**Study of interactions and stability of pyrethroids and cellulose allomorphs for controlled release applications**

by

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Abstract

The study of controlled release materials is a growing field for applications like agricultural, biomedical, and insecticidal fibers. Cellulose, because of its abundance and ability to be modified and regenerated into many forms, is a sustainable and practical choice of controlled release substrate. In the search of active bio-based materials, the use of cellulose as a sustainable and renewable carrier for active ingredients as an alternative to synthetic polymeric systems such as polyesters; however, the understanding of the underlying interactions between relevant compounds such as insecticides and cellulose still need to be studied. Belonging to a class of insecticides called pyrethroids, deltamethrin and permethrin commonly used for killing disease carrying arthropods such as mosquitoes, therefore, it is important to investigate its interactions with various surfaces. Due to resistance being built up against these insecticides, synergists like piperonyl butoxide (PBO) are being added to products to inhibit the resistance of the mosquito against the pyrethroids for a short time. For this reason, these components were studied in this work to evaluate the behavior and interactions with different cellulose allomorphs using a model film approach through surface sensitive techniques such as Atomic Force Microscopy (AFM), Quartz Crystal Microbalance with dissipation monitoring (QCM-D), and Surface Plasmon Resonance (SPR). AFM was used to generate images of these films and confirm full coverage of the sensor by the sample. QCM-D and SPR were used in combination to quantify surface interactions with hydrophobic model films surfaces such as polystyrene and silica. Thus, the adsorption onto these model films would resemble the expected charges found in cellulose due to its hydrophilic nature, or other common polysaccharides such as chitosan with a positive charge, and lignin's hydrophobic nature. Cellulose and other sustainable and renewable biobased materials have drawn interest as possible replacement of harmful synthetic polymeric

systems for the purpose of carrying an active ingredient. This as various industries like agriculture and textiles aim to substitute fossil-based materials in controlled -release of fertilizers or pesticides, for example. However, it is important to first understand the basic interactions between the carrier materials and the active ingredients. In addition, Nuclear Magnetic Resonance (NMR) was used to determine the stability of these chemicals in common cellulose solvent. In this study, in order to resemble the fiber- making process, ionic liquid was used to regenerate the native cellulose I to cellulose II for the interactions study with pyrethroids. Over time, at a controlled temperature, these insecticides were tested, and their degradation compounds were monitored to model their behavior in dry jet wet spinning. This work will be used in the future to determine the possibility of these being applicable to regenerated cellulose products (i.e. fibers, foams) for controlled release of insecticides.

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List of Abbreviations

| | |
|---|---|
| [APPH][OAc] | 1-(3-aminopropyl)-2-pyrrolidone acetate |
| [DBNH][OAc] | 1.5-diazabicyclo[4.3.0]non-5-ene acetate |
| AFM | Atomic Force Microscopy |
| AI | Active Ingredient |
| APPAc | 1-(3-aminopropyl)-2-pyrrolidone |
| CNF | Cellulose Nanofibrils |
| DBN | 1.5-diazabicyclo[4.3.0]non-5-ene |
| DES | Deep-eutectic Solvent |
| IL | Ionic Liquid |
| HMBC | Heteronuclear  Multiple Bond Correlation |
| LLIN | Long-lasting Insecticide Nets |
| NMR | Nuclear Magnetic Resonance |
| PBO | Piperonyl Butoxide |
| HSQC | Heteronuclear Single-Quantum Correlation Spectroscopy |
| PEI | Polyethylenimine |
| PS | Polystyrene |

| | |
|---|---|
| QCM-D | Quartz Crystal Microbalance with Dissipation |
| SPR | Surface Plasmon Resonance |

# 1. Chapter 1

# Cellulose: Surface Studies and Regeneration

## 1.1 Introduction to Cellulose and Lignocellulosic Materials

Cellulose is the world's most abundant natural polymer and renewable material. Its sources include all types of wood, agricultural waste, and even some bacteria (Abol-Fotouh et al., 2020). With all these different types of feedstock, there is much variation in the material properties which allows for celluloses' application in a variety of products, but it is insoluble in most common solvents. This challenge is of interest to many because regenerated cellulose has superior properties. To process this polysaccharide into useful forms, it should be first dissolved and then regenerated, and this is a significant topic of interest among those who wish to potentially use bio-based polymers as a replacement for common petroleum- based polymer, like single-use plastics, due to the environmental concerns that surround these materials. Cellulose can also be used to develop value-added products for current environmental and health issues like uptake of pollutants in natural water sources or to allow for the slow release of active ingredients for fertilizing fields or protecting individuals from disease-causing pests.

## 1.2 Cellulose and Lignocelluloses Cell Wall Chemistry

Before it can be used to make these products, the cellulose must be isolated from the other components in lignocellulosic biomass. These components include cellulose, hemicellulose, and lignin, primarily, and the composition can vary based on the source of the biomass as it is found in wood cells along with those of other plants (Trygg et al., 2013). Lignocellulosic biomass refers to plant sources of softwood or hardwood as well as non-wood biomass. These lignocellulosic materials are used primarily in the pulp and paper and building material industries, but there is an interest in applying integrated biorefineries to create more value-added products than only paper and packaging materials such as nanocellulose and energy (Fernando et al., 2006).

The polysaccharides, hemicelluloses can be made up of these main sugars: d-xylopyranose, d-glucopyranose, d-galactopyranose, l-arabinofuranose, and d-mannopyranose. They usually consist of multiple sugars and can have different functional groups because of this. Their purpose is related to the function of cellulose in the cell wall (Uraki & Koda, 2015). There is a difference in hemicellulose composition based on hardwoods or softwoods. For hardwoods, the prominent type of hemicellulose is xylan, but the wood also contains a small percentage of glucomannan. On the other hand, softwood contains majority galactogluomannans with only xylans that are half as common in these woods as they are in hardwoods. The exact amount depend heavily on the species of the tree, but compositions are consistent across these two categories of woods (Timell, 1967). They interact with cellulose fibrils to add strength and structure, sometimes interacting with lignin, as well. Their function in research is of less interest than cellulose and lignin, but it still has important applications in consumer products (Roger et al., 2012).

## 1.3 Lignin

The bases of lignin's structure are known as p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. These come together to build an amorphous phenolic network whose function is to bind the cell walls together (Harmsen et al., 2010). Demonstrated by the differences in physical properties between the types of wood, softwood and hardwood vary in their total lignin content. Softwoods contain 25 to 35%, and hardwoods contain 18 to 25% lignin. Due to these interesting physical properties, the isolation of lignin apart from the rest of the components is of great interest to scientists. It has been successfully studied as a controlled-release material with respect to fertilizers and pesticides, similarly to many cellulose derivates (Mulder et al., 2011).

## 1.4 Surface Interactions

Cellulose, one of the most useful lignocellulosic materials, acts as the main structural component found in trees and is derived from natural sources including forest biomass and agricultural waste. It is a linear homopolymer made from repeating glucose units attached at C1 and C4 with 3 hydroxyl groups at C2, C3, and C6 which act as the functional groups analyzed by surface sensitive instruments (Olszewska, 2013). Surface interactions are being studied in terms of solid liquid interfaces to evaluate the adsorption kinetics based on surface charges and functional groups (Pefferkorn, 1999). It is being applied in the field of natural polymeric materials with goals that include solving biomedical problems or replacing synthetic polymers which are nonbiodegradable and nonrenewable. To study cellulose for these applications, a deep understanding of the surface is needed because that is where much of the action is taking place. Cellulose crystals are tightly packed and rigid due to intermolecular interactions like hydrogen bonding, so the surface is only able to interact or be modified by chemical processes. These leads to the relevance of cellulose films, an important tool for analyzing surface chemistry and interactions. These films are often made from either nanocellulose or regenerated cellulose. Nanocellulose, or nanofibrillated cellulose, is a form of cellulose resulting from the breaking down of cellulose pulp into units of small fiber diameter. The amorphous regions can be removed to produced cellulose nanocrystals, a useful material due to their superior mechanical properties. Regenerated cellulose is also known as cellulose II, the product of the dissolution of cellulose I, the native form of cellulose found in trees (Olszewska, 2013).

### 1.4.1 Cellulose Allomorphs

Cellulose is considered to be a linear homopolymer of β-1,4-glycosidic linked d-glucopyranose units, also called anhydroglucose units, and the conformation causes the hydroxyl groups of the carbon rings to be located at the outside, or the surface, of the polymer structure (Klemm, 2002). This is why cellulose has the ability to be functionalized easily and why it is such a challenge to dissolve with common solvents (Klemm, 2002). Cellulose can occur in different allomorphs that subsequently change the functionality of the material, and this change is normally achieved through dissolution. Cellulose I is the native form of cellulose, but after it is dissolved and regenerated, the new structure is called cellulose II. The intermolecular bonding of cellulose I differs from the bonding within cellulose II because of the structural changes that occur. Cellulose I's intermolecular and intramolecular hydrogen bonds and subsequent van der Waals hydrophobic interactions cause its rigid structure, and its molecules have both disordered amorphous and highly ordered crystalline regions (Nagarajan et al., 2017). For example, cellulose II has an anti-parallel chain formation which means that the nonreducing ends (C4-OH group) switch direction (Zlenko et al., 2021). This causes the materials to be much more thermodynamically stable. Cellulose I and II can thus be transformed into cellulose $III_I$ and $III_{II}$, respectively from liquid ammonia at -80 °C. These can then be transformed to cellulose $IV_I$ and $IV_{II}$, respectively by glycerol treatment 260 °C. The main difference between cellulose II and the other discussed allomorphs is that there are different hydrogen linkages between the chains in crystal regions of cellulose II, and this bond network is weaker than the original glycosidic linkage of cellulose I. This and the amorphization of the cellulose I have an effect on the rigidity (Valeri, 2010). Cotton linter is another type of cellulose material used for regeneration; it is the short fibers of the cotton plant seed. For dissolving wood pulp, the trees used most often are softwoods spruce and pine or hardwoods beech and eucalyptus (Chen, 2016).

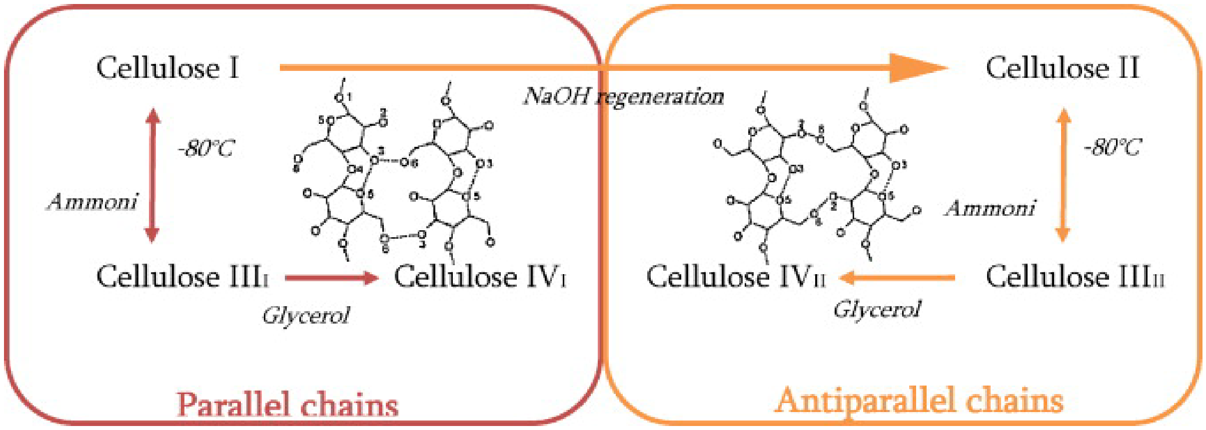


Figure 1. Cellulose Allomorphs. Reprinted from (Lavoine et al., 2012) with permission from Elsevier.

1.5 Cellulose Solubility and Common Solvents

One of the primary challenges associated with working with cellulose is its solubility in common organic solvents and solvent systems. Its insolubility in water is caused by intermolecular hydrogen bonding between cellulose chains. Cellulose is insoluble in common solvents like water and typical organic solvents due to the formation of a strong hydrogen bond network between the hydroxyl groups within and with other adjacent chains; as well as the hydrophobic crystalline face that is naturally formed in the ensemble of the fibers (Medronho et al., 2012). The effectiveness of the dissolution process depends on mixing time, mixing temperature, and properties like the crystallinity and degree of polymerization of the starting material. Therefore, an efficient cellulose solvent should be able to reduce the crystallinity of cellulose during the process of its dissolution and regeneration ideally at ambient temperatures and pressures (Pinkert et al., 2010). It is also important to do this without significant degradation of the cellulose. Advances in the understanding of this material has led to the identification of some solvents that aim to break this network to successfully dissolve cellulose, allowing processing and regeneration. Cellulose I was proposed to be an amphiphilic compound because all three hydroxyl groups of the anhydroglucose units have an equatorial orientation making it hydrophilic and the H atoms of its C–H bonds have an axial orientation making it hydrophobic (Nagarajan et al., 2017).

### 1.5.1 NaOH and Urea

A commonly used technique to dissolve cellulose quicky involves 7 wt% NaOH and 12 wt% urea at cold temperatures. Before this process, though, dissolving pulp needs pretreatment to help break down the fibers by using ethanol and hydrochloric acid (Gericke et al., 2013). After this treatment, the respective amounts of NaOH and urea are added with water to a cold beaker at -11 °C containing 2% solids of cellulose (Huber et al., 2016). This solid content can be adjusted depending on the needs of the experiment. The mechanism has been found to be that NaOH is attracted to cellulose chains through the formation of new hydrogen-bonded networks, and the urea functions as a shell surrounding the NaOH hydrogen-bonded cellulose to form an inclusion complex with a sheath like structure (Wang et al., 2016). Despite using the same technique, there are differences in regenerated films based on the source of the starting material. According to Li et al, wood, bamboo, and ramie cellulose sources all were able to dissolve in 2 minutes under the same conditions, but there was some variation in the properties of the regenerated films though the crystallinity and morphology was similar between all sources (Li et al., 2015). For the regeneration, a strong acid like nitric acid at a concentration of 2 M is used and has found to produce a stronger structure than that of the same strong acid at 6M, because this high concentration interfered with formation of agglomerates. Thus, this will result in fine structures and thin fibrils that are less strong under force than that of the 2 M acid bath where larger agglomerates contribute to a higher strength (Gericke et al., 2013).

### 1.5.2 Viscose and Rayon – Carbon disulfide

The most common commercial process for cellulose regeneration of fibers, made from wood dissolving cellulose, is called the viscose process. These steps involve the derivatization of cellulose to cellulose xanthate by carbon sulfide. The derivative is then soluble in aqueous NaOH and can be regenerated in a strong acid bath like the previous process, but there are environmental concerns with this method because carbon disulfide is toxic, flammable, and harmful to the environment. Additionally, this method is known as derivatizing approach because the raw cellulose dissolving pulp needs to be converted before dissolution. The acid solution for regeneration then should remove these functional groups to return a pure cellulose regenerated fiber (Wang et al., 2016). There have been some efforts to improve the viscose process such as recovering the toxic carbon disulfide gas by up to 75%.

Also, freezing alkali cellulose prior to xanthation has been found to protect the structure with respect to temperature and alkali concentration. It changes the degree of substitution for the xanthation step which will affect the dissolving capability of the resultant cellulose II and the functionalization ability (Roggenstein, 2010).

One example of a practical use of viscose is treatment by dielectric barrier discharge which allows for the adsorption of copper and silver ions to create an antimicrobial material, useful in many applications. This electrical treatment allowed for better wettability and adsorption of the antimicrobial ions to the fibers, a good example of how surface modifications of cellulose have many different problem-solving capacities (Kramar et al., 2013). An alternative to viscose is the conversion of cotton fibers from cellulose I to cellulose II by applying microwave irradiation during the mercerization process. Utilizing this method, Guo et al. synthesized cellulose carbamates using the radiation in urea which was then spun via the Carbacell process (Guo et al., 2010). The Carbacell process spins fibers comparable to that of viscose via wet-spinning but using urea instead of harmful $CS_2$ to derivatize cellulose (Fink et al., 2014).

### 1.5.3 Ionic Liquids

Ionic liquids (ILs) are usually composed of imidazolium, pyridinium, or organic ammonium cations and anions such as chloride, bromide, or more complex structures such as hexafluorophosphate, trifluoromethyl sulfonate, bis(trifluoro-methylsulfonyl) imide and 1-allyl-3-methylimidazolium chloride ([Amim]Cl) (Sayyed et al., 2019). A goal of researchers is to find a successful ionic liquid without the imidazolium cation because ILs comprised of this have a high melting point and corrode the spinning equipment (Hummel et al., 2016). Regardless of the type of IL, as there are many, the overall mode of action depends on the presence of a cation and an anion (Mohd et al., 2017). A benefit of these ILs is that water can be used as the regeneration bath and the ionic liquid can be recovered (Hauru et al., 2012). The interest of recycling the ionic liquid is a major concern to the commercialization, and it has been shown that at a pilot scale, ionic liquids can be purified from the water bath for reuse in further cellulose dissolution and regeneration cycles (Ahmad et al., 2016; Walger et al., 2017).

Drawbacks associated with ILs are their high cost of production, high viscosity, and sensitivity to moisture content (Medronho & Lindman, 2015). This is not to mention the use of harsh chemicals during synthesis such as acetic acid, and they are not able to biodegrade which is a main concern for those looking for a more environmentally friendly option for dissolving cellulose pulp (Sayyed et al., 2019).

1.5.3.1 Lyocell – NMMO

Another development in the dissolution of cellulose is the use of *N*-methylmorpholine *N*-oxide (NMMO) and water in the commercial Lyocell process. This solvent belongs in category of amphiphilic solvents, meaning they have polar and nonpolar components, which is vital to the dissolution of cellulose if hydrophobicity is an interaction of concern (Medronho et al., 2012). A benefit of NMMO as a solvent is that it is nonderivatizing, enabling direct dissolution (Sayyed et al., 2019). The mechanism of NMMO shows the solvents ability to form solvent complexes with the hydroxyls by forming new hydrogen bonds where the water was previously interacting. This process is done at temperatures between 70 to 100 °C to promote mobility of the groups in question. In this process, there are many side reactions occurring that are being studied to effectively control them. Stabilization of the cellulose and NMMO solution can be achieved by trapping byproducts which are radicals of formaldehyde and *N*-(methylene)iminium ions (Wang et al., 2016). After regeneration, over 99% of the NMMO can be recovered, making it a green option for cellulose dissolution (Rosenau et al., 2001).

1.5.3.2 Ioncell

The Ioncell process utilizes direct solvent, 1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH][OAc]), a superbase ionic liquid, to dissolve cellulose pulp, then, it uses dry-jet wet-spinning in a cold water bath which washes away the solvent, leaving behind cellulose II in the shape of a thin fiber. More specifically, prehydrolysis kraft pulp is ground up and mixed at 70 to 80 °C with the [DBNH][OAc] until a homogenous mixture is reached.

This dope is filtrated and then extruded through a spinneret via an air gap into a cold water bath where the solvent is removed. These fibers get their properties by drawing the filament in the air gap. The speed of the take-up godet stretches the filament and thus results in alignment of the cellulose molecules within the filament. The ionic liquid can be recovered from the spin bath through evaporation of the water, allowing for the recycling of the IL (Parviainen et al., 2015; Stepan et al., 2016).

### 1.5.4 Deep Eutectic Solvents

Deep eutectic solvents (DESs) are a relatively new class of cellulose solvent systems and have not yet become widely commercially available, though they are of great interest to researchers because of their environmentally-friendliness and their ability to be extracted from the regeneration bath and reused many times over. Some consider DESs to be within the category of ionic liquids, but there are characteristics that set them apart. DESs function, similarly, behaving as both a hydrogen bond donor and a hydrogen bonds acceptor which allows for the hydrogen bonding to occur between the components of the solvent rather than the cellulose chains. Unlike ILs, though, the synthesis of DESs is done by adding a certain composition of two solids, usually choline chloride and other solid such as urea or an acid, at the eutectic composition which means that the mixture has a lower melting temperature than each of the constituents itself. This often allows DESs to be liquid at room temperature, like ILs, but they do not receive the same criticism as ILs in that DESs are significantly less toxic and present more biodegradability (Zhang et al., 2020).

The issue with DESs, though, is that the solubility of cellulose is more limited than that of ILs. According to (Tenhunen et al., 2016), ChCl + urea DESs have no effect on the fiber morphology of cellulose and only slight electrostatic forces at work when treated, and others have used a strong acid and choline chloride to develop a DES that effectively regenerates cellulose I into cellulose II (Tenhunen et al., 2016). Due to their safety and low cost, DESs are continually being studied as a green solvent system for cellulose pulp.

## 1.6 Chitosan

Cellulose and lignin are not the only bio-based polymers with a variety of uses. Chitosan is derived from chitin, a natural polysaccharide and the second most abundant biopolymer in the world after cellulose. The presence of acetyl groups in chitosan make it useful for controlled-release applications after being converted from chitin (Rinaudo, 2006). The reason this is more usable than chitin is because these groups have interacting characteristics with metal ions. The mechanisms by which these are taking place include adsorption, ion-exchange, and chelation (Ninan et al., 2012). For controlled release, adsorption is a good measure of a materials viability.

## 1.7 Model Surfaces and Characterization Techniques

Model surfaces are ultrathin films fabricated by methods including layer-by-layer assembly, self-assembled monolayer techniques, or the Langmuir-Blodgett method (Park et al., 2018). One layer-by-layer method, the primary and simplest way, is to cast from a solution, either from the solvent in the case of regenerated cellulose or from an aqueous dispersion in the case of nanocellulose. They are important because they help identify interfacial forces in cellulose systems. These can be composites, pure cellulose, or a cellulose derivative, but the surface allows for the specific functional groups to be studied with great accuracy. Creating a thin surface is necessary for sensitive instruments to be able to detect the phenomena that occurs and having an even and homogenous surface is crucial to producing good results (Hubbe et al., 2017). Spin coating is a popular technique for creating supported films from solution. It usually done at a rate of 1000 to 6000 rpm depending on the viscosity of the solution. The steps are deposition, spin-up, spin-off, and evaporation. These steps refer to a droplet of solution at a calculated concentration being deposited on a sensor, the rotation beginning, the sample being pulled from the center to the edges, and the solvent evaporating resulting in a thin film (Taajamaa, 2014).

Other ways of fabricating ultrathin films are self-assembled monolayering and the Langmuir-Blodgett method. Self-assembled monolayers are created by submerging the gold sensor or other substrate in the solution of surface-active material. At the interface of the substrate, one end group of the compound in solution has chemisorption at the surface. The parameters including concentration and time will depend on the materials, but in order to create a monolayer, the compounds should attach directly to the substrate (Ulman, 1996). The Langmuir-Blodgett includes arranging the molecules on the surface in a fixed configuration by two steps. The first step involves the single layer of molecules being deposited on a water surface and then forced into a fixed shape to pack them more tightly together. The molecules and water must have an anisotropic relationship in order for the layer to remain single and no interactions occur between the molecules of the layer. After this layer is formed, the substrate is passed through the liquid and this layer is deposited onto the surface. This can be repeated as many times as necessary for the experiment (Peterson, 1990).

### 1.7.1 Atomic Force Microscopy

Such instruments that utilize thin film surfaces include the Atomic Force Microscopy (AFM) which is a mechanical technique used to generate topographical images of the surface of a thin film. AFM is important for the characterization of polymeric materials because from these images, details about fiber morphology can be analyzed. Scanning is conducted across the sample surface by a probe with a sharp microscopic tip at the end of a cantilever allowing for the oscillating movement of the tip generated by a piezoelectric element at its resonance frequency (Rugar, 1990). This instrument can be run in either tapping mode or contact mode. In tapping mode, the damping of the oscillation amplitude, caused by the interaction of the surface of the sample and the tip, is detected by the lever. Not only is the oscillation difference monitored, but the bending and torsion of the cantilever is also noted by the instrument. For contact mode, the cantilever oscillation is set at a certain value, so the tip is constantly in contact with the surface. Tapping mode is often used for polymers, because although contact mode usually results in a higher resolution image, it can easily damage a surface like cellulose (Magonov & Reneker, 1997).

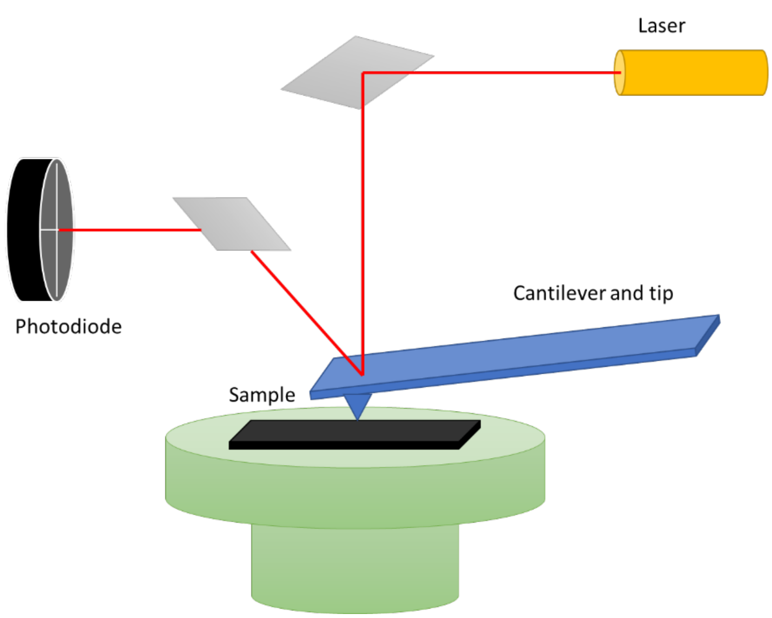


Figure 2. AFM Configuration

### 1.7.2 Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D)

Another instrument that works by using thin films is the Quartz Crystal Microbalance with Dissipation (QCM-D). Frequency and dissipation changes obtained from QCM-D experiments can be modeled using the Saurbrey equation and determine the mass adsorbed onto a polymer surface as well as some viscoelastic properties (Bratek-Skicki et al., 2021). The Sauerbrey equation is only valid, though, if the films is considered rigid which can be identified using the dissipation measurement (Sohna Sohna & Cooper, 2016). Soft viscoelastic materials need such a large correction to this equation that it is not considered useful for materials like proteins (Kankare, 2002). A benefit of QCM-D is that it shows real time measurements of adsorption and desorption which can indicate whether the interactions are reversible or irreversible. It can achieve this very sensitive detection of mass change by measuring resonance of piezoelectric materials, the most common being α-quartz, or crystalline $SiO_2$. Piezoelectric materials have a unique property where mechanical strain causes an electrical field within the material, and an electrical field within the material subsequently causes mechanical strain. This phenomenon is utilized in QCM-D by applying an oscillating electric field to a sensor, and resonance occurs as a function of frequency of these oscillations and the mass of the sensor (Höök, 1997). A solution is flowed across the surface to evaluate this change in mass. Since the mass of the adsorbed material is considered to be mass of the sensor, there is a frequency change when adsorption is successful. Dissipation is another aspect that is measured by the instrument which gives information about the damping of the oscillations, and therefore, the rigidity of the material on the sensor, an important viscoelastic property to consider for some experiments (Liu et al., 2011).

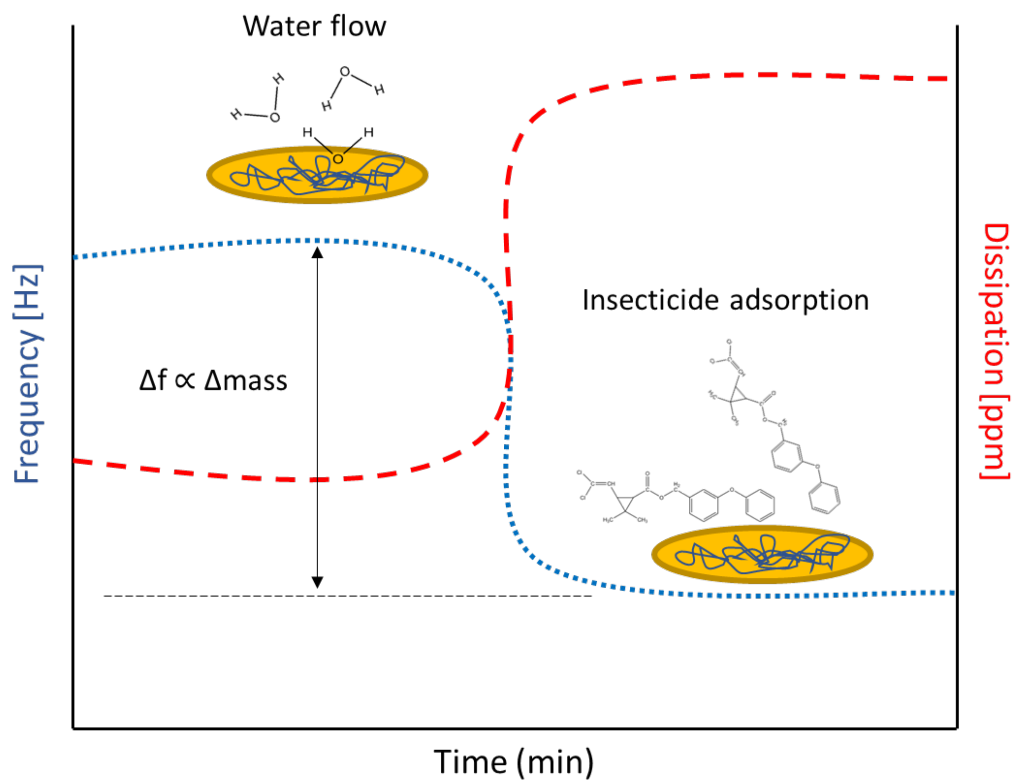


Figure 3. QCM-D Mechanism

1.7.3Multi- Parametric Surface Plasmon Resonance

Surface Plasmon Resonance (MP-SPR) is often used in conjunction with QCM-D to confirm its findings. Surface plasmons refer to electromagnetic waves that propagate along a thin metal interface. This metal interface is usually gold, and it can be coated with a polymer like cellulose to measure the interactions when different solutions are flowed across the surface, much like QCM-D. It uses the change in refractive index to indicate surface or conformation changes with respect to time (sensogram) by directing p-polarized light through a prism to the sensor. At this point the plasmons become excited and the peak minimum is shifted (Bionavis, 2020; Granqvist, 2014). The peak minimum represents the angle at which the light is no longer reflected by the sensor and is instead absorbed by the surface plasmons. Therefore, this method uses different physics to determine the surface interactions between the solution and the material, but it displays a similar curve in the sensogram as the results for QCM-D (Homola, 2008). The combination of QCM-D and SPR is important because it utilizes a gravimetric technique and optical technique to verify the data being collected.

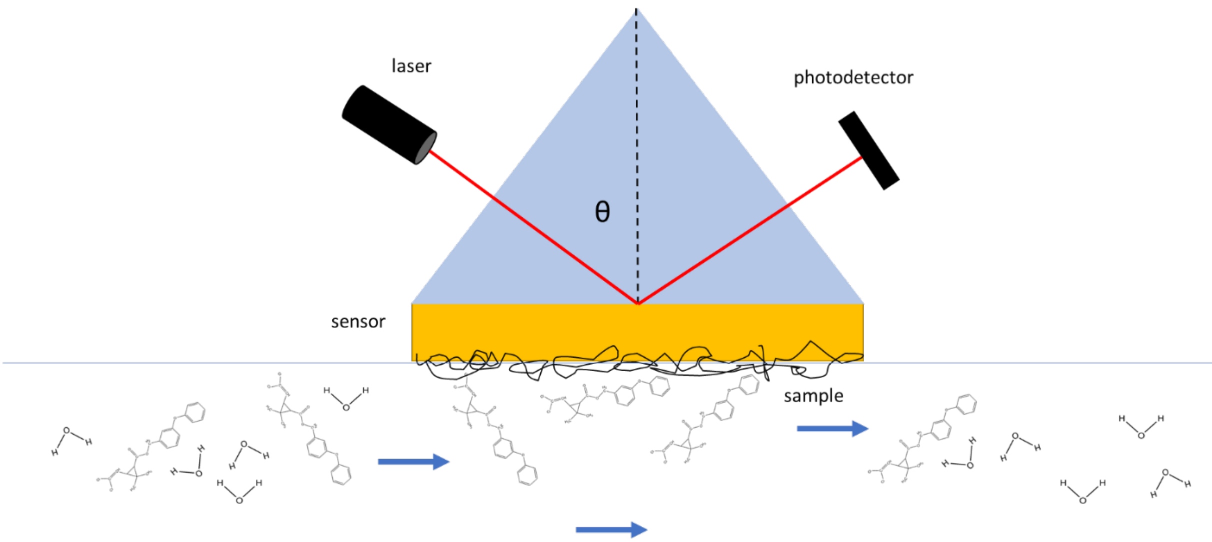


Figure 4. SPR Mechanism

1.7.4 Nuclear Magnetic Resonance

The last technique used in this work is Nuclear Magnetic Resonance (NMR), a high-resolution method for determining the structure of compounds based on ½ spin nuclei. Nuclear Magnetic Resonance (NMR) is a method used in this work to study the stability of pyrethroids in ionic liquid, a common cellulose solvent. The functionality of NMR depends on their nuclear spin quantum number being nonzero, so only some nuclei exhibit NMR. The signals produced by this test represent the resonant frequency of the nucleus, and the energy transition is affected by the electron shielding of the nucleus (Claridge, 2016). For the purpose of this study, proton (1H) and carbon 13 (13C) are the isotopes used to generate spectra because they provide sufficient 1D and 2D spectra for the analysis of the pyrethroids in question. Heteronuclear single quantum coherence spectroscopy (HSQC) is a useful NMR test that correlates the hydrogens in a compound with the carbons and presents subsequent chemical shifts depending on the structure.

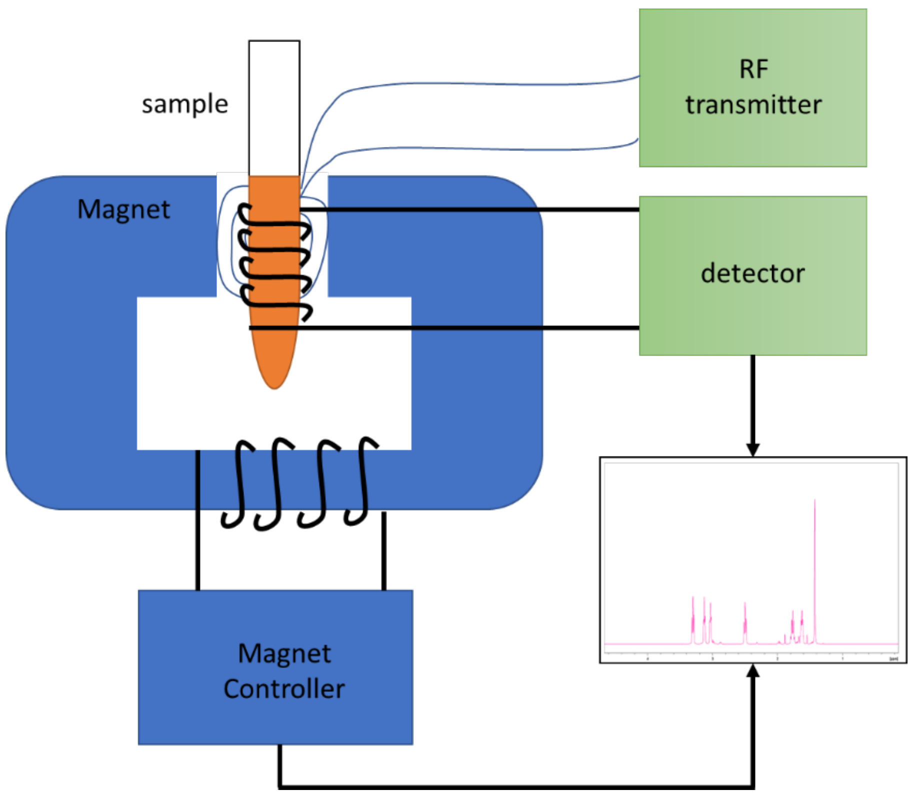


Figure 5. NMR Mechanism

1.7.5 Encapsulation and controlled release of active ingredients

The purpose of studying surface interaction is to evaluate the potential mechanisms of controlled release by physical or chemical means. Cellulose is commonly researched as the medium for controlled release of active ingredients like pesticides and fertilizers due to the many forms it can take and its ability to modified. Release rate controlled physically can occur one of two ways: by permeation or by absorption (Pavaloiu et al., 2014). Although there are many options for the material of choice including hydrogels and crosslinked membranes, permeation occurs by first swelling the membrane or hydrogel containing the chemical in water which allows the chemical inside to dissolve and form a saturated solution. Then, it can permeate through the surface because of the concentration gradient between the center of the material and the environment. In stable conditions, this permeation rate will be constant, but this rate is determined by the free volume fraction of the cellulose material. Factors that most strongly affect this are hydrophilicity and crosslinking density (Pang et al., 2019).

Another way this can occur is by absorption where the active ingredients are absorbed into the matrix of the polymer and is either released by slowly diffusing out if there is a low concentration in the surrounding environment or burst releasing by shrinking due to changes in things like temperature or pH. For diffusion, the concentration gradient between the inside and the outside of the material determines the release rate, and because the concentration of active ingredient on the inside is reduced, the release rate will decrease over time in stable conditions. Because of this, the release rate is much higher initially (Pang et al., 2019).

The other mechanism by which active ingredients can be released is chemically. For this to occur with cellulose specifically, it can be modified or unmodified. Unmodified cellulose contains hydroxyl groups at which active ingredients can attach, and modified cellulose will link to the chemicals via a functional group such as the case with the cellulose derivative cellulose acetate which contains acetyl groups at the locations of the hydroxyls. Cellulose can interact with chemicals unmodified, as well, via the hydroxyls with hydrogen forces. Then, the active ingredients will link directly or indirectly (Pang et al., 2016).

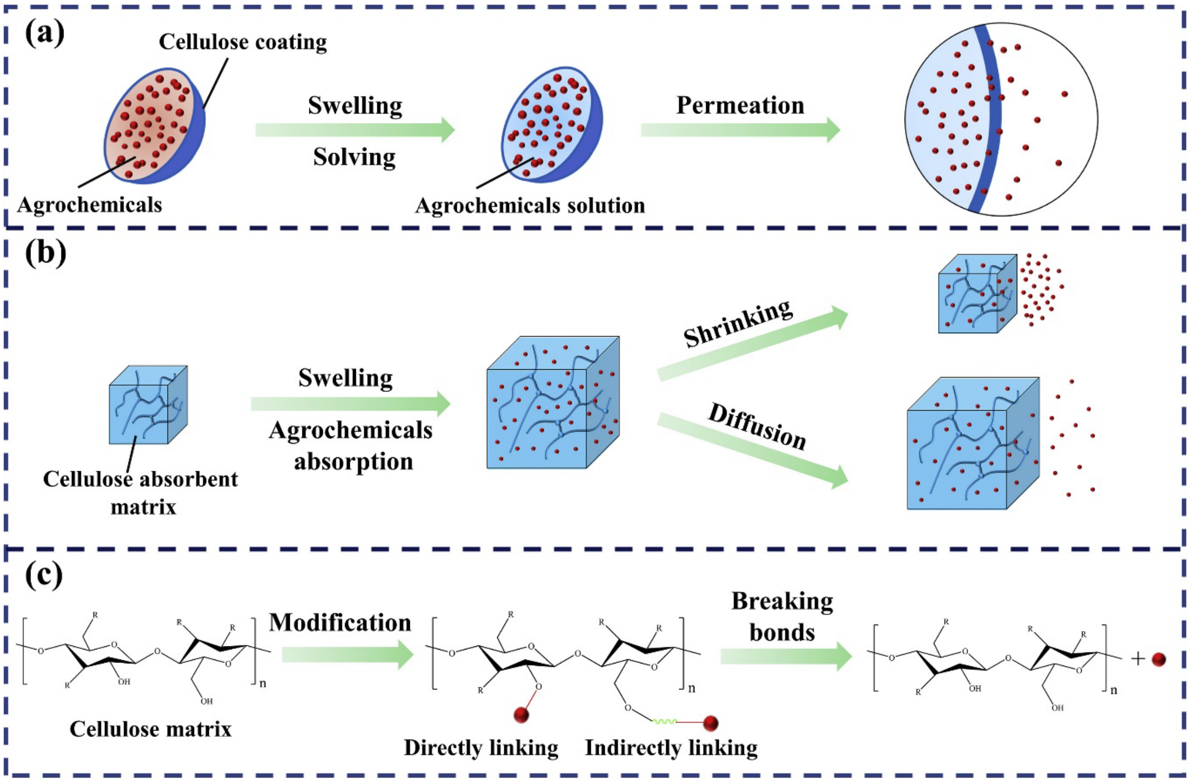


Figure 6. Controlled Release Mechanisms. Reprinted from (Pang et al., 2019) with permission from Elsevier.

## 1.8 Long-lasting insecticide nets

One application of controlled release that can be potentially improved by biobased materials is called a long-lasting insecticide net (LLIN). These malaria control devices are made from extrusion of a synthetic, petroleum-based polymer, polyethylene or polyester with either the insecticidal compounds incorporated within the filament or coated with a combination of insecticide and binder on the surface. These compounds migrate to the surface via diffusion if incorporated (Ramanathan & Samiappan, 2013). Pyrethroids, are the insecticides used in these products because of their cost effectiveness and approval by the World Health Organization along with some other additives. Some additional synergists have been a necessary addition to LLLINs due to the built up resistance of mosquitoes to the pyrethroids only. Piperonyl butoxide is a synergist that functions to reduce the resistance to pyrethroids, allowing them to function effectively to kill malaria parasite carrying mosquitos. This additive in particular has had a significant impact on the ability of the nets to protect people from malaria, so it should be used in conjunction with the other active ingredients (Protopopoff et al., 2018). For this reason, permethrin, deltamethrin, and piperonyl butoxide are used in this work.

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## Hypothesis

Currently, lignocellulosic materials and other bio-based materials like chitosan are being used in many different applications, including controlled release of active ingredients (AI) but require preliminary data on the interactions between the AI and the substrate. In this work, pyrethroids are tested for their affinity with cellulose allomorphs and other biobased polymers and their stability within a useful cellulose solvent system. Pyrethroids and common additives for insecticide nets can have irreversible interactions with biobased materials and be stable in cellulose solvent systems. Therefore, biobased materials can be utilized for controlled release of insecticides.

# Objectives

## General Objective

The objective of the work is to gather and analyze preliminary data to support the hypothesis that bio-based materials can be used as insecticidal controlled release systems while also gathering useful fundamental data on the behavior of pyrethroids in cellulosic environments including solvents and typical processing parameters. This is an application of this work, but another objective is to develop methods that can be used to gather fundamental information on active ingredients and how they can be implemented in a bio-based controlled release device.

## Chapter 1 Objectives

The objective of Chapter 1 is to provide the necessary background to give context for the following experimental chapters. This includes details on the materials and methods that were used and why they are of interest in this work.

## Chapter 2 Objectives

The objectives of Chapter 2 are to evaluate the adsorption of deltamethrin, permethrin, and PBO onto surface films. These films include 3 allomorphs of cellulose and 3 different surface groups intended to model other biobased materials such as chitosan and lignin. These represent the behavior of the insecticides in a controlled-release device in terms of its ability to remain bound to the material in a reversible or irreversible manner.

## Chapter 3 Objectives

The primary objective of this section is to study the degradation potential of deltamethrin, permethrin, and PBO in the solvent [DBN][OAc], a commonly used ionic liquid for the dissolution and regeneration of cellulose. Future work involves using this solvent to spin cellulose fibers that contain the insecticide, so it is important to evaluate the behavior of the insecticides modeled in those temperature and time conditions.

# 2. Chapter 2

## Interactions between pyrethroids and model surfaces

### 2.1 Introduction

Interfacial interactions of model films of different forms of cellulose: nanofibrillated cellulose, dispersed cellulose, and cellulose II along with model surfaces: silica, polystyrene, and polyethylenimine (PEI) tested with permethrin, deltamethrin, and PBO. The nanofibrillated cellulose is in the native cellulose form, cellulose I. Ionic liquid, [DBN][OAc], dissolved cellulose is cellulose II, because it has been regenerated. Deep eutectic solvent, ChCl/urea, is not successful at dissolving cellulose, but it has a dispersion and swelling effect on the fibrils, so it is not considered cellulose II, but it can have some different adsorption effects from cellulose I. Because DESs are being studied recently for their effects on cellulose as a green solvent, the interactions between cellulose dispersed in DES and pyrethroids are of interest. These materials will be used in this chapter to create model films. In addition, some model surfaces are used. Silica surfaces contain hydrophilic hydroxyl groups like that of cellulose, isolating that possible interaction of the pyrethroids with cellulose. Also, the surface of PEI contains amine groups with a positive charge so it can interact with negatively charged particles. This is similar to chitosan which is often used as an adsorbent of metal ions in aquatic environments, it can be functionalized to achieve many different purposes due to its known adsorption capability (Rinaudo, 2006). Polystyrene, the final model surface, contains many aromatic groups at the solid-liquid interface and behaves hydrophobically. Hydrophobic biobased materials are used for practical applications. One example is lignin. Lignin-based controlled release materials include lignin gel for pesticides and coatings for fertilizers. Its hydrophobic nature and ability to be crosslinked make it a good candidate for these applications and should be considered when working with insecticides, as well (Mulder et al., 2011). The objective of this work is to model the adsorption of pyrethroids on the surfaces of the allomorphs of cellulose and the model films to see how both morphological changes in cellulose or functional groups added to the surface change the adsorption capability.

Nanocellulose was used in this section which is known as a colloidal suspension with an anionic surface charge. Nanocellulose can have unique solid-liquid interactions with different substances due to the many hydroxyl groups at the surface. Using nanocellulose will provide these groups at the surface to interact strongly with the active ingredients during surface sensitive testing (Olszewska, 2013). Interactions between charged particles include van der Waals forces and electrostatic repulsions. Van der Waals forces refer to the attraction of two particles in a short range depending on their respective properties (Benselfelt et al., 2019). Electrostatic forces become present when ions and charges are interacting within an aqueous environment. This should be overcome in order for noticeable irreversible adsorption. In addition, other forces present include hydrophobic, steric, and hydration forces which can have an effect, but this also depends on the particles being studied (Berg, 2009).

### 2.1.1 Active Ingredients of Interest

Because of the consideration of bio-based materials being used in the future as the material of LLINs, the AIs in this study are based on those that prove effective for that application. Currently, only two types of insecticides are approved for net use, pyrroles and pyrethroids, and pyrethroids are universally utilized (CDC). Initially, only one class of insecticides had been used in nets, but due to increased development of insecticide resistance in mosquitoes, different additives have been commercially employed to counteract resistance through various modes of action. The original insecticides used in the nets are called pyrethroids

(Organization; Organization; Organization). Examples of this category of insecticides include permethrin, alpha-cypermethrin, and deltamethrin. All commercially available and approved LLINs use one of these types of pyrethroids because they are readily available, cost effective, and have been widely studied and used for many years (Shafer et al., 2005).

Commonly used additives include piperonyl butoxide (PBO) and pyrroles. Pyrroles are used as insecticidal additives, but not all additives are insecticides on their own. Some additives, such as PBO, may act as synergists which can serve to enhance the functional role of the insecticide by modifying susceptibility to pyrethroids (Birhanu et al., 2019). PBO, for example, breaks down the insect's natural resistance to pyrethroids, allowing them to function normally to kill the insect (Gleave et al., 2018).

The objectives of this work are to evaluate the adsorption of deltamethrin, permethrin, and PBO onto surface films by detecting a change on the surface via frequency in QCM-D and peak minimum angle change in SPR. This information gives important preliminary data about the behavior of the insecticides in a controlled-release device and their ability to remain bound to the material reversibly or irreversibly.

## 2.2 Materials and Methods

### 2.2.1 Synthesis of Solvents

Ionic liquid [DBNH][OAc] was synthesized by using 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) from VWR at a 1:1 molar ratio with glacial acetic acid from VWR (56.16g DBN, 27.16g/25.86mL acetic acid). The DBN was stirred at 70 °C in the fume hood and the acetic acid was added dropwise. Then, it is left for an additional 20 minutes to mix. The deep eutectic solvent was used by combining a 1:2 molar mixture of choline chloride (64.8g) from VWR and urea (48.9g) from VWR in an enclosed container at 100°C until a clear liquid is formed.

2.2.2 Preparation of Nanocellulose Suspensions

Bleached cellulose nanofibrils were prepared from cellulose pulp using Masuko Supermasscolloider (MKZA10-15J). The cellulose I sample was created from this by diluting to 1.67 g/L with miliQ water. The dispersed cellulose sample used the same nanofibrils, but deep eutectic solvent was added so the solids would be the same as the previous sample. The additional water in this sample does not have an effect on the ability of the deep eutectic solvent's function because the DES is not very soluble in water. On the other hand, to dissolve the aqueous colloidal suspension of nanocellulose in ionic liquid, it had to first be solvent exchanged with acetone. The ionic liquid is washed away by water leaving regenerated cellulose, so water should be kept from the system until regeneration. To achieve this, the nanocellulose was solvent exchanged by adding acetone, mixing, and filtrating until no more water remained. This is necessary to avoid agglomeration of the nanocellulose suspension that occurs when it dries. After the solvent exchange, the solid content was remeasured and then 1.67 grams of solid content was added to 1 L of ionic liquid. Then, the ionic liquid mixture with the solvent exchanged nanocellulose was heated at 60°C until no more acetone could be detected and the nanocellulose was dissolved in the ionic liquid. To get supernatant from these samples, they were centrifuged for 45 minutes at 10500 rpms at room temperature. The cellulose I solids gathered at the bottom, but the solids in DES and IL did not, so the centrifuging was not necessary for these samples, and seen by the AFM images, a coated surface was achieved despite failing to remove the extra larger solid particles as was done in the cellulose I. These 3 mixtures have distinct allomorphic (structural) differences, seen in Fig. 7, 8, and 9 (AFM).

The PEI only sensor was created using this method without spin coating the cellulose layer on top. The polystyrene (PS) and silica sensors were purchased from Nanoscience and used without further preparation or swelling with water prior to the experiment.

### 2.2.4 Model Film Formation

Thin film development is necessary for AFM, QCM-D, and MP-SPR. All of the sensors were prepared using this method, only the AFM utilizes silica wafers instead of gold that is used for QCM and SPR, purchased from Nanoscience. Before adding the thin films of nanocellulose, the sensors were cleaning with miliQ water and ethanol twice, then they were placed in UV ozone, Digital UV Ozone System – PSD Series by Novascan, for 20 minutes. After this, they were submerged in a PEI solution 1 g/L for 15 minutes, rinsed with miliQ, then stored in miliQ until spin coating (about 5 min). Spin coating was done using Laurel Model WS-650MZ-2323NPPB. The spin coater uses vacuum and nitrogen gas to hold the sensor in place and create a stable environment for coating. Once the sensor is in place, the program runs which is set to intervals that correspond to the following steps. First, 180 μL of miliQ water is added to the surface using a micropipette to ensure an even surface of PEI for the cellulose to bond with. This spins for 30 seconds at 10000 rpms. Before the cellulose suspension is added, there is a pause to allow for another addition of 180 μL of the supernatant cellulose suspension that is spun for 1 minute at 10000 rpms. This is repeated so another layer of cellulose is added to ensure an even coat over the PEI. After all sensors were coated, they were dried in an 80°C oven for 10 minutes and then stored in enough miliQ water to cover the surface to swell before use the following day.

### 2.2.5 Atomic Force Microscopy Operation (AFM)

Imaging of the morphology of the different cellulose samples was conducted using an Anton Paar Tosca 400 Atomic Force Microscope in tapping mode. At the end of a cantilever, a diamond tip is making contact with the surface by oscillating at a resonance frequency and scanning across the surface. Bending of the cantiliever due to changes in interactions between the surface and the tip is how topographical image is generated because a laser is reflected off the top and the change in angle is received by the detector. This method was used to verify the theoretical changes in cellulose morphology based on the solvent system.

### 2.2.6 AFM Image Optimization and Processing

To gather the images from the AFM, some parameters should be changed to optimize the result. First, the cantilever tip is loaded into the actuator which is loaded into the AFM cabinet. For tapping mode, the laser must be aligned to the tip and the cantilever must be tuned to find the resonance frequency. After moving to the desired position on the sample, the parameters used to optimize the images in the images can be adjusted. I Gain controls the feedback in order to minimize the noise that can occur when it is too high. This is dependent on the size of the area being captured in the image. The setpoint indicates the contact force of the between the cantilever and the sample, so it should be optimized based on the sample. Resolution determines the number of lines and the data points per line, and rate is the scan speed in lines per second. One line per second, 400 resolution, and 100 I gain are used for good quality surface images. These changes can be modified in real time as the image is being generated to improve the clarity and detail of the image. Two samples were made from each material, and 2 to 3 images were generated for each to ensure an even coating and consistency. Then, they were processed using Gwyddion software.

### 2.2.7 Interactions Studies

As discussed previously, QCM-D and SPR are used in conjunction to evaluate the interactions between a surface and a compound, so both use the same insecticide solution. The deltamethrin was purchased from VWR and the permethrin (a mix of cis and trans isomers) was purchased from Sigma Aldrich. The deltamethrin and permethrin were prepared at 2 mg/mL by dissolving the insecticide in a small amount of acetone and then adding miliQ water to the desired concentration. This is necessary because these compounds are very hydrophobic. Then, half was separated and diluted to 1 mg/ml. The PBO was used at a different concentration 5 mg/mL and 10 mg/mL due to practical applications often having much higher PBO content relative to the permethrin/ deltamethrin.

### 2.2.8 Quartz Crystal Microbalance with Dissipation and Surface Plasmon Resonance

The QCM-D is set up by placing 2 sensors per test in the holders so the changes in frequency and dissipation can be detected. After these are enclosed, the pump is hooked up and the tubing is placed first in only miliQ water which is flowed across the surfaces until the frequency and dissipation is stable, around 10 minutes. After this, the 1 mg/ mL insecticide is flowed until stability is achieved (10-20 minutes), water is flowed again, the 2 mg/mL concentration is flowed, and water is flowed last. These are all flowed until the frequency and dissipation becomes stable. The SPR is used in a similar way to measure the change in peak minimum angle except the autosampler is programmed to switch samples automatically.

## 2.3 Results and Discussion

### 2.3.1 Preliminary Dissolution and Regeneration Tests

Initial regeneration tests were done to evaluate the behavior of pulp in the deep eutectic solvent, ChCl + urea, and the ionic liquid, [DBNH][OAc], compared to nanocellulose in water. This is to see the dissolution of cellulose in each solvent before making thin films to check adsorption.

Figure 7. Nanocellulose in Water

Nanocellulose in water, 1 wt%, creates a colloidal suspension and when the water is evaporated, it leaves a film close to native cellulose, cellulose I. This is the same form of cellulose used in the surface interactions testing.

Figure 8. Cellulose Pulp in DES

Pre-hydrolysis kraft birch dissolving pulp sent from Aalto University was used at 13 wt% in ChCl + urea to disperse the cellulose. The DES was synthesized according to the section 2.2.1. The pulp was shredded by hand and then mixed in the DES at 80 ℃ for an hour. Other trials were conducted to see if more time mixing could help with dissolution, but after 1 hour, no more changes were observed so this procedure was used to avoid any degradation of the cellulose.

Some sources claim that DESs can be used to dissolve high concentrations of cellulose pulp but others that have attempted with ChCl + urea to regenerate cellulose yarns have determined that this DES only is successful at dispersing or swelled cellulose pulp rather than full dissolution (Tenhunen et al., 2018). Based on the result in Fig. 4, this was the case observed during the preliminary experiment. This does not mean that the DES has no use for controlled release materials, but it does not fully dissolve and thus provide regenerated cellulose II.

Figure 9. Cellulose Pulp in IL

It can be seen in Fig. 5. that after 13 wt% cellulose dissolving pulp was mixed in IL [DBNH][OAc] at 70 ℃ for one hour, regenerated cellulose was produced as film. IL is washed away with water during the regeneration process. This ionic liquid's ability to dissolve cellulose is supported by the literature, so this result was expected (Hummel et al., 2016).

These results were taken into account for thin film development and line up with the structures in the AFM images in the following section.

2.3.2 Morphological Studies on Model Films

The images shown in figures 10-12 are a result of spin coating nanocellulose suspensions from various solvents onto silica AFM sensors.

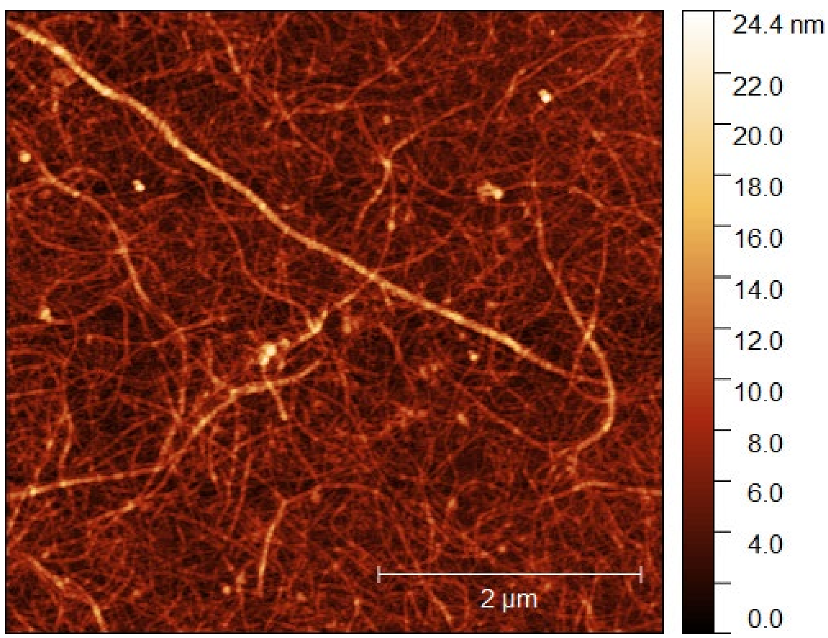


Figure 10. Bleached Nanocellulose Suspension in Water

The AFM image in Fig. 10 is the thin film used in the QCM-D and SPR measurements. This image shows the morphology of the nanocellulose, many long thin chains with many hydroxyl groups for interacting with the insecticide or respective AI. This confirms the methods used for interfacial interactions testing will have a fully covered sensor and the insecticides will be in contact primarily with the nanocellulose rather than the PEI.

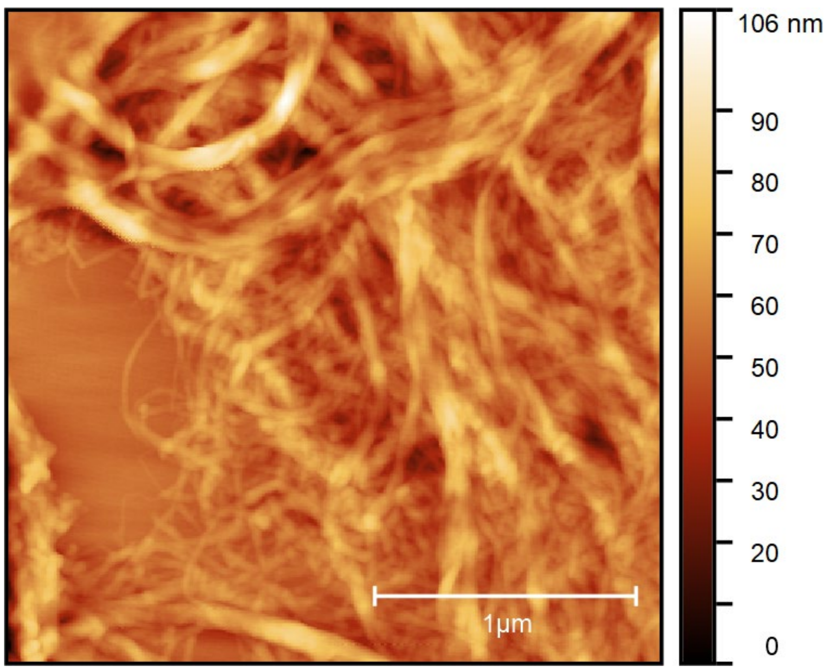


Figure 11. Bleached Nanocellulose Suspension in Deep Eutectic Solvent

The AFM image in Fig. 11 confirms the results from the preliminary dissolution test that the DES does not sufficiently dissolve the cellulose nor the nanocellulose, but the surface is coated as evenly as possible given that the nanocellulose is only dispersed from dissolving pulp.

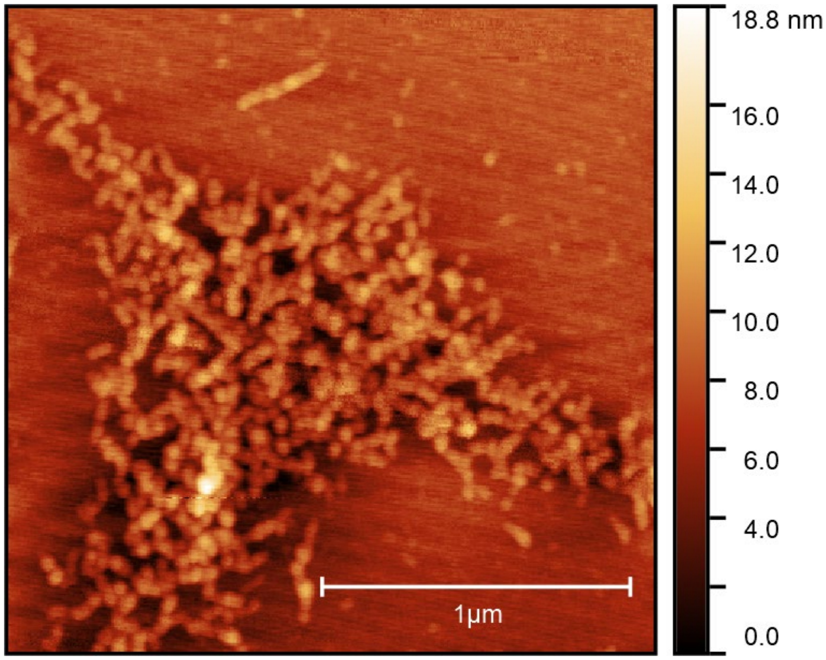

Figure 12. Bleached Nanocellulose Suspension in Ionic Liquid

Fig. 12 shows the coverage of regenerated nanocellulose thin film on the AFM sensor. In this image, the cellulose chains have clearly been broken successfully by the IL given the small particles.

It can be seen that there is a significant difference between the structures of nanofibrillated cellulose (cellulose I), dispersed cellulose, and dissolved cellulose (cellulose II). Although all of these are still cellulose with hydroxyl groups at the surface, there is more surface area for hydrogen interactions.

The PEI is used to bind the cellulose to the surface more securely using its amine groups, but as seen in the AFM images, the dispersed and regenerated cellulose is not a perfectly even layer due to the solvents used. In the nanocellulose (cellulose I) system, it was possible to remove large particles and agglomerates by centrifuging and use the supernatant, so these fibrils are more evenly spaced unlike those in the other sensors. This can cause some of the PEI on the surface to be exposed, which can interact with the AIs. Overall, the different forms of cellulose are covering the surfaces sufficiently to evaluate their interactions with the insecticides.

### 2.3.4 QCM-D and SPR Interactions Studies

After the analysis of the model films to ensure full coverage, these along with the surfaces PEI, PS, and silica can be studied for their interactions with the active ingredients of interest. Each sample of QCM was repeated to ensure reproducibility. Then, the set of data with the least noise was chosen to show in the figures below. In addition, a baseline correction was applied to all data and the final changes in frequency, dissipation, and peak minimum angle are summarized in table 2.

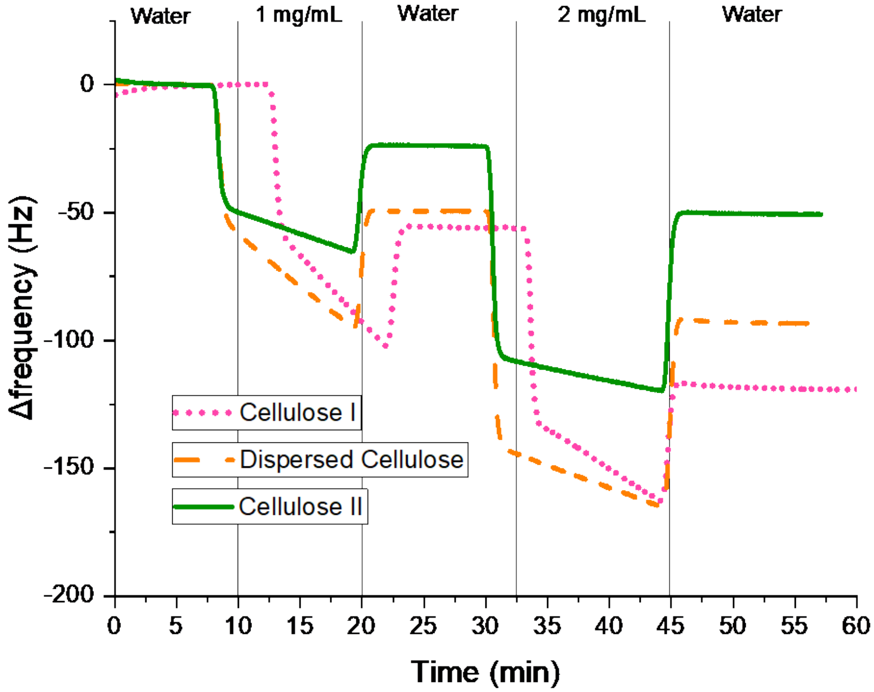

Figure 13. Frequency Results for Permethrin in Cellulose Allomorphs (Model Films)

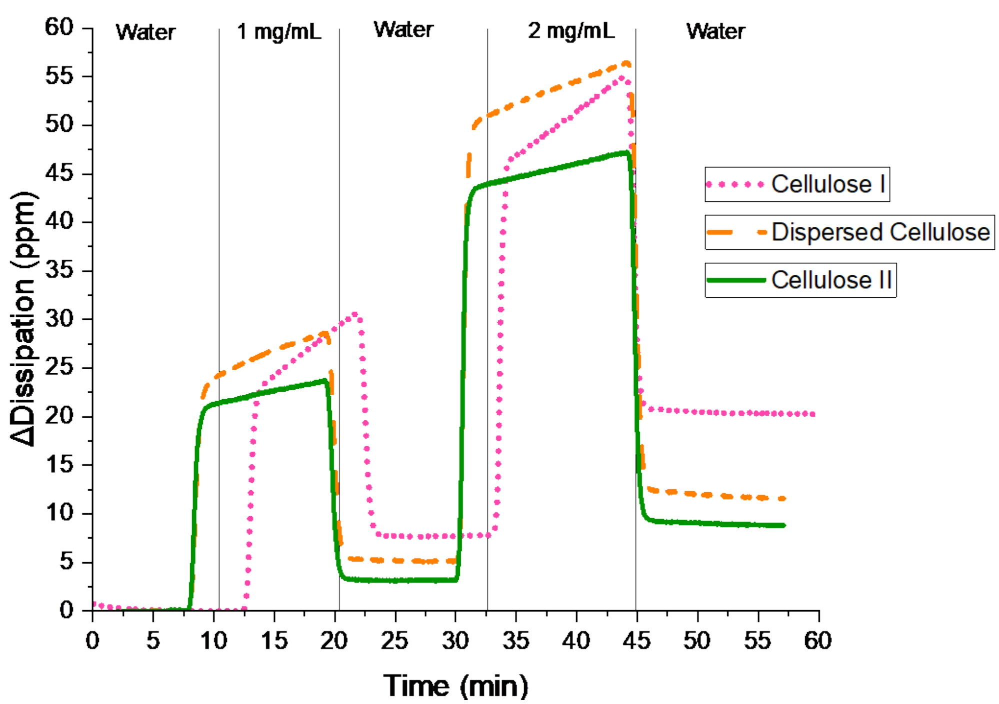

Figure 14. Dissipation Results for Permethrin in Cellulose Allomorphs (Model Films)

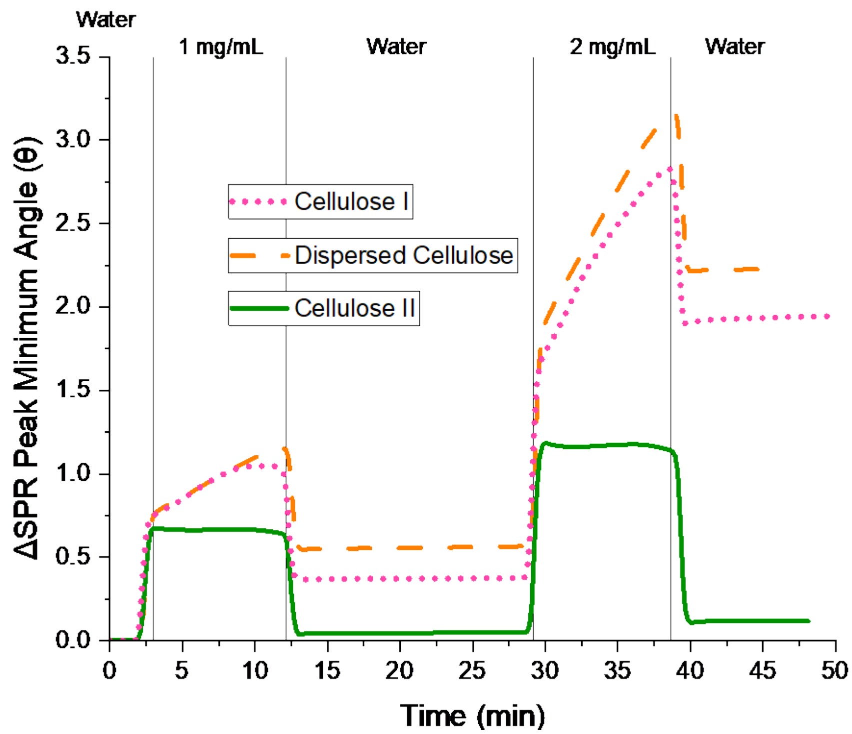


Figure 15. SPR Results for Permethrin in Cellulose Allomorphs (Model Films)

For permethrin, according to the change in frequency and dissipation measurements, there were interactions with all three allomorphs, especially cellulose I. Although, the SPR peak min angle change is less significant for the regenerated cellulose, there is still some interaction that is noticeable in the SPR measurement. It can also be seen that there was more irreversible change for the higher concentration. This can be due to the difference in surface area from the nanofibrillated cellulose (cellulose I) to the cellulose II allomorph. Because the cellulose I model film has so much surface area and hydroxyl groups at the interface of the permethrin, it can be the reason that it has the most interactions compared to the dispersed cellulose and cellulose II.

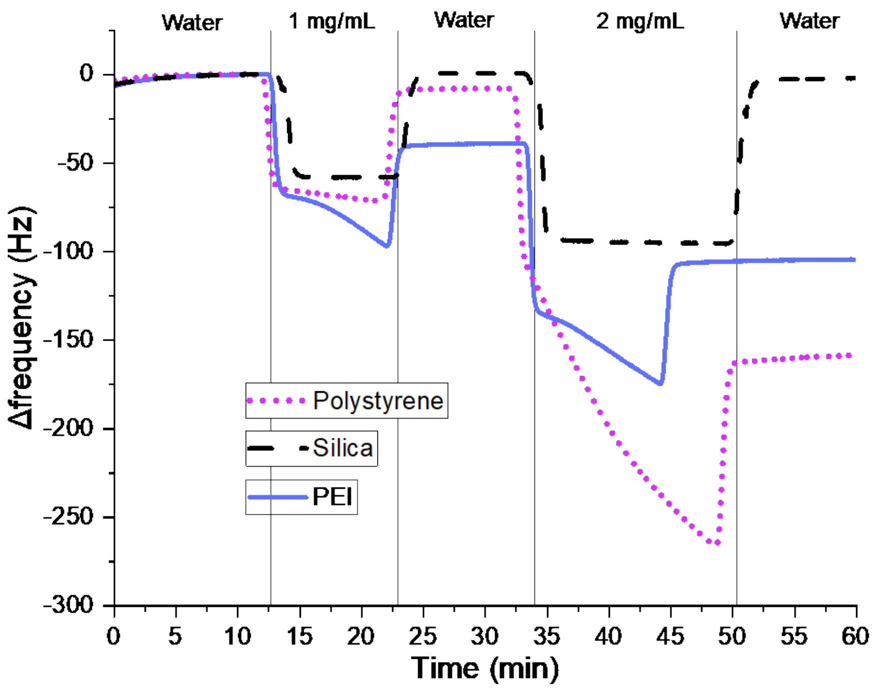


Figure 16. Frequency Results for Permethrin in Model Surfaces

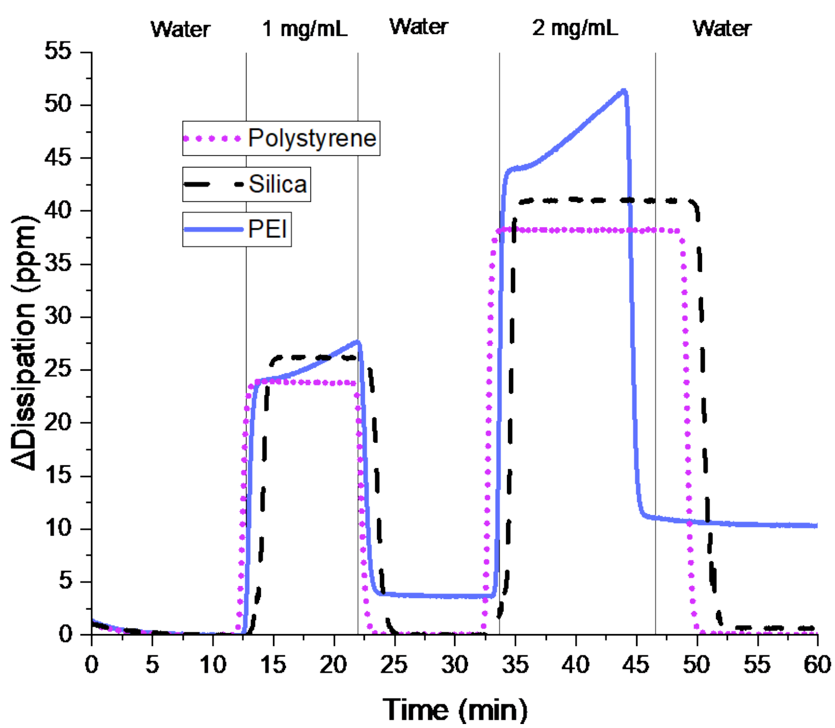


Figure 17. Dissipation Results for Permethrin in Model Surfaces

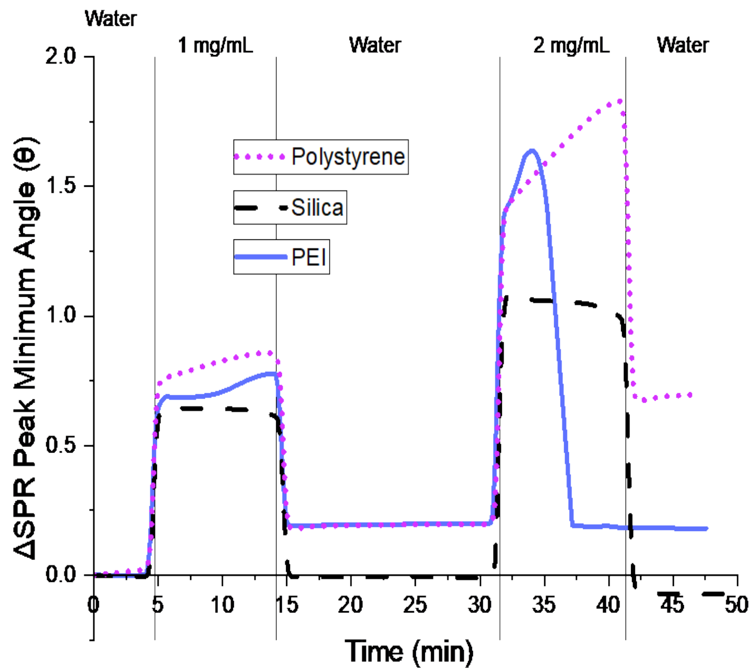


Figure 18. SPR Results for Permethrin in Model Surfaces

The permethrin flowed onto the model surfaces show that polystyrene shows higher adsorption than the other surfaces according to the QCM-D and the SPR. Though it did not have an effect on the dissipation, so the permethrin did not change the properties of the polystyrene. This is an important consideration for controlled release materials, because modifying the viscoelastic properties of the material can change the way they can be processed into different forms, affecting the manufacturing capability of the final products.

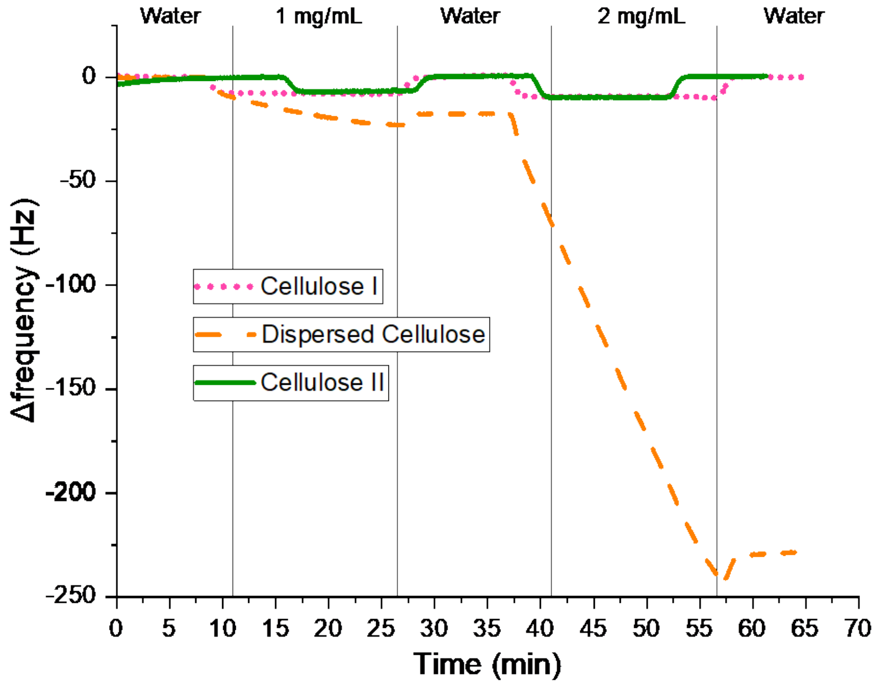


Figure 19. QCM-D Results for Deltamethrin in Cellulose Allomorphs (Model Films)

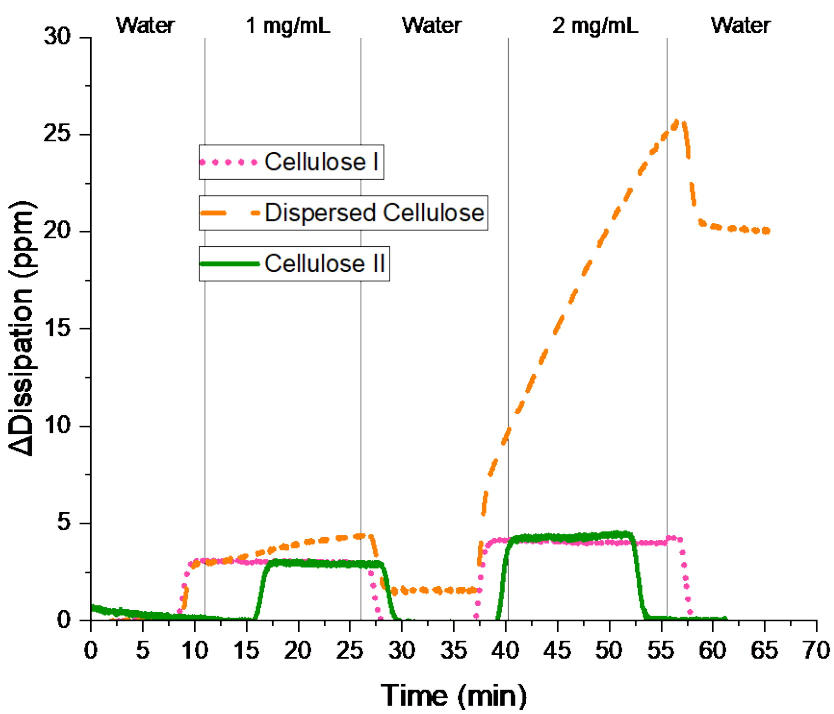


Figure 20. Dissipation Results for Deltamethrin Cellulose Allomorphs (Model Films)

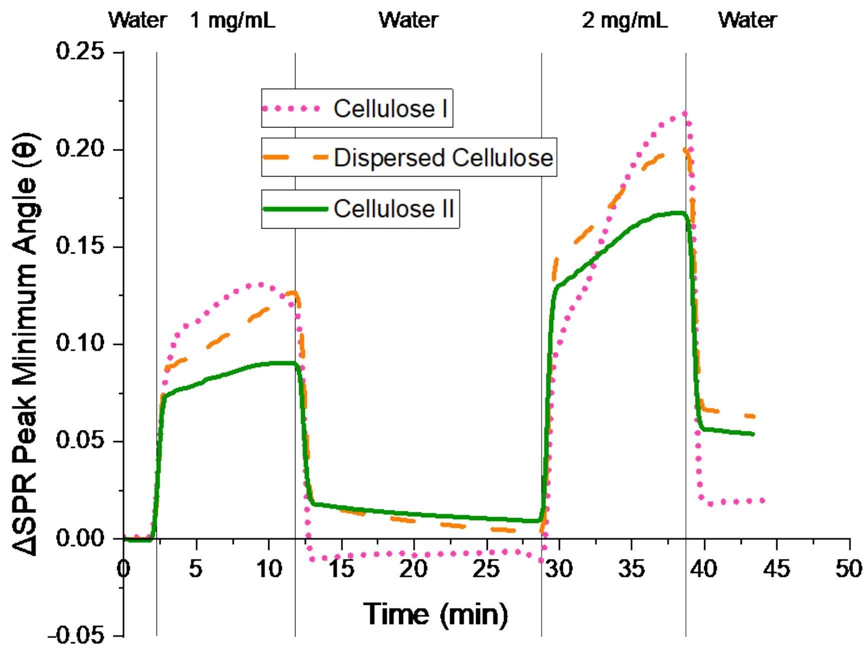


Figure 21. SPR Results for Deltamethrin in Cellulose Allomorphs (Model Films)

These results for the deltamethrin show an extremely high interaction with the dispersed cellulose for the QCM-D, but this is not supported by the SPR, so this result could be due to the interactions seen with the PEI. Due to the hydrophobicity of the AIs, there could have been an agglomeration of the deltamethrin particles in the aqueous media that caused this to happen, but it follows the SPR data that the higher concentration used results in more interactions with the DES dispersed cellulose.

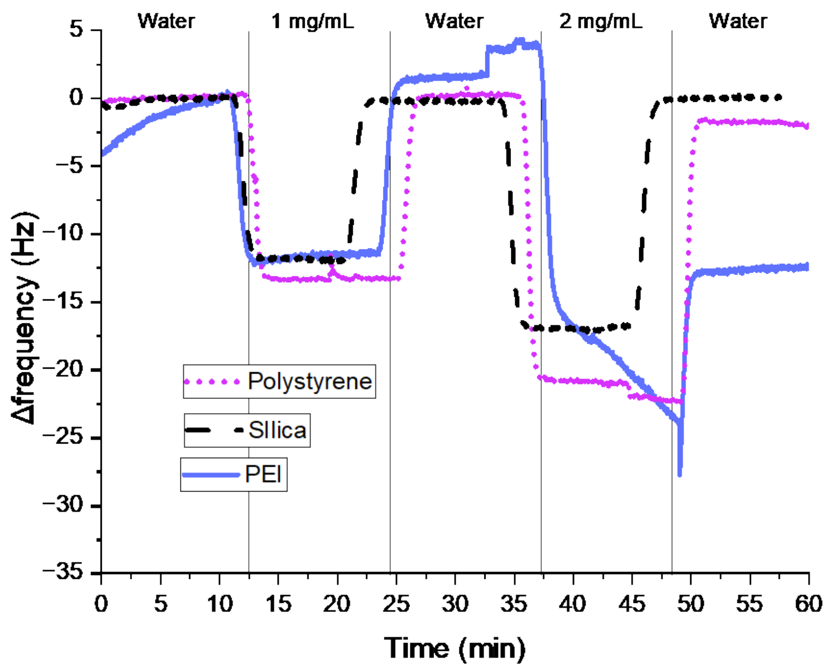


Figure 22. Frequency Results for Deltamethrin in Model Surfaces

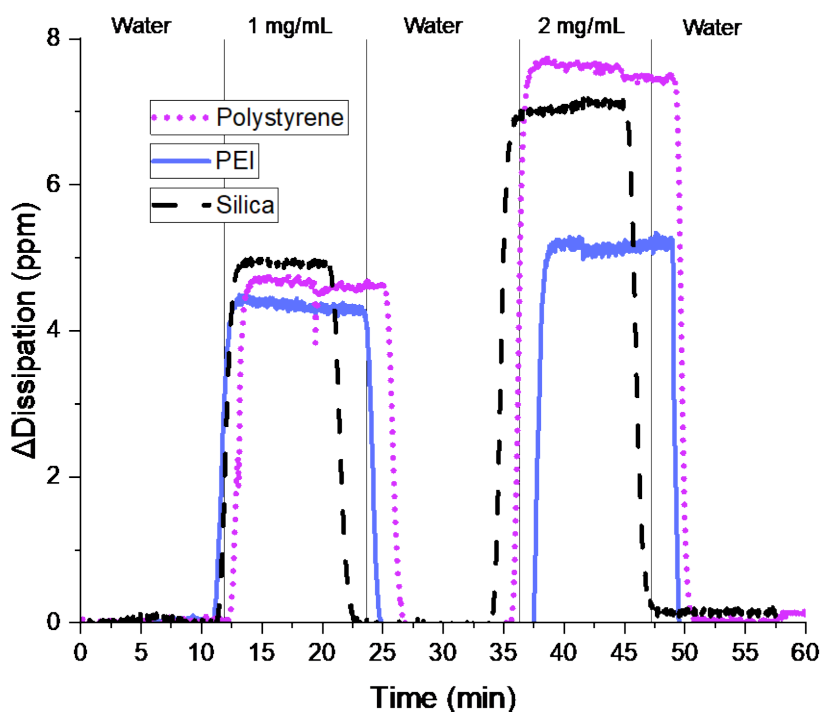


Figure 23. Dissipation Results for Deltamethrin in Model Surfaces

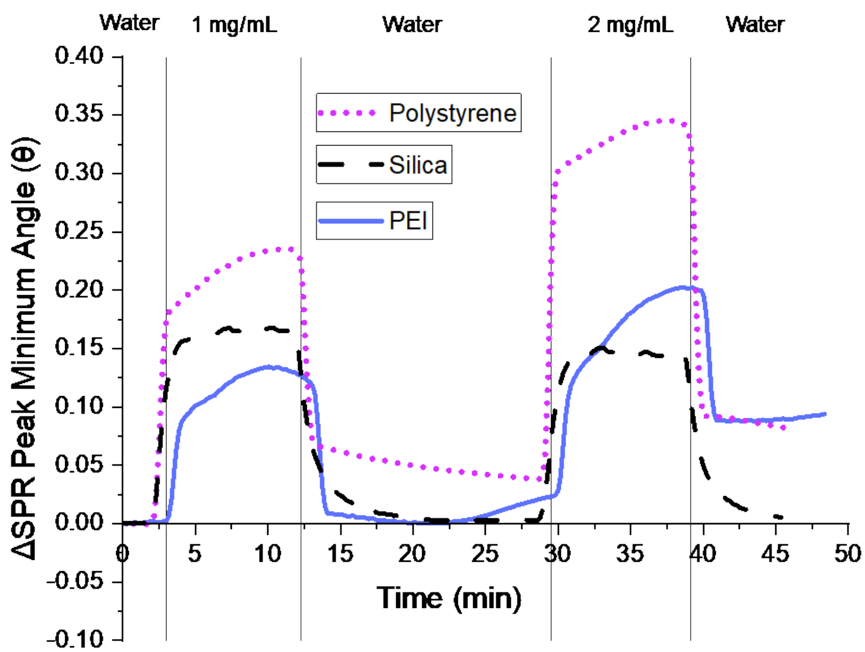


Figure 24. SPR Results for Deltamethrin in Model Surfaces

These results show that there are some significant irreversible interactions between PEI and deltamethrin which cannot explain the high change in frequency and dissipation for the dispersed cellulose. Because there is PEI underneath the different cellulose allomorphs, it is important to consider that some interactions can be a result of some PEI being exposed to the deltamethrin, but in the case of the dispersed cellulose, there was also a strong change of dissipation while this did not occur with PEI. Therefore, it can be seen that this PEI interaction is not the reason for the results of deltamethrin in the DES dispersed cellulose.

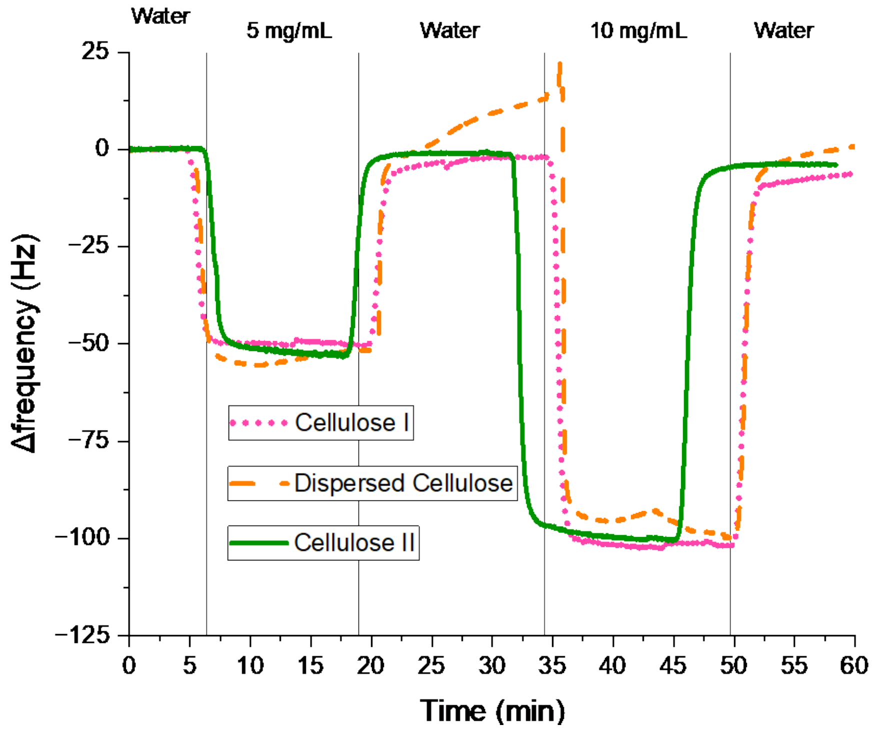


Figure 25. Frequency Results for Piperonyl Butoxide in Cellulose Allomorphs (Model Films)

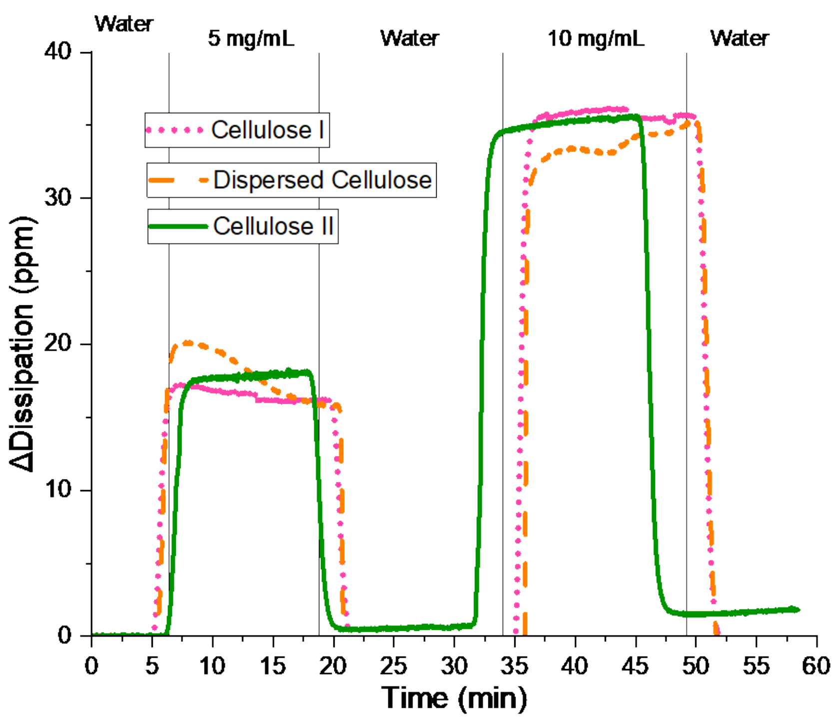


Figure 26. Dissipation Results for Piperonyl Butoxide in Cellulose Allomorphs (Model Films)

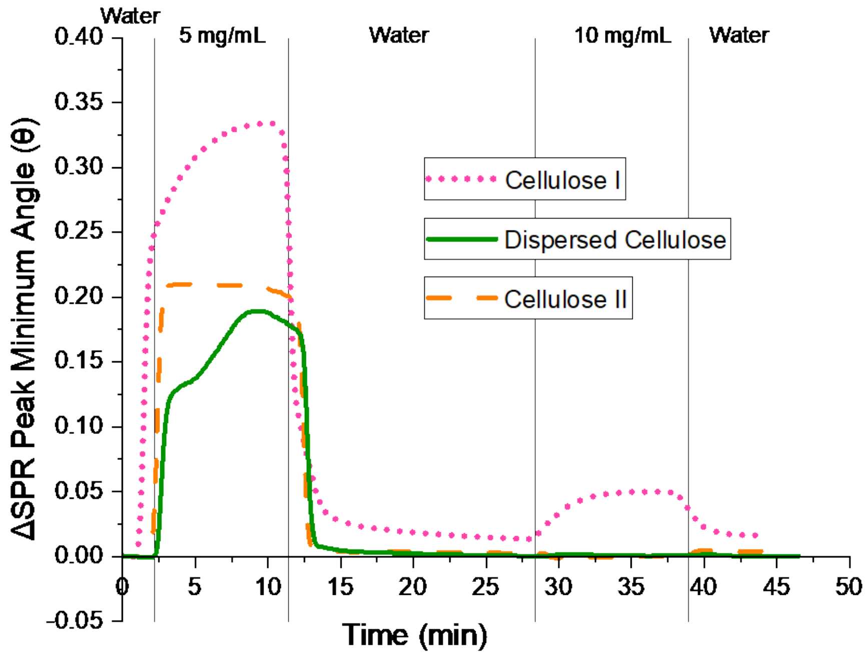


Figure 27. SPR Results for Piperonyl Butoxide in Cellulose Allomorphs (Model Films)

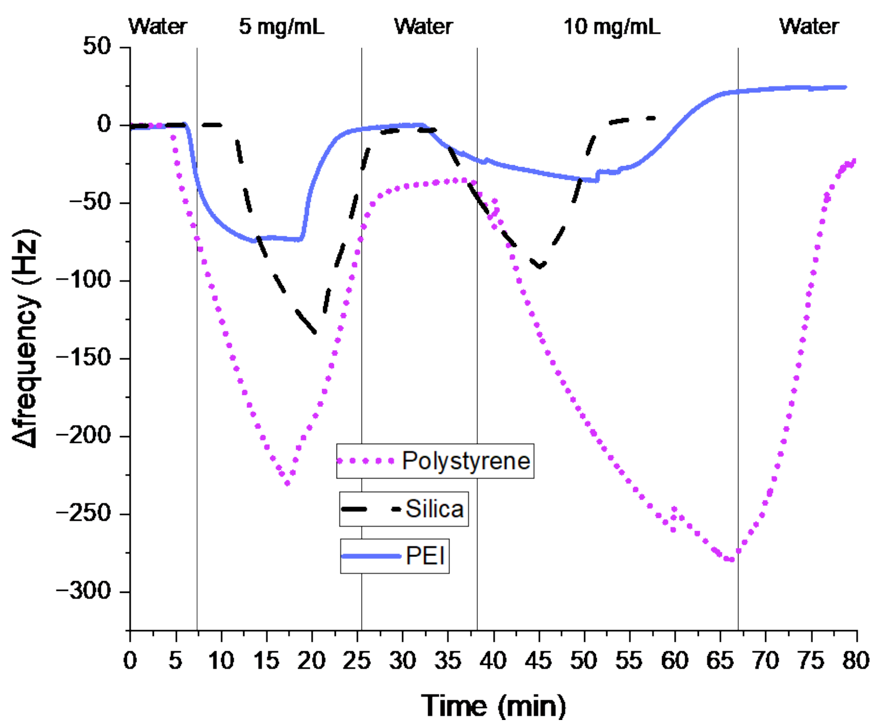


Figure 28. QCM-D Results for Piperonyl Butoxide in Model Surfaces

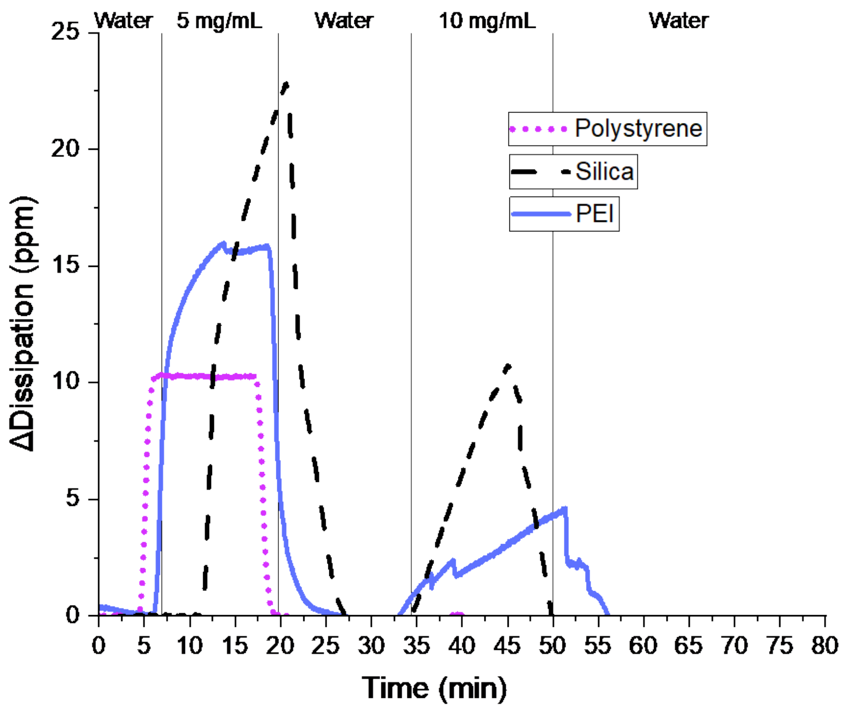


Figure 29. Dissipation Results for Piperonyl Butoxide in Model Surfaces

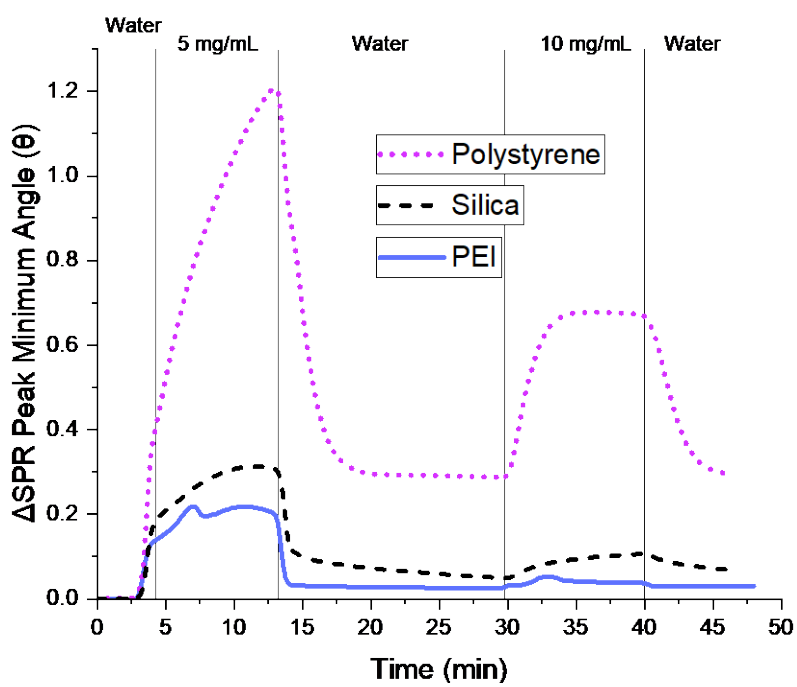


Figure 30. SPR Results for Piperonyl Butoxide in Model Surfaces

PBO has little to no irreversible interactions with any of the cellulose morphologies. This, along with the results from the silica shows that there are negligible interactions between PBO and hydroxyl groups no matter how many there are due to differences in surface area. It does, though, have some with polystyrene's aromatic groups. This could be because of the higher PBO concentration, but it can be seen in Fig. 21 that there was a large change in the surface of the polystyrene, but it was mostly reversible with only little PBO staying attached to the model surface. PBO also had no irreversible reactions with the any allomorphs of cellulose. Because PBO is now an essential component of insecticidal textiles for LLINs, its interactions with certain groups crucial. The pyrethroids, in most cases, cannot function properly without the presence of PBO, making it a deciding factor in what materials are valid for this type of purpose.

Table 1. Summary of QCM-D and SPR Results

| | **Δf (Hz)** | | | **Δd (ppm)** | | | **Δpeak min angle (θ)** | | |
|---|---|---|---|---|---|---|---|---|---|
| | **Delta** | **Perm** | **PBO** | **Delta** | **Perm** | **PBO** | **Delta** | **Perm** | **PBO** |
| **Surfaces** | | | | | | | | | |
| Silica | 0 | 2.28 | 0 | 0.18 | 0.66 | 0 | 0 | 0 | 0.062 |
| PS | 2.5 | 159 | 25 | 0.08 | 0 | 0 | 0.08 | 0.69 | 0.29 |
| PEI | 12 | 104 | 0 | 0 | 10 | 0 | 0.08 | 0.18 | 0.013 |
| **Allomorphs** | | | | | | | | | |
| Cellulose I | 0 | 119 | 6 | 0 | 20 | 0 | 0.018 | 1.94 | 0.01 |
| Dispersed | 243 | 93 | 39 | 20.19 | 11.7 | 0 | 0.06 | 2.23 | 0 |
| Cellulose II | 17 | 50 | 4 | 0.01 | 8.9 | 1.75 | 0.05 | 0.118 | 0.04 |

* Delta = deltamethrin, Perm = Permethrin, PBO = piperonyl butoxide

* Δf = change in frequency, Δd = change in dissipation

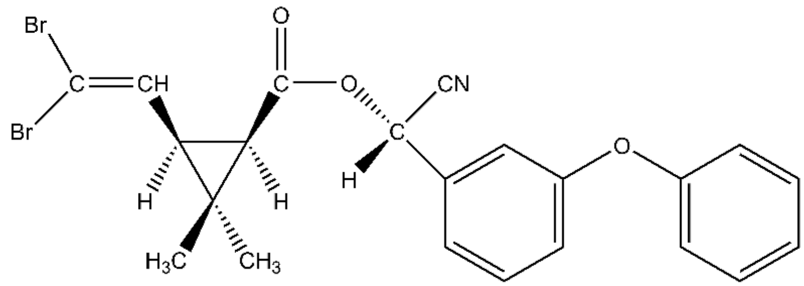

Figure 31. Deltamethrin Structure

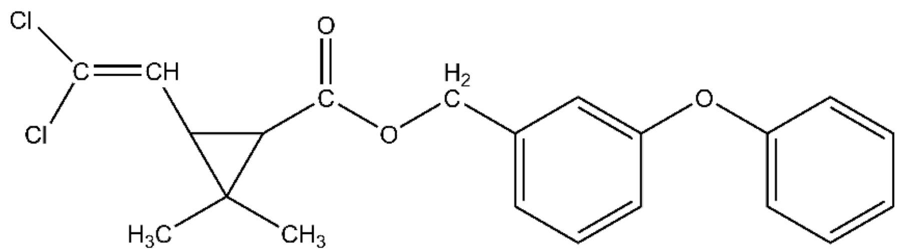

Figure 32. Permethrin Structure

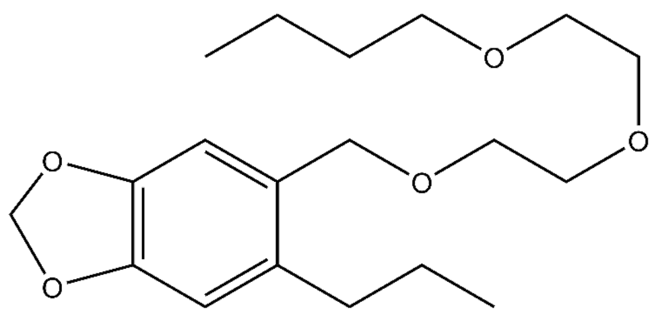

Figure 33. Piperonyl Butoxide Structure

Figure 34 shows the functional groups being modeled by the model films polystyrene, silica, and PEI. The purpose of using silica, polystyrene, and PEI sensors to quantify interfacial interactions with pyrethroids is to model different functional groups. Seen in Fig. 24, silica has hydroxyl groups, polystyrene has aromatic groups, and PEI has amine groups. These model the surfaces with various isolated functional groups with unique characteristics for adsorption seen in the Figure.

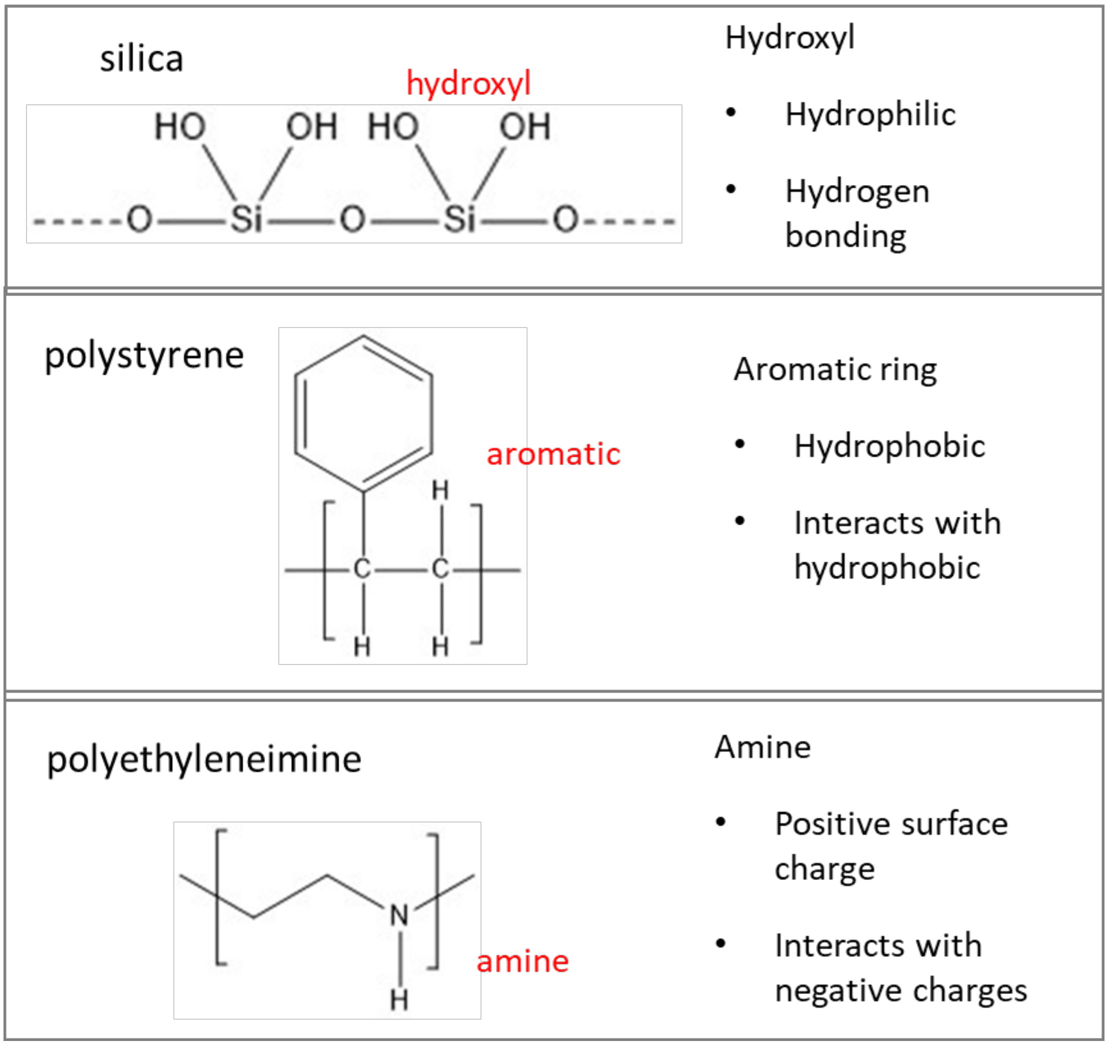


Figure 34. Model Films and Functional Groups

When the frequency goes down during adsorption of the active ingredient and this change is non zero after rinsing, then there is some irreversible change in mass. These can be explained by strong interactions and intermolecular forces (Israelachvili, 2011). For example, PS has strong hydrophobic interactions due to the aromatic structure, and because the deltamethrin, permethrin, and PBO are also hydrophobic, they both push away the water molecules and have these irreversible interactions consistently. Surface wettability would not have much effect in this set of experiments because the sensors are pre swelled in water, and water was flowed across the surfaces until stability was reached in the case that they were not sufficiently swelled prior to the experiment.

Often, the adsorption of pyrethroids is studied in soils and sediments, and one conclusion that has been reached is that due to their nature, more interactions can be seen with hydrophobic and nonionic compounds (Chaaieri Oudou & Bruun Hansen, 2002). According to (Zhou et al., 1995), aromatic groups of the surface sample is very important for the adsorption of nonionic, aromatic compounds. In this case, it explains the interactions between all the pyrethroids with the polystyrene surface due to the hydrophobicity of both.

Different interactions can occur between the pyrethroids and cellulose due to various fundamental interaction forces. In general, permethrin had higher interactions with most of the cellulose allomorphs than the other compounds. Looking at the structure of the permethrin versus the deltamethrin, there are few significant changes including deltamethrin containing Br instead of Cl. There is also an additional nitrogen in deltamethrin. These should be the only difference that is causing interactions.

Another aspect to consider is the potential of ionic liquid remaining on the surface even after it should be washed away with the water during storage and first step during the QCM-D and SPR. There could be some interaction of particles of the ionic liquid with the PEI surface underneath which causes it to remain on the surface with the cellulose II. Using what was found by Zhou, this ionic residue on the surface could explain why the pyrethroids had little to no interaction with those surfaces.

The deep eutectic solvent has more of a likelihood of remaining on the surface of the sensor, because they were only rinsed with water, and the DES used in these experiments is soluble in ethanol, showing more resistance to washing from water. This would leave behind the components of the deep eutectic solvent, the hydrogen bond donor and hydrogen bond acceptor

## 2.4 Conclusions

The driving force of the interactions is likely strongly related to the hydrophobicity of the active ingredients and the aromatic groups present in the permethrin and deltamethrin and the polystyrene surface. Lignin has been studied with hydrophobic active ingredients for this same reason. It has strong irreversible interactions with other hydrophobic particles, similar to that of the pyrethroids and PBO in this study. The objective to evaluate the interactions for a potential controlled release material for these substances shows that cellulose in forms other than in deep eutectic solvent show little interaction. A device made from biobased sources should include a component or a coating that is considered hydrophobic in nature. For example, unbleached cellulose, meaning cellulose pulp prior to the removal of lignin, would most have the best adsorption capability for these active ingredients.

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# 3. Chapter 3

## Stability of pyrethroids in ionic liquid

### 3.1 Introduction

The objectives of this work are to evaluate deltamethrin, permethrin, and PBO's ability to be manufactured into a regenerated cellulose fiber yarn using the Ioncell® process. The Ioncell® process utilizes ionic liquid [DBNH][OAc] to dissolve 13 wt% cellulose dissolving pulp under a temperature of 90 ℃. Similar to LLINs, the processing opportunities involve incorporation of insecticides within the fiber matrix or using a coating on the surface. A superior net is made when incorporation is the method of choice, because it will result in a longer lasting net. This also applies to many other controlled release applications, so testing the ability of the AIs to remain stable during the dissolution of the cellulose.

#### 3.1.1 Properties of Pyrethroids

Pyrethroids chemical properties include their hydrophobicity. This is also true of PBO. They also have many carbon-hydrogen bonds which makes most of the major degradation easy to identify in the spectra. Ester cleavage can also be seen in NMR which is another mechanism of degradation of pyrethroids which could be seen via NMR. These changes will cause a reduction in the function of the compounds, removing their insecticidal properties. Thermal stability of pyrethroids have been studied primarily in aqueous environments and soils.

### 3.1.2 NMR Techniques

In order to identify peaks with Nuclear Magnetic Resonance, multiple different bond correlations are necessary. In order to see any changes in the structure, only proton and HSQC is necessary due to the common degradation compounds. For characterization of the unknown peaks in the spectra, though, more tests including HMBC are needed. For this reason, these peaks were interpreted from existing references in this work (Claridge, 2016). Degradation of compounds under certain processing conditions is important to evaluate prior to conducting any small or large scale trials. The goal of this work is to identify potential degradation compounds of permethrin, deltamethrin, and PBO in [DBNH][OAc] under time and temperature conditions similar to that of the Ioncell® process because it is an effective method for regenerating cellulose on a commercial scale.

## 3.2 Materials and Methods

### 3.2.1 Sample preparation

Pyrethroids were tested in [DBNH][OAc], an ionic liquid that can successfully dissolve cellulose. The tubes used were Wilmad 17.8 cm length and 0.38 mm wall thickness that can be used with frequencies up to 600 MHz. For this set of experiments, no cellulose was added to ensure the solution wouldn't become too viscous and prevent a good reading by the NMR. The equipment requires a fully dissolved sample in order to conduct solution state tests. By analyzing the stability of the insecticides in the solvent system, an accurate prediction can be made of the stability during the spinning process.

The insecticides permethrin, deltamethrin, and piperonyl butoxide were dissolved directly into the ionic liquid, and there were no solids that disrupted the NMR test which proved this dissolution was successful. These are the same materials that were used in the QCM-D and SPR.

10 wt% of permethrin was dissolved into ionic liquid (preparation in Section 2.2.1). Before heating (0 hours), a 200 µL sample was taken and mixed with 400 µL of deuterated DMSO. A deuterated solvent ($D_2O$) is necessary for running NMR spectra because the hydrogens in water would overwhelm the spectra and make it difficult to identify the peaks of the compounds of interest. This mixture was heated at 90 °C in a water bath and 200 µL samples were taken at 2 hours for deltamethrin, 0, ½, 1, 2, 3, 4, 5, and 8 hours for permethrin, and 0, 2, 4, and 8 hours for PBO.

### 3.2.2 Nuclear Magnetic Resonance Studies and data processing

The tests were conducted using a Bruker 500 MHz NMR in solution state. For each sample, a proton spectrum was collected using zg30 pulse program with 16 scans, and an HSQC (Heteronuclear Single-Quantum Correlation Spectroscopy) was collected using hsqcetgp pulse program and 2 scans. All the spectra were processed with Fourier transform and baseline corrections as well as calibrated against the DMSO peak at 2.5 ppm.

## 3.3 Results and Discussion

### 3.3.1 Assignment of Peaks

The HSQC spectra can be seen in Figs. 25-27 which correlate the hydrogens in the compound to the carbons to which they are connected by a singular bond.

The assignments of the peaks were done in collaboration with Alistair King at VTT and adapted from the Spectra Database for Organic Compounds (SDOC) using a combination of Heteronuclear Single Quantum Correlation (HSQC) and Heteronuclear Multiple Bond Correlation (HMBC). The deltamethrin HSQC in Fig. 25 shows an area where no significant peaks of the ionic liquid could be found because the ionic liquid blocked many of the signals of the deltamethrin at lower ppm.

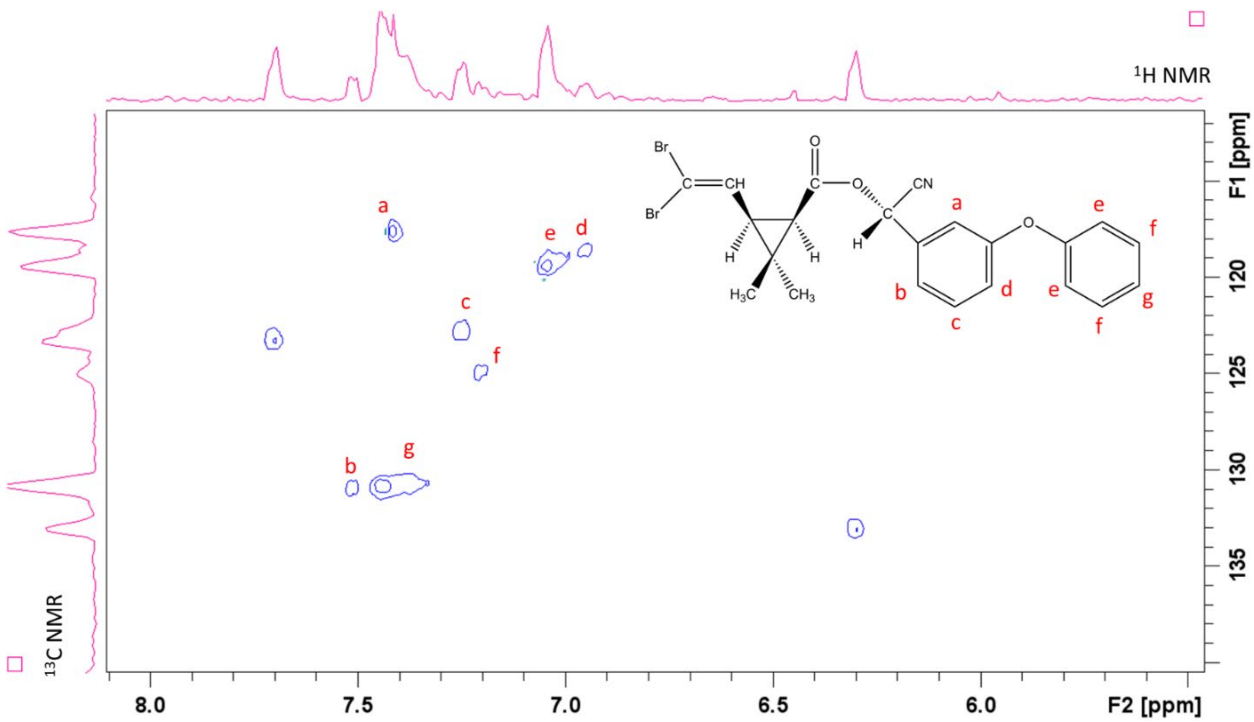



Figure 35. Deltamethrin Peak Assignments from HSQC

In Figure 35, many of the deltamethrin peaks can be identified via the hydrogen and carbon singular connections. Because the deltamethrin was in combination with ionic liquid in this sample, some of the peaks can be obscured by those of the solvent. The DMSO, though, does not obstruct any of the peaks.

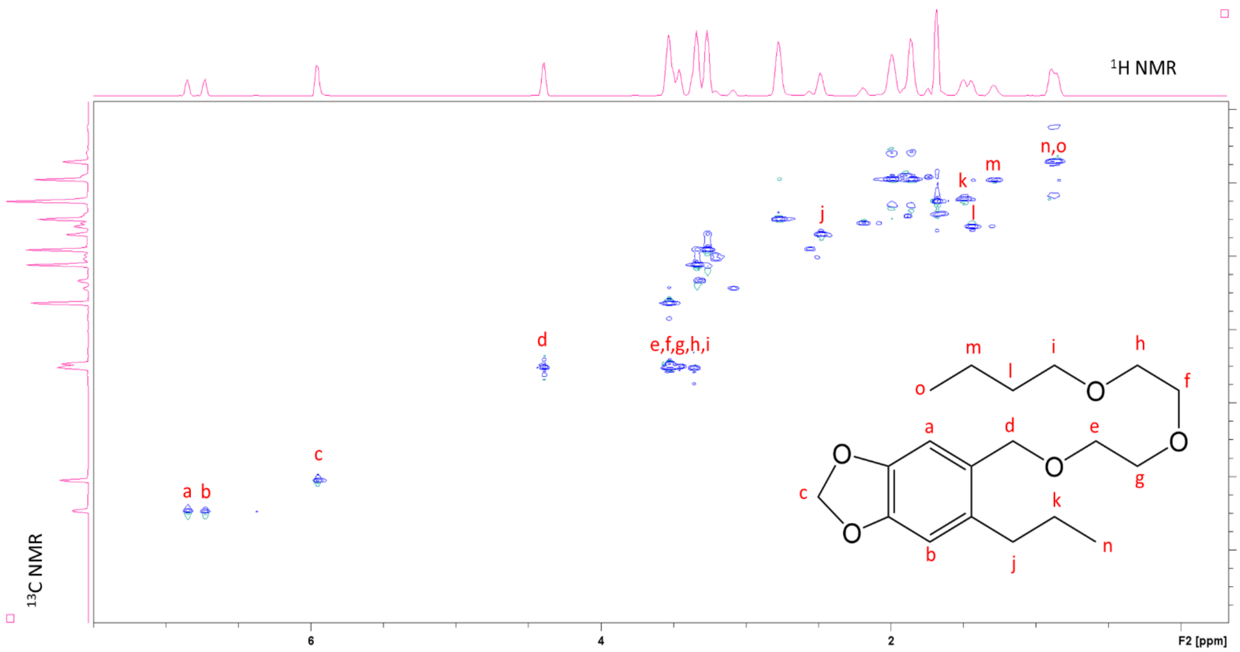



Figure 36. Piperonyl Butoxide Peak Assignments from HSQC

The HSQC measurement of PBO can be seen in figure 36. Because much of the structure is hydrogen-carbon singluar bonds, many of the identifiable peaks can be shown. This was determined from external sources and compared to the measurement of the ionic liquid alone to determine which peaks were visable and did not overlap with those if the ionic liquid.

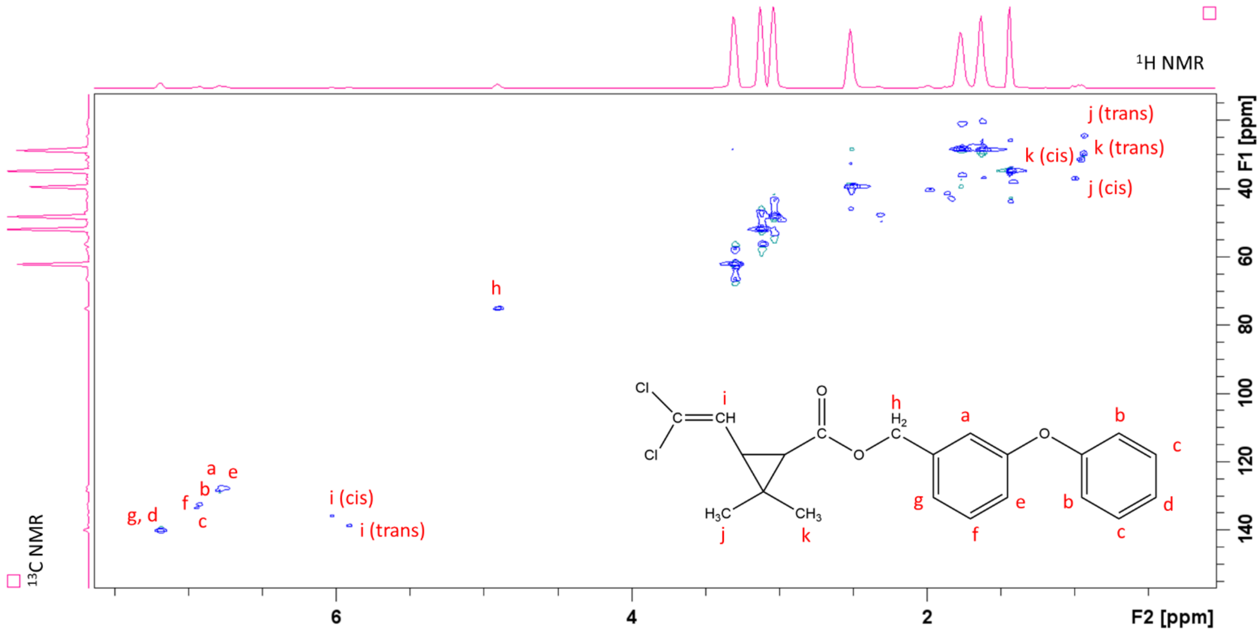



Figure 37. Permethrin Peak Assignments from HSQC

The permethrin peak assignments shown in the HSQC spectrum were also interpreted from the reference library which assigned these peaks using a combination of HSQC and HMBC. Because the product used to make this sample had a mixture of cis and trans isomers, there are different peaks labeled for cis and trans carbon-hydrogen correlations. This is important to identify in the sample because in some conditions, trans-permethrin was degraded more rapidly (Qin & Gan, 2006).

3.3.2 Degradation Study

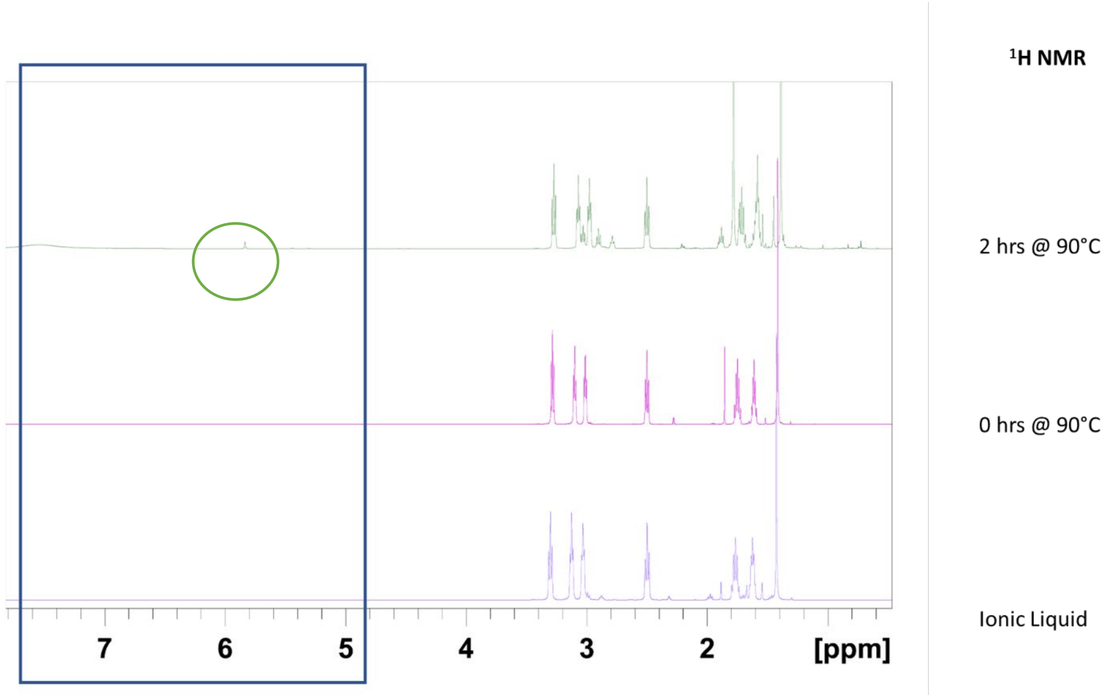



Figure 38. Deltamethrin Degradation by Proton NMR

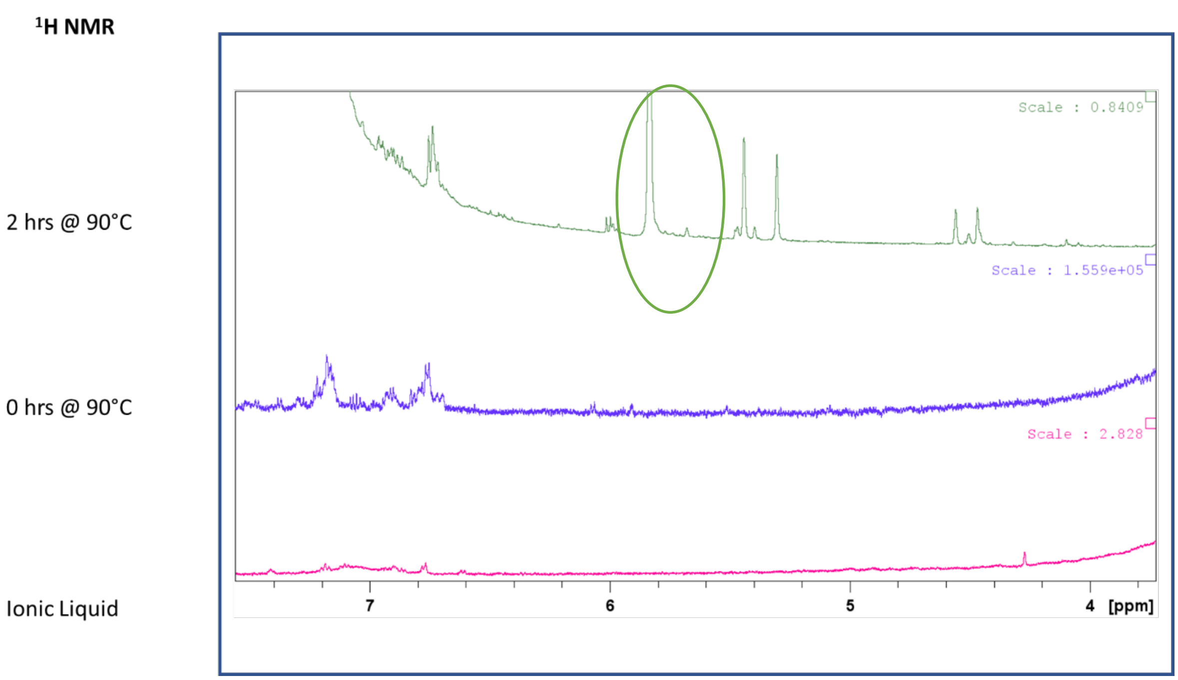



Figure 39. Deltamethrin Degradation Detail by Proton NMR

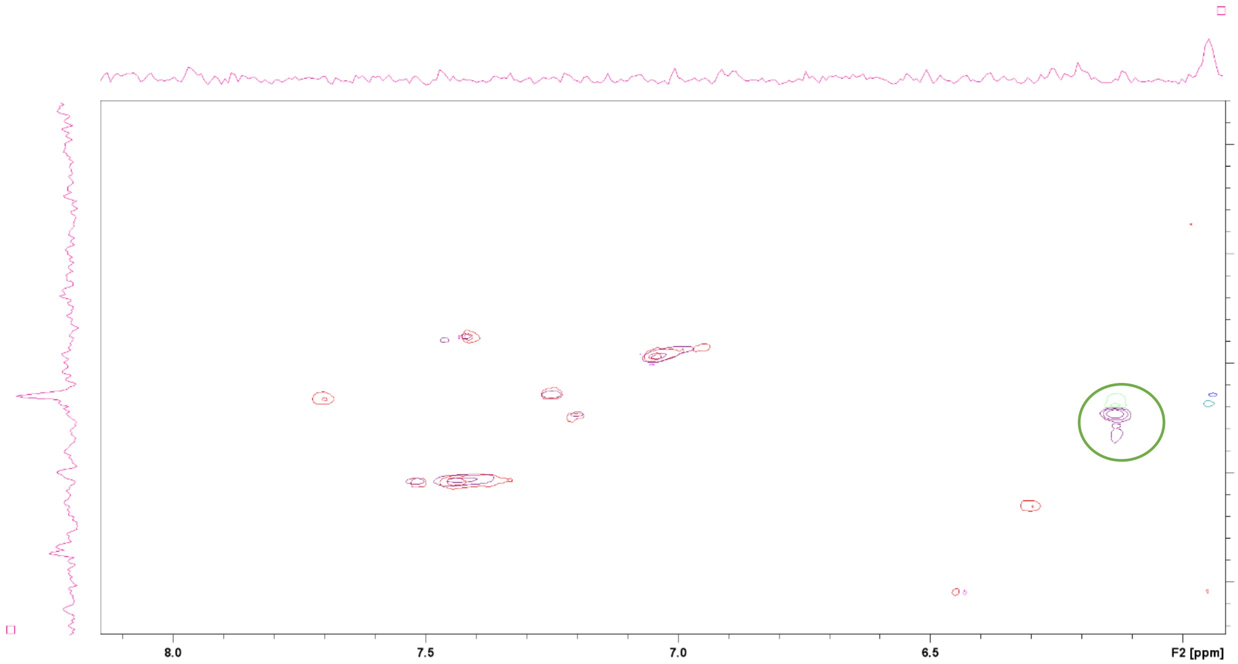



Figure 40. Deltamethrin Degradation Detail by HSQC

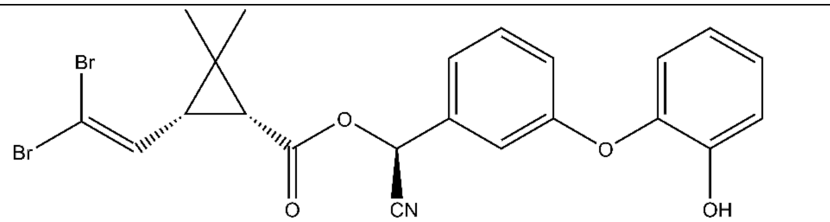
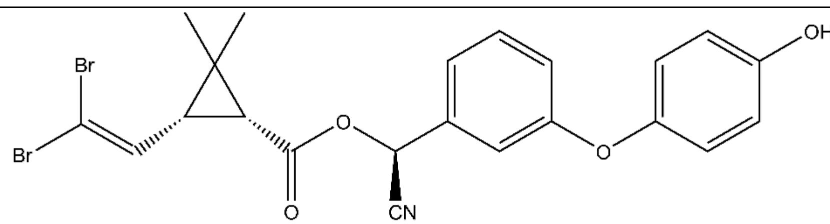
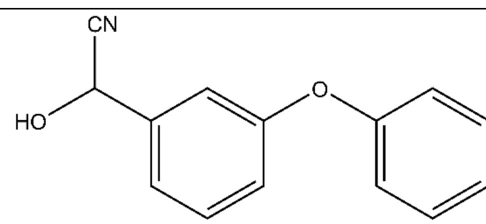
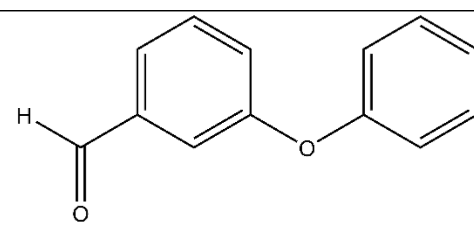
3.3.2.1 Degradation Compounds of Deltamethrin

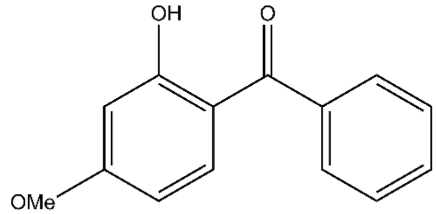
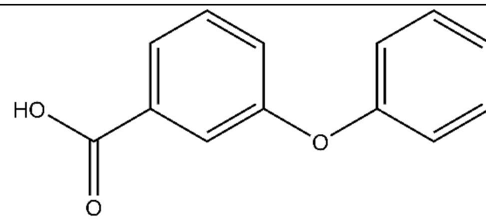
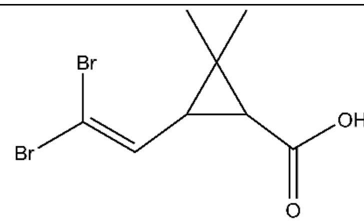
In this spectrum, the purple is representative of the deltamethrin, and the red is representative of the ionic liquid peaks. As seen the Fig. 29, around the proton chemical shifts 5 to 8 ppm where some of the characteristic deltamethrin peaks occur, no ionic liquid peaks can be seen, but new ones can be found in the comparison of the spectra.

There are some known degradation compounds of deltamethrin, and it has been studied previously how easily it can be hydrolyzed and oxidized in aqueous solvent systems (Aiello et al., 2021). This can be an issue when trying to use the insecticide in ionic liquid since it absorbs water easily despite it being reversible. Additionally, regeneration of cellulose from ionic liquid dissolution is done in a water bath, so it is highly likely that any deltamethrin left in the cellulose II system would degrade into these non-insecticidal degradation products.

Since there are new peaks appearing in the proton spectra, it suggests that new protons are attaching to the structure. Looking at the HSQC in Fig. 30 can give more detail on the carbon hydrogen bonds. There is a new carbon hydrogen correlation circled in Fig. 29 that is not present in the ionic liquid or unheated. These could be due to a shift that occurs when changing into 2-OH or 4-OH deltamethrin since a carbon hydrogen is being replaced by an OH group.

Table 2. Deltamethrin Degradation Products

| Name | Chemical Structure |
|---|---|
| 2-OH deltamethrin |   |
| 4-OH deltamethrin |   |
| α-hydroxy-3-phenoxy-benzeneacetonitrile |   |
| 3-phenoxybenzaldehyde |   |

| | |
|---|---|
| 2-hydroxy-4-methoxy benzophenone |  |
| 3-phenoxybenzoic acid |  |
| *cis*-decamethrinic acid |  |

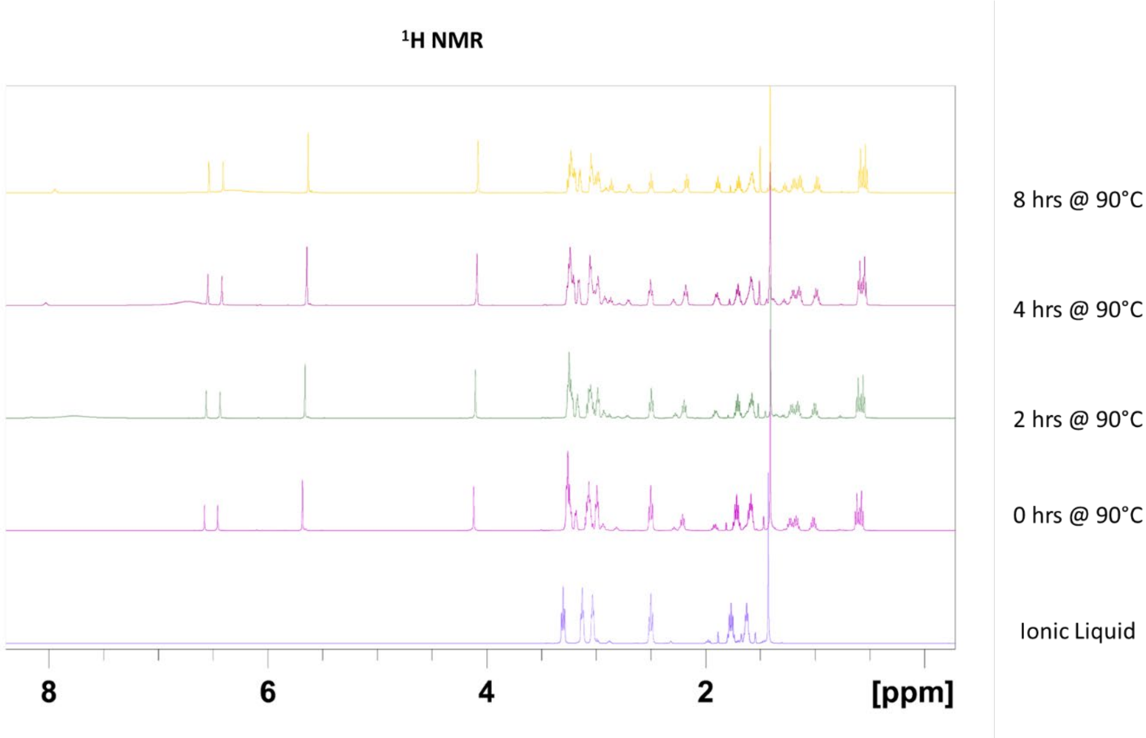



Figure 41. PBO Degradation by Proton NMR

It can be seen in Figure 41 that there is no significant reduction in peaks or new peaks to be found. Due to PBO's structure, it would be very clear if any breakage of hydrogen bonds had occurred because of its many hydrogens as well as hydrogen-carbon correlations. Its structure of carbon- carbon connections should be very stable against thermal degradation in the ionic liquid, but these would be more visible in a carbon-carbon correlation spectrum.

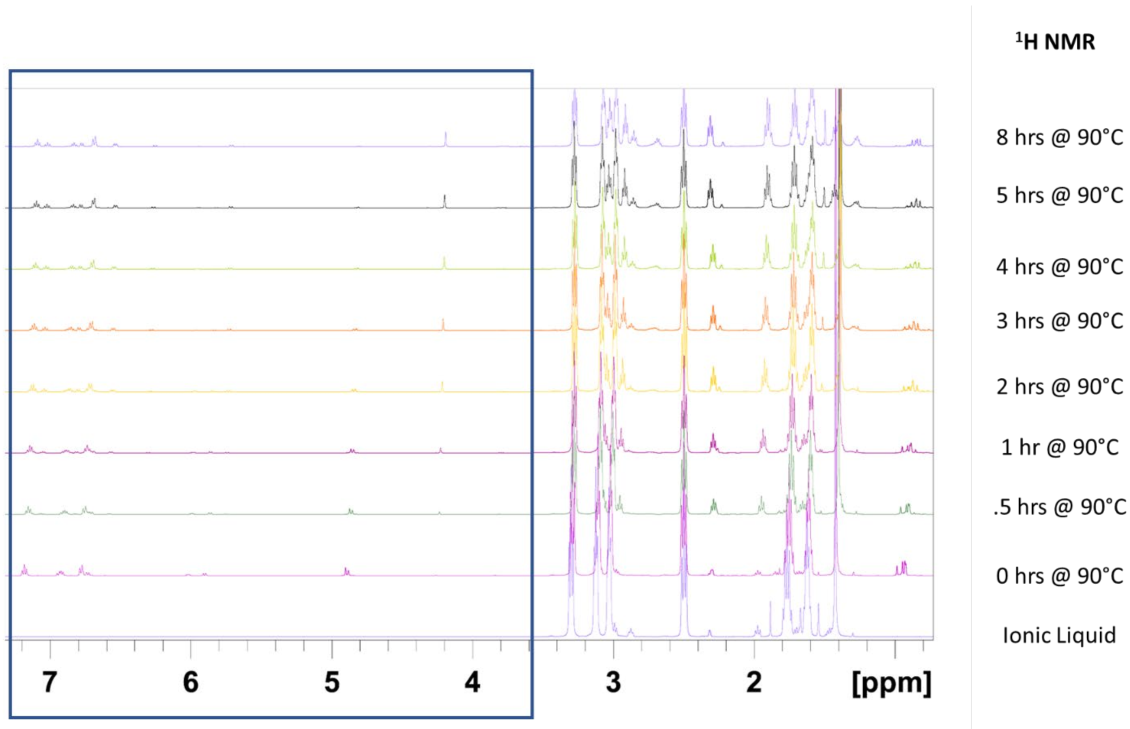



Figure 42. Permethrin Degradation by Proton NMR

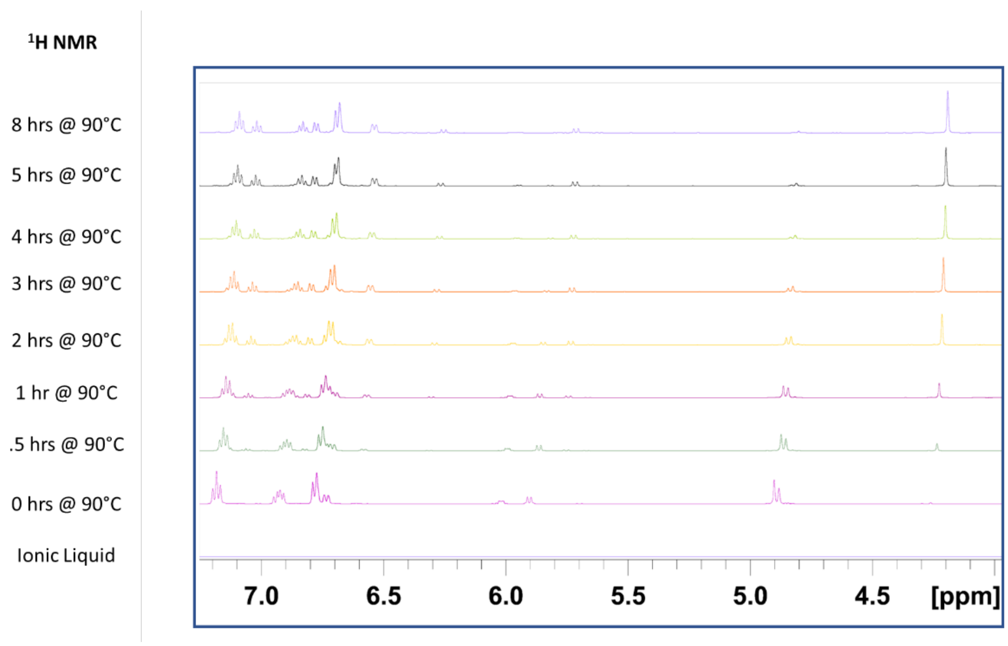



Figure 43. Permethrin Degradation Detail by Proton NMR

3.3.2.2 Degradation Compounds of Permethrin

Many studies of the resultant degradation compounds of permethrin in sediment and soil environments (Qin et al., 2006). These degradation pathways can predict the ways in which permethrin may degrade in controlled ionic liquid environments. In soil, both cis and trans permethrin has been found to undergo ester cleavage in addition to hydrolysis (Qin & Gan, 2006).

Hydrolysis products have also been studied in terms of the different types of pyrethroids. Pyrethroids can be categorized into two types: Type I pyrethroids are esters of primary alcohols, whereas type II pyrethroids are esters of secondary alcohols that contain a cyano group at the α-carbon of the alcohol. Permethrin is considered a type I pyrethroid and deltamethrin is type II (Nishi et al., 2006). These differences in structure can have an effect on the way they degrade in certain solvents, and the presence of water during the dry jet wet spinning process. Seen in Figure 44, these degradation products remove a hydrogen from the system, so the only possibility is that the h hydrogen in figure 43 is being removed and bonding with the ionic liquid or one of its degradation products. This shows that if something is degrading within the permethrin structure, it is not resulting in one of the compounds seen in figure 44, so it can still have its insecticidal impact.

In the environment, though, it has been found that permethrin is more stable that other pyrethroids. For example, permethrin remained undecomposed after 10 days when other pyrethroids were decomposed within 24 hours, although deltamethrin was not considered in this study (Miyamoto, 1976). Many studies on the degradation of permethrin also refer to microbial degradation which is different than the results expected from thermal degradation in an ionic solution, so more tests should be gathered on this topic pertaining specifically to ionic liquids.

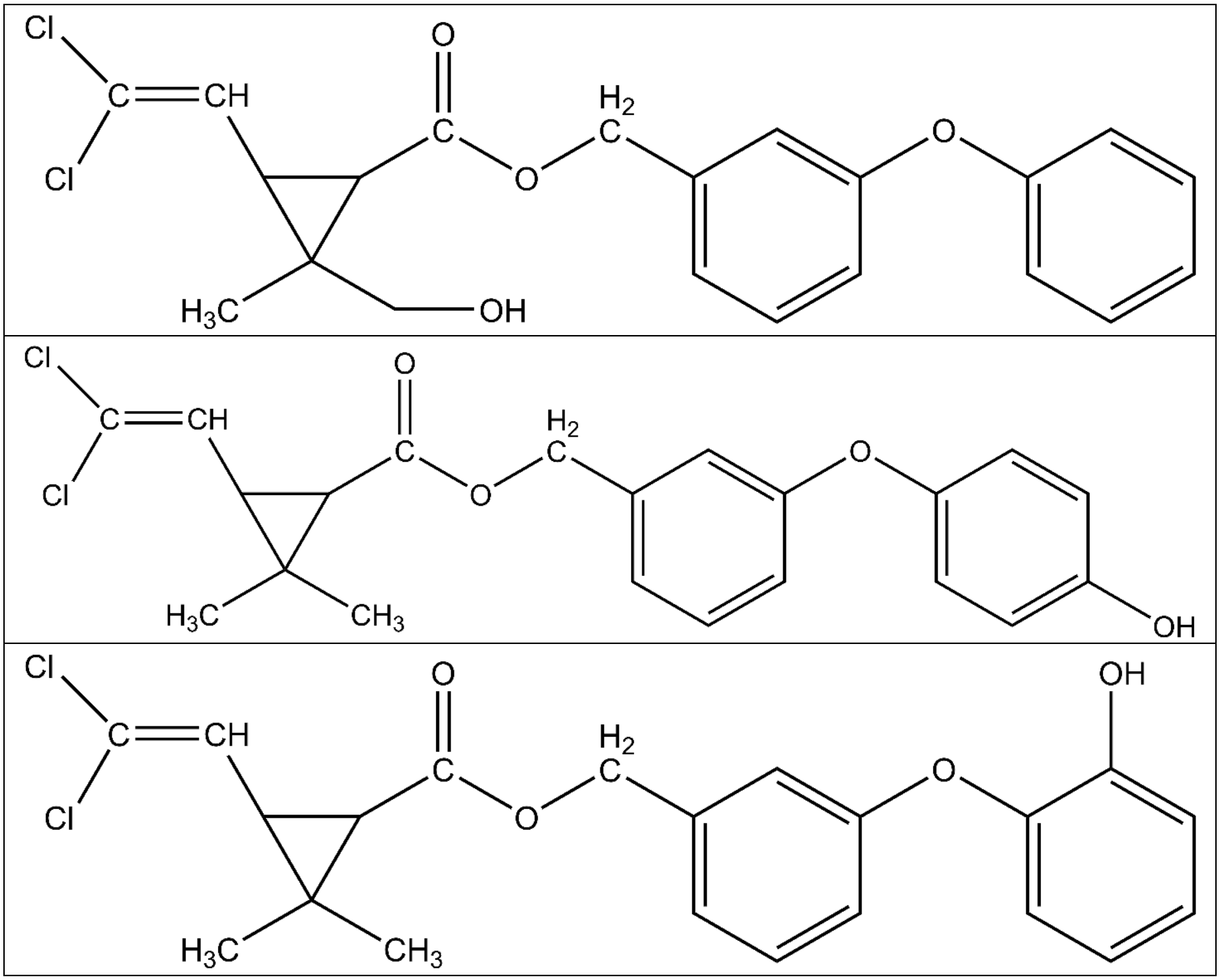


Figure 44. Permethrin Degradation Compounds

3.3.2.3 Degradation Compounds of Ionic Liquid

Degradation was not found to occur for permethrin or PBO, but the ionic liquid has been found to undergo reversible hydrolysis at prolonged temperatures. Seen in Fig. 34, hydrolysis of the ionic liquid can result in [APPH][OAc] and then condense into APPAc (Guizani et al., 2020). These would not be detected by the NMR spectra, but the degradation compounds can have some unknown reactions with the insecticide. Further studies and more data will need to be collected to correctly identify the new compounds in the spectra.

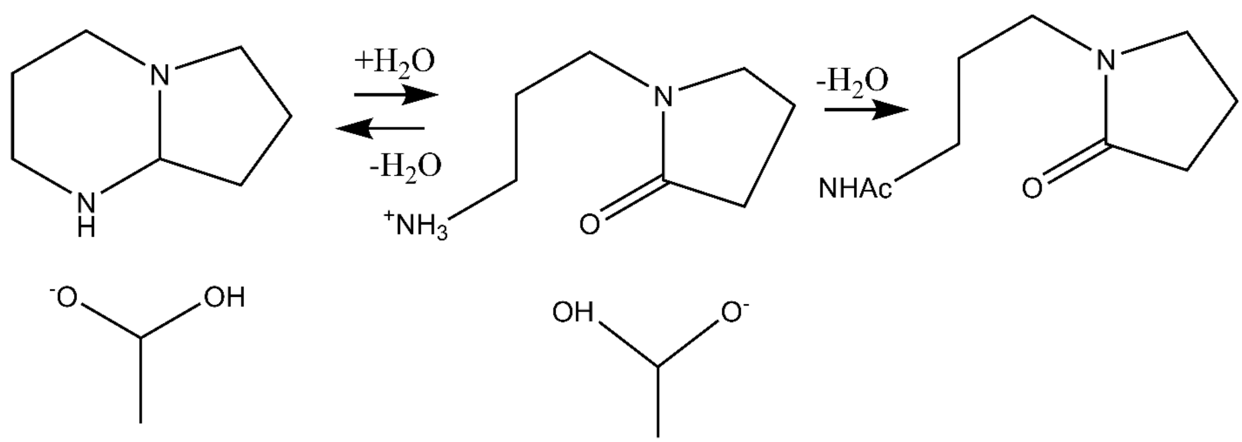



Figure 45. Degradation of Ionic Liquid

## 3.4 Conclusions

According to the objectives of this work, it appears that permethrin and PBO remain relatively stable in the ionic liquid environment although there is something occurring within the structure of permethrin. Deltamethrin degraded significantly after only 2 hours under 90 °C. In addition, there can be some slight degradation and hydrolysis happening to the ionic liquid under these conditions, which has been studied and confirmed to still be effective at dissolving and supporting the regeneration of the cellulose pulp (Guizani et al., 2020). More information should be collected to identify exactly the new peaks in the system, but permethrin and PBO are the best choices for utilization in biobased LLINs based on the Ioncell® method of fiber spinning.

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SDOC. *Spectral Database for Organic Compounds*

# 4. General Conclusions and Future Work

The purpose of these studies is to decide what kind of materials and methods will work well for the absorption of insecticides for controlled release applications. Seeing that permethrin and PBO had little degradation in the ionic liquid solvent, they should be good options for regenerated cellulose materials. One problem with this is that PBO had very little interactions with the cellulose II, and permethrin only had some irreversible bonding. A hydrophobic material is ideal for these insecticides, because it will reduce the likelihood of the ionic liquid absorbing water and degrading it and the insecticide as well as encourage stronger interactions leading to longer lasting controlled release materials.

The pulp and paper industry has developed ways of dissolving lignin, but it would be ideal in this case to be able to directly dissolve lignin-containing cellulose in the ionic liquid for generating insecticidal fibers. It has been found that [DBNH][OAc] can dissolve lignin contents over 15%, so one proposed method of spinning insecticidal cellulose fibers is to utilize unbleached raw material in order to optimize the adsorption capability (Wang et al., 2019).

Overall, permethrin and PBO have the most potential to be used in controlled release regenerated cellulose materials, but the release rate can be optimized by using coatings with deep eutectic solvents or other biobased materials like lignin containing nanocellulose.

References

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