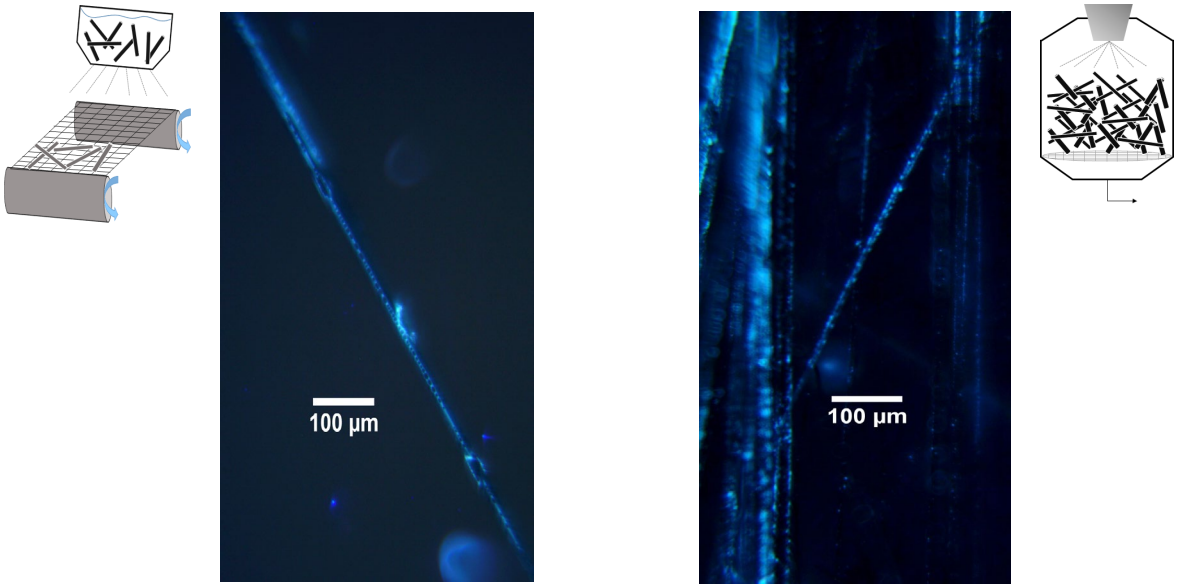


(a) (b) (c)

Figure 9. Liquid extruded coating results for jetting into water (a) and acetone (b) and dripping into water (c).

3.3.3 Pilot Scale Methods

In order to develop more large scale dip coating methods for relevant batches of carbon fiber, two pilot scale techniques were developed. The first, conveyer coating, is a versatile method which is capable of operating in both the drying and quenching modes. For example, we have used a formulation of 0.1 % PEI in chloroform with a low volume fraction of fibers dispersed before coating. The fibers are deposited on the conveyer and allowed to dry quiescently. A resulting coating is shown in Figure 10a. From this technique, reasonable consistency across the batch is obtained. This is likely because the support screen confines the coating formulation near the fiber during drying, leading to less variability than individually dipped fibers. The coatings show a characteristic imperfection across a continuous film. This defect is caused by the dewetting during drying which eventually freezes the contact line on the surface of the fiber. This is the same phenomena that was observed previously, however the confinement effect seems to reduce the speed of dewetting (because the evaporation occurs over a larger surface area) thus preventing full dewetting before drying. This method, however generates a large amount of unrecoverable solvent. Also, because the fiber volume fraction must be kept low to avoid processing issues, the amount of product compared to the lost solvent is unmanageable.



(a) (b)

Figure 10. Pilot scale coating results from conveyer (a) and spray column (b) coating.

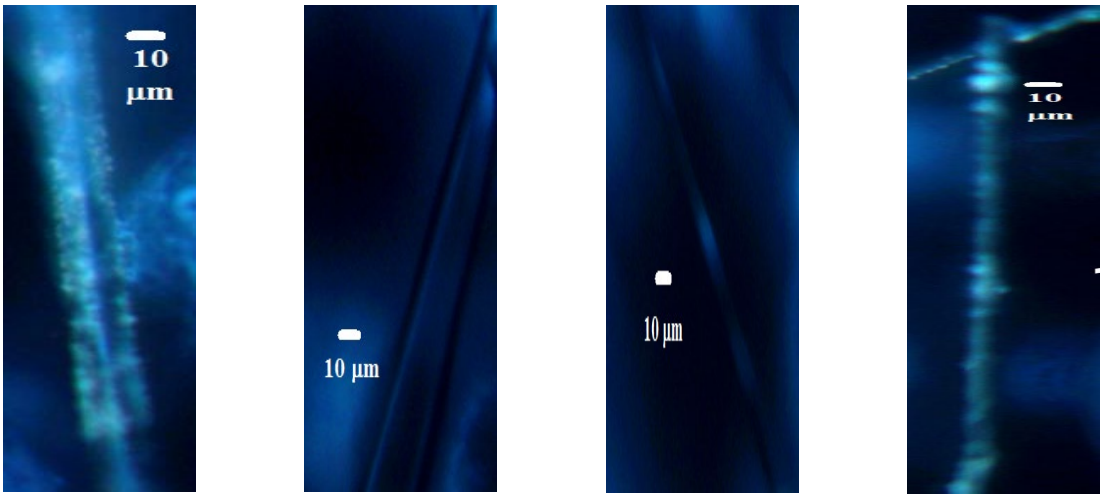
The spray column improves the dip coating process by containing the waste streams and drastically increasing the amount of fibers processed in a single batch. Additionally, because the coating is applied to dry fibers, fiber attrition is greatly reduced. The spray column results, shown in Figure 10b, also show successful scaling of the results shown in Figure 6b and Figure 7. Excellent consistency across the batch is achieved. Individual fibers show consistent coatings, with particulate polymer across the fiber. The benefits to this method over that of the conveyer are the decreased time and volume of solvents required to achieve coatings on large mass of fibers. Furthermore, the times at which quenching occurs is controllable meaning fiber dewetting

can be avoided leading to more uniform films on the fiber surface. Further investigation of processing parameters is needed to improve the coating morphology and increase the throughput of both processes.

3.4 Surface Treatments

One possibility for optimizing coating quality and reproducibility is modification of fiber surface chemistry. Many studies of carbon fiber adhesion have shown that improved surface wettability can be achieved chemically [4][5]. In this work we have used oxidation, reduction, and silanization as examples of techniques to improve surface coatings formed via solution coating. We use the dipping method as an example for the coating procedure. Figure 11 compares the resulting coatings. Both oxidation and reduction of the surface appear to decrease the amount of coating to almost nothing, when compared to the as-received fiber. This is likely due to the increase in the number of hydrophilic chemical groups on the surface with both oxidation and subsequent reduction. Because chloroform is hydrophobic, the introduction of hydroxyls has decreased the wettability resulting in inferior coatability.

Silanization was performed after reduction taking advantage of the increased bonding sites on the surface to attach APES. The APES molecule contains a sizable hydrophobic moiety. This has drastically improved the coatability from the reduced surface to the silanized surface. The resulting coatings show an increased thickness over that of the as-received fiber. The coating defect wherein the contact lines formed during dewetting are present in the dried coating are not as pronounced on the silanized surface leading to more uniform coatings. Clearly the surface chemistry of the fiber can be used as a tool to tune the coating process, however, this chemistry must be compatible with the coating formulation in order to be successful. Further investigation of surface modification processes must include matching surface chemistry to desired coating parameters. Additional work has been completed using the silanization process and is presented elsewhere [6].



(a) As Received (b) Oxidized (c) Reduced (d) Reduced + Silanized

Figure 11. Surface pretreatment results.

4. CONCLUSIONS

In this work we have demonstrated several multi-scale approaches to the formation of a high performance thermoplastic coated short carbon fibers for use in prepreg. We show that while conventional particle coating techniques can be successfully applied to large aspect ratio particles, several factors must be considered to achieve successful, scalable processes. Large aspect ratio particles are more challenging than small, uniform particles because of the size of the surface. We have shown that solution based coatings are preferable over melt coating because of higher scalability and repeatability as well as low fiber attrition rate. Additionally, SEM indicates good adhesion of polymer films directly to the fiber surface indicating useful properties for composite manufacture. Figure 12 summarizes the coating methods demonstrated in this work along with their major challenges.

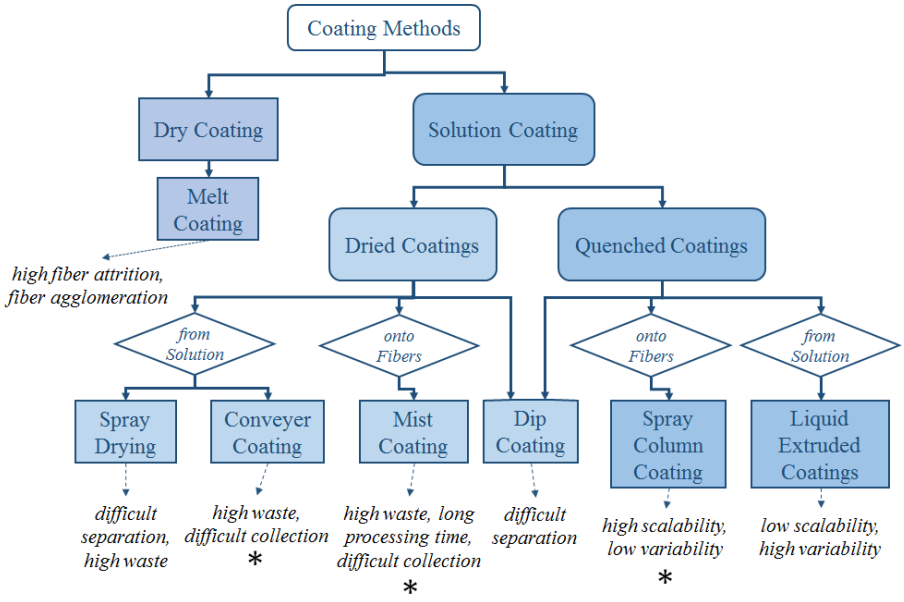


Figure 12. Summary of coating techniques and major drawbacks to implementation.

For solution based methods, drying of the coating is successful only when the coating solidifies before dewetting the surface. Solidifying the coating with an anti-solvent, or quenching, is of greater interest than drying because of the ability to control the coating morphology. When using a mutually soluble anti-solvent, coatings are formed by particulates near the surface leading to uniform, repeatable coatings. When there is an interface between coating formulation and anti-solvent, the coating forms at the interface leading to highly conformal coatings with low repeatability. The methods with the highest success rates (indicated with a *) involve processes which control the solidification of the coating, promoting solidification before dewetting by either confining the coating formulation near the fiber, or quick solidification via quenching.

Further investigation of the optimal process parameters and technical development is needed to improve the coating quality for a variety of systems. For example, the surface chemistry of the fiber surface is critical to the solution based coating process as well as final composite performance. The optimal surface is achievable chemically but depends on the coating

formulation properties. Further investigation is required to determine the post-processing methods required to meet specific performance specifications. Additionally, the most successful techniques developed in this work require optimization of both the operating parameters, coating formulations, and surface treatments to develop a wide variety of tunable coatings for prepregs. We expect that the techniques demonstrated in this work will serve as a starting point for further coating processes and prepreg formulations.

5. ACKNOWLEDGEMENTS

The effort depicted was sponsored by the Defense Advanced Research Projects Agency and was accomplished under Cooperative Agreement Number HR0011-16-2-0014. The views and conclusions contained in this document are those of the authors and do not necessarily reflect the position or the policy of the Government. No official endorsement should be inferred.

The authors would like to thank the Center for Composite Materials for their input in multiple stages of development.

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