ABSTRACT


With the advance of technology, new challenges and new problems, raise the need for the new materials. Organic-inorganic hybrid materials aim to solve some of these problems by incorporation of the organic and inorganic components at very fine scales. Using sol-gel chemistry and metal organic frameworks, many functional hybrid materials have been introduced in the literature for long time. New techniques such as molecular layer deposition (MLD) and layer-by-layer (LbL) film formation have also been presented recently to meet new technological demands such as precise thickness control and conformality. Sequential vapor infiltration (SVI) is also one of the recent techniques that forms hybrid materials by heterogeneous reactions, taking place between a solid phase polymer and gas phase organometallic precursor.

SVI is conducted in an atomic layer deposition (ALD) reactor, using common ALD precursors, has advantage of being a solvent free technique. However being a batch process, limits the technique in terms of high throughput production and detailed understanding of the mechanism is necessary in order to overcome this problem. To this day, studies on SVI mechanism are very limited and one of the aims of this work is to improve the understanding mechanism of SVI. In this work, process parameters of SVI, such as temperature, pressure, exposure conditions and different substrates has been studied. It has been found that temperature has a profound effect on the mechanism of SVI and this effect is attributed to the mechanism being a combination of diffusion and chemical reaction. At high temperatures in general low mass gain observed is an effect of quick barrier layer formation at the surface of
the polymer, which prevents further diffusion of the precursors. Pressure effect at low temperatures was also less pronounced comparing to high temperatures. Furthermore in this work SVI process was conducted at atmospheric pressure for the first time, showed promising results for roll-to-roll application of the process. It is also shown that, at atmospheric pressure reduced diffusivity of the precursor in the reactor chamber can enable effective patterning of SVI on the substrate. Effect of exposure conditions on SVI showed significant dependence on the substrate chemistry. SVI on polyethylene terephthalate (PET) substrates showed amount of the precursor in the reactor chamber, holding time, and number of cycles are all interrelated to each other. However, the reaction extent in polyamide 6 (PA6) substrates showed primary dependence on the amount of the precursor in the reactor.

During the mechanistic SVI analysis on PET it is discovered that the optical properties of fibers changed by incorporation of alumina. PET shows weak photoluminescence due to UV light absorption by aromatic units on the backbone of the polymer. It is shown that SVI hybrid materials can intensify the photoluminescence intensity of the PET up to 13 times. This phenomenon further analyzed by internal quantum efficiency analysis which showed the efficiencies is increasing up to ~24% indicating not only the luminescence increases in the material but also the mobility of the charge carriers are also increased. Higher charge carrier mobility of a semiconductor material can also increase the photocatalytic activity of it. As a demonstration of the photocatalytic activity of hybrid materials, silver and gold particles were deposited onto SVI treated fabrics out of aqueous metal salt solutions. It is also presented that by controlling the light exposure of the substrate selective photoreduction of these particles is also possible, which is promising for flexible electronic applications.
A detailed analysis of photoluminescence structure analysis showed that SVI mainly takes place in amorphous regions of the polymer and the increased emission is due to amorphous hybrid material. Thermal analysis of SVI treated PET fabrics revealed that temperature stability of the substrates are increased with hybrid materials formation.
Formation of Organic-Inorganic Hybrid Materials by Sequential Vapor Infiltration

by

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DEDICATION

To my parents Mustafa and Seher, my wife Elif, my son Mustafa Bilal and my daughter Esma.
BIOGRAPHY

Halil Ibrahim Akyildiz was born in Iskenderun, Turkey in 1985 as first child of Seher and Mustafa Akyildiz. He studied Textile Engineering and earned his Bachelor of Science degree from Uludag University in 2007. Prior to coming to the US he worked at ISKO weaving company, a prominent denim fabric producer where he is accepted to scholarship program of Republic of Turkey, Ministry of National Education. He received his Master of Science Degree in Textile Engineering from North Carolina State University in 2011. During his M.S. he studied with Dr. Stephen Michielsen on synthesis of water soluble acrylic acid and styrene copolymers. He continued his study at North Carolina State University to pursue a Ph.D. degree in Fiber and Polymer Science and co-majoring in Materials Science and Engineering. Halil has been married to Elif since 2008 and they have a handsome boy Mustafa Bilal and a beautiful girl Esma.
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TABLE OF CONTENTS

LIST OF TABLES .................................................................................................................. viii

LIST OF FIGURES ................................................................................................................. ix

Chapter 1 Introduction ........................................................................................................ 1

Chapter 2 Literature Review ............................................................................................. 6

2.1. Definition of Hybrid Material ..................................................................................... 6

2.2. Organic-Inorganic Hybrid Materials Formation Techniques ..................................... 6

2.2.1 Sol-gel .......................................................................................................................... 7

2.2.2 Layer by Layer Deposition ......................................................................................... 8

2.2.3 Metal-Organic Frameworks ....................................................................................... 9

2.2.4 Atomic Layer Deposition .......................................................................................... 10

2.2.5 Molecular Layer Deposition ...................................................................................... 13

2.2.6 Vapor Infiltration Techniques .................................................................................. 15

2.3. Applications and Properties of Organic-Inorganic Hybrid Materials ....................... 20

2.3.1 Optical Applications and Properties of Hybrid Materials ....................................... 20

2.3.2 Catalytic Activity and Applications of Organic Inorganic Hybrid Materials .......... 23

Chapter 3 Temperature and Exposure Dependence of Hybrid Organic–Inorganic Layer

Formation by Sequential Vapor Infiltration into Polymer Fibers ................................... 41
Chapter 4 Formation of Novel Photoluminescent Hybrid Materials by Sequential Vapor
Infiltration into Polyethylene terephthalate Fibers ......................................................... 71

Chapter 5 Atmospheric Pressure Synthesis of Photoluminescent Hybrid Materials by
Sequential Organometallic Vapor Infiltration into Polyethylene terephthalate Fibers........ 96

Chapter 6 Organometallic Exposure Dependence on Organic-Inorganic Hybrid Material
Formation in PET and PA6 Polymer Fibers ................................................................. 119

Chapter 7 Photoluminescence Mechanism and Photocatalytic Activity of Polyester Based
Organic-Inorganic Hybrid Material Fibers ...................................................................... 133

Chapter 8 Structure Photoluminescence Relationship of Organic-Inorganic Hybrid Materials
Formed by Sequential Organometallic Vapor Infiltration into Polyethylene Terephthalate
Films ............................................................................................................................. 153

Chapter 9 Thermal Properties and Pyrolysis of Organic-Inorganic Hybrid Materials Formed
by Sequential Organometallic Vapor Infiltration into Polyethylene Terephthalate ........... 161

Chapter 10 Conclusions and Future Work ....................................................................... 172

REFERENCES .................................................................................................................. 175
LIST OF TABLES

Table 7-1. Absorption and internal quantum efficiency values of pristine and SVI treated samples.................................................................................................................................................. 152

Table 9-1. SVI mass gain values vs. TGA residue amounts. ........................................................................................................ 171
LIST OF FIGURES

Figure 1.1. Number of articles published in the last 25 years and the number of the citations to these articles in the field of organic-inorganic hybrid materials on Web of Science.\textsuperscript{8} ........... 5

Figure 2.1. Schematic of sol gel process.\textsuperscript{12} ........................................................................................................... 25

Figure 2.2. Illustration of thin film formation via Layer by layer technique.\textsuperscript{28} ......................... 26

Figure 2.3. a) Flowchart of MOF productions and optical images b) SEM image of Zn-MOF 5 samples.\textsuperscript{38} ........................................................................................................................................ 27

Figure 2.4. Building block and structure relationship of MOFs.\textsuperscript{34} ................................................. 28

Figure 2.5. Schematic description of ALD surface reactions for Al₂O₃ film deposition using TMA and H₂O precursors. ........................................................................................................................................ 29

Figure 2.6. Growth per cycle as a function of temperature plot used for determination of ALD window. ........................................................................................................................................ 30

Figure 2.7. Cross-section TEM micrographs of 100 cycle ALD Al₂O₃ films formed on a) cotton fiber and b) polypropylene fibers.\textsuperscript{56} ........................................................................................................................................ 31

Figure 2.8. a) TEM image of PA6 film cross section after 100 cycle Al₂O₃ ALD showing a distinct hybrid layer formation b) EDX spectrum obtained from approximately circled region a).\textsuperscript{54} ........................................................................................................................................ 32

Figure 2.9. Schematic of ideal MLD reactions by using two co-reactants.\textsuperscript{67} ......................... 33

Figure 2.10. Schematic of the process to create nanoscopic materials using sequential infiltration synthesis and self-assembled block copolymers.\textsuperscript{89} ........................................................................................................................................ 34
Figure 2.11. a) Difference of ALD film formation on rigid substrate and hybrid material formation using MPI on soft substrate b) Stress strain tests of inorganic infiltrated spider silk showing significant improvement of substrate’s toughness. 90

Figure 2.12. Schematic of SVI process showing the separation of exposures of each reactant with number of cycles. 141

Figure 2.13. Alumina-polymer hybrid material formation and reaction mechanisms during SVI on polyestersas suggested by Gong et al. 64

Figure 2.14. a) PBT nonwoven fiber mat before and after SVI treatment and annealing b) SEM image of fibers before SVI treatment c) and d) SEM micrographs of SVI treated and annealed samples shows fibrous structure is preserved. 64

Figure 2.15. Schematic of different mechanisms of luminescence in MOFs. 43

Figure 2.16. Schematic of photoreduction and photooxidation mechanism in TiO$_2$. 138

Figure 3.1. Schematic of the viscous flow tube type ALD reactor used for SVI experiments.

Figure 3.2. Evaluation of the effect of consecutive TMA sub-cycles (xNA) in an SVI process on percentage mass increase of PA6 fabrics (3 m2/g). The mass of the fabrics were evaluated before SVI processing and after processing with a 2-3 hr ambient stabilization.

Figure 3.3. Mass increase of PA6 fabrics with 10 consecutive TMA sub-cycles in an SVI process, evaluated at as a function of exposure temperature. Data is shown for samples with and without a 120 °C in situ anneal prior to SVI processing.
Figure 3.4. a) QCM analysis of mass gain per cycle resulting from 10 consecutive TMA exposures at temperatures of 60, 100 and 150 °C b) Mass gain in the first cycle at 60, 100 and 150 °C is plotted as an Arrhenius-type plot.

Figure 3.5. Mass increase of PA6 fabrics with 10 consecutive TMA sub-cycles in an SVI process sequence as a function of holding time for TMA dose times of 0.2 to 2 sec.

Figure 3.6. Mass increase of PA6 fabrics as function of consecutive TMA sub-cycles in an SVI process at a TMA dose time of 2 sec and 0-30 sec hold periods.

Figure 3.7. FT-IR spectra of PA6 fabrics untreated and with SVI processing (10 TMA sub-cycles) comparing a) processing at 60 °C and 150 °C, and b) SVI processing with and without an in situ anneal. An untreated PA6 spectra is provided in both (a) and (b) for comparison.

Figure 3.8. Cross-sectional TEM analysis of PA6 fibers after SVI processing at exposure temperatures of a) 60 °C, b) 90 °C, and c) 150 °C. (d) TEM image of PA6 fiber sample with SVI processing at 60 °C, after which calcination is performed to remove the organic component. All samples were treated with 60 TMA SVI sub-cycles.

Figure 3.9. Higher magnification cross sectional TEM analysis of PA6 fibers with SVI processing at exposure temperatures of a) 60 °C, b) 90 °C, and c) 150 °C. All samples were treated with 60 TMA cycles.

Figure 3.10. Mass increase of PA6 fabrics with 10 consecutive TMA sub-cycles in an SVI process as a function of holding time for TMA dose times of 0.2 to 2 sec.

Figure 4.1. Mass gain of a) round fibers b) winged fibers as function of number TMA cycles at temperatures varying between 60 °C and 150 °C. TMA cycles were conducted with a
sequence of 0.5 s dose/ 30 s hold/ 30 s purge and H2O cycles of approximately half number of the TMA cycles were conducted with a sequence of 0.2 s dose/ 30 s hold/ and 30 s purge.

Figure 4.2. SEM micrographs of a) untreated b) 3 cycle, c) 15 cycle, and d) 30 cycle SVI treated winged fibers (WF) and e) untreated and f) 30 cycle SVI treated round fibers (RF) showing the change in the fiber morphology upon SVI treatment. All the treatments are at 60 °C.

Figure 4.3. FTIR spectra of SVI treated fabrics made of round fibers after a) 10 TMA cycles and b) 60 TMA cycles. Samples are treated under similar exposure conditions (TMA cycle: 0.5 s dose/30 s hold/30 s purge; H2O cycle: 0.2 s dose/30 s hold/30 s purge).

Figure 4.4. TEM micrograph of cross-section of round fibers treated with a) 90 cycles TMA SVI at 60 °C and b) 60 cycles TMA SVI at 90 °C.

Figure 4.5. X-Ray diffraction spectra of the control and samples treated with SVI at 60 and 90 °C.

Figure 4.6. AFM-IR spectra and AFM images of round fiber cross sections treated with a) high wavenumber (normalized at 2972 cm$^{-1}$), b) low wavenumber (normalized at 1268 cm$^{-1}$) 60 cycle TMA SVI at 150 °C c) high wavenumber (normalized at 2968 cm$^{-1}$), d) low wavenumber (normalized at 1268 cm$^{-1}$) 90 cycle TMA SVI at 90 °C e) high wavenumber (normalized at 2964 cm$^{-1}$), f) low wavenumber (normalized at 1268 cm$^{-1}$) 90 cycle TMA SVI at 90 °C after 1 hour heat treatment at 150 °C.

Figure 4.7. Comparison of untreated PET samples and those treated with SVI at 60 °C, 90 °C and 150 °C under a) natural lighting and b) under UV illumination.
Figure 4.8. Room temperature PL spectra conducted on control fabrics and 90 and 150 °C SVI treated fabrics excited at $\lambda_{ex} = 355$ nm. ................................................................. 95

Figure 5.1. Mass gain of samples treated with SVI at a) 2.5 Torr and b) 760 Torr as a function of number of TMA cycles at various process temperature................................. 112

Figure 5.2. Comparison of mass gain for samples treated by SVI process with 60 cycles of TMA at 2.5 and 760 Torr for process temperature between 60 °C and 150 °C. ............... 113

Figure 5.3. FTIR spectra of samples treated with SVI a) 30 cycles, b) 60 cycles at 2.5 Torr and c) 30 cycles, b) 60 cycles at 760 Torr for process temperature between 60 °C and 150 °C. ................................................................. 114

Figure 5.4. Consumption of C=O peak in FTIR spectra as function of temperature after 30 and 60 cycle SVI treatment at a) 2.5 Torr and b) 760 Torr. ............................................. 115

Figure 5.5. Calculated diffusivity values of TMA molecules in $N_2$ as a function of pressure at 60, 90, 120 and 150 °C.................................................................................................................. 116

Figure 5.6. Optical images of samples masked during 30 cycle TMA exposure SVI experiments at 60 °C at 2.5 Torr ((a) and (c)) and 760 Torr ((b) and (d)) under normal light ((a) and (b)) and UV illumination ((c) and (d)). ................................................................. 117

Figure 5.7. Schematic of hybrid materials formation through the fabric cross-section in the case of a) ideal masking, b) low resolution masking at low pressures, and c) good resolution masking at high pressures. ................................................................. 118

Figure 6.1. Schematic of SVI process a) with batch processing b) envisioned roll-to-roll processing with precursor cycling and c) envisioned roll-to-roll SVI processing with elongated single exposure................................................................. 128
Figure 6.2. Mass gain of PET round and winged fibers at 60 °C as a function of number of TMA cycles................................................................. 129

Figure 6.3. Mass gain of high surface area PET winged fibers as a function of number of TMA cycles at different holding time................................................................. 130

Figure 6.4. Mass gain of PET samples as a function of dosing time after 10 cycle and 60 cycle SVI using a) 30 s hold and b) 60 s hold time. ........................................... 131

Figure 6.5. Mass gain of a) PET and b) PA6 fibers as a function of product of dosing time, holding time and number of cycles................................. 132

Figure 7.1. Optical images of the PET fabric samples a) under ambient light and b) under UV illumination................................................................. 145

Figure 7.2. UV-Vis spectroscopy of the samples treated with 60 cycle TMA SVI at various temperatures................................................................. 146

Figure 7.3. Photoluminescence Excitation (PLE) mapping and spectroscopy analysis results of SVI treated a) and b) winged fiber at 90 °C, c) and d) round fiber at 150 °C. ............... 147

Figure 7.4. Optical images of samples after 15 minutes of UVA exposure a) pristine PET and b) SVI treated PET in AgNO₃, SVI treated PET in c) HAuCl₄. ................................. 148

Figure 7.5. XRD spectra of pristine and SVI treated samples after 15 minutes of UVA exposure in aqueous AgNO₃ and HAuCl₄ solutions........................................... 149

Figure 7.6. SEM images of SVI treated samples after 15 minutes of UVA exposure in a) AgNO₃ and b) HAuCl₄ solutions........................................... 150
Figure 7.7. a) Approach used for printing metal nanoparticles of with a mask b) optical image of resulting patterns as prepared with masking approach c) schematic of approach using a laser for printing metal nanoparticles with resulting pattern................................. 151

Figure 8.1. Photoluminescence spectra of pristine PET samples of different thicknesses and crystallinities. ($\lambda_{\text{excitation}}=325$ nm) ................................................................................................................................. 158

Figure 8.2. Photoluminescence of the PET films with different thicknesses and crystallinities after SVI treatment at 60 °C. ($\lambda_{\text{excitation}}=325$ nm) ............................................................................................................. 159

Figure 8.3. Photoluminescence of the PET films with different thicknesses and crystallinities after SVI treatment at 150 °C. ($\lambda_{\text{excitation}}=325$ nm) ............................................................................................................. 160

Figure 9.1. Thermogravimetric analysis curves of pristine and SVI treated samples. ....... 167

Figure 9.2. Optical images of pristine and SVI treated PA6 and PET fiber mats after high speed pyrolysis. (Heating rate: 200 °C/min)......................................................................................................................... 168

Figure 9.3. SEM images of pristine and SVI treated samples before and after pyrolysis. .. 169

Figure 9.4. Raman spectra of PET samples after pyrolysis a) pristine vs. SVI treated b) SVI treatment at different temperatures. ................................................................................................................. 170
Chapter 1 Introduction

As the technological improvements challenge the conventional materials, scientists and engineers found new ways to create novel materials. Organic-inorganic hybrid materials, with the synergetic combination of the organic and inorganic components, can result in novel properties. There is a growing research interest in the area of hybrid materials for solving new contemporary problems of catalysis,\textsuperscript{1-2} optical,\textsuperscript{3-4} electrical,\textsuperscript{5} and biotechnology\textsuperscript{6-7} applications. In Figure 1.1 citation report for “organic-inorganic hybrid materials” topic shows that number of papers and the number of the citations to those papers increased significantly in the last two decades.

Different approaches can be used to synthesize hybrid materials. Among them topic of this document, sequential vapor infiltration (SVI) is a newly developed technique that depends on diffusion of organometallic precursors into the polymeric substrates which then reacts with the available functional groups and forms hybrid materials. This work aims to explore the effect of SVI process parameters, such as temperature, exposure, and pressure on hybrid materials formation in the polymer. This is vitally important for applications of the SVI for industrial purposes in future. Furthermore this works investigates the optical properties of the materials formed by SVI to expand the applications of SVI into different areas.

In the following chapter, first a brief survey of hybrid materials formation techniques is provided. The main aim of the review is to compare and contrast advantages of different techniques without going into details about the processes. Wide variety of applications is projected for hybrid materials in the literature. In the second part of the literature review, a
brief survey of projected applications of these materials with the properties aimed to be improved is discussed. Since the optical properties of the hybrid materials formed by SVI is prominently studied in this work, we try to focus on the optical properties and applications of hybrid materials.

In Chapter 3 a published report from this work is reprinted. In the report we studied the effect of temperature and exposure time on SVI mechanism into Polyamide 6 (PA6) high surface area fibers. It has been found that PA6 fibers show a rapid saturation during SVI at around 10 TMA cycles under different temperatures. But the reaction extent, which is measured by mass gain, has shown temperature dependency. As the process temperature increased, the amount of the mass gain decreased that is attributed to the higher reaction rates at high temperatures leads a rapid hybrid layer formation preventing the further infiltration of precursors.

Chapter 4 is a reprinted manuscript on formation of photoluminescent hybrid materials in poly(ethylene terephthalate) (PET) fibers, published in Journal of Materials Research. In this section effect of surface area, temperature and exposure conditions during SVI is discussed with mass gain of the PET fibers. Furthermore using FTIR–ATR analysis chemical changes in the PET substrates during SVI is discussed. Cross-sectional TEM and AFM-IR analysis showed differences in the formation of hybrid materials during SVI at different temperatures. XRD analysis conducted to investigate the structure of the hybrid materials formed. In addition to the mechanistic analysis, for the first time change in the optical properties of PET fibers after SVI treatment is presented with optical images and photoluminescence spectroscopy.
In Chapter 5 reprint of a report on atmospheric pressure SVI processing published in Journal of Applied Physics is presented. In this report for the first time an infiltration method is presented at atmospheric pressure, which is considered very important for roll-to-roll applications of the SVI process. SVI at atmospheric pressure showed similar materials conversion to low pressure infiltration. We explain the differences in the mass gain patterns observed at different pressures by the change in the diffusivity of the precursor in the gas phase. Furthermore as demonstration of the pressure effect, increased pattern-ability of the SVI by forming a marker on the fabric that is only visible under UV illumination. Under similar conditions atmospheric pressure SVI showed very well defined pattern whereas low pressure SVI showed poor definition.

In Chapter 6 effect of exposure conditions on SVI processing is discussed in relation to the roll-to-roll process ability of SVI process. Effect of dosing, holding time and number of cycles is discussed for different surface area and different polymers. It is found that for PET holding time and dosing time are interrelated meaning one’s effect is dependent on another while the primary parameter that affects the reaction extent for PA6 is the amount of TMA dosed. In this letter we also envision different approaches for roll-to-roll processing of SVI.

In Chapter 6 optical properties of SVI treated PET fibers are studied in relation to the photocatalytic activity of the hybrid materials. Upon SVI treatment fibers showed an order of magnitude increase in photoluminescence intensity with a red shift comparing to pristine PET, which shows luminescence due to the cyclic groups on the backbone of the polymer. Photoluminescence excitation spectroscopy revealed low temperature and high temperature
SVI treated samples show different absorption and emission patterns. Absorption and internal quantum efficiency study demonstrated SVI treated samples show very high absorption rates more than 90% both in UV and in visible spectrum. Furthermore samples showed up to 5-fold increase in the internal quantum efficiency values upon SVI treatment. As a result of increased internal quantum efficiency values an increase in photocatalytic activity of the materials is shown by successful deposition of silver and gold particles on fibers.

In Chapter 7 the relationship between the photoluminescence mechanisms of SVI treated PET films and their structure is studied. Polymer films prepared with different expected crystallinity and their photoluminescence is studied. Data suggests that after SVI treatments photoluminescence due to the amorphous regions are enhanced while the photoluminescence due to the crystalline regions show no significant change.

In Chapter 8 thermal properties of SVI is studied using thermogravometric analysis (TGA). It is shown that SVI treated fabrics show three step degradation. One phase is attributed to the degradation of oligomer species forming by chain scission reactions as proposed in the literature. Second degradation is attributed to the polymer and the last one is attributed to the hybrid material degradation. It is also shown that hybrid material increases the thermal stability of the fibers by high heating rate pyrolysis of the hybrid materials.
Figure 1.1. Number of articles published in the last 25 years and the number of the citations to these articles in the field of organic-inorganic hybrid materials on Web of Science.⁸
Chapter 2 Literature Review

2.1. Definition of Hybrid Material

In order one to talk about hybrid materials it is necessary for him/her to define the phenomena. In the literature many different definitions can be found, however all these definitions have one thing in common; hybrid materials are formed by synergetic combination of more than one constituent materials. Debate for the definition arises on two aspects, one is the size scale of the materials and the second is the nature of the bonding between the components of the hybrid materials. Some define every size scale of the constituent materials and considering even the composite materials as hybrid materials whereas there are also people who define a material as hybrid material only if the constituents are interacting or mixed at the atomic or molecular scales.\(^5\) Latter size definition is the most common and literature starts to agree on less than 100 nanometer scales. Second debate is on the bonding nature of the component materials. While the opinion of hybrid materials should have primary bonding between the constituents is dominant in the literature, in some cases secondary bonds and interactions between the constituents also considered as hybrid materials.\(^5,9\) In our work the materials formed are considered as hybrid materials from every point of view in the literature since they are formed as a result of chemical reactions taking place between the polymer and the precursor at the atomic scale.

2.2. Organic-Inorganic Hybrid Materials Formation Techniques

In this section of the dissertation common organic-inorganic hybrid materials formation techniques particularly their advantages and disadvantages are discussed. Then
Atomic Layer Deposition (ALD) and Molecular Layer Deposition (MLD) techniques are introduced focusing on their role on organic-inorganic hybrid material synthesis. Finally hybrid material formation via organometallic infiltration is reviewed with the background of the techniques.

2.2.1 Sol-gel

Sol-gel is one of the most commonly used techniques for creating organic inorganic hybrid materials. It was originally invented as polymerization reactions of inorganic materials such as glasses and ceramics.\footnote{Technique drew a lot of attention because of low temperature processing of inorganic materials. Then organic-inorganic hybrid materials synthesis led a new area and many articles and reviews in this field have been published. In this technique small molecules (monomers) form colloids in a proper solvent and this colloidal solution is called “sol”. After proper reactions colloidal particles can form a polymer like network which is called “gel”.}

Once the solution of precursors is prepared different routes can be taken to prepare materials in different forms as shown in Figure 2.1. When colloids in the solutions starts to form by hydrolysis or polycondensation reactions, thin films can be created via spraying, dip coating, or spin casting.\footnote{Another option is to create fibers by drawing the solution. If the solution is dried at this stage colloids will form a nanoparticle powder. By changing the temperature, solution pH or by adding chemicals, colloids can form a network structure, referred to as a gel. Structure of the material formed via sol-gel technique is depends on process conditions a lot. Drying the gel is one of the processes that determines the final product properties such as density and porosity. A normally dried gel will lead to xerogel}
structure. However when it is dried under supercritical conditions, an aerogel structure is formed. Dense ceramics can be obtained through post-process sintering.

Sol-gel technique is very well understood for the formation of materials. Relatively recent reports on creating organic-inorganic hybrid materials formation using sol-gel have been reported. These materials are interest for their electronic, optical and catalytic applications. Even though the sol-gel technique is well-established, there are some drawbacks in the use of this process: the predominant use of organic solvents and the long process time for drying (which is predicated on the solute-solvent interaction). Another drawback is that every step of sol-gel process needs precise control of conditions for the repeatability of product. For example, even a small amount of solvent left in the material, can cause unwanted structure changes.

2.2.2 Layer by Layer Deposition

Layer by layer (LbL) deposition is a thin film formation technique, which depends on electrical charges of molecules in solvents. In order to deposit materials using LbL, materials should get ionized in the solution and the substrate should have a charged surface. In this technique charged substrate is dipped into solution of an ion with an opposite charge and materials are deposited onto the substrate via columbic attractions. As shown in Figure 2.2 four batches prepared for the process 1st and 3rd batches are the solutions of materials with opposite charges to deposit. 2nd and 4th batches are rinsing batches in which substrate is dipped to cleanse from any excess material freely standing on the surface. Sample is dipped in to these batches sequentially and 4 dipping is called a cycle and thickness of the coating depends on number of cycles.
LbL is very useful in terms of creating hybrid materials because using more number of batches many different blends can be deposited. Many different materials have been deposited using LbL, including polymer-polymer blends and ceramic-polymer blends. Some of these films are including but not limited to, branched polyethylenimine-sodium montmorillonite clay,\textsuperscript{29} poly(sodium phosphate)-poly(allylamine),\textsuperscript{30} polyethylenimine-carbon nanotube-poly(acrylic acid),\textsuperscript{31} polyhedral oligomeric silesquioxane,\textsuperscript{32} alumina coated silica-silica nanoparticles,\textsuperscript{33} and chitosan-montmorillonite clay based multilayers. LbL is of interest for organic electronics, tailoring surface wetting properties, flame retardant coatings, and integrated optics and sensor applications.

Even though LbL is in general very simple and versatile for depositing hybrid materials, there are some shortcomings in its use. Solution processing of the technique limits the substrate choice because substrate should show very good stability in the solution. Also, substrates, which cannot be easily charged, are not very suitable for the technique. Another limitation of the technique is the materials have to be ionized in a proper solvent in order to be deposited. Furthermore, the formation of thick films using LbL demands very long process times, which makes practical applications very difficult.

\textbf{2.2.3 Metal-Organic Frameworks}

Metal organic frameworks (MOF) are a group of materials that can be considered as a supramolecular solid, consisting of metal ions and organic ligands connecting the metal ions called as linkers.\textsuperscript{34-35} This group of materials can form large crystal structures with high porosity and the structure and spacing can be tailored by changing the size and coordination of the metal ions and the organic ligands.\textsuperscript{36-37} A principle flow chart for MOF production is
Multifunctional organic molecule and metal precursors are batch processed in certain solvents and precipitated. During or after precipitation, crystallization of the MOFs takes place. As seen from the schematic the process is conducted in solvent media, usually using environmentally unfriendly solvents. For environmental and cost reasons solvent recovery is necessary. In Figure 2.3 (b) it is also seen that large crystals of the MOF are formed as a result of the process in Fig. 2.3 (a).

Even though the MOFs are using highly undesirable solvents and produced by usually long reaction processes, they have very desirable properties such as high surface area. A gram of MOF can have area of 40 tennis courts,\textsuperscript{36, 39} makes these materials for many applications such as, gas storage,\textsuperscript{40} catalysis\textsuperscript{41} and biomedicine.\textsuperscript{36, 42} Furthermore production of MOFs, gives great flexibility to the producer to tailor the shape and the size of the pores in MOFs. A schematic representation of MOF precursors in Figure 2.4 shows some of the very different structures that can be formed. It is also possible to tailor the functionality of the MOF by simply changing the metal ions or the bridging ligands. For example using luminescent bridging ligands luminescent materials can be formed\textsuperscript{43} or changing ions or the ligands the catalytic activity of the material can be changed.\textsuperscript{44}

2.2.4 Atomic Layer Deposition

Atomic layer deposition (ALD) is a thin film deposition technique used for formation of metal oxide and metal coatings at angstrom to nanometer scales. Due to the self-limiting nature of sequential binary precursor reactions during exposure of a precursor, reaction takes place between surface of the substrate and the precursor. Thus conformal films even at high aspect ratio substrates are achieved. In Figure 2.5 a schematic ALD surface reactions are
depicted. For a surface finished by –OH functional groups and Al₂O₃ film is formed on the surface using trimethylaluminum (TMA) and H₂O precursors which are the most commonly reported precursors in the literature. A purge is applied to clean up the surface from unwanted physisorbed water molecules. Than substrate is exposed to first precursor TMA and via Lewis acid-base ligand exchange reactions between –CH₃ and –OH groups Al is attached to O on the surface and CH₄ forms as a byproduct. Upon a purge step remaining unreacted precursor molecules and byproducts are disposed. Then second half reaction starts via exposure of water, which reacts with the methyl groups which oxidizes the Al containing ligand again with a Lewis acid base reaction mechanism. A purge step cleans the byproducts and remaining water from the reactor and what is called a cycle is completed. In a cycle under ideal circumstances one layer of aluminum oxide is deposited that covers all surface of the substrate.

In order to achieve ALD film deposition chemisorption of precursors to the surface of the substrate is required. Commonly ALD is called as type of chemical vapor deposition (CVD) technique mainly because of this common requirement. However there are differences between these techniques, which are the main reasons for comformality. In CVD precursors are introduced to the system all at once and in comparison in ALD precursors are dosed in sequential cyclic manner. Furthermore CVD is usually conducted at high temperatures so not every substrate is compatible for this technique. On the contrast ALD can be conducted at relatively lower temperatures defined by a temperature window unique to precursors selected. A generic temperature window plot is given in Figure 2.6. Below ALD window temperatures depending on precursor, high growth via condensation or
incomplete reactions due to low thermal energy can occur. Similarly at high temperatures decomposition or desorption of precursor or surface species might happen. Being the ALD window of common precursors at low temperatures, many substrates can be treated with ALD.

ALD is a good technique to create organic-inorganic hybrid structures using polymer substrates mainly because of the low temperature processing conditions. Also it is a vapor phase technique dealing with solvents during the process is eliminated. ALD on polymers attracted attention for flexible electronic applications, vapor and gas barrier applications, and optical applications. Different precursor chemistries have been studied to deposit Al₂O₃, TiO₂, ZnO, SnO₂, HfO₂, ZrO₂ thin films and their mixtures on polyamide, polyester, polyolefin, polyacrylate, polystyrene, cellulose, polytetrafluoroethylene, polyimide, poly(vinyl alcohol), and biomolecules.

Depending on the chemical structure of the polymers, nucleation of inorganic ALD films on polymers showed differences. Polymers have plenty of functional groups (e.g. –OH groups) on the surface such as cotton, showed a conformal coating on the surface of the polymer with no evidence of infiltration into the polymer. A TEM micrograph of a fiber cross section treated with 100 cycle Al₂O₃ ALD is given in Figure 2.7 a). ALD on polymers with no reactive functional groups such as PE and PP, was enabled by diffusion of precursors and the trapping of precursors without reacting with the polymer. As seen in Figure 2.7 b) this type of growth shows an intermixed hybrid structure which forms isolated inorganic regions. Depending on the processing temperature this isolated inorganic regions can coalesce and form a uniform ALD films. QCM studies also showed that during this type of
nucleation there is a certain number of cycle is needed for nucleation before a normal ALD growth to be observed.

Another different nucleation pattern was observed during ALD on polymers with C=O functional groups. As seen in Figure 2.8 an organic-inorganic hybrid layer beneath the inorganic thin film was observed as a result of diffusion of precursor into the polymer matrix and reaction between the polymer and precursor\textsuperscript{54, 56, 64}. This diffusion pattern was interpreted as a result of lower functional group density on the surface and slower reaction mechanisms between C=O groups and TMA comparing to the one with –OH groups. This hybrid layer is also formed conformally beneath the ALD film and it shows much more uniform inorganic infiltration comparing to the PP case. This type of nucleation showed temperature dependency, higher the reaction temperature lower the hybrid layer formation was. In Figure 2.8 cross sectional TEM micrograph of hybrid layer formed during ALD on PA6 film at 60° is given with an EDX spectra obtained from the hybrid layer region which shows an Al peak\textsuperscript{54}.

\textbf{2.2.5 Molecular Layer Deposition}

Molecular layer deposition (MLD) is a thin film formation technique that is used for deposition of organic molecule networks such as polymers or organic-inorganic hybrid network molecules. Technique is named after atomic layer deposition because in this technique during each dose theoretically a layer of a molecule is deposited. Vapor phase synthesis of polymers dates back to 1930s\textsuperscript{65}. With growing interest in the purity of polymer films especially in conducting polymers\textsuperscript{66}, there is an increasing interest in the vapor phase
Vapor phase deposition of polymers is conducted under vacuum conditions and the monomer feed is controlled carefully so that high purity polymers can be achieved. Furthermore, it is a solvent free technique which eliminates the solvent removal step after polymerization.

During MLD multifunctional molecule precursors (monomers) are introduced to a functional surface sequentially similar to ALD. Figure 2.9 shows schematic of MLD surface reactions. A functional surface is exposed to reactant A in a self-limiting pattern. In order to achieve a conformal coating, the exposure time should be sufficient to saturate the surface species. Then an inert gas purge removes the residual reactants and by-products from the surface. The purge step should be long enough in order to pursue film conformality. By this step, the first part of an MLD cycle, a so called “half cycle”, is completed. Then reactant B is exposed to new functionality on the surface. This reactant is typically the co-monomer and has functional groups that are solely reactive towards the new surface species. Similar to the first half reaction a purge step is applied and an MLD cycle is completed. Typically, one cycle creates one repeat unit of the polymer on the surface that is terminated with the functional groups that can further react with reactant A.

There are a variety of polymers deposited by MLD such as polyamides, polyimides, polyaramids, conjugated polymers, polyurea, polythiourea, and polyurethane. These conformal, high quality thin films are of interest for electronic, catalytic, protective, barrier and drug delivery applications. It is also possible to deposit organic-inorganic hybrid networks using MLD. Using MLD hybrid networks
including Al₂O₃, ZnO, TiO₂ and ZrO₂ inorganic constituent using common ALD precursors along with organic precursors such as ethylene glycol, glycidol and hydroquinone.

Along with the important benefits of the technique there are also some limitations or additional necessities. Since large organic molecules are used as precursors their vapor pressures in ambient conditions are not sufficient for the process. Heating the precursor or using a bubbler system is necessary in these cases. Furthermore to get more reactivity halogenated precursors are used and in this case corrosive byproducts are created during the process. These corrosives can be trapped in the film as an impurity or can etch the product film and lower the growth amount.

### 2.2.6 Vapor Infiltration Techniques

Using the idea of extended exposure, to take advantage of the infiltration of precursors into polymers processes have been developed, for example; sequential infiltration synthesis (SIS), multiple pulsed infiltration (MPI), and sequential vapor infiltration (SVI). Demonstrations of potential applications have included mechanical strengthening of protein-based organics, modification of surface energy, formation of highly porous materials, and nanopatterning. Each of these vapor infiltration methods possesses subtle differences in their vapor exposure sequences. In this section of the literature review, these processes will be introduced and their short comings and advantages will be discussed.

#### 2.2.6.1 Sequential Infiltration Synthesis

One of the techniques proposed to use infiltration of ALD precursors is called Sequential Infiltration Synthesis. Infiltration in this process is reliant on an extended
exposure time of all of the reactants, which provides sufficient time periods for diffusion and reaction within the polymer. This technique is mainly proposed for creating hybrid materials for block copolymer lithography where they used self-assembly polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) and polystyrene-block-polydimethylsiloxane (PS-b-PDMS) block copolymers as substrates. Jeffrey Elam and his group at Argonne National Laboratories proposed the technique to create nanoscale patterned hybrid materials for energy, sensor, data storage and biomedicine applications.

When the block copolymers are synthesized, different ratios of repeat units, form different self-assembly nano to micro structures. This is a result of lack of solubility of each constituent in each other. Peng et al. and Tseng et al. used this technique to create nanoscopic materials generation by stepwise selective reactions within self-assembled block copolymer templates. A schematic of reaction mechanisms is given in Figure 2.10. In this report of Peng et al. used (PS-b-PMMA) which form self-assembled PMMA nanorods in PS medium. PS doesn’t have any functional group that can react with the organometallic precursor but PMMA has C=O groups that can react and form hybrid materials. By removing the organic template via different etching techniques inorganic nano size patterned materials has been produced.

Using SIS it is also possible to utilize a binary set of reactions in which the hybrid material formation of the first reaction with the polymer promotes the nucleation of the second reaction sequence that is otherwise non-reactive. For examples while C=O groups readily react with TMA, the reaction between DEZ (i.e. Zn precursor) and C=O groups are very slow. That’s why this type of hybrid materials formation is not observed with DEZ.
Using SIS TMA was first infiltrated and then oxidized by water exposures. This first half of the reactions created –OH groups, so when DEZ exposures are conducted it can react with them.

2.2.6.2 Multiple Pulsed Vapor-Phase Infiltration

Multiple pulse infiltration (MPI) is another technique proposed by Mato Knez and his research group at Max-Planck Institute. The MPI technique is similar to SIS, an increase in the exposure is performed by the use of a hold step (H) between the precursor exposure and inert purge in a sequence, similar to ALD, defined by: (A/H/I/B/H/I)xN. The hold step isolates the reactor from the gas flow and vacuum pumping such that the polymer substrate is contained in a volume consisting of the reactant species. A schematic in Figure 2.11 (a) shows the differences between ALD and MPI processes. In this technique along with the hybrid material formed with in the organic material via infiltration, also an inorganic thin film on the surface of the substrate is formed.

Using the idea they have infiltrated Al₂O₃ and TiO₂ into spider silk, which eventually increased the toughness of the fibers up to 2 orders of magnitude higher values, which is shown in Figure 2.11 (b). Considering spider silk having a very high toughness values by itself, this significant achievement drew a lot of attention on hybrid materials formation via infiltration techniques. Along with spider silk some other biomolecules such as collagens and feritin was also studied with MPI.⁹⁰-⁹².⁹⁹ One common property of these protein based materials is they have the carbonyl groups as pendant groups as a part of amino acid groups, which allowed the infiltration because of the low reactivity towards the ALD precursors. At
the same time they are reactive enough that they can form these hybrid structures within the material.

### 2.2.6.3 Sequential Vapor Infiltration

Sequential vapor infiltration (SVI) also incorporates a hold step to increase exposure however; this technique separates exposure of the precursors. First multiple repetitions (xN<sub>A</sub>) of the precursor exposure is conducted to replenish the reactant species during the hold step. After a certain number of repetitions of the initial reactant exposure, the co-reactant is introduced in a similar manner (xN<sub>B</sub>). The resulting sequence is defined as (A/H/I)<sub>xN_A</sub>/(B/H/I)<sub>xN_B</sub> of which a schematic is given in Figure 2.12. The total exposure of a reactant is dictated by the number of consecutive sub-cycles and the hold period in between exposures. A key difference between SVI and other infiltration processes is that SVI does not cycle between the reactant and co-reactant. That is, only one total exposure of each species is performed in SVI. That’s why an inorganic thin film is not formed on the substrate.

Gong et al. showed the reactions take place between TMA precursor and during SVI process on PET and PBT polymers using an in-situ FTIR enabled ALD reactor. In Figure 2.13 suggested reaction mechanism is explained on a schematic of SVI process on fiber. While conducting the TMA exposures ligand exchange reactions between TMA and C=O group on the backbone of the polymer takes place which breaks the double bond and O bounds to Al while the methyl group bounds to C on the backbone. Then after all the TMA cycles are completed number of water cycles is conducted similar to TMA cycles when unreacted CH<sub>3</sub> groups of TMA are oxidized. This way Polymer-Alumina structure is created.
Few applications have been proposed for the hybrid materials formed via SVI. In one of those studies scaffold PET and PBT fibers are infiltrated with TMA and TiCl₄ precursors. Hybrid materials are calcinated at high temperatures in order to burn out the organic component. Remaining was very high surface area oxide materials that can be used for catalysis applications. In Figure 2.14 it is shown that inorganic structure keeps the shape of the sacrificial fibers after calcination step. Another application was proposed for SVI was using the hybrid layer as a buffer layer to increase the stability of the ALD films formed on PDMS films. ALD films on PDMS were deposited to change the surface wetting properties. However it was observed that wetting transition resulted by ALD films were not stable in time. In order to increase the stability SVI was utilized and a hybrid buffer layer was created. Then ALD film applied to the surface which showed higher stability comparing to ALD films without SVI layer.

Even though there are some studies explained the chemical reactions that take place during SVI along with useful applications of the technique, there is a need for thorough investigation of the SVI mechanism. Process parameters such as substrate, temperature, exposure, and pressure need to be explored. There is also need for investigation of materials properties and their relation to processing conditions. This study aims to investigate these missing parts of the literature.
2.3. Applications and Properties of Organic-Inorganic Hybrid Materials

2.3.1 Optical Applications and Properties of Hybrid Materials

Organic-Inorganic hybrid materials are interest for many optical applications such as electroluminescence, and photovoltaic. Many researchers showed hybrid materials have certain advantages over organic or inorganic optical materials including flexibility. Here we briefly discuss some of the approaches to form these materials.

2.3.1.1 Light Emitting Diodes

Organic LEDs are getting a lot of interest for flexible electronic applications. Many different polymers and organic molecules have been synthesized. At the same time many researchers worked on forming hybrid materials showing light emission for such applications. One of the problems of the current materials is the low durability of the active organic material against moisture and oxidation. It is projected that inorganic substances will increase the durability of these materials by increasing hydrophobicity in the materials.

One of the ways to incorporate inorganic materials is simply to mix inorganic nanoparticles into organic medium. Even though it is not considered as hybrid material for some researchers, it is common that they are called as hybrid materials in the literature. Using this approach it is possible to form many different hybrid materials especially using luminescent nanoparticles like CdS. For example Tamborra et al. reported CdS/PMMA nanocomposites focusing on how the optical properties of CdS particles change in these polymers. With this approach it is also possible to combine many different polymers with various luminescent nanoparticles. Alternatively a luminescent inorganic (i.e. CdSe
nanoparticles) with conjugated polymers (i.e. PPV) also demonstrated in a LED application with varying colors. Similarly in another article GaN and InGaN quantum dots were incorporated into light emitting organic molecules and it was reported that with this incorporation color of the light coming out of the device could be tailored by blue emission of the inorganic. Even though these materials are not considered as hybrid materials according to some of the definitions in the literature, they can be considered as nanocomposites and they show enhanced luminescent properties comparing to constituent materials.

Another approach is to produce luminescent hybrid materials by chemically attaching organic and inorganic components to each other. Sol-gel and metal organic frame works are used for this purpose. Using sol-gel method silanes modified with hole transporting or electron transporting molecules can be used as precursors to form organic-inorganic hybrid materials. There are also reports showing the effect of lanthanide specifically europium doping in the optical response of the sol-gel base hybrid materials. Many papers showed the europium and other lanthanides can improve the quantum yield of these hybrid materials compared to many organic and hybrid LED systems. Metal organic frameworks (MOFs) or metal coordination polymers as referred previously are also capable of producing luminescent hybrid materials. MOFs can be luminescent by three mechanisms in general; i) linker based luminescence, ii) metal based luminescence and iii) guest phase emission as shown in the Figure 2.15. For linker based emission organic molecules with conjugated structures are used as linker and ligand to metal or metal to ligand charge transfer results in
emission. In the case metal emission transition metals or lanthanides are used. Using different chemistries the color and intensity of the emission can be adjusted.

There is also another phenomenon that is called as hybrid light emitting diodes (HyLED), where an oxide layer is used as hole injection layer that increases the device performance of polymer light emitting diodes (pLED). In this case thin films of TiO$_2$, ZnO, Ga$_2$O$_3$, or SnO$_2$ is deposited on top ITO to serve as hole injection layer. This design aims to improve charge transfer efficiencies between the layers therefore increasing the emission out of the active polymer layer. Another benefit of the design is to improve the air encapsulation of the material therefore providing longer lifetimes for the device.

2.3.1.2 Photovoltaics

Photovoltaic is another area of optical materials where we come across with the term hybrid materials. In this case the hybrid material is commonly referred to the nano-composites of conjugated polymers and inorganic particles. In this approaches it is aimed that the processability of the organic components along with high absorption values, can be improved by addition of inorganic nanoparticles. Inorganic particles being more stable than organic components, more robust devices are aspired. Inorganic materials can enhance the light absorption of these materials for better performance. Furthermore it is also shown that by controlling the size and shape of the inorganic component it is possible to modify the band structure of the hybrid phase. Many organic polymer has been used with this approaches including polyphenylene vinyledene (PPV) and Poly(3-hexylthiophene) (P3HT), with silicon nanowires, CdSe, Cd$_2$, TiO$_2$, ZnO, and many other inorganic materials.
2.3.2 Catalytic Activity and Applications of Organic Inorganic Hybrid Materials

Catalysis enables many technologies today and undoubtedly is one of the fundamental areas of research nowadays. Organic inorganic hybrid materials are very commonly referred as good candidates for catalytic applications. Especially solid catalyst preparation with sol-gel and MOFs is projected in the literature very often. Solid catalysts are great because they are easy to recover after desired reactions take place however they are slower in reaction rates compared to the homogenous catalysts and it is not easy to form organic solid materials that is not soluble in the medium of reaction.\(^1\) By introducing inorganic component to the catalyst material it is expected to increase the reaction rates.\(^{124}\) Furthermore the solubility of the material is prevented by hybridization.\(^1\)

It is possible to find wide variety of organic-inorganic hybrid materials are formed with sol gel technique for many different applications.\(^{124-125}\) Metal organic frameworks are also very good candidate materials for catalysis and some applications of the MOFs for different catalysis applications have been demonstrated in the literature.\(^{34, 126-128}\) Sol-gel and MOFs materials can be produced mesoporous therefore can be very useful for catalysis because higher surface are will enable them high conversion rates.\(^{36, 38, 129}\)

Another approach towards use of organic inorganic hybrid materials for catalysis is to using the hybrid material as a sacrificial template. In this case organic inorganic hybrid material is synthesized with a certain technique and later by carbonization or calcination. Remaining porous material can be utilized as catalyst\(^64\) or used as a template for incorporation of catalyst material.\(^{130}\) Previously using sequential vapor infiltration
mesoporous TiO$_2$ and Al$_2$O$_3$ materials were prepared by calcination of sacrificial organic-inorganic hybrid material. 64

2.3.2.1 Photocatalysis

Photocatalysis first introduced to literature by Fujishima and Honda by the water splitting reactions on TiO$_2$ electrodes in 1972. 131 Since then studies have been published to investigate the photocatalytic activity of the TiO$_2$ and other semiconductor materials. 132 As shown in Figure 2.16 exposure to light excites electrons from valance band to conduction band in these semiconductors, which can create free radicals by splitting the water and start series of reactions on the surface of the semiconductor. 133 Another words light here is not the catalyst itself it sensitizes the actual catalyst the semiconductor. 134 TiO$_2$ is the most widely studied molecule for photocatalysis, can absorb UV light and then it can undergo reactions to create the surface radicals. Many studies dedicated to improve the visible light absorption of titania to improve the photocatalytic activity in the visible spectrum as well. 135 This photocatalytic systems can be used for H$_2$ production, 131 remediation of waste waters 136 and self-cleaning systems. 137 Photocatalytic activity of material can be defined as the ability of the material when they are exposed to light. Organic-inorganic materials showing light absorption and light emission are also projected to be used for photocatalysis applications.
Figure 2.1. Schematic of sol gel process.\textsuperscript{12}
Figure 2.2. Illustration of thin film formation via Layer by layer technique.²⁸
Figure 2.3. a) Flowchart of MOF productions and optical images b) SEM image of Zn-MOF 5 samples.
Figure 2.4. Building block and structure relationship of MOFs.\textsuperscript{34}
Figure 2.5. Schematic description of ALD surface reactions for $\text{Al}_2\text{O}_3$ film deposition using TMA and $\text{H}_2\text{O}$ precursors.
Figure 2.6. Growth per cycle as a function of temperature plot used for determination of ALD window.
Figure 2.7. Cross-section TEM micrographs of 100 cycle ALD Al₂O₃ films formed on a) cotton fiber and b) polypropylene fibers.⁵⁶
Figure 2.8. a) TEM image of PA6 film cross section after 100 cycle Al₂O₃ ALD showing a distinct hybrid layer formation b) EDX spectrum obtained from approximately circled region a).⁵⁴
Figure 2.9. Schematic of ideal MLD reactions by using two co-reactants.\textsuperscript{67}
Figure 2.10. Schematic of the process to create nanoscopic materials using sequential infiltration synthesis and self-assembled block copolymers.\cite{89}
Figure 2.11. a) Difference of ALD film formation on rigid substrate and hybrid material formation using MPI on soft substrate b) Stress strain tests of inorganic infiltrated spider silk showing significant improvement of substrate’s toughness.
Figure 2.12. Schematic of SVI process showing the separation of exposures of each reactant with number of cycles.\textsuperscript{141}
Figure 2.13. Alumina-polymer hybrid material formation and reaction mechanisms during SVI on polyesters as suggested by Gong et al.\textsuperscript{64}
Figure 2.14. a) PBT nonwoven fiber mat before and after SVI treatment and annealing b) SEM image of fibers before SVI treatment c) and d) SEM micrographs of SVI treated and annealed samples shows fibrous structure is preserved.64
Figure 2.15. Schematic of different mechanisms of luminescence in MOFs. ⁴³
Figure 2.16. Schematic of photoreduction and photooxidation mechanism in TiO$_2$. $^{138}$
Chapter 3 Temperature and Exposure Dependence of Hybrid
Organic–Inorganic Layer Formation by Sequential Vapor Infiltration into
Polymer Fibers

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Abstract: The characteristic processing behavior for growth of a conformal nanoscale hybrid
organic-inorganic modification to polyamide 6 (PA6) by sequential vapor infiltration (SVI) is
demonstrated. The SVI process is a materials growth technique by which exposure of
organometallic vapors to a polymeric material promotes the formation of a hybrid organic-
inorganic modification at the near surface region of the polymer. This work investigates the
SVI exposure temperature and cycling times of sequential exposures of trimethylaluminum
(TMA) on PA6 fiber mats. The result of TMA exposure is the preferential subsurface
organic-inorganic growth by diffusion into the polymer and reaction with the carbonyl in
PA6. Mass gain, infrared spectroscopy, and transmission electron microscopy analysis
indicate enhanced materials growth and uniformity at lower processing temperatures. The
inverse relationship between mass gain and exposure temperature is explained by the
formation of a hybrid layer that prevents the diffusion of TMA into the polymer to react with
the PA6 upon subsequent exposure cycles. As few as 10 SVI exposure cycles are observed
to saturate the growth, yielding a modified thickness of ~75 nm and mass increase of ~14 wt %.
Removal of the inherent PA6 moisture content reduces the mass gain by ~4 wt% at low
temperature exposures. The ability to understand the characteristic growth process is critical
for the development of the hybrid materials fabrication and modification techniques.

Introduction

Hybrid organic-inorganic materials and hybrid surface modifications to materials are
of interest for altering mechanical, electronic, catalytic, and optical properties, in addition to their ability to fabricate bioactive scaffolds and nanostructured materials. In general, hybrid materials take advantage of combined material properties by unifying inorganic and organic materials. Facile processing techniques are sought to exploit these properties on a wide range of substrates, including non-planar polymeric materials. Here in, the use of a vapor infiltration method is explored that utilizes organometallic vapors, typically used as precursors in ALD processing, in order to form a hybrid modified layer on polymer substrates such as fibrous textiles.

Atomic layer deposition is a process by which vapor precursors are sequentially
exposed to a surface, leading to a self-limited materials growth away from the surface. In a
standard ALD process, precursors (A and B) are exposed in sequence to complete a reaction
on a surface and separated by an inert (I) purge step, following an A/I/B/I sequence.
Defining the sequence timing and the temperature window is critical to the understanding of
an ALD process space. This includes consideration of the reactor design (size, flow rate, pump speed), precursor exposure, inert purge time and available reaction sites. With optimized sequencing and process temperatures, ALD growth is conformal on textured surfaces. The definition of the process characteristics is also important for the implementation and understanding of similar processes such as the SVI technique defined in this work.

As a result of the low process temperature window characteristic of many ALD growth chemistries, its application to polymers has been investigated. The vapor phase surface-promoted reaction typical of an ALD process allows for conformal materials growth on complex polymer surfaces such as a fibrous textiles. As such, ALD has shown unique ability to control the surface characteristics of a polymer and produce novel architectures for electronic, catalytic, and barrier applications. Materials nucleation on polymers has been shown to be different in comparison to processing on inorganic surfaces. Specifically, ALD materials nucleation is dependent on precursor-polymer interactions, leading to vapor precursor infiltration into the polymer. Subsurface ALD material nucleation is observed on inert thermoplastics such as polypropylene, (C\text{\textsubscript{3}}H\text{\textsubscript{6}})\textsubscript{x}, as a result of vapor diffusion into the surface. In materials such as poly(methyl methacrylate) (PMMA), poly(butylene terephthalate) (PBT), and nylon-6 (PA6), subsurface growth is shown to result in a reaction between the precursor and the polymer functional groups or polymer backbone, forming a hybrid organic-inorganic covalently bonded material.

Processes have been developed, for example; sequential infiltration synthesis (SIS), multiple pulsed infiltration (MPI), and sequential vapor infiltration (SVI), which exploit
the reactive vapor infiltration mechanism. Demonstrations of potential applications have included mechanical strengthening of protein-based organics, modification of surface energy, formation of highly porous materials, and nanopatterning. Each vapor infiltration method mentioned previously possess subtle differences in their vapor exposure sequences. For example, SIS utilizes a binary set of reactions in which the hybrid material formation of the first reaction with the polymer promotes the nucleation of the second reaction sequence that is otherwise non-reactive. Infiltration in this process is reliant on an extended exposure time of all of the reactants, which provides sufficient time periods for diffusion and reaction within the polymer. The MPI technique is similar to SIS, except that an increase in the exposure is performed by the use of a hold step (H) between the precursor exposure and inert purge in a sequence, similar to ALD, defined by: (A/H/I/B/H/I)xN. The hold step isolates the reactor from the gas flow and vacuum pumping such that the polymer substrate is contained in a volume consisting of the reactant species. Finally, SVI also incorporates a hold step to increase exposure however, this technique allows for multiple repetitions (xN_A) of the precursor exposure to replenish the reactant species during the hold step. After a certain number of repetitions of the initial reactant exposure, the co-reactant is introduced in a similar manner (xN_B). The resulting sequence is defined as (A/H/I)xN_A/(B/H/I)xN_B. The total exposure of a reactant is dictated by the number of consecutive sub-cycles and the hold period in between exposures. A key difference between SVI and other infiltration processes is that SVI does not cycle between the reactant and co-reactant. That is, only one total exposure of each species is performed in SVI.
Understanding the saturation behavior of these processes allows for their application to materials with complex dimensions as well as methods to increase their process throughput. This study examines the temperature dependence and evolution of an organic-inorganic hybrid layer in PA6 by sequential exposure subcycles of TMA followed by H$_2$O. The TMA/H$_2$O pair to create Al$_2$O$_3$ is one of the most extensively studied ALD processes and TMA has been shown in ALD and SVI processing to be reactive towards C=O groups that are present in PA6. To examine this saturation behavior, a high surface area PA6 fabric is utilized that allows for a more accurate analysis of mass gain per cycle as compared to a planar PA6 film material. We demonstrate that the SVI process saturates after a number of consecutive TMA sub-cycles and that the degree of saturation is dictated by the processing temperature, in addition to the dosing and holding times of the TMA exposure. The infiltration and hybrid modification of PA6 fibers is shown to be more conformal at low temperatures. Finally, the effect of the water presence in the PA6 is observed, which allows for additional control over the infiltration and saturation behavior.

**Experimental**

SVI experiments were conducted with a custom-designed viscous flow tube reactor, also designed for ALD processing. A schematic design of the reactor is provided in Figure 3.1. The reactor chamber consists of a stainless steel conflate-sealed tube, 90 cm in length and 20 cm in diameter. The reactor is able to achieve a base pressure of <20 mTorr with the use of an Alcatel 2021SD mechanical pump. During all processing, inert N$_2$ (Airgas National Welders, 99.999%) is delivered to reactor after it is further purified with an Entegris Gatekeeper® inert gas purifier that reduces impurities and moisture content to below 10 parts
per trillion. Flow rate of the N₂ is controlled using an MKS (Model: PR4000B) flow controller and 1 Torr pressure in the reactor is reached with a flow rate of approximately 300 SCCM. The reactor is heated using Omegalux® fiberglass heating tapes and the temperature is controlled by Omega (Model: 616) temperature controller. Exposure of TMA (STREM chemicals CAS#: 75-24-1, 98% purity) and high purity water (Sigma Aldrich, biotechnology performance certified grade, CAS#: 7732-18-5) was delivered to the N₂ flow through the use of Swagelok® ALD pneumatic valves. The valves sequencing is controlled using a custom Labview® program.

SVI processing was evaluated on PA6 (T_g ~50 °C, T_m ~220-230 °C) hydroentangled nonwoven fabric mats (Allasso Industries) consisting of ~10 µm diameter fibers and a surface area of 3 m²/g. The fiber cross-section has a lobed-shape, which enhances the surface area and allows for a better understanding of the conformal behavior of the hybrid surface modification. Fabric samples were used as received and cut into sections ~20 cm² in dimension and a mass of ~0.2 g. The use of fabric samples for this analysis allows for increased resolution of the mass gain observed through SVI processing. The mass gain resolution is directly related to the areal density (i.e. sample surface area per unit mass), which is much higher for fabrics in comparison to deposition on a planar film. SVI was conducted at temperatures ranging from 30 to 150 °C for 1-60 consecutive TMA cycles at a process pressure of 1 Torr. Prior to placement into the system, the mass of the PA6 nonwoven fabric samples was recorded. Upon entry into the reactor, the samples were allowed to thermally equilibrate in a N₂ flow for a period of 5 min prior to SVI processing. For experiments exploring exposure temperature effects, a single SVI processing cycle
consists of a TMA sub-cycle that is defined by an TMA exposure (0.5 seconds), a hold period (30 seconds) in which the system was isolated from the vacuum pump and N₂ flow, and a N₂ purge (30 seconds) to remove all unreacted TMA and reaction products from the system. After a number of consecutive TMA exposure sub-cycles, the system was pumped without N₂ flow for 300 sec prior to performing sequential H₂O exposure sub-cycles (0.2 sec exposure, 30 sec hold, 30 sec purge). Effect of exposure was investigated at 60 °C and the number of TMA sub-cycles (1-10 cycles), dosing time (0.2-2 sec) and holding time (0-60 sec) of the SVI process was varied. To examine the effect that pre-adsorbed H₂O in the polymer had on SVI processing, some fabric samples were subjected to a 120 °C in situ bake prior to TMA exposure. This bake was conducted in the reactor at vacuum for 15 min under a flow of N₂ (100 SCCM). The reactor was then cooled to the desired SVI processing temperature under N₂ flow. SVI processing was conducted without removing the samples from the reactor. The mass of the PA6 samples was again evaluated after SVI processing after a 2-3 hour period at room temperature and humidity. Growth was also evaluated on silicon wafer pieces placed in the reactor chamber in close proximity to the PA6. Spectroscopic ellipsometry evaluation showed typically <10 Å of Al₂O₃ growth on the Si, which is anticipated given the SVI cycling sequence that isolates the total exposure of TMA and H₂O. Some growth is anticipated due to moisture outgassing from the fabrics.

In-situ quartz crystal microgravimetry (QCM) was used to explore the mass gain of PA6 thin films infiltrated with multiple doses of TMA at 60, 100 and 150 °C. Initially, a 3 wt. % PA6 solution was prepared by dissolving PA6 pellets (Ultramid®) in 95 % purity Formic Acid (reagent grade, Sigma Aldrich Inc.). The solution was mixed for 12 hours in a
closed container at room temperature. PA6 thin films were spun cast (Laurell Technologies) at 3000 rpm for 1 minute onto unpolished, gold plated quartz crystals (Inficon, resonant frequency, 6 MHz). Ellipsometry measurements of PA6 films formed on silicon wafers showed that the film thickness was ~300 nm. The polymer coated quartz crystals were annealed at 90 °C on a hot plate for 1 minute to remove residual solvent. The PA6 coated quartz crystals were secured to a crystal drawer (Inficon) with a conductive silver epoxy (Electron Microscopy Sciences), which was then inserted into a sensor head inside the main reaction chamber and allowed to equilibrate to the processing temperature. During the TMA exposure, the frequency of the oscillating quartz crystal was recorded every 0.25 seconds. To prevent build-up of inorganic material around the electrical contacts between the sensor head and the quartz crystal, N₂ gas was continuously purged on the backside of the quartz crystal. The mass gain of the as a result of the TMA exposure was calculated using the Sauerbrey relationship.

Fourier transform infrared spectroscopy (FTIR) of the PA6 fabrics was obtained using a Nicolet Nexus 470 FTIR attenuated total reflectance (ATR) spectrophotometer equipped with a germanium crystal. For the sample measurements, the fabric is oriented between the germanium crystal and a metal tip (3 mm diameter) and an orthogonal force is applied to the tip in order to increase the material contact with the crystal surface. A sequence of 64 scans over a range from 4000 to 700 cm⁻¹ was performed and averaged for each data set reported. Transmission electron microscopy (TEM) samples were prepared using Leica UC7 Cryo Ultramicrotome. The microtome samples were prepared by first embedding the fibrous mat samples in Spurr low-viscosity epoxy resin (Ladd Research...
Industries) and then cured overnight at room temperature. The blocks were then cut to a thickness of ~70 nm using a Leica Ultracut diamond knife microtome and floated onto TEM grids with an ultrathin amorphous carbon film. Transmission electron microscopy analysis of the microtome prepared specimens was conducted using a Hitachi HF 2000 with a 200 kV cold emission source. Energy dispersive X-ray Microanalysis (EDS) was unable to be performed with suitable spot size dimension to resolve the constituents of the organic-inorganic hybrid SVI layer without damaging the PA6.

**Results and Discussion**

The growth behavior of the sequential vapor infiltration of TMA into PA6 was analyzed by evaluating the mass gain of the fabric samples. The saturation behavior of the TMA into the PA6 was examined by increasing the number of consecutive sub-cycle exposures of TMA (xN_A). Ambient stabilization after SVI processing was necessary to complete any moisture re-gain into the fabric that was lost during process. As a control, PA6 samples held in the reactor at 120 °C for 30 min showed ~4 wt% decrease compared to the initial mass measurement, but regained the full mass loss after 2-3 hour stabilization (25 °C, >40% relative humidity). This is consistent with the weight percent of H_2O in PA6 of ~4 wt% (at 20°C and 60% relative humidity).\(^{155}\)

Figure 3.2 provides an evaluation of percent mass change of the PA6 fabric samples evaluated as a function of consecutive TMA exposures (xN_A) at processing temperatures ranging from 60 to 150 °C. The mass gain was consistently higher for processing at a temperature of 60 °C and decreased with increasing temperature up to 150 °C. For the entire temperature range evaluated in this study, the significant portion of the mass increase occurs
over the initial 1 to 10 TMA exposure sub-cycles (i.e. 10 consecutive cycles of a 0.5 sec TMA exposure, 30 sec hold, and 30 sec purge). At 150 °C, only a 0.7% mass gain was observed from the 1st to the 60th TMA sub-cycle. At 60 °C a more gradual mass increase is shown that saturates by the 10th TMA sub-cycle. It is noted that similar evaluation of consecutive H$_2$O exposure sub-cycles, with a constant TMA exposure, showed no mass difference after post process stabilization. To be sure that the reported % mass gain values are reliable, we performed all tests using samples from a single fiber source, with a measured starting surface area of 3 m$^2$/g. In addition, fabric mass was consistent for all samples such that the total chemical reactant exposure required to saturate the reaction was not altered.

Evaluation of the mass uptake after 10 TMA sub-cycles for a temperature range of 30 to 150 °C is provided in Figure 3.3. At 30 °C, a mass increase of 14.2 wt% was observed and decreases with increasing temperature. At 150 °C, the mass gain was ~1 wt%. Given the high weight percentage of water in the PA6, it is apparent that some mass gain is due to TMA reaction with the H$_2$O. To determine the mass gain effect of the water content in PA6, a separate set of fabric samples underwent SVI process after an in situ bake, consisting of an initial drying in the reactor at a temperature of 120 °C. The samples were subsequently cooled under vacuum with N$_2$ flow prior to SVI processing with a temperature range from 30°– 120 °C. The percent mass gain for samples with and without the in situ bake is compared in Figure 3.3a. The difference in the trend with and without the in situ bake is attributed to TMA reaction with the H$_2$O to form Al$_2$O$_3$. The percent mass gain of the samples with drying was decreased in comparison to the samples without drying, showing an 11 wt% and 2 wt% mass gain at 30 and 120 °C, respectively. The mass gain observed after
the *in situ* bake is attributed to the mass gain only through reaction between the TMA and PA6.

An Arrhenius plot (ln(mass gain(wt%)) vs. 1000/T (1/K)) of the mass gain is provided in Figure 3.3b and shows that the mass gain increases linearly on a logarithmic scale with decreasing temperature. The slopes of the lines for both *in situ* bake treated and untreated samples are similar which suggests effect of temperature on mass gain is independent of the PA6 water content. To support this observation, the mass gain of TMA exposure was further analyzed by QCM of spuncast PA6 films. The data obtained from the mass gain per cycle during 10 TMA only multi-doses is plotted in Figure 3.4. Again, an Arrhenius plot (Figure 3.4b) of the mass gain related to the TMA exposure (0.5 s) cycle shows a decreasing mass gain with temperature. This data suggests that at high exposure temperatures, in which less mass gain is observed, the reaction between the TMA and the PA6 is more favorable, likely resulting in a hybrid modification with higher density at the surface of fiber. This modification serves as a barrier to TMA diffusion into the PA6 and as such, the total mass gain saturates after few exposure cycles, as observed in Figure 3.2.

The influence of the dose time and the hold time were examined by determining the percent mass gain of PA6 after 10 SVI exposure cycles at 60 °C. The mass gain of these samples is presented in Figure 3.5. With a dose time of 2 sec, a corresponding 15 sec hold time is required to achieve a saturated mass gain between ~14-15%. The mass gain is shown to decrease as the dose time decreases. Considering the mass gain saturation obtained in Figure 3.2 for a 0.5 sec dose time at 60 °C is ~9-10%, it can be concluded that the higher dose time does in fact influence the highest obtainable mass gain. In addition, the hold time
required to reach this mass gain increases with an increasing dose time. In general, a 15-20 sec hold time at a corresponding 2 sec dose time is required to reach saturation. It is important to note that a 9.5% mass gain is observed even for a 0 sec hold time, which directly corresponds to a 20 sec TMA exposure to PA6.

To elucidate the significance of the hold time, and explore rapid rate of mass gain, nonwoven PA6 was exposed to an increasing number of cycles at hold times ranging from 0 to 30 sec using a 2 sec TMA dose time. The results of this investigation are presented in Figure 3.6. In agreement with prior observations in Figure 3.2, a minimum of 10 SVI cycles is required to reach a saturated mass gain. A single SVI cycle results in a mass gain of 7-10%, and is shown to increase with the hold time. After 10 SVI cycles, the percent mass gain ranges between 9.5 and 12.5%, consistently remaining higher for increased hold times. As such, the hold time also appears to affect the maximum achievable percent mass gain although, to a lesser effect than the dose time. As shown in Figure 3.5, the influence of the hold time is more prominent at higher dose times.

FTIR-ATR spectral analysis was conducted to examine the change in functional groups after the SVI processing. Figure 3.7(a) and (b) shows the spectra of SVI processing at temperatures of 60 and 150 °C as compared to untreated PA6 and the effect of an in situ bake of the PA6 at an SVI process temperature of 60 °C, respectively. In each figure, the broad spectra from 3600 to 3250 cm\(^{-1}\) and the peak at 3300 cm\(^{-1}\) are representative of O-H stretching and N-H stretching in the polymer, respectively. The peak at 1640 cm\(^{-1}\) represents C=O stretching. The general magnitude of the interaction between the TMA and PA6 can be observed quantitatively through changes in the characteristic peaks’ intensities.
since the substrate modification thickness is much less than the depth of profiling (for germanium crystal FTIR about 0.5 µm, whereas TEM shows surface modification of <0.075 µm at 60 °C). As compared to the untreated polymer, SVI processing at 60 °C shows an increase in the broadening and peak intensity of the O-H stretching (Figure 3.7a) and a corresponding decrease in the C=O and N-H related peaks. When the process temperature is increased to 150 °C, the O-H stretching is reduced while the C=O and N-H related peak intensities increase. These observations indicate that at lower temperature processing, the O-H content is increased and extent of the reaction between the PA6 and TMA may be increased in the surface region of the polymer analyzed. The latter observation may be due to the aforementioned Al₂O₃ formation, which can make the intensity of the polymer peaks decrease. To again examine the effect of inherent moisture in the PA6, Figure 3.7b compares PA6 prior to processing, SVI processing at 60 °C, and SVI processing at 60 °C after a 120 °C in situ bake. The in situ bake is shown to have a higher C=O and N-H peak intensities and similar O-H broadening as compared to the samples with no in situ bake. This suggests that the Al₂O₃ formation from the reaction between moisture in the PA6 and TMA can reduce the C=O and N-H peak intensity. In addition, the O-H formation is as prevalent as the sample without the Al₂O₃ formation, suggesting that the reaction product between the TMA and C=O still allows for reaction with H₂O. This is also in agreement with previous in situ FTIR analysis of ALD on PA6 films.154

The conformity and growth behavior of the hybrid film formed after 60 consecutive TMA exposure sub-cycles to PA6 was examined by cross sectional TEM. Low magnification images provided in Figure 3.8(a-c) of PA6 with SVI processing at 60, 90 and
150 °C show that the growth behavior becomes more conformal as the process temperature is lowered. It is noted that the differences in the cross-section appearance of the fibers are due to differences in the fiber orientation during the microtome sample preparation, but has minimal influence on the analysis of the coating. At 60 °C, and to a somewhat lesser extent at 90 °C, the conformity of the coating on the edges of the winged fiber is consistent even within the gaps of the individual fiber lobes. At 150 °C, the coating is thicker in the gap regions, consistent with preferential growth in these areas. In order to examine the conformity of the SVI coating processed at 60 °C along the fiber axis, a fiber sample was calcined in air at 450 °C for 2 hrs, resulting in an alumina construct shown in Figure 3.8 (d). As the inset figure shows, the uniformity of the coating is consistent along the fiber. Higher magnification TEM images of samples processed at 60, 90 and 150 °C are provided in Figure 3.9 (a-c). A more conformal thickness of the hybrid layer growth is shown at lower process temperatures, with significant non-uniformity observed between 90 and 150 °C processing. At 60 °C, a thickness of ~75 nm is measured, whereas the thickness decreases to 65 nm at 90 °C. Interestingly at 150 °C, a graded film is observed that makes estimation of the thickness more difficult, but also suggests varying density of the hybrid layer on the PA6 surface. It would be expected that the density of the film processed at the lower temperatures may be higher due to alumina formation from the reaction between TMA and the water content in the PA6. Given that all samples had the same surface area, the mass increase data can be used to approximate the magnitude of the density differences. The mass increase is shown in Figure 3.3 (a) to be ~50% higher at 60 °C compared to 90 °C, where the thickness is only ~20%
higher. This discrepancy suggests a higher density of the modification at 60 °C. The TEM results are also consistent with the FT-IR analysis, in which the peaks intensity from the polymer functional groups are increased for the thinner hybrid layers processed at increased temperatures.

The observations in this work allow for a better understanding of the vapor phase organometallic infiltration into the polymer. Of particular importance are the observations that the mass uptake decreases with increasing process temperature and that the mass saturation behavior is conformal in thickness at lower process temperatures. For understanding these observations, it is important to take into account that based on the SVI exposure sequence, growth is only achieved by interaction between the organometallic precursor and the polymer or material in the polymer (i.e. H$_2$O in PA6). It is natural then to think of the infiltration as being dictated by both precursor diffusion into the polymer and the reaction between precursor and the components of the polymer.

Diffusion of vapor into a polymer is generally proportional to the available free volume in that polymer. As is the case with thermoplastics, the free volume increases with temperature which can markedly increase the diffusion rate of vapors into that polymer. For example, ALD processing of alumina on polypropylene, an inherently inert material that shows no reaction with TMA, does show increased subsurface growth of alumina with temperature due to diffusion into the polymer.\textsuperscript{19} Compared directly to the present work, the thermal expansion coefficients are similar for polypropylene and PA6 (1x10$^{-4}$ °C$^{-1}$ and 0.5x10$^{-4}$ C$^{-1}$, respectively) and the resulting polymer free volume increase should be similar upon heating. The observation in this work of the limited growth at higher exposure
temperatures is an indication that the reaction between the PA6 and TMA does limit the overall modification of the polymer. A likely reason is that the materials product between the TMA and PA6 is of higher density when the exposure temperature is increased. Prior literature has shown that the ALD film density increases with temperature.\textsuperscript{55} In addition, calcined PBT fabrics after an SVI process show a decrease in pore size with increased exposure temperatures.\textsuperscript{11} The low density of the hybrid modification produced at decreased exposure temperatures is projected to provide a resistance to diffusion between that of the original polymer and the high temperature hybrid material. As this modification increases in thickness (i.e. increase in TMA sub-cycles), the time required for TMA to diffuse to unreacted PA6 increases, resulting in the saturation behavior observed in this work.

It is reasonable to consider that the presence of H\textsubscript{2}O in the PA6 may affect the dynamics of the hybrid organic-inorganic formation process. For example, reaction between the TMA and H\textsubscript{2}O in the polymer to form Al\textsubscript{2}O\textsubscript{3} in the hybrid layer should increase the layer density and prevent diffusion and alter the subsequent saturation condition. It is also possible that the critical thickness of the hybrid layer is controlled, not only by the relationship between the reaction and diffusion process, but also by the water content in the polymer. As observed in Figure 3.3, when the H\textsubscript{2}O is removed from the PA6, the inverse relationship between the mass gain and temperature remains. Other unbound materials in the polymer, such as PA6 monomer (caprolactam, (CH\textsubscript{2})\textsubscript{5}C(O)NH), may also affect the hybrid formation. PA6, in general has an ~1 wt % monomer in the final polymer and has a vapor pressure of ~0.07 Torr at 60 °C and increases to ~1.4 Torr at 100 °C.\textsuperscript{156} At exposure temperatures below 100 °C, the outgassing of the caprolactam from the PA6 is minimal in comparison to H\textsubscript{2}O.
outgassing. At higher temperatures where the caprolactam outgassing is substantial, the effects on the materials growth may be dependent on the reaction affinity for TMA with the PA6 or the caprolactam. Additional testing is required to understand the role of the water and monomer in the saturation conditions of the hybrid modification.

Finally, it is important to consider the exposure in a single SVI cycle and how this is affected by the dose and hold times. Typically, exposure reported in units of Langmuir (1 L = 10^6 torr ·sec), is the amount of time a quantity of reactant (i.e. vapor pressure) is present over a surface. This relationship for an ALD process is depicted in Figure 3.10 (a), where the exposure is a quantification of the area under the curve (vapor pressure vs. time). The exposure is dictated by the reactant dose time and rate of at which the reactant species is consumed or evacuated from the reactor during the purge step. The asymptotic decrease shown in Figure 3.10 (a) is used as a means for description and does not represent actual data. It is noted that in ALD, the reaction occurring on the surface starts with the initial dose and the purge step quickly evacuates the reactant from the system. The exposure required for each reactant dose needs to be sufficiently high to saturate the surface with reactant. For an SVI process the exposure scenario is very different. Figure 3.10 (b) depicts an exposure for an increasing number of TMA sub-cycle exposures. The results in this work indicate the reactant can be fully consumed through the hold step, such that multiple SVI cycles are required to saturate the mass gain. Once the polymer is saturated and the reaction is extended to its end, additional SVI cycles serve no purpose in terms of materials growth and therefore the vapor pressure remains constant through the hold period. It is obvious that the initial exposure (in an unsaturated condition) is going to be higher when the dose and hold
times are increased. As indicated by the data presented in Figures 3.5 and 3.6, the maximum achievable mass gain increases with both the dose and hold times.

For the conditions of the process outlined in this work, the amount of precursor delivered to the system for the SVI cycle is increasing with dose time. Given the dimensions of the reactor and carrier gas flow rate, the gas velocity of the reactant through the reactor is ~6 cm/sec and the residence time is ~8 sec. Therefore, a dose time of at least 8 sec is necessary to achieve a maximum quantity of reactant species to be contained within the reactor dimensions during the hold period. All of the dose times examined in this work are lower than the 8 sec. As such, the concentration of the reactant outside of the polymer is increasing with dose time and the related driving force is a likely reason for the change in maximum achievable mass gain with increasing dose times. Higher hold times also allows the precursor to infiltrate to its maximum capacity. If either the hold or dose times are disproportionately low, additional SVI cycles are required to achieve the maximum achievable mass gain. Therefore, it can be concluded that both dose and hold conditions provides the ability to controllably engineer the mass increase of the modified material.

Additional factors may be projected for influencing the characteristics hybrid surface modification of polymers by infiltration of reactive organometallic vapors. For example, control of the amount of reactant can be controlled not only by vapor pressure of the precursor delivered, but also the dimensions of the reactor. Given the influence of diffusion rate vapor into the polymer, the pressure can also be projected to have a significant influence, particularly as pressure is increased up to atmospheric conditions where continuous, roll-to-roll manufacturing is more accessible and is a necessity for high throughput processing of
organic electronics and textiles. All of these scenarios allow for a means to achieve a desired hybrid modification to a polymer surface.

**Conclusions**

In this study the processing space of SVI hybrid layer formation was examined using consecutive TMA exposure sub-cycles to PA6. At lower temperatures, the hybrid layer formation thickness was enhanced as compared to higher temperature. This observation is attributed to a reaction that forms a higher density surface modification and hinders the ability of the additional reactant exposure to react with the polymer. Saturation conditions are demonstrated at low exposure temperatures and the thickness of the hybrid surface modification is shown to be as high as ~75 nm on the polymer surface. The mass uptake is highly dependent on the water content that is present in the polymer, which accounts for ~4% of the mass increase at lower temperatures and is attributed to Al₂O₃ formation within the hybrid material. The effect of the exposure time on mass gain showed that the saturation conditions are highly dependent on the amount of TMA present in the chamber. Studying different holding times with various dosing times showed a minimum of 15-20 sec of holding is needed to reach saturation. Furthermore, at different holding times, the number of TMA sub-cycles required to reach saturation is observed to be ~10. While the data presented in this work is based on TMA exposure to PA6, the SVI process has been shown to occur on a wide range of polymers exposed to various organometallic vapors. This work is important for the advancement of hybrid modification processes on polymer surface, including fibrous textiles, in which properties are desired that take advantage of individual inorganic and organic constituents.
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Figure 3.1. Schematic of the viscous flow tube type ALD reactor used for SVI experiments.
**Figure 3.2.** Evaluation of the effect of consecutive TMA sub-cycles (xNA) in an SVI process on percentage mass increase of PA6 fabrics (3 m2/g). The mass of the fabrics were evaluated before SVI processing and after processing with a 2-3 hr ambient stabilization.
Figure 3.3. Mass increase of PA6 fabrics with 10 consecutive TMA sub-cycles in an SVI process, evaluated as a function of exposure temperature. Data is shown for samples with and without a 120 °C in situ anneal prior to SVI processing.
Figure 3.4. a) QCM analysis of mass gain per cycle resulting from 10 consecutive TMA exposures at temperatures of 60, 100 and 150 °C b) Mass gain in the first cycle at 60, 100 and 150 °C is plotted as an Arrhenius-type plot.
Figure 3.5. Mass increase of PA6 fabrics with 10 consecutive TMA sub-cycles in an SVI process sequence as a function of holding time for TMA dose times of 0.2 to 2 sec.
**Figure 3.6.** Mass increase of PA6 fabrics as function of consecutive TMA sub-cycles in an SVI process at a TMA dose time of 2 sec and 0-30 sec hold periods.
Figure 3.7. FT-IR spectra of PA 6 fabrics untreated and with SVI processing (10 TMA sub-cycles) comparing a) processing at 60 °C and 150 °C, and b) SVI processing with and without an in situ anneal. An untreated PA6 spectra is provided in both (a) and (b) for comparison.
Figure 3.8. Cross-sectional TEM analysis of PA6 fibers after SVI processing at exposure temperatures of a) 60 °C, b) 90 °C, and c) 150 °C. (d) TEM image of PA6 fiber sample with SVI processing at 60 °C, after which calcination is performed to remove the organic component. All samples were treated with 60 TMA SVI sub-cycles.
Figure 3.9. Higher magnification cross sectional TEM analysis of PA6 fibers with SVI processing at exposure temperatures of a) 60 °C, b) 90 °C, and c) 150 °C. All samples were treated with 60 TMA cycles.
Figure 3.10. Mass increase of PA6 fabrics with 10 consecutive TMA sub-cycles in an SVI process as a function of holding time for TMA dose times of 0.2 to 2 sec.
Chapter 4 Formation of Novel Photoluminescent Hybrid Materials by Sequential Vapor Infiltration into Polyethylene terephthalate Fibers

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Abstract: Fibrous polyethylene terephthalate (PET) was modified by organometallic vapor exposure to form hybrid materials with unique photoluminescent characteristics. Using sequential vapor infiltration (SVI) process, elongated exposures of trimethylaluminum (TMA) to PET were examined. As the infiltration temperature increased, evidence of changes in the reaction between the organometallic vapor and the polymer was observed as well as significant changes in the infiltration depth into the polymer fiber, owing to variation
in the reaction mechanisms of the hybrid material formation. At TMA exposures of 60 °C, the mass of the polymer fiber increased by ~55 wt. %, whereas exposures at 150 °C were limited to ~25 wt. % infiltration. Photoluminescence analysis of the PET after TMA infiltration shows an intensity increase of up to ~13x and an increasing red-shift with increasing infiltration temperature, attributed to the variations in the reaction mechanism to form the hybrid modification observed through the spectroscopy analysis.

**Keywords:** infiltration (chemical reaction), luminescence, organometallic,

**Introduction**

Polymeric substrates are of interest for flexible electronic applications because of their flexibility, relative ease of production and lower cost. However many conventional polymers are insulators and their electronic properties don’t meet the requirements for device applications. Hybridization of such polymers can alter their electronic properties along with many properties which can enable those low cost conventional polymers to be used for flexible electronic applications. Hybrid materials consisting of mixed organic and inorganic constituents are showing the ability to create novel materials for applications including biosensing, electronics, optics and catalysis. Techniques to fabricate these materials including sol-gel, molecular layer deposition and layer-by-layer deposition form such hybrid materials by incorporation of organic and inorganic building blocks via chemical synthesis. An alternative approach to form hybrid materials is to modify either organic or inorganic materials with reactive precursors to incorporate the other kind of material. The process, referred to herein as sequential vapor infiltration (SVI) is like similar vapor
phase infiltration methods (such as multiple pulsed vapor phase infiltration, sequential infiltration synthesis) that utilize organometallic precursor vapors to modify polymers.

These infiltration processes, originally inspired by atomic layer deposition (ALD) on polymers, have shown three primary nucleation behaviors based on the chemical structure of the polymer. First, polymers whose surface is covered with reactive functional groups that strongly react with the ALD precursor, such as trimethylaluminum (TMA) exposed to cellulose, form a conformal coating on the polymer surface with no evidence of infiltration into the polymer. Second, ALD on polymers with no reactive functional groups such as polyethylene and polypropylene shows significant diffusion of the precursors into the polymer, particularly at high temperatures. Subsequent exposures to the secondary ALD reactant (i.e. H\textsubscript{2}O), with the organometallic precursor still in the bulk of the polymer, produces a CVD-like island growth in the subsurface of the polymer. Finally, and of importance to this work, is the observation of an intermediate state in which both diffusion and reaction can occur between the organometallic and the polymer. That is, polymers with functional groups that are susceptible to ALD reaction (i.e. C=O) have shown evidence of an organic-inorganic hybrid layer beneath the ALD inorganic thin film, resulting from the organometallic diffusing into the polymer and reacting during ALD cycling.

Each of the proposed infiltration techniques have slight differences in processing, yet they all depend on extended exposures to ensure diffusion and reaction of the precursors in the bulk polymer. In particular, SVI employs an elongated hold stage in which the organometallic is isolated with polymer substrate to increase the exposure. This hold stage can be repeated with a new precursor dose in order to extend the reaction. In practice, SVI
can produce the hybrid modification in a single exposure and hold sequence. Using infiltration methods, improvement in mechanical properties of biopolymers, enabling block copolymer lithography for formation of nanoscopic structures, and synthesis of mesoporous structures for catalysis applications has been demonstrated in the literature on many carbonyl containing polymers such as polyamides, polyesters, poly(methyl methacrylate), and spider silk. This work is intended to examine how the process behavior can enable control over the hybrid modification and for the first time demonstrate the effect that this materials processing has on the optical behavior of the polymer.

Prior work has reported SVI hybrid film formation on polyamide 6 (PA6) high surface area fabrics using trimethylaluminum (TMA) is dependent on temperature and exposure conditions, showing a maximum of ~15 wt. % increase after 10 exposure cycles of 2 s dose and 60 s hold. Here we present data on SVI of polyethylene terephthalate (PET) fibers using same precursor chemistry and demonstrate increased materials growth (up to ~55 wt. %). The influence of temperature on the change in chemical composition and structure were analyzed using Fourier Transform IR (FTIR) spectroscopy as well as cross-sectional analysis using transmission electron microscopy (TEM) and AFM-IR technique.

Finally, demonstrations of change in luminescent characteristics of the polyethylene terephthalate fibers were investigated by using Photoluminescence (PL) spectroscopy. Polyesters are commonly used in textiles, food packaging and electrical insulation due to ease of their production and high resistance to chemicals and temperature. Electroluminescence and photoluminescence of polyesters has been studied previously in
relation to the space charge that is accumulated on these polymers as result of its insulating nature. Following UV excitation, PET shows two photoluminescence bands in the blue spectrum. The band with lower energy has been attributed in the literature to the luminescence of monomers, and the higher energy luminescence is attributed to the polymer chain interactions called excimer emission. Upon alumina-hybrid infiltration, intensity of luminescence increased an order of magnitude with a slight red shift. This is attributed to the increase in excimer emission of the materials from alumina attachment to the carbonyl groups of the polymer. These significant changes in the optical properties of PET show promising capabilities of SVI in terms of optical tailoring of organic molecules. Specifically, formation of these materials on high surface area porous textile structures, can enable new means for flexible/wearable electronics, including platforms for sensing based on optical characteristics.

Experimental

SVI experiments were conducted using a custom-designed flow tube type reactor described previously. Precursors trimethylaluminum (TMA) (STREM chemicals CAS no. 75-24-1, 98% purity) and high purity water (Sigma Aldrich, biotechnology performance certified grade, CAS no. 7732-18-5) were used as obtained. Precursors delivered to the system via N₂ (Airgas National Welders, 99.999%) flow, and the pressure of the system was maintained at 1 Torr during purge cycling. Following an initial 5 minutes purge, samples were exposed to TMA cycles consisting of 0.5 s dose, 30 s hold and 30 s purge. After the TMA cycles are completed, the reactor chamber is evacuated for 5 minutes, before exposure
to H$_2$O cycles to oxidize any unreacted methyl groups with a sequence of 0.2 s dose, 30 s hold, and 30 s purge.

PET round and winged fibers were treated with SVI, and their mass gain is calculated as a weight percentage using the initial and final weight of the sample. The final mass of the samples were measured after the samples were equilibrated for approximately 2 hours. This time was found to be more than sufficient for PET because of its low inherent moisture gain (0.4%). Other polymers, such as PA-6 (4%) require longer equilibration times due to their high moisture content.\textsuperscript{141} Round fibers with average diameter of ~25 µm were obtained in the form of woven fabric form made of 100% PET 330/70 denier multifilament yarns with a 2/1 twill structure. High surface area (3 m$^2$/g) winged fibers with average diameter of 1 µm were obtained from Allasso Industries as hydroentangled nonwoven fiber mats. During SVI experiments, temperature varied from 60 °C to 150 °C and exposure conditions were varied by number of TMA cycles (1 to 90).

SEM micrographs were obtained using a Phenom G1 desktop SEM. Prior to imaging samples are sputter coated with ~10 nm gold/palladium thin films using a Quorum Technologies SC7620 Mini Sputter Coater. FTIR analysis was conducted using a Nicolet Nexus 470 FTIR spectrophotometer with attenuated total reflectance (ATR) equipment using a germanium crystal. 64 scans were performed over a range from 4000 to 700 cm$^{-1}$ and averaged for each spectrum reported. Samples for AFM-IR were prepared using Leica UC7 Ultracut diamond knife microtome. The microtome samples were prepared by first embedding the fibrous yarn samples in Devcon 2 Ton epoxy resin and then cured overnight at room temperature. The blocks were then cut to a thickness of 200-300 nm at room
temperature. All AFM-IR images and spectra were collected on a nanoIR™ instrument (Anasys Instruments) and a 450 µm-long contact mode cantilever (0.1 N/m). For TEM analysis, fibrous yarn samples were embedded into Spurr low viscosity epoxy resin (Ladd Research Industries) and then cured overnight at room temperature. A Leica Ultracut diamond knife microtome was used to cut films to ~100 nm in thickness. Films were floated on deionized water to place them on a Cu TEM grids coated with ultrathin amorphous carbon. TEM micrographs were obtained by using Hitachi HF 2000 with a 200 kV cold emission source. Energy dispersive X-ray microanalysis (EDX) was unable to be performed with a suitable spot size dimension without damaging the PET. XRD data was obtained using a Panalytical Empyrean X-ray diffractometer using a Cu anode producing K-Alpha x-rays with 1.54 Å.

Photoluminescence (PL) spectra were obtained from samples mounted in air a 30 cm grating spectrometer and a Princeton Instruments Spec-10 liquid nitrogen cooled charge coupled device detector. The light source was a continuous wave Xenon arc lamp with a monochromator used to adjust the wavelength.

**Results and Discussions**

Figure 4.1 (a) and (b) shows mass gain of both round fibers (low surface area) and winged (high surface area), respectively, measured as a function of number of consecutive SVI cycles of TMA at reactor temperatures from 60 to 150 °C. For both low and high surface area samples, a decrease in the highest mass gain is observed as the process temperature increases. This is consistent with our previous analysis of TMA SVI on PA6 fibers. In that analysis, mass gain saturation occurred for all temperatures within ~10 SVI
cycles. Here, the saturation on PET fibers shows a dramatic delay with decrease in temperature. At 60 °C a nearly linear increase of mass gain up to 90 SVI cycles is observed with no sign of saturation in mass gain. At an infiltration temperature of 90 °C, a saturation behavior is observed by around 15 cycles for low surface area fabric and 30 cycles for high surface area fabric. As the temperature increases, the number of cycles to saturation continues to decrease from 120 °C to 150 °C.

SVI is enabled by the diffusion of precursors and diffusion is limited by high reaction rates at higher temperature. Data in Fig. 4.1 supports this previously proposed reaction mechanism. At low temperatures (i.e. 60 °C), the linear growth per TMA cycle suggests diffusion of the precursor into polymer matrix is possible until all the available sites (free volume and reactive sites on the backbone of the polymer) are satisfied. However, the slope of the line at 60 °C is lower comparing to linear parts of the high temperature samples. This can be attributed to the slower diffusion rates at lower temperatures. As we increase the process temperature, a rapid increase in the mass gain is observed with a corresponding increase in initial slope. At the higher temperatures, the mass gain saturates quickly indicating that no precursor is diffusing into the samples for subsequent reaction. We think this deceleration of diffusion is a result of higher reaction kinetics, which forms a dense hybrid layer close to the surface so the penetration of the additional precursors is blocked.

The influence of the surface area Fig. 4.1(a) vs Fig. 4.1(b) is evident. The increased surface area allows for an increased mass gain. However, inspection by SEM, provide in Figure 4.2 (a-d), shows the morphology of the high surface area fibers undergo a dramatic change after SVI processing, whereas round fibers retain their shape. This coalescence of the
winged structure is observed as the number of the SVI cycles increases. Cracks are formed on the surface of the fibers along with the coalescence of the winged structure. In contrast, low surface area PET round fibers do not show fiber coalescence, but still form cracks on the surface, as shown in Figure 4.2 (e) and (f).

Figure 4.3 (a) and (b) presents FTIR-ATR results after 10 and 60 TMA SVI cycles, respectively, of round PET fibers at reactor temperatures of 60, 90, 120, and 150 °C. As shown in Fig. 4.3 (a), the peak related to the C=O group at ~1735 cm\(^{-1}\) decreases in intensity after SVI processing and generally decreases in intensity with an increase in temperature. This trend is also observed after 60 SVI cycles in Fig. 4.3 (b), although the peak intensity is much lower in comparison to the untreated control sample. This C=O feature can be considered to follow the extent of the reaction in the near surface region of the polymer.\(^{64, 154}\)

As such, the lower temperature processing results in less near surface consumption of the PET C=O functionality by the ligand exchange reactions between TMA and C=O groups as explained in the literature.\(^{64, 141, 167}\) At 10 SVI cycles, this is in agreement with mass gain analysis (Fig. 4.1(a)): initial extent of reaction is higher at increased temperatures, but it is less clearly differentiated than at higher numbers of SVI cycles.

Other than the reduction of the C=O peak intensity, there is additional spectral evidence of the formation of an organic-inorganic- hybrid structure. First, the peak emerging at ~2975 cm\(^{-1}\) is evidence of CH\(_3\) stretching, resulting from groups that form in ligand exchange reactions between the TMA precursor and the C=O group.\(^{64}\) Second, the broad peak spanning from 3000 to 3750 cm\(^{-1}\) is due to the OH groups that form by the oxidation of Al(CH\(_3\))\(_x\) ligand groups formed within the polymer matrix by the TMA polymer reactions,
during water cycles. Furthermore, Al-O interactions show up with a weak and wide peak at ~775 cm$^{-1}$ and have higher intensity at increased processing temperature.

Most interesting, are the new peaks that form in the fingerprint region, especially of the spectra obtained for 120 and 150 °C samples. After 10 SVI cycles, all samples are showing a low intensity peak at ~1610 cm$^{-1}$ which is in the literature attributed to Al-H Van der Waals interactions.$^{168-169}$ Other peaks may also be attributed to the deformation of polymer groups that are formed by addition of TMA into the polymer. The peak at ~1592 cm$^{-1}$ may be attributed to a different conformation of C=O group formed during SVI reactions as a result of CH$_3$ addition to the ester group.$^{170}$ In the literature the peak at ~1537 cm$^{-1}$ is attributed to the CCO stretch in CH$_2$CHO$^{171}$ group, a functional group whose structure is very similar to what is formed by the SVI process. Literature reports a peak location of ~1425 cm$^{-1}$ for CH$_3$COO$_2^{172-173}$ deformation or a methyl radical deformation.$^{174}$ There is also another report showing it can represent the -OH scissor group in water.$^{175}$ However, the latter is not likely since it would be expected for other samples as much as for the 150 °C sample. The intensity of these peaks for 120 and 150 °C samples increases after 60 cycle SVI whereas these peaks are still not observable for low temperature samples. This is an evidence of different reaction mechanisms for higher temperature samples.

Transmission electron microscopy was conducted on the round PET fiber cross-sections to examine the extent of the reaction into the subsurface region of the polymer at exposure temperatures of 60 °C and 150 °C, as presented in Figure 4.4. The SVI treatment at 60 °C sample shows no distinct formation of a hybrid material, which would be indicated by a high light contrast compared to the polymer. In comparison, a distinct hybrid layer
formation is observed for samples exposed at 150 °C. In addition, mechanical properties show a much more brittle material, as indicated by the cracks that are formed during the microtome cross-section preparation. Given the high mass gain of the 60 °C sample, it is predicted that the reacted vapor infiltration is more thorough and evenly dispersed into the cross-section of the fiber. Note that in Fig. 4.1 (b), the 150 °C data is discontinued at 15 cycles because samples started to come out fractured after the SVI processing and an accurate mass couldn’t be measured. The brittleness is attributed either tension created by the dense SVI layer near the surface of the fiber or to chain scission reactions in the polymer. As observed through handling, the brittleness is greater for higher temperature SVI processing on the high surface area winged fibers.

In order to understand the brittle nature of the hybrid materials observed in Figure 4.4, the effect of SVI on the structure of the polymer, was analyzed with X-ray diffraction. XRD spectra of the pristine PET and samples treated with SVI at 60 and 90 °C is given in Figure 4.5. Control samples showed three diffraction peaks at 2θ = 17, 22.5 and 25.5° corresponding to (100), (010) and (110) reflections respectively which defines the triclinic structure of the polymer as given in the literature.176-177 These peaks are observed on top of a broad peak spanning from ~5 to ~35° degrees which identifies the amorphous regions of the polymer. After SVI processing XRD spectra of the samples did not show significant changes except for a broad peak observed from ~3.5 to ~8° at both SVI treatment temperatures. These broad peaks are most likely attributed to the hybrid material formation. The broadness of the peak identifies the amorphous nature of the alumina-polymer hybrid materials and the low angle reflects the large size of the structures. The XRD data also suggests that the SVI
reactions primarily occur within the amorphous regions of the polymer and the resulting in a possibly more brittle material between the crystalline regions of the PET. However flexibility of the polymer coming from the amorphous regions present in the polymer is decreased by the addition of the AlO$_x$ to the backbone of the polymer as seen in TEM images in Fig. 4.4.

AFM-IR analysis was performed to examine the chemical constituent through the fiber cross-section in more detail. Figure 4.6 (a) provides the high wavenumber spectra of the PET round fiber treated with 60 cycle of TMA SVI at 150 °C. In the figure, three spectra are collected from each point shown in the AFM image. Of particular interest are peaks located at 3436, 2972 and 2908 cm$^{-1}$ wavenumbers. The peak at 3436 cm$^{-1}$ is likely coming from the overtone band of the C=O group in PET. This peak is not visible in FTIR-ATR analysis due to broad and strong OH peak presence. Peaks at 2972 and 2908 cm$^{-1}$ can be attributed to the anti-symmetric and symmetric stretches of CH$_2$ groups in the PET respectively. Closer to the fiber surface intensity of these peaks decreases can be indication of the more hybrid material close to the surface. In Figure 4.6 (b) provides the low wavenumber region of the sample treated at 150 °C, showing peaks at 1720, 1410, 1340, 1268, 1104 and 1020 cm$^{-1}$; each normalized to the polymer C-O stretch at 1268 cm$^{-1}$. All these peaks are attributed to the polymer functional groups that can be observed in the control sample except for 1020 cm$^{-1}$ which can due to AlO$_x$ formation in the fiber. This peak is not seen in the control sample and formed only after SVI processing. It can either be a peak directly associated with AlO$_x$ vibrational modes as reported in the literature or coming from a mode of PET that is activated by AlO$_x$ modification. Through normalization of the peaks, we are able to see that
all the peaks coming from polymer are showing similar intensities, however the C=O peak showing a sharp decrease as the analysis is performed closer to the surface. This transition point is emphasized in the spectra by showing low carbonyl amount colored as pink and rest colored green. At this point, the AFM image also shows a higher topography, which is attributed to the hardness change and corresponds to the dense surface layer observed in the TEM micrographs Fig. 4.4 (b).

In Figure 4.6 (c) and (d) high and low wavenumber spectra of the sample treated with 90 TMA cycles SVI at 90 °C, are given. At high wavenumber region we see peaks at 3436, 3064, 2968, 2920 and 2860 cm\(^{-1}\). Again, peak at 3436 cm\(^{-1}\) is attributed to the overtone band of the C=O group in PET and peak at 2968 is attributed to the anti-symmetric stretch of CH\(_2\) group in the PET. The 2908 cm\(^{-1}\) peak observed in Fig. 4.6 (a) can be observed as a shoulder on the 2920 cm\(^{-1}\) peak. Peaks at 2920 and 2860 cm\(^{-1}\) are attributed to the methyl (CH\(_3\)) stretches\(^{180-181}\) attached to the polymer backbone as a result of reactions taking place between C=O groups and TMA precursor.\(^{64, 167}\) These peaks showing higher intensity closer to the surface suggesting more TMA polymer reactions takes place closer to the surface. The low wavenumber region shows peaks at exactly at same wavenumbers as the 150 °C sample. However, all the peaks show similar intensities. Since CH\(_3\) peaks and AlO\(_x\) peak are observed, this can be attributed to a more homogeneous composition of the sample within the measured section.

To further investigate the reasons for the differences of different temperature samples spectra, the same cross-sectioned sample in Fig. 4.6 (c) and (d) is heated for 60 min at 150 °C under an ambient atmosphere. Spectra of high wavenumber and low wavenumber regions are
given in Figure 4.6 (e) and (f) respectively. In the high wavenumber region we observe that spectra are very similar to the spectra in Fig. 4.6 (a) with the peaks at 2964 and 2904 cm\(^{-1}\). The peaks observed at 2920 and 2860 cm\(^{-1}\) in Fig. 4.6 (c), disappears. This can be an indication hybrid material structure that is formed at low temperatures is forming metastable metal organic coordination complexes as suggested in the literature.\(^{167}\) Upon heat treatment these complexes transition to more stable chemistries or structures. Furthermore, in the lower energy spectra intensity of the peak at 1020 cm\(^{-1}\) is decreased at the surface. This is attributed to the change in the AlO\(_x\) structure by further oxidation of these groups.

Of high interest is the ability to create new hybrid materials characteristics within the textile construct. In this work, photoluminescence of the PET fabrics has shown significant changes upon SVI processing. Figure 4.7 shows PET round fiber, woven fabrics emit stronger photoluminescence after SVI processing when they are exposed to UV illumination. The samples processed at 60 and 90 °C samples showing similar color and intensity illumination to the eye whereas sample treated SVI at 150 °C shows green hue. Even though samples do become more rigid after SVI process, the textile is still flexible and the luminescent appearance is not changed with flexing or handling. Samples treated at higher temperatures come out of the reactor with a bright yellow color whereas low temperature samples come out with original white color. As we discussed during FTIR-ATR analysis high temperature SVI processed samples show various peaks associated with different species formation. This color change can be due to the color providing nature of some of those species. For example quinone radicals, which are known to be giving yellow color, show FTIR peaks at 1518, 1536, and 1504 cm\(^{-1}\) due to the C=O stretching mode as reported
in the literature. The FTIR peaks in the fingerprint region discussed above can be attributed to the quinone like structures.

To analyze the visible wavelength emission of the fibers, room temperature PL spectroscopic analysis at $\lambda_{\text{ex}} = 355$ nm was conducted on control fabrics and on samples treated by SVI and resulting spectra is given by Figure 4.8. The control, untreated, fabric shows peaks at 400 and 425 nm, and have been attributed in literature to monomer emission and inter chain interactions (i.e. excimer), respectively. After the SVI treatment at 90 °C, the PL intensity is increased by ~13x with a slight red shift, showing an emission band at 425 nm and a shoulder at 450 nm wavelengths. This strong emission at 425 nm can be attributed to the increased inter chain interactions as a result of Al-OH formation during SVI. Treatments at 150 °C on the other hand show ~3x increase in the PL intensity and a higher red shift then 90 °C samples with a single broad emission band at 472 nm. This shift in the emission can be seen optically in Figure 4.7 as well.

These optical responses can be explained by the difference in reaction mechanisms at different temperatures as presented in the FTIR and AFM-IR analysis. Thus, process temperature of SVI determines the chemical and physical structure of the hybrid material. Difference in photoluminescence mechanism can be caused by subtle differences in chemical species forming at the different temperatures. For example, at low temperatures metal organic coordination complexes can be formed via TMA carbonyl group reactions whereas at higher temperatures chain dissociation by TMA can be more effective, which likely results in different emission mechanisms. The difference in intensity can be explained by the lower
mass gain observed at higher temperatures (Fig. 4.1) or by the absorption of the emitted light by the color providing structures formed at high temperature SVI processing.

**Conclusions**

The effects of temperature, exposure conditions and surface area on the SVI process into PET fibers are explored. Increasing process temperature decreases the mass gain of the SVI process as a general trend. A linear mass increase with number of TMA cycles was observed at 60 °C but at higher temperatures such as 90, 120 and 150 °C initial cycles shows a rapid increase in mass gain before saturation behavior is observed. Saturation behavior becomes clearer as the temperature increases to 150 °C. This phenomenon is interpreted as the increasing temperature speeds the reaction kinetics, forming a barrier layer at the surface of the polymer that slows down the diffusion of the reactant. This idea is supported with the FTIR-ATR and AFM-IR analysis of these fibers and TEM micrographs of fiber cross sections. The structure of the hybrid materials formed during SVI is studied with XRD, which showed hybrid materials formed during SVI shows amorphous nature. Photoluminescence analysis of SVI treated PET fabrics shows the ability for tailoring the luminescent behavior of organic materials. Furthermore, the mechanism of SVI process is shown to affect the resulting material optical properties. In general, luminescence is increased by incorporation of alumina into the bulk polymer while the substrate remains flexible and porous. As a result of this work, many carbonyl containing polymers often made inexpensively and applied range of constructs (including textiles), may be enabled by SVI processing toward applications in organic/flexible electronics.
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Figure 4.1. Mass gain of a) round fibers b) winged fibers as function of number TMA cycles at temperatures varying between 60 °C and 150 °C. TMA cycles were conducted with a sequence of 0.5 s dose/ 30 s hold/ 30 s purge and H2O cycles of approximately half number of the TMA cycles were conducted with a sequence of 0.2 s dose/ 30 s hold/ and 30 s purge.
Figure 4.2. SEM micrographs of a) untreated b) 3 cycle, c) 15 cycle, and d) 30 cycle SVI treated winged fibers (WF) and e) untreated and f) 30 cycle SVI treated round fibers (RF) showing the change in the fiber morphology upon SVI treatment. All the treatments are at 60 °C.
Figure 4.3. FTIR spectra of SVI treated fabrics made of round fibers after a) 10 TMA cycles and b) 60 TMA cycles. Samples are treated under similar exposure conditions (TMA cycle: 0.5 s dose/30 s hold/30 s purge; H2O cycle: 0.2 s dose/30 s hold/30 s purge).
**Figure 4.4.** TEM micrograph of cross-section of round fibers treated with a) 90 cycles TMA SVI at 60 °C and b) 60 cycles TMA SVI at 90 °C.
Figure 4.5. X-Ray diffraction spectra of the control and samples treated with SVI at 60 and 90 °C.
Figure 4.6. AFM-IR spectra and AFM images of round fiber cross sections treated with a) high wavenumber (normalized at 2972 cm$^{-1}$), b) low wavenumber (normalized at 1268 cm$^{-1}$) 60 cycle TMA SVI at 150 °C c) high wavenumber (normalized at 2968 cm$^{-1}$), d) low wavenumber (normalized at 1268 cm$^{-1}$) 90 cycle TMA SVI at 90 °C e) high wavenumber (normalized at 2964 cm$^{-1}$), f) low wavenumber (normalized at 1268 cm$^{-1}$) 90 cycle TMA SVI at 90 °C after 1 hour heat treatment at 150 °C.
Figure 4.7. Comparison of untreated PET samples and those treated with SVI at 60 °C, 90 °C and 150 °C under a) natural lighting and b) under UV illumination.
Figure 4.8. Room temperature PL spectra conducted on control fabrics and 90 and 150 °C SVI treated fabrics excited at $\lambda_{ex} = 355$ nm.
Chapter 5 Atmospheric Pressure Synthesis of Photoluminescent Hybrid Materials by Sequential Organometallic Vapor Infiltration into Polyethylene terephthalate Fibers


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Abstract: Exposing a polymer to sequential organometallic vapor infiltration (SVI) under low pressure conditions can significantly modify the polymer’s chemical, mechanical and optical properties. We demonstrate that SVI of trimethylaluminum (TMA) into polyethylene terephthalate (PET) can also proceed readily at atmospheric pressure, and at 60 °C the extent of reaction determined by mass uptake is independent of pressure between 2.5 Torr and 760 Torr. At 120 °C, however, the mass gain is 50% larger at 2.5 Torr relative to that at 760 Torr, indicating that the precursor diffusion in the chamber and fiber matrix decreases at higher source pressure. Mass gain decreases in general as the SVI process temperature increases both at 2.5 Torr and 760 Torr attributed to the faster reaction kinetics forming a
barrier layer which prevents further diffusion of the reactive species. The resulting PET/Al-Ox product shows high photoluminescence compared to untreated fibers. A physical mask on the polymer during infiltration at 760 Torr is replicated in the underlying polymer, producing an image in the polymer that is visible under UV illumination. Because of the reduced precursor diffusivity during exposure at 760 Torr, the image shows improved resolution compared to SVI performed under typical 2.5 Torr conditions.

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**Introduction**

Organic-inorganic hybrid materials have drawn attention for advanced electronics, biotechnology, optics and catalysis applications. Sequential vapor infiltration (SVI) is one of the techniques where hybrid materials are formed within organic materials by exposure to an organometallic precursor vapor. The technique is inspired by observations from atomic layer deposition (ALD) on polymers with moderate reactive functional groups (i.e. C=O) toward the ALD precursors. During ALD, an organic-inorganic hybrid material layer is observed at the interface of the inorganic film and polymer substrate. Motivated by these hybrid materials formation, techniques using the idea of extended ALD precursor exposures to form hybrid materials such as multiple pulsed vapor-phase infiltration (MPI), sequential infiltration synthesis (SIS), and SVI have been proposed. While the techniques vary by slight differences in processing, to all incorporate a common elongated exposure in order to enhance the infiltration. Biomolecules such as spider silk and collagens processed with MPI demonstrated improved strength by this hybridization. SIS has been studied for the formation of nano-patterning by selective infiltration into self-
assembly block copolymers composed of one polymer that can react with the ALD precursor to form hybrid material and the other is inert towards the same precursor. The unreacted polymer is removed by plasma etching process while hybrid material remains and hence nano-sized patterns are created.\textsuperscript{89, 95-96, 98}

SVI utilizes a series of precursor exposures in a separated manner different from other infiltration methods. An exposure consists of an organometallic vapor dose into a reactor volume, whereafter the vapor is held in the reactor for a period of time and then purged from the reactor volume with inert gas. This dose-hold-purge can be repeated to increase the overall exposure of the organometallic vapor within the reactor. Afterwards, an oxidation agent (i.e. H\textsubscript{2}O) is also cycled in same sequential order to oxidize the material.\textsuperscript{141} The SVI mechanism has been studied as a function of temperature, exposure conditions and surface area on C=O containing polymers such as polyamides and polyesters.\textsuperscript{141, 183} SVI on PET and polybutylene terephthalate (PBT) fibers have been studied to create mesoporous hybrid materials for catalysis applications.\textsuperscript{64} Also, SVI on PET fibers showed the ability to tune optical properties of organic materials by formation of PET-alumina coordination complexes.\textsuperscript{183}

Sol-gel is the common technique for organic-inorganic hybrid material formation, in which precursors reacts in an appropriate solvent.\textsuperscript{148} Solvent removal during the sol-gel process adds time and expense. One key advantage of SVI is that it utilizes precursors in the vapor phase thus allowing dry processing of the polymers and eliminates liquid solvents post processing. Furthermore, hybrid materials formation can be performed on a polymeric material that is already shaped as film or fiber. Therefore, the integration of the SVI process
into polymer production lines, which is known for high throughput production, can produce hybrid materials or modify polymers with high throughput rates. Previous studies have shown that shape of the pristine polymeric material is mostly preserved even after high temperature calcination process plasma etching.\textsuperscript{64, 95} This offers SVI additional advantages from a materials processing perspective since polymers may be molded into more complex shapes and structures that can subsequently be modified with the hybrid materials afforded through SVI. To this point, one major limitation of the SVI process is that it has been only conducted under low to medium vacuum conditions with batch processing, which reduces the materials production speed. It is highly desired to have atmospheric pressure conditions, to apply the process for roll-to-roll manufacturing of hybrid materials. Operating at atmospheric pressure provides the opportunity to eliminate the time needed for reactor evacuation and pressure control, and facilitates integration for in-line manufacturing. This work provides the first investigation of the SVI mechanism as a function of pressure and aims to investigate feasibility of the roll-to-roll SVI under atmospheric pressure conditions. PET is one of the most common polymers used in textiles, packaging, and electrical insulation applications. Due to its high chemical and thermal resistance and low moisture permeability, PET has shown application as a substrate for flexible electronics.\textsuperscript{184-186} With respect to optical applications, PET shows a weak photoluminescence by absorption of UV light both in solid state and in solution due to the presence of pi electrons on the polymer backbone.\textsuperscript{165-166, 187} Prior work by our team has shown SVI processing of PET fibers to increase the photoluminescence intensity by an order of magnitude.\textsuperscript{183} Here along with the mechanistic analysis of SVI process at various pressures we also demonstrate advantages for atmospheric
pressure SVI to selectively modify optical properties of the substrate with improved resolution.

**Experimental**

PET fabrics were obtained with 2/1 twill woven structure, made of 100% PET round fibers in a 330/70 denier multifilament yarn and were used as received. Fabrics are cut into 2x1” pieces and the 2-3 yarns from each side is pulled out to make sure they are not separated during later handling of the samples, hence the initial mass for the samples remain same. Fabric samples are weighed prior to SVI processing and they were in the range of 0.25-0.3 g. SVI treatments were conducted in a custom made viscous flow type ALD reactor described previously that has special system design that allows variable pressure operation up to 760 Torr.\(^{188-190}\) The ability of precursor delivery at pressures higher than the vapor pressure of the precursor is enabled by pressurization of a hold cell on the gas delivery line. The evacuated hold cell is filled with the precursor or oxygen source (charge time) and then pressurized with N\(_2\) (pressurizing time). Afterwards, the hold cell is opened to the reactor through the main N\(_2\) line (dose time). In order to conduct the SVI hold steps (hold time), a pneumatic gate valve is added to the end of the reactor, either on vacuum side or atmospheric pressure exhaust side depending on the SVI operation pressure. The gate valve is opened during the reactor purging after each hold step (purge time).

Following the sample loading, the reactor chamber was evacuated for 5 minutes by opening the pump side of the exhaust before every run. The chamber was then purged at the operation pressure for 10 minutes. To achieve 2.5 Torr operation pressure, the N\(_2\) flow rate was 0.5 slm and for 760 Torr the flow rate was 5 slm. SVI process is conducted by first
cycling trimethylaluminum (min. 98%, Strem Chemicals) in a dose/hold/purge sequence, followed by H₂O (deionized) cycles in the same sequence. An inert purge step for 5 minutes is conducted in between TMA and H₂O cycles. After the process is completed, 2 minutes of purging is conducted and the samples are removed to ambient conditions. For the mass gain calculations, the PET samples were weighed before loading to the reactor and after sitting at ambient conditions for 30 minutes after infiltration. For masking during the SVI processing, premium vinyl adhesive films (Silhouette) were cut to a desired pattern using a Silhouette Cameo die cutting tool. The adhesive-backed films were stuck on the fabric surface and pressed manually.

In order to analyze the changes in chemical structure of the fibers, Fourier transform infrared (FTIR) spectra of the untreated and treated fabrics are obtained using a Nicolet Nexus 470 FTIR spectrometer with a germanium crystal attenuated total reflectance (ATR) attachment. Samples were placed on a germanium crystal and a force normal to the crystal surface is applied using a 3 mm diameter metal tip. Each FTIR-ATR measurement consisted of 64 scans from 700 to 4000 cm⁻¹.

**Results and Discussion**

In order to be consistent between low pressure and high pressure conditions we first investigated the optimum dosing conditions that allowed for consistency in the amount of TMA delivered to the reactor. Since the hold cell is always charged with TMA up to 18 Torr, the pressurizing and dose times need to be adjusted to ensure that a maximum amount of TMA molecules are delivered to the reactor under both pressure conditions to achieve a saturated reaction between the sample and TMA (as observed by mass gain). For an ideal
gas, the known hold cell temperature, volume and pressure gives the number of TMA moles in the hold cell, \( n \sim 2.8 \times 10^5 \). At 2.5 Torr, 0.5 s \( N_2 \) charge and 0.5 s dose conditions are sufficient for saturation for SVI at 120 °C. At 760 Torr and 120 °C, a 10 s \( N_2 \) charge and a 6 s dose is required for saturation. Furthermore we investigated effect of purge time at different temperatures, with 6 s and 35 s purge at 2.5 Torr and with 15 s and 45 s at 760 Torr. At both pressures longer purge times resulted in slightly lower mass gain values. In order to minimize effect of left over TMA in the reactor we fixed the purging time to >35 s. We therefore fixed these exposure conditions at the temperature and pressure values studied.

Figure 5.1 (a) and (b) presents the mass gain observed at 2.5 Torr and 760 Torr, respectively, as a function of number of TMA cycles in a temperature range of 60-150 °C. At 2.5 Torr, highest mass gain values are observed at 90 °C with a linear increase as a function of number TMA cycles. At 60 °C slightly lower mass gain is observed, also with a linear trend. However as the temperature increases the mass gain deviates from linearity as a higher mass gain is observed at 120 °C than at 150 °C. In Fig. 5.1 (b) 760 Torr samples show a pronounced mass gain decrease as the process temperatures increases. At 60 and 90 °C a linear mass gain increase is observed and with increasing temperature a saturation behavior begins to be observed. It is interesting to note that the mass gain trend at 60 °C is independent of pressure and as the temperature increases the difference due to pressure becomes clear. This result is important for determining the feasibility of the process for atmospheric pressure. The scale of the mass gain is very similar for both pressures (between 2-10 wt. %), which is promising for the application of the SVI process at higher pressures and low temperatures.
In Figure 5.2, the mass gain of the PET fabrics after 60 TMA SVI cycles at 2.5 and 760 Torr is compared as a function of temperature. The first observation is the marginal difference in mass gain of the samples processed at 60 and 150 °C. At 2.5 Torr, mass gain is highest at 90 °C whereas the maximum mass gain occurred at 60 °C at 760 Torr. Mass gain of the samples at 2.5 Torr and 760 Torr shows a ~3 wt. % difference for 90 °C and 120 °C samples. This behavior is a consequence of the process being a combination of precursor diffusion along the reactor, fiber matrix (between fibers), and polymer bulk as well as chemical reactions taking place between precursor and polymer functional groups at the surface and in the bulk of the polymer. Reaction rate is only affected by temperature, for constant TMA partial pressure. As discussed above we optimized the dosing conditions such that it can be anticipated that the amount of TMA delivered into chamber doesn’t change. However, diffusion of the precursor in the gas phase is affected by both temperature and pressure, which will affect the precursor delivery speed to the surface of the fibers. As discussed in previous studies,\textsuperscript{54, 141, 183} for constant pressure the reaction rate between precursor and the polymer is reduced at low temperatures which permits diffusion, and is observed as higher mass gain in the sample. This statement remains true for this study as at 60 °C for both pressures showing that diffusion of the TMA in N\textsubscript{2} is changing with the pressure although the diffusion in the bulk polymer is dependent on temperature mainly. As the temperature increases, it is expected that the reaction rate between the precursor and C=O groups increases, as well as the diffusion of the TMA in N\textsubscript{2} and polymer. While we see an increase in mass gain at 2.5 Torr, mass gain slightly decreases at 760 Torr. Considering the diffusion of the precursor in polymer matrix is primarily dependent on the temperature, we
can attribute this difference to the pressure dependency of the precursor diffusion in N\textsubscript{2}. Faster diffusion will keep the surface concentration of TMA higher at 2.5 Torr resulting in higher mass gain. Furthermore, faster reaction kinetics starts to show effect at 760 Torr which can lead to a barrier layer at the close to the surface and result in less mass gain. As the temperature increases to 120 °C, mass gain decreases at both pressures are an indication that the reaction rate starts to dominate over the diffusion. Finally, as the process temperature reaches 150 °C, the reaction dominates the diffusivity and the barrier is formed prevents the added diffusion and both pressures gives similar mass gain results. However the evolution of the mass gain by increasing number of TMA cycles is very different for different pressures as can be seen in Fig. 5.1. It can be seen that at low pressure this barrier layer starts to form at initial cycles whereas at high pressure it forms gradually. This can be attributed to slower kinetics at the surface at high pressures due to the lower partial pressure of the precursor as a result of slower diffusion.

To examine the reactivity of the TMA and PET as a function of pressure and temperature, FTIR analysis was conducted on samples using an attenuated total reflectance (ATR) set up, the spectra of which are provided in Figure 5.3. All spectra show two common features, independent of the SVI temperature and pressure that are related to the TMA-PET reaction, and have been previously determined in literature.\textsuperscript{64, 141, 167, 183, 191} The first feature is the peak at 1716 cm\textsuperscript{-1} that upon SVI processing is decreased due to the ligand exchange reaction taking place between TMA and C=O groups. The second feature is a broad peak from 3000 to 3600 cm\textsuperscript{-1} wavenumber, which is attributed to the formation of OH groups by oxidation of Al-CH\textsubscript{3} groups during water exposures.
As an indication of the reaction extent in the probing depth of the ATR setup, we calculated the consumption of the C=O peaks in Figure 5.3 following: Carbonyl Consumption (\%) = 100 \times \frac{\text{Peak Intensity}_{(\text{control})} - \text{Peak Intensity}_{(\text{sample})}}{\text{Peak Intensity}_{(\text{control})}}.

In Figure 5.4 (a) and (b), the C=O consumption of the SVI treated samples are provided as a function of temperature at 2.5 Torr and 760 Torr respectively. After 30 cycles at 2.5 Torr (Fig. 5.4 (a)), a maximum consumption of C=O peak is observed for the 120 °C sample followed by 90, 150 and 60 °C respectively. In contrast, the mass gain analysis in Fig. 5.1(a) is quite different than the ATR analysis. Recall that in the mass gain analysis the samples processed at 60, 120 and 150 °C samples show similar mass gain and the 90 °C sample shows higher mass gain. The difference in the analysis can be attributed to the surface sensitivity and ultimate probe depth is limited in the ATR method. This surface sensitivity provides important inferences as to the characteristics of the SVI materials modification to the PET at different pressures. First, the discrepancy in the relative magnitude of the mass gain and C=O consumption at 120 °C can be attributed to the reaction occurring close to the surface of the PET fiber. At low temperatures, the higher mass gain means that precursor diffuses more into the material and the consumption of the C=O groups close to the surface, is lower. After 60 cycles at 2.5 Torr, the trends for mass gain and ATR analysis of the C=O consumption changes. As Fig. 5.4 (a) shows, a marked decrease in the C=O concentration is observed at all temperatures except 60 °C. Even though after 60 cycles of SVI the mass gain increased significantly at 60 °C, the C=O concentration (at the surface) is not considerably higher than 30 cycle SVI. In comparison, at all other temperatures, the C=O peak is nearly
all consumed. This can be interpreted that the surface is nearly saturated with AlO₄ at higher temperatures.

A similar analysis is performed for the samples processed at 760 Torr, as provided in Figure 5.4 (b) for 30 and 60 SVI cycles. After 30 cycles, the highest C=O consumption occurs at 150 °C then 90, 120 and 60 °C respectively. In comparison, mass gain of 150 °C sample is slightly lower whereas other temperatures are very similar. As compared to the 2.5 Torr, the 30 cycle C=O consumption values in Fig. 5.4 (a), show a wider dispersion then 760 Torr samples. This suggests that the change of diffusivity of the precursor shows little dependence on temperature at high pressures and much higher dependence at low pressures. After 60 cycles, the ATR spectra in Fig. 5.3 (d) suggests that all the samples have similar C=O peak intensities. However, mass gain of the samples increases as the processing temperature decreases. Once more by comparing to the mass gain, it can be observed that diffusivity of the TMA in the samples is more temperature dependent at low pressures.

In order to support the discussion above of the operating pressure effect on TMA diffusion along the reactor and consequently its concentration at polymer surface, diffusion coefficients of TMA in N₂ is calculated using the equation suggested by Fuller et al.¹⁹² as derived from Chapman–Enskog.

\[
D_{\text{TMA}-N_2} = 10^{-8}T^{1.75} \left( \frac{1}{M_{\text{TMA}}} + \frac{1}{M_{N_2}} \right)^{\frac{1}{2}} \frac{1}{p \left( (\Sigma_{\text{TMA}} v_1)^{\frac{1}{3}} + (\Sigma_{N_2} v_1)^{\frac{1}{3}} \right)^{\frac{1}{2}}}
\]
where $T$ is the gas mixture temperature, $p$ is the total pressure, $M$ is the molecular weight of the gas components, and $v$ is diffusion parameters considering the molecule structure of the diffusing species.

Calculated diffusion coefficients of TMA in $N_2$ as a function of temperature at the low and high pressures during the hold step, 14 and 760 Torr respectively, are given in Figure 5.5. At higher pressure, the diffusion coefficients show significant lower values comparing to low pressures. Therefore, the overall mass gain at high pressure is expected to be lower than that observed at lower pressure. At lower pressure, TMA molecules have higher diffusion in $N_2$ along the reactor and between fibers than at atmospheric pressure. This is especially true at lower temperatures, where at 60 °C the time required to diffuse one centimeter is ~0.04 sec at low pressure and ~2.04 sec at 760 Torr. The diffusion times were calculated based on the equation derived from Fick’s first law as calculated by Mousa et al.\textsuperscript{189} Due to the faster diffusion along the reactor and between fibers at low pressure, a constant TMA partial pressure is maintained at the polymer surface, especially at high temperature, while a much lower TMA partial pressure is expected at polymer surface at atmospheric pressure. The TMA molecules that will react with the polymer surface will not be quickly substituted by new TMA molecules at atmospheric pressure due to the very slow diffusion rate along the reactor and between fibers. Such low TMA partial pressure at polymer surface will consequently lead to low TMA diffusion through the polymer bulk due to the low TMA concentration gradient between polymer surface and bulk.

It can also be noted from Fig. 5.5 that the change in diffusion coefficients with temperature at 760 Torr (0.74 cm$^2$/sec at 150 °C to 0.49 cm$^2$/sec at 60 °C) is much lower than
the change at low pressure (40.4 cm$^2$/sec to 26.6 cm$^2$/sec). The difference in TMA diffusion coefficients is a good estimate for the difference in the precursor diffusion through the polymer. As noted earlier, the higher the diffusion coefficient, the faster molecules will diffuse along the reactor and between fibers, thus maintaining constant high TMA partial pressure at the polymer surface and consequently higher diffusion. If that is the case, then the difference in diffusion coefficients shown if Fig. 5.5 can explain the temperature dependence of mass gain observed in Fig. 5.1 and Fig. 5.2. An increase in temperature from 60 °C to 90 °C at 2.5 Torr shows an increase in mass gain as a result of the higher TMA diffusion in the polymer. However for the same temperature values at 760 Torr, the mass gain is low as a result of a small increase in the diffusion coefficient. As the temperature increased to 120 °C and 150 °C, a decrease at both high and low pressures is a result of change in reaction rate between the polymer and the precursor rather than change in diffusion coefficient. Higher reaction rates at these temperatures, leads to formation of a barrier layer close to the fiber surface, which eventually reduces the diffusion of the precursor. Samples treated at 150 °C, show similar mass gain and C=O consumption in the FTIR spectra at both pressures which is attributed to the reaction rate being the primary factor that determines the mass gain values at this temperature.

While it has been shown that the lower diffusion of TMA through the polymer matrix at high pressure affects the mass uptake, the diffusion in the fiber matrix (between fibers) will also be altered. We investigated the effect of TMA diffusion through the fiber matrix by noting the percentage decrease in mass uptake after masking ~82% of the sample upper
surface. The change in mass uptake due to masking was noted by comparing the values for masked and bare samples, following:

\[
\text{Change in mass uptake}_{\text{masking}} = \frac{\text{Mass uptake}_{\text{bare}} - \text{Mass uptake}_{\text{masked}}}{\text{Mass uptake}_{\text{bare}}} \times 100
\]

The samples were masked using a film with a vinyl adhesive and subsequently treated with SVI at different pressures. The sample processed at low pressure at 60 °C with 30 TMA cycles showed ~20% lower mass uptake compared to the unmasked sample. On the other side the masked sample processed under similar conditions but at high pressure (low TMA diffusion) showed ~80% lower mass uptake as compared to the unmasked sample. The lower TMA diffusion through the fiber matrix at higher pressure may have strategic benefits in patternning. To demonstrate the diffusion differences at low and high pressures, the pattern resolution of masked fabric was investigated. As previously demonstrated, SVI of TMA can induce an increase in the photoluminescence of PET. Optical images of the treated fabrics with and without UV illumination are provided in Figure 5.6. It is observed that all of the treated samples do not show any indication of the patterned SVI process under normal light conditions. When the samples are exposed to UV light in dark room, a photoluminescent pattern appears, as observed in Fig. 5.6 (a-d). The resolution of the luminescent pattern is a direct indicator of the diffusion behavior of the TMA into the fiber matrix as pressure is altered. The sample treated at 2.5 Torr and 60 °C is not readable because precursor reached the masked sites because of its high diffusivity at low pressure. By increasing the pressure to 760 Torr, the resolution of the pattern is greatly improved due to the lower diffusion into the masked regions because of the low precursor diffusion.
Assuming an infinitely large mask on top of a fabric surface on which there is a finite opening for precursor diffusion into the substrate; the cases of ideal, low, and good resolution are given schematically in Figure 5.7. For best pattern resolution, precursor should diffuse into the fiber matrix through only the exposed part of the mask. Penetration depth through the fiber matrix should also be very limited and hybrid modification happens only in the fibers close to the surface (Fig. 5.7 (a)). For the demonstrated masked sample at 2.5 Torr, masking is limited to small areas under the label and precursor diffuses beyond the pattern definition and the resolution is very low (Fig. 5.7(b)). At 760 Torr, diffusion coefficients are much lower and the masking is significantly more effective (Fig. 5.7 (c)). Limited and very low diffusion through the pattern definition results in better resolution. The ability to have fine photoluminescent patterning using the SVI process at atmospheric pressure has the potential for unique applications in flexible electronics and protective identification applications.

Conclusions

This research demonstrates the mechanistic differences for the synthesis of hybrid materials formed via sequential vapor infiltration of TMA at vacuum and atmospheric pressure. Results showed that SVI can be conducted at atmospheric pressures which very important for utilization of the process for roll-to-roll polymer material (fiber and film) modification applications. Differences in the extent of infiltration into the polymer matrix, as determined through mass gain and FT-IR analysis, are related to the precursor diffusion in N₂ along the reactor and between fibers as well as its diffusion through the polymer and the reaction rate with the functional groups on polymer surface and bulk. The much slower diffusion of TMA in N₂ at atmospheric pressure, leads to lower TMA partial pressure at the
polymer surface and thus lower diffusion rate through the polymer bulk as compared to processing under lower pressure. Also, at higher temperatures, faster reaction kinetics leads to the formation of a barrier hybrid layer that prevents the reactants diffusion into and through the samples resulting in lower mass gain values in general. Finally, the effect of diffusion through the fiber matrix (between fibers) on the ability to pattern the photoluminescent behavior of the hybrid materials is shown improved with increasing pressure. Patterns created at higher pressure showed more defined edges, which shows great advantage for the feasibility of the pattern-based roll-to-roll processing of SVI.

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Figure 5.1. Mass gain of samples treated with SVI at a) 2.5 Torr and b) 760 Torr as a function of number of TMA cycles at various process temperature.
Figure 5.2. Comparison of mass gain for samples treated by SVI process with 60 cycles of TMA at 2.5 and 760 Torr for process temperature between 60 °C and 150 °C.
Figure 5.3. FTIR spectra of samples treated with SVI a) 30 cycles, b) 60 cycles at 2.5 Torr and c) 30 cycles, b) 60 cycles at 760 Torr for process temperature between 60 °C and 150 °C.
Figure 5.4. Consumption of C=O peak in FTIR spectra as function of temperature after 30 and 60 cycle SVI treatment at a) 2.5 Torr and b) 760 Torr.
Figure 5.5. Calculated diffusivity values of TMA molecules in N$_2$ as a function of pressure at 60, 90, 120 and 150 °C.
Figure 5.6. Optical images of samples masked during 30 cycle TMA exposure SVI experiments at 60 °C at 2.5 Torr ((a) and (c)) and 760 Torr ((b) and (d)) under normal light ((a) and (b)) and UV illumination ((c) and (d)).
Figure 5.7. Schematic of hybrid materials formation through the fabric cross-section in the case of a) ideal masking, b) low resolution masking at low pressures, and c) good resolution masking at high pressures.
Chapter 6 Organometallic Exposure Dependence on Organic-Inorganic Hybrid Material Formation in PET and PA6 Polymer Fibers

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Abstract: The effect of exposure conditions and surface area on hybrid material formation during sequential vapor infiltrations of trimethylaluminum (TMA) into polyamide 6 (PA6) and polyethylene terephthalate (PET) fibers are investigated. Mass gain of the fabric samples after infiltration was examined to elucidate the reaction extent with increasing number of sequential TMA single exposures, defined as the times for a TMA dose and a hold period. An interdependent relationship between dosing time and holding time on the hybrid material formation is observed for TMA exposure PET, exhibited as a linear trend between the mass gain and total exposure (dose time x hold time x number of sequential exposures). Deviation from this linear relationship is only observed under very long dose or hold times. In comparison, amount of hybrid material formed during sequential exposures to PA6 fibers is found to be highly dependent on amount of TMA dosed. Increasing the surface area of the
fiber by altering its cross-sectional dimension is shown to have little on the reaction behavior but does allow for improved diffusion of the TMA into the fiber. This work allows for the projection of exposure parameters necessary for future high-throughput hybrid modifications to polymer materials.

**Introduction**

Organic-inorganic hybrid materials are of interest for a variety of applications including electronics, catalysis and optics. Traditional and nontraditional techniques such as sol-gel and molecular layer deposition, have been investigated in the literature for formation of such materials. Sequential vapor infiltration (SVI) is a recently proposed technique that utilizes extended exposures of atomic layer deposition (ALD) precursors that have an affinity to diffuse and react into the subsurface of a polymer. Elongated and separated exposures of organometallic precursors results in infiltration into the polymer matrix and reaction with available functional groups thus forming hybrid structures rather than forming a thin film on the surface as in ALD. SVI and similar techniques (i.e. sequential infiltration synthesis and multiple pulsed vapor-phase infiltration) has been investigated on polyamides, polyesters, polyacrylates, and biopolymers. The hybrid materials formed with these infiltration methods have shown opportunities for mechanical strengthening of fibers, fabrication of patterned nanostructures, sacrificial template formation for high surface area structures, and fabrics with enhanced photoluminescence.
The infiltration methods are conducted in batch reactors, as seen in Figure 6.1 (a), designed traditionally for ALD-type processing under controlled vacuum conditions. Future development of high-throughput processing in a roll-to-roll approach to SVI with cycling precursors can be envisioned as seen in Figure 6.1 (b) since the processing includes sequential exposures to a single precursor reactant at a time. Moreover, the technique can be more simply employed if a single elongated exposure is employed as seen in Figure 6.1 (c). Prior work by our team has examined fundamental process parameters that influence the hybrid formation in a range of polymers including amides, esters, and acrylates.\textsuperscript{141, 183, 194, 201} In general, precursor exposure at lower temperatures results in higher mass gain values observed comparing to higher temperatures, as a result of the slower reaction kinetics between TMA and polymer functional groups.\textsuperscript{141, 183, 194} As the process temperature increases, it is observed that a hybrid material layer forms at initial stages of the exposure close to the surface of the fibers, which prevents further diffusion afterwards.\textsuperscript{141, 183} Processing at atmospheric pressure, a significant enablement of high-throughput processing, has shown that the diffusivity of the precursor is reduced, resulting in slightly reduced mass gain particularly at higher temperatures.\textsuperscript{200} Hybrid materials formation at low temperatures at atmospheric conditions is comparable to at observed under vacuum.

This study serves to investigate the effect of the exposure condition on TMA SVI into PET and PA6 fibers comparatively, and represents a major advancement in determining the feasibility of high-throughput SVI process. Similar to the previous studies, the mass gain of the samples is employed as an indication of the reaction extent during SVI process. We report here the impact of that dosing, holding and number of sequential exposure cycles has
on the hybrid materials modification to polymers. These results provide the exposure conditions necessary in a high throughput process to achieve a desired modification.

**Experimental**

SVI treatments were done at 60 °C in a heated wall flow tube ALD reactor described elsewhere. Trimethylaluminum (Strem Chemicals, Inc., CAS#: 75-24-1, 98% purity) was used as aluminum source and high purity water (Sigma Aldrich, biotechnology performance certified grade, CAS#: 7732-18-5) was used as the oxygen source. Precursors were delivered into the reactor using ultra high purity N\(_2\) (Airgas National Welders, 99.999%), after filtering with an Entegris Gatekeeper inert gas purifier. PET round fibers were obtained in the form of woven fabric with 2/1 twill structure, consisting of 330/70 denier multifilament yarn. PET and PA6 high surface area winged fibers were obtained in the form of hydroentangled nonwoven fiber mats from Allasso Industries and used as received. 2”x1” cut fabric samples were placed into the reactor followed by 5 minutes of N\(_2\) purge. Afterwards, samples were exposed to TMA cycles and the reactor was evacuated for 5 minutes after completion of TMA cycles. After a N\(_2\) purge for 2 minutes, water cycles were conducted and the samples were finally removed from the reactor. Weight of the samples were recorded before and after SVI process. To eliminate any effect of moisture regain by the fibers, samples were weighed after waiting 2-4 hours after removal from the reactor. Percent mass gain values are calculated by the ratio of mass increase to the initial weight.

**Results and Discussions**

The mass gain of PET winged and round fibers after SVI is provided in Figure 6.2 as a function of number of TMA cycles at 60 °C. It is very interesting that both of the fibers
demonstrate a linear relationship between mass gain and number of cycles. When we investigate the slopes, high surface area winged fibers show 0.8% mass gain per cycle whereas round fibers are showing 0.24% mass gain per cycle. Surface area of winged fibers given by the company is \( \sim 3 \text{ m}^2/\text{g} \) and the calculated surface area of the round fiber fabric is about \( \sim 0.1 \text{ m}^2/\text{g} \). It is obvious that surface area has an effect on the mass gain of the fiber but it is not the only factor affecting the mass gain.

In order to evaluate the effect of holding time during TMA cycles, we conducted SVI experiments at 60 °C with 0.5 s dosing time. The mass gain values, provided in Figure 6.3, shows that increasing the holding time of each cycle from 30 s to 60 s, does not change the linear relationship of the mass gain vs. number of cycles but slope of the line is increased as the holding time increased. The slope of 60 s hold data is approximately double the slope of 30 s hold data. Mass gain of the sample, which is related to the reaction extent during SVI process, is linearly dependent on holding time under this dosing condition. This linear correlation of holding time suggests that TMA in the chamber during the hold process is not fully infiltrated into the material. It also indicates that the diffusion rate is constant in this experimental boundary, which is expected since the temperature and the concentration of TMA at the surface remains constant.

In Figure 6.4 we change dosing time of the TMA cycles with 30 s and 60 s holding time to determine the relation between the dosed TMA amount and the mass gain. By increasing the dose time we increase the initial TMA concentration in the chamber available for diffusion. All four samples sets are showing an increase in mass gain as the dosing time is increased. However the pattern of the increase is changing with holding time. Both 10 cycle
and 60 cycle samples with 30 s holding time show a linear increase in mass gain as the dosing time increases. As the holding time increases to 60 s the mass gain starts to show a deviation from linearity with increasing TMA exposures, which indicates that longer holding times provides adequate time to saturate the diffusion. In totality, these preceding results are an indication that dosing time and holding time are interrelated when it comes to defining the saturation conditions of TMA infiltration in an SVI process. Furthermore these effects can be better understood by the solution of the Fick’s second law for diffusion where concentration of the diffusing species at the surface ($c_s$) is constant over time.\textsuperscript{202}

\[
\frac{c_x - c_0}{c_s - c_0} = \left(1 - \text{erf}\left(\frac{x}{2(Dt)\frac{1}{2}}\right)\right)
\]

where $c_x$ is the concentration the diffusing gas at point $x$ within the bulk of the substrate and $c_0$ is concentration at the point $x$ at $t=0$. $D$ is the diffusion coefficient and $x$ is the distance from the surface. Fick’s second law shows that as the concentration at the surface increases, the concentration in the bulk $c_x$ increases (i.e. results in higher mass gain) in time. As the time increases, the error function goes to zero and concentration at point $x$ again increases. Consequently in Fig. 6.4 we only see the deviation from linearity in mass gain with longer dose (i.e. surface concentration) and hold times.

In traditional ALD processing, exposure can be quantified in Langmuir, or Torr·sec, evaluated most often by the dose time and pressure rise in the reactor area around the sample. This evaluation serves the useful purpose of defining saturation quantities required for ALD growth, and in effect can be used as a point of reference for researchers. In the case of the SVI process, a similar ‘exposure’ to TMA can be defined by the combined multiplication of
the dose time, hold time and number of TMA singular exposures. To see the relationship between all the parameters affecting the exposure of the precursor, we calculated the product of dosing time, holding time and number of TMA cycles. In Figure 6.5, the product term is presented vs. mass gain. In this calculation, dosing time is considered to be directly proportional to the amount of TMA present in the system, which is reasonable considering that the residence time of the reactor is ~8 seconds (as calculated by the flow rate and the pumping speed). In Fig. 6.5 (a), the initial part of the PET mass gain curve follows a linear pattern, which deviates from linearity as the dosing time increased 1 s suggesting that there is a limit after which effect of TMA concentration diminishes. This plot also shows that at 60 °C, exposure time can be defined as product of number of cycles and holding time. It is observed that a 60 s hold x 30 cycles and 30 s dose x 60 cycles show similar mass gain values when the dosing times are same. This indicates that the mass gain of the PET can be simply adjusted by controlling both the holding time of the precursor and the number of precursor cycles. Likewise, using processing conditions of 0.5 s dose x 60 s hold x 60 cycles gives similar mass gain values as 1 s dose x 30 s hold x 60 cycles. It is important to make note that this relationship is dependent on the polymer that is being infiltrated upon. As an example, mass gain as a function of SVI exposure upon PA6 fibers with winged fiber cross section is provided in Fig. 6.5 (b). For PA6, the mass gain is primarily dependent on amount of the precursor available in the reactor. It was also shown previously that mass gain of the PA6 samples saturated after 10 TMA cycles independent of the temperature of the process.\textsuperscript{141} This difference in the mechanism can be attributed to the different reactivity of the functional groups of the polymers; PET has C=O on the ester group, whereas PA6 has a C=O group on
the amide group. This key difference results in amide groups being able to form hydrogen bonds between polymer chains, and are therefore a limiting factor for the hybrid forming reactions. Ester groups are not expected to be part of such interactions. From this data set we also observe that the initial period of the exposure results in the formation of hybrid material that prevents further diffusion of the precursor.

The prior analysis aids in defining the characteristic exposure scales required to achieve a roll-to-roll process to impart a dedicated degree of hybridization to a polymer surface. In the experimental work conducted in batch reactors in this work, the exposure was dictated by simply increasing the hold time of the TMA precursor in the reactor. To obtain similar scales of exposure in a roll-to-roll system with sequential TMA exposures, as envision in Fig. 6.1(a), it is possible to simply control the web speed or the distance between the upper and lower rollers. Moreover, as Figure 6.5 shows, the infiltration to form a hybrid material can be performed as a single elongated exposure. A roll-to-roll process for a single exposure, envisioned in Fig. 6.1(c), would be simply dictated by web speed, roller spacing, and number of rollers. It is important to note that this work in a batch reactor required the TMA in the reactor to be replenished in every cycle such that the surface concentration would be maintained. This can be achieved in roll-to-roll by a design by maintaining a continuous flow of precursor to keep concentration of TMA constant in the chamber.

**Summary and Conclusion**

In this paper we explain effects of exposure conditions and surface area on the SVI process into PET and PA6 fibers envisioning it is necessary to study these parameters for roll-to-roll realization of SVI. A linear mass increase with number of TMA cycles was
observed at 60 °C independent of the surface area of the PET fabrics. However, with the increasing surface area higher mass gain values are observed. Increasing holding time increases the mass gain, yet its effect is dependent on the amount of the TMA precursor dosed. Longer dose times are required to observe saturation in the mass gain. It is also found that for PET exposure conditions show interrelated effects on mass gain of the fiber at 60 °C, whereas a primary factor effecting the mass gain of PA6 is the TMA amount in the reactor at same temperature. This work aids in the process development of hybrid modification to polymer surface in both batch and roll-to-roll processing, and experimentally shows that the degree to infiltration can be simply controlled by a the exposure of the precursor to the polymer. The roll-to-roll processing sequence envisioned in this work is not too different than existing thin film and textile based roll-to-roll treatments.

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Figure 6.1. Schematic of SVI process a) with batch processing b) envisioned roll-to-roll processing with precursor cycling and c) envisioned roll-to-roll SVI processing with elongated single exposure.
Figure 6.2. Mass gain of PET round and winged fibers at 60 °C as a function of number of TMA cycles.
Figure 6.3. Mass gain of high surface area PET winged fibers as a function of number of TMA cycles at different holding time.
Figure 6.4. Mass gain of PET samples as a function of dosing time after 10 cycle and 60 cycle SVI using a) 30 s hold and b) 60 s hold time.
Figure 6.5. Mass gain of a) PET and b) PA6 fibers as a function of product of dosing time, holding time and number of cycles.
Chapter 7 Photoluminescence Mechanism and Photocatalytic Activity of Polyester Based Organic-Inorganic Hybrid Material Fibers

Reprint of a manuscript in preparation for publication.

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Abstract: Organic-inorganic hybrid materials formed by sequential vapor infiltration (SVI) of trimethylaluminum into polyester fibers increased photoluminescence of the fibers. Optical changes in the material analyzed by UV-Vis, it is observed that upon SVI treatment hybrid fibers absorb in the visible spectrum. Mechanism of photoluminescence studied by photoluminescence excitation (PLE) showed the mechanism of photoluminescence in these hybrid materials is dependent on the process temperature. At low temperatures one excitation band and two emission bands observed whereas at high temperatures two distinct absorption
and one emission band observed suggesting the physical and chemical structure of the resulting hybrid material significantly depends on the SVI temperatures. While SVI treatment increased the photoluminescence intensity of the PET fibers, internal quantum efficiency values also increased up to 5-fold. Furthermore it is shown that hybrid materials were able to reduce metal particles on fiber surfaces via photocatalytic activity of the hybrid material. Results of the optical analysis are used to explain the increased photocatalytic activity of these materials formed with SVI. Increased photocatalytic activity is attributed to the increased internal quantum efficiency of the hybrid materials. Silver and gold nanoparticles deposited on to hybrid material fibers via photoreduction effect. XRD and SEM analysis showed that it is possible to deposit larger gold particles than silver particles. For flexible electronics applications, the patterning of the photo-depositions is demonstrated using a masking approach and laser excitation approach and both approaches successfully created well-defined patterns.

**Introduction**

Organic-Inorganic hybrid materials are of interest for electronic, catalytic and optical applications. Different techniques including sol-gel, layer-by-layer thin film formation and atomic layer deposition on polymers have been proposed to create such materials. Atomic layer deposition is a thin film formation technique utilizing self-limiting reactions between substrate surface and vapor phase precursors. Polymers are soft materials and they contain free volume, which led diffusion of precursors into these available sites during ALD on polymeric substrates. Precursors reacting with functional groups within the polymers formed organic-inorganic hybrid materials. Idea of taking advantage of this infiltration inspired new
techniques to create organic-inorganic hybrid materials such as multiple pulse infiltration, sequential infiltration synthesis and sequential vapor infiltration especially using C=O containing polymers such as polyamides, polyesters, polyacrylates and silk for various applications. These techniques depend on same idea of extended precursor exposures even though they show subtle differences in the sequence of precursor exposures.

Conventional polymers like polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) can show weak photoluminescence due to the presence of pi electrons on the phenyl groups. These pi electrons are excited by absorption of UV light and decay of the electrons show emission in the blue region of the visible spectrum. This emission is studied by many reports in the literature to understand the space charge accumulation on these polymers during insulation applications, which caused degradation of the polymer eventually. Polyesters showed two emission bands in these studies. First band was attributed to the monomeric emission which can be explained by the excitation of mobile sp² electrons and their relaxation to ground state. The second emission is attributed to inter chain interactions of the polymer. But when it comes to mechanism of the second emission there is some disagreement between reports. First opinion is this emission is an excited state dimer (excimer) emission which arises from interaction of excited species. However second opinion claims excimer emission for PET should be same as monomer emission so this secondary emission is due to ground state dimers which are excited by photons.

There is a growing interest in production of electronic devices using organic molecules and polymers to enable flexible devices for many different applications. Furthermore using polymeric materials it is projected that roll-to-roll high throughput will be
enabled for inexpensive device production may be even disposable devices. Many conductive and light emitting polymers and organic molecules have been synthesized for this purpose. Many of these molecules and polymer are still relatively expensive comparing to conventional polymers such as polyesters. In our group we are interested in modifying conventional inexpensive polymers by infiltration of organometallic vapors used in ALD, so we can change their electronic and optical properties by increasing the inter-chain interactions. In this study we explain the mechanism of photoluminescence in alumina-PET hybrid materials formed with sequential vapor infiltration. We also present the effect of these changes on the electronic transitions in the material showing induced photocatalytic activity of the fibers.

**Experimental**

PET fabrics were obtained in the form of 2/1 twill woven form, made of 330 denier multifilament 100% PET fibers. PET winged fibers were obtained from Allasso Industries. Fabrics were used as received and no pretreatment was conducted. Samples treated with SVI at different temperatures using a flow tube type ALD reactor described elsewhere. Precursors trimethylaluminum (TMA) (STREM chemicals CAS no. 75-24-1, 98% purity) and high purity water (Sigma Aldrich, biotechnology performance certified grade, CAS no. 7732-18-5) were used as obtained. Precursors delivery and purging to the system were done via N₂ (Airgas National Welders, 99.999%) flow, and the pressure of the system was maintained at 1 Torr during purge cycling. After placement of the samples into the reactor, chamber was purged for five minutes. Afterwards TMA cycles were conducted with a sequence of 0.5 s dose/ 30 s hold/ 30 s purge. It is important to note that during the hold step chamber was
isolated from the pump and nitrogen flow was stopped. After TMA cycles completed reactor chamber was evacuated for five minutes before water cycles were conducted. H₂O cycles were carried with 0.2 s dose/ 30 s hold/ 30 s purge. Before samples were taken out of the reactor SVI process was completed with 2 minutes of purging.

Optical properties of samples were investigated using UV-Vis and Photoluminescence spectroscopy. Thermo Scientific Evolution 300 BB UV-Vis spectrometer and an integrating sphere were used for to obtain transmission and reflection spectra of the samples. Then, relative absorption values were calculated with the equation

\[ A\% = 100 - T\% - R\% \]

Photoluminescence measurements were done at US Army, Aviation and Missile Research Development and Engineering Center (AMRDEC) at Alabama. Photoluminescence (PL) spectra are obtained with a 30 cm grating spectrometer and a Princeton Instruments Spec-10 liquid nitrogen cooled detector, using a Xenon lamp as a light source and a monochromator used to adjust the wavelength while holding samples in air. For Photoluminescence Excitation PLE measurements the wavelength of the excitation is changed and the PL strength is measured at each excitation. Absorption and quantum efficiency measurements were completed in a 10cm integrating sphere at optimum wavelengths obtained by PLE measurements.

For photoreduction experiments 0.1 M AgNO₃ (Sigma-Aldrich, CAS# 7761-88-8) and 10⁻³ M HAuCl₄ (Sigma-Aldrich, CAS# 27988-77-8) solutions were prepared by using DI water. 1”x1” cut fabrics were embedded into 25 ml salt solution and exposed to UVA light source (Intelli-Ray 400, ~75mW/cm²). After samples are taken out of the solution, they were
rinsed with DI water and dried in an oven at 60 °C. XRD data was obtained using a Panalytical Empyrean X-ray diffractometer using a Cu anode producing K-Alpha x-rays with 1.54 Å. SEM images are obtained using FEI Verios 460 L SEM. First approach metal reduction patterning experiments were conducted using a plastic mask placed on top of the fabric in 25 ml solution. Than fabrics are exposed to the UVA light for 15 minutes. Second approach patterning experiments were done using a near UV laser. Fabrics were embedded into the solution and then using a gantry stage, laser beam moved on the sample with a pattern.

**Results and Discussions**

In Figure 7.1, the optical images of the SVI treated fabric samples under ambient and UV light conditions are given. As shown in Fig. 7.1 (a) under ambient light conditions polymer changes color especially with increasing SVI temperature. We previously reported that, as the process temperature increases in general the mass gain of the samples decreases (which is related to the reaction extent of the process). After 60 cycles of SVI 60 and 90 °C SVI treated samples even show more mass gain than 120 and 150 °C SVI treated samples. Therefore the color change observed here is not a result of the reaction extent rather it is due to the chemical differences explained previously. Another important change observed after SVI processing of the samples is the interesting photoluminescence emission observed when these samples are exposed to the UV illumination in a dark room as shown in Fig. 7.1 (b). The weakest emission is observed from the sample treated 5 TMA cycles of SVI at 60 °C, which also shows the lowest mass gain among the other samples. As the amount of the hybrid material formation increases with increasing number of TMA cycles, stronger
emission is observed. At 90 °C samples show similar trend that is observed at 60 °C, however stronger emissions observed more rapidly. As previously reported SVI mass gain increases more rapidly at 90 °C than at 60 °C. Emission colors of the 60 and 90 °C samples are also very similar to the eye after 60 cycles. At 120 °C samples starts to show change in the emission color which is parallel to the optical color change of the samples. Color change is more intense at 150 °C and as the number of cycles increases the brightness of the emission decays.

In order to further understand the optical changes in the samples we conducted a UV-Vis absorption spectroscopy analysis on the samples and resulting spectra are given in Figure 7.2. PET shows UV absorbance in the range of 200-375 nm due to the short rate conjugation of pi electrons on the backbone of the polymer. However above 375 nm it doesn’t show any absorption as many conventional polymers. Upon SVI treatment higher wavelength absorption starts to be observed with a trend that the amount of the absorption dependent on the SVI temperature. As the process temperature increases, more red shift and higher absorption values are observed. The samples here are treated with 60 cycles of SVI and their mass gains are highest at 90 °C and then 60, 120 and 150 °C sequentially. However highest amount of the absorption is observed at 150 °C with highest red shift, reaching absorption values up to 90 % in the range of 375 nm to 475 nm. This strong absorption is the reason for the yellow color observed in the material. At 120 °C amount of the absorption still reaches up to 80% in the range of 375 nm to 425 nm. As the temperature decreases to 90 °C absorption drops below 60% an eventually at 60 °C absorption decreases below 40%. Even though the mass gain values are 3-4 times higher at 60 and 90 °C the highest absorption at 150 °C
confirm that the chemical nature of the materials forming is different in these samples. Furthermore the change in the cut off wavelengths of the samples suggests that band gap structure of these materials is different as well.

In order to investigate the mechanism of excitation and emission in these samples photoluminescence excitation (PLE) mapping and spectroscopy were conducted and the results are given in Figure 7.3. Difference in temperature of SVI treatment cause significantly different absorption and emission patterns. In Fig. 7.3 (a) PLE mapping of 90 °C SVI treated sample is given excitation wavelength on the y-axis and emission wavelength on the x axis. Mapping shows a broad band of excitation results two distinct emission bands from the samples. In Fig. 7.3 (b) the PLE and PL emission spectra of the sample are given as normalized manifests the excitation band is at 372 nm and two emission bands observed at 424 and 452 nm. In Fig. 7.3 (c) the PLE mapping of samples treated with SVI at 150 °C is given. In this case we observe two excitation bands for one emission band. In Fig. 7.3 (d) PLE spectrum shows two absorption bands at 372 nm and 424 nm and PL spectrum shows one emission band in the sample at 472 nm. At low temperatures one absorption band suggests that we have single product of SVI process, which is uniform as discussed in previous work. However at high temperature processing we have two absorption bands suggesting we have two distinct phases forming in the material, one is similar to the one forming at low temperatures absorbing at 372 nm and the other is a different material forming at 424. The material formed at low temperature has an emission band at 424 and interestingly the materials formed at high temperature shows a strong absorption at this wavelength show. This can explain the fact that the intensity of the emission is an order of
magnitude lower at high temperature processed sample (Fig 7.3 (a-c)) and there is one emission band in high temperature SVI material.

To further understand the optical changes in the materials we investigated the amount of absorption and the internal quantum efficiency of the materials at the excitation bands found above using the technique reported by de Mello et al. and results are given in Table 7.1. We first studied the absorption and IQE by exciting samples at 355 nm. At this wavelength PET absorbs up to 70% of UV light however the internal quantum efficiency of the material is very low. After SVI processing we see that absorption values increasing above 90% and the internal quantum efficiency increases up to ~24% for the 90 °C SVI treated sample. When the samples are excited at 372 nm SVI treated samples show similar values in terms of absorption and IQE however, the absorption of the control sample drops 50%. When control and high temperature samples, excited at 424 we see that the absorption of pristine PET drops to 8% whereas sample treated with SVI at 150 °C still show more than 90% absorption. Increase in the internal quantum efficiency after SVI processing suggests that more electron-hole pairs are forming in the material. Photocatalytic activity of a material depends on the amount of the e-h pairs it can form upon light exposure. In this case IQE can be linked to the photocatalytic activity of the material therefore upon SVI exposure PET samples show higher photocatalytic activity.

To test that hypothesis given above pristine and SVI treated samples are embedded into metal salt solutions and exposed to a UVA light source. In Figure 7.5 optical images of pristine and SVI treated samples after 15 minutes of UVA exposure in AgNO₃ and HAuCl₄ are given. Pristine sample in Fig. 7.4 (a) only shows very few stains on the fabric after the
UVA exposures and this behavior doesn’t change significantly up until 1 hour of UVA exposure. Samples treated with SVI in Fig. 7.4 (b) and (c) in AgNO3 and HAuCl4 respectively, changed their colors upon 15 minutes of UVA exposure, which is attributed to the deposition of metal nanoparticles onto the surface of the PET fibers. Black stains start to form during silver deposition and it continues to keep the color whereas in the gold chloride solution black stains starts to form and then color of the fabrics remain black for a while and then the fabric starts to turn into reddish color.

XRD spectroscopy was conducted on the same sample set shown in Fig. 7.4 for further analysis and resulting spectra are given in Figure 7.5. Pristine PET sample after 15 min UVA exposure in AgNO3 solution, showed three diffraction peaks at 2θ =17, 22.5 and 25.5°. These peaks are attributed to the (100), (010) and (110) reflections of triclinic structure of polymer respectively as given in the literature.\textsuperscript{176-177} Other than these peaks no significant peaks observed especially at the high degrees especially due to the metal presence. SVI treated sample in AgNO3 solution forms a new peak at 38° which is the most intense peak for silver and attributed to reflection from (111) plane of Silver. Since we carry the photoreduction in an aqueous solution it is also possible that this peak might be due to the reflection from (110) of silver oxide. However the latter is less likely since silver oxide has also another strong peak appear at 33°, which is not seen in our case. Similarly SVI treated sample in gold chloride solution shows a peak at 38° for (111) plane reflection. In addition to that, another peak is observed 44° for reflection from (200) plane as well. An important difference between the spectra of silver reduced sample and gold reduced sample is, the
intensity of the (111) plane peak. In the case gold we observe more intense peak, which can be indication of the average size of the gold particles, is larger than the silver particles.

SEM micrographs SVI treated samples after 15 minutes of UVA exposure in silver nitrate and gold chloride is given in Figure 7.6 (a) and (b), respectively. Silver deposition results in very small nanoparticles with the size range less than 100 nm. On the other hand gold deposition results in larger particles formation, which is in agreement with the color change observed in the material and the XRD spectrum data. This SEM analysis was made without any sputtering using a Verios SEM by applying bias to the sample holder. During the analysis it is also observed that there is textured surface between the large particles, which can be very small gold particles similar to what is observed during silver deposition.

It is of interest to control the reduction of the nanoparticles selectively on a flexible substrate such as fabrics, so printing metal particle for flexible and wearable electronic applications would ne possible. We followed two approaches to realize such patterning on fabric substrates as given in Figure 7.7. First approach depends on using a mask to block the light reaching the undesired areas and exposes it to the UVA light in only for patterning (Figure 7.7 (a)). To serve this purpose we prepared a plastic black mask and shined UVA light on the samples. Optical image of this sample is given in Figure 7.7 (b) with very well defined patterns. It should be noted here in the masked regions sample is colored slightly as well. Another approach for patterning could be the selective excitation of the substrate using a fine light source such as a laser beam as shown in Figure 7.7 (c). In Figure it is shown that using a laser beam wavelength of 410 nm is capable of reducing nanoparticles with a well-defined patterns of silver.
Conclusions

In this work we present photocatalytic activity of organic-inorganic hybrid materials formed with sequential vapor infiltration of trimethylaluminum precursors into polyethylene fibers. We explain the photocatalytic activity of the hybrid materials to the optical properties especially mechanism of photoluminescence and the internal quantum efficiency. Depositions of silver and gold nanoparticles are carried out successfully by photoreduction out of aqueous solutions of metal salts. XRD and SEM analysis showed gold particles are larger than the silver particles. We also demonstrate that it is possible to control the photoreduction by selective excitation of the samples by either using a mask or laser beam.

Acknowledgement

Authors would like to acknowledge the funding sources National Science Foundation; University Industry Copperative Centers: Center for Dielectrics and Piezoelectrics, and Republic of Turkey, Ministry of National Education.
Figure 7.1. Optical images of the PET fabric samples a) under ambient light and b) under UV illumination.
Figure 7.2. UV-Vis spectroscopy of the samples treated with 60 cycle TMA SVI at various temperatures.
Figure 7.3. Photoluminescence Excitation (PLE) mapping and spectroscopy analysis results of SVI treated a) and b) winged fiber at 90 °C, c) and d) round fiber at 150 °C.
Figure 7.4. Optical images of samples after 15 minutes of UVA exposure a) pristine PET and b) SVI treated PET in AgNO₃, SVI treated PET in c) HAuCl₄.
Figure 7.5. XRD spectra of pristine and SVI treated samples after 15 minutes of UVA exposure in aqueous AgNO₃ and HAuCl₄ solutions.
Figure 7.6. SEM images of SVI treated samples after 15 minutes of UVA exposure in a) AgNO₃ and b) HAuCl₄ solutions.
Figure 7.7. a) Approach used for printing metal nanoparticles of with a mask b) optical image of resulting patterns as prepared with masking approach c) schematic of approach using a laser for printing metal nanoparticles with resulting pattern.
Table 7-1. Absorption and internal quantum efficiency values of pristine and SVI treated samples.

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<thead>
<tr>
<th>Sample</th>
<th>Absorption @ 355nm</th>
<th>Internal QE @ 355nm</th>
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</thead>
<tbody>
<tr>
<td>Control</td>
<td>69.00%</td>
<td>1.87%</td>
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<tr>
<td>SVI at 90 °C</td>
<td>90.02%</td>
<td>24.88%</td>
</tr>
<tr>
<td>SVI at 150 °C</td>
<td>96.72%</td>
<td>9.99%</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorption @ 372nm</th>
<th>Internal QE @ 372nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>30.89%</td>
<td>4.59%</td>
</tr>
<tr>
<td>SVI at 90 °C</td>
<td>89.42%</td>
<td>23.54%</td>
</tr>
<tr>
<td>SVI at 150 °C</td>
<td>97.44%</td>
<td>7.33%</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorption @ 424nm</th>
<th>Internal QE @ 424nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>8.14%</td>
<td>3.19%</td>
</tr>
<tr>
<td>SVI at 150 °C</td>
<td>92.84%</td>
<td>8.02%</td>
</tr>
</tbody>
</table>
Chapter 8 Structure Photoluminescence Relationship of Organic-Inorganic Hybrid Materials Formed by Sequential Organometallic Vapor Infiltration into Polyethylene Terephthalate Films

by Halil I. Akyildiz,1,2 Gee Simmons,3 Henry O. Everitt,3,4 and Jesse S. Jur1

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Introduction

Organic-inorganic hybrid materials are of interest for flexible optical applications such as flexible displays. Polyethylene terephthalate is a polymer used in the textiles, packaging and flexible electronic applications. PET shows weak photoluminescence due to returning of pi electrons present on the polymer backbone to the valance band after they are excited by UV light absorption. Emission in these molecules shows two significant emission bands in the literature. The lower wavelength emission is attributed to the monomeric emission and the higher wavelength is attributed to the excited state dimer emission. It is previously shown that this weak emission can be enhanced during sequential vapor
infiltration (SVI) of organometallic precursors process. In this work the emission of the SVI treated PET film samples, which has different crystallinity amount, has been studied using photoluminescence spectroscopy.

**Experimental**

PET is obtained from Eastman and dissolved in trifluoroacetic acid. To prepare different thicknesses of films 3 wt% and 7 wt% solutions were prepared. Samples are spin coated on fused silica glass slides using Laurell Technologies spin coater at 1500 and 3000 rpm for 1 minute. Spin coating of 3 wt. % solution at 3000 rpm gave approximately 300 nm thick films. Spin coating of 7 wt. % solutions at 1500 rpm resulted in approximately 1700 nm thick films. After spin coating samples are annealed on a hot plate at 100 and 160 C which are expected to have different crystallinity amounts.

Photoluminescence (PL) spectra were obtained from samples mounted in air a 30 cm grating spectrometer and a Princeton Instruments Spec-10 liquid nitrogen cooled charge coupled device detector. The light source was a HeCd laser with a monochromator used to adjust the wavelength.

**Results and Discussion**

In order to understand the effect of crystallinity and the film thickness on emission PL spectra of pristine PET films were studied at $\lambda_{ex}=325$ nm and the results are given in Figure 8.1. First thing observed in the data is the significant effect of the thickness of the films on PL intensity. 300 nm samples show very similar emission in terms of intensity independent of the expected crystallinity. However the emission patterns of the samples are different than each other. As the thickness increases there is a pronounced difference between the films
with different expected crystallinities. It is also observed that irrespective of the thickness or crystallinity there are four emission bands observed at 342, 364, 386 and 414 nm wavelengths. Higher temperature annealed samples show stronger emissions at 342 and 364 nm wavelengths, which is an indication of the emission due to the crystal regions in the polymer occurs at these wavelengths.

In Figure 8.1 the PL spectra of the same sample set is given after SVI treatment at 60 °C. First thing noticed is the increased intensity of the photoluminescence of the all samples except the one with high crystallinity thick sample. In this thick highly crystalline sample still we see the four emission bands with similar intensities. This is an indication of the SVI process takes place primarily, in the amorphous regions of the polymer. All the other samples doesn’t show any change in the emission intensity at 342 and 364 nm wavelengths while showing significant changes in the 386 nm and 414 nm emission bands. Emission at 386 nm of these samples showed a red shift to 396 nm with an evident increase in the intensity. The emission at 414 while remaining at the same band showed an apparent increase in the intensity. Furthermore a shoulder around 432 nm is also observed for these samples.

In Figure 8.2 the PL spectra of the same sample set is given after SVI treatment at 60 °C. First thing noticed is the increased intensity of the photoluminescence of the all samples except the one with high crystallinity thick sample. In this thick highly crystalline sample still we see the four emission bands with similar intensities. This is an indication of the SVI process takes place primarily, in the amorphous regions of the polymer. All the other samples doesn’t show any change in the emission intensity at 342 and 364 nm wavelengths while showing significant changes in the 386 nm and 414 nm emission bands. Emission at 386 nm of these samples showed a red shift to 396 nm with an evident increase in the intensity. The emission at 414 while remaining at the same band showed an apparent increase in the intensity. Furthermore a shoulder around 432 nm is also observed for these samples.

In Figure 8.3 PL spectra of the samples treated with SVI at 150 °C is given. In these samples a completely different emission mechanism is observed compared to the pristine and SVI treated samples at 60 C. All the bands observed in Fig. 8.1 and Fig. 8.2 disappears in these spectra. Samples show significant red shift in the emission with two emission bands for all the samples. Thinner and high crystalline films show two emission bands at 414 and 432 nm bands and the rest of the samples show emission bands at 444 nm and 464 nm. The difference of the emission mechanism supports the previous discussion on the difference of
the chemistry of forming materials at different SVI temperatures. In this sample set we also see that less crystalline substrates show higher intensity emission compared to the low crystalline samples. However it is very interesting not see any emission due to the crystalline regions of the samples. Which can be explained by the previous PLE study on SVI treated samples. It was reported in Chapter 6 that high temperature SVI process results in two absorption bands and one of the absorption bands was at the emission band of the low temperature samples. Therefore the absence of the lower wavelengths can be attributed to reabsorption in the material.

Another important difference between the Fig. 8.2 and Fig. 8.3 is the scale of the y-axes. After SVI at high temperatures, up to 20 times higher PL intensities are observed compared to the low temperature SVI treated samples. This is not in agreement with PL data of SVI treated fiber samples reported previously where we reported higher PL intensities for low temperature SVI processed samples. This can be explained by the reaction extent in the material. The fiber samples at low temperatures showed higher mass gain, which is an indication of the reaction extent, compared to the high temperature samples. It was observed that at high temperatures rapid saturation takes place due to a barrier layer formation at the surface of the fibers whereas at low temperatures mass gain increased slower without saturation. This was an indication of the slower diffusion and reaction kinetics at low temperatures. So in a planar substrate such as the films in the study the hybrid material formation would be even lower whereas at high temperatures more material would form rapidly. Therefore the difference between the studies can be attributed to the difference in the amount of material formed.
Conclusion

In summary, in this study we explain the relationship between the structure and the photoluminescence of the pristine and SVI treated PET films. There are four emission bands observed in pristine PET films. Two of them showed stronger emissions in high crystallinity films attributed to the crystalline regions of the samples. The other two, showed stronger emission in low crystallinity films attributed to the amorphous regions. After the SVI process at 60 °C only the emissions attributed to the amorphous regions showed increase indicating SVI primarily effective in the amorphous regions of the polymer. After SVI at 150 °C shows very high red shift and emission mechanism changes completely suggesting the reactions taking place at high temperatures are different than low temperature SVI processing.

Acknowledgement

I would like to thank Prof. Henry Everitt and Gee Simmons at Army Aviation and Missile Research, Development, and Engineering Center for the collaboration for the optical analysis.
Figure 8.1. Photoluminescence spectra of pristine PET samples of different thicknesses and crystallinities. ($\lambda_{\text{excitation}}=325$ nm)
Figure 8.2. Photoluminescence of the PET films with different thicknesses and crystallinities after SVI treatment at 60 °C. ($\lambda_{\text{excitation}} = 325$ nm)
Figure 8.3. Photoluminescence of the PET films with different thicknesses and crystallinities after SVI treatment at 150 °C. ($\lambda_{\text{excitation}}=325$ nm)
Chapter 9 Thermal Properties and Pyrolysis of Organic-Inorganic Hybrid Materials Formed by Sequential Organometallic Vapor Infiltration into Polyethylene Terephthalate

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Introduction

Organic inorganic hybrid materials are of interest for wide variety of applications including flexible electronics and catalysis. Many different hybrid materials formed with different techniques including sequential vapor infiltration. Thermal stability is one of the desired properties of these materials. Thermal properties of organic-inorganic hybrid materials formed by trimethylaluminum (TMA) SVI into PET fibers are investigated by thermogravimetric analysis. Furthermore increased thermal stability of polymer-alumina hybrid materials showed by pyrolysis of SVI treated PA6 and PET fiber mats with very high heating rates.

Experimental

Round fibers were obtained in the form of woven fabric form made of 100% PET round fibers 330/70 denier multifilament yarns with a 2/1 twill structure. SVI experiments
were conducted using a custom-designed flow tube type reactor described in details previously. Precursors trimethylaluminum (TMA) (STREM chemicals CAS no. 75-24-1, 98% purity) and high purity water (Sigma Aldrich, biotechnology performance certified grade, CAS no. 7732-18-5) were used as obtained. Precursors delivered to the system via N2 (Airgas National Welders, 99.999%) flow and the pressure of the system was maintained at 1 Torr during purge cycling. Following an initial 5 minutes purge, samples were exposed to TMA cycles consisting of 0.5 s dose, 30 s hold and 30 s purge. After the TMA cycles are completed reactor chamber is pumped down for 5 minutes. Afterwards samples were exposed to H2O cycles to oxidize any unreacted methyl groups with a sequence of 0.2 s dose, 30 s hold and 30 s purge.

TGA was performed using a Perkin Elmer Pyris 1 TGA on PET-Alumina hybrid fabric samples that were cut to 2-5 grams. Heating rate was 20 °C/min, and N2 gas was used. Samples were heated from room temperature to 800 °C. A static gun is used to remove any excess static or debris surrounding the sample to limit the tendency to obtain a false reading. The 60 °C and 150 °C 60 cycle SVI round fiber samples were heat treated for 24 hours in a preheated oven at 120 °C and 150 °C under ambient atmosphere. A Phenom SEM was used to analyze the heat treated SVI samples for cracks and effects of heat treatment. Samples were coated with ~10 nm Gold/Palladium mixture.

**Results and Discussion**

Thermogravimetric analysis was conducted to see the degradation patterns of the pristine and SVI treated fabrics and the resulting curves are given in Figure 9.1. The control sample show an onset temperature for polymer degradation for the polymer at 428 °C. The
residue left after the polymer degradation is about 12%. After SVI treatment samples show slightly different degradation patterns depending on the SVI temperature. 60 and 90 °C SVI treated samples show an additional degradation step before the polymer degradation observed at 428 °C as observed for the polymer. During this degradation step which starts around 150 °C sample lost about 8% more mass gain then control sample. After this step the polymer degradation takes place as observed with the control sample. After weight of the sample is reduced to 26-27% we see another degradation step in the material which start around 625 °C. After 800 °C both samples show about 19% residue. Sample treated with SVI at 150 °C doesn’t show the degradation step before the polymer degradation as seen for low temperature SVI processed samples. However it does show the same degradation step observed at low temperature samples starting after ~35% weight is left. After 800 °C high temperature SVI sample shows 21% residue.

The initial weight loss of the polymer can be result of two factors. At low temperature processed samples there is –OH group formation occurs upon SVI treatment is shown in previous FTIR studies and desorption of these –OH groups can be one of the reasons. Considering the amount of mass gain is around 5% for the high temperature SVI treated sample, it is understandable that it doesn’t show up on these samples. Another reason for this weight loss can be the formation of low molecular weight oligomer groups caused by chain scission during SVI as suggested by the studies in the literature. If the latter is the case then it is absence in the data of high temperature SVI processed samples can be attributed to the elimination of these groups during the SVI process. Other weight loss around 500 °C and
ending near 650 °C is most likely due to the decomposition of the PET-Alumina hybrid material, which would have slightly more thermal stability due to the addition of alumina.

The mass gain of the samples during SVI is compared to the residue after TGA in Table 8.1. It is observed that even though the mass gain observed at 150 °C is lower comparing to the low temperature SVI samples it still show higher residue amount. This dramatic difference can be attributed to the difference in the formation of the hybrid materials at different temperatures. As previously reported a dense hybrid layer formation occurs during high temperature process, which can be acting as a heat resistant shell that prevents the degradation of the polymer inside this shell. The heat in this case can be consumed to form stable carbon structures and results in higher residue amount.

One application of this slower degradation of the SVI hybrid materials can be applied to formation of carbon fiber formations. In Figure 9.2 optical images of pristine and SVI treated PET and PA6 fibers after pyrolysis under Argon atmosphere with very high heating rates reaching up to 200 °C/min is given. Pristine PA6 sample after pyrolysis shows basically little carbon residue on the quartz slides whereas SVI treated sample remains its fabric format after the pyrolysis. In the case of PET after pyrolysis of pristine fibers a film of carbon is left on the surface of the fiber. This can be attributed to the chemical structure of the PET containing aromatic structures are capable of more stable towards the temperature. Even though they are not capable of preserving the fiber form they can turn into another form without degrading completely. SVI treated PET fibers can also their fabric structure. The greyish color of the sample after the pyrolysis can be attributed to the higher amount of the alumina presence in the sample.
To further analyze the samples in Fig. 9.3 SEM images of the pristine samples and SVI treated samples before and after pyrolysis are given. After SVI treatment of PA6 fibers no significant morphology changes observed and after pyrolysis with slight changes the fibers still show high surface area morphology. It should be noted here after the pyrolysis samples become very brittle and that’s why handling breaks many fibers. After SVI processing of PET fibers, however coalescence of the winged structure is observed as reported previously. After pyrolysis fibers still retain their shape even though they are coalesced.

Raman spectroscopy analysis of these samples confirms the graphitic and disordered carbon structures formation by formation of G and D peaks as shown in the Figure 9.4. G and D peak ratios of the samples doesn’t show significant changes with the processing indicating with this high heating rates SVI Processing conditions are not effective on the structure of the final material.

**Conclusions**

The thermal analysis of these hybrid materials was useful in characterization. Future tests could allow the characterizations to be more completely explained. The use of XRD to examine the crystalline structure of the residue after TGA could confirm what occurs with the material and show whether or not cylindrical compounds are forming in the 150°C SVI samples. Increasing the temperatures for future heat treatments of the fiber samples would be useful in determining the possibility to completely fill in the cracks viewed in SEM. Since many electronic applications make use of films rather than fabrics, the use of a hot press process to attempt to melt the fibers and create a film would be of particular interest. The
film would then be viewed under SEM to determine if the cracks in the fiber were properly melted to create a smooth material.

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Figure 9.1. Thermogravimetric analysis curves of pristine and SVI treated samples.
Figure 9.2. Optical images of pristine and SVI treated PA6 and PET fiber mats after high speed pyrolysis. (Heating rate: 200 °C/min)
Figure 9.3. SEM images of pristine and SVI treated samples before and after pyrolysis.
Figure 9.4. Raman spectra of PET samples after pyrolysis a) pristine vs. SVI treated b) SVI treatment at different temperatures.
Table 9-1. SVI mass gain values vs. TGA residue amounts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% SVI Mass Gain</th>
<th>% TGA Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>60 °C SVI</td>
<td>16</td>
<td>19</td>
</tr>
<tr>
<td>90 °C SVI</td>
<td>18</td>
<td>19</td>
</tr>
<tr>
<td>150 °C SVI</td>
<td>5</td>
<td>21</td>
</tr>
</tbody>
</table>
Conclusions and Summary

In this study mechanism of SVI for PA6 and PET, has been studied as a function of temperature, pressure, and exposure conditions. Diffusion and reaction rate being dependent on temperature, competition between them determines resulting mass gain. In general it has been observed that at low temperatures diffusion is dominant over reaction rate and higher mass gain result can be observed, as the temperature increases the reaction rate takes over the diffusion and a barrier layer at the surface of the polymer is observed. Pressure studies showed that SVI could be conducted at atmospheric pressure, which is very important for roll-to-roll application of the process. Along with the mechanism analysis of SVI, photoluminescence of the SVI hybrid materials reported for the first time. This optical change in the PET fibers is attributed to the enhancement of inherent PL of the polymer. Detailed analysis of optical properties showed internal quantum efficiency of the substrates was also increased significantly along with the photoluminescence. Increased quantum efficiency effect is demonstrated with the increased photocatalytic activity of the substrates by photodeposition of silver and gold nanoparticles out of metal salt solutions. Study relationship between polymer structure and optical properties, revealed the enhancement of the photoluminescence mainly was due to the enhancement of certain emission bands attributed to the amorphous regions of the polymer. Thermal analysis of the SVI treated fibers showed hybridization of the polymer improves the thermal stability of the fibers.
Future Work

With the shown potential in the literature and through this study, there are a lot to discover for SVI technique. In general future work on SVI can focus two main routes. First route should focus on enhancing the knowledge of the mechanism of the SVI process. This is necessary for the future industrial applications of SVI. For example roll-to-roll SVI process has great potential for industrial applications therefore possible hardware designs should be studied. Another important aspect of this route is further analysis of the hybrid materials formation in different polymers with different precursors. As shown in this work, mechanism of the SVI changes simply with the choice of polymer. One important thing missing in the literature is the detailed analysis of the chemical reactions at different temperatures using in situ characterization techniques. As found emphasized in this work properties of the resulting materials and ex situ characterization suggests the materials formed at different temperatures are very different. Furthermore in situ analysis and studies of the very fine scale structure using advanced light sources can improve the knowledge of the physical structure of the hybrid materials.

Second route is to study different material systems such as different oxides and different organic materials with SVI. In this study main focus is on alumina infiltration into PET and PA6, however inorganic materials with more interesting optical properties such as ZnO and TiO$_2$ can be studied in the future. This study shows optical properties of the organic molecules can be tailored by incorporation of inorganic materials. Optically more interesting polymers such as conjugated polymers with carbonyl groups can be studied as well. With that it would be very interesting to see band gap tailoring of conductive polymers and using
these hybrid materials in device applications. It is also important that promising results on thermal stability of the SVI should be further analyzed to improve thermal stability of other polymers.
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