Fabrication and characterization of novel polymer-matrix nanocomposites and their constituents

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Fabrication and characterization of novel polymer-matrix nanocomposites and their constituents

by

Rui Ding

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Materials Science and Engineering

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Iowa State University
Ames, Iowa
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ABSTRACT

Two main issues for the wide application of polymer-matrix nanocomposites need to be addressed: cost-effective processing of high-performance nanomaterials, and fundamental understanding of the nanofiller-polymer interaction related to property changes of nanocomposites.

To fabricate inexpensive and robust carbon nanofibers (CNFs) by the electrospinning technique, an organosolv lignin for replacing polyacrylonitrile (PAN) precursor was investigated in this work. Modification of lignin to its butyl ester alters the electrospinnability and the thermal mobility of the lignin/PAN blend precursor fibers, which further affect the thermostabilization and carbonization processes of CNFs. The micromorphology, carbon structure, and mechanical properties of resultant CNFs were evaluated in detail. Lignin butyration reveals a new approach to controlling inter-fiber bonding of CNFs which efficiently increases the tensile strength and modulus of nonwoven mats.

A commercial vapor-grown CNF reinforcing of room-temperature-vulcanized (RTV) polysiloxane foam has potential impact on the residual tin catalyst in composites and consequently the aging and the long-term performance of the materials. Elemental spectra and mapping were employed to analyze the distribution and the composition of tin catalyst residues in the CNF/polysiloxane composites. Thermal analysis revealed a significant increase of thermal stability for CNF-filled composites. Further, the glass transition properties of polysiloxane are not evidently influenced by the physical interaction between CNF filler and polysiloxane matrix.
Nanocomposites consisting of anthracene, a model polycyclic aromatic hydrocarbon (PAH) compound, and a thermosetting epoxy was matrix was studied to interpret the reinforcing effect on the glass transition temperature ($T_g$) by different routes: physical dispersion and/or covalent modification. The molecular dynamics of the relaxation processes were analyzed by broadband dielectric spectroscopy (BDS). By parametric fitting using the Havriliak-Negami (HN) function, the Arrhenius diagram was obtained to evaluate the temperature dependence of the relaxation processes at different length scales for the nanocomposites. The segmental $\alpha$ relaxation was strongly affected by the reinforcing approaches and the correlation of $T_g$-scaled fragility to molecular structures provides the explanation for the mechanisms of the nanofiller-polymer interaction.

In addition, the accelerated chemical aging of nylon 6 polymer, a common material for wire insulations, was monitored by a nondestructive dielectric/capacitive method. The correlation between dielectric properties and electrical breakdown strength was found dependent on the polarity of the aircraft fluids to which nylon 6 was exposed. It was concluded that permittivity/capacitance measurement offers a feasible nondestructive method for diagnosing the breakdown strength of chemically immersed nylon 6.
CHAPTER 1: INTRODUCTION

1.1 General Introduction

Nano-scale reinforcements for polymer-matrix composites (PMCs) have been attracting increased attention in recent decades because they not only improve the mechanical properties of the host polymers, but also impart multifunctional characteristics, such as thermal and electrical conductivity, charge dissipation, chemical resistance, low permeability of gas, etc. The improved performance and unique properties of polymer nanocomposites are attributed to the enhanced molecular interaction between polymer chains and nanofillers which have very small length scale and ultra large interfacial area per volume.

Carbon nanofibers (CNFs) are an important one dimensional (1-D) nanomaterials for PMCs which find expanding applications in aerospace, automotive, and microelectronics industries due to CNFs’ excellent mechanical, thermal, and electrical properties. A critical issue that has precluded the large-scale use of CNFs (and carbon fibers (CFs)) in structural applications is their high cost compared to that of the host polymers. Reducing the cost of precursors is considered the most efficient, but most challenging way to reach the economical goal for CNFs and CFs. A growing amount of research has been dedicated to exploring low-cost, renewable alternatives to the petroleum-based polyacrylonitrile (PAN) precursors to produce CNFs (and CFs), meanwhile improving their properties to meet high-performance demands in reinforcing PMCs. In another aspect, studies have shown that the aging of PMCs upon service can be affected by the addition of nanofillers. PMCs used as industrial products sometimes consist of reactive species that are detrimental to their service lifetime. Investigation of the chemical interplay between nanofillers and polymer systems, and its influence on the material properties, is therefore of practical
interest. In addition, the inclusion of nano-scale fillers with large specific surface area to polymer matrices can lead to a remarkable changes of physical properties due to not only the intrinsic properties of the nanofillers but also the interaction between polymer chains and nanofiller surfaces. The physical relationships between nano-scale structural variables and the macro-scale properties of polymer nanocomposites is worth further understanding.

This dissertation encompasses my efforts on the following research aspects: First, develop inexpensive lignin/PAN blends for electrospinning precursor fibers and processing subsequent continuous CNFs. The morphology, structure and properties of CNFs are controlled by the judicious molecular modification of lignin. Second, an industry-formulated room-temperature-vulcanized (RTV) polysiloxane foam reinforced by vapor grown carbon nanofiber (VGCNF) is chosen to investigate the nanofiller’s effect on the residual tin catalyst and foam networks. Third, a novel group of molecular nanofillers – polycyclic aromatic hydrocarbon (PAHs) – are incorporated into an epoxy thermoset to study the change of molecular dynamics in response to different nanofiller-polymer interactions, via broadband dielectric spectroscopy (BDS). Finally, the dielectric properties of nylon 6 polymer, a simplified example of wire insulation composites, is monitored dielectrically under controlled chemical exposure. Observed variation in the dielectric properties indicates that nondestructive evaluation (NDE) based on capacitive measurements is feasible for monitoring the chemical aging of nylon 6.

1.2 Dissertation organization

This dissertation is laid out in six chapters including four research topics. Chapter 1 serves as a general introduction to cover the relevant backgrounds: structure, properties and preparation of CNFs, CNF-polymer composites and their properties, molecular dynamics study of polymers
and their nanocomposites using dielectric analysis, and dielectric measurements for developing capacitive NDE techniques to monitor wire aging. The specific polymer (matrix) used in each study is introduced briefly in each chapter. The main characterization techniques used in the whole work include dielectric analysis – broadband dielectric spectroscopy (BDS); thermal analyses – differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA); microscopic analyses – optical microscopy (OM) and scanning electron microscopy (SEM); spectroscopic analyses – Fourier transform infrared (FTIR), Raman, nuclear magnetic resonance (NMR), energy-dispersive X-ray (EDS), and X-ray photoelectron (XPS); and property measurements – rheological, mechanical, thermal, electrical and dielectric properties. In this chapter BDS and dielectric measurement are reviewed in detail due to their central role in two of the pieces of research (Chapters 4 and 5) and their likely being less familiar than the other characterization methods mentioned.

Chapter 2 discusses the usage of an organosolv lignin as a biorenewable precursor to develop low cost, high performance continuous carbon nanofibers by the electrospinning technique. The structure and mechanical properties of lignin-based electrospun CNFs are compared to those of conventional PAN CFs. By modifying the thermal mobility of lignin, inter-fiber bonding is achieved and provides a significant mechanical enhancement for CNF mats. As structural reinforcement, the CNF mats are potentially applicable in laminated fiber-reinforced epoxy composites.

Chapter 3 describes the exploration of the effect of nanofillers on the structure and thermal properties of the VGCNF-reinforced RTV siloxane syntactic foams synthesized for industrial application. SEM-EDS and XPS are applied to characterize the composition and distribution of catalyst and nanofillers in the pristine foams. To develop understanding of accelerated oxidation
of the residual tin catalyst in the presence of VGCNF is attempted by studying structural morphology, molecular dynamics and thermal properties of the foam composites. Beyond the preliminary investigation, post-curing and accelerated thermal degradation of the pristine foam materials are proposed, to further understand the observations.

Chapter 4 emphasizes the use of BDS to analyze the increased $T_g$ of epoxy composites modified with anthracene by hybrid reinforcing routes. The dielectric loss as a function of frequency and temperature is the main focus and is investigated with models of dielectric relaxation. Parameters related to the glass transition are extracted from dielectric relaxation modeling, providing complementary information to conventional thermal analysis and explaining the mechanisms for observed increases in $T_g$ due to the incorporation of anthracene.

Chapter 5 details the dielectric monitoring of the complex permittivity response of nylon 6 to various chemical exposures over time. The correlation between dielectric properties and electrical breakdown strength is found dependent on the polarity of the aircraft fluids to which nylon 6 is exposed. Permittivity/capacitance measurement is examined for its potential to diagnose the breakdown strength of chemically aged nylon 6.

Chapter 6 summarizes the conclusions drawn from the entire work and provides recommendations for extended study on each topic. Appendices A and B provide supplementary data for chapters 2 and 3, respectively.

1.3 Literature review and background

1.3.1 Carbon nanofibers

Carbon nanofibers constitute a class of 1-D carbon nanomaterials that have attracted ongoing attention in recent decades [1-3]. Depending on the preparation approach, two types of
carbon nanofibers are produced with distinct morphologies and characteristics: continuous carbon nanofibers based on the nonwoven electrospinning technique, and vapor grown carbon nanofibers (VGCNF) based on catalytic chemical vapor deposition (CVD). Both CNFs will be reviewed in the following.

Continuous CNFs, prepared by electrospinning of carbon precursors, usually have fiber diameter from 10 nm to ~1 μm (nanometer to submicron range) which is much smaller than the ~5-μm-diameter of commercial CF manufactured by conventional wet spinning. The structure of this type of CNF, similar to the commercial CFs, is of oriented and ordered carbon crystallites composed of turbostratic and bent carbon layers [3]. The carbon layers are equivalent to sp²-hybridized graphene layers with vacancy defects. The processing strategy for the continuous CNFs follows precursor spinning, thermal stabilization, carbonization and graphitization, regardless of the source of the precursors, from petroleum-based feedstocks such as PAN or pitch to biorenewable sources such as lignin, cellulose, and other biomass [4]. The CNF structure evolves depending upon the maximum temperature during thermal treatment as shown in Figure 1-1.

The first step, precursor spinning, is very important because the dimension, structure and good final mechanical and other physical properties of CFs are highly dependent on the properties of precursor fibers. Electrospinning is a practical and versatile technique that was popularized in the early 1990s due to the great achievement of turning a wide range of organic polymers into nanoscale filaments via this method [5]. Compared to conventional spinning methods using a mechanical or shear force, electrospinning draws fibers by electrostatic force under an external electric field, which dramatically reduces the fiber diameter. Electrospinning exhibits the further advantage that there is little restriction on the chemical composition of the
Figure 1-1. Upper: TEM images of PAN-based electrospun CNFs carbonized at (a) 550 °C, (b) 950 °C and (c) 2800 °C [3]. Bottom: corresponding model for the carbon layer structures at different temperature stages from TEM studies [4].

materials that may be electruspun successfully, allowing all the aforementioned CF precursors and their hybrid blends to form nanofibers.

The basic setup for electrospinning is quite simple, consisting of three major components: a high-voltage power supply, a metal spinneret, and a grounded collector, shown schematically in Figure 1-2. The electrospinning dope, usually a polymer solution (or melt), is fed through the spinneret, which is connected to a syringe. The syringe pump provides the dope flowing at a constant and controllable rate. Under an applied high voltage (1 to ~30 kV), the pendant droplet formed at the tip of the spinneret becomes highly charged. Meanwhile, electrostatic repulsion overcomes the surface tension of the polymer solution, causing a distortion of the liquid drop and finally the ejection of a liquid jet. The conical shape formed due to the electrostatic force is
known as the Taylor cone [6]. The charged liquid jet is then elongated and thinned by a whipping process, resulting in the formation of long, uniform fibers with nano/submicron-scale diameters. Attracted by the grounded collector placed opposite to the spinneret, the charged fiber is often deposited as a randomly oriented, non-woven mat, see the inset of Figure 1-2.

Due to different selections of precursors and corresponding heat treatments, the mechanical properties of electrospun CNFs are varied just like micro-sized CFs. For the same precursor, however, recent studies proved that the electrospun CNF exhibited some superior mechanical properties when compared to its micro counterpart. Based on in situ TEM tensile testing with aid of a microelectromechanical system (MEMS) device, it has been reported that the PAN-based CNFs exhibit extraordinary increase in tensile strength and modulus when the fiber diameter decreases to 150 nm, reaching strength of 7.3 GPa and modulus of 262 GPa with 108 nm

Figure 1-2. Schematic diagram of the electrospinning setup.
diameter [7]. Smaller fiber diameter for CF precursors can be readily prepared via the electrospinning process, leading to both a higher degree of molecular orientation and fewer defects in the structure, which are critical to the increase of the final mechanical properties of CNFs [7-9]. There is still much room to optimize the mechanical properties of electrospun CNFs by modifying the precursor formula and the thermal treatment procedure [10].

VGCNFs are also high aspect ratio nanofibers with 50-200 nm in diameter and up to 100 μm in length. One common structure of VGCNFs is a hollow core surrounded by single or double layers of rolled graphene sheets stacked either parallel to each other or at a certain angle from the nanofiber axis, as shown in Figure 1-3. This tilted-stacking structure features reactive graphene edges on both inner and outer surfaces of these VGCNFs, which can be readily modified through chemical functionalization or thermal treatments, if necessary, to facilitate covalent bonding with the matrix. Different structures and morphologies of VGCNFs can be obtained by varying the gas feedstock, metal catalyst, and operating conditions [11]. VGCNFs are typically included in property comparisons with carbon nanotubes (CNTs) because of their similarity as well as diverse advantages. Table 1-1 summarizes the typical properties of electrospun CNF, VGCNFs, single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), and commercial PAN-based CFs [1].
Figure 1-3. A schematic illustrates the cup- stacked structure of a single layer VGCNF. (referred from pyrografproducts.com)

Table 1-1. A comparison of typical properties of electrospun CNF, VGCNF, SWNT, MWNT and CF.

<table>
<thead>
<tr>
<th>Property</th>
<th>Electrospun CNF [7]</th>
<th>VGCNF</th>
<th>SWNT</th>
<th>MWNT</th>
<th>CF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (nm)</td>
<td>100 - 300</td>
<td>50 - 200</td>
<td>0.6 - 1.8</td>
<td>5 - 50</td>
<td>7300</td>
</tr>
<tr>
<td>Length (μm)</td>
<td>-</td>
<td>50–100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aspect ratio</td>
<td>&gt; 1000</td>
<td>250 - 2000</td>
<td>100 - 10000</td>
<td>100 - 10000</td>
<td>-</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.6~1.8</td>
<td>2</td>
<td>~1.3</td>
<td>~1.75</td>
<td>1.74</td>
</tr>
<tr>
<td>Thermal conductivity (W/m K)</td>
<td>-</td>
<td>1950</td>
<td>3000–6000</td>
<td>3000–6000</td>
<td>20</td>
</tr>
<tr>
<td>Electrical resistivity (Ω cm)</td>
<td>-</td>
<td>$1 \times 10^{-4}$</td>
<td>$1 \times 10^{-3} - 1 \times 10^{-4}$</td>
<td>$2 \times 10^{-3} - 1 \times 10^{-4}$</td>
<td>$1.7 \times 10^{-3}$</td>
</tr>
<tr>
<td>Tensile strength (GPa)</td>
<td>4 - 7.3</td>
<td>2.92</td>
<td>50 - 500</td>
<td>10 - 60</td>
<td>3.8</td>
</tr>
<tr>
<td>Tensile modulus (GPa)</td>
<td>60-260</td>
<td>240</td>
<td>1500</td>
<td>1000</td>
<td>227</td>
</tr>
</tbody>
</table>
The data presented in Table 1-1 shows clearly that VGC NFs have larger fiber diameter and higher density than CNTs, at the same time possessing weaker mechanical properties and lower thermal conductivity. Despite the fact that VGC NFs receive less research focus academically, they are competitive over CNTs in industry at the moment due to their advantages in two other aspects: ease of dispersion/processing and lower cost. The dispersion of CNTs into a solution or resin matrix is usually difficult due to strong Van der Waals forces existing for nanomaterials with high aspect ratio. Sonication with the aid of dispersants in solvent is often employed to enhance dispersion of CNTs [12], which is not desirable for industrial-scale production. In contrast, VGC NFs are less affected by Van der Waals forces and can be well dispersed through direct melt mixing [13]. In order to improve interfacial bonding between nanofillers and the matrix, CNTs require additional functionalization, such as exposure to strong acids, plasmas and UV light to create reactive functional groups on their surfaces. This functionalization step is not necessary for VGCNF/polymer composites, however. In addition to the extra cost resulting from the complexity of processing CNTs into nanocomposites, the raw material cost of VGC NFs is much lower than CNTs. According to economic data published in 2013, the prices of VGC NFs, MWCNTs, and 90 % pure SWCNTs were 0.1 – 5 $/g, 0.1 – 25 $/g, and 50 – 400 $/g, respectively [14]. The continuing drop in price associated with their growing market makes VGCNFs an excellent alternative to CNTs and conventional CFs for composite applications.

1.3.2 CNF/polymer nanocomposites and their properties

Since VGCNFs exhibit excellent balance among mechanical, electrical, and thermal properties, VGCNF-reinforced polymer nanocomposites are promising for structural and other multifunctional applications, such as electromagnetic interference (EMI) shielding, electrostatic discharge (ESD) protection, thermal conductivity of spacecraft materials, batteries and
electronics, and reduced coefficient of thermal expansion (CTE) materials for aerospace systems [1]. In order to achieve further property improvement with lower nanofiber loading for the isotropic VGCNF/polymer nanocomposites, three main factors - the nanofiber dispersion and distribution, the nanofiber aspect ratio, and the filler-matrix interfacial properties – need to be balanced simultaneously. In the example of melt mixing, which is a common processing approach for compounding polymer composites in industry, a good dispersion of VGCNFs without reducing the aspect ratio at a moderate shear mixing condition is essential for efficiently increasing mechanical and electrical properties of the composites [1, 13]. The interfacial tension between the VGCNFs and the polymer matrix affects the dispersion and distribution of the nanofibers, which can be adjusted by surface treatment with oxidation [13]. The processing-structureProperty relationships of VGCNF/polymer nanocomposites have been studied for quite a number of thermoplastic polymers, including polyethylene (PE) [15], polypropylene (PP) [16-24], nylon, poly(ethylene terephthalate) (PET) [25], polystyrene (PS) [26-29], poly(methyl methacrylate) (PMMA) [15, 30-32], poly(ether ether ketone) (PEEK) [33], and polycarbonate (PC) [24, 34-36], etc; and other thermosetting polymers, such as epoxy [34, 37-40].

1.3.3 Molecular dynamics study using dielectric analysis

Broadband dielectric spectroscopy (BDS) is capable of measuring the complex permittivity of dielectric materials in a wide frequency range from $10^{-5}$~$10^{10}$ Hz (or time domain, occasionally) of oscillating electric field and at ambient or varied temperature. Polymeric materials, including their composites, normally contain a certain concentration of dipole groups and/or trace ions so that they are dielectrically sensitive to BDS measurement. BDS is becoming a very powerful and popular technique to study polymeric materials, because it has the following advantages compared to other thermal analysis techniques:
- Relatively large changes may be observed in the complex permittivity during physical transitions (glass transition, secondary transition), compared to small changes in heat capacity, volume and enthalpy measured via DSC, TMA and DTA.

- The available frequency range of the electrical stimulus is much wider than that of mechanical stimulus in DMA and rheometry, revealing more dynamic information.

Permittivity is one of electrical properties for a dielectric describing how easily it polarizes in response to an external electric field. For a polymeric material i.e. condensed matter, the response of the material to an oscillating electric field generally depends on the frequency of the field, because a material’s polarization does not respond instantaneously to the applied field. This relation is therefore represented by a complex permittivity as a function of the angular frequency of the applied field \( \omega \): \( \varepsilon^*(\omega) \), which is composed of the real and imaginary parts:

\[
\varepsilon^* = \varepsilon'(\omega) - i \varepsilon''(\omega) \quad (1-1)
\]

in which \( \varepsilon' \) and \( \varepsilon'' \) are the real and imaginary parts, respectively. \( \varepsilon' \) and \( \varepsilon'' \) are available by measuring the capacitance (\( C \)) and conductance (\( G \)) of the material placed in a parallel-plate capacitor under an alternating voltage of angular frequency (\( \omega \)), via the following equations:

\[
C(\omega) = \varepsilon_0 \varepsilon'(\omega) \frac{A}{d} \quad (1-2)
\]

\[
G(\omega) = \omega \varepsilon_0 \varepsilon''(\omega) \frac{A}{d} \quad (1-3)
\]

where \( A \) and \( d \) are the sample’s cross-sectional area and thickness, respectively, and \( \varepsilon_0 \) is the permittivity of vacuum. Real permittivity \( \varepsilon' \) expresses the ability of the dielectric medium to store energy, whereas \( \varepsilon'' \) represents the energy losses due to the material medium. The complex permittivity for a dipolar relaxation process in a condensed dielectric medium can be described
by various empirical relaxation models, which are all extended from the single-relaxation-time model of Debye:

\[ \varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1+i\omega\tau} \quad (1-4) \]

where \( \varepsilon_{\infty} \) is the unrelaxed permittivity at the high frequency limit and \((\varepsilon_0 - \varepsilon_{\infty})\) is the dielectric strength of the relaxation process.

The collected dielectric data can be displayed as either isothermal or isochronal plots, depending on the purpose of analysis. Isothermal plots, namely the permittivity as a function of frequency at constant temperature, are convenient for studying the relaxation characteristics and their temperature dependence. A couple of dynamic models have been historically established to describe the temperature dependence of dielectric relaxation based on different mechanisms and molecular environment, exemplified in the schematic Arrhenius diagram of Figure 1-4. The Arrhenius equation well describes uncorrelated dipole rotations, and the Vogel-Fulcher-Tammann (VFT) equation is representative for non-Arrhenius behavior.

Within the intermediate frequency range, \(10^{-5}-10^{10}\) Hz, the polarization observed in polymers originates from the rotational mobility of permanent group dipole moments. The polarization, known by the net dipole moment per volume, can reflect different molecular motion processes of various length scales (localized motions, segmental motions, and global chain motions), as illustrated in Figure 1-5. Each process corresponds to a dielectric relaxation process, characterized by a peak in \(\varepsilon''\) and a step-like decrease of \(\varepsilon'\) in the frequency domain. The relationship between \(\varepsilon'\) and \(\varepsilon''\) for such dipolar relaxation processes are described by the Kramers-Kronig relations [42].
Figure 1-4. Schematic of an Arrhenius diagram for mechanisms commonly observed in polymers. The straight lines correspond to Arrhenius-like processes and the curves correspond to VFT-like relationships between the relaxation time and temperature [41].

Figure 1-5. Molecular motion processes categorized by length scales in polymer systems. (referred from Wübbenhorst's tutorial “Polymers and Nano-composites” at the 6thIDMRCs, Rome, 2009)
1.3.4 Dynamic study of epoxy and its nanocomposites

Epoxy resin is a class of common but important thermosetting polymers that have wide applications in coatings, adhesives, electrical insulations and composites. The basic constituent of epoxy resin primarily used in industry is diglycidyl ether of bisphenol A (DGEBA), with trade name Epon 828. DGEBA bears 2 epoxide groups at chain ends which are readily reactive to various curing agents, such as amines, anhydrides, phenols and thiols. Due to the versatility of the epoxy resin, the studies with the aid of BDS techniques have been carried out for different research purposes. One in particular is for the purpose of understanding the evolution of molecular dynamics of epoxy resins during network-forming progress. A couple of epoxy systems at different processing stages, including neat DGEBA [43-45], the unreacted mixtures of DGEBA with hardeners [46-52], the partially polymerized products at various degrees of cure [46-56], and the completely polymerized products [48, 50], have been investigated by dielectric spectroscopy. The \( \beta \) relaxation, determined as a Johari-Goldstein (JG)-type secondary relaxation, was found to change correspondingly with the primary relaxation regarding the relaxation time and strength when the system converts towards the cross-linked structure. A coupling model and other models were developed to link the changes in relaxation behavior to the changes in the molecular structure [45, 57, 58].

In another aspect, the influence of reinforcing nanofillers on the dynamics of epoxy thermosets is also attracting interest because it is closely related to the improvement of thermal, mechanical, and electrical properties [59]. For a certain polymer system, it has been realized that complicated factors determining nanofiller-polymer interaction are at play, such as the types of nanofillers (e.g. Montmorillonite nanoclay [60, 61], carbons [62], polyhedral oligomeric silsesquioxane (POSS) [63-65], nanosilicate [66, 67], nanoaluminum oxide [68], and
nanotitanium oxide [69, 70]), the nanofiller geometry (particles, fibers, and layers), concentration, dispersion (self-assembly versus aggregation), surface chemistry (surface modification), and others. Among the molecular mechanisms on different length scales mentioned earlier, the change of glass transition behavior, which is associated with segmental motions, after incorporating nanofillers is of particular interest and has not been widely studied in epoxy cross-linked systems. The interfacial relaxation, due to polarization of the intrinsic immobilized free charges at the interfaces between the two phases of different dielectric properties (nanofillers and polymer matrix in this case), is also of interest to understand the interfacial interaction.

1.3.5 Capacitive nondestructive evaluation of wire insulation

Wiring insulation provides electrical and physical separation of wire conductors in order to guarantee the safe electrical power or signal transmission in many systems, including space/aircraft systems. A variety of polymers have been developed historically and are being used widely in commercial aircraft until the present day. A representative list of the big insulating polymer family is given in chronological order: Nylon/PVC (polyvinyl chloride), aromatic polyimide such as Kapton® and Apical®, cross-linked ETFE (ethylene-tetrafluoroethylene) such as XLTefzel®, PTFE (polytetrafluoroethylene) such as Teflon®, polymer composites such as Teflon-Kapton-Teflon (TKT). Although these insulating polymers generally exhibit an excellent combination of dielectric, mechanical, thermal and chemical properties, they still suffer from degradation over extended periods of extended service due to environmental exposure factors such as heat, ionizing radiation, immersion in water/chemicals, concentrated electrical fields, mechanical stress, etc. Degradation in electrical wiring insulation is one of the leading causes of wire failure, which increases the risk of short-circuiting or loss of control function in aircraft.
Therefore, the inspection of the wiring insulation conditions on aircraft become necessary to detect the actual and potential insulation faults for improving the aircraft safety.

A number of nondestructive testing methods intended for wiring insulation inspection have been developed on the basis of monitoring the structural and property changes of insulators, such as infrared thermography [71], portable pulsed X-ray system [71], ultrasonic methods [72], acoustic and impedance testing methods [73], partial discharge analysis methods [74], and capacitive methods [75-77]. The capacitive method based on delicate models and sensors is capable of relating quantitatively the measurable capacitance to the dielectric properties of wires at specific locations under test, allowing effective determination of wire insulation status.

The polarization of dielectric materials, such as polymers, is characterized by the dipolar polarization mechanism, in which the separation of charges is caused by the rotation and distortion of permanent dipoles in molecules, by the external electric field. A dipole moment aligned in the field direction is therefore created and defined by:

\[ p = qd \]  

(1-4)

where \( p \) is the induced dipole moment in the field direction, and \( d \) is the distance vector between charges \(-q\) and \(+q\). The presence of polarization means that more charges are stored on the capacitor electrodes and the capacitance of the system is thereby increased. The relationship among the induced dielectric polarization \( P \), a static external electric field \( E \) and the electrical displacement \( D \) is established by:

\[ D = \varepsilon_0 E + P \]  

(1-5)

Due to the linear relationship between the capacitance and the permittivity, \( D \) is also expressed as:

\[ D = \varepsilon_0 \varepsilon E \]  

(1-6)
Using a typical inductance-capacitance-resistance (LCR) meter coupled with a parallel-plate electrode tester, as in this research, the complex permittivity as a function of frequency can be readily determined by relating Eq (1-2), Eq (1-4), and Eq (1-5) from the measured capacitance $C$ and dissipation factor $D$, as the real and imaginary part of complex capacitance $C^*$, respectively.

$$C^* = C(1 - jD) \quad (1-7)$$

$$D = \frac{\varepsilon''}{\varepsilon'} \quad (1-8)$$

The measurement of capacitance for wire insulations with complicated geometry requires sophisticated computational models and electrode design. Figure 1-6 shows that the interdigital capacitive methods developed in our group were capable of detecting dielectric property changes in realistic aircraft wires (MIL-W-81381/12) due to thermal and hydrolytic exposures [77].

Figure 1-6. Schematic of cylindrical interdigital capacitive sensor designed for on-aircraft wire insulation monitoring [77].
1.4 Research Objectives

1.4.1 Processing and Characterization of Low-Cost Electrospun Carbon Fibers from Organosolv Lignin/Polyacrylonitrile Blends

The development of low-cost, high-performance CNFs by electrospinning aims to: 1. Tune the electrospinnability, molecular miscibility and thermal mobility of lignin/PAN precursor blend fibers by butyration of hydroxyl groups on lignin molecules; 2. Optimize the processing conditions for electrospinning lignin/PAN precursor fibers by investigating the factors - blend ratio, viscosity and conductivity, enabling production of bead-free, uniform, continuous fibers with maximum lignin content; and 3. Evaluate the morphology, structure, and mechanical properties of carbonized nanofiber mats based on different precursor compositions.

1.4.2 The influence of carbon nanofibers on the aging of Tin (II)-catalyzed RTV polysiloxane foams

The investigation of CNF-reinforced RTV polysiloxane foam composites aims to: 1. Characterize the foam structure and the morphology of CNF nanofiller and residual tin catalyst in polysiloxane via scanning electron microscopy (SEM); 2. Identify and quantify the tin and other elements based on surface techniques: energy dispersive spectrometry (EDS) and X-ray photoelectron spectroscopy (XPS); and 3. Evaluate the effect of CNF loading on thermal properties and the temperature dependence of polymer dynamics in the nanocomposites.

1.4.3 Dynamics of a model polycyclic aromatic hydrocarbon compound/epoxy composites:

A dielectric study

The dielectric study of model PAH/epoxy nanocomposites aims to: 1. Investigate the $T_g$ increment of anthracene-reinforced epoxy nanocomposites by hybrid strategies via broadband
dielectric relaxation spectroscopy over a wide frequency and temperature range; 2. Analyze dielectric spectra with a parametric model fitting technique to identify and quantify DC conductivity, interfacial polarization (Maxwell-Wagner-Sillars) relaxation, $\alpha$-, and $\beta$- relaxations of the epoxy system; and 3. Interpret the molecular interaction between the anthracene nanofiller and epoxy polymer chain in nanocomposite samples and the mechanisms underlying the observed changes in the glass transition behavior as a function of sample composition.

1.4.4 Permittivity and Electrical Breakdown Response of Nylon 6 to Chemical Exposure

Chemical exposure of nylon 6 in six aircraft fluids with different polarity was designed and the study aims to: 1. Conduct permittivity measurement using parallel plate electrodes and electrical breakdown measurement; 2. Apply two-parameter Weibull analysis of breakdown strength data to evaluate the effect of chemical immersion; and 3. Investigate the correlation between permittivity and electrical breakdown strength, providing experimental benchmarks of measured capacitance as a function of chemical immersion time and validating the efficacy of the capacitive sensing method in this context.

1.5 References


CHAPTER 2: PROCESSING AND CHARACTERIZATION OF LOW-COST ELECTROSPUN CARBON FIBERS FROM ORGANOSOLV LIGNIN/POLYACRYLONITRILE BLENDS

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2.1 Abstract

The esterification of lignin with butyric anhydride decreases both the viscosity of lignin/PAN blend spinning solutions and their glass-transition temperature compared to unmodified lignin/PAN blends. The effect of blending PAN with lignin before or after butyration on the electrospinnability, miscibility and thermal stability of precursor blend fibers was investigated by morphological, rheological, and thermal analysis. The micromorphology, carbon structure, and mechanical properties of resultant carbonized fibers (CFs) were further evaluated. This study reveals a new approach to controlling inter-fiber bonding of lignin-based carbon nanofiber mats by manipulating the molecular structure of lignin while following a standard procedure of thermo-stabilization and carbonization treatment. Characterization results indicate

\[ \text{--------------------------} \]
that inter-fiber bonding in electrospun CF mats, induced by the high thermal mobility of butyralated lignin, favorably affected their mechanical properties.

2.2 Introduction

The last decades have seen increasing demand for carbon fibers in a variety of industrial applications. Carbon fibers (CF) are by far the most important commercialized carbon-reinforcing material for polymer composite applications. They exhibit not only exceptional mechanical properties such as high strength-to-weight ratio and fatigue resistance, but also can be produced at the lowest cost compared to other carbonaceous materials with potential for application in structural composites, e.g., vapor grown carbon nanofiber (VGCNF) [1], multi-walled carbon nanotube (MWCNT), and single-walled carbon nanotube (SWCNT) [2]. Carbon fibers can be woven into fabric sheets or plied together to form composite laminates, resulting in high fiber content and superior reinforcement, properties other particulate fillers typically do not achieve. On the other hand, the growth rate in the CF-manufacturing industry is too low to satisfy the fast growing demand, mostly because the main precursor for CFs, polyacrylonitrile (PAN), is expensive and – as a petroleum derivate – not sustainable [3]. In order to overcome the manufacturing restrictions caused by PAN, low-cost CF alternatives based on bio-renewable, inexpensive precursors are the focus of current investigations. These alternatives include lignin [3, 4], cellulose [5], and biomass resins [6].

Lignin is the second most abundant biopolymer next to cellulose, and it is available as a major by-product of the paper industry. There is a wide selection of lignin candidates as CF precursors, characterized by the particular lignin source and isolation process. The most common sources are hardwood lignin, softwood lignin, and grass lignin, which differ in their chemical
structure due to the varying percentage of three basic repeating units: cumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [7]. Lignins obtained through different isolation processes, such as lignosulfonates, alkali lignin, kraft lignin, and organosolv lignin, are characterized by their different purity and lignin fraction size. These variations influence their fiber spinning performance and, consequently, the quality of the resulting CFs. Organosolv lignin, with its low inorganic impurities such as ash and sulfur, is being explored expansively as a potential precursor for the conversion to CFs [8-11]. Baker [3] used a thermal pretreatment and reported tensile strength of CFs melt-spun from a purified organosolv lignin as high as 0.71 GPa. However, the mechanical properties of lignin-based CFs produced by conventional spinning methods are still comparatively low and need further improvement, such as to seek more suitable lignin precursors and to optimize the fiber fabrication and treatment techniques.

Electrospinning is emerging as a reinvented processing technique that permits fabrication of robust, multi-functional fibrous materials [12, 13]. Ultrathin fibers with submicron to nanometer (from $10^{-2}$ to 1 μm) diameters can be fabricated by continuously stretching of a viscoelastic jet under an external electric field applied during the process. Recent studies on electrospun PAN fibers showed that the reduction of the fiber diameter down to the nanoscale enabled a significant increase in modulus, strength, and toughness compared to micro-scale fibers [14, 15]. It was reported that precursor fibers obtained by electrospinning exhibited improved mechanical properties and molecular orientation, critical for the manufacture of stronger CFs. In addition to the effect of diameter size on mechanical properties, the higher specific surface area of electrospun fibers that is the result of the smaller diameter shows a promising pathway to improving poor interfacial bonding between the microfibers and the polymer matrix in composites. Electrospun nonwoven membranes have been reported to reinforce neat epoxy
matrices [16, 17] and increase the interlaminar/fracture toughness of a high-performance composite laminates [18, 19].

Direct electrospinning of lignin is challenging in most cases due to its susceptibility to “beading”. Non-uniform fibers are often the result of lignin’s relatively low molecular weight and low viscosity in solution [20]. A straightforward approach for tuning electrospinnability is to blend lignin with high-molecular-weight polymer additives such as polyethylene oxide (PEO) [8, 11, 21, 22], polyvinyl alcohol (PVA) [23, 24], or PAN [25-28]. Particularly, using PAN as an additive in electrospinning would theoretically improve the mechanical performance of lignin-based CFs because PAN is already known as the best precursor to produce CFs with high carbon yield and excellent properties [29]. Some extra attention need to be paid to the PAN content in order not to compromise the general economical goal.

Fiber fusion is generally considered a detrimental process in the production of conventional lignin-based carbon fibers [4]. Recently, however, investigations showed unexpected improvements in a variety of material properties after inter-fiber fusion in ultrafine electrospun fibers after thermal treatment. Fused fibrous carbon mats obtained from an organosolv lignin (Alcell) blended with 10 wt.% of PEO plasticizer exhibited superior charge capacity than non-fused carbon fibers, an effect that was even enhanced by nitrogen-doping [11]. Kadla reported that electrospun fibers based on a mixture of Kraft lignin fractions with different molecular weights ($M_w$) and glass transition temperatures ($T_g$) showed inter-fiber fusion after thermostabilization [30, 31]. The resulting inter-connected carbon fibers exhibited an order of increase in electrical conductivity as well as significant improvement in mechanical properties compared to non-bonded fibers. Inter-fiber fusion occurs when the $T_g$ of the precursor fibers shifts below the heating temperature due to slow cross-linking during the thermostabilization
stage. Incorporation of a certain percentage of low-melting point PEO additive or low-\(T_g\) lignin fraction modifies the \(T_g\) and induces thermal softening of the lignin-based precursor fibers, which is key to controlling the inter-fiber bonding that occurs during the thermostabilization process.

In the present work, we report that a low-molecular weight organosolv lignin blended with PAN precursor was readily electrospun into ultrafine fibers and that inter-fiber bonding of the CFs was attained through lignin butyration. Esterification of lignin by butyration transforms the alcohol groups to butyl esters, which improves the miscibility of lignin with low-polar solvents [32], monomers [33], and plasticizing polymers [34]. The \(T_g\) of lignin decreases after esterification due to increasing the molecular thermal mobility by reducing intermolecular interaction [35]. The effect of lignin butyration on electrospinnability, miscibility and thermal properties of the precursor blend fibers was investigated by morphological, rheological, and thermal analysis. The carbon structure and mechanical properties of the resultant CF mats were characterized by Raman spectroscopy and tensile testing. The mechanism for the improvement in mechanical performance of CF mats associated with inter-fiber bonding will also be discussed.

2.3 Experimental

2.3.1 Materials and Sample Preparation

Polyacrylonitrile (PAN, average \(M_w = 150,000\)), butyric anhydride, and 1-methylimidazole (1-MI) were supplied by Sigma-Aldrich (St. Louis, MO) and used as received. N, N-dimethylformamide (DMF) and hexane were obtained from Fisher Scientific (Fair Lawn, NJ). The organosolv lignin (referred to as lignin in the following) used here was a grass-type lignin isolated from corn stover using the organosolv process, supplied by Archer Daniels Midland (ADM) Company (Decatur, IL). The as-received lignin was purified by washing with dilute
hydrochloric acid solution (HCl, 0.1M) according to a reported approach [36] in order to limit the inorganic impurities to less than 0.1 wt.%. The empirical formula of the purified organosolv lignin was determined by CHN elemental analysis as C_{10.2}H_{12.2}O_{3.8}N_{0.2}. Gel Permeation Chromatography (GPC, Waters, ACQUITY UPC system) indicated that the average molecular weight ($M_n$) and its distribution (PDI) were 4000 and 1.25, respectively. The purified lignin was dried in a vacuum oven at 70 °C for 24 h before further chemical modification or mixing.

Butyrated organosolv lignin (B-lignin) was synthesized according to a modified method of butyration described in [33]. The reaction scheme of lignin butyration is illustrated in Figure 2-1. Organosolv lignin (200 g), butyric anhydride (400 g) and 1-methylimidazole (1-MI) (5 g) were added in this order to a 2 L round-bottomed flask. The mixture was allowed to react in nitrogen atmosphere under vigorous stirring at 60 °C for 3 h. After natural cooling to room temperature, the reaction mixture was transferred to a beaker and washed three to five times with 500 mL of n-hexane, stirring vigorously with a rod during each wash. Between each wash the mixture was allowed to precipitate for a few minutes. Then 1 L of DI water was added to the washed, chalky, crude butyrated lignin and stirred vigorously overnight. The water-lignin mixture was then vacuum-filtered with water wash three times, followed by drying in a vacuum oven at 60 °C for 12 h. The B-lignin was then ground into a fine powder and stored in a desiccator.
Figure 2-1. Reaction scheme of lignin butyration to convert hydroxyl groups to esters.

2.3.2 Precursor Fiber Preparation: Blending and Electrospinning

Electrospinning dopes of lignin/PAN and B-lignin/PAN blends were prepared at a total concentration of 20 wt.% in DMF solvent with the (B-)lignin; the PAN mass ratio varied from 30:70 to 70:30. The required amount of PAN powder was mixed into 12 g DMF in a 30 ml glass vial and then processed in a high-speed planetary mixer (Mazerustar KK50S, KURABO Industries Ltd., Japan) for 15 min until PAN was completely dissolved. Subsequently, weighed lignin or B-lignin was homogenized into the clear PAN solution for another 15 min. The planetary mixing shortened the normal dissolving process time significantly: from hours to 30 min. Pure PAN solutions at concentrations of 10 to 15 wt.% were also prepared as reference for the comparison of dope electrospinnability, fibrous morphology, structure, and properties at different stages of thermal treatment.

In a horizontal electrospinning setup, 2.8 mL of dope solution was loaded into a 10 ml syringe capped with a flat-tip 22 gauge needle (0.41 ± 0.02 mm inner diameter), which was autopumped at a constant flow rate of 5 μL/min. The high-voltage power supply was set to 15 kV potential difference between the needle tip and the cylindrical collector, separated by 20 cm. The
cylindrical copper collector (length 23 cm, diameter 5.5 cm) was connected to a rotating motor to receive the fiber mats. The copper was wrapped in smooth aluminum foil for ease of removal of the finished mats. Electrospinning was performed at room temperature and 25 % relative humidity. The resulting fibrous mats were dried at 60 °C in a vacuum oven overnight to remove any residual DMF.

2.3.3 Carbon Fiber Fabrication: Thermostabilization and Carbonization

The precursor fiber mats (16 cm × 16 cm) were thermally stabilized in a Thermolyne F79300 tube furnace in an oxidizing atmosphere (air flow, 150 cm³ STP/min). The mats were fixed along the short edges by clipping to the vessels in order to provide tension against shrinkage during stabilization. The furnace temperature was increased from room temperature up to 200 °C at a heating rate of 0.2 °C /min. Thereafter the temperature was held at 200 °C for 12 h. After natural cooling to ambient temperature, the furnace was switched to an inert atmosphere (argon flow, 150 cm³ STP/min). The stabilized fibers were subsequently carbonized at 1000 °C for 0.5 h at a heating rate of 5 °C /min. The carbonization temperature was adopted due to the practicability for comparison to other studies on lignin-based carbon fibers. The precursor fiber yields after thermostabilization and carbonization were determined by weighing the mats after each process.

2.3.4 Structural and Morphological Characterization

Nuclear magnetic resonance (¹H-NMR) and Fourier transform infrared spectroscopy (FTIR) were performed to confirm the butyric modification of the organosolv lignin. To obtain ¹H-NMR spectra, unmodified lignin, and B-lignin were dissolved in dimethyl sulfoxide-d₆ (99.9 %, Cambridge Isotope Laboratories, Inc., Andover, MA) and tested using a Varian MR-400 spectrometer featuring a narrow bore 9.4 Tesla 400 MHz magnet. FTIR spectra were recorded by
a Bruker IFS66 V spectrometer with a scanning range from 500 to 4000 cm\(^{-1}\) at a spectral resolution of 4 cm\(^{-1}\). In this case, the sample pellets were prepared by mixing with ground KBr powder. The micro-morphology of precursor, stabilized, and carbonized fibers was examined using a field-emission scanning electron microscope (FE-SEM) (FEI Quanta 250) operating at 10 kV under high vacuum. The fiber diameters and their distribution were obtained by image analysis (ImageJ) of 100 fibers that were randomly selected. The carbon structure of the carbonized fibers was analyzed using Raman spectroscopy and the spectra were recorded on a Renishaw Dispersive Raman Spectrometer with back-scattered light from a 480 nm laser. The Raman shift was scanned from 1000 to 2000 cm\(^{-1}\) with a spectral resolution of 2 cm\(^{-1}\). Flat and smooth samples were placed on a glass side for testing. Elemental composition (percentage C, H, and N) of the fibers at different stages was determined using a PE 2100 Series II combustion analyzer (Perkin Elmer Inc., Waltham, MA).

**2.3.5 Rheological, Thermal and Mechanical Analysis**

The dynamic viscosity of the electrospinning dope was measured using an AR2000ex stress-controlled rheometer (TA Instruments), utilizing a 40 mm diameter cone geometry (1° cone angle, 28 μm truncation) and Peltier temperature control stage. Flow continuous ramp test at 25 °C was performed at shear rates decreasing from 660 s\(^{-1}\) to 0.1 s\(^{-1}\) and the data were recorded at 5 points per decade in the overall duration of 4 min. This test protocol aimed to minimize flow instability as well as evaporation of the lignin blend solutions. Five replicate measurements were taken for each dope sample to determine the standard deviation and 0.2 mL of dope solution was applied for every measurement. The electrical conductivity of dope solutions was measured using a conductivity meter (Mettler Toledo S47 SevenMulti\textsuperscript{TM}) coupled with a Inlab 720 conductivity probe at room temperature. Glass transition temperatures (\(T_g\)) of
the lignin blends were measured using a differential scanning calorimeter (DSC, Q20, TA Instruments) in order to investigate the miscibility between PAN and lignin/B-lignin. Precursor fiber samples as well as butyrated and non-butyrated lignin samples were scanned from 0 to 200 °C at a heating rate of 10 °C/min under nitrogen gas purge. Thermogravimetric analysis (TGA, Q50, TA Instruments) was conducted to evaluate the thermal stability of the precursor fiber mats and the carbon contribution from the lignin content. The porous fibers were pressed into solid pellet samples prior to measurements. Approximately 5 mg samples were heated from room temperature to 800 °C at a heating rate of 20 °C/min under nitrogen atmosphere with a purge flow of 50 mL/min. The mechanical properties of the carbonized fiber mats were evaluated by uniaxial tensile testing using an Instron universal testing machine (Model 5569) equipped with a 50 N load cell. According to ASTM C1557-03, a modified approach for test specimen preparation was adopted. Here, a fast-curing epoxy adhesive was used to adhere a fiber mat sample (40 mm length × 5 mm width) to a paper mounting tab with gauge length of 20 mm. The tensile test started when the specimen was securely gripped and cut away both sides of the tab, as shown in Figure A-3. The strain rate was 0.2 mm/min.

2.4 Results and Discussion

2.4.1 Lignin Butyration

$^1$H NMR spectra of organosolv lignin before and after butyration are presented in Figure 2-2. For butyrate lignin, three distinct signals emerging in the chemical shift between 0.5 - 2.4 ppm corresponded to -CH$_3$ ($\delta$ 0.8-1.1 ppm), $\alpha$-CH$_2$ ($\delta$ 1.3-1.8 ppm), and $\beta$-CH$_2$ ($\delta$ 2.0-2.4 ppm) groups, which qualitatively confirmed the attachment of butyl ester chains to lignin molecules. Proton signals attributed to methoxyl (-OCH$_3$) groups ($\delta$ 3.3-4.1 ppm) and aromatic protons ($\delta$
6.3-7.9 ppm) of lignin were barely affected by the butyration modification. Complete conversion of hydroxyl groups to esters was further confirmed by FTIR spectra, as shown in Figure 2-3. The broad and strong peak at 3430 cm\(^{-1}\), corresponding to O-H stretching of hydroxyl groups in lignin, was weakened significantly after butyration. In addition, an increase in the peaks at 2940-2840 cm\(^{-1}\) and at 1765-1705 cm\(^{-1}\) for butyrated lignin was observed, corresponding to C-H stretching of the aliphatic and aromatic structures (Al & Ar) and C=O stretching of the carboxylic groups, respectively. In agreement with the \(^1\)H NMR spectroscopy results, the existence of butyl ester was established. It was expected that the replacement of aliphatic and aromatic hydroxyl groups by esters would modify the intermolecular interaction and the thermochemical properties of lignin, which is critical for the electrospinnability and processability of carbon fibers.

![Figure 2-2. \(^1\)H NMR spectra of unmodified and butyrate...](image-url)
Figure 2-3. FTIR spectra of unmodified and butyrated organosolv lignin. Peak labels represent (a) O-H at 3430 cm\(^{-1}\): stretching of hydroxyl groups (b) C-H (Al & Ar) at 2940-2840 cm\(^{-1}\): stretching of the aliphatic and aromatic structures (c) C=O at 1764-1706 cm\(^{-1}\): stretching of the carboxylic groups.

2.4.2 Effect of Viscosity on the Electrospinnability of Precursor Solutions

A critical initial step for the fabrication of high-quality carbon nanofibers is the acquisition of bead-free, uniform, fine precursor fibers with high lignin content through electrospinning. The formation of “bead on the string” structure, which is an unfavorable phenomenon during electrospinning, will generally appear when the surface tension of spinning solution prevails over the effects of electrostatic repulsion and viscoelastic force, the two other combined factors governing the ejection of electrospinning jet [37]. Several studies have been conducted to
determine how the intrinsic parameters, including surface tension, conductivity, and viscosity (or concentration), affect the electrospinnability of lignin-based electrospun fibers [10, 23]. It is worth noting that for a solution with given polymer and solvent, the surface tension changes moderately with the polymer concentration whereas the viscosity and the conductivity of solution can be significantly varied to affect bead formation on electrospun fibers [38]. In the present study, the viscosity and the conductivity were investigated in relation to electrospinnability in order to determine the optimal precursor composition for stable electrospinning. In the case of a bi-component lignin-PAN-DMF solution system, the viscosity can be tuned by varying either the total precursor concentration or the lignin:PAN mass ratio. The lignin (B-lignin)/PAN concentration of the electrospinning solution was set at 20 wt.% in DMF, while allowing the lignin (B-lignin) fraction to vary from 30 % to 70 % in the solid. The precursor solutions of various compositions were stable viscous fluids, not showing any precipitation after 24 hours.

The viscosities of 20 wt.% solutions of lignin (B-lignin)/PAN blends and pure PAN precursor solutions at 10 to 15 wt.% concentrations were measured as a function of shear rate in the range of 0.1 to 660 s\(^{-1}\) (see Figure A-1). Typical shear thinning behavior occurred at above shear rate of 10 s\(^{-1}\) in all solution samples, indicating the viscoelasticity of high molecular weight liquids essential for electrospinning. The viscosity of both lignin blends with different polymer mass ratios was plotted in comparison to that of pure PAN solutions in various concentrations at a shear rate of 0.1 s\(^{-1}\) in Figure 2-4, which approximates the intrinsic characteristics under Newtonian plateau. It is demonstrated that at constant concentration, increasing the fraction of lignin (butyrated or non-butyrated) with relatively low molecular weight decreased the viscosity of both precursor blend solutions, showing analogous effect of decreasing concentration on the
viscosity of PAN solution. For example, the viscosity of the lignin/PAN blend solution decreased from 10.7 ± 0.3 Pa·s for 30 % lignin fraction to 2.10 ± 0.01 Pa·s for 50 % lignin fraction, comparable to the decrease from 7.8 ± 0.3 Pa·s at 15 wt.% to 2.36 ± 0.01 Pa·s at 12 wt.% for the pure PAN solutions. A further reduction to 0.91 ± 0.02 Pa·s for lignin/PAN at 60 % lignin fraction was very close to the value of pure PAN solution at 10 wt.% (0.93 ± 0.05 Pa·s). The viscosities of B-lignin/PAN blends were gently lower than those of the lignin/PAN blends at the same mass ratio as expected, due to the reduction of strong intermolecular attraction between lignin hydroxyl groups and polar dipoles of PAN/DMF solutions. On the other hand, Fig.4 shows that the electrical conductivity of 20 wt.% lignin/PAN blends decreased with addition of lignin, of which the values were significantly lower than that of pure PAN solution ranging 10 to 15 wt.%. These indicate that lignin is a weaker charge-carrier than PAN. A further drop of conductivity about 5 to 16 μS/cm for B-lignin/PAN from lignin/PAN blend solutions exhibited the negative effect of butyration of lignin on conductivity by removing hydroxyl groups.

The lignin(B-lignin)/PAN blend solutions with lignin fractions varying from 30 % to 70 % were electrospun under the same operational conditions (including voltage supply, feeding rate, and tip-to-collector distance) as described in the experimental section, and the SEM morphologies of their resulting precursor fibers are shown in Figure 2-5. Randomly-ordered, bead-free, and uniform electrospun fibers were formed for lignin/PAN blend solutions with lignin fraction up to 60 %. In contrast, occasional, large-size beads emerged in the fibers from B-lignin/PAN blend solutions with B-lignin fraction of 60 %. The further incorporation of lignin or B-lignin into precursor polymers to 70 % led to an increasing density of beads and to non-uniform fiber diameters. Meanwhile, the fiber diameter decreases with increasing the lignin fraction for both precursor blends from 1.8 μm to 0.6 μm approximately.
Figure 2-4. Viscosity at a shear rate of 0.1 s⁻¹ (filled symbols) and conductivity (open symbols) of 20 wt.% lignin(B-lignin)/PAN solutions with varied lignin fraction in comparison to pure PAN solutions in different concentrations. The value of viscosity is averaged based on at least three measurements and the standard deviation is given in the form of error bars.

The diameters of bead-free precursor fibers electrospun from three selected solutions were investigated and the results are shown in Figure 2-5. The solutions had the following similar viscosities but varied conductivity (see Figure 2-4): pure PAN 12 wt.% (2.36 ± 0.01 Pa·s, 121.6 μS/cm), lignin/PAN 50-50 blend 20 wt.% (2.10 ± 0.01 Pa·s, 79.0 μS/cm) and B-lignin/PAN 50-50 blend 20 wt.% (1.48 ± 0.09 Pa·s, 62.7 μS/cm). Correspondingly, the diameter of electrospun fibers from pure PAN 12 wt.% solution, measured as 950 ± 180 nm, was significantly smaller
than that of the fibers spun from lignin blends, lignin/PAN 50-50 and B-lignin/PAN 50-50, with $1920 \pm 150$ nm and $1690 \pm 70$ nm, respectively. The higher conductivity (or the charge density which is proportional to conductivity) led to stronger repulsive force to stretch the electrified fluid jet and consequently thinner solidified fibers. When tailoring the lignin:PAN mass ratio, both viscosity and conductivity were altered to affect the electrospinnability. It demonstrated that the viscosity is competing the conductivity in a predominant way on controlling the fiber diameter, confirmed by the fact of thinner electrospun fibers with deceasing both viscosity and conductivity. This effect may also result in the slight decrease in fiber diameter for B-lignin/PAN 50-50 compared to lignin/PAN 50-50 fibers. If both viscosity and conductivity are lower than critical levels, beading on fibers occurs due to insufficient resistance to capillary and sinusoidal instability [38, 39]. In order to obtain the bead-free, thinner lignin-based electrospun fibers down to nanoscale, methods such as adding conductive additive or solvent to reduce critical viscosity should be achieved. It was concluded that in this study a 50 % lignin content represented the optimal composition for comparing lignin and B-lignin/PAN blends in 20 wt.% DMF solution.
Figure 2-5. SEM images of precursor fibers electrospun from 20 wt.% DMF solutions with lignin:PAN ratios of (a) 30:70 (b) 40:60 (c) 50:50 (d) 60:40, and (e) 70:30; and B-lignin:PAN ratios of (f) 30:70 (g) 40:60 (h) 50:50 (d) 60:40, and (j) 70:30. Scale bar = 10 μm.
Figure 2-6. Comparison of the diameters of electrospun fibers prepared from different precursors: PAN, lignin/PAN 50-50, and B-lignin/PAN 50-50 at different processing stages.

2.4.3 Phase Miscibility of Blend Precursor Fibers

The investigation of glass transition temperatures ($T_g$) by differential scanning calorimetry (DSC) is a convenient and reliable method to study the phase behavior of polymer blends. Figure 2-7 shows the DSC thermograms of the individual components (pure PAN, lignin, and B-lignin) and their blends (lignin/PAN 50-50 and B-lignin/PAN 50-50). Both lignin and B-lignin exhibited single and sharp glass transition regions, but the $T_g$ of butyrated lignin was 13 °C lower than that of unmodified lignin, indicating that butyl ester attached to the lignin molecules exhibited a plasticizing effect by enhancing lignin molecular mobility. Pure PAN fibers showed a clear glass transition at 100.2 °C. After blending PAN with lignin, a single but broad glass transition in a range from approximately 65 °C to 110 °C was identified for both lignin/PAN 50-50 and B-lignin/PAN 50-50 blends, indicating that good miscibility between PAN and lignin was retained.
Figure 2-7. Glass transition temperature ($T_g$) of lignin, B-lignin, and precursor fibers based on PAN, lignin/PAN 50-50, and B-lignin/PAN 50-50 measured by DSC.

after butyration. It should be noted that B-lignin/PAN 50-50 blends exhibited a $T_g$ region similar to that of lignin/PAN 50-50, whereas the $T_g$ of butyrated lignin was much lower than that of pristine lignin, indicating a favored binding interaction between PAN chains and butyrated lignin molecules.

2.4.4 Compositional, Structural, and Morphological Analysis of Carbonized Fibers

Table 2-1 summarizes the elemental compositions of fibers electrospun from different precursors together with the yields at the stabilization and carbonization stages. The carbon content of all precursor fibers was almost identical; however, the lignin-based fibers exhibited
higher oxygen contents because of the hydroxyl groups/ester groups before and after butyration and the methoxyl groups existing in lignin. The carbon content of all carbonized fibers was consistently above 90% without large variations, indicating that the carbonization temperature of 1000 °C allows a sufficient conversion of lignin-based to carbon materials. Higher temperatures or longer dwelling times may be employed to further eliminate the residual non-carbon content. The stabilization yield for the lignin-based fibers was lower than for PAN-based fibers which was attributed to the ease of releasing volatile compounds in lignin at stabilizing temperatures. Due to the already-oxidized state of lignin, degradation, such as demethoxylation, was initiated at temperatures of approx. 200 °C by driving off CO₂ and CO during the stabilization of the precursor fibers [9, 40]. This effect was confirmed by early weight loss of lignin-based fibers which occurred at temperatures approx. 100 °C lower than for pure PAN fibers according to our thermogravimetric results (Figure A-2). The significant increase in carbon content for PAN fibers during carbonization corresponded to the rapid weight loss region in TGA, stemming from the evolution of H₂, NH₃, and HCN between 300 to 400 °C and evolution of oligomers from the uncyclized portion of the polymers at higher temperature [41]. In contrast, although the conversion of lignin/PAN 50-50 to carbon appeared to be retarded on the basis of thermal degradation curves, it resulted in higher carbonization yields (~39.4%), which could be related to the contribution of the aromatic moiety of lignin. B-lignin/PAN 50-50, however, was subjected to a relatively fast degradation process, with the maximum rate of weight loss at approx. 360 °C, resulting in a decrease in carbon residue and carbon fiber yield. This effect is probably caused by the scission of butyl ester groups, resulting in a loss of carbon content.
Table 2-1. Elemental composition of different fibers acquired by CHN analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CHN analysis</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C (%)</td>
<td>H (%)</td>
</tr>
<tr>
<td>PAN</td>
<td>67.4</td>
<td>5.7</td>
</tr>
<tr>
<td>Lignin/PAN 50-50</td>
<td>66.5</td>
<td>5.6</td>
</tr>
<tr>
<td>B-lignin/PAN 50-50</td>
<td>66.4</td>
<td>6.0</td>
</tr>
<tr>
<td>PAN SF&lt;sup&gt;a&lt;/sup&gt;</td>
<td>66.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Lignin/PAN 50-50 SF</td>
<td>64.3</td>
<td>4.0</td>
</tr>
<tr>
<td>B-lignin/PAN 50-50 SF</td>
<td>65.8</td>
<td>4.4</td>
</tr>
<tr>
<td>PAN CF&lt;sup&gt;b&lt;/sup&gt;</td>
<td>92.4</td>
<td>0.8</td>
</tr>
<tr>
<td>Lignin/PAN 50-50 CF</td>
<td>92.3</td>
<td>0.6</td>
</tr>
<tr>
<td>B-lignin/PAN 50-50 CF</td>
<td>91.7</td>
<td>0.6</td>
</tr>
</tbody>
</table>

<sup>a</sup> SF represents fibers after thermo-stabilization.

<sup>b</sup> CF represents fibers after carbonization.

<sup>c</sup> O % was determined by subtraction of C %, H % and N % from the total composition.

* The uncertainty of C % from CHN analysis was within 1.2 %.

Raman spectroscopy was employed to compare the carbon structure formed during the carbonization process of different stabilized fibers. Figure 2-8 shows the example of a normalized first-order Raman spectrum of carbonized nanofibers (produced from lignin/PAN 50-50 blends) deconvoluted by a combination of four fitted Gaussian-shaped bands. The two major broad peaks centering at about 1360 and 1585 cm<sup>-1</sup> in the spectrum are referred to as D and G band, respectively [42]. The G band is attributed to an in-plane stretching mode of sp<sup>2</sup> carbon bonds existing in the ideal graphitic lattice. The D band originates from a hybridized vibrational mode related to graphene layer edges, indicating the number of defects in the graphitic structure. The disordered carbon is also indicated by two additional bands resolved at about 1190 cm<sup>-1</sup> (D<sub>1</sub>
band) and 1490 cm$^{-1}$ ($D_A$ band) in the Raman spectrum. According to earlier studies on different types of carbonaceous materials [43], the $D_I$ band is related to ionic impurities or defects from heterogeneous structure, which could be induced here by residual nitrogen and oxygen atoms caused by incomplete volatilization at 1000 °C during the carbonization process. The $D_A$ band corresponds to amorphous carbon, indicating interstitial defects rather than in-plane defects that are responsible for the $D$ band [44]. In order to evaluate the degree of structural order of different carbonized nanofibers, we chose the following critical band parameters obtained by Raman deconvoluted spectra for comparison: the relative integrated band intensities, which are determined by the ratio of single integrated band intensity to the total integrated intensity ($I/I_{\text{total}}$) [43], full width at half maximum (FWHM), and band position of each band.

As seen in Figure 2-9 (a), the relative integrated band intensities for all bands of lignin/PAN 50-50 CF showed little differences compared with PAN CF, considering the experimental uncertainty. The same observation was made for the plots of FWHM and band positions, indicating that the incorporation of lignin at 50 wt.% into the blend precursor did not evidently alter the formation of ordered graphitic structure in the PAN-based carbon fibers. However, B-lignin/PAN 50-50 CF presented a detectable decrease of $I_G/I_{\text{total}}$ accompanying an increase of $I_{DA}/I_{\text{total}}$, while $I_D/I_{\text{total}}$ and $I_{DI}/I_{\text{total}}$ remained the similar value to those of the other fibers. To confirm the increasing degree of disorder for B-lignin/PAN 50-50 CF indicated by the relative intensity results, it is essential to investigate the FWHM of each band in detail, shown in Figure 2-9 (b). Both $G$ band and $D$ band of B-lignin/PAN 50-50 CF seem to be narrower than those of lignin/PAN 50-50 CF or PAN CF, which indicated an inverse shifting tendency of the degree of disorder. Normally higher degrees of disorder in carbonaceous materials occur at lower heat treatment temperatures, evidenced by widening FWHM of both the $G$ and $D$ band and decreasing
G band intensity [45, 46]. A possible explanation for narrowing G band with a decrease in $I_G/I_{\text{total}}$ observed for B-lignin/PAN 50-50 CF could be the formation of a smaller fraction of ordered graphitic crystallites under the same carbonization condition compared to PAN CF and lignin/PAN 50-50 CF. The weaker signal intensity of the G band caused by the less pronounced graphitic structure may have resulted in a slight decrease in FWHM, assuming the crystal size did not change. The increase in $I_{\text{DA}}/I_{\text{total}}$ of B-lignin/PAN 50-50 CF, on the other hand, indicates a higher content of amorphous carbon. Although the average FWHM of the $D_A$ and $D_I$ bands increased for B-lignin/PAN 50-50 CF, it may need further validation considering the larger experimental uncertainty compared to the D and G band. The positions of all bands in Figure 2-9(c) were constant for the three carbon fibers, indicating band position may not be sensitive to probe slight differences in the structural order.

Figure 2-8. Raman deconvoluted spectra of carbonized fibers derived from B-lignin/PAN 50-50 blend.
Figure 2-9. (a) Relative integrated band intensity; (b) FWHM; (c) band position for each band determined by Raman deconvoluted spectra of different carbonized fibers.
Figure 2-10. SEM images of thermo-stabilized fibers (top: (a) series) and carbonized fibers (bottom: (b) series) based on different precursor compositions: (1) pure PAN, (2) lignin/PAN 50-50, and (3) B-lignin/PAN 50-50. Scale bar = 10 μm.

In Figure 2-10, the (a)-series illustrates the micromorphology of stabilized fibers based on PAN, lignin/PAN 50-50, and B-lignin/PAN 50-50. Moderate inter-fiber bonding was observed for B-lignin/PAN 50-50 stabilized fibers without losing fiber structure, while PAN and lignin/PAN 50-50 stabilized fibers remained straight and single. The diameters of carbonized fibers from different precursors, shown in Figure 2-10 in the (b)-series, decreased significantly after further carbonization treatment at 1000 °C, as was expected. As was seen earlier in Figure 2-6, the shrinkage from as-spun fibers to carbonized fibers for precursor blends with lignin content ranged from 40 to 45 %, much lower than the 56 % measured for fibers from PAN precursors. The difference in fiber diameters between fibers from lignin-containing precursors diminished after carbonization.
2.4.5 Tensile Properties of Carbonized Fibers

For the practical purpose of carbon fiber reinforcing material application, the mechanical properties of the carbonized fiber mats were only investigated using uniaxial tensile tests. Because of the porous nature of this fibrous material, the true stress of fiber mats is calculated from the specific stress, given as:

\[
\text{Specific stress (N tex}^{-1}) = \frac{\text{Load (N)}}{\text{specimen width (mm)/Areal density (g m}^{-2})}
\]

The areal density is the mass (g) of the carbon fiber mat specimen divided by its area. The specific stress (N tex\(^{-1}\)) was converted into the true tensile stress (MPa) by multiplication with the density of the carbon fibers, which was determined between 1.6 and 1.7 g cm\(^{-3}\) depending on the samples (Table A-1), comparable to general PAN-based carbon fibers with moderate mechanical properties [47]. The change in specimen width during tensile testing was negligible because of the very small transverse strain on the carbon fiber mats. The stress-strain curves for carbonized fibers derived from three different precursors are shown in Figure 2-11. The corresponding tensile results, including tensile strength, Young’s modulus, and strain at break, are listed in Table 2-2; the standard deviation was based on 5 replicate measurements.

All mats obtained from different precursors generally exhibited linear elastic behavior without yielding, substantiated by the fact that their strain at break ranged from 0.8 to 1.5 %. It is worth noting that carbon fibers derived from lignin-incorporated precursor blends (lignin/PAN 50-50 and B-lignin/PAN 50-50) exhibited higher strain at break than PAN-based carbon fibers. The observation is contrary to the common embrittlement of the precursor polymer fibers by incorporating lignin content [48, 49]. Compared to lignin/PAN 50-50 CF, slight increase of strain at break of B-lignin/PAN 50-50 CF indicates increase in ductility. Significant difference in tensile strength and Young’s modulus were observed between the carbon fiber mats with lignin
Figure 2-11. Representative tensile stress-strain curves of carbonized fiber mats derived from different precursors.

Table 2-2. Tensile strength, Young’s modulus, and strain at break of carbonized fiber mats.

<table>
<thead>
<tr>
<th>Fiber sample</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Strain at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN CF</td>
<td>41 ± 5</td>
<td>6.4 ± 0.4</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>Lignin/PAN 50-50 CF</td>
<td>22 ± 1</td>
<td>2.4 ± 0.2</td>
<td>1.2 ± 0.1</td>
</tr>
<tr>
<td>B-lignin/PAN 50-50 CF</td>
<td>83 ± 17</td>
<td>6.1 ± 0.6</td>
<td>1.4 ± 0.2</td>
</tr>
</tbody>
</table>

content. B-lignin/PAN 50-50 CF demonstrated the highest tensile strength, about 3.8 times higher than that of lignin/PAN 50-50 CF. The Young’s modulus of B-lignin/PAN 50-50 CF was
approx. 1.9 times higher than that of lignin/PAN 50-50 CF. The superior tensile strength and modulus properties demonstrated by B-lignin/PAN 50-50 CF mats even matches those of PAN-based CF mats, which is probably related to the inter-fiber bonding.

Interpreting the mechanical property differences between the three mats from different carbon fibers is complicated because the final mechanical properties of the nonwoven mats made from electrospun fibers were not only controlled by the intrinsic fiber properties, but also by the mats’ microstructure. Pai’s fabric microstructure model [50] demonstrates that mat structure parameters, such as the porosity of mats, fiber diameter, radius of curvature, and distance between inter-fiber junctions, significantly affect the Young’s modulus of electrospun nonwoven mats. According to his curved fiber model, a correlation between the Young’s modulus of fiber mats \(E_{\text{mat}}\) and that of the constituent curved fibers \(E_{\text{fiber}}\) can be established by introducing the stiffness ratio \(SR = E_{\text{fiber}}/E_{\text{mat}}\) as a function of fiber diameter, radius of curvature, and junction length. The model also showed that the stiffness ratio decreased when these three factors are all decreased so that it was possible to achieve increase in mat moduli. This model can be used to explain the present case of significant increase in mechanical reinforcement observed in bonded B-lignin/PAN 50-50 CF mats compared to lignin/PAN 50-50 CF mats. Although the intrinsic fiber modulus was not acquired due to difficulty in direct measurement, it is reasonable to assume that intrinsic fiber modulus is nearly equal between lignin/PAN 50-50 CF and B-lignin/PAN 50-50 CF, regarding the fact that the differences of fiber diameter, chemical composition and carbon structure characterized by Raman between the two carbonized fibers are very subtle. Since the fiber diameter is similar, irreversible inter-fiber fusion occurred during thermostabilization played an important role that would lead to decrease of the radius of curvature and the junction length, as shown by bending of fibers as well as forming immobilized
fiber junctions in the SEM image of B-lignin/PAN 50-50 CF (Figure 2-10 (b-3)). According to the expression derived from Pai’s curved fibers-based model, the apparent mat modulus increases by decreasing the stiffness ratio. Inter-fiber bonding improved the mechanical properties of the mats analogous to the effect of cross-linking of thermosets on the molecular level, compensating for the intrinsic weakness of the lignin-based carbon fibers.

2.5 Conclusion

Cornstover organosolv lignin before and after butyration and PAN, serving as a plasticizing additive, were blended in DMF solvent to prepare electrospun ultrafine fibers, resulting in biodeviced, low-cost carbon nanofibers. The effect of viscosity and blend composition on electrospinnability was examined, and the optimal composition that obtained bead-free, uniform fibers was determined. Butyrated lignin decreased the viscosity of lignin/PAN blends due to weakened intermolecular interaction and led to a reduction of the as-spun fiber diameter. Sufficient miscibility between PAN and lignin was obtained after butyration, as indicated by single and broad glass transitions in the DSC thermograms. Precursor fibers derived from B-lignin/PAN exhibited lower carbon yield than lignin/PAN after pyrolysis/thermal treatment; however, the yield was comparable to that of PAN-based fibers. Inter-fiber bonding occurred with B-lignin/PAN 50-50 fibers during the oxidative thermostabilization at 200 °C (0.2 °C/min) because of enhanced thermal mobility of the modified lignin molecules. After carbonization at 1000 °C, the resultant fused CF mats showed significant improvement in mechanical properties compared to non-bonded lignin/PAN 50-50 carbonized fibers. The reinforcing mechanism was attributed to the change of the fabric network features. Raman spectra revealed a slight decrease in the structural order of the B-lignin/PAN 50-50 carbon fibers. This study demonstrated a new
approach to manipulating inter-fiber bonding using an inexpensive lignin/PAN blend precursor system to produce fibrous nano-carbon materials with promising characteristics for fiber-reinforced composite applications.

Acknowledgments

The authors thank Dr. Chunhui Xiang of the Department of Apparel, Events, and Hospitality Management at Iowa State University for her assistance with developing the electrospinning setup and conducting pilot experiments for this study.

Supplementary data related to this chapter can be found in Appendix A.

2.6 References


[29] P.J. Bissett, C.W. Herriott, Fiber dope solution, useful for producing fibers e.g. precursor, oxidized and carbonized fibers, which are useful in e.g. composite materials, comprises lignin and polyacrylonitrile or polyacrylonitrile copolymer in an organic solvent, Patent US2012003471-A1.


CHAPTER 3: THE INFLUENCE OF CARBON NANOFIBERS ON THE AGING OF TIN (II)-CATALYZED RTV POLYSILOXANE FOAMS

Manuscript in preparation

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3.1 Abstract

The tin octoate residue in room-temperature-vulcanized (RTV) polysiloxane foams reinforced by carbon nanofiber (CNF) is of interest due to its potential impact on the aging and the long-term performance of the foams. In this study, scanning electron microscopy coupled with energy-dispersive spectrometry (SEM-EDS) measurements shows that tin catalyst residues are concentrated in the foam cellular structure as thin layers. EDS mapping indicates that the tin-rich layer is a complex organotin compound containing Sn, Si, O, and C. X-ray photoelectron spectroscopy (XPS) analysis on cut cross-sectional surfaces of the polysiloxane foams reveals that the tin catalyst was oxidized slightly faster with the addition of a small amount of CNF to the foam. Thermogravimetric analysis reveals a significant increase of thermal stability of the foam in inert atmosphere after the incorporation of CNF. The glass transition temperature of polysiloxane determined by differential scanning calorimetry (DSC) shows no evident change after adding CNF. In broadband dielectric spectroscopy, the segmental α relaxation process was well resolved from the dielectric loss spectra at low temperatures, and therefore analyzed with
parametric model fitting. The temperature dependence of the \( \alpha \) relaxation and fragility of the polysiloxane are not apparently influenced by the incorporation of CNF.

### 3.2 Introduction and background

Polysiloxane is a group of polymeric organosilicon materials containing the Si-O-Si linkage. The most widely used and studied polysiloxane is polydimethylsiloxane (PDMS), often referred to as silicone. In silicones (or polysiloxanes), the main constituting bonds are the Si-O and Si-C bond, which have bond energies of 452 kJ/mol and 318 kJ/mol respectively. The Si-O bond energy is high compared to that of a C-C bond (347 kJ/mol) found in common hydrocarbon polymers and this difference accounts for the excellent thermal stability of silicones, demonstrated by its degradation starting at around 400 °C [1]. On the other hand, the rotation barriers of the siloxane linkage are much lower than that in hydrocarbon polymers, giving rise to the high flexibility of the siloxane chain. As the polar Si-O bonds shielded by side methyl groups, the flexible chains become loosely entangled due to the low interchain interactions, resulting in silicones’ uniqueness in high viscoelasticity and low glass transition temperature.

The room-temperature-vulcanization (RTV) process for producing polysiloxane elastomers, coatings and foams became popular in the 1960s, replacing vulcanization with peroxides which required elevated curing temperature [2]. The RTV curing process follows one of two methods, either ‘one-part’ (with the system in contact with atmospheric humidity) or ‘two-part’ (in which two components are mixed). The former system is crosslinked with moisture-sensitive multifunctional silane-terminated polymers in a two stage reaction. The latter system requires alkyl silicate as a cross-linking agent and a small amount of catalyst to accelerate the reaction. Organotin compounds such as dialkyltindicarboxylates and tindicarboxylates are the preferred
catalysts because they limit undesirable side reactions and are relatively inert which is convenient for long-period storage. The foam structure is created by incorporating hydride functional (Si-H) siloxanes into silanol terminated elastomer formulations. A dehydrogenative coupling reaction occurs between the two components, resulting in the emission of hydrogen as the blowing agent. A schematic of the curing reactions for polysiloxane foams is illustrated in Figure 3-1 [3]. Commonly, mineral fillers and some other additives are incorporated to improve the mechanical properties of the polymer network.

Figure 3-1. Reaction scheme of the synthesis of RTV polysiloxane foams: foaming and cross-linking.
Carbon/polysiloxane nanocomposites have been investigated for various applications, including as flexible strain sensors for example, since the discovery of carbon nanomaterials such as carbon nanofibers, carbon nanotubes and graphenes [4-11]. Since these carbon nanomaterials have high mechanical, electrical and thermal properties, their integration to polysiloxane would enable a variety of application such as high-performance elastic and flexible conductors, electrode materials for supercapacitors and lithium ion batteries, thermal interface materials for electronic devices, actuators and controllable dampers. Recently, a novel three-dimensional interconnected graphene, also called graphene foam (GF), was synthesized by template-directed chemical vapor deposition based on nickel catalytic foam [4]. It has been reported that GF/PDMS with a very low GF loading of 0.5 wt.% exhibited a relatively high electrical conductivity of ~10 S cm\(^{-1}\), about 6 orders of magnitude higher than ordinary graphene sheet (GS)-based composites. In another study, 0.7 wt.% GF/PDMS was reported having 20% higher thermal conductivity and 36% lower coefficient of thermal expansion compared to GS/PDMS composite with the same graphene loading [11].

Polysiloxane containing residual tin catalyst is subject to aging in normal environment conditions, such as exposure to atmospheric oxygen and moisture [12, 13]. The continuing reactivity of the catalyst would influence the long-term mechanical properties of RTV silicone materials. Both polymerization and decomposition of siloxane linkages is associated with the hydrolysis of tin carboxylates. Van der Weij has proved that vulcanization of condensation-type silicone rubbers does not occur under anhydrous conditions and that other protic substances like silanols or alcohols do not initiate the vulcanization process [14]. It has also been pointed out that the hydrolysis product of tin carboxylates actually serves as the catalyst. The products of partial hydrolysis of tin carboxylates in the presence of moisture, namely tin hydroxide and
carboxylic acid as shown in the proposed reaction scheme in Figure 3-2, is thought to possess higher catalytic reactivity [14]. The presence of carboxylic acid in the vulcanized silicone rubber, on the contrary, could promote degradation by protonating the siloxane chain and then reducing the energy barrier for hydrolysis of the polymer [15].

A variety of chemical structural characterization techniques have been applied to analyze polysiloxane foam samples aged in service in comparison with artificially aged samples. $^{119}$Sn Mössbauer spectroscopy (MS) was used as a sensitive probe to identify the chemical state of tin residues [3, 16, 17]. Two residual tin species, tin (II) and tin (IV), were detected in RTV polysiloxane foams catalyzed by tin octoate. The oxidation from Tin (II) to tin (IV) in pristine polysiloxane over aging time was observed to be different to that under a simple hydrolysis process [3]. The tin (IV) species has been found to lose catalytic activity for the silanol condensation reaction, implying the degradation of the catalyst by oxidation [18]. $^1$H, $^{13}$C and $^{29}$Si nuclear magnetic resonance (NMR) has been used to characterize the reactive functional groups and functional siloxane linkages of aged samples [3, 17, 18]. The use of attenuated total reflectance – Fourier-transform infrared (ATR-FTIR) and micro X-ray fluorescence (MXRF) spectral imaging has been instrumental in revealing the change of chemical components near the surface between differently aged polysiloxane foams [3, 19].

ROCO—Sn—OCOR $\xrightarrow{H_2O}$ ROCO—Sn—OH + HOOCR

\[ R = \text{CH(CH}_2\text{CH}_3\text{)}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]

Figure 3-2. Reaction scheme of the partial hydrolysis of tin carboxylates
This work aims to investigate the effect of the presence of vapor-grown carbon nanofibers (VGCNFs) on the changes of the residual tin (II) catalyst in RTV polysiloxane foams. VGCNFs are relatively low-cost, commercially-available one-dimensional carbon nanofillers that are recognized as an alternative to carbon nanotubes for large-scale industrial applications. Scanning electron microscopy was coupled with energy-dispersive spectrometry (SEM-EDS) to study the morphology and composition of tin residues in the foam structure. X-ray photoelectron spectroscopy (XPS) was also employed to investigate the difference in oxidation state of the tin residues. Thermogravimetric analysis (TGA) was performed to investigate the effect of VGCNFs on thermal degradation of RTV polysiloxane foams. Differential scanning calorimetric (DSC) measurements were employed to determine the glass transition temperature and broadband dielectric spectroscopy (BDS) was conducted to reveal the dynamics of the primary relaxation process, which is associated with glass transition.

3.3 Experimental Section

3.3.1 Materials preparations

The neat siloxane foam was synthesized according to the protocol of SX358 foams previously established by Honeywell. The starting polysiloxane gumstock included 75 wt% dihydroxyl-terminated polydimethylsiloxane (HO-PDMS-OH), 5 wt% diphenylmethyl-silanol (DPMS), 3 wt% polymethyl-hydrosiloxane (PMHS), and 2 wt% tetrapropyl orthosilicate (TPS); all of which were supplied by NuSil Technologies. The dihydroxyl-terminated PDMS consisted of a mixture of about 17 wt% low molecular weight (Mw = 2350), 14.5 wt% medium molecular weight (Mw = 29,400), and 43.5 wt% high molecular weight (Mw = 54,300). The uncured resin were blended with 15 wt% of diatomaceous earth filler (Imerys, San Jose, CA) to impart
reinforcement to the cured polymers. Various loadings (0.1 wt% and 0.5 wt%) of carbon nanofiber (Pyrograf®-III PR-25-XT-PS grade, Sigma-Aldrich, St. Louis, MO) (CNF) were added for further property tuning. The fillers were mechanically dispersed by a mixer with 2500 rpm for 30 s. The resin blend was then stored in a refrigerator at 4 °C for 7 days and allowed to form a viscous prepreg for the subsequent curing procedure.

The foams were cured by condensation reactions between silanols on dihydroxyl-terminated PDMS, and DPMS and silanes on PMHS, producing hydrogen gas. Condensation between silanols and TPS also contributed to cross-linking, with evolution of n-propyl alcohol. Both condensation reactions were catalyzed by tin octoate, which is also known as tin(II) 2-ethylhexanoate (Sigma-Aldrich, St. Louis MO). The procedure was performed by quick mixing of 5 wt% tin octoate into the polysiloxane gumstock for 15 s, and allowing it to cure at room temperature into a mold to obtain a chosen thickness (the average thickness of pristine samples was 1.22 ± 0.02 mm) and density (about 0.4 g/cm³). The amount of tin catalyst is necessary in order to produce foams of high-quality. The composition profile of siloxane foams with the different loadings of CNF was summarized in Table 3-1.

3.3.2 Structural Characterization

The cross-sectional morphology of the polysiloxane foam and its CNF-reinforced composites was characterized using a FEI Quanta 250 field-emission scanning electron microscope (FESEM) at 10 kV under high vacuum. The cross-section surfaces of the samples were sputter coated with iridium of 2 nm thickness to avoid electrostatic charging during examination. Backscattered electrons (BSE) mode, which detects the reflected electrons from the elastic scattering interaction with specimen atoms, was employed to reveal not only topography but also compositional differences.
### Table 3-1. Composition of siloxane foams, with different loadings of CNF.

<table>
<thead>
<tr>
<th>Parts</th>
<th>Composition</th>
<th>Concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastomeric matrix</td>
<td>Dihydroxyl-terminated polydimethylsiloxane (HO-PDMS-OH)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mw =2,350 (low)</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>Mw =29,400 (medium)</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>Mw =54,300 (high)</td>
<td>43.5</td>
</tr>
<tr>
<td></td>
<td>Diphenylmethylsilanol (DPMS)</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Polymethylhydrosiloxane (PMHS)</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Tetrapropyl orthosilicate (TPS, crosslinker)</td>
<td>2</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Tin octoate (Tin II 2-ethylhexanoate)</td>
<td>5</td>
</tr>
<tr>
<td>Filler</td>
<td>Diatomaceous earth</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Carbon nanofiber (CNF)</td>
<td>0.1; 0.5</td>
</tr>
</tbody>
</table>

In order to precisely determine and quantify the element composition of the samples, Oxford Aztec energy-dispersive spectrometer (EDS) installed on FESEM was used to characterize the X-ray photons for their energy (or wavelength) and abundance. Element mapping was performed to generate two-dimensional images that show the abundance and relative distribution of different elements in selected areas of a sample. EDS was performed at 6 kV, 10 kV and 15 kV in order to vary the interaction depth of the electron beam with the sample materials and isolate features of particular interest.

XPS analysis was conducted on Kratos Amicus X-ray Photoelectron Spectrometer with an Al Ka radiation source (1486.7 eV). The survey spectra were initially collected from 0 to 1100 eV and then followed by scanning high-resolution spectra at narrow binding energy ranges for specific elements. The flat, as-received surfaces and planar cross-sectional surfaces of three samples were both examined. CasaXPS software was employed for identifying and analyzing peaks from XPS spectra.
3.3.3 Thermal and dielectric analysis

Differential scanning calorimetry (DSC, Q2000, TA instruments) was used to determine physical transitions and residual cure reactions of the samples. A small amount of samples (7~8 mg) were sealed into a Tzero aluminum hermetic pan. The sample pan was then loaded in the DSC cell and was subsequently scanned between -160 °C and 350 °C with a heat - cool - heat cycle at a constant rate of 10 °C/min under helium gas purge (50 mL/min). Thermogravimetric analysis (TGA, Q50, TA Instruments) was conducted to evaluate the thermal stability and degradation process of samples. Approximately 5 mg samples were heated from room temperature to 900 °C at a heating rate of 20 °C/min under different atmospheres (nitrogen and air) with a purge flow of 50 mL/min. Dielectric relaxation spectra was measured using a Novocontrol Broadband Dielectric spectrometer (Novocontrol Technologies, Germany). The sample cell, consisting of 20-mm-diameter parallel plate brass electrodes, was housed in an automatic temperature-controlled chamber. The measurement was conducted at a voltage of 1 V, over a frequency range from $10^{-2}$ to $10^{6}$ Hz, and temperature range from -150 °C to 250 °C with a 10 °C increment. The temperature increment was reduced to 3 °C for detailed investigation of glass transition.

3.4 Results and discussion

Figure 3-3 shows the SEM morphology of pristine carbon nanofibers (Pyrograf®-III PR-25-XT-PS grade) at different magnifications. In the name of these nanofibers, “XT” represents an improved debulking method that creates loose structures of the CNF bundle, and “PS” represents a pyrolytic stripping process for the as-produced fiber to remove polyaromatic hydrocarbons from the fiber surface. This grade of CNF features an average fiber diameter of about 100
Figure 3-3. SEM morphology of the pristine CNF at different magnifications, from left to right: 5000 ×, 15000 ×, and 50000 ×. The highlighted areas indicate the impurities and residual iron catalyst in the pristine CNF.

nanometers and a tubular structure. The distribution of large chunks and bright spots in the CNF bundles (the highlighted areas in Figure 3-3) observed under BSE mode indicates the presence of impurities and a trace amount of residual iron catalyst, respectively.

Figure 3-4 shows the foam morphology imaged on cut, cross-sectional surfaces of polysiloxane and CNF-reinforced polysiloxane composite samples at different magnifications. At the lowest magnification, the bubble structure is identified by round, bright areas, and the remaining dark background corresponds to the polysiloxane matrix. The black patches inside the bubble and the matrix indicate the breakages of bubbles resulting in a lack of electron signals. The bubble diameter ranges from 50 µm to 250 µm and does not vary apparently between the samples with different CNF loading. Higher magnification was applied to seek more details of the bubble structure and fillers. Apart from the roughness apparent on the cut surface due to the
rubbery character of polysiloxane, spinal morphology is observed in Figure 3-4 (a) with 5000x magnification, which is attributed to the diatomaceous earth. Figures 3-4 (b) and (c) with the addition of CNF exhibit fibrous morphology. It is noteworthy that the “fiber-like” structure may also result from the diatomaceous earth, which causes extra difficulty to distinguish the distribution of each type of filler. On the other hand, the bright areas observed under BSE mode indicate the different elemental compositions, comprising higher atomic numbers, compared to the dark background. EDS analysis was therefore performed to further investigate the inhomogeneity of the foam structure.

Figure 3-4. SEM images showing the morphology of the fracture surfaces of (a) neat polysiloxane (b) 0.1% CNF/polysiloxane, and (c) 0.5% CNF/polysiloxane at different magnifications: from left to right: 150 ×, 500 ×, 1500 ×, and 5000 ×. The arrows in the rightmost figure indicate the topology of diatomaceous earth (and CNF).
Two morphologically distinct areas were selected in one SEM image of neat polysiloxane, Figure 3-5 (a), for EDS scanning. The beam voltage was selected to be 10 kV as a practical starting standard. The results are shown in Figure 3-5 (b) and, based on these observations, the selected area based on the bright flakes is denoted as “Sn-rich” due to the appearance of a series of strong tin signals. The area denoted “matrix” exhibited no trace of Sn signal but abundance of Si, O and C, consistent with the chemical composition of polysiloxane (H is not detectable by EDS). Figure 3-5 (c) displays the distribution of the determined elements (C, O, Al, Si and Sn) corresponding to the image shown in Figure 3-5 (a). The significant contrast between the “Sn-rich” area and the “matrix” area in the tin map confirms that the presence of Sn is exclusive to the thin layers of the bubble wall. The silicon map shows that the Si signal appears to be universal but fades in the “Sn-rich” area, for this relatively high beam voltage due to the likelihood that the beam penetrates through the layer and into the matrix below.

(a)

Figure 3-5. (a) SEM image of neat polysiloxane at 3000x magnification under BSE mode
Figure 3-5. (b) EDS spectra of two selected spots in the SEM image (yellow – elemental composition of overall area; orange - elemental composition of selected area denoted “matrix” in (a); red - elemental composition of selected area denoted “Sn-rich” in (a)); (c) distribution maps of different elements (C, O, Si and Sn) corresponding to the SEM image (a).
Figure 3-6 shows the atomic fraction of elements identified by EDS at three different electron beam voltages and its dependence on the thickness (number) of tin-rich layers observed in neat polysiloxane. The thickness is defined as the number of Sn-rich layers that are apparently overlapped in the image. Figure 3-6 (a) demonstrates that the atomic fractions of Sn and Si are stable at around 12% and 8% respectively for single, double and triple Sn-rich layers measured with 6 kV beam voltage. This indicates that the interaction depth of the electron beam at 6 kV is comparable to the thickness of a single Sn-rich layer. For a beam voltage of 10 kV, however, the atomic fraction of Si decreases with increasing number of Sn-rich layers, Figure 3-6 (b), implying a certain extent of electron beam penetration into the matrix through one or two Sn-rich layers. Figure 3-6 (c) indicates excessive electron penetration into the matrix by identifying a low value of Sn % compared with that measured at lower beam voltages, and that increases as the number of Sn-rich layers increases. It is concluded that the lowest beam voltage employed here, 6 kV, is optimal for the quantification of tin in the Sn-rich layers. The elemental composition of the Sn-rich layer can be determined roughly as Sn:Si = 1.4~1.6, O:Sn = 2~2.5, and O:Si = 3.3~3.6.
Figure 3-6. Dependence of the atomic fraction of elements identified by EDS on the thickness (number) of tin-rich layers examined, and the electron beam voltage for neat polysiloxane. EDS beam voltages are 6 kV (a), 10 kV (b), and 15 kV (c).
Figure 3-7 shows XPS spectra of the cross-sectional surfaces of three samples, neat polysiloxane, 0.1% CNF/polysiloxane and 0.5% CNF/polysiloxane from survey scans and the atomic concentrations for each element are summarized in Table 3-2. It can be seen that there is little obvious difference of elemental composition between the neat polysiloxane and its nanocomposites incorporating low loadings of CNF.

In order to determine the relative prevalence of Sn (II) and Sn (IV) oxidation states, high resolution scans were performed on the identified element peak at around 487 eV. The 3d$_{5/2}$ peak can be deconvolved into two components, Sn 3d(II) (486.2 eV) and Sn 3d(IV) (486.8 eV ), as illustrated in Figure 3-8. The relative fractions of the two oxidation states of Sn were calculated by this analysis for different samples and are listed in Table 3-3. The results indicate that the fraction of Sn 3d (IV) increases slightly as the CNF loading increases, suggesting that the presence of CNF may accelerate the oxidation of any residual tin (II) catalyst.

![Figure 3-7. XPS survey scans of the cross-sectional surfaces of three samples: neat polysiloxane, 0.1% CNF/polysiloxane and 0.5% CNF/polysiloxane.](image-url)
Table 3-2. The characteristic binding energies and calculated atomic concentration of elements determined by XPS.

<table>
<thead>
<tr>
<th>Signal</th>
<th>Position (eV)</th>
<th>Atomic Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>neat</td>
</tr>
<tr>
<td>O 1s</td>
<td>532.3</td>
<td>28.8</td>
</tr>
<tr>
<td>Sn 3d $_{5/2}$</td>
<td>486.7</td>
<td>0.5</td>
</tr>
<tr>
<td>C 1s</td>
<td>284.8</td>
<td>48.3</td>
</tr>
<tr>
<td>Si 2p</td>
<td>102.25</td>
<td>22.3</td>
</tr>
</tbody>
</table>

Figure 3-8. High resolution XPS scans of the Sn 3d$_{5/2}$ peak of the cross-sectional surface of neat polysiloxane. Deconvolution of the Sn(II) (blue) and Sn(IV) (red) peaks and their sum (green) are shown superimposed over experimental data (black).
Table 3-3. The characteristic binding energy of Sn 3d\textsubscript{5/2} components and calculated concentration of each component, determined by XPS. The uncertainty is approximately 5\% of these values.

<table>
<thead>
<tr>
<th>Signal</th>
<th>Position (eV)</th>
<th>Atomic Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>neat</td>
</tr>
<tr>
<td>Sn 3d (II)</td>
<td>486.2</td>
<td>27.1</td>
</tr>
<tr>
<td>Sn 3d (IV)</td>
<td>486.8</td>
<td>72.9</td>
</tr>
</tbody>
</table>

The thermal degradation of polysiloxane and its CNF-reinforced composites in N\textsubscript{2} atmosphere is shown in Figure 3-9 and the relevant data are summarized in Table 3-4. The neat polysiloxane exhibits a simple decomposition process with the maximum degradation rate occurring at approximately 397 °C. The addition of CNF at 0.5\% loading increases T\textsubscript{max} by up to 40 °C and meanwhile engenders an additional degradation stage at adjacent higher temperature (430~600 °C). The residue at 900 °C for neat polysiloxane is about 18.5 \% and higher value is obtained for CNF-reinforced polysiloxanes.

![Figure 3-9. Thermogravimetric curves and their derivatives of three samples: neat polysiloxane, 0.1\% CNF/polysiloxane and 0.5\% CNF/polysiloxane. The test is conducted at heating rate 20 °C/min in N\textsubscript{2} atmosphere.](image)

Table 3-4. Thermogravimetric data of three samples obtained from Figure 3-10.

<table>
<thead>
<tr>
<th>Samples</th>
<th>T₅ (°C)</th>
<th>Tₘₐₓ (°C)</th>
<th>Tₙₑ₉ (°C)</th>
<th>Wᵣ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat siloxane</td>
<td>375.9</td>
<td>397.3</td>
<td>-</td>
<td>18.5</td>
</tr>
<tr>
<td>0.1% CNF siloxane</td>
<td>368.3</td>
<td>436.6</td>
<td>489.8</td>
<td>20.8</td>
</tr>
<tr>
<td>0.5% CNF siloxane</td>
<td>370.9</td>
<td>430.8</td>
<td>486.7</td>
<td>22.5</td>
</tr>
</tbody>
</table>

* T₅: degradation temperature at 5 wt.% weight loss  
Tₘₐₓ: degradation temperature at maximum weight loss rate (primary derivative peak)  
Tₙₑ₉: degradation temperature at secondary derivative peak  
Wᵣ: residual weight at 900 °C

The glass transition temperature (T₉) was obtained from DSC thermograms determined by the average temperature at the half height of the heat capacity increase (1/2Cₚ) on the second heating thermal curve, shown in Figure 3-10. The three samples exhibit T₉ close to each other around -123 °C, indicating the negligible influence on T₉ of the addition of CNF at the low loadings considered in these samples.

Figure 3-10. DSC curves showing the glass transition temperature for three samples: neat polysiloxane, 0.1% CNF/polysiloxane and 0.5% CNF/polysiloxane.
Figures 3-11 (a) and (b) show the temperature and frequency dependence of the real and imaginary parts of complex permittivity for neat polysiloxane, as an example. Only one relaxation process located near -120 °C was observed for both spectra and identified as the $\alpha$ relaxation. At high temperature, imaginary permittivity $\varepsilon''$ increases significantly due to the ionic conduction.

In order to quantify the relaxation characteristics and probe how the molecular dynamics of polysiloxane is affected by CNF, the empirical Havriliak-Negami (HN) function is applied to describe the $\alpha$ relaxation process in the frequency domain [20]:

$$
\varepsilon''(\omega) = -\Im\left\{\frac{\Delta\varepsilon}{1 + (i\omega\tau_{HN})^{1-\alpha_{HN}}}^{\phi_{HN}}\right\} \tag{3-1}
$$

![Figure 3-11. Three dimensional plots of (a) measured real permittivity and (b) measured imaginary permittivity of neat polysiloxane as a function of frequency and temperature.](image-url)
where $\varepsilon''(\omega)$ is the imaginary part of the permittivity, $\omega$ is the angular frequency ($\omega = 2\pi f$), $\Delta\varepsilon$ is the relaxation strength of the process, $\tau_{HN} = 1/(2\pi f_{HN})$ is the characteristic relaxation time, and $a_{HN}$ and $b_{HN}$ are two shape parameters ($0 \leq a_{HN}, b_{HN} \leq 1$). The former governs the peak intensity and breadth of the relaxation process and the latter governs its skewness. Best fits were achieved at each temperature by adjusting the fitting parameters and minimizing the error between model and experimental data by the least squares fitting technique.

The characteristic frequencies at which $\varepsilon''(\omega)$ is maximum ($f_{\text{max}}$) for a single dielectric relaxation at each temperature is obtained by the following relation between $f_{HN}$, $a_{HN}$ and $b_{HN}$:

$$f_{\text{max}} = f_{HN} \left( \frac{\sin \left[ \frac{\pi(1-a_{HN})b_{HN}}{2(b_{HN}+1)} \right]}{\sin \left[ \frac{\pi(1-a_{HN})}{2(b_{HN}+1)} \right]} \right)^{-1/2}$$  \hspace{1cm} (3-2)

The temperature dependence of relaxation times (in the form of inverse of $f_{\text{max}}$) for $\alpha$ relaxation processes are plotted for all three samples in Figure 3-12. The temperature dependence of the $\alpha$ relaxation can be further well described by the Vogel-Fulcher-Tammann (VFT) law [21, 22]:

$$f_{\text{max}} = f_0 \exp \left( -\frac{D T_0}{T-T_0} \right)$$  \hspace{1cm} (3-3)

where $D$ is the strength parameter, the temperature $T_0$ is the Vogel temperature, and $f_0$ is the frequency pre-exponential factor. Table 3-5 lists the fitted parameters of the $\alpha$ relaxation plots shown in Figure 3-12. The glass transition temperature defined by dielectric spectroscopy ($T_{g,die}$) is empirically obtained from the VFT fit of the segmental $\alpha$ relaxation time $\tau_\alpha = 100$ s, corresponding to $f_{\text{max}}^\alpha = 1.6 \times 10^{-3}$ Hz:
In addition to $T_g$, fragility index $m$ is also determined, to characterize the breadth of the glass transition and how rapidly the transport properties change with temperature when approaching $T_g$. The fragility index $m$ is a measure of the cooperative motions from the $\alpha$ relaxation for glass-forming polymers and is determined by evaluating the slope of the temperature dependence of $\tau_\alpha$ approaching $T_g$ [23, 24]:

$$m = \left. \frac{d \log(\tau_\alpha)}{d(T_g/T)} \right|_{T=T_g}$$  \hspace{1cm} (3-5)$$

$$m = \frac{T_g}{\ln(10)} \frac{D\tau_\alpha}{(T_g-T_o)^2}$$  \hspace{1cm} (3-6)$$

The calculated values of $T_{g\text{, die}}$ and $m$ for the three polysiloxane composite samples are reported in Table 3-5. The results show that the molecular dynamics of polysiloxane are not obviously affected by the incorporation of CNF, which supports the observation that the glass transition temperature, obtained from DSC measurement, is unchanged regardless of CNF concentration in these composites.

### 3.5 Summary and Conclusion

The effect of vapor grown carbon nanofibers (VGCNFs) on the changes of the residual tin (II) catalyst in RTV polysiloxane foams has been investigated. Characterization using SEM-EDS showed that tin catalyst residues are concentrated in the bubble structure as thin layers. Elemental mapping indicated that the tin-rich layer is a complex organotin compound containing
Figure 3-12. Arrhenius diagram showing the $\alpha$ relaxation process for three samples: neat polysiloxane, 0.1% CNF/polysiloxane and 0.5% CNF/polysiloxane, fitted by the VFT relation, Eq. (3-3).

Table 3-5. Parameters from the VFT fit of $\alpha$ relaxation in Figure 3-12; $T_g$ and $m$ for three siloxane samples containing various CNF loadings.

<table>
<thead>
<tr>
<th>CNF weight %</th>
<th>$f_0$ (s$^{-1}$)</th>
<th>D</th>
<th>$T_0$ (K)</th>
<th>$T_{g,\text{diel}}$ (°C)</th>
<th>$T_{g,\text{DSC}}$ (°C)</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.5 ± 0.3</td>
<td>3.0 ± 0.1</td>
<td>-131.5 ± 0.7</td>
<td>-117.5 ± 0.8</td>
<td>-122.9 ± 0.7</td>
<td>148 ± 10</td>
</tr>
<tr>
<td>0.1</td>
<td>10.1 ± 0.3</td>
<td>2.6 ± 0.1</td>
<td>-130.2 ± 0.6</td>
<td>-117.5 ± 0.8</td>
<td>-122.7 ± 0.6</td>
<td>158 ± 12</td>
</tr>
<tr>
<td>0.5</td>
<td>10.5 ± 0.2</td>
<td>3.0 ± 0.1</td>
<td>-131.7 ± 0.6</td>
<td>-117.4 ± 0.8</td>
<td>-123.2 ± 0.3</td>
<td>146 ± 10</td>
</tr>
</tbody>
</table>

Sn, Si, O, and C. The oxidation state of residual tin species in the different polysiloxane nanocomposites was determined approximately by using XPS. Observation from the cross-sectional surface of the foam samples revealed that the oxidation of the tin catalyst was slightly
accelerated with the addition of a small amount of CNF to polysiloxane. In addition to the structural characterization, thermal analyses were carried out to investigate the change of thermal properties of the CNF/polysiloxane composites. TGA results exhibited a significant increase of thermal stability of polysiloxane incorporating CNF in inert atmosphere. The glass transition temperature of polysiloxane determined by DSC, on the other hand, did not show significant change with addition of CNF. In broadband dielectric spectroscopy, the segmental α relaxation process was well resolved from the dielectric loss spectra at low temperatures, and analyzed with parametric HN model fitting. The temperature dependence of the α relaxation and fragility of the polysiloxane are not apparently influenced by the incorporation of CNF.

Acknowledgments

The authors thank Dr. Warren Straszheim and Dr. Dapeng Jing, of the Materials Analysis and Research Laboratory at Iowa State University, for their technical assistance and thoughtful discussions in SEM-EDS analysis and XPS analysis, respectively.

Supplementary data related to this chapter can be found in Appendix B.

3.6 References


4.1 Abstract

A model polycyclic aromatic hydrocarbon (PAH) compound, anthracene, was incorporated into a cross-linking epoxy matrix as a reinforcing moiety via one of or a combination of two routes: physical dispersion and chemical modification. In order to understand the “additive effect” of glass transition temperature \( T_g \) observed with the variation of free anthracene (AN) and bonded 2-aminoanthracene (2-AM) loading, the relaxation dynamics were investigated by broadband dielectric spectroscopy. Within the measurement range of 0.01 Hz to 1 MHz and -60 to 130 °C, three relaxation processes, namely normal mode (n-mode) relaxation, \( \alpha \) relaxation and \( \beta \) relaxation were observed for all compositions. The n-mode relaxation occurring at low frequencies above \( T_g \) for the rigid epoxy system is revealed after eliminating the strong effect of ionic conduction by using the logarithmic derivative approximation \( \varepsilon'' \propto \frac{\partial \varepsilon}{\partial \ln \omega} \), derived from the Kramers-Kronig relations. The Arrhenius diagram showing the temperature dependence of each relaxation process for the PAH/epoxy composites was obtained after parametric fitting using the Havriliak-Negami (HN) function in the frequency domain. The segmental \( \alpha \) relaxation was affected more strongly than the long-range n-mode relaxation by the different reinforcing
approaches. The correlation of $T_g$-scaled fragility to molecular structures reveals the different mechanisms for the retardation effects on cooperative segmental and chain relaxation time. The localized $\beta$ relaxation below $T_g$ was not apparently affected by the incorporation of bound or/and unbound anthracenes as indicated by the characteristic relaxation time and the activation energy.

**4.2 Introduction**

A variety of research has been conducted on different nano-scale fillers with the hopes of improving many properties in polymeric matrices such as rheological properties, thermal stability, and mechanical strength. It has been shown that some molecules are able to provide reinforcement to the overall composite in a similar way to traditional nanofiller materials, such as nanoclays, nanosilica, and carbon nanotubes. These molecular nanofillers, such as fullerene ($C_{60}$), polyhedral oligomeric silsesquioxane (POSS), and boron cage compounds (BCCs) have smaller sizes than traditional nanofillers, and interact effectively with the polymer chains. Previous work has focused on incorporating specific molecular nanofillers into elastomer matrices [1]. However, many of these other molecular nanofillers are difficult and costly to obtain and manipulate leading to limited utility.

Asphaltenes offer an abundant supply and relatively inexpensive option for a molecular nanofiller. Asphaltenes have been studied in large part due to their ability to aggregate and adsorb onto surfaces. This phenomenon has led to many challenges for the petroleum industry, specifically with respect to well production, transportation, and oil refining [2]. These materials are composed of non-uniform arrangements of aromatic structures and various sulfur and nitrogen containing systems. They also have a large percentage of fused aromatic carbons present. Moreover, the $\pi-\pi$ stacking exhibited by asphaltenes further reduces their solubility [2].
Asphaltenes are often noted as the component of crude oil that is insoluble in n-alkanes, such as n-heptane or n-pentane, while still being soluble in benzene or toluene.

Prior attempts to use asphaltenes as inexpensive nanofiller materials have experienced many complications. The lack of uniformity in the samples makes chemical modification difficult while agglomeration promoted by π-π stacking further reduces the feasibility of proper dispersion for asphaltenes as nanofillers. As such, a more modifiable, representative polycyclic aromatic hydrocarbon (PAH) system (Figure 4-1) is sought as a surrogate for asphaltenes. Anthracene is one of the simplest PAH molecules, consisting of three fused benzene rings, which is interesting for investigation as a polymer additive because of its fluorescent, scintillator, and optical wave guide properties enabling sensor and semiconductor applications. Anthracene is designated as a simplified model for asphaltene due to its similarity to the aromatic core structure of asphaltenes. Moreover, Anthracene is merely bonded by π-π stacking interaction and its readily functionalized compounds allow for alterations in solubility and dispersion in a polymer matrix. Studying the process of incorporating anthracene into an epoxy model matrix provides insight into the development a better dispersion process for asphaltenes in polymer systems.

![Figure 4-1. Examples of the chemical structures of PAHs in different classes: (a) naphthalene (b) anthracene (c) perylene (d) asphaltene (referred from [3]).](image-url)
In this work, broadband dielectric spectroscopy measurements and analyses are conducted on anthracene/epoxy composites subjected to different reinforcing routes, in order to elucidate the mechanism(s) underlying the observed increase of glass transition temperature by the incorporation of the molecular fillers. Anthracene is not subject to dipolar and charge-transfer interactions due to its non-polar structure. In broadband dielectric spectroscopy of anthracene-incorporated polymers, therefore, the molecular dynamics of the modified polymer can be investigated without complications due to independent contributions to the dielectric polarization, from the filler. The model epoxy matrix selected in this study has a moderate $T_g$ above room temperature presenting both cooperative chain (n-mode) and segmental ($\alpha$) relaxations within the bounds of the measurement conditions. The relationship among glass transition temperature, temperature-dependent $\alpha$ relaxation time and fragility of the anthracene/epoxy composites were analyzed.

4.3 Experimental section

4.3.1 Material preparation

The model epoxy system selected for this study was Epon 828 and amine curing agent Epicure 3270, supplied by Momentive Specialty Chemicals (Houston, TX). Epon 828 is diglycidyl ether of bisphenol-A (DGEBA), a viscous glass-forming liquid with an epoxy equivalent weight of about 190. Epicure 3270 is a modified aliphatic amine mixture containing n-aminoethyl piperazine and diethylene triamine. It is a yellow, viscous liquid with amine hydrogen equivalent weight of 142. The mixing weight ratio of Epon 828 to hardener is 100:75. Anthracene and 2-aminoanthracene are obtained from Sigma-Aldrich (St. Louis, MO). At room temperature anthracene (melting point (m.p.) = 215 °C) appears as light-colored crystalline
particles and 2-aminoanthracene (m.p. = 241 °C) appears as a dark yellow powder. Tetrahydrofuran (THF, HPLC grade) is obtained from Fisher Scientific (Fair Lawn, NJ) and used without further purification.

2-aminoanthracene was mixed with Epon 828 at various loadings (0 % and 5 % of total material by weight) in 20 mL THF and stirred until 2-aminoanthracene completely dissolved into solution. The solution was then transferred to a 100 mL round-bottom flask and heated at 80 °C for 2 hours under reflux. After the reaction the solution was removed from the heat and allowed to cool under ambient conditions. Separately, a stoichiometric amount of Epicure 3270 hardener and anthracene at various loadings (0 %, 2.5 % or 5 % of total material by weight) were mixed together by hand using a spatula. The 2-aminoanthracene/epoxide and the hardener/anthracene mixtures were then combined and mixed thoroughly. The resulting epoxy resin mixture was poured into a silicone rubber mold consisting of a cylindrical cell 25 mm in diameter and 3 mm in height. The samples were degassed in a vacuum oven and allowed to cure at ambient temperature overnight. Finally, the samples were heated under vacuum at 110 °C for between 60 and 72 hours to fully drive off any residual THF.

An example resulting chemical structure of 2-AM/AN epoxy composites is illustrated schematically in Figure 4-2. The quality of filler dispersion in the six different samples was examined by optical microscopy, Figure 4-3. Figures 4-3 (a) to (c), for epoxy composites without 2-aminoanthracene, reveal that a dense micro-crystal phase was formed after the addition of anthracene, with crystal dimensions ranging from several to hundreds of microns. In Figures 4-3 (d) to (f), for epoxy composites containing 5% 2-aminoanthracene, the miscibility between anthracene and the epoxy matrix was significantly enhanced, revealed by a reduction in the density of crystallites.
Figure 4-2. A schematic chemical structure of 2-AM/AN epoxy composites.

Figure 4-3. Optical micrographs showing the morphology of composites with no 2-aminoanthracene: (a) neat epoxy, (b) 0% 2-AM/2.5% AN, and (c) 0% 2-AM/2.5% AN; and composites with 5% 2-aminoanthracene: (d) 5% 2-AM/0% AN, (e) 5% 2-AM/2.5% AN, and (f) 5% 2-AM/5% AN.

4.3.2 Characterization by thermal and dielectric analysis
The glass transition temperature \( (T_g) \) of the epoxy composites with varied PAH filler loading was measured using a differential scanning calorimeter (DSC, Q20, TA Instruments). Samples with approximate mass 4 to 6 mg were each sealed in a Tzero hermetic pan and scanned with heat/cool/heat progress from -90 to 110 °C at a ramping rate of 10 °C/min for 4 cycles, under a helium purge gas flow rate of 50 ml/min.

The complex permittivity of PAH epoxy composites was measured using a Novocontrol dielectric spectrometer (Novocontrol Technologies, Germany) in which the sample cell, consisting of 20-mm-diameter parallel plate electrodes, was housed in a temperature-controlled chamber. The complex permittivity \( \varepsilon^*(\omega) \) is inferred from the measured complex impedance \( Z^*(\omega) \) of the sample material as it forms the dielectric insulation layer between the parallel electrodes at controlled temperature. Thin, disc-shaped samples with uniform thickness of around 0.3 mm and less than 5 % thickness variation from sample-to-sample and smooth surfaces were prepared by polishing the sample from 400 to 800 grit. A pair of brass spacers with the same diameter as the electrodes were applied to fix sample between the electrodes when conducting the dielectric measurement. The overall uncertainty in measured permittivity is estimated to be around 1 %, introduced by the sample thickness variance and the error of the analyzer. The measurement was conducted at a voltage of 1.0 V, over a frequency range from \( 10^{-2} \) to \( 10^6 \) Hz, and temperature range from -60 °C to 130 °C with a 10 °C increment. The upper temperature limit was determined by the starting temperature at which massive decomposition of the sample occurs, as indicated from thermogravimetric analysis.

### 4.4 Results and discussion
4.4.1 Glass transition temperature measured by DSC

Glass transition temperature ($T_g$) obtained from DSC thermograms was determined by the average temperature at the half height of the heat capacity increase ($1/2C_p$) on the last three heating thermal curves. $T_g$ for epoxy composites with varied anthracene and 2-aminoanthracene loading is shown in Figure 4-4 as a 3D bar graph. The addition of 2.5 % anthracene increases the $T_g$ of neat epoxy by 11±5 °C, whereas no further increase in $T_g$ is observed with 5% of anthracene loading. As anthracene is a typical PAH molecular crystal bonded by weak intermolecular forces, it is inclined to disperse physically into the epoxy matrix at the molecular level [4]. The concentration of anthracene filler at 2.5 % and beyond appears to exceed its critical solubility in epoxy and therefore precipitates as a second micro-crystal phase as seen in the optical microscope images [5-7] (Figures 4-3 (b) and (c)). The correlation of $T_g$ results to the morphology suggests that the increase of $T_g$ is associated with the molecularly dispersed anthracene rather than micro-scaled anthracene crystallites. Similar findings have been reported by several studies on the influence of micro and nanoscale particles on the glass transition of epoxy [8].

By the other route of chemical modification with 5 % of 2-aminoanthracene, the $T_g$ of epoxy was increased by 12±4 °C. For the composition of 5% 2-AM/2.5% AN, the epoxy incorporated with both fillers exhibits a nearly additive effect on the increase of $T_g$ ($\Delta T = 24±4 \, ^\circ C$). Combined with the observation from the corresponding morphology, it is apparent that the macromolecular dynamics of epoxy was significantly changed by the interplay of anthracene and 2-aminoanthracene fillers included. In order to interpret how the physical or/and covalent types of
polymer-filler interactions affect the segmental dynamics relating to glass transition and other relaxations beyond, an in-depth analysis by broadband dielectric spectroscopy was therefore performed on the four samples: neat epoxy, 0% 2-AM/2.5% AN, 5% 2-AM/0% AN, and 5% 2-AM/2.5% AN.

4.4.2 Dielectric spectra

Figures 4-5 (a) and (b) show the temperature and frequency dependence of the real and imaginary part of permittivity for the neat epoxy sample, as an example. The glass transition, or \( \alpha \) relaxation process, is allocated as the step of \( \varepsilon' \) shift and the relaxation peak in \( \varepsilon'' \) occurring at around 50 °C. The \( \alpha \) relaxation is associated with cooperative motions of the chain segments.
triggered by the relaxation of polar side groups [9]. At temperatures below the $\alpha$ relaxation, a relaxation process with lower intensity in $\varepsilon''$ was identified as a $\beta$ relaxation, associated with the local motions of polar side groups. In this material system, the $\beta$ relaxation is recognized as crankshaft motions of the hydroxyl groups from the epoxy moiety [10, 11]. At increasing temperatures above that of the $\alpha$ relaxation, there occurs another significant step increase in $\varepsilon'$ whereas the corresponding relaxation process in $\varepsilon''$ was hard to distinguish from a gradient increase of $\varepsilon''$, indicating strong ionic conductivity effect at low-frequency (between $10^{-2}$ and $10^0$ Hz) and high-temperature (100 to 130 °C) region. Meanwhile, the corresponding sharp increase in $\varepsilon'$ indicates the electrode polarization, resulting from the accumulation of charges at the electrode-dielectric interface.

In order to separate the intrinsic dielectric phenomena at low-frequency, above-$T_g$ region from the ionic conduction, a logarithmic derivative expression which is a first order approximation of the Kramers-Kronig relation was applied to the permittivity data as follows [12]:

$$
\varepsilon''_{deriv} = -\frac{\pi}{2} \frac{\partial \varepsilon'(\omega)}{\partial \log \omega} \approx \varepsilon'' \quad \text{(Eq. 4-1)}
$$

This formula transforms the real part $\varepsilon'$ into an imaginary part $\varepsilon''_{deriv}$ that originates only from dipolar relaxation phenomena. The derivative eliminates the direct current (dc) conduction and sharpens the loss peaks, which gives good separation for broad peaks such as $\alpha$ and $\beta$ relaxation process. The imaginary permittivity obtained by Eq.4-1 (denoted as $\varepsilon''_{deriv}$) for neat epoxy is presented in Figure 4-5 (c), in which three relaxation processes are clearly visible in the spectral map.
Figure 4-5. Three dimensional plots of (a) measured real permittivity (b) measured imaginary permittivity and (c) imaginary permittivity obtained from logarithmic derivative approach of neat epoxy as a function of frequency and temperature.
The slow relaxation process above glass transition at low frequencies is observed universally, for all six cured epoxy samples with and without PAH fillers, and is herein attributed to the normal mode (n-mode) relaxation. The n-mode dielectric relaxation reflects the long-range motion of the end-to-end dipole vector along the polymer chains. The relaxation mode exists on the polymers with dipoles of type-A parallel to the chain contour [13]. Dielectric spectroscopic studies on uncured or partially-cured epoxy monomers, mainly DGEBA [14-16], revealed no trace of such relaxation mode due to dipole moment offset by the monomer’s chain symmetry of inversion. Previously, the observation of n-mode relaxation in cured epoxy systems has been reported only for rubbery epoxies with low \( T_g \) which have been cross-linked by reactive prepolymer intrinsic of type-A dipoles [17, 18]. However, it is noteworthy that n-mode relaxation is perceptible in this glassy epoxy system cured by aliphatic amines, probably because the amine linkages newly formed after curing such as -R\( _2 \)N-CH\( _2 \)-CHOH- serve as type-A dipoles on the main chains by disrupting the chain symmetry structure.

For n-mode relaxation with Debye characteristic, the derivative expressed in Eq.1 results in peaks which are significantly narrower than the measured loss peaks. In order to attain to preferable HN fitting at isothermal conditions above \( T_g \), the following approximation is therefore more appropriate [12]:

\[
-\frac{\pi \partial \varepsilon'(\omega)}{2 \partial \log \omega} \approx (\varepsilon'' \omega)^2 \quad \text{(Eq.4-2)}
\]

In the low-frequency dispersion region (for frequencies in the range \( 10^{-2} \) to \( 10^0 \) Hz and temperatures greater than 80 °C) the measured imaginary permittivity \( \varepsilon'' \) was fitted by the power law relation \( \varepsilon''(\omega) = \sigma/(\varepsilon_0 \omega^\delta) \), where \( \sigma \) is the conductivity, \( \varepsilon_0 \) is the permittivity of free space,
and $S$ is the exponent $(0 \leq S \leq 1)$. The exponent $A$ was found to be 0.98 or 0.99 for the neat epoxy sample and 0.97 or 0.98 for the 2-AM/AN composites, respectively. This exponent value close to unity indicates that the ionic conduction effect is mainly attributed to dc conduction. DC conduction-free $\varepsilon''_{\text{deriv}}$ curves such as shown in the low-frequency dispersion region of Figure 4-5 (c) reveals that there remains additional conductivity, which may be due to the electrode polarization.

4.4.3 Parametric model-fitting and molecular dynamics

In order to quantify the relaxation characteristics and probe how the molecular dynamics of epoxy is affected by 2-AM and AN fillers, firstly the empirical Havriliak-Negami (HN) function is applied to describe a single dielectric relaxation process in the frequency domain [19]:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + i\omega\tau_{HN}^{1-\eta_{HN}}}^{\eta_{HN}} \quad \text{(Eq.4-3)}$$

where $\varepsilon^*$ is the complex permittivity, $\omega$ is the angular frequency ($\omega = 2\pi f$), $\varepsilon_\infty$ is the permittivity well above the relaxation frequency (without the contributions of dipole orientation and free charge migration), $\Delta\varepsilon$ is the relaxation strength of the process, $\tau_{HN} = 1/(2\pi f_{HN})$ is the characteristic relaxation time, and $a_{HN}$ and $b_{HN}$ are two shape parameters ($0 \leq a_{HN}, b_{HN} \leq 1$). The former governs the peak intensity and breadth of the relaxation process and the latter governs its skewness.

The imaginary part of the permittivity, $\varepsilon''(\omega)$, at isothermal conditions, was resolved by a superposition of multiple Havriliak-Negami functions representing the identified relaxation processes and a conductivity term, expressed in the following general form:
\[ \varepsilon''(\omega) = -\text{Im} \sum_{i=1}^{n} \left\{ \frac{\Delta \varepsilon_i}{\left[ 1 + (i\omega \tau_{HN})^{3-a_{HN}} \right]^{b_{HN}}} \right\} + \frac{\sigma}{\varepsilon_0 \omega^A} \quad \text{(Eq.4-4)} \]

Parametric fitting was conducted on the basis of two sets of isothermal data of \( \varepsilon''(\omega) \): logarithmic derivative results \( \varepsilon''_{\text{deriv}} \) above glass transition (40 °C), Eq.4-1, and measured \( \varepsilon'' \) for temperatures below the glass transition. At low frequency and above \( T_g \), the remaining conductive process was included to fit \( \varepsilon''_{\text{deriv}} \). Best fits were achieved at each temperature by adjusting the fitting parameters and minimizing the error between model and experimental data by the least squares fitting technique.

Figure 4-6 shows an example of \( \varepsilon''_{\text{deriv}} \) at 110 °C for all four samples fitting suitable combinations of relaxation functions to measured experimental data. Samples of neat epoxy and 5% 2-AM/0% AN with homogenous structure, yields a good fit to the data through a combination of conductivity, n-mode, and \( \alpha \) relaxation. For 0% 2-AM/2.5% AN and 5% 2-AM/2.5% AN sample, best fits entail an additional relaxation peak between the n-mode relaxation and conductivity, arising from the effect of Maxwell-Wagner-Sillars (MWS) interfacial polarization due to the boundaries induced between the epoxy matrix and the distributed anthracene crystallites.

The characteristic frequencies at which \( \varepsilon''(\omega) \) turns maximum \( (f_{\text{max}}) \) of a single dielectric relaxation at each temperature is obtained by the following relation between \( f_{HN} \), \( a_{HN} \) and \( b_{HN} \):

\[
f_{\text{max}} = f_{HN} \left\{ \sin \left[ \frac{\pi(1-a_{HN})b_{HN}}{z(b_{HN}+1)} \right] \right\}^{-1/(1-a_{HN})} \quad \text{(Eq.4-5)}
\]
Figure 4-6. Imaginary permittivity by derivative $\varepsilon''_{\text{deriv}}$ for different samples: neat epoxy, 5% 2-AM/0% AN, 0% 2-AM/2.5% AN and 5% 2-AM/2.5% AN at 110 °C, with fitted HN relaxation processes.

The temperature dependence of relaxation times (in the form of inverse of $f_{\text{max}}$) for relaxation processes above and below $T_g$ are plotted for all four samples in Figure 4-7. As clearly seen, the $\alpha$ and n-mode relaxations exhibit distinct shifting behaviors for each composite sample from neat epoxy, as temperature cools down towards that of the glass transition. In order to quantify the change of both relaxation processes, the ratio of relaxation times for 2-AM/AN epoxy composites to neat epoxy is plotted as a function of temperature in Figure 4-8.
Figure 4-7. Arrhenius diagram showing all relaxation processes for neat epoxy, 0% 2-AM/2.5% AN epoxy and 5% 2-AM/2.5% AN epoxy. The symbols represent the HN model-fitted relaxations from the measured imaginary permittivity (triangle: α relaxation, circle: β relaxation, square: n-mode, and diamond: MWS relaxation). The solid lines represent the fits of the VFT law to n-mode and α relaxations and of the Arrhenius law to β relaxations. The dashed line indicates the frequency of $1.6 \times 10^{-3}$ Hz ($\tau = 100$ s) at which the dielectric $T_g$ is defined [9].

For 0% 2-AM/2.5% AN, the α relaxation time ($\tau_\alpha$) is slower than that of neat epoxy at temperatures near $T_g$ and the ratio $\tau_{\text{composite}}/\tau_{\text{neat,\alpha}}$ converges to 1 at higher temperature above $T_g$. The change of n-mode relaxation time ($\tau_n$) is similar but $\tau_{\text{composite}}/\tau_{\text{neat,n}}$ decrease towards a value less than unity, indicating slightly accelerating dynamics. The $\tau_{\text{composite}}/\tau_{\text{neat,\alpha}}$ for 5% 2-AM/0%
AN exhibits entirely different behavior, shifting from $10^2$ towards $10^3$ as temperature increases, exhibiting a prominent retardation of $\alpha$ relaxation compared to neat epoxy. In contrast, the n-mode relaxation of 5% 2-AM/0% AN is faster than that of any other sample above $T_g$. The $\alpha$ relaxation behavior of 5% 2-AM/2.5 AN resembles the characteristics of 0% 2-AM/2.5% AN at temperatures well above $T_g$ and 5% 2-AM/0% AN at temperatures near $T_g$, showing the rapid decay of $\tau_{\text{composite}}/\tau_{\text{neat,}\alpha}$ with increasing temperature. The decreasing $\tau_{\text{composite}}/\tau_{\text{neat,n}} (>1)$ as temperature decreases shows the retardation of n-mode relaxation time when approaching glass transition. These results show that the form of anthracene incorporation influences the change of $\alpha$ relaxation time with temperature more than for the n-mode relaxation.

Figure 4-8. Ratio of $\alpha$ relaxation (filled symbols) and n-mode relaxation (open symbols) for the PAH epoxy composites to that of the neat epoxy.
The temperature dependence of the n-mode and $\alpha$ relaxation can be further well described by the Vogel-Fulcher-Tammann (VFT) law [20, 21]:

$$f_{\text{max}} = f_0 \exp\left(-\frac{D}{T-T_0}\right) \quad \text{(Eq. 4-6)}$$

where $D$ is the strength parameter, $T_0$ is the Vogel temperature, and $f_0$ is the frequency pre-exponential factor. Table 4-1 lists the fitted parameters of n-mode and $\alpha$ relaxation curves plotted as solid lines in Figure 4-7.

The glass transition temperature defined by dielectric spectroscopy ($T_{g,\text{diel}}$) is empirically obtained from the VFT fit of the segmental $\alpha$ relaxation time $\tau_\alpha = 100$ s, corresponding to $f_{\text{max}}^\alpha = 1.6 \times 10^3$ Hz:

$$T_{g,\text{diel}} = T_0 - \frac{D T_0}{\ln(f_{\text{max}}^\alpha/f_0)} \quad \text{(Eq. 4-7)}$$

Table 4-1. Parameters from the VFT fit of n-mode and $\alpha$ relaxation times.

<table>
<thead>
<tr>
<th></th>
<th>n-mode relaxation</th>
<th>$\alpha$ relaxation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>log$_{10} f_0$ (s$^{-1}$)</td>
<td>$D$</td>
</tr>
<tr>
<td>Neat epoxy</td>
<td>6.1 ± 0.2</td>
<td>8.6 ± 0.3</td>
</tr>
<tr>
<td>0% 2-AM/2.5% AN</td>
<td>7.7 ± 0.2</td>
<td>11.5 ± 0.3</td>
</tr>
<tr>
<td>5% 2-AM/0% AN</td>
<td>7.2 ± 0.3</td>
<td>8.3 ± 0.3</td>
</tr>
<tr>
<td>5% 2-AM/2.5% AN</td>
<td>7.4 ± 0.2</td>
<td>10.0 ± 0.2</td>
</tr>
</tbody>
</table>
In addition to \( T_g \), fragility is also investigated as an important parameter characterizing the breadth of the glass transition and how rapidly the transport properties change with temperature when approaching \( T_g \) [22]. The fragility index \( m \), a measure of the cooperative motions from \( \alpha \) relaxation for glass-forming polymers, is introduced by evaluating the slope of the temperature dependence of \( \tau_\alpha \) approaching \( T_g \) [23]:

\[
m = \left. \frac{d \log(\tau_\alpha)}{d(T/T_g)} \right|_{T=T_g} \quad (\text{Eq.4-8})
\]

\[
m = \frac{T_g}{\ln(10)} \frac{D \tau_\alpha}{(T_g-T_0)^2} \quad (\text{Eq.4-9})
\]

As proposed in earlier studies [24, 25], a glass-former with high value of \( m \) (up to \( \sim 250 \)) is defined as “fragile” because it indicates a steep variation close to \( T_g \) corresponding to non-Arrhenius temperature dependence of \( \tau_\alpha \). On the contrary, a glass-former is “strong” with low value of \( m \) (down to \( \sim 16 \)) and tends to resist the variations in transport properties (such as viscosity, thermal conductivity, and diffusion coefficient, etc.) with temperature, behaving nearly Arrhenius dependence of \( \tau_\alpha \).

Table 4-2. Glass transition parameters \( T_g \) and \( m \) for all samples.

<table>
<thead>
<tr>
<th>Glass transition parameters</th>
<th>( T_{g, \text{DSC}} ) (°C)</th>
<th>( T_{g, \text{dieu}} ) (°C)</th>
<th>( m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat epoxy</td>
<td>32 ± 4</td>
<td>45 ± 3</td>
<td>83 ± 6</td>
</tr>
<tr>
<td>0% 2-AM/2.5% AN</td>
<td>39 ± 4</td>
<td>56 ± 2</td>
<td>94 ± 7</td>
</tr>
<tr>
<td>5% 2-AM/0% AN</td>
<td>41 ± 4</td>
<td>57 ± 1</td>
<td>65 ± 4</td>
</tr>
<tr>
<td>5% 2-AM/2.5% AN</td>
<td>48 ± 4</td>
<td>69 ± 1</td>
<td>88 ± 6</td>
</tr>
</tbody>
</table>
The calculated values of $T_g \text{ _d i e l}$ and $m$ for the 2-AM/AN epoxy composite samples are reported in Table 4-2. $T_g \text{ _d i e l}$ shows a trend in good agreement with $T_g \text{ _D S C}$ obtained previously while the values of $T_g \text{ _d i e l}$ for all samples appear to be between 13 and 20 °C lower than $T_g \text{ _D S C}$. In contrast, the change of fragility $m$ is not in proportion to the shift of $T_g$, substantiated by the fact that 0% 2-AM/2.5% AN becomes more fragile whereas 5% 2-AM/0%AN is less fragile than neat epoxy as both of $T_g$s increase. This implies that $m$ could be a key parameter to correlate to the different mechanisms in tailoring glass transition processes.

0% 2-AM/2.5% AN behaves in a way that is characteristic of merely physical interaction between anthracene and epoxy because free anthracene fillers without functional groups are not capable of chemically participating in cross-linking of epoxy network. As pointed out earlier in Section 4.4.1, two forms of anthracene fillers were assumed to exist in this binary molecular filler-polymer blend: the nano-scale fillers that are miscible with the polymer matrix on the molecular level at the critical solubility and the micro-scale fillers that appear as a second crystallization phase due to the excessive concentration of unbound anthracene. Despite the fact that the distribution of micro crystallites may lead to mechanical reinforcement, they were proven to have negligible impact on modifying $T_g$ and polymer dynamics due to lack of sufficient filler-matrix interfacial area [26]. The anthracene nanofiller dispersed molecularly at much lower concentration than 2.5 % in the epoxy network is supposed to play an important role in increasing $T_g$. According to recent findings on the effect of adding nano-sized fillers - nanoparticles or molecular additives - on the glass-formation in polymers, both experimentally [27, 28] and theoretically [29], it is shown that $T_g$ and $m$ change proportionally at low nanofiller loading depending on the nature of the filler-polymer interaction. Attractive interaction between filler and polymer increases both $T_g$ and fragility, characterized by slowing down of dynamics
and disrupting molecular packing of polymer chains. Conversely, repulsive interaction decreases both $T_g$ and fragility, corresponding to the acceleration of dynamics and improvement of polymer packing. For 0% 2-AM/2.5% AN, $T_g$ rises in consistency with the increase of $\tau_\alpha$ observed in Figure 4-8, indicating the characteristic of attractive interaction. The retarded $\alpha$ relaxation dynamics of 0% 2-AM/2.5% AN could possibly be attributed to the restraining effect on segmental motions by introduced positive $\pi-\pi$ stacking interactions between the aromatic rings of anthracene molecules and of bisphenol A moieties contained in the epoxy network, as shown in Figure 4-9. The anthracene molecules located near the epoxy mainchains do not only increase the reorientation energy for hydroxyl group-involved segments but also disrupt the local molecular packing efficiency by substituting the original free volume, which leads to increase of $m$.

Neat epoxy used in this study exhibits the feature of relatively high $T_g$ (45 ± 3 °C by DSC) and high $m$ (83 ± 6), which is mainly attributed to the rigid bisphenol A moiety constituting the backbone. Except for the backbone flexibility as the primary parameter controlling $T_g$, the stiffness and bulkiness of side groups is also an effective parameter to shift $T_g$. Hence, increase of $T_g$ observed in the 5% 2-AM/0% AN sample is attributed to the pendant anthracene groups incorporated into the epoxy network by the chemical modification. The steric hindrance of the bulky side groups inhibits the chain configurations and elevates energy barriers for the segmental motion that is responsible for the glass transition. Compared to neat epoxy, the significant shift of $\tau_\alpha$ towards slower segmental relaxation agrees with $T_g$ elevation due to the intrinsic change in the chemical structure of 5% 2-AM/0% AN. On the other hand, the single functionality of 2-aminoanthracene could lower $T_g$ by creating less cross-linking sites for epoxy network (observed at high loading of 2-aminoanthracene), but this counter factor appears to be secondary compared
to the sterically hindering effect at the relatively low 2-aminoanthracene loading of 5%. On the other hand, the $m$ of 5% 2-AM/0% AN exhibits a significant decrease, by about 20%, compared with $m$ for neat epoxy, which appears to be contradictory to the literature reports that polymer fragility usually increases with substitution of stiff and bulky side groups [30]. A qualitative structural parameter, the relative stiffness of side groups to the backbone, was introduced to explain this non-intuitive phenomenon. According to the fragility map of polymers in Figure 4-10, a polymer is expected to have the lowest fragility when the side group stiffness matches that of the backbone. The fragility increases with varying the relative stiffness of side groups to the backbone according to two opposite pathways: (i) increasing the backbone stiffness (towards left side of map) or (ii) adding bulky and inflexible side groups to the polymers with flexible backbones (towards right side of map). Since epoxy is classified as a polymer with a relatively stiff backbone, such as polycarbonate (PC), polyethylene terephthalate (PET) and polyetherimide (PEI), attaching anthracene side group with similar stiffness in 5% 2-AM/0% AN diminishes the difference between side group and backbone stiffness, resulting in the shift of $m$ downwards.

The hybrid system 5% 2-AM/2.5% AN is a blend of free anthracene with epoxy modified by 2-aminoanthracene. The solubility of anthracene in modified epoxy is enhanced due to addition of the compatible aromatic moiety, which is substantiated by the lower density and smaller size of micro-crystalline anthracene. The increased dependence of $\tau_\alpha$ on temperature also confirmed the concentration effect of attractively interactive nano-fillers. Figure 4-9 schematically illustrates all the possible interactions between the epoxy mainchain, attached anthracene side group, unbound anthracene molecules and anthracene crystallites in 5% 2-AM/2.5% AN. The two different factors increasing $T_g$, namely the stiffer side group induced by 2-aminoanthracene and hindered segmental mobility by attractively-interactive anthracene, are
combined to drive $T_g$ of 5% 2-AM/2.5% AN towards a higher value than either of the composite samples with single filler incorporation. The effects of chemical modification and physical dispersion on the fragility are opposite, therefore compromising $m$ to an intermediate value between 5% 2-AM/0% AN and 0% 2-AM/2.5% AN.

Figure 4-9. Schematic diagram showing different intermolecular interactions in 2-AM/AN epoxy composites.
Figure 4-10. Fragility map showing the structural parameter controlling fragility of various polymers whose acronyms are listed in Table 4-3 (adapted from [30, 31]).

Table 4-3. Abbreviation of polymers in Figure 4-10.

<table>
<thead>
<tr>
<th>Acronyms</th>
<th>Full names</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA</td>
<td>diglycidyl ether of bisphenol A</td>
</tr>
<tr>
<td>PC</td>
<td>polycarbonate</td>
</tr>
<tr>
<td>PDMS</td>
<td>polydimethylsiloxane</td>
</tr>
<tr>
<td>PEI</td>
<td>polyetherimide</td>
</tr>
<tr>
<td>PE</td>
<td>polyethylene</td>
</tr>
<tr>
<td>PET</td>
<td>polyethyleneterephthalate</td>
</tr>
<tr>
<td>PHMA</td>
<td>polyhexylmethacrylate</td>
</tr>
<tr>
<td>PIB</td>
<td>polyisobutylene</td>
</tr>
<tr>
<td>PIP</td>
<td>polyisoprene</td>
</tr>
<tr>
<td>PMMA</td>
<td>polymethylmethacrylate</td>
</tr>
<tr>
<td>PMPS</td>
<td>polymethylpheynylsiloxane</td>
</tr>
<tr>
<td>POE</td>
<td>polyoxyethylene</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PSF</td>
<td>polysulfone</td>
</tr>
<tr>
<td>PTHF</td>
<td>polytetrahydrofuran</td>
</tr>
<tr>
<td>PVC</td>
<td>polyvinylchloride</td>
</tr>
</tbody>
</table>
The linear temperature dependence of the $\beta$ relaxation time shown on the Arrhenius plot in Figure 4-7, is described by the Arrhenius equation:

$$f_{\text{max}} = f_0 \exp\left(\frac{-E_a}{k_B T}\right) \quad (4-10)$$

where $E_a$ is the activation energy of the $\beta$ relaxation process, $k_B$ is the Boltzmann constant, and $f_0$ is the $\beta$ relaxation frequency prefactor. The fitted parameters $f_0$ and $E_a$ are presented in Table 4-4. The temperature-dependent curves of $\beta$ relaxation shift slightly towards increasing relaxation time $\tau_\beta$ after incorporating 2-AM or/and AN additives in epoxy but this change is subtle and not definitive, considering the fitting error. The effect of AN and/or 2-AM additives on the activation energy of $\beta$ relaxation appears also to be insignificant, indicating that the local motions of hydroxyl groups as the origin of $\beta$ relaxation are not affected by either of the changes in molecular environment: the adjacent attachment of pendent anthracene; and attractive $\pi-\pi$ interactions between the anthracene (free molecules or/and chemically bonded moiety) and bisphenol A moiety from epoxy.

**Table 4-4. Parameters from the Arrhenius fit of $\beta$ relaxation times**

<table>
<thead>
<tr>
<th></th>
<th>$\beta$-relaxation</th>
<th>$\log_{10} f_0$ (s$^{-1}$)</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat epoxy</td>
<td></td>
<td>16.0 ± 0.3</td>
<td>62.0 ± 1.7</td>
</tr>
<tr>
<td>0% 2-AM/2.5% AN</td>
<td></td>
<td>15.8 ± 0.2</td>
<td>61.8 ± 0.8</td>
</tr>
<tr>
<td>5% 2-AM/2.5% AN</td>
<td></td>
<td>16.0 ± 0.2</td>
<td>63.4 ± 1.0</td>
</tr>
<tr>
<td>5% 2-AM/0%AN</td>
<td></td>
<td>16.0 ± 0.2</td>
<td>63.3 ± 1.0</td>
</tr>
</tbody>
</table>
4.5 Conclusions

Novel epoxy nanocomposites incorporating anthracene are here explored as a simple model compound for polycyclic aromatic hydrocarbons. Different reinforcing strategies exhibited improvements in the thermal, rheological, and mechanical properties. Specifically, characterization by DSC showed a nearly additive effect on increasing the glass transition temperature of epoxy after the simultaneous physical dispersion and chemical modification by anthracene and its derivative, respectively. Optical microscopy displayed the enhanced miscibility between the unbound anthracene and the epoxy matrix with covalently-attached anthracene groups compared to the epoxy without. Broadband dielectric spectroscopy was applied to further investigate the influence of interplay of the two types of anthracenes on the universal macromolecular dynamics of the nanocomposites.

Parametric fitting of the dielectric loss spectra with HN functions revealed that both n-mode relaxation and $\alpha$ relaxation, representing global chain motion and segmental motion respectively, exist above $T_g$ for all 2-AM/AN epoxy composite samples. Physical dispersion of anthracene into epoxy behaves as the attractive polymer-filler interaction, verified by retardation of $\alpha$ relaxation time with temperature as well as the proportional increase of $T_g$ and fragility. Chemically anthracene-modified epoxy was subjected to significant decrease of $\alpha$ relaxation time due to the constraining effect on the segments from pendent anthracene groups, as evidenced by increase of $T_g$. Instead, the fragility decreases inversely because of the intrinsic change of the relative stiffness of side groups to the backbone as the main controlling factor. The combination of both reinforcing routes magnifies the temperature dependence of $\alpha$ relaxation time, indicating the increasing loading effect of unbound anthracene fillers upon the increased $\pi-\pi$ interaction. In this
way, $T_g$ was elevated while the fragility was kept comparable to the original epoxy matrix. The n-mode relaxation was found less sensitive to the incorporation of anthracene fillers than $\alpha$ relaxation.

MWS interfacial relaxation occurs in the samples with freely dispersed anthracene at high temperatures due to the boundary interaction between anthracene micro-crystallites and matrix. The $\beta$ relaxation corresponding to the local motions of hydroxyl groups below $T_g$ was not apparently affected by the incorporation of bound or/and unbound anthracenes as indicated by no significant observed change in the characteristic relaxation time and the activation energy of the $\beta$ relaxation across the samples studied.

Acknowledgments

The authors thank Mr. Kun Chen of the Department of Electrical and Computer Engineering and Mr. Weixing Sun of the Department of Materials Science and Engineering at Iowa State University for their contribution in optimizing the model fitting codes in Matlab.

4.6 References


CHAPTER 5: PERMITTIVITY AND ELECTRICAL BREAKDOWN RESPONSE OF NYLON 6 TO CHEMICAL EXPOSURE

A paper published in IEEE TDEI

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5.1 Abstract

Environmental stress such as unintended exposure of aircraft wire insulation to aviation-related fluids is one cause of wire aging that increases the risk of electrical failure. In this paper, the dielectric properties of nylon 6, a common wire insulation material, were investigated under chemical exposure for up to 8 days in six fluids: distilled water, cleaning fluid, isopropyl alcohol, deicing fluid, jet fuel and hydraulic fluid. Real permittivity \( \varepsilon' \) and dissipation factor \( D \) of aged samples were measured using an LCR meter over frequency range from 100 Hz to 1 MHz in an ambient environment (23 °C). It was found that \( \varepsilon' \) and \( D \) of aged nylon 6 exhibit distinct shifting behavior according to the polarity of the fluids in which it is immersed. Immersion in polar fluids gives rise to a strong effect of fluid absorption on the increase of polarizability of nylon 6, showing significant increase in \( \varepsilon' \) and \( D \), along with moving of relaxations to higher frequencies. Electrical breakdown strength of nylon 6 was also observed to reduce dramatically following exposure to polar fluids. A two-parameter Weibull distribution was applied to analyze the distribution of electrical weak sites in chemically-aged nylon 6 and it is concluded that a different electrical breakdown mechanism could be responsible for the narrower distribution observed after polar chemical exposure than for the pristine material. Nylon 6 displayed
resistance to aging in non-polar fluids, showing no significant change in complex permittivity and electrical breakdown strength.

Index Terms -- Nylon 6, chemical exposure, permittivity, dissipation factor, breakdown strength, Weibull distribution

5.2 Introduction

An early type of wiring insulation, polyvinylchloride (PVC)/nylon, still serves widely to protect electrical conductors on commercial aircraft [1], including M5086/2 and Boeing BMS 13-5 wires, for example. The installation of PVC/nylon wiring traces back to the 1950s on aircraft such as the Boeing 707, 727 and 737. As aircraft continue to be operated beyond their original design life, the risk of wire deterioration increases due to their vulnerability to aging stresses [2]. It is important, therefore, to understand the aging characteristics of this legacy polymeric insulation under different aging stresses.

Nylon (polyamide) is a major component of wiring insulation, often serving as the outer layer jacketing PVC in the electric wire. Dry nylon is generally a good insulator to protect electrical conductors in low-frequency, moderate voltage applications, exhibiting unusually good combination of dielectric, mechanical, thermal and chemical properties. Nylon is, however, susceptible to severe degradation under various aging conditions. It has been reported that combined hydrolytic and oxidative degradation occur in nylon after long-time exposure to hot water or steam, in which the estimated service life of nylon 6,6 was reduced by 80 % as the exposure temperature was raised from 71 °C to 100 °C [3]. Another study showed that nylon fibers in the presence of moisture exhibited faster oxidation [4]. Nylon components used under exposure to automatic transmission fluid were found to undergo color changes and lose tensile strength [5]. In the aircraft operation environment,
the exposure to aviation fluids may have significant influence on the dielectric properties and electrical breakdown strength of wiring insulation polymers.

In the present work, we investigate the effect of chemical exposure on nylon 6 at room temperature by two types of aircraft chemical fluids: polar fluids mainly composed of water and alcohols, and nonpolar fluids composed of hydrocarbons. In particular, the chemical aging impact on the dielectric properties and electrical breakdown strength is studied. The change in real permittivity and dissipation factor as a function of aging time over frequency range 100 Hz to 1 MHz was monitored by dielectric spectroscopy. Electrical strength with Weibull distribution analysis was performed to reveal the dispersity of electrical failure locations. At the same time, mass gain was monitored during chemical exposure and WAXD patterns were utilized to analyze the amorphous phase of nylon 6 in relation to chemical aging. The association between the change in the dielectric properties and the change in polymer structure is discussed. Based on this and other information it is intended to develop an in-situ capacitive non-destructive evaluation technique to assess the degradation state of wire insulation [6-9].

5.3 Sample Materials

Extruded nylon 6 sheets with thickness between 0.5 and 0.6 mm were purchased from theplasticsshop.co.uk. Nylon 6 is a thermoplastic polymer, polymerized by a ring-opening polymerization of caprolactam in the presence of a catalytic amount of water at about 200 °C [10]. As shown in Figure 5-1, the chemical structure of nylon 6 consists of repeating methylene units and amide linkages that are arranged in the same direction. Due to the regular chain configuration and strong hydrogen bonding between polar amide groups, nylon 6 tends to be highly crystalline. Nylon 6 can occur in either of two stable crystal structures: the α form, which
is monoclinic structure; and the \( \gamma \) form, characteristic of the hexagonal/ pseudo-hexagonal structure [10-12]. The melting point of nylon 6 is 220 °C, much higher than the upper operating temperature limit of M5086/2 aircraft wire which is 105 °C. In addition, nylon 6 is well qualified for low-frequency, moderate-voltage applications because of its low dielectric constant and relatively small dependence on frequency, and relatively high dielectric strength. Selected properties of the purchased nylon 6 sheet are listed in Table 5-1 [10, 13].

Nylon 6 is moisture sensitive owing to its high affinity to water molecules through hydrogen bonding. Moisture content in nylon 6 not only decreases mechanical strength but also has a significant effect on electrical/dielectric properties, including increased frequency dependence of \( \varepsilon' \) and \( D \), and decrease in volume resistivity and dielectric strength. Therefore, drying pristine nylon 6 is required to guarantee obtaining effective and comparable data.

Thermogravimetric analysis (TGA) was used to determine the heating temperature to effectively remove water from nylon 6. A sample was kinetically scanned from ambient conditions to 800 °C in nitrogen at a heating rate of 20 °C/min. An initial weight loss of 1.9 % appeared around 120 °C, which is attributed to loss of water during the heating process. Prior to chemical aging, therefore, pristine nylon 6 was dried at 120 °C for one hour for all samples studied in this work.
Figure 5-1. Ring-opening polymerization and chemical structure of nylon 6.

Table 5-1. Physical and electrical properties of pristine nylon 6 [10, 13].

<table>
<thead>
<tr>
<th>Property</th>
<th>Nylon 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm$^3$)</td>
<td>1.13-1.14</td>
</tr>
<tr>
<td>Water absorption (wt. %)</td>
<td></td>
</tr>
<tr>
<td>Saturation in air (23°C / 50% RH)</td>
<td>2.6-2.8</td>
</tr>
<tr>
<td>Saturation in water (23°C)</td>
<td>9.0-9.5</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>220</td>
</tr>
<tr>
<td>Glass transition temperature (°C)</td>
<td>47-57, measured by DSC*</td>
</tr>
<tr>
<td>Dielectric strength (kV/mm)</td>
<td>25</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td></td>
</tr>
<tr>
<td>Dry</td>
<td>3.9 at 100 Hz, 3.3 at 1 MHz</td>
</tr>
<tr>
<td>50% RH</td>
<td>7.4 at 100 Hz, 3.8 at 1 MHz</td>
</tr>
<tr>
<td>Dissipation factor</td>
<td></td>
</tr>
<tr>
<td>Dry</td>
<td>0.019 at 100 Hz, 0.021 at 1 MHz</td>
</tr>
<tr>
<td>50% RH</td>
<td>0.13 at 100 Hz, 0.06 at 1 MHz</td>
</tr>
</tbody>
</table>

*DSC, differential scanning calorimetry
5.4 Chemicals

A variety of aircraft chemicals were chosen for chemical aging of nylon 6, based on their applicability and possible contact with wiring during the service life of an aircraft. Six fluids were chosen for this study: distilled water, cleaning fluid, isopropyl alcohol, deicing fluid, Jet A fuel, and hydraulic fluid. The cleaning fluid selected was AV-8 Concentrated Aircraft Cleaner. AV-8 cleaner is a general purpose cleaner conforming to the Boeing D6 specification, designed for use on both interior and exterior surfaces of aircraft. The cleaner is used in water with volume ratio of 1 part cleaner to 9 parts water. The deicing fluid selected was commercially named as Cryotech Polar Plus, donated by Cryotech. It is a Type I propylene glycol based fluid, commonly applied to the exterior of large aircraft. Some other ingredients essential in deicer include corrosion inhibitor, surfactant and colored dye. The deicer is used as a diluted solution with water in 1:1 ratio, which conforms to the specifications in the Boeing document D6-17487 on MIL-A-8243D Type I fluid. Isopropyl alcohol was also chosen for this study, as it is commonly used to clean aircraft wires during maintenance. The isopropyl alcohol used was 70% alcohol by volume. Jet A fuel is the most common type of aircraft fuel used in the United States. It is composed of kerosene with additives. The hydraulic fluid used in this study is Phillips 66 X/C, which conforms to the MIL-H-5606 specification. This hydraulic fluid is a red-dyed mineral oil based fluid commonly used in aircraft hydraulic and brake systems. The fluids described above are summarized in Table 5-2. As can be seen, cleaning fluid, isopropyl alcohol and deicing fluid contain a significant percentage of water and are polar whereas jet fuel and hydraulic fluid are non-polar. In Section 5.6, the dielectric response of exposed nylon 6 is therefore grouped according to the polarity of the fluids in which it is immersed.
Table 5-2. Aircraft-related fluids in which nylon 6 was aged.

<table>
<thead>
<tr>
<th>Aircraft fluid category</th>
<th>Main components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>Cleaning fluid</td>
<td>0.5 % ethoxylated C$_{9-11}$ alcohol, and 99.5 % water</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>70 % isopropanol, and 30% water</td>
</tr>
<tr>
<td>Deicing fluid</td>
<td>44 % propylene glycol, and &lt; 56% water</td>
</tr>
<tr>
<td>Jet A fuel</td>
<td>Kerosene, hydrocarbon of C$_{6-16}$</td>
</tr>
<tr>
<td>Hydraulic fluid</td>
<td>mineral oil, hydrocarbon of C$_{15-50}$</td>
</tr>
</tbody>
</table>

5.5 Experiment

5.5.1 Sample preparation and chemical exposure

Nylon 6 samples were cut from the large purchased sheet into a bundle of rectangular strips with several sizes: square samples around 0.5 g were prepared in order to monitor the mass gain as a function of immersion time in each fluid. Samples with dimensions 120 × 60 mm$^2$ and 60 × 40 mm$^2$ were prepared for permittivity and breakdown voltage measurements, respectively. Prior to fluid immersion, sample strips were cleaned with ethanol and wiped dry with a Kimwipe. All samples had smooth, defect-free surfaces. Then, samples were stacked between glass plates and placed in an oven at 120 °C for 1 hour in order to remove absorbed moisture. This step also served to anneal the samples, relieving any residual stress from the extrusion process. Samples were afterwards stored in a desiccator overnight.

Chemical exposure was carried out by immersing nylon 6 samples in each chemical fluid for up to 8 days. Immediately before the measurements of mass gain, permittivity, or breakdown voltage, the chemically-aged samples were removed from the fluids and their surfaces were wiped dry at room temperature. Permittivity and breakdown voltage measurements were
performed immediately on separate strips for each chemically-aged nylon 6 sample in order to minimize the effect of fluid evaporation during and between tests.

5.5.2 Permittivity measurement

Before and after controlled chemical aging, nylon 6 samples were tested using an Agilent E4980A LCR meter coupled with a 16451B dielectric test fixture capable of complex permittivity measurement over frequency range from 100 Hz to 1 MHz at room temperature, in order to explore the changes in permittivity and dielectric relaxations in response to degradation. The guarded electrode with 38 mm diameter was used for the measurement. Permittivity is a parameter that characterizes the relative charge storage capability of dielectrics in the presence of an electric field. Permittivity is usually in a complex form as a function of the frequency of the applied alternating field, denoted $\varepsilon^* = \varepsilon' - j\varepsilon''$. The real permittivity $\varepsilon'$ is calculated from the equation: $C = \varepsilon_0 \varepsilon' A/d$. $C$ is the capacitance (F), $A$ is the surface area (m$^2$) of sample sandwiched between parallel electrodes, $d$ is the thickness (m) of the sample, and $\varepsilon_0$ is vacuum permittivity with value $8.854 \times 10^{-12}$ Fm$^{-1}$. The dissipation factor $D$ (or tan $\delta$) is defined by $D = \varepsilon''/\varepsilon'$, describing the rate of energy loss with respect to the frequency of alternating electrical field. $\varepsilon'$ and $D$ were measured at three nominally identical spots on each sample. The sample thickness was also measured at the same locations, using a digimatic caliper with uncertainty of 0.01 mm. Given that 12 thickness measurements on each sample yielded a low standard deviation (less than 0.4 %), the smoothness of the nylon 6 film was considered sufficiently good for direct contact permittivity measurement without sputtering the surface of the sample. Further, the time required for the sputtering process is sufficiently long that evaporation of fluids from the sample would have occurred, especially because of the state of vacuum in the chamber, leading to loss of accuracy in the permittivity measurement. The average
value and standard deviation of three permittivity values measured on each sample are illustrated as solid symbols and error bars, respectively, in the figures shown in Section 5.6.

### 5.5.3 Electrical breakdown strength measurement

Another essential property of insulating materials is their electrical breakdown strength, the critical magnitude of electric field at which the insulator breaks down i.e. at which electrical discharge occurs. Electrical breakdown of nylon 6 was measured before and after degradation using a dielectric rigidity 6135 test apparatus that is capable of supplying alternating voltage up to 60 kV. According to ASTM D-149 [14], type 3 opposing cylindrical electrodes with diameter of 6.4 mm were equipped for standard tests. Insulating liquid bath filled with Envirotedef® FR3® fluid was used as an insulation and cooling medium in order that samples fail in puncture mode without surface discharge. In the measurement, the voltage ramp rate was 0.5 kV/s and applied current was 10 mA. The value of electrical breakdown strength $E_{bd}$ (kV/mm) is obtained from the ratio of measured breakdown voltage to the thickness of the sample at the point where failure occurred. Data was collected at 20 nominally identical points on each sample and thicknesses were measured using a digital micrometer with uncertainty of 1 μm.

### 5.5.4 Wide angle X-ray diffraction

To characterize the degree of crystallinity, WAXD patterns of pristine and chemically-aged nylon 6 with 8 days immersion in all six fluids were conducted using a Scintag XDS 2000 powder diffractometer. The radiation is sourced by CuKα with a wavelength of 1.542 Å, scanning from 5° to 35° at a rate of 0.02° per second. Nylon 6 samples with dimension 25 × 25 mm² were braced with a quartz sample holder between clamps in order to flatten the surface in line with the direction of equatorial scans. At first, to confirm whether the orientation of crystal phase of extruded nylon 6 is isotropic in the planar direction, the pristine sample was measured
for 0° and 90° rotation. The two resulting diffraction patterns overlapped with each other, indicating that the crystal orientation is quite uniform. The resulting plots of X-ray intensity versus 2θ were analyzed using OriginPro 9 software to deconvolve the amorphous and crystalline phases.

5.6 Results

5.6.1 Mass gain during chemical exposure

The mass change of nylon 6 immersed in various aircraft fluids over time is shown in Figure 5-2. The mass gain behavior is divided into two groups on the basis of the polarity of fluids. For the polar fluids: distilled water, cleaning fluid, isopropyl alcohol and deicing fluid, nylon 6 shows rather significant absorption due to the strong hydrogen bonding effect between molecular chains and solvents. The maximum water absorption of nylon 6 (immersed in distilled water) observed eventually stabilizes at + 9.4% of the original mass, which conforms to the reference value given in Table 5-1 [10, 13]. As cleaning fluid used for immersion comprises 99.5% water, the mass gain of nylon 6 in this case is nearly identical to that observed for immersion in pure water. It is noted that the total absorption of isopropyl alcohol by nylon 6 appears to be higher than for any other fluid, reaching saturation at + 15.2% of the original mass after 4 days immersion. Clearly the exceptionally high value of absorption in this case indicates that not only water molecules but also a certain amount of alcohol diffuses into the polymer matrix.
Figure 5-2. Mass gain (wt %) of nylon 6 immersed in various chemical fluids for up to 16 days.

The absorption rate of distilled water and cleaning fluid by nylon 6 is similar to that for isopropyl alcohol during the first day, increasing up to +9.7 % after 2 days immersion. The absorption rate of deicing fluid compared to that of the previous fluids, however, is somewhat slower, increasing by only +4.7 % of the original sample mass after immersion for one day. In fact, deicing fluid does not reach equilibrated saturation in nylon 6 even for 16 days immersion, demonstrating a “retarded” characteristic of chemical absorption in this case. Only swollen surface and softening of material was observed as the effect of polar chemical exposure.

In contrast, the mass of nylon 6 shows independence to long exposure to nonpolar fluids: hydraulic fluid and jet fuel even up to 16 days, indicating nylon’s resistance to the interaction with non-polar hydrocarbon molecules.

5.6.2 Real permittivity and dissipation factor

Figures 5-3 and 5-4 show how real permittivity and dissipation factor of nylon 6 behave as a
function of frequency ranging from 100 Hz to 1 MHz for different exposure times in polar chemical fluids, obtained by taking the mean of measurements on three nominally identical samples. Error bars indicate one standard deviation in these measurements. As shown in Figure 5-3, the real permittivity of pristine nylon 6 with no water content presents to be a downward curve, decreasing from 4.1 at 100 Hz to 3.2 at 1 MHz. The $\varepsilon'$ obtained in experiment agrees within ±0.2 of literature data, Table 5-1. The standard deviation in measured real permittivity of the pristine samples is low at around 0.1 %, whereas it increases substantially with longer time of immersion in polar fluids. This value varies from 1.6 % to 7.2 % depending on the type of fluid.

The $\varepsilon'$ of nylon 6 immersed in distilled water, shown in Figure 5-3(a), increases rapidly with exposure time up to 16.4 ± 0.3 at 100 Hz in 12 hours (0.5 day). After 4 days immersion, the value of $\varepsilon'$ changes only slightly and stabilizes at 21.2 ± 0.5 at this frequency, increasing by a factor of five compared to the pristine value. It is noted that the increasing behavior of $\varepsilon'$ corresponds with the water uptake shown in the mass-gain measurement, Figure 5-2. In the case of samples immersed in cleaning fluid and isopropyl alcohol, shown in Figures 5-3(b) and 5-3(c), $\varepsilon'$ develops in a way analogous to the case of distilled water. At 100 Hz, the value of $\varepsilon'$ reaches equilibrium around 23 ± 2 and 22.1 ± 0.5, for cleaning fluid and isopropyl alcohol, respectively. For nylon 6 immersed in deicing fluid, Figure 5-3(d), a similar result to those shown in (a) to (c) was obtained, showing stepwise increase in $\varepsilon'$ with longer exposure time. After 8 days immersion, $\varepsilon'$ attains to the highest value of 20 ± 1 at 100 Hz. The data reveals a much slower set of changes across the exposure period than for distilled water, cleaning fluid and isopropyl alcohol, however, reflecting possibly much slower diffusion of the propylene glycol into nylon 6. Additionally, the decrease of $\varepsilon'$ as a function of frequency is amplified after immersion in all polar fluids, indicating a stronger frequency dependence.
Figure 5-3. Real permittivity of nylon 6 immersed in polar fluids: (a) distilled water, (b) cleaning fluid, (c) isopropyl alcohol and (d) deicing fluid at room temperature for different exposure times as a function of frequency. Error bars indicate the standard deviation in measurements on three nominally identical samples.
Figure 5-4. As for Figure 5-3 but for dissipation factor, $D$.

The dissipation factor $D$ of pristine nylon 6 exhibits one relaxation peak with the highest value at about 20 kHz over the measured dielectric spectrum, shown in Figure 5-4. This
dielectric relaxation peak is attributed to the $\beta$-relaxation of nylon 6, which corresponds to the localized motion of the polar NH-CO groups and their neighboring H-bonds [15-18]. The $\alpha$-relaxation, which occurs around the glass transition temperature, is associated with the cooperative movement of a few dozens of caprolactam repeating units in the case of nylon 6. The $\alpha$-relaxation of pristine nylon 6 is not observed on the measured spectrum at room temperature due to the fact that the $T_g$ of nylon 6 is 47–57 °C, as listed in Table 5-1.

As shown in Figure 5-4, nylon 6 exposed to distilled water, cleaning fluid, isopropyl alcohol and deicing fluid share similar shifts in the dissipation factor $D$, with increasing exposure time. In the low frequency range from approximately 100 Hz to $10^3$ Hz, $D$ ascends significantly as the exposure time increases, with a sharp decline as the frequency increases. This is attributed to the appearance of $\alpha$-relaxation. The broad peak associated with the $\beta$-relaxation at frequency around 20 kHz, moves to higher frequencies as exposure time increases. Meanwhile, the relaxation intensity exhibits a sharp increase under the initial exposure (~ 0.5 day) in distilled water, cleaning fluid and isopropyl alcohol, seen in Table 5-3.

**Table 5-3. Dissipation factor data of nylon 6.**

<table>
<thead>
<tr>
<th>Nylon 6 samples (pristine or after 0.5 days exposure)</th>
<th>$D_{\text{max}}$</th>
<th>$f$ of $D_{\text{max}}$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>0.0496 ± 0.0001</td>
<td>22</td>
</tr>
<tr>
<td>Distilled water</td>
<td>0.26 ± 0.01</td>
<td>280</td>
</tr>
<tr>
<td>Cleaning fluid</td>
<td>0.232 ± 0.005</td>
<td>280</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>0.205 ± 0.005</td>
<td>220</td>
</tr>
<tr>
<td>Deicing fluid</td>
<td>0.152 ± 0.006</td>
<td>60</td>
</tr>
</tbody>
</table>
Figures 5-5 and 5-6 show measured results for real permittivity and dissipation factor of nylon 6 as a function of frequency ranging from 100 Hz to 1 MHz for different exposure times in non-polar chemical fluids. Nylon 6 immersed in jet fuel and hydraulic fluid finally exhibits a slight reduction (5 %, similar to the percentage of the uncertainty in the measurement) in $\varepsilon'$ after 8 days, in contrast to the significant increase (~ 250 %) observed for immersion in polar fluids. The percentage values indicating the change in $\varepsilon'$ are the minimum observed over the measured frequency range. $D$ of aged nylon 6 in both fluids remained within the range 0.03 to 0.06 over the entire measured frequency range, and the frequency of relaxation peak appears to be independent of exposure in these non-polar fluids.

![Figure 5-5](image.png)

Figure 5-5. Real permittivity of nylon 6 immersed in non-polar fluids: (a) jet fuel and (b) hydraulic fluid at room temperature for different exposure times as a function of frequency. Error bars indicate the standard deviation in measurements on three nominally identical samples.
5.6.3 Electrical breakdown strength and Weibull distribution

In order to explore the possibility of measuring real permittivity $\varepsilon'$ as an indicator of dielectric breakdown strength $E_{bd}$ of chemically-aged nylon 6 in polar and non-polar aircraft fluids, average $\varepsilon'$ measured at 1 kHz is plotted as a function of average $E_{bd}$, in Figure 5-7. 1 kHz was chosen because at this frequency the $\varepsilon'$ data displays significant change for all chemicals as a function of time. As the immersion time increases, nylon 6 under exposure of polar fluids displays a two-stage process: $\varepsilon'$ increases approximately linearly as $E_{bd}$ decreases initially (seen in the approximate range from 34 to 25 kV/mm in Figure 5-7); then at a certain point of immersion time, which varies slightly according to the fluid, $\varepsilon'$ appears to become independent of $E_{bd}$ as $E_{bd}$ continues to decrease (seen in the approximate range from 25 to 20 kV/mm in...
Figure 5-7). The electrical breakdown strength of pristine nylon 6 is measured to be 34±2 kV/mm, decreasing to 22.6±0.5 kV/mm in distilled water, 20.2±0.4 kV/mm in cleaning fluid, 21.8±0.7 kV/mm in isopropyl alcohol and 23.6±0.8 kV/mm in deicing fluid after 8 days immersion. On the other hand, nylon 6 under exposure to non-polar fluids exhibits decreasing $E_{bd}$ to 30±1 kV/mm in jet fuel and 30.0±0.8 kV/mm in hydraulic fluid after 8 days of immersion with no significant change in $\varepsilon'$.

The Weibull distribution, as the most popular statistical analysis tool for solid insulation materials, is used here to analyze the electrical breakdown behavior. The expression for the cumulative distribution function (CDF) for the two-parameter Weibull distribution is given by [19]:

$$F(E) = 1 - e^{-(E/E_0)^\beta}$$
\[ F(E_{bd}; \alpha, \beta) = 1 - \exp \left( -\left( \frac{E_{bd}}{\alpha} \right)^\beta \right) \]  

(5-1)

where \( F \) is the probability of electrical breakdown strength \( E_{bd} \) of the insulator under test, \( \alpha \) is the scale parameter, and \( \beta \) is the shape parameter. With large data sets of typically at least 20 values, one can safely use the least-squares regression technique to estimate the two parameters with good accuracy. Benard’s approximation for the median rank is applied to estimate the probability of failure \( F(E_{bd}) \), given by

\[ F(i, N) = \frac{i - 0.3}{N + 0.4} \]  

(5-2)

where \( i \) is the assigned rank when \( E_{bd} \) values are listed in order from low to high and \( N \) is the total number of measured values. Details of how the Weibull plot is established are available in reference [20].

The two-parameter Weibull CDFs of electrical breakdown data of nylon 6 immersed in polar and non-polar aircraft fluids are plotted in Figures 5-8 and 5-9, respectively. Inspection of each chemically-aged data set reveals a deviation from Weibull slope for high \( E_{bd} \), although the majority of data points fit well to the Weibull distribution. The Weibull plots for nylon 6 after polar-chemical aging, shown in Figure 5-8, display a significant shift towards lower electrical breakdown strength with longer exposure time.
Figure 5-8. The CDF of the measured dielectric strength of nylon 6 immersed in polar fluids: (a) distilled water, (b) cleaning fluid, (c) isopropyl alcohol, and (d) deicing fluid from 0.5 to 8 days at room temperature compared to the result for a pristine sample. Symbols represent experimental data and lines represent the linear fit to the data. Open symbols are excluded from the linear fit.
$E_{bd}$ for nylon 6 aged in non-polar fluids exhibits a much lesser shift, as shown in Figure 5-9. Table 5-4 gives an example comparison between samples aged in a polar (cleaning fluid) and non-polar (hydraulic fluid) liquid in terms of the dependence of the scale parameter ($\alpha$) and the shape parameter ($\beta$) on the exposure time. The parameter values for other polar and non-polar fluids show similar trends to those presented in Table 5-4. Figure 5-10 compares the Weibull plots for nylon 6 immersed in polar fluids and non-polar fluids for 8 days.

Figure 5-9. As for Figure 5-8 but for nonpolar fluids: (a) jet fuel and (b) hydraulic fluid.
Table 5-4. The Weibull-statistical scale parameter ($\alpha$) and the shape parameter ($\beta$) of chemically-aged nylon 6.

<table>
<thead>
<tr>
<th>Exposure time of nylon 6 (days)</th>
<th>Polar fluid (eg. cleaning fluid)</th>
<th>Non-polar fluid (eg. hydraulic fluid)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$ (kV/mm)</td>
<td>$\beta$</td>
</tr>
<tr>
<td>0</td>
<td>34.8</td>
<td>19.8</td>
</tr>
<tr>
<td>0.5</td>
<td>28.0</td>
<td>27.9</td>
</tr>
<tr>
<td>1</td>
<td>24.1</td>
<td>27.0</td>
</tr>
<tr>
<td>2</td>
<td>23.2</td>
<td>64.3</td>
</tr>
<tr>
<td>4</td>
<td>21.5</td>
<td>53.8</td>
</tr>
<tr>
<td>8</td>
<td>20.4</td>
<td>56.5</td>
</tr>
</tbody>
</table>

Figure 5-10. A comparison of the cumulative distribution function of the measured dielectric strength between a pristine nylon 6 sample and samples immersed in various aircraft fluids for 8 days at room temperature. Symbols represent experimental data and lines represent the linear fit to the data. Open symbols are excluded from the linear fit.
5.6.4 X-ray diffraction and semicrystalline structure

Studies concerning the effect of molecular structure, molecular order [18, 21], and moisture [22, 23] on the dielectric properties of nylon polymers indicate that the amorphous phase containing the freely orientable amide group dipoles in the chains is critical in adjusting dielectric constant and dissipation factor.

Figure 5-11 illustrates the crystalline and amorphous peaks separated from an X-ray diffraction curve of pristine nylon 6 using the profile fitting technique (Peak Analyzer in OriginPro 9 software). The background drift has been corrected by subtracting the baseline drawn between the end points of the spectrum ($2\theta = 5^\circ$ and $35^\circ$). The $2\theta$ location of $\alpha$- and $\gamma$-crystalline forms were identified by peak intensities occurring at $2\theta = 20.3$ to $20.4^\circ$ and $23.3$ to $23.4^\circ$ for the $\alpha$- form, and $21.6$ to $21.8^\circ$ for the $\gamma$- form. The amorphous peak location, although not being acquirable directly from its broad distribution in the diffraction pattern, was determined at $21.43 \pm 0.01^\circ$ using the amorphous template [11, 24]. The two other crystalline peaks, located at $9.5^\circ$ and $28.6^\circ$, are attributed to the combination of both $\alpha$- and $\gamma$-crystalline forms appearing in meridional scans [10]. The appearance of meridional peaks could be due to imperfect crystallization induced in unoriented direction during the extrusion process. This portion of crystallinity is not taken into account as only equatorial crystallinity of extruded nylon 6 is considered here. Crystalline peaks of each sample, including pristine and chemically-aged nylon 6, were fitted with Gaussian peaks. The coefficients of determination, $R^2$, are above 0.98 for all samples, exhibiting good agreement between the modeled and experimental data. Areas under the peaks calculated from the fitting curve were used to estimate the degree of crystallinity, $X_c$, of nylon 6, which is expressed by:
\[ X_c = \frac{\text{area under crystalline peak}}{\text{area under total curve (crystalline + amorphous)}} \] (5-3)

Figure 5-11. A representative example of an X-ray diffraction pattern (this one for pristine nylon 6) and the profile fitting technique used to deconvolve the crystalline and amorphous phases.

The crystallinity data, including the total crystallinity, and the proportion of \( \alpha \)- and \( \gamma \)-crystalline phases for pristine and chemically-aged nylon 6, after 8 days exposure, are presented in Table 5-5. The uncertainty of the crystallinity values is estimated to be about 3% of the average values obtained through three measurements on each sample. It should be noted, however, that larger uncertainty due to the differences in scattering factor of the crystalline and amorphous phases and the ways in which these are modified by the presence of diffused molecules cannot be quantified. It is expected that scattering from the amorphous phase increases to some extent due to molecular diffusion into it, influencing \( X_c \) in addition to other factors. According to the data of Table 5-5, however, the calculated decrease in \( X_c \) for the samples
Table 5-5. Crystallinity data calculated from WAXD patterns of nylon 6 after 8 days exposure. Uncertainty in these values is approximately 3 %.

<table>
<thead>
<tr>
<th>Nylon 6 samples (pristine or after 8 days exposure)</th>
<th>$X_c$ (total)</th>
<th>$\alpha$-form</th>
<th>$\gamma$-form</th>
<th>% of total γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>0.48</td>
<td>0.42</td>
<td>0.050</td>
<td>10.3</td>
</tr>
<tr>
<td>Cleaning fluid</td>
<td>0.41</td>
<td>0.37</td>
<td>0.023</td>
<td>5.7</td>
</tr>
<tr>
<td>Deicing fluid</td>
<td>0.43</td>
<td>0.38</td>
<td>0.028</td>
<td>6.5</td>
</tr>
<tr>
<td>Distilled water</td>
<td>0.43</td>
<td>0.39</td>
<td>0.024</td>
<td>5.6</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>0.40</td>
<td>0.36</td>
<td>0.019</td>
<td>4.8</td>
</tr>
<tr>
<td>Jet fuel</td>
<td>0.45</td>
<td>0.39</td>
<td>0.042</td>
<td>9.3</td>
</tr>
<tr>
<td>Hydraulic fluid</td>
<td>0.47</td>
<td>0.42</td>
<td>0.029</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Immersed in polar fluids tends to be larger than for those immersed in non-polar fluids. When further investigating the crystallinity of individual phases, it is revealed that the percentage of $\gamma$-crystal in total equatorial crystallinity is reduced. The $\gamma$-phase fraction of nylon 6 decreases to between 38 and 56 % of its value in pristine nylon 6 after 8 days exposure to polar chemicals.

5.7 Discussion

The mass-gain measurement result reveals that the variation of alcohol composition (concentration and variety) may affect the maximum mass gain or/and absorption rate of nylon 6 exposed to water-based protic aircraft fluids. As shown in Figure 5-2, nylon 6 exposed to isopropyl alcohol, containing 30% water, exhibits the highest mass gain while deicing fluid, an aqueous solution composed of 44% propylene glycol, is absorbed less than any other of the polar fluids by nylon 6, during the early days of immersion. Similar to water molecules, the alcohols
possess high polarity and strong H-bonding tendency and we postulate that the alcohols also participate actively in the interaction with polar nylon 6 molecular chains. Water and alcohol content are, therefore, taken to be primary factors contributing to the observed changes in dielectric properties of nylon 6 under chemical exposure. As observed in Figure 5-3, $\varepsilon'$ of chemically-aged nylon 6 increases with immersion time, as the fluid uptake increases. One possible explanation for this is that the association of protic molecules, including water and alcohol, with polar amide groups in nylon 6 increases the polarizability of the polymer chains [15, 21]. Based on the principal dipole orientation mechanism in a semi-crystalline nylon polymer, dipole orientation is controlled by inter-chain H-bonding in the amorphous regions. The H-bonds between neighboring amide groups in the amorphous regions are less ordered compared to those existing between efficiently-packed chains in crystallites, and thus hinder but still allow certain freedom of rotation in chain segments. When the protic molecules enter the amorphous regions, the inter-chain amide-amide H-bonds are replaced by amide-water/alcohol H-bonds, resulting in a plasticizing effect [15, 16, 25]. The mobility of the chain segments is enhanced by weakening of the inter-chain binding forces and, therefore, an increase in $\varepsilon'$ is observed as evidence of the increasing polarizability of nylon 6 with incorporation of fluid molecules.

Figure 5-4 shows that, as polar fluid content increases in nylon 6, the peak in the dissipation factor, which is associated with the $\beta$-relaxation mode, increases in magnitude and migrates to higher frequencies. This shift of peak dissipation factor to higher frequency is a result, to some extent, of the plasticizing effect of protic molecules. In the fluid absorption process, the number of orienting dipoles or their dipole moment increases due to additional water/alcohol molecules forming bonds with the amide groups. The dipole motions involved in the $\beta$-relaxation become more independent, appearing to be proportional to the relaxation intensity [16]. The increasing
freedom of motion of amide groups due to interaction with water has been verified by reduction in the activation energy of the $\beta$-relaxation process in the case of other nylon types [15, 25]. Similarly, the $\alpha$-relaxation, which is related to long chain segment motions, was observed to move to higher frequencies and increase in intensity on $D$ with the increase of water uptake [23]. Within the frequency range of our study, the high-frequency end of the $\alpha$-relaxation was detected to overlap with $\beta$-relaxation in the approximate frequency range from $10^3$ to $10^4$ Hz, Figure 5-4 but is not observed in its entirety.

The structural change related to increased interaction between protic molecules and nylon 6 chains is evidenced by WAXD, which shows a decreasing tendency of between 10 and 17 (± 3) % in the fraction of crystalline phase in nylon 6 after polar chemical exposure, Table 5-5, although the cautionary comments made following Eq. (3) should be kept in mind. A fractional transition from crystalline to amorphous phase may be induced due to incorporation of small molecules into amorphous regions as well as intercrystalline regions. The $\gamma$-crystal, a less stable crystal form, could be subjected to dissociation by enhanced movement of interphase chain segments and thus exhibits greater loss in percentage.

As can be seen by inspection of Figures 5-8 and 5-9, the higher electrical breakdown strength values (consisting of 2 or 3 data points, which corresponds to 10 to 15 % of the data) appear to deviate consistently from the 2-parameter Weibull fit for most data sets of polar and non-polar chemically-aged nylon 6. Given that these high $E_{bd}$ values make a relatively small contribution and are of less importance than low $E_{bd}$ in insulation practice, we follow the precedent of excluding these points from the linear fit [26]. The excluded points are indicated by open symbols in Figures 5-8 and 5-9. The fit quality of 2-parameter Weibull distribution can be examined by a simple correlation coefficient, $P$ by comparing to the critical correlation.
coefficient (CCC) [19]. If P is larger than the CCC, it means the data follow 2-parameter Weibull distribution with 90 % confidence, indicating a good fit. For 20 breakdown tests, CCC is 0.937 and thus P is expected to be above 0.937 for a good fit. It was found here that, except for two cases (4 days immersion in distilled water (P = 0.932) and 2 days immersion in isopropyl alcohol (P = 0.920)), P values were greater than the CCC, indicating the good quality of the 2-parameter Weibull fit.

The scale parameter $\alpha$, representing the $E_{bd}$ at which the failure probability is 63.2 %, decreases from 35 to 20 ~ 25 and 30 ~ 31 for polar and non-polar chemical aging, respectively, shown in Table 5-4, as the exposure time increases. The shape parameter $\beta$, representing the width of the Weibull distribution, intriguingly, increases as the exposure time increases, corresponding to a steeper slope of Weibull fit for both polar and non-polar aged nylon 6. The effect of polar chemical aging on slope shifting is more significant than non-polar chemical aging. The increase of $\beta$ indicates that $E_{bd}$ occupies a smaller range of values after aging, which is contrary to the trend that was reported previously in a study of polyimide (PI) degradation [20]. One possible reason for this result may be transformation to a different electrical breakdown mechanism for nylon 6 after aging. Given nylon 6’s high absorption of polar molecules (water absorption of nylon 6 is 9.4 %, compared to the much lower value of 1.8 % in the case of PI), the dominant conduction route through defects within polymer chains may be replaced by the new linkage formed between fluid molecules and polymer chains after absorption. In this case chemically-aged nylon 6 exhibits improvement of structural homogeneity along with decreasing electrical breakdown strength.
5.8 Conclusion

Aging of wire and cable insulation is a major concern in aviation, nuclear power and other industries in which components are being kept in service beyond their original design life. This study investigates the dielectric and electrical breakdown response of nylon 6 following chemical exposure to various aviation fluids at ambient temperature. The aging response of nylon 6 is distinguished according to the polarity of the fluids in which it is aged. Following exposure to polar fluids: distilled water, cleaning fluid, isopropyl alcohol and deicing fluid, significant increase in real permittivity and dielectric relaxation intensity was observed. On the other hand, only small changes were observed after exposure of nylon 6 to non-polar fluids: jet A fuel and hydraulic fluid. In addition, the way in which $\varepsilon'$ and $D$ of nylon 6 shift as a function of immersion time depends on the absorption kinetics. These, in turn, are determined by the composition of the polar fluids. The observed dielectric changes of nylon 6 after aging in polar fluids are interpreted as the enhancement of polarization caused by reduced interaction between molecular chains. Decrease of crystallinity confirms increased interaction between fluids and chains in the amorphous phase.

The influence of chemical exposure on electrical breakdown behavior of nylon 6 was evaluated by the 2-parameter Weibull distribution. The electrical breakdown strength was observed to decrease as exposure time increases, but to occupy a smaller range of values, especially after aging in polar fluids. Based on these results, it can be concluded that it is possible to correlate aging-induced changes in measured permittivity with changes in electrical breakdown strength. This points to the potential for capacitive NDE to diagnose the breakdown strength of nylon 6 wire insulation exposed to polar chemicals based on measurements of its permittivity.
Acknowledgment

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5.9 References


CHAPTER 6: GENERAL CONCLUSIONS

6.1 General discussion

Motivated by the demand of developing low-cost, high-performance carbon nanofibers (CNFs) for polymer matrix composite applications, the first study deals with fabricating ultrafine CNFs based on electrospinning precursor blends of low-molecular-weight organosolv lignin and polyacrylonitrile (PAN). The functionalization of the lignin with butyl groups (butyration) was adopted to tune the miscibility and thermal mobility of the precursor blend fibers, and confirmed by DSC characterization. The effect of blend composition, viscosity and conductivity on electrospinnability was examined, and the optimal composition enabling bead-free, uniform electrospun fibers was determined. Butyration of lignin led to lower viscosity of lignin/PAN blend solutions and smaller diameter of resulting as-spun fibers. The carbon yields of the precursor fibers derived from the blends of PAN and lignin before and after butyration are comparable or even higher than that of PAN-based fibers. Raman spectroscopy revealed a slight decrease in the structural order of the butyrated lignin (B-lignin)/PAN 50-50 carbon fibers. The modified lignin was endowed with higher thermal mobility, resulting in inter-fiber bonding between B-lignin/PAN 50-50 fibers during the oxidative thermostabilization. The resultant fused CF mats after carbonization showed significant increase in tensile strength and modulus compared to non-bonded lignin/PAN 50-50 carbonized fibers. The observed reinforcement was attributed to the cross-linking feature of the fabric network. This study demonstrated an effective approach to manipulating inter-fiber bonding using an inexpensive lignin/PAN blend precursor system to produce fibrous nano-carbon materials. The strengthened bonding characteristic is promising for fiber-reinforced composite applications and beyond.
The effect of a vapor grown carbon nanofiber (VGCNF) on the changes of the residual tin (II) catalyst in RTV polysiloxane foams has been investigated. Characterization using SEM-EDS showed that tin catalyst residues are concentrated in the bubble structure observed in these composite samples, as thin layers. Elemental mapping indicates that the tin-rich layer is a complex organotin compound containing Sn, Si, O, and C. An effort to determine the oxidation state of residual tin species in different polysiloxane nanocomposites was made using XPS. Observation of the cross-sectional surface of the foams reveals that the oxidation of the tin catalyst was possibly slightly accelerated with the addition of a small amount of CNF to polysiloxane. In addition to the structural characterization, thermal analyses were also carried out to investigate the change of thermal properties of the CNF/polysiloxane composites. TGA results exhibited a significant increase of thermal stability of polysiloxane incorporating CNF in inert atmosphere. The glass transition temperature of polysiloxane determined by DSC did not show evident change after adding CNF. In broadband dielectric spectroscopy, the segmental α relaxation process was well resolved from the dielectric loss spectra at low temperatures, and analyzed with parametric Havriliak-Negami (HN) model fitting. The temperature dependence of the α relaxation and the fragility of the polysiloxane are not apparently influenced by the incorporation of CNF.

In order to shed light on the complicated interaction between advanced polycyclic aromatic hydrocarbon (PAH) nanofillers and a host polymer, a model system consisting of epoxy incorporating anthracene (AN) with different reinforcing strategies was explored. Broadband dielectric spectroscopy was applied to investigate the “additive” increase of glass transition temperature \( T_g \) of epoxy incorporating two types of anthracenes, physically dispersed AN and covalently bonded AN, observed from DSC characterization. Parametric fitting of the dielectric
loss spectra with HN functions revealed the macromolecular dynamics of the epoxy composites at different length scales: n-mode relaxation, α relaxation, and β relaxation. Maxwell-Wagner-Sillars (MWS) interfacial relaxation was observed in the epoxy composites incorporating unbound AN at high temperatures due to the boundary interaction between AN micro-phases and the matrix. Physical dispersion of AN into epoxy behaves with an attractive polymer-filler interaction, verified by retardation of the α relaxation time with temperature as well as the corresponding increase of $T_g$ and fragility. Chemically AN-modified epoxy was subjected to significant decrease of α relaxation time due to the constraining effect on the segments from pendent AN groups, as evidenced by increase of $T_g$ observed for those samples. On the other hand, the fragility decreases in chemically AN-modified epoxy because the intrinsic change of the relative stiffness of side groups to the backbone is the main controlling factor. The combination of both reinforcing routes enhanced the solubility of AN in the epoxy matrix, and therefore magnifies the temperature dependence of the α relaxation time, as indicated by the increasing loading effect of unbound AN fillers upon the increased π-π interaction. In this way, $T_g$ was elevated in the case of chemically AN-modified epoxy while the fragility was kept comparable to that of the neat epoxy. The n-mode relaxation and the β relaxation were found less sensitive to the incorporation of AN fillers than α relaxation. The mechanism for the change of glass transition behavior due to various molecular interactions of nanofillers was elucidated by analyzing the characteristic relaxation parameters extracted from BDS.

The dielectric and electrical breakdown response of nylon 6 following chemical exposure to various aircraft fluids at ambient temperature was investigated. The aging response of nylon 6 was distinguished according to the polarity of the fluids to which it was exposed. Significant increase in real permittivity ($\varepsilon'$) and dielectric dissipation factor ($D$) was observed for nylon 6
following exposure to polar fluids: distilled water, cleaning fluid, isopropyl alcohol and deicing fluid. In contrast, only small changes were observed after exposure to non-polar fluids: jet fuel and hydraulic fluid. Additionally, the fashion in which $\varepsilon'$ and $D$ of nylon 6 shift as a function of immersion time depends on the absorption kinetics of the polar fluids. The influence of chemical exposure on electrical breakdown behavior of nylon 6 was evaluated by the 2-parameter Weibull distribution. The electrical breakdown strength was observed to decrease as exposure time increases, but to occupy a smaller range of values, especially after aging in polar fluids. Based on these results, it can be concluded that a correlation exists between chemical immersion-induced changes in measured permittivity and changes in electrical breakdown strength, for nylon 6. This points to the potential usefulness of a capacitive NDE method for diagnosis of the breakdown strength of nylon 6 wire insulation exposed to polar chemicals based on measurements of its permittivity.

6.2 Recommendations for future research

Regarding the development of low cost and high performance electrospun carbon nanofibers, up to 50 wt.% of lignin was used to successfully substitute PAN to fabricate carbon fibers. Further improvement to the structure and properties of the CNFs could be explored in terms of the following aspects. CNFs with smaller fiber diameters should be produced in order to evaluate the nano-size effect on the mechanical properties of the resulting non-woven CNF mats. Studies on the PAN-based CNFs [1] and other polymeric nanofibers [2-4] by electrospinning have shown that there is a threshold of nanofiber diameter (about 200 nm) below which an extraordinary increase in tensile properties of materials occurs. A few approaches could be considered to reduce the as-spun fiber diameter and not to induce beads or non-uniform
structure, such as decreasing the feed rate and adding salts to increase the charge density of the spinning solutions [5]. In addition to inter-fiber bonding, uniaxial alignment of nanofibers is another approach to tailor the mat micro-structure which would render anisotropic properties. Considering other properties, the electrical, thermal, and adsorption properties of the electrospun CNFs with the proposed structural variations are also important to investigate for potential application in laminated polymer nanocomposites.

Considering the presented study of CNF/RTV polysiloxane foam composites, the tin catalyst residues in the pristine samples were examined. Future work will be carried out on investigating the foams after post-curing and subsequent accelerated thermal aging in order to probe the kinetic effect of CNF on the oxidation state of residual tin species and the network structure of polysiloxane. It has been shown that the existence of moisture (from environment) and acid (from hydrolytic by-product) would promote the hydrolysis reaction and bond-exchange reactions in polysiloxane catalyzed by tin (II) species [6]. Therefore, a control of pH level for accelerated thermal aging may be instrumental in monitoring the chemical interplay between CNF, residual tin species and polysiloxane during aging. Besides, additional characterization techniques such as FTIR and NMR could be employed for structural analysis.

In the dielectric study of anthracene-reinforced epoxy nanocomposites presented here, interfacial (MWS) relaxation was induced in the composites incorporating freely dispersed anthracene due to the formation of boundaries between the epoxy matrix and the micro-crystal phases of undissolved anthracene molecules. A lower concentration of anthracene fillers well dispersed in epoxy could be investigated, in relation to their effect on $T_g$, in order to remove the complexity resulting from structural heterogeneity resulting from the presence of the micro-crystals. For the analysis of dielectric spectra, some more relaxation and structural parameters,
such as relaxation strength, shape and skewness parameters, molecular cooperativity [7], and intermolecular coupling parameter [8] could be extracted for in-depth evaluation of the molecular interactions within the nanocomposites. For an extension of this study, polyaromatic hydrocarbons (PAHs) with more complex structure should be investigated with respect to the effect of dispersion and molecular interaction between the nanofillers and the polymer matrix with the ultimate goal of successfully developing asphaltene-filled polymer composites.

On the topic of dielectric monitoring of chemically-immersed nylon 6, measurements were made on samples at different stages of chemical absorption, a largely reversible change of state, rather than on samples having undergone irreversible aging. The accelerated aging stress with regards to chemical exposure time and temperature were not strong enough in this study to induce significant irreversible change of nylon 6, such as hydrolytic depolymerization. Further investigations with different stress factors, such as chemical exposure at elevated temperature, longer periods of exposure or periodical chemical exposure may be adopted for better simulating the practical effects of long-term aging conditions.

6.3 References


Figure A-1. Viscosity as a function of shear rate for different spinning solutions: lignin-PAN blends and B-lignin/PAN blends (mass ratio of 70:30, 50:50, and 30:70) in 20 wt.% DMF solution; PAN with 10 wt.%, 12 wt.%, and 15 wt.% in DMF solution.
Figure A-2. Weight loss and derivative weight loss curves of precursor fibers based on PAN, lignin/PAN 50-50, and B-lignin/PAN 50-50 measured by TGA in N\textsubscript{2} atmosphere.
Figure A-3. Laboratory setup for tensile testing of as-spun and carbonized fiber mats customized from ASTM C1557-03.

Figure A-4. Representative tensile stress-strain curves of as-spun fiber mats derived from different precursors.
Inset shows the elastic behavior at the initial tensile stage. Here, the measured tensile stress represents a nominal value with comparative meaning only; it was obtained from the measured load divided by the pristine cross-sectional area during stretching.

**Table A-1. Density of carbonized fibers based on PAN, lignin/PAN 50-50, and B-lignin/PAN 50-50**

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<th>Fiber sample</th>
<th>Density (g cm(^{-3}))</th>
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<tr>
<td>PAN CF</td>
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<tr>
<td>Lignin/PAN 50-50 CF</td>
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<td>B-lignin/PAN 50-50 CF</td>
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True fiber density was determined using Mettler Toledo balance and density kit according to a modification to ASTM B962 – 13. Three replicate measurements were performed to determine the mean value and uncertainty. The auxiliary liquid used is pure ethanol for good wetting and low uncertainty. Table A-1 shows the measured density values between electrospun CFs from different precursors are close to each other.
APPENDIX B: SUPPLEMENTARY INFORMATION FOR CHAPTER 3

B.1 SEM-EDS results of 0.5% CNF/polysiloxane

(a)

Figure B-1. (a) SEM image of 0.5% CNF/polysiloxane at 3000x magnification under BSE mode.

(b)

Figure B-1. (b) EDS spectra of three selected spots in the SEM image (yellow – elemental composition of overall area; orange - elemental composition of selected area denoted “matrix”; red - elemental composition of selected area denoted “Sn-rich”; blue - elemental composition of selected area denoted “O-rich”)
Figure B-1. (c) distribution maps of different elements (C, O, Al, Si and Sn) corresponding to the SEM image.
B.2 SEM-EDS results of neat polysiloxane at different voltages of electron beams

Figure B-2. SEM image of neat polysiloxane at 10000x magnification under BSE mode.
Figure B-3. EDS spectra of five selected spots with different thickness/layers of Sn in the SEM image Figure B-2 (yellow – non Sn-rich area; orange – single layer of Sn-rich area; red – double layer of Sn-rich area; cyan – triple layer of Sn-rich area; blue – thicker than triple layer of Sn-rich area) at (a) 6 kV; (b) 10 kV; and (c) 15 kV.
Table B-1. Atomic fractions of selected areas in Figure B-2 measured at (a) 6 kV, (b) 10 kV, and (c) 15 kV of electron beams.

(a)

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B.3 SEM-EDS results of 0.5% CNF/polysiloxane at different voltages of electron beams

0.5% CNF in siloxane 10kx bse

Figure B-4. SEM image of 0.5%CNF/polysiloxane at 10000x magnification under BSE mode.
Table B-2. Atomic fractions of selected areas in Figure B-4 measured at (a) 6 kV and (b) 10 kV of electron beams.

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