

# Chemi-Code: An Innovative Method for Wood Product Tracking

by

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# Abstract

Chain of custody in the forest sector is very dependent on effectively tracking products through the supply chain and manufacturing processes, including sawmilling, drying, planing, and pulp processes. The effectiveness of a tracking system is largely influenced by the characteristics of the process it works within, the nature of the tracking system being used, and increasingly by the penetration of technologically advanced material tracking methods into on-the-ground CoC practices. A variety of CoC systems that exist in the global marketplace accommodate the use of advanced materials tracking systems as a tool for their implementation. These advances not only offer the potential to reinforce the traceability of products in inventory, but also promote maintenance of their certified status between the various organizations that exist along the wood product supply chain, and ultimately to the end consumer.

In the past, a number of different product tracking methods have been used, all of which suffer certain shortcomings in the challenging environment of the forest industry, and the extremely complex nature of Chain of Custody tracking. This work explores the development of a novel material tracking method using the innate IR signatures of polymeric compounds, varied by compound and concentration to develop millions of potential combinations, and consequently millions of unique identities. The combined variation of multiple IR peak frequencies and magnitudes provide the conceptual basis of a chemical barcode system, named “Chemi-Code”, to be explored.

To prove the validity of this concept, a series of polymers were assayed for suitability in such a system by tracking their IR response stability in the presence of solar UV radiation and over time. As well, the feasibility of vary-

## *Abstract*

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ing polymer concentration, and subsequently identification of concentrations by DRIFT spectroscopy was explored by constructing response curves between polymer concentration and peak absorbance, and assessing associated error.

Seven polymers were identified and assessed. Only two of these polymers were found to be sufficiently stable for use in the context of the forest industry, and of those two, only one behaved in a manner that would allow peak absorbance to be used as an identifiable chemical variable. Although only one of the seven polymers was suitable for use in the “Chemi-Code” system, the study did demonstrate the validity of the concept by showing that polymers can be exploited for use in such a system.

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# Statement of Co-Authorship

The third chapter of this manuscript-based thesis (DRIFT Response Reproducibility of Aged and UV-Exposed Wood Surface Coatings) was prepared with the assistance of research scientist Dr. Robert Franich of Ensis Forest Products Division, New Zealand. His assistance was offered in interpreting spectral data from stability assays, and the production of the manuscript.

All research was supervised by Dr. Paul McFarlane, Professor of Wood Science at the University of British Columbia. He was instrumental in developing the intellectual foundations of this research, and provided guidance in the development of its design and methodology.

Bryce Smiley, the primary author of this thesis, developed the experimental design of the reported works under the supervision of Dr. McFarlane, carried out all experimentation and data analysis, and produced the entirety of this thesis.

# Chapter 1

## Innovative Methodologies in Wood Tracking: The Chemi-Code Concept

### 1.1 Introduction

Chain of Custody has been applied increasingly within the forest sector over the last decade as a response to the industry's mounting demands for ways to track and certify the validity of the various sustainability claims made by forest product producers (Nussbaum & Simula, 2005). As sustainable forest management (SFM) certification continues to grow in developed countries, and increasingly penetrates into developing nations, chain of custody (CoC) certification expands with it (Kraxner *et al.*, 2006). The primary need for CoC certification lies in its ability to confirm the links between certified forests and certified products in the marketplace. These clear links not only increase consumer awareness about the concepts of "sustainable forestry" but also help consumers make educated purchasing decisions (Rametsteiner and Simula, 2003). Secondly, there are many benefits to effective material tracking within a manufacturing line, and throughout the value chain (Maness, 1993). Since materials tracking is a foundational element of CoC, these value chain benefits may also provide further incentive for businesses to invest in updating their material management systems to conform to CoC practices.

One of the cornerstones of effective material traceability is an appropriate product identification method (Wall, 1995). Barcode labels, radio frequency ID (RFID) tags, paints, chisels, and conventional labels are several of the methods currently used in the forest industry (Dykstra *et al.*, 2003). As well, microtaggants, genetic fingerprints, and aromatic signatures are also being investigated (Brack *et al.*, 2002, Dykstra *et al.*, 2003, Murphy and Franich, 2004). However, an ideal identification system requires a balance of durability, cost-effectiveness, ease of use, specificity and security. Many methods used to date have weaknesses in one or more of these areas. Barcode labels, for instance, are easily dislodged and lost, per-unit costs of RFIDs are quite high, and paints and chisels are easily forged (Brack *et al.*, 2002, Curtin *et al.*, 2007). The forest products industry is presently making do with the methods currently available and dealing with the shortcomings that exist in manufacturers' respective systems of choice. This practice will continue until new technologies are created, or existing ones are refined to create more practical solutions for materials tracking in the wood products industry. For example, long term potential may exist in genetic and chemical fingerprinting for security and specificity and branding products at a biological level, but until the technology has matured, the labour involved makes their use unfeasible for industry-scale consumption in forestry (Dykstra *et al.*, 2003). The same situation exists, but to a lesser extent, with RFIDs which, despite a great deal of progress, are still highly delicate (especially lower-cost models) and work primarily with passive (very short range) communication technologies.

This thesis will survey current Chain of Custody requirements, including current practices and the demands they impose on industrial material tracking methods. Based on this foundation, the following manuscripts propose the development of a new method of material marking and identification. Using a three-level approach to chemical tagging, the proposed system will take advantage of the inherent security of infrared (IR) absorbance responses of stable polymers, the ease of use and economics of paint-style product applications, and the simple, yet durable nature of polymer coats. In addition,

this work seeks to develop sufficient resolution to create several millions of unique codes based on a variety of unique polymer identifiers. This “chemical barcode” system (abbreviated to “Chemi-Code”) will be comprised of unique mixtures of IR-absorbent polymers solutions. These solutions can be applied like a paint to the surface of a wood product. Upon drying, a thin polymer film will be left that will be barely detectable by the naked eye. This film, like paint, is not easily removed, and should endure harsh weather conditions. Scratches and dirt should not interfere since it is not read visually. The applied “marker” will be read by means of an IR spectrophotometer utilizing the Diffuse Reflectance IR Fourier Transform (DRIFT) method, which is a simple, non-destructive means of reading the IR spectrum of unprepared surfaces. Using the spectrophotometer, the film can be characterized by the combination of “absorbance peaks” in the IR spectrum. This spectrum will be the unique “signature” by which the product is identified.

A major part of the development process will be investigating how to engineer unique customized IR spectrum from combinations of polymers. This research will be approached by selecting polymers which exhibit a “candidate peak” in a suitable area of the IR spectrum. In the following studies a candidate peak is defined as a single peak whose magnitude can be quantified to determine the amount of polymer used to create it, and is therefore a single peak that is representative of a polymer. The combination of candidate peaks present, and the relative intensities will be used as a multi-polymer code in the mid-IR region.

## 1.2 IR Spectrometry in Wood Identification

IR Spectrometry has been used in the past as a means of identifying wood, but mainly for the purpose of interspecific differentiation. Although IR profiling of wood components can be found as early as the 1940s, with the discovery of the IR spectrum of lignin (Jones, 1948), a good deal of the momentum that now exists in IR wood spectroscopy has developed in the more

recent decades. Investigations into the uses of IR spectroscopy in the field of wood science were done by Culler *et al.* (1984), using FTIR to characterize the lignin content of pulp wood to optimize pulp treatment operations. Owen and Thomas (1989) followed this research with the use of DRIFT technology to discern between gymnosperms (softwoods) and angiosperms (hardwoods) by assessing the ratio of lignin to cellulose by inference from the lignin and cellulose characters of resulting spectra. Nault and Manville (1997) used DRIFT spectroscopy to assess not only the principal components of wood (holocellulose and lignin) as done previously by Owen and Thomas, but also evaluated absorptions from the extractive chemicals present in wood species samples. By introducing these additional factors, their system was somewhat successful in differentiating species within lumber mixes (spruce, pine, fir). Investigations have also been undertaken in the near-infrared (NIR) region of the wood spectrum (NIRS) with the same objective. Brunner *et al.* (1996) developed new methodologies using the Fourier Transform method (FT-NIR) to identify wood products, and demonstrated that these methods could be used as a means of wood product identification, or determining wood's geographical origin, and Meder *et al.* (1999) used DRIFT methods to assess structural attributes of wood products. Tsuchikawa *et al.* (2003) continued with NIR investigation of wood products, moving further to use NIR spectroscopy to discriminate between not only different wood species, but also different engineered wood products. They surveyed a number of chemometric interpretation methods, namely Mahalanobis' generalized distance (Mark and Tunnell, 1985), K nearest neighbor (Kowalski and Bender, 1972), and soft modeling of class analogy (Sharaf *et al.*, 1986). K nearest neighbor was found to perform best in the NIR region, providing a 98% validation rate of samples. The nature of their work, which dealt primarily with the mathematical profiling of various wood substrates worked well to elucidate variances between the different species. Replication of their multi-variate methodologies would not have been appropriate in a situation such as the chemical barcode system proposed in this work. The intentions of most reviewed works involved the profiling of wood products in some way. Conversely, the IR characteristics we look to investigate are those which we

have engineered, and intend to view them in the simplest way possible, that is, by following a single absorption peak maximum for each polymer applied.

Studies have been undertaken to develop species-specific chemical identities using biochemical profiles of wood species through pyrolysis (Challinor, 1996), and progress has even been made in wood identification based on emitted volatile compounds (Murphy and Franich, 2004). Work has also been done with DNA markers in tree species for species identification and tracking of geographical origin for certification purposes. Deguilloux (2003) investigated the origins of high-value oak species using chloroplastidial DNA (cpDNA) microsattelites, and reviews much of the previous work which cpDNA wood identification was founded upon. It was found that, in addition to being a rather time-consuming process, extracting sufficient amounts of DNA from dried wood products was often problematic, and that this technology remains unfeasible in any industrial application. These approaches do have potential in the long term, because they assess the chemical structure of wood products as a means of identification. This inherent security is a great asset to these approaches, as the chemistry of the wood is not easily modified and is relatively consistent. This project seeks to take the concept of chemical wood identification a step further by effectively engineering the chemistry of the wood surface by applying a customizable chemical signature.

Spectroscopy has been used extensively in the past as a means of non-destructively analyzing compounds. IR spectroscopy is used for many applications, especially in structural determination of compounds (Skoog *et al.*, 1998). The basic principle of IR spectrophotometry is that multi-atomic molecules can absorb different frequencies of IR radiation and in different amounts, depending on what functional groups are present, the location of these functionalities, the concentration, and the sample position relative to the spectrophotometer (Skoog *et al.*, 1998). IR radiation is absorbed by chemical bonds within molecules when the radiation's frequency is synchronized the bond's vibrational modes. When this synchronization occurs,

the bond absorbs radiation, becoming excited, and thus less IR radiation is transmitted through (or reflected from) the sample. A frequency (or wavenumber) at which this occurs exhibits an “absorbance” response, and these frequencies are determined primarily by stretching vibrations of intermolecular bonds. For simple systems, the absorbance frequency can be approximated by application of Hooke’s Law, likening the relationship between bonded molecules to that of “spring” connected masses. Hooke’s law is expressed:

$$v = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

where  $k$  represents the force constant of the connecting “spring”,  $\mu$  represents the relationship between the two masses (the reduced mass), and  $c$  is the velocity of light (Skoog *et al.*, 1998). The amalgamation of the absorbance responses for all frequencies produces an IR spectrum that characterizes the sample scanned.

### 1.3 The Concept

The chemical barcode system proposed will be based on three different variables. The multiplicative permutations allowable by this three-level system will not only address the need for millions of unique identifiers, but also contribute significantly to the inherent security of the system.

#### 1.3.1 Level 1 - Polymer Presence

The presence or absence of a modified chemical surface (polymer film) on a wood product is the first and simplest aspect of the system, and is essentially binary. All that is necessary to recognize this level of chemical marking is the ability to detect the presence of a polymer on the wood surface. Knowing the chemical functionalities of a coating polymer and the characteristic IR spectrum of untreated wood will allow this recognition *via* the simple and relatively accessible method of IR spectrometry. However, with this level

of simplicity, there are only two possible identities discernible—marked and unmarked.

Suitable polymers for the proposed system must be easily applied to wood products and give a characteristic spectrum in the IR range, so that their presence can be detected by spectrometric methods. As well, an ideal polymer for application to wood should have minimum toxicity (maximizing the ease with which it can be manipulated in industrial contexts), be readily soluble in a common solvent (to allow easy production, storage, and transport of polymer solutions) and allow liquid application (for methodical continuity within the study), but be solid in standard conditions and thus adhere well to wood products, ensuring that it remains on the product after application. Different application methods may be of use in the future, but for the purpose of demonstrating the concept of this system, and the relative simplicity of the solvent application method in a laboratory environment, only dissolved polymer applications were investigated in this thesis.

Although the economics of the system would benefit from using polymers readily available from chemical suppliers, there is an increased security in the use of custom-synthesized polymers. By using polymers that are not commercially available, production of counterfeit markers is made more difficult. As well, the development of custom polymers may open new areas of the spectrum in which common functionalities cannot elicit an IR response peak.

The IR spectrum of wood shows IR absorbance in ranges upwards of  $2500\text{ cm}^{-1}$  and less than  $1800\text{ cm}^{-1}$  (Figure 1.1). The majority of the common organic functionalities exhibit IR peaks at wavenumbers less than  $1800\text{ cm}^{-1}$  (Owen and Thomas, 1989), so a great deal of signal intensity is observed in this area of the wood spectrum. The area between these two ranges,  $2500\text{--}1800\text{ cm}^{-1}$  shows very little IR activity in wood. For this reason, polymers with functionalities absorbing in this range were sought out to ensure a readily recognizable IR response on top of the wood IR background. Polymers with candidate peaks in the “busy” ranges mentioned above must

produce strong, sharp peaks which can be identified on top of the interference caused by the IR spectrum of the wood background.

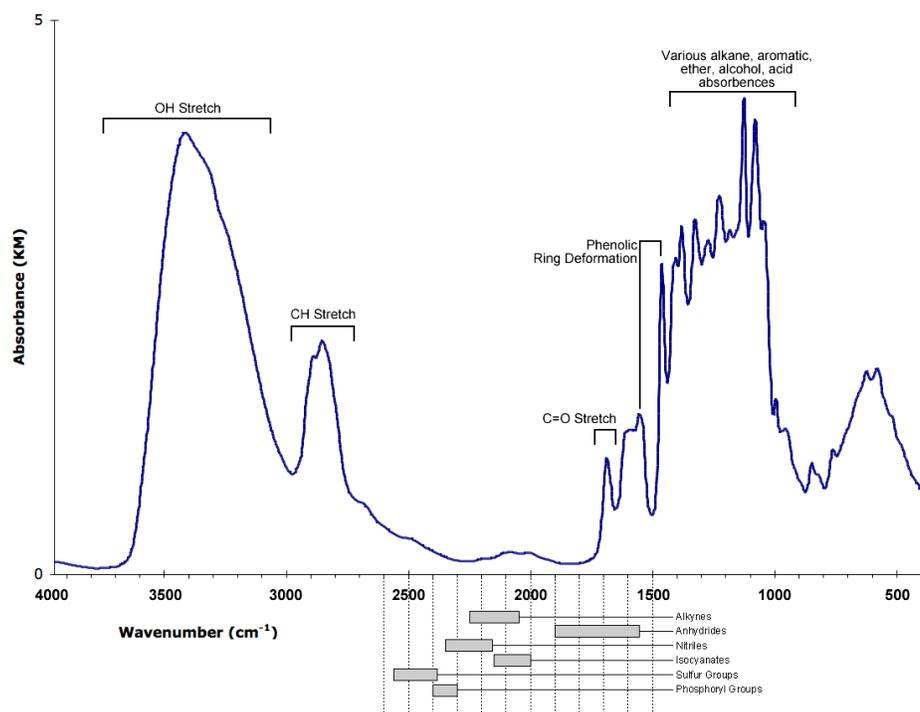


Figure 1.1: Characteristic IR spectrum of White spruce (*Picea glauca*), illustrating the range of the spectra not affected by chemical species in wood (2700–1800 cm<sup>-1</sup>). Ranges below show areas in which novel functionalities may be used to manufacture new peaks outside the major influence of the wood spectrum. (Skoog *et al.*, 1998)

Polymers that would be easiest to identify on the wood background are those which are chemically different from the principle constituents of wood, namely holocellulose (composites of cellulose and hemicellulose) and lignin. Polymer functionalities that are in common with those in these compounds could be easily interfered with, or blend in with the background of the wood spectrum. For this reason, novel functionalities should be sought out in polymers so that new peaks can be created and identified in the wood spectrum. Figure 1.1 illustrates where absorbance peaks would appear

with the application of polymers containing alkynes, anhydrides, nitriles, isocyanates, sulfuryl and phosphoryl compounds.

### **1.3.2 Level 2 - Polymer Combination**

The second level to be used to diversify the range of identities in the proposed system is the combination of polymers in the marking system. If numerous polymers can be applied in a mixed system, assuming they are spectrometrically discernable by infrared, it is possible to create  $2^n$  unique permutations of polymers, where  $n$  equals the number of polymers. With the addition of more polymers, the system has multiple variables (polymers) which are able to exhibit two different states. For example, if 8 IR-discernable polymers were available, this would equate to 256 unique permutations.

Using multiple polymers in a system may cause variability based on chemical interactions, between applied polymers, and with wood surfaces. For this reason, studies must be done to ensure that no significant polymer interactions occur, and to quantify the extent to which addition of one polymer may affect the IR response of another. As well, when selecting polymers to be used in concert, it is imperative that candidate peaks in the IR spectrum do not overlap or cause interference with the reading of others.

### **1.3.3 Level 3 - Polymer Load Variation**

In a system intended for uniquely identifying products and batches in an industrial context (as would be required in a Chain of Custody system), 256 would not be a sufficient number of unique identifiers to mark and discern among individual products. Furthermore, no reasonable multiple of this number would suffice either. For this reason, the third level of variability, polymer load, is necessary. Using varying polymer loads allows the number of values for each polymer (variable) to increase from two (binary) to the number of statistically discernable polymer amounts available from the given polymer. If 8 polymers were used, and each was able to contribute 10

different discernable concentration points, the system would have potential for  $10^8$  unique permutations.

Beer's law states that absorbance at a given wavenumber is directly proportional to chemical concentration of the absorbing compound thus creating a linear relationship between the polymer concentration and absorbance at a given wavenumber in transmission systems. Empirically, Beer's law is expressed as:

$$A = \varepsilon c \ell = -\log T$$

where  $\varepsilon$  is molar absorbtivity of the examined species,  $c$  is the concentration, and  $\ell$  is the path length (Skoog and West, 1998). Beer's law is applied only to transmission spectra, but for reflectance systems, Kubelka-Munk theory describes a similar relationship (Blitz, 1998). However, at high polymer concentrations which will be used in this study, and with the influence likely to be imposed by a wood-spectrum background, this linear relationship can break down beyond a certain concentration level (Culler *et al.*, 1984). For this reason, preliminary studies will be undertaken to develop calibration curves for each polymer that might be used in the system (Figure 1.2).

These curves will define the expected relationships between polymer load and peak absorbance to allow translation of characteristic spectral elements to polymer concentration values. As well, the maximum number of unique points should be defined along these calibration curves to allow the greatest possible number of potential "barcode combinations".

Also, in order to determine the range of peak absorbance intensities a given polymer amount can exhibit, numerous scans of each sample and each concentration will be collected to construct confidence intervals, allowing automated readers to translate a values from a continuous scale (peak height) into discreet categories (which concentration it represents). Minimizing these intervals will allow maximum "resolution" of the system by allowing the most numbers of concentration designations, and thus the greatest number of unique identifiers for certified products.

An ideal CoC product tracking system is one which is economical to apply

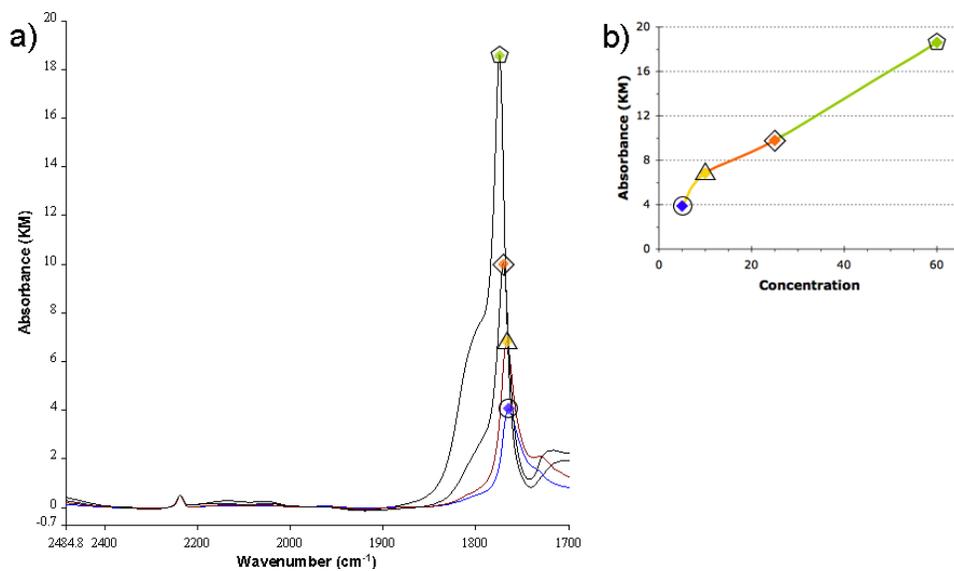


Figure 1.2: Translation of IR spectra to a polymer calibration curve. Spectra for each polymer concentration are collected, averaged (a), and compared by maximum peak height at the candidate absorbance wavenumber of each respective polymer (b).

and read information from, difficult to forge, physically robust, weather-proof, able to operate at industrially acceptable speeds, exact and reproducible in its marking specificity, and able to be read from a distance (Dykstra *et al.*, 2003). The use of polymeric compounds in a system similar to paint coatings should satisfy the requirements of simplicity, economics and durability, and the modifiable IR structure offers great potential for security, specificity, and applicability within industry. What remains to be found is how reproducible chemical markers of this nature can be, and the degree to which the system can offer marking specificity (resolution).

This thesis will begin by outlining the current state of modern Chain of Custody certification and defining the important attributes of effective material tracking systems in Chapter 2. The two subsequent chapters will report on the primary steps taken in developing the Chemi-Code system described above. Chapter 3 will describe the assessment of a series of polymers for use in the system based on stability. Chapter 4 will describe the investigation of candidate polymer IR absorbance characteristics with respect to concentration, and derive preliminary insights into these polymers' abilities to effect quantitative changes to IR spectral elements of the wood surface. The final chapter of this thesis outlines conclusions of the research and comments on its impact towards creation of a functional material tracking system. This work is the first report on the research and development of the Chemi-Code system.

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## Chapter 2

# International Forest Certification Systems and Their Chain of Custody and Eco-Labeling Requirements

### 2.1 Introduction

The continuously evolving market pressures on the forest industry, and the increased visibility of environmental factors in issues of corporate social responsibility are resulting in certified forests becoming increasingly common in developed countries and slowly advancing into developing regions (Rametsteiner & Simula, 2003). As forest certification continues to gain momentum, it exerts an increasing influence on forest management organizations, timber producers, and retail companies to buy, sell and manufacture certified products (Nussbaum and Simula, 2005). Sustainable forest management (SFM) certification is on the rise, having increased from 60 million to almost 270 million hectares between 2000 and 2006, and chain of custody certificate numbers are continuing to grow as well, having increased by 375% from 2000 to 2006 (UNECE, 2006). SFM refers to the first, and generally most

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<sup>0</sup>A version of this chapter will be submitted for publication.

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visible of the principal elements of forest certification. In addition to SFM certification, there is also Chain of Custody (CoC) certification, and product eco-labelling, which are intended to trace certified products along the value chain (Hansen 1997, Nussbaum and Simula 2005). SFM certificates are issued by an independent, third party certification organization to confirm that a specified forest area is managed and harvested in compliance with the criteria set by the accrediting certification scheme (Nussbaum and Simula, 2005). There are more than 20 of these schemes currently operating in the world, including the CSA (Canadian Standards Association), FSC (Forest Stewardship Council), PEFC (The Programme for the Endorsement of Forest Certification), and SFI (Sustainable Forestry Initiative) (Rupert, 2001). Many schemes also require separate certification of Chain of Custody (CoC). These certificates are also issued by third party accredited certification organizations, and they reflect an organization's capacity to maintain an appropriate certification status on wood products of certified origin through harvest, manufacture and transport (Nussbaum and Simula, 2005). Unlike SFM certification, CoC certificates are issued to organizations existing between the harvest site and the customer (such as sawmills, furniture manufacturers, or other processing plants). Conversely, eco-labeling is not a certification but it addresses how certified materials are identified as such in the marketplace (Anderson and Hansen, 2003). Generally, every certification scheme has its own unique set of criteria dictating how their claims are to be presented.

The major motivator for businesses to adopt a third party certification has been to proactively increase market share (Merry and Carter, 1997), not desire for price premiums or realized potential managerial improvements (Hubbard & Bowe, 2005). With the greatest demand for certified wood products coming from large-scale lumber distributors, most chain of custody certificates have been issued to organizations in the primary processing sector of the forest industry (UNECE, 2006). The demand for certified wood from lumber retailers has come from pressure exerted by non-governmental organizations (NGOs) and competing retailers to adhere to "socially responsible

business practices” (Nussbaum and Simula, 2005). However, relaying the message of the environmental stewardship to general consumers has been weak, resulting in only a small group of consumers being aware of, and avoiding products procured through environmentally damaging practices. Many of these consumers still are unwilling to pay price premiums for products that are produced sustainably (Ozanne & Vlosky, 1996). In addition to a lack of regard in the marketplace, the impact of forest certification on consumers is diluted by the diversity of claims presented (Irland, 2007). Making CoC certification more attractive to forest product manufacturers in markets less involved in certification, as well as aligning claims of the certification schemes in existence, may produce a more potent impact on the commercial marketplace, leading to better consumer understanding, and perhaps even an increased demand for certified products. With the benefits of certification often being indirect and unapparent to many manufacturers, overcoming these barriers is paramount to propagation of certified products in the marketplace (Vidal et al., 2005).

It seems that this is the direction in which certification is moving. Chain of custody certification has the potential to become more attractive to manufacturers as it develops, so long as the increasing comprehensiveness of certification does not render it too cumbersome to create benefits for wood product manufacturers. Voluntary certification also requires a delicate balance between costs of being certified and benefits perceived by certified organizations (Hubbard & Bowe, 2005). The continued success of forest certification depends on increasing the benefits without allowing them to be outweighed by associated costs. Use of advanced material tracking methodologies may not be required by CoC systems, but implementation of such systems may, over time, decrease the costs of certification by streamlining operations and inventory management processes. As technology develops, decreased costs and increased benefits may emerge. In practice, inventory management technologies are required to be robust in the face elemental adversity, inexpensive and simple to implement, and extremely accurate and specific in linking certified products to supporting documentation or prod-

uct information. As methods are developed which can fulfill all these needs, managerial and financial benefits of CoC implementation may become more obvious, and better realized by manufacturers.

This paper examines the differences and similarities of the various chain of custody systems currently in use by the major international forest certification schemes (namely FSC, PEFC, and SFI), their eco-labeling requirements, and issues with harmonization. It also explores whether the evolution of CoC has produced sufficient supply chain management options to accommodate the diverse industry it services. The current state of chain of custody certification will be examined, and assessed for compatibility with the new material tracking technologies that are becoming available, notably the potential of the ChemiCode system for use within a CoC system.

## **2.2 Fundamental Principles of Chain of Custody**

The core elements of chain of custody are confirmation of inputs, use of a documented control system, defined product claims, and secure product labeling. These fundamental principles are common to all CoC systems, but each scheme has developed its own criteria due to the many opportunities for variance and distinction in policy and definitions in the historical development of CoC frameworks. The following section will use these core elements to assess the distinctions in methodology between the three major forest certification schemes: FSC, PEFC, and SFI.

### **2.2.1 Confirmation of Inputs**

All chain of custody schemes require that the origin of the inputs received by any process line must be confirmed before they are manufactured into certified products. This requirement applies to all inputs including raw, and pre-processed and recycled wood and fibre materials. There are a number

of categories into which wood inputs can be divided. Most schemes have slightly different definitions of pure certified, recycled/reclaimed, uncertified, and controlled uncertified wood material inputs. The input categories present in the three schemes investigated are presented in Table 2.1 (FSC 2004a, PEFC 2005a, SFI 2006).

Table 2.1: Input category comparison by CoC system.

Classification	FSC	PEFC	SFI
Certified Pure	✓	✓	✓
Certified Mixed	✓		✓
Post-consumer Reclaimed	✓		✓
Other Reclaimed	✓		
Controlled Sources	✓	✓	
Neutral		✓ *	

\*PEFC considers post-consumer reclaimed fibre to be “neutral”, and it does not play a part in certified volume calculations.

Similarly, all three schemes exclude wood from controversial sources. However, as presented in Table 2.2, the definition of a controversial source varies among schemes, with PEFC and SFI categorizing illegally harvested materials and those that don’t comply with all local laws as arising from a controversial source. FSC has more stringent requirements that preclude the use of materials from high conservation value forests, areas where civil or traditional rights are violated, the use of genetically modified trees and the conversion of forests into plantations or non-forested land uses. Stringent sourcing requirements can affect the operations of producers buying from such “controversial” sources or those that cannot be verified as non-controversial. This stringency is one of the simplest ways in which forest certification attempts to hamper the illicit use of forests. However, compared to other schemes, these regulations may sway producers from using the FSC certification, or becoming involved in certification at all. Compliance with more stringent requirements, however, can allow companies to more strongly assert their commitment to socially and environmentally re-

sponsible activities, which has been suggested to be an asset to business performance (Miles and Covin, 2000).

Table 2.2: Considerations for the definitions of controversial wood sources. (Wingate and McFarlane, 2005)

Classification	FSC	PEFC	SFI
Failure to comply with all laws and regulations	✓	✓	✓
Illegal harvest of area protected by law	✓	✓	✓
Illegal harvest of area planning to be protected by law	✓	✓	✓
Logging of high conservation-value forest	✓		
Harvesting in areas where traditional/civil rights are violated	✓		
Use of genetically modified tree species	✓		
Conversion of forests into plantation/non-forest uses	✓		

For all three schemes, the main objective is to verify that inputs originated from certified forest areas are confirmed by the documentation accompanying the log or product. Such documentation may be either a valid SFM certificate if the materials originated from a forest area, or a CoC certificate if they were previously processed. Similarly, for recycled and other controlled wood sources, verifiable proof of the claimed status must be provided. Logistically, attaching a certificate or another relevant document to wood products within an industrial setting can be very challenging. All CoC systems are flexible in their allowances for methodologies for attaching these claims to wood products. This opportunity, along with the necessity to attach very specific certifications to a somewhat homogeneous resource (in the context of industrial manufacture) encourages the adoption of industrial material tracking systems.

### 2.2.2 Use of a documented control system

The effectiveness of a chain of custody system is heavily dependant on the individuals that implement it. In order to ensure transparency of the system, a consistent framework and competence of the implementing staff, all three CoC schemes require a documented control system (FSC 2004a, PEFC

2005a, SFI 2006). A documented control system is a resource for staff and for auditors that describes all of the workings of a chain of custody system.

All three certification schemes require that the documented control system provides written instructions for all procedures involved in the system, and communicates plainly the responsibilities of all staff involved in CoC activities. Such documentation is instrumental in avoiding errors due to negligence, as well as quickly and easily tracking the source of discrepancies in order to uncover unscrupulous activities, and to maintain confidence in the system. Such a documented control system could be integrated into the human resources operations of a facility relatively simply. Not only would explicit documentation of individual roles and responsibilities reinforce the transparency of a CoC system, but also the understanding and competencies of the associated labor force.

Of the three schemes, SFI and PEFC requirements stand out in that they explicitly require the flow of wood products to be mapped throughout the entire system for the reference of staff and auditors alike. This feature of the documented control system should prove useful to identify high-risk points in the process chain.

### **2.2.3 Defined Product Claims**

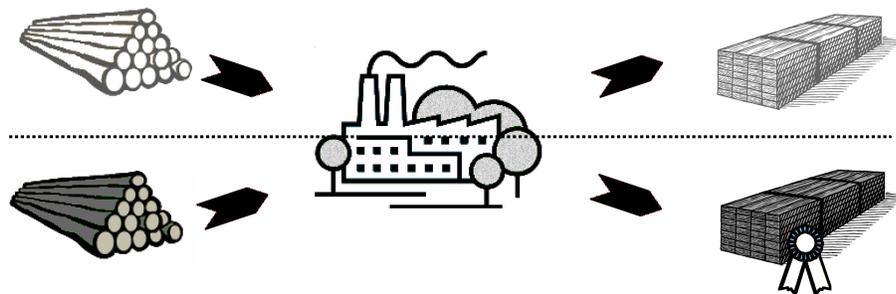
All three certification schemes addressed have different claims that they attach to their products. Ensuring the accuracy of these claims is one of the most important roles of a chain of custody system.

#### **Pure Claims**

All schemes have some form of a “pure” claim, but the definition of this claim varies from scheme to scheme. FSC requires that all products carrying this claim and eco-label have been made from 100% FSC-certified wood. Consequently, these products will contain only certified wood. FSC

makes no mention of any requirements for physical segregation in claiming products to be 100% certified, and states only that the rolling average of the material used in the product group is 100% FSC-Pure (FSC, 2004a). Physical segregation is a common method of ensuring that no uncertified material is included in certified products, involving segregation of certified and uncertified products and inputs. As illustrated in Figure 2.1, there is no accounting or mixing of certified and uncertified materials involved, ensuring a very transparent product claim (Nussbaum and Simula, 2005). SFI certified products can carry the same claim of 100% certified material both if the product is actually 100% certified material, or if managed by a volume credit accounting method (see section 2.2.3) to the value of 100%. Therefore, SFI pure products will, as the label states, contain no uncertified material. PEFC's standard is nearly identical in this respect, with all inputs used in products that are labeled as arising "From sustainably managed forests" having to be physically separated from all uncertified wood sources throughout all steps of the chain of custody (PEFC, 2005b).

## Physical Segregation



**FSC:** "Product groups manufactured with 100% FSC-certified material (FSC 2004b)  
**PEFC:** "From sustainably managed forests." (PEFC 2005b)  
**SFI:** "100 percent of the fiber used in this product comes from independently certified forests" (SFI 2006)

Figure 2.1: Physical separation methodology in chain of custody accounting. White products represent uncertified products, and grey represents certified products. When physical segregation is being implemented, these two classes of wood are kept separate at all times. The included captions are the claims which each certification scheme attaches to wood products managed in this way.

## Mixed Claims

Mixed claims refer to environmental claims made about products that do not contain 100% certified wood, but rather a portion of certified wood, and a portion of uncertified wood. Mixed claims were developed as a pragmatic solution to shortages of certified materials, and to promote manufacturers' uptake of certification and eco-labeling schemes. Since its inception, there has been a convergence to two main methodologies of calculating the certified percentage claims: the minimum threshold method, and the credit accounting method (FSC 2004a, PEFC 2005a, SFI 2006).

The minimum threshold approach calculates the percentage of certified material in a product based on the total inputs of a product line. For instance, if 70 of the 100 tonnes of wood used to make a batch of I-joists were from certified sources, all (100%) of the I-joists would be considered 70% certified material. This method usually requires a minimum percentage of certified material to be considered certified.

FSC allows CoC certificate holders to use a minimum threshold system, where the minimum is 70%. If a product contains more than 70% certified wood, the FSC label will not communicate the exact percentage of certified material, unless it contains 100% FSC-pure certified material (FSC 2004a). PEFC and SFI follow the same principle of minimum threshold, where 70% is the minimum for a mixed claim with PEFC, and 66% for SFI (PEFC 2005a, SFI 2006). PEFC has recently permitted optional inclusion of certified percentage values on eco-labels, and the same allowance is made by SFI to their CoC certificate holders.

The mass flow method was originally used to offer a binary means of describing certified status of mixed inputs. The original principle was that the percentage of certified material created by a producer would be the same as the percentage of certified inputs. For example, if a given batch of lumber was created from 70m<sup>3</sup> of certified roundwood and 30m<sup>3</sup> of uncertified roundwood (basis of mass or volume is determined by the scheme), 70% of the lumber produced would be certified, while the remainder would be un-

certified. Certification schemes have previously permitted the use of either a mass or volume accounting methodology, but in recent years most schemes have moved away from their use. None of the major schemes described in this review use such a system. The more complex credit accounting systems which replace them allow the certified inputs and outputs to be modified by “input accounting” over batches or time. For instance, for a composite product to carry an FSC Mixed eco-label, it must have come from 70% certified inputs. However, if a producer can only source 35% of his inputs from certified sources, he may sell 50% of the outputs as FSC-Mixed, and the other half as uncertified. Similar accounting can be done with respect to time, to provide flexibility to producers that may not be able to source enough certified materials at all times to maintain the requirements of the eco-label. Figure 2.2 demonstrates how credit accounting can be used to modify percentage claims over product batches or over time.

Mixed claims were developed to allow producers easier access to markets demanding certification in spite of the challenges in accessing certified raw materials. It allowed them to include both certified and uncertified inputs into their products. However, the increased flexibility for product inputs has created a demand for more comprehensive management systems to effectively track inputs and outputs. Although this approach may exert pressure on manufacturers to put in place effective inventory and input tracking systems, these systems can be beneficial when integrated into other facets of the business. For example, such a comprehensive inventory management system, or a real-time material tracking system may be used to optimize material turnover (Christianson, 1996).

### **Recycled Product Claims**

The inclusion of recycled products in certified materials was a necessity if the goals of certification were truly to promote sustainability within the forest sector. The incorporation of recycled products into certified products, however, proved to be a complicated endeavor, and one that was handled

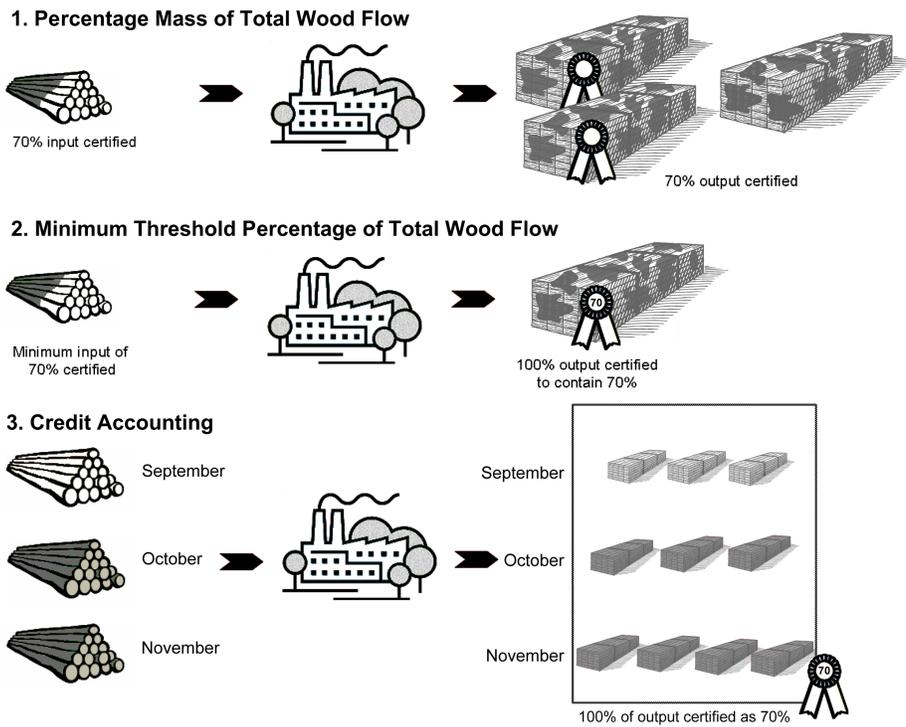


Figure 2.2: Mixed claims methodologies in chain of custody accounting. White products represent uncertified, while grey products represent certified. Batches (right) showing grey and white contain both types of inputs.

differently by the various certification schemes. FSC allows recycled materials to be present in FSC Recycled and FSC Mixed products. When recycled contents are used, FSC takes into account two different values, the mass/volume percentage of certified inputs, and the mass/volume percentage of post-consumer reclaimed input. In order for a product to be labeled as 100% recycled, that product's batch must have come from 100% post-consumer reclaimed inputs. To be labeled as "FSC Mixed" containing no uncertified material, the recycled inputs must surpass a threshold of 90% FSC certified inputs, while the remainder of the inputs must be FSC-certified. To be marked as "FSC Mixed" containing certified, recycled, and uncertified materials, a product batch must be produced from at least 70% post-consumer reclaimed material, 10% FSC-certified material, and the remainder may be uncertified controlled wood. These stringent requirements, together with the publication of percentage reclaimed figure on eco-labels, makes FSC's system very transparent, but possibly confusing to the uninformed consumer (FSC 2004a).

FSC draws strict divisions between post-consumer and pre-consumer reclaimed products. Only post-consumer reclaimed products may be incorporated into FSC products as "recycled" material. Any manufacturing by-products which could be re-incorporated, such as fibre, paper or sawdust (i.e. pre-consumer reclaimed products) cannot be used as "recycled content". If collected, recorded and sequestered from uncertified materials, these pre-consumer materials can be incorporated into products as inputs of the same percent certification as the inputs from which they were derived.

PEFC and SFI operate very similarly with respect to recycled materials. Both require that products marked as containing certified recycled materials contain at least 70% recycled material (PEFC 2005b, SFI 2006).

#### **2.2.4 Secure Product Labeling**

All forest certification schemes examined in this paper have requirements regarding how certified products are to be marked in the mill, in the mar-

ketplace, and when in transit.

The FSC Guide for On-Product Labeling requires that all certified outputs be securely identified as their respective product group with an accompanying CoC registration number, in a manner that will not come loose or be degraded (FSC 2004a). How this is done, however, is not specified, enabling end users to innovate and promote the adoption of advanced material tracking methodologies. With the complexity of the certified product value chain, use of an automated product identification system would be much more efficient than trying to attach physical documentation to a product through the mill, or in transit. Also, it is the responsibility of the producer to ensure that the eco-labels provided by the FSC are managed properly and are not attached to any non-certified products (FSC 2004b).

The eco-label usage requirements of the PEFC are somewhat more flexible than those of the FSC. Producers are given options regarding what information is to appear on their products' certification statement. PEFC only requires that their logo and a logo license registration number appear on the eco-label. In addition, it is optional to include environmental claims, SFM or CoC certificate numbers, identity of the accredited certification body that issued the certificates and raw material properties (PEFC 2005a). The logo usage rules are quite flexible because of the PEFC's framework methodology. It is likely that most subsidiary certification schemes will have their own eco-labeling restrictions and it is important that PEFC facilitates the integration of their own requirements into those already existing in the national certification schemes under the PEFC umbrella. PEFC does have very strict guidelines regarding who is allowed to use and reproduce the PEFC eco-label. The PEFC requires that only forest management and forest industry companies holding either a valid SFM or CoC certificate in addition to a logo license are allowed to produce the PEFC mark on-product. These companies, in addition to national PEFC governing bodies and educational/promotional organizations with valid logo licenses, are allowed to produce the PEFC logo for off-product uses (where the logo makes no claim to any product) (PEFC 2005b). As well, as a measure of product secu-

rity, PEFC requires that certification bodies maintain detailed records of all agencies and producers to whom they issue certificates, and who thereby are allowed to apply the PEFC mark to their products or promotional materials.

SFI's standard for eco-labelling states that all organizations applying their label must maintain an SFI program license, as well as demonstrate compliance with the Fibre Sourcing requirements of the SFI. Registration and management of licenses is maintained by the SFI (SFI 2006). SFI has many different eco-labels that are used in different applications, dictated by an organization's position in the supply chain (primary or secondary producer), the material management system used (segregation, percentage, or credit accounting), and the claims being communicated (pure, mixed, recycled, or combinations). With the very specific logos being used in very specific scenarios, the labels are relatively transparent to those who know and understand the requirements, but they may be confusing to the average consumer due to the variety of labels and the vague and nondescript claims.

## 2.3 Discussion

It is often not taken into account how chain of custody certification can benefit organizations beyond the most visible aspect of access to a new, certified market (Vidal *et al.*, 2005). Implementation of CoC systems requires considerable expense, but the potential benefits may also be quite substantial. For instance, one of the major deterrents of manufacturers from implementing a CoC system is the cost associated with segregation of inputs (Hansen, 1997). However, this segregation/input identification system that is necessary to run a certified operation, if approached smartly, can be integrated into an overall inventory management system capable of optimizing inventory turnover, forecasting input demands, and potentially saving a great deal of money (Christianson, 1996). Current chain of custody requirements are sufficiently flexible that they can be implemented into

many different systems, and integrated into an organization's business plan. In fact, CoC offers much more potential this way, rather than as a superimposed process used only to meet requirements of CoC and SFM policy. With the introduction of new methodologies such as credit accounting, and the broadening requirements for product tracking and control systems, there no longer needs to be a divide between profit-maximizing business strategies, and the environmental objectives of a certification scheme. Implementation of technologically advanced tracking systems within a Chain of Custody framework could streamline the manufacture of certified materials without interfering with input processing.

One of the major issues currently facing CoC certification is the sourcing restrictions that come along with being a certified manufacturer. When an organization puts forth the time and monetary investment to become certified, it generally desires to maximize the amount of product that can be sold as "certified" to those buyers who demand it. For many manufacturers, the most tangible benefit of CoC certification is this market access. In essence, this is what they are paying for. Currently, the various certification schemes, and their CoC systems are running in parallel, redundantly, but not offering mutual recognition of one another. Mutual recognition of CoC systems would allow manufacturers certified by one scheme to include certified materials from another in their products (as certified volume). When certain products of certified origins are not allowed to be used by organizations certified by a "competing" scheme, bottlenecks are formed, and pressure is exerted on manufacturers to procure inputs from only certain "brands" of certification. For example, as certified products increase in proportion in the total forest product pool, PEFC and FSC (two such "competing" schemes) may eventually need to be co-processed in manufacture. Under today's certification policy, this is not allowed. However, if it comes to the point where manufacturers are co-processing blended certified products, or are forced to produce products certified by different schemes in parallel, accurate identification of inventory and inputs will be essential. Ultimately, there may be an opportunity to adopt a global chain of custody standard to serve as a bridge

between the certification organizations that currently compete against each other. As the standard of material tracking technology improves, probability of this opportunity being manageable and efficient in implementation is greatly increased.

Sustainable forest management flourishes under local development, as the unique issues and idiosyncrasies of a particular region's forest and society are identified and addressed, allowing the forest management side of certification to be tailored to the environment in which it is used. Enforcing a uniform, global forest certification standard would be neither possible, nor desirable (Eba'aaty & Simula, 2002). Chain of custody standards, on the other hand, could benefit from global rationalization and increased mutual acceptance among the diversity of sustainable forest management schemes currently operating. No longer should chain of custody be thought of as a chain linking operations along a linear pathway from the forest to the consumer. Development of a "network of custody" where certified materials could flow freely among suppliers registered under different forest certification schemes is likely to alleviate bottlenecks in the supply chain, while offering new material sourcing options to certified forest product producers. With the technology needed to implement such a system now increasingly available (telecommunication networks, real-time data analysis and collection systems, and the development of effective, industry-focused material tracking systems), such a goal is now much more feasible. Furthermore, such a system does not require the merging of all forest certification schemes into a single entity, but allows the many regional schemes to use their diverse strengths to flourish while using one common, or a few compatible, chain of custody systems to connect them to the marketplace.

There is also the possibility that harmonization never occurs and certification schemes will stay in possession of their own CoC systems. Competition provides some benefits, as it ensures progress, assists accountability and avoids issues of management corpulence in monopoly. On the other hand, in competing for the subscription of manufacturers who would prefer to do less than more, unless kept in balance by consumers or environmental

groups, a duopoly in the CoC area could catalyze a “race to the bottom” (Fischer et al., 2005).

If there is not a global initiative to develop a single chain of custody standard to cover all certification schemes, the governance of the CoC standards will remain with the individual bodies. If any certification scheme is unwilling to take part in the development of an international CoC standard, continued independence of its CoC standard would occur, making it unlikely that an independent, global CoC standard could be developed. The evolution of CoC certification is therefore coming to a fork in the road, and the direction which it will take is uncertain. There will be benefits and detriments, whether the major forest certification schemes cooperate, or stand divided, over the development of a global CoC standard. Organizational unity provides logistical freedom, but also may result in conflicts of interest and complacency due to monopolization. With active competition comes improvement, but also the threat of diluting standards to remain competitive.

The continued efforts of PEFC and FSC to develop CoC standards, remove logistical bottlenecks and facilitate the supply of certified forest products to the market place may eventually result in a global network of custody. Conversely, deepening the divide between the PEFCs unified organization of schemes and the grass-roots environmental ideals of the FSC may lead to the development of a competitive duopoly in the realm of CoC certification. Either way, the technological landscape of materials tracking offers a great deal of potential to create solutions to improve the efficiency with which certified production are delivered to markets.

## **2.4 Conclusions**

As SFM and chain of custody systems develop into more efficient and effective processes, the major contenders in forest certification are developing increasingly similar CoC systems, in terms of policy on input confirmation,

documented control systems, defined product claims, and secure product labelling. The systems continue to evolve by further developing their principles and resolving the problems that presently afflict chain of custody systems. Simultaneously, industry continues to seek more efficient ways of implementing CoC systems. As the framework for the CoC evolves, certified organizations are left with the freedom to decide what methods will maximize the effectiveness of the CoC system, and the benefit to their organization. This freedom creates a wealth of opportunity for innovators to develop methods to service these organizations. With the increasingly robust systems available to track and manage inputs and inventory, CoC practices are becoming more diverse. Advanced material tracking systems offer the potential to make on-the-ground CoC management more effective, transparent, and economical for producers. As CoC systems evolve, technological intervention will provide the solutions to effectively remove, or loosen, many process bottlenecks and increase the potential material supply for processors holding CoC certificates.

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## Chapter 3

# DRIFT Response Reproducibility of Aged and UV-Exposed Wood Surface Coatings

### 3.1 Introduction

The forest-to-product supply chain has need for a new, tamper-proof means of tracking materials. In contrast to many manufacturing processes where individual components are assembled to produce a final product, wood product manufacturing always involves a disassembly step, *viz*, conversion of a log to sawn lumber pieces. A single log, depending on its dimensions, the sawing pattern and the products manufactured may be converted to many tens, hundreds, or thousands of components. Tracking all of these products through the supply chain requires a stable, durable, traceable code that may be applied to logs and also carried on each component throughout the entire supply chain.

Many labeling systems are being used for the purposes of Chain of Custody and materials tracking, but there remain a number of problems to be addressed in the complex nature of the forest product supply chain. Continual development in the material tracking industry has brought about a

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<sup>0</sup>A version of this chapter will be submitted for publication.

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variety of methods of tracking wood through this supply chain. These methods have included Radio Frequency Identification tags (RFID), nail-based barcode labels, microtaggant tracers and chemical paints (Dykstra *et al.*, 2003). However, barriers have arisen with many of these technologies due to limited robustness of complex technologies, or unfeasible associated expense (Chapter 1).

In this study, the development of a tracking system with the required attributes has been investigated using chemical functional group infrared (IR) signatures to build a chemical “barcoding” system using combinations of polymers with characteristic IR absorption bands. By applying polymers to logs or wood products, an invisible, stable identifier which can be read using reflectance IR spectroscopy may be devised.

In evaluating candidate polymers to be used in this study, it was important to address key attributes to ensure effectiveness of a barcoding system. Some properties of an ideal polymer for this application would include long shelf-life, stability in solution (to be applied to log or other product surfaces), chemical stability on wood over time, resistance to weathering, robustness at elevated temperature and presence of a clear, unique and reproducible absorption band in an ideal wavenumber region of the infrared spectrum. This study investigated seven candidate polymers against these criteria, and determined whether they were suitable for further use in the proposed barcoding system.

Although the literature provided much information regarding photooxidation and thermostability of some of the polymers assayed, the proposed application which involves polymer films applied to wood surfaces was expected to produce significantly different results. Substantial variation may have arisen from the complex biological background upon which the polymers were placed and against which the spectral properties would be determined, as well as the extensive potential for chemical interaction between the IR-detectable and chemically active moieties in wood and polymers. This study was undertaken to lay a foundation for the development of a chemical

barcode for wood products using polymer infrared spectroscopic responses, and spectroscopic behavior of multi-polymer blends.

## 3.2 Methods

### 3.2.1 Compound Selection

The polymeric and oligomeric compounds used in this study (henceforth referred to as polymers) were selected based on properties related to the ideal criteria which were germane to the proposed application. The primary criterion for selection was the presence of a clear, unique absorption band in the IR spectrum of the pure polymer. Peaks were sought which existed in areas of the spectrum sparsely populated by other chemical responses to minimize background interference and simplify discernment among different polymers in order to minimize interference from IR responsive compounds in the wood substrate. This initial screen was done using various polymer IR libraries (Pouchert 1975, Keller 1986, NIAIST 2006). After candidates were selected from this search, the pool was narrowed by investigating the physical properties of the pure polymers, such as handling characteristics, solubility in dichloromethane (DCM), toxicity and phase under standard conditions. The initial range of polymers selected for assessment and their absorption maxima are presented in Table 3.1. All polymers apart from poly(styrene-co-acrylonitrile) (SAN) were commercially available. SAN was prepared as presented below. All polymers selected were found to be soluble in DCM, and to exhibit an absorption band in an area of the IR spectra with the range of 2600–1550  $\text{cm}^{-1}$ . Slight differences between the absorption maxima reported in the literature and those measured in on wood surfaces were observed (Table 3.1).

Table 3.1: Compounds selected for study, their published absorption maxima and measured values in DCM.

Compound (Abbreviation)	Candidate Peak (Literature $\text{cm}^{-1}$ )*	Candidate Peak (DCM $\text{cm}^{-1}$ )
<i>o</i> -Carborane (CARB)	2600	2594
Poly(methylhydrosiloxane) (PMHS)	2242	
Poly(styrene-co-acrylonitrile) (SAN)		2238
Poly(methyl methacrylate) (PMMA)	1728	1740
Polycyclohexanone (PCH)	1715	1715
Poly(vinyl phenyl ketone) (PVPK)	1670	1700
Polysulfone (PSF)	1590	1590
Poly(propylene carbonate) (PPC)	1764	1770

\*Pouchert, 1975

### 3.2.2 Preparation of Poly(styrene-co-acrylonitrile) (SAN)

Absolute ethanol (117 mL), 2-butoxyethanol (13 mL) and azoisobutyronitrile (0.05 g) were added together in a round-bottomed flask fitted with a reflux condenser, and stirred, while a continuous stream of nitrogen was bubbled through the solution. The mixture was then heated to 80°C. Styrene (10 mL) and acrylonitrile (10 mL) were dissolved in absolute ethanol (18 mL) and 2-butoxyethanol (2 mL) and added drop-wise to the stirred mixture. The reaction was left to proceed for 18 hours. At the end of this period, the mixture was cooled to ambient temperature (20°C), and the liquid decanted off leaving the precipitated hard, white solid in the bottom of the flask. The co-polymer was dissolved in dichloromethane and transferred to a foil-lined glass dish. The dish was placed in a vacuum oven held at 50°C until the co-polymer had reached dry weight. The glassy solid was crushed and stored in a glass vial. Two preparations were carried out. The first gave a yield of 7.0 g (40%), and the second gave a yield of 6.8 g (39%) IR (KBr disc)  $\text{cm}^{-1}$  2238 ( $\text{C}\equiv\text{N}$ ), 1602 (Ar).

### 3.2.3 Solution Preparation

Polymer masses required to make 25 mL of a desired concentration were calculated, and polymers were weighed using an electronic balance (Ohaus ExplorerPro - Model EP214C) to 0.01 mg accuracy. The polymer samples were then transferred to DCM-washed 25 mL volumetric flasks (Kimax, Kimble, USA). The flask was filled to approximately 0.5 cm below the neck, sealed with a glass stopper, and left overnight for the polymer to fully dissolve. By not filling the flasks into the neck, the formation of solvent-swollen polymer “plugs”, especially with higher-concentration polymer solutions, was avoided. After the polymer had fully dissolved, the flasks were filled to the 25 mL mark, stoppered, and left for at least 1 hour before the solution was applied to prepared spruce wood specimens (see below). After the solutions were applied to the wood surface, they were transferred to 45 mL glass vials for storage and kept in the dark. In order to avoid any contamination of the polymer solutions from plastic labware, degradation of seals and consequent evaporation of solutions, these were kept for long-term in vials of either glass or Teflon<sup>®</sup>.

### 3.2.4 Sample Preparation

White spruce (*Picea glauca*) wood specimens, selected as a model of the SPF (spruce pine fir) wood mixes common to Northwestern forest operations, all cut from the same 2”x12” air-dried slab were prepared with dimensions of 2.2mm x 28mm with grain parallel to the length of the slide. These pieces were cut into 75mm veneers (2.2 x 28 x 75 mm), in the number required for a given experiment. If more than one piece was necessary to produce enough veneers, pieces with similar grain qualities were selected. Veneers were labeled on the back-side with solution ID, slide number (for duplicates of the same solution ID) and the date. Veneer specimens were weighed using an electronic balance to 0.01 mg.

The veneers were uniformly coated with 0.5 mL of the prepared polymer

solution using 1 mL disposable graduated borosilicate pipettes (Fisherbrand) with a 5mL hand pump, and then left to dry for at least 1 hour to ensure that all DCM solvent had evaporated. Slides were re-weighed to determine the polymer weight applied. This was done to compare weights calculated from solution volume applied and final weight after solvent evaporation.

Prior to IR spectrum acquisition, cores were then sampled from the prepared veneers using a cork borer (E. H. Sargent & Co., USA) with a 6 mm diameter bit. Typically, for every polymer solution prepared, veneers were prepared in duplicate, from which 3 cores were sampled, resulting in 6 cores being analyzed per applied polymer solution.

### 3.2.5 Spectrum Acquisition

Samples were placed in the macrocup sample holder of the Perkin Elmer DRIFT Accessory within a Perkin Elmer SpectrumOne Spectrophotometer (Perkin Elmer, Shelton, CN), and IR spectra were collected from samples in the range of 4000–450  $\text{cm}^{-1}$  in Kubleka-Munk (KM) units, with a scan resolution of 2  $\text{cm}^{-1}$ . Four spectra were taken from each sample, at different grain orientations: 45, 135, 225 and 315 degrees. Multiple grain angles were assessed to account for effects of grain angle on IR absorbances observed in preliminary studies. Spectra were saved in the default format, \*.sp and converted to ASCII files (\*.asc) for numerical analysis and manipulation.

### 3.2.6 Spectrum Quantification

Spectra were normalized to the SAN absorption band using Perkin-Elmer Spectrum Software. It was observed that polymer load, as well as many other factors could influence the overall attributes of a raw spectrum (i.e. the unmodified output of the DRIFT spectrophotometer). SAN peaks, and other peaks could be amplified or diminished, and the baseline of the spectrum could fluctuate substantially. When comparing two spectra of similar character (similar relative peak height and ratio values), differences in base-

lines, general amplification or masking of IR absorbances could skew peak calculations (such as reflectance difference and ratio) to near insignificance if examined in absolute terms. The spectral normalization process corrected for general masking effects by scaling the entire spectrum to proportionality to a fixed internal standard (SAN) peak height, and forced alignment of all spectra compared to a common minimum baseline to decrease the effects of a general spectral shift (on the  $y$ -axis). Combined, these two factors greatly improved the comparability of different spectra of similar character. The following parameters were used to scale spectra to the SAN C $\equiv$ N peak and to assign the baseline to zero at the base of the same peak.

- Peak<sub>high</sub>: 2268 cm<sup>-1</sup>
- Peak<sub>low</sub>: 2205 cm<sup>-1</sup>
- Ordinate: 0.5
- Zero: 2268 cm<sup>-1</sup>

Using the ASCII versions of these normalized spectra, it was possible to compare and analyze spectral data using Microsoft Excel to calculate the average height of peak apices and the variation of these averages. Averages for all polymer peaks were based on the maximum peak height, rather than KM response at a fixed point. Analysis sheets were programmed to extract maximum values in polymers' apex ranges.

### 3.2.7 SAN Stability

The reproducibility of the DRIFT response of the internal standard Poly-(styrene-co-acrylonitrile) (1:1) (SAN) was paramount to the success of this experiment. Previous studies had established that SAN is stable under exposure to light, as the cyano group has proven to be quite stable chemically due to infrequent restructuring of bonds within C $\equiv$ N functionalites (Jelinek and Schlueter, 1960). SAN (1:1) was used instead of polyacrylonitrile (PAN) to provide solubility of the internal standard polymer, as PAN is not soluble

in DCM. Very limited literature exists on the photo- and thermal-stability of this copolymer, and none is available on its stability on wood. Mailhot and Gardette (1994a) showed previously that this copolymer is susceptible to thermal and photooxidation when exposed to long and short wave UV radiation. The degree to which SAN surface coatings would oxidize when applied to wood, and to what degree the IR spectra might be affected was investigated by collecting spectra from samples coated with SAN solution at 10 mg/mL, and comparing them to each other with respect to baseline-subtracted peak height of the C $\equiv$ N stretch (height of peak minus calculated height of background at 2238 cm<sup>-1</sup>).

### 3.2.8 SAN Stability in Solution (Shelf Life)

In order to ensure that peaks were scaled correctly, it was imperative that normalized SAN peaks maintained a similar shape with a high degree of accuracy to allow meaningful comparison of other peaks in the spectrum. In order to assess spectral fit, integrated areas beneath SAN peaks were compared from initial applications, rescans (five months later) and on new pieces of wood treated with five-month old solution of SAN 10 mg/mL in order to assess the stability of SAN in solution. All samples were kept in dark conditions, with the exception of when they were being scanned in the DRIFT cell.

### 3.2.9 Polymer Response Reproducibility

Candidate polymer responses were compared over time to determine stability on wood. Core samples coated with 25 mg/mL of respective polymer were scanned and the spectra collected were normalized to a common SAN-C $\equiv$ N peak. Ranges of values of height (in Kubelka-Munk Absorbance units (KM)) for candidate peaks were compared by mean and 95% confidence intervals. After initial scans (at t=0) half of the sample cores were placed in a North-facing window, exposing the samples to glass-filtered sun rays at

seasonal levels (between February and July). These samples were used to determine any changes in polymer response due to light exposure. The remaining half of the samples were kept in the dark, undessicated conditions. Both sample sets were re-scanned every 6 weeks. Changes in response ranges were investigated over time, and between samples kept under light versus dark conditions.

### **3.3 Results**

#### **3.3.1 SAN Stability**

The major concern associated with the use of SAN as an internal standard was whether it would degrade significantly, or if chemical changes would be small enough that the resulting IR spectra ( $C\equiv N$  peak, particularly) would not deviate over time. The temporal changes in SAN's cyano-group peak height with and without exposure to the sun are presented in Figure 3.1.

Both light and dark treated SAN polymer samples suggested stability over time. Neither sample sets exhibit noticeably increasing or decreasing trends, inferring that the SAN peak is stable over time both in dark conditions, and when exposed to indoor sunlight.

SAN has been used as the normalization standard for all candidate polymer coatings in this study, and if it is to serve as an effective internal standard, it must be reproducible relative to the rest of the spectrum. The SAN  $C\equiv N$  peak was forced to certain parameters during normalization, and all other peaks were scaled to the same order.

#### **3.3.2 SAN Shelf Life**

Peak integrations of the  $C\equiv N$  stretch (internal standard peak) from new samples, on-wood aged samples, and in-solution aged samples of SAN 10

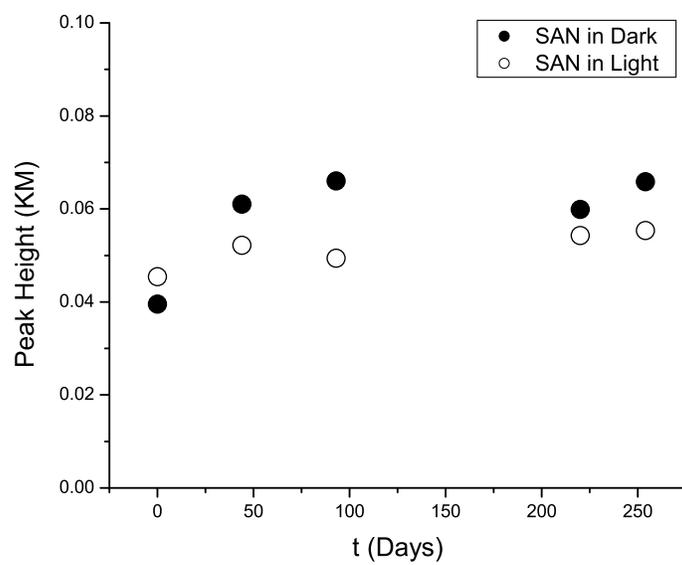


Figure 3.1: Changes in peak intensity of  $V_{C\equiv N}$  (baseline subtracted) between on-wood SAN samples exposed to light and kept in dark over time illustrated by mean values of collected data.

mg/mL are presented in Figure 3.2.

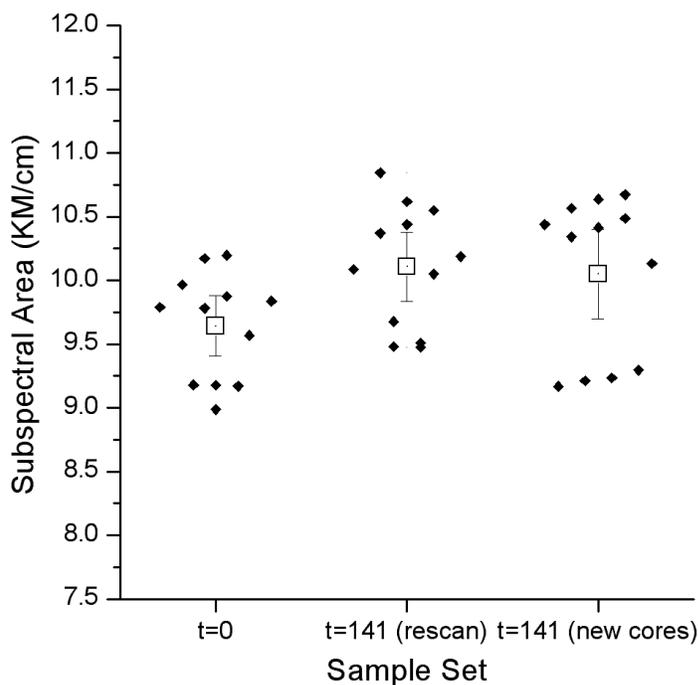


Figure 3.2: Comparison of subspectral area of SAN peaks derived from spectra collected from newly prepared samples with newly prepared SAN10 solution (initial), aged samples (same cores) and freshly prepared samples with aged SAN10 solution (new cores). Open squares represent arithmetic means, whiskers represent 95% confidence intervals, and the three clusters of black dots represent data values ( $n=12$ ) for each of the three sample times. Sample set ( $x$  axis) is measured in time elapsed in days.

Figure 3.2 shows a slight shift in the distribution of points. The slight increase in peak area, when attributed to peaks forced to certain zero and apex values (normalized) suggests a relative decrease in peak magnitude. However, overlapping 95% confidence intervals indicate that the means are not statistically significant, meaning SAN does give a statistically reproducible peak at the  $C\equiv N$  absorbance band ( $2238\text{ cm}^{-1}$ ) over the study period.

### 3.3.3 Peak Reproducibility

Using SAN as the internal standard, normalized spectra were compared to establish their ability to deliver reproducible responses over time and in the presence of solar UV radiation. The normalized IR responses of candidate polymers at different points in time are presented in Figure 3.3. The paired-sample means t-test was applied to the same data to extract conclusions regarding “significant change” from these scatter plots and the results are presented in Table 3.2, with the sampling timeline defined in Table 3.3.

Table 3.2: Results of paired-sample t-tests. Each value represents the  $P(T \leq t)$  value derived from comparison of dark and light treated samples at progressive sampling intervals. Values greater than 0.05 (shown in bold) denote a lack of significant change ( $\alpha = 0.05$ ).

Period	Treatment	PVPK	PSF	PMMA	PCH	PMHS	CARB	PPC
$t_0 - t_1$	Dark	0.000	0.003	<b>0.039</b>	<b>0.024</b>	0.000	<b>0.462</b>	<b>0.690</b>
	Light	0.001	0.013	0.000	0.000	0.000	0.000	0.001
$t_1 - t_2$	Dark	0.012	0.000	<b>0.222</b>	<b>0.146</b>	0.000	0.010	0.001
	Light	<b>0.117</b>	0.019	0.000	0.001	<b>0.687</b>	0.026	<b>0.801</b>
$t_2 - t_3$	Dark	0.018	0.000	<b>0.243</b>	<b>0.317</b>	0.000	<b>0.451</b>	
	Light	0.000	<b>0.181</b>	<b>0.160</b>	0.022	<b>0.998</b>	<b>0.052</b>	
$t_3 - t_4$	Dark	<b>0.560</b>	<b>0.251</b>		0.000		<b>0.738</b>	
	Light	<b>0.964</b>	<b>0.823</b>		0.000		<b>0.793</b>	
$t_5 - t_6$	Dark				0.000		0.000	
	Light				0.000		<b>0.266</b>	

Table 3.3: Sample period definitions for polymer stability assay. Values represent number of days after sample preparation each data set was collected.

Sampling	PVPK	PSF	PMMA	PCH	PMHS	CARB	PPC
$t_1$	44	57	45	75	50	53	52
$t_2$	93	106	116	112	113	87	94
$t_3$	220	213	147	162	148	136	
$t_4$	254	240		221		197	
$t_5$				247		225	

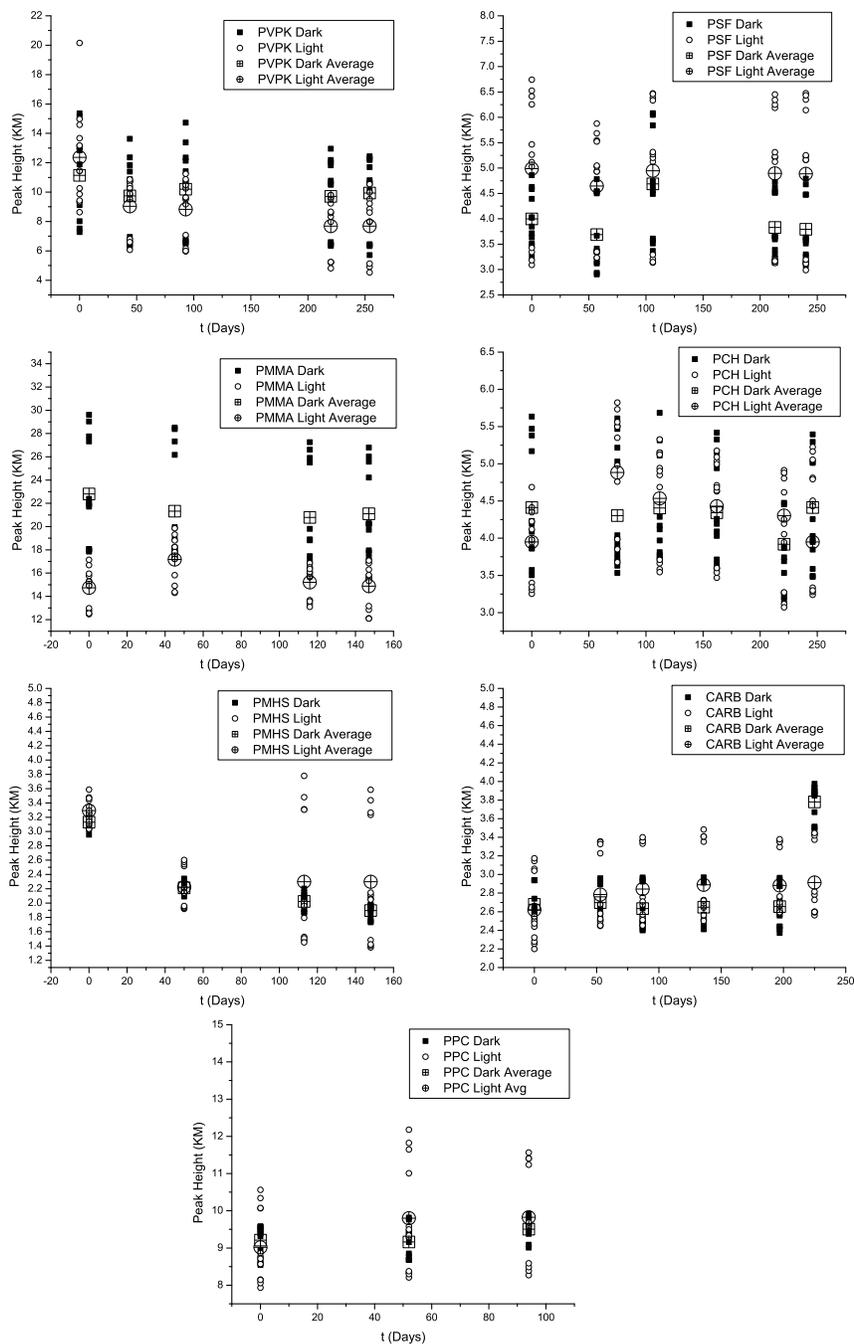


Figure 3.3: Temporal scatter plot of repeated DRIFT sampling of candidate polymer films on wood surfaces. Data points represent baseline corrected candidate peak heights derived from spectra normalized to the PAN internal standard. KM = Kubelka-Munk units. 47

A data point which does not fit within a linear pattern may suggest some change in the system, but if the curve returns to linearity, such points may be due to experimental error.

Photochemically, and over time, the PVPK peak appeared to be unreliable, as both the dark and the light treated samples changed significantly. In darkness, the PVPK changed significantly within three of the four intervals, and in light conditions significant shifts were seen within two of the intervals. Figure 3.3 shows a progressive decrease in both light and dark-exposed sample ranges.

PMMA appeared to be stable with respect to time in the dark. However, until the  $t_3$  sampling, the light-treated samples changed significantly within each interval (Table 3.2). Investigation of the data shows an increased average in the  $t_1$  sample set, and a  $t_2$  showing similarity to  $t_0$ , causing the significant increase and decrease in the  $t_0$  to  $t_2$  range. These data formed a response curve that was slightly parabolic, whilst the paired sample t-test revealed a lack of significant change between the data range at  $t_0$  and the end of the assay. Although this may suggest stability over time, the significant variance in the interim may be problematic for the system.

The response stability data showed by PSF gave relatively consistent averages, with the exception of the  $t_3$  light sampling, which was notably higher than the other light-treated samples. This outlying average caused significant changes in light-treated sample intervals (Table 3.2). Figure 3.3 does suggest relatively consistent readings, despite this outlying average. The parabolic nature of the average curve is similar to that of PMMA, and consequently suggests fluctuation over progressive sampling intervals. In the long term, however, the absorbance responses appear relatively stable.

PMHS did not give a reproducible peak on wood over time. Light treatment did not cause significant differences in the behavior of the PMHS stability curves, compared to dark treatment. For both dark controlled and light treated samples, all ranges beyond  $t=0$  were lower than the initial values for all samples. Table 3.2 suggested that light-treated samples did not change

beyond  $t_2$ , however inspection of data (Figure 3.3) showed similar means at a lower absorbance, and a notable increase in variance.

In the dark, PCH initially gave a reproducible peak (consistent between  $t_0$  and  $t_3$ ), as the ranges did not appear to vary until the  $t_4$  and  $t_5$  samplings. When exposed to light, the PCH peak exhibited a complete lack of peak reproducibility.

The CARB peak appeared reproducible with respect to both time and exposure to light showing only a slightly increasing trend in CARB peak response with light exposure, and an overall absorbance increase in dark-treated samples (Figure 3.3). The results of the paired-sample t-test showed that CARB exhibited a significant shift between  $t_1$  and  $t_2$ , stayed stable until the end of  $t_4$ , and shifted again toward the end of the assay. Light treated samples shifted from  $t_0$  until  $t_2$ , and beyond this point remained stable. Examination of Figure 3.3 showed an increasing trend in the beginning of the assay.

PPC exhibited a strong peak that varied significantly between samplings in both light and dark treated sample sets. The range of the data points appeared to increase in light-treated wood.

Response uncertainties were correlated with the intensity of all polymer candidate peaks in this study, especially for samples stored in the dark (Figure 3.4). Polymers such as PMMA, PVPK and PPC gave much more intense peaks, and therefore exhibited higher uncertainty. This observation is primarily due to procedural error associated with normalizing peaks larger than the internal standard.

The regression surface for both light and dark samples suggests a positive mean-variance relationship. However, statistical assessment showed that both sample sets violate the assumptions of normality and uniform variance. Associated residual plots (not shown) show a widening trend suggesting changing variance. As well, Shapiro-Wilk tests applied to both data sets showed a lack of normality for both light and dark treated sample variances, suggesting that these results must be approached with caution.

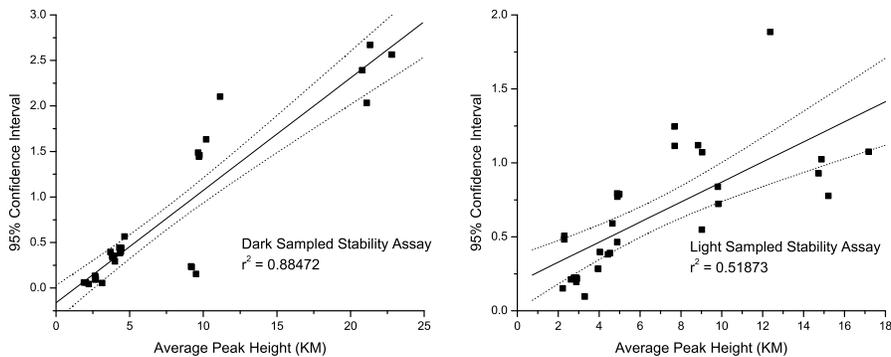


Figure 3.4: Regression between degree of uncertainty and increasing absolute peak height for light and dark treated wood samples.

### 3.3.4 Spectral Interference

Investigation of sample spectra revealed that light exposure created changes in the spectra of all the compounds studied in the  $1700\text{--}1800\text{ cm}^{-1}$  range. In some cases these changes resulted in peaks that were close enough to the candidate peaks to cause interference. In order to illustrate the impacts that light exposure and time had on the spectra of candidate polymers, difference spectra were constructed to illustrate the spectral areas in which the DRIFT response changed the most (Figure 3.5).

All polymers exhibited “peak shouldering” in the  $1700\text{--}1800\text{ cm}^{-1}$  range in light-treated sample sets. Although wood surfaces were coated with a polymer, the observation that all samples showed the same peak growth in the  $1760\text{ cm}^{-1}$  area suggested that it was an effect of wood photodegradation. Exposure of wood to UV radiation has been reported to result in an increased IR spectrum within the  $1710$  and  $1763\text{ cm}^{-1}$  areas as unconjugated carboxyl groups are created (Tolvaj and Faix, 1995). In addition to wood photodegradation, some polymers tested were also capable of being photooxidized into the carbonyl photoproducts which could contribute to this shoulder. It has been reported that PVPK (Rabek, 1995), PAN (Mailhot

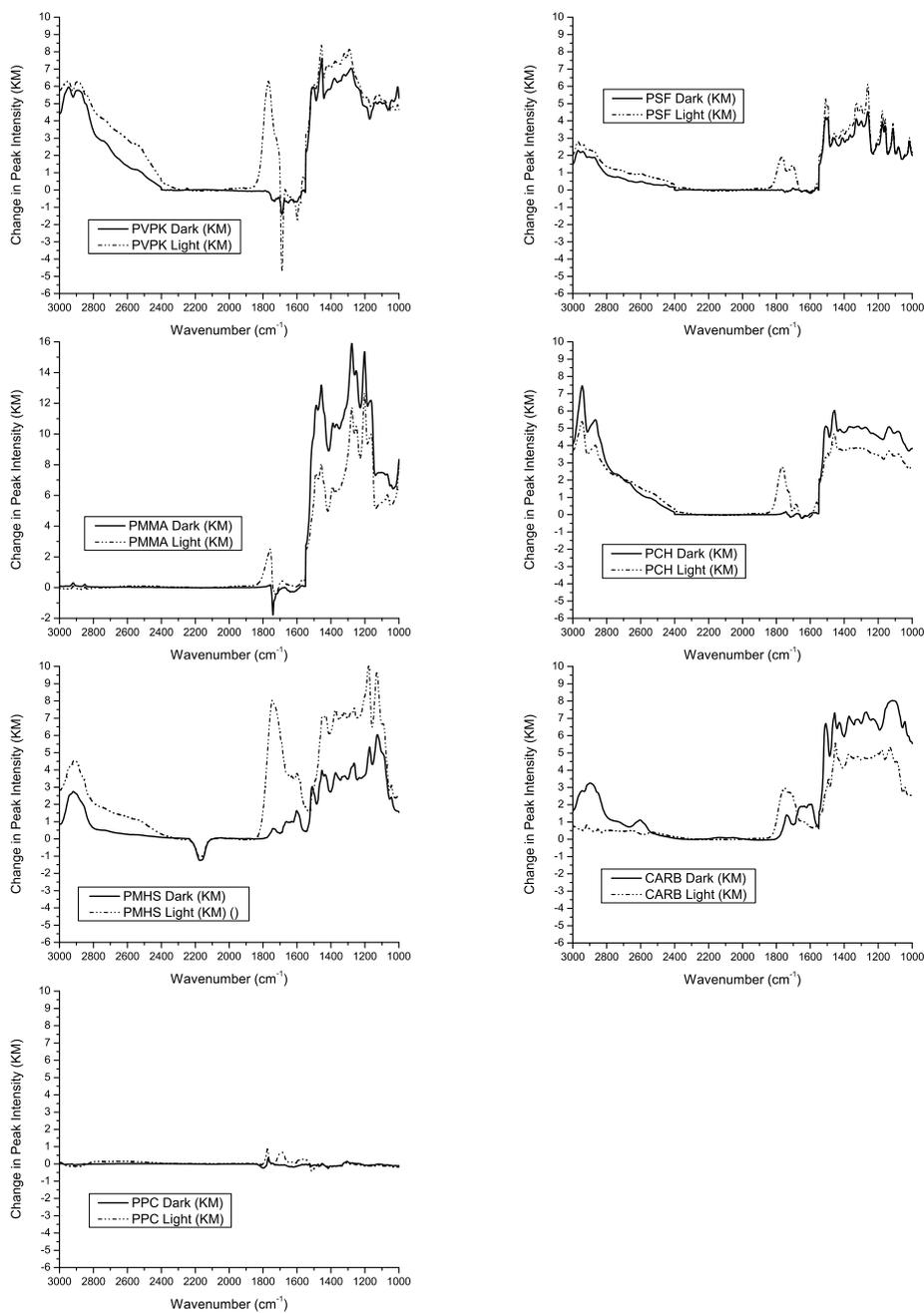


Figure 3.5: Difference spectra of candidate polymers after 8 months of treatment (either dark or light). Spectra represent Kubelka-Munk value differences between spectra at  $t=8$  months and those of spectra collected at  $t=0$ .

and Gardette, 1994b) and PSF (Rivaton and Gardette, 1999) also produce photoproducts which would manifest a response in this area. PPC, by contrast, was reported to be gradually oxidized to released CO<sub>2</sub> when irradiated, explaining its relative lack of activity in that region (Liu *et al.*, 2002).

CARB showed a notable increase in the 1550–1800 cm<sup>-1</sup> range with exposure to light, and displayed the same increase, to a lesser extent, in the dark samples. PMMA exhibited a notable increase in the 1763 cm<sup>-1</sup> area of the spectrum, accompanied by a hypsochromic shift in the 1738 cm<sup>-1</sup> (PMMA peak) area of approximately 0.5 KM units when exposed to light. However, when kept in the dark, the PMMA peak decreased by 2 KM units in the absence of light-induced spectral effects.

PVPK, when exposed to light, showed a consistently decreasing PVPK peak (1714 cm<sup>-1</sup>) while the overall 1710–1800 cm<sup>-1</sup> region exhibited a notable increase in spectral activity. PSF spectra showed increases in the spectra in two areas, with maxima at 1770 and 1670 cm<sup>-1</sup>. The double peak was likely due to the production of unconjugated carbonyls, which absorbed in the region of a peak already present in the spectrum, thus demonstrating the increases in the flanking regions of an already existing C=O absorbance in wood (1741 cm<sup>-1</sup>) (Tolvaj and Faix, 1995). With a peak already existing in that position, the relative increase was less than in surrounding areas. In darkness, PSF remained relatively stable. PPC showed a relatively small increase in the same two areas as PSF (1770 and 1670 cm<sup>-1</sup>). For PPC, the candidate peak was located at 1770 cm<sup>-1</sup> reflecting the carbonate C=O group. A 0.91 KM increase in this peak was observed with light exposure, in addition to a 0.66 KM increase in the 1670 cm<sup>-1</sup> area. PCH appeared stable in dark conditions, but under light exposure showed a 2.6 KM increase at the 1770 cm<sup>-1</sup> wavenumber, and exhibited increases in the range between 1770 and 1700 cm<sup>-1</sup>, effectively enveloping the PCH candidate peak. PMHS appeared to cause particularly dramatic changes in the 1800–1500 cm<sup>-1</sup> range of the spectra. During the assay, areas between 1900 and 1600 cm<sup>-1</sup> had increased in intensity to a great degree with maximum increase at 1745 cm<sup>-1</sup> (increased 7.9 KM units in the presence of light). An increasing peak

was also visible at  $1595\text{ cm}^{-1}$ , increasing by 3.7 KM units in the course of five months sun exposure. Also, a notable decrease in response from the PMHS peak area ( $2166\text{ cm}^{-1}$ ) was shown by the difference spectra of both light treated and dark treated samples. This observation illustrated either PMHS' instability on wood, or its inability to remain adhered to the wood surface.

### 3.3.5 Shelf Life

Reproducibility of response is imperative for both polymer coatings on wood, and polymers in solution. To ensure that polymers were not changing in a way that would jeopardize the fidelity of the resulting IR peaks, polymers were applied to wood when solutions were freshly prepared, and again once the solutions had aged (in the dark for more than 6 months). The results obtained are presented in Figure 3.6.

When the collected spectra were normalized, very close alignment of spectra was observed within the same sample sets, but narrow 95% confidence intervals showed significant differences between some of the peaks (Figure 3.6). Only PCH, PMMA and PSF gave statistically similar responses when the same polymer reagents were applied to different wood on later dates, changing 6, 10 and 6% respectively. The responsiveness of CARB, PMHS, PPC and PVPK changed significantly over the study period.

## 3.4 Discussion

### 3.4.1 SAN as an Internal Standard

The SAN  $\text{C}\equiv\text{N}$  peak was found to be an acceptable internal standard for use in the proposed chemical barcode system as it produced a reproducible response over time, both in solution (data not shown) and on wood. Initially selected for its favorable position in the IR spectrum ( $2238\text{ cm}^{-1}$  region),

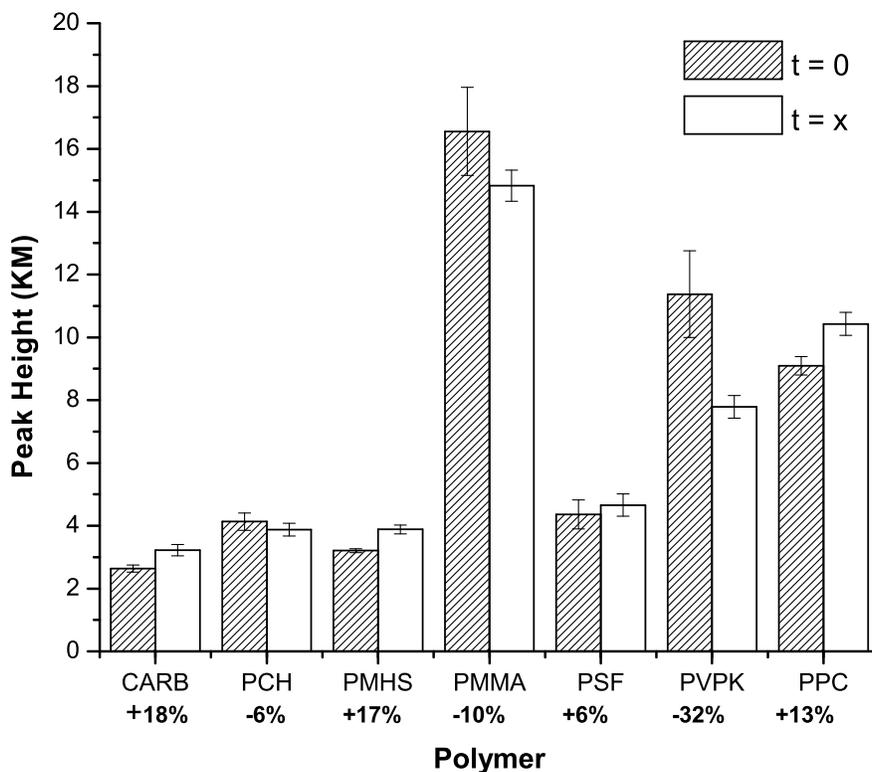


Figure 3.6: Shelf life of polymers in solution was determined by comparison of polymer responses (absolute maxima of SAN-normalized spectra) with respect to time applied to wood. Bars represent geometric means of peak responses (n=24 each, geometric mean was found to better represent non-normal data distributions of certain polymers), whiskers represent 95% confidence intervals. Days elapsed (x) = CARB-219, PCH-240, PMHS-181, PMMA-212, PSF-213, PVPK-253, PPC-238. Values below polymer identities indicate the percentage difference between initial and final samples.

separated from most interference caused by wood spectra (Tolvaj & Faix, 1995), SAN gave a statistically stable DRIFT response through aging, on wood and in solution and under exposure to the suns UV rays. The  $2238\text{ cm}^{-1}$  peak which was used as an internal standard in this study was stable due to the large amount of energy required to chemically degrade the the cyano ( $\text{C}\equiv\text{N}$ ) group (Mailhot and Gardette, 1994b). Any degradation that does occur in SAN can be attributed to chain scission, which leaves the  $\text{C}\equiv\text{N}$  groups intact, and occasional  $\text{C}\equiv\text{N}$  cyclization, which creates polyimines along polymer backbones (Mailhot and Gardette, 1994b). In addition, this peak is found in a spectral range between  $2400\text{--}1850\text{ cm}^{-1}$  that contains little absorbance from wood components or byproducts of wood and polymer degradation. SAN is therefore an ideal polymer to be used as an internal standard.

### 3.4.2 Polymer Peak Reproducibility

This experiment investigated the behavior of polymer IR responses when applied to wood surfaces. The study emphasized the impacts of wood background spectral elements on the reproducibility of candidate peaks, which are the components of each polymer's IR spectrum with which the proposed chemical "barcodes" will be built. Four of the polymers assayed presented a candidate peak identified with the same functionality. PVPK, PPC, PCH and PMMA all gave candidate peaks in the same area of the spectrum ( $1700$ ,  $1770$ ,  $1714$  and  $1744$ , respectively) owing to presence of carbonyl groups in each compound's structure (Figure 3.7). The common carbonyl functionalities in PVPK, PPC, PCH and PMMA caused the candidate peak for each polymer to be situated in close proximity in the IR spectrum. This effect prevented the use of any combination of these four polymers, due primarily to the serious issue of differentiating between peaks, as well as the potential for chemical interplay of these functionalities and production of similar byproducts through thermo- and photo-oxidation. In addition, the  $1700\text{--}1800\text{ cm}^{-1}$  area of the wood spectrum is populated with responses from oxidized by-

products of wood-based phenolics (mainly unconjugated carbonyls), as well as photo- and thermo-oxidized products of candidate polymers (Mitsui *et al.*, 2003, Mailhot and Gardette, 1994b, Liu *et al.*, 2002). Discerning more than one peak in such a chemically active area of the spectrum would not be feasible. Therefore, the best performing of these polymers must be chosen for use in the chemical barcode system. Of the four, PMMA exhibited the best reproducibility over time and sunlight exposure on wood. PMMA also exhibited superior shelf-life reproducibility compared to PVPK and PPC. The PCH peak was significantly affected by interference from by-product accumulation, due to a relatively weak IR peak, and would therefore cause problems in industrial use.

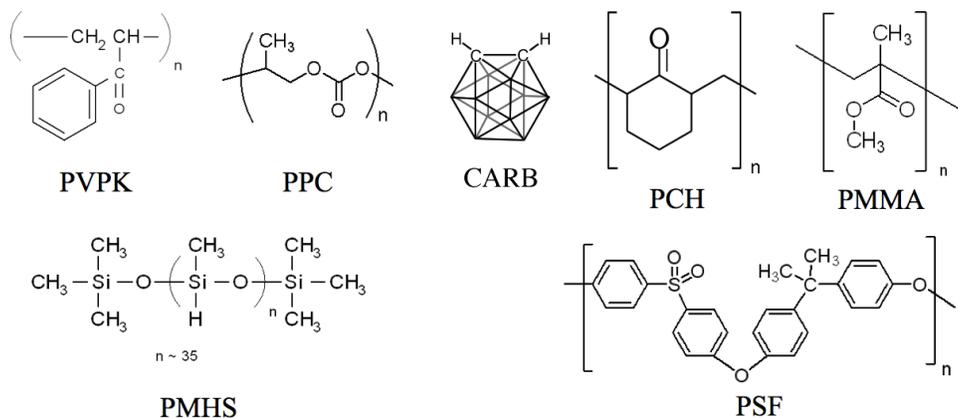


Figure 3.7: Chemical structures of PVPK, PPC, PCH, PMMA, PMHS, PSF and CARB candidates.

In the presence of sunlight, wood treated with PPC gave an IR spectrum which changed the least. This observation may be due to PPC's propensity to eliminate CO<sub>2</sub> rather than produce lactones and other unconjugated carbonyl derivatives (Liu *et al.*, 2002), or to a greater UV "protecting" effect associated with PPC, which did not allow the wood to be affected to the same extent as other polymers. However, PPC in surface protectants has not been investigated in the literature. Although PPC performed well in the scope of this study, previous investigations raised questions of its durability in the harsher context of industrial use. PPC is well known for its

biodegradability, and is being extensively investigated in naturally decomposing plastics (Du *et al.*, 2004). This property comes from the propensity, previously mentioned, to eliminate CO<sub>2</sub>. This chemical property makes PPC extremely susceptible to acid hydrolysis and photodegradation. In a log yard or shipping facility, the chemical compounds proposed will be repeatedly exposed to moisture and pH variation (rain, fresh- and salt-water) as well as extreme sun conditions. In these cases, PPC could be degraded significantly, since exposure to the most ideal outdoor conditions can cause PPC mass losses of up to 5% (Du *et al.*, 2004). As carbon dioxide is lost from the polymer system, the functionality that produces the candidate peak of PPC will become less present, leading to changes in the IR response, and consequently the chemical barcode. For this reason, of the four polymers, PMMA is considered the best carbonyl candidate for use in the proposed system.

PSF performed well in this assay in reproducibility on wood over time, with exposure to sunlight, and in solution over time. Rivaton and Gardette (1999) found that PSF was susceptible to photodegradation in the presence of O<sub>2</sub> which raises a concern. Upon degradation, most products still contain the S=O stretch that contributed to the candidate IR peak, apart from the trace amounts of SO<sub>2</sub> that may have been eliminated (Rivaton and Gardette, 1999). Also, PSF is quite susceptible to weathering when exposed to the full range of elemental stresses (Dilks & Clark, 1981). These two studies suggest that even though PSF produced a stable response over time, this response could be reflecting more than one product, one of which may be soluble in water. If oxidized S=O byproducts were produced, this study could not demonstrate the effects of byproduct loss on IR peak reproducibility (such as would occur under regular exposure to weather). Therefore, although PSF appears to perform well in laboratory tests that did not include exposure to water, further experimentation is recommended to confirm its appropriateness for use in more practical applications.

PMHS gave the same results with and without exposure to light, suggesting photostability. However, these consistent results included a notable decrease

in the PMHS IR peak response over time. While polymethylsiloxane is very stable, polymethylhydrosilane is much less so, as the Si—H bonds are reactive towards both water and polar functional groups leading to substitution reactions and poly-condensation (Pionteck *et al.*, 2005). The loss of absorbance intensity for the Si—H peak in this assay was assumed not only to be a consequence of oxidation, but also due to polymer loss due to poor adhesion to wood. In addition, the absorbance peak for PMHS ( $2166\text{ cm}^{-1}$ ) was within close enough proximity to the  $\text{C}\equiv\text{N}$  peak ( $2238\text{ cm}^{-1}$ ) from SAN to influence its peak characteristics, and therefore posed the issue of interfering with the SAN internal standard. For these reasons, PMHS was not considered to be a suitable polymer for use in the proposed polymer barcode system.

*o*-Carborane initially appeared to be a promising candidate, with the compound exhibiting reflectance peak-response reproducibility on wood over time and after sunlight exposure. The chemical stability of the carborane ring structure is well established (Korshak *et al.*, 1976) suggesting that this compound would be a suitable candidate for a chemical barcode. However, it gave a significantly different response when the *o*-carborane solution was re-applied to new wood samples after having been kept in DCM solution for five months. This observation suggests instability of *o*-carborane in the solvent DCM. One advantage of *o*-carborane was the large IR reflectance response for a relatively small amount of the compound applied to the wood surface. Due to apparent instability in DCM solution, *o*-carborane was rejected for further use in the proposed chemical barcode system. Such polymers which exhibit differences in spectrum when stored in solution cannot be used effectively, because they would exhibit divergence from established parameters even before being exposed to the elements.

Of the seven polymers assayed, only two proved to be usable in the proposed chemical barcode system, based on requirements of stability over time and under solar UV exposure (Table 3.4). This number of polymers is not sufficient for the development of a prototype system, due to the lack of resolution in the system caused by the small number of variables (candidate peaks).

Table 3.4: Summary of polymer response with respect to aging techniques investigated. ✓ denotes stability in a given assay (lack of significant change), while  $x$  denotes instability

Polymer (peak $\lambda$ , $\text{cm}^{-1}$ )	On Wood		In Solution	ChemiCode
	Aging	Sunlight	Shelf Life	Suitability
CARB (2600)	$x$	$x$	$x$	$x$
PCH (1715)	✓	$x$	✓	$x$
PMHS (2166)	$x$	✓	$x$	$x$
PMMA (1744)	✓	✓	✓	✓
PSF (1590)	✓	✓	✓	✓
PVPK (1700)	$x$	$x$	$x$	$x$
PPC (1770)	$x$	$x$	$x$	$x$

The present study has been limited to commercially available polymer compounds. To develop a broader assortment of IR-peak producing candidates, further studies will need to investigate the potential for the synthesis of polymers with novel IR signatures to be exploited, mainly with peaks in the 2400–1800  $\text{cm}^{-1}$  wavenumber area of the spectrum. Not only would such polymers be expected to display better responses on a wood background, but also custom synthesis would make illicit reproduction much more difficult, thus increasing the security of the system. In addition, further investigation into methods of effectively blinding the wood background spectrum should be undertaken. Removing the interference caused by wood background would make new regions of the IR spectrum available and permit the application of polymers with IR peaks outside the 2400–1800  $\text{cm}^{-1}$  range.

### 3.5 Conclusion

Important properties for an ideal polymer to be used in a chemical barcode system for wood products are long shelf-life in solution, stability on wood surfaces over time, resistance to weathering, and presence of a strong, identifying peak in an ideal part of the spectrum. Two polymers of the seven

initially assayed PMMA and PSF, were deemed acceptable for use in the proposed chemical barcode system, based on factors mentioned above as well as their IR-response reproducibility on wood in darkness, in presence of sunlight, and in DCM solution. Those that did not meet the desired criteria were PCH, PMHS, CARB, PPC and PVPK. SAN was selected from the three acceptable polymers for use as an internal standard because of the ideal location of its nitrile ( $C\equiv N$ ) peak in the spectrum and its consistent peak response.

Polymers that may be considered to be stable in ideal conditions were shown to perform differently in the presence of UV radiation and in contact with the chemically active wood surface. Due to the extensive overlap of common polymer functionalities and wood compounds in the IR-spectra, uses of polymers with candidate peaks derived from carbonyl, alkene, alkyne, or nitrous functionalities were severely limited. More polymers containing functionalities giving peaks in the  $2400\text{--}1800\text{ cm}^{-1}$  area of the spectra must be found, or some means of removing the wood background spectrum in the  $1800\text{--}1550\text{ cm}^{-1}$  IR range must be developed.

A system allowing sufficient resolution cannot yet be produced with only the two candidate polymers and single internal standard selected from this study. Further investigation is required to select a range of polymers sufficient to be used in concert to produce a sufficient number of chemical permutations. Further measures may include use of novel functionalities, such as conjugated allenes (Kijima *et al.*, 2002) or sulfur-containing compounds (Skoog *et al.*, 1998), or making available more of the spectrum frequencies by using techniques to mask the background and offer additional possibilities for candidate polymers in this proposed chemical barcode system.

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## Chapter 4

# DRIFT Response Dependency on Polymer Concentration in Wood Surface Coatings

### 4.1 Introduction

Material tracking methods have taken many forms in the past, including conventional on-product labels (barcode, paint, and chisel), radio frequency identification tags, and microtaggant tracers (Chapter 1). Some tracking technologies have been developed for security, some for accuracy, and some for economics or ease of use (Chapter 1). This study continues the initiative to develop a new method of material tracking using the inherent security of IR signatures, the resolution of certain fingerprint methodologies, and the reasonable economics of commercially available feedstock polymers. Foundational research into the principle of the chemical barcode system (Chapter 1) was previously undertaken by assaying polymers for appropriate polymer stability (Chapter 3), and has been further investigated to predict potential resolution of such a system, based on the response between the polymer IR signatures and increasing concentration.

This study is founded on the rule that reflectance responses expressed in

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<sup>0</sup>A version of this chapter will be submitted for publication.

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Kubelka-Munk units (KM) should show a positive slope with respect to increasing concentrations of polymer applied to a surface (Skoog *et al.*, 1998). However, KM theory is based on ideal samples of infinite depth (Liang *et al.*, 1999). Samples observed in non-ideal conditions will show an IR-response plateau at high concentrations (Culler *et al.* 1984). In light of this behavior, polymers which maximize the potential resolution of the system, thus behaving ideally, will plateau at higher concentrations, allowing more concentration points to be included in the upward-sloped portion of the concentration-IR response curve.

For each compound examined, the relationship between concentration and IR absorbance response was assessed, to illustrate that polymer's potential utility in the chemical barcode system. The utility of each compound was characterized by the slope of the polymer concentration-absorbance response curve between the minimum and the maximum point before a plateau occurs, and determining the number of discernible concentration points that can exist in this range. An "ideal" polymer, as previously mentioned, should exhibit a concentration-absorbance response curve with a positive slope with increasing polymer concentration, or plateau only at high concentrations, and have linearly distributed data points that represent statistically unique ranges. Response curves which increase continuously, or plateau at high concentrations are ideal because concentration points which lie beyond an apex or plateau cannot be utilized in the proposed chemical barcode system. It is necessary that a given KM value falls into a unique range to be associated with a given concentration, therefore, if the same KM value can arise from two different concentrations (as would occur in the event of a plateau or apex), there would exist ambiguity in the interpretation of the data. Consequently, a plateau or apex effectively caps the number of possible concentrations. In an ideal situation (uniform upward linearity, such as in Figure 4.1), there is no limit to the number of concentration points which may be used in such a chemical barcode system. However, in non-ideal conditions a plateau or apex defines a range of usable concentration points, and thus potentially limits the resolution of the system.

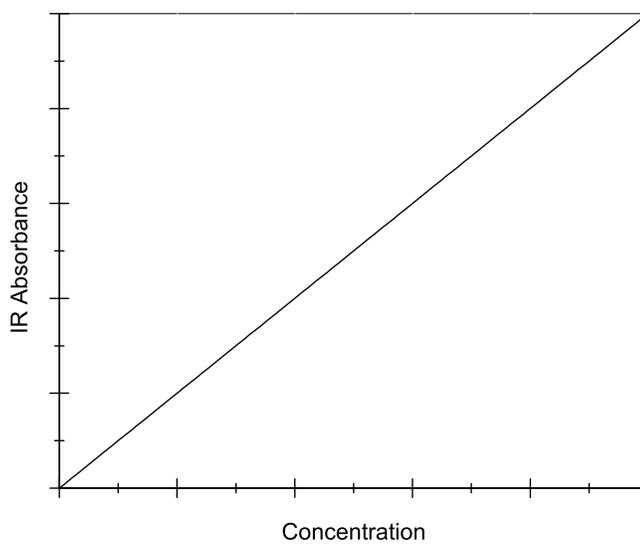


Figure 4.1: An ideal polymer concentration–IR absorbance curve. According to Beer’s law for transmission spectroscopy, and the Kubelka-Munk Equation for reflectance spectroscopy, absorbance is proportional to concentration of the absorbing compound. In ideal conditions, the resulting curve is linear at all concentrations.

Increased numbers of concentration points between the curve minimum and plateau allows for greater resolution in the overall system, since numbers of concentrations per polymer will factorally increase the number of discreetly identifying permutations the system can provide.

The objective of this study was to determine the suitability of each candidate polymer for use in a chemical barcode system. This judgement was based on the resolution which each could accommodate in their polymer concentration–absorbance response curves, when derived from a singular “candidate” peak. The suitability of each compound was to be further assessed by investigating the responses of the candidate polymers according to the criteria of ideal behavior: the slope of increasing concentration range and number of statistically discernable concentration ranges within it.

## 4.2 Methods

### 4.2.1 Sample Preparation and Spectra Collection

Sample preparation and spectral collection methods have been previously outlined in Chapter 3. Data used in the response curves was collected immediately after solution and sample preparation for all sample sets, in order to avoid potential changes in reflectance response due to degradation or light exposure. Individual sample sets were created for each polymer concentration, allowing for meaningful comparisons by 95% confidence intervals.

### 4.2.2 Data Analysis

Spectra were converted to ASCII files at the resolution of one data point per  $2\text{ cm}^{-1}$ , and collected into polymer-specific spreadsheets. Average spectra for selected polymer concentrations were calculated by individually averaging reflectance values for each wavenumber ( $\lambda$ ), and compiling the average values into a spectrum. Spectral data used for this study were nor-

malized to the poly(styrene-co-acrylonitrile) (SAN) peak ( $2237\text{ cm}^{-1}$ ), and set to a common zero located at the base of the internal standard peak. The resulting normalized spectra were monitored for changes in individual candidate peaks depending on the polymer they represented. Absorbance-concentration curves were generated by spreadsheets programmed to extract a maximum value within the candidate peak ranges described in Table 4.1. The peak ranges cited are the wavenumbers at which peak maxima would be expected based on literature values. Peak heights were extracted from narrow wavenumber ranges to ensure that true maxima were being represented in the data.

Table 4.1: Candidate peak wavenumber ranges ( $\text{cm}^{-1}$ ), at which candidate peak apexes were observed.

Compound Name (Abbreviation)	Peak Range ( $\text{cm}^{-1}$ )	Literature Value* ( $\text{cm}^{-1}$ )
<i>o</i> -Carborane (CARB)	2604 - 2598	2600
Polycyclohexanone (PCH)	1714 - 1712	1714
Polymethylhydroxylsiloxane (PMHS)	2174 - 2162	2166
Polymethylmethacrylate (PMMA)	1748 - 1736	1740
Polypropylene carbonate (PPC)	1774 - 1768	1764
Polysulfone (PSF)	1594 - 1586	1590
Polyvinylphenyl ketone (VPPK)	1690 - 1678	1686

\*Pouchert, 1975

Polymer-specific peak maxima were averaged from the sample readings ( $n = 24$ ), and 95% confidence intervals were calculated. Notable shifts were observed in a number of the polymers between observed values and those expected. Because literature values were based on pure polymer FTIR spectra, and the peak ranges noted in Table 4.1 are derived from polymer films applied to wood surfaces, the background wood spectra impacted the observed peak locations. Polymers characterized by a carbonyl functionality peak (PCH, PMMA, PPC, and VPPK) were most affected by this factor due to the great number of carbonyl and hydroxyl species present in wood and hydrogen bonding that occurred between them and the polymer coating (Kolling, 1999).

To define the number of unique, discernible data ranges available from the IR data collected, one-way ANOVA was used to determine presence or absence of significant difference between peak height means (grouped by polymer concentration). A Tukey *post hoc* test was used to define pairwise relationships between means, and illustrate similarities or significant differences among them.

## 4.3 Results

### 4.3.1 Determination of Internal Standard Concentration - SAN

The internal standard serves as a foundation for the rest of the study, as all polymer concentration data were quantified with respect to this standard. Investigation of the concentration-response curve of SAN showed a positively sloped reflectance-concentration curve from 0 mg/mL to 100 mg/mL. With a steep slope, and relatively narrow confidence intervals, SAN was considered to be the most ideal polymer of those investigated in this study, thus reaffirming the appropriateness of using it as an internal standard (Figure 4.2).

The concentration of SAN to be used as an internal standard was determined by a number of factors. First, the concentration chosen would be required to give a reproducible peak. Increasing SAN concentrations were shown to give increasing 95% confidence intervals, thus increasing uncertainty (Figure 4.2a). This error should be minimized, but modest error should be balanced with maximal peak intensity. When used in ratio-based quantification methods, too small an internal standard peak can cause an unnecessary inflation of error in quantification of candidate peaks. In balancing these two factors, it must also be ensured that concentration is not too high, in order to minimize materials required, control solution viscosity, and avoid unnecessary polymer interactions in solution. With these factors taken into consideration, SAN concentration of 10 mg/mL was chosen as

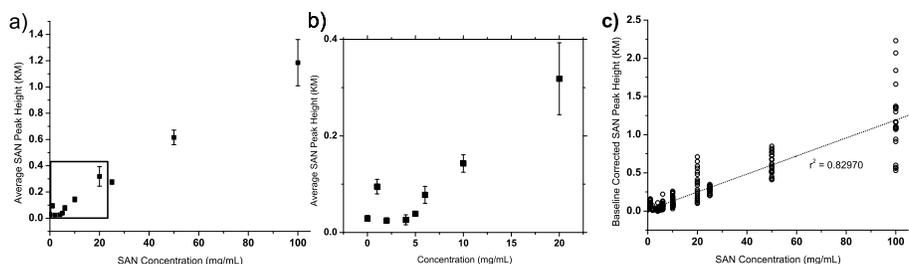


Figure 4.2: Baseline corrected SAN peak height with respect to SAN concentration. Averages are shown to the left (a), with whiskers representing the 95% confidence intervals associated with the ranges of absorbance values for each concentration. (b) shows the low-concentration points at a higher magnification. The individual data points are shown in (c) along with the  $r^2$  value obtained from linear regression of these data.

the internal standard.

### 4.3.2 Concentration Response of *o*-Carborane

*o*-Carborane (CARB) gave a non-ideal response curve (Figure 4.3a). The IR response in the CARB region increased substantially with the addition of CARB to the system, but progressive increases in concentration resulted in decreases in reflectance response. The characteristics of the peak remained relatively uniform with increasing concentration. Although the overall magnitude of the peak decreased beyond the 5 mg/mL concentration, rounded shoulders on either side of the peak remained consistent (Figure 4.3b,c).

### 4.3.3 Concentration Response of Polycyclohexanone

Poly(cyclohexanone) (PCH) exhibited an increasing trend with increasing polymer concentration. However, each point was not consistently higher than the previous (Figure 4.4a). As well, a number of ranges in the positively sloping region exhibited overlapping 95% confidence intervals, making some

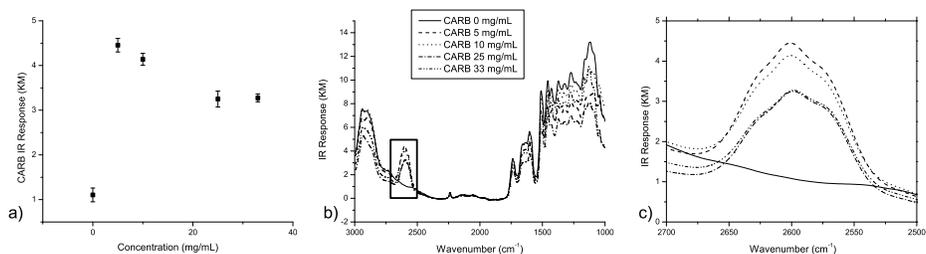


Figure 4.3: *o*-Carborane IR spectral responses with respect to increasing concentration. Part (a) illustrates quantification of candidate peak at given concentration (x); part (b) illustrates changes in the IR spectrum with increasing concentration (by line), with the boxed area expanded in (c).

points statistically indistinguishable from those surrounding them. Beyond 20 mg/mL, the PCH peak decreased significantly, making points greater than this concentration unusable. Figure 4.4b and c show the emergence of the small PCH response from between two wood-spectrum peaks as concentration increases, and a progressive increase and then decrease of these neighboring peaks. The unpredictable behavior of the response curve and its wide confidence intervals may have been due to the great number of competing responses in this range in response to changing concentration.

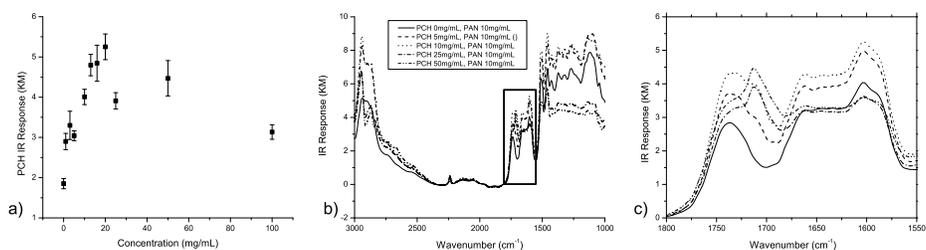


Figure 4.4: PCH IR spectral responses with respect to increasing concentration. Part (a) illustrates quantification of the PCH candidate peak ( $1714\text{ cm}^{-1}$ ) at given PCH concentration (x); part (b) illustrates changes in the IR spectrum with increasing concentration (by line), with the boxed area expanded in (c).

### 4.3.4 Concentration Response of Polymethylhydrosiloxane

Poly(methyl hydrosiloxane) (PMHS) failed to exhibit a sufficient sensitivity between concentration and IR peak response. The overall data did not adhere tightly to any apparent curve (Figure 4.5a). However, if data between concentration points 0-20 mg/mL were only considered, some linearity was exhibited. Considering the erratic behavior of the data beyond this concentration, the reproducibility of linear curve was questionable. Increasing concentration also showed an increasing level of influence of the PMHS peak on that of the internal standard, SAN (Figure 4.5c). As the PMHS peak increased in magnitude, the SAN peak was progressively flattened into somewhat of a plateau in the flanking region of the PMHS peak. For this reason, and that of questionable reproducibility, PMHS was not considered suitable for use in a chemical barcode system.

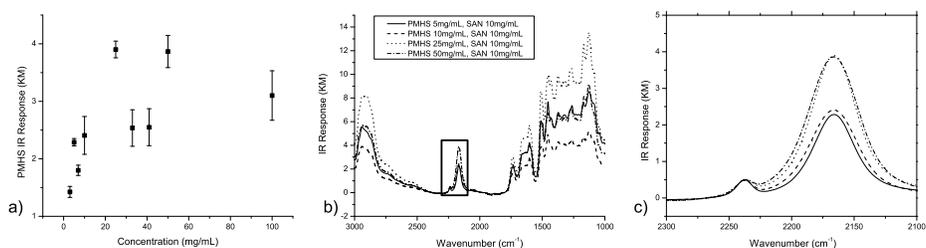


Figure 4.5: PMHS IR spectral responses with respect to increasing concentration. Part (a) illustrates quantification of PMHS candidate ( $2166\text{ cm}^{-1}$ ) peak at given PMHS concentration (x); part (b) illustrates changes in the IR spectrum with increasing concentration (by line), with the boxed area expanded in (c).

### 4.3.5 Concentration Response of Polymethylmethacrylate

The IR response peak of poly(methylmethacrylate) (PMMA) increased until 25 mg/mL, beyond which it plateaued and decreased slightly (Figure

4.6a). Some of the ranges in the 0-20 mg/mL concentration range showed overlap of the 95% confidence intervals. PMMA's candidate peak was sharp and was very responsive to increasing polymer concentration (Figure 4.6b), showing relatively large increases in intensity with increasing polymer concentration. This intensity may be responsible for overpowering the interference that affects the quality of the other candidate polymers which elicit a less-intense peak. It has been shown, however, that IR peaks too intense exhibit significantly increased error in their quantification (Blitz, 1998). A raw peak reflectance value beyond 70% is said to cause such effects, and PMMA gave values greater than this magnitude for concentrations higher than 20 mg/mL. Although the error bars (shown by 95% confidence intervals) did increase at these higher concentrations, the values are consistent enough to show at least two distinct, differentiable ranges before the curve maximum. Also, a slight shift is visible upon close examination of the candidate peak (Figure 4.6c), showing a progressive shift of approximately  $10\text{ cm}^{-1}$  with increasing concentration.

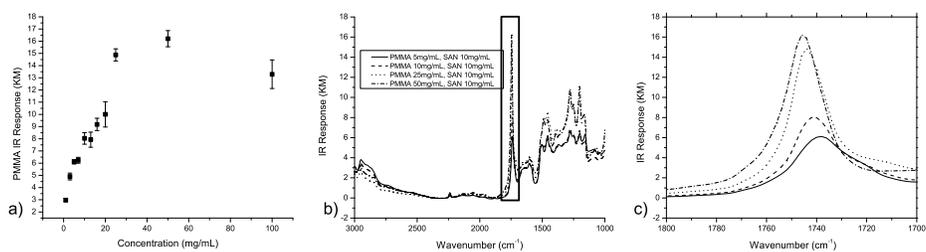


Figure 4.6: PMMA IR spectral responses with respect to increasing concentration. Part (a) illustrates quantification of the PMMA candidate peak ( $1740\text{ cm}^{-1}$ ) at given PMMA concentration ( $x$ ); part (b) illustrates changes in the IR spectrum with increasing concentration (by line), with the boxed area expanded in (c).

### 4.3.6 Concentration Response of Polypropylene carbonate

The poly(propylene carbonate) (PPC) reflectance-concentration relationship behaved ideally from 0-65 mg/mL (Figure 4.7a). The narrow confidence intervals of each range formed a nearly linear upward trend with increasing polymer concentration. Beyond 65 mg/mL, the response of the PPC candidate peak decreased significantly, and therefore could not be used. The slope of the increasing range of the PPC response curve was quite steep due to the large magnitude of the PPC peak, but compared to most other compounds it reached a maximum at a high concentration. This fact combined with the very high IR reproducibility within each concentration allowed for a large number of IR ranges to be discerned. It is worth noting that like PMMA, PPC gave peaks higher than 70% reflectance at concentrations beyond 15 mg/mL, which has been shown to affect the accuracy of peak height quantifications (Blitz, 1998). However, PPC also continued to show distinct, differentiable, increasing peak height ranges beyond this concentration, suggesting that error remained within tolerable levels. Also like PMMA, increasing PPC concentration elicited a shift in the candidate peak of approximately  $10\text{ cm}^{-1}$  (Figure 4.7c).

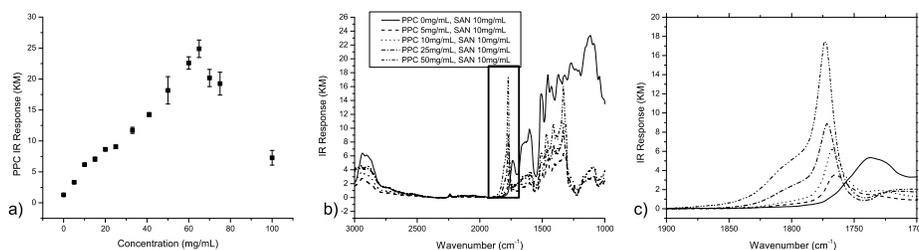


Figure 4.7: PPC IR spectral responses with respect to increasing concentration. Part (a) illustrates quantification of PPC candidate peak ( $1764\text{ cm}^{-1}$ ) at given concentration (x); part (b) illustrates changes in the IR spectrum with increasing PPC concentration (by line), with the boxed area expanded in (c).

### 4.3.7 Concentration Response of Polysulfone

Polysulfone (PSF) showed a gradual increasing trend of IR response with increasing PSF concentration. The candidate peak quantified for PSF reflected the S=O stretch of the PSF backbone, and existed at a slightly lower wavenumber than most of the other carbonyl moieties discussed ( $1590\text{ cm}^{-1}$ ). With the exception of the certain outliers (eg.  $[\text{PSF}] = 5, 20\text{ mg/mL}$ ), the ranges formed an upward trend from zero to  $100\text{ mg/mL}$  PSF. However, the error (95%CI) associated with the PSF peak was relatively large due to the increased high level of interference observed in area of the spectrum at lower wavenumbers than  $1600\text{ cm}^{-1}$ . Figure 4.8c shows the emergence of the PSF peak from a shoulder in the wood IR spectrum. The peak showed much lower intensity than those of other polymers such as PPC and PMMA, and was difficult to define at all concentration levels (Figure 4.8b,c).

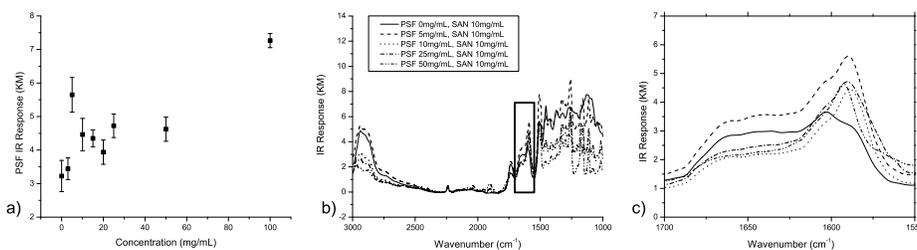


Figure 4.8: PSF IR spectral responses with respect to increasing concentration. Part a illustrates quantification of PSF candidate peak ( $1590\text{ cm}^{-1}$ ) at given concentration of PSF (x); part b illustrates changes in the IR spectrum with increasing PSF concentration (by line), with the boxed area expanded in (c).

### 4.3.8 Concentration Response of Poly(vinyl phenyl ketone)

Poly(vinyl phenyl ketone) (PVPK) exhibited a weak relationship between polymer concentration and IR reflectance response. Although a slight up-

ward trend could be seen, increasing concentration in many cases did not elicit an increase in reflectance response, creating a serpentine response curve. Also, like PMMA and PPC, PVPK's candidate peak was intense and sharp, but exhibited a shift with increasing polymer concentration (Figure 4.9b,c). Despite the sharpness of the PVPK peak, the unpredictable behavior of its polymer response curve made it unfeasible for use in the chemical barcode system.

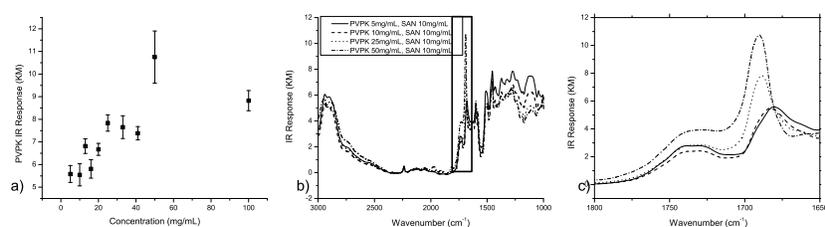


Figure 4.9: PVPK IR spectral responses with respect to increasing concentration. Part (a) illustrates quantification of the PVPK candidate peak ( $1686\text{ cm}^{-1}$ ) at given PVPK concentration ( $x$ ); part (b) illustrates changes in the IR spectrum with increasing PVPK concentration (by line), with the boxed area expanded in (c).

### 4.3.9 Differentiable Ranges Within Sampled Polymer Concentrations

Figures 4.3-4.9 illustrated a number of different concentration response behaviors from the various compounds tested. The results of one-way ANOVA tests of IR peak height data, and Tukey *post hoc* comparison of means are presented in Figure 4.10, showing the statistically discernible peak height ranges within the increasing parts of these curves.

The ordering of the CARB ranges are skewed, due to the immediate plateau and dropoff of the CARB IR response with increasing concentration. PCH exhibited an steeply increasing response at low concentrations, and from the concentrations examined, there appears to be four spectrometrically

CARB	00	25	50	10	05						
PCH	00	01	05	03	10	13	16	20			
PMHS	03	07	05	10	25						
PMMA	01	03	05	07	13	10	16	20	25	50	
PPC	00	05	10	15	20	25	33	41	50	60	65
PSF	00	03	20	15	10	50	25	05	100		
PVPK	10	05	16	20	13	41	33	25	50		

Figure 4.10: Graphical representation of Tukey comparison of means between polymer concentrations. Rows of numbers represent polymer concentrations, and are ordered by increasing mean of respective peak height data. Polymers whose peak height did not progressively increase, therefore, will show concentration values out of numerical order. Underlining represents lack of significant difference ( $\alpha = 0.05$ ) between IR peak height means.

discernible concentration levels prior to the curve apex. The response curve of PMHS did not progressively increase, so no progressive IR ranges could be determined. Within the response curve of PMMA, if the 10 mg/mL concentration point is removed, there were seven statistically discernible IR ranges. Like PMMA, due to its aggressive slope and tight confidence intervals, PPC delivers a large number of discernible IR ranges. If the 15mg/mL concentration is omitted, eight progressive ranges can be determined. PSF's lack of progressively increasing absorbance made it impossible to extrapolate a response curve, or meaningful IR ranges within it. PVPK also showed lack of progressively increasing absorbance behaviour and wide confidence intervals, thus not allowing any number of progressive IR ranges to be determined.

## 4.4 Discussion

This research assessed a number of candidate polymers (Table 4.2) for feasibility of use in a chemical barcode system. This was achieved by comparing the polymers' changes in IR absorbance response with increasing polymer concentration against a number of ideal behavior criteria. As mentioned in the introduction of this paper, these criteria were: exhibition of an increasing IR response with increasing concentration (positive slope of response curve), exhibition of response linearity (no plateau), or otherwise reaching a maximum only at high concentrations (positive slope not so steep as to limit the number of concentration points usable), and being comprised of concentration points which are statistically different from each other (reflected by non-overlapping confidence intervals).

When exhibiting all these behaviors, the polymer would achieve the greatest number of concentration points within the concentration-absorbance response curve, thereby allowing maximum number of polymer/concentration permutations to be exploited in the proposed barcode system. In the laboratory environment in which this experiment was performed, due to the

Table 4.2: Number of measurable ranges extrapolated from polymer response assays, and the concentration assayed at which each compound exhibited the highest absorbance. These data are based on normalized maximum absolute peak values.

Compound	Ranges	[Polymer] $_{MaxKM}$	Slope $_{min-max}$
<i>o</i> -carborane	-	5 mg/mL	0.66973
poly(cyclohexanone)	4	20 mg/mL	0.17001
poly(methylhydroxysiloxane)	-	25 mg/mL	0.11264
poly(methylmethacrylate)	7	25 mg/mL	0.49590
poly(propylenecarbonate)	8	65 mg/mL	0.36390
polysulfone	-	100 mg/mL	0.04043
poly(vinyl phenyl ketone)	-	50 mg/mL	0.11485

lack of the infinite depth which the assumption of linearity is based on, and the imposition of the measured compounds upon the complex profile of the wood surface, significant diversions from ideal behavior were observed. The assumption that what is presented in a spectrum is due only to the behavior of the polymer film cannot be made—rather, one must assess the relationship between concentration, path length, and absorbance, and examine a deeper and more complex system. The influence of a IR-reactive and varying biological background, the progressively increasing film depth, and a continuously changing perspective of the wood-polymer interface add additional dimensions of variation to a system which already diverges significantly from the ideal systems upon which Beer’s law and the theory of Kubelka-Munk are based on. Many polymers assessed showed some form of plateau in their response curve (Figure 4.11), which was to be expected (Culler *et al.* 1984) at high polymer concentrations. Also, some polymers gave slightly parabolic response curves. The redundancies introduced by this type of curve would cause ambiguity in interpreting spectra at higher concentration as one absorbance value could indicate more than one concentration (Figure 4.11). Therefore data beyond the apex cannot be used for a chemical barcode system. The same applies to plateau-forming curves. Points beyond the last statistically differentiable concentration cannot be used, in order to avoid ambiguity (Figure 4.11).

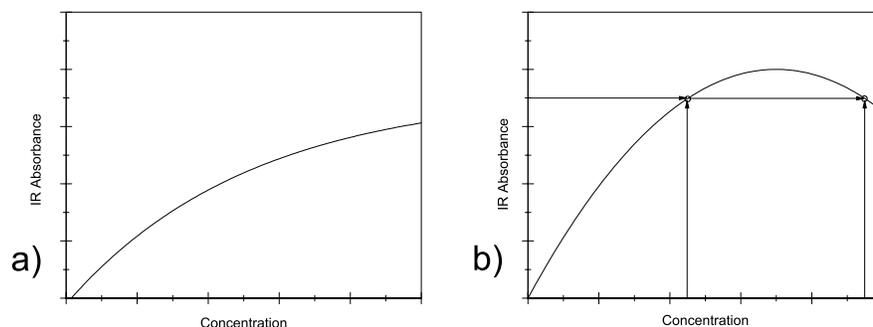


Figure 4.11: Non-ideal concentration-IR absorbance response curves. Outside ideal conditions, linearity of response curves breaks down at high concentration, forming a plateau (a). This study also observed parabolic curves, which showed decreasing absorbances at higher concentrations (b).

CARB's response appeared to be approximately binary (Figure 4.3a). When no polymer was present in the system, the  $2600\text{ cm}^{-1}$  peak response was absent, but with addition of progressive amounts of polymer, no trend of increasing response intensity was observed. Rather, the maximum IR response was achieved at or less than  $5\text{ mg/mL}$ . When the concentration increased beyond  $5\text{ mg/mL}$ , the peak height decreased. In exhibiting a lack of concentration-response sensitivity, which gave rise to a parabolic response curve, CARB was not appropriate for use in a chemical barcode system.

PCH's IR-response presented a better sensitivity to increasing polymer concentration than CARB. However, the points recorded did not consistently increase with increasing concentration (Figure 4.4a). A number of points exhibited a lower response when representing a higher concentration, or vice-versa. However, static analysis showed four unique IR ranges (Figure 4.10).

PMHS showed poor linearity of IR responses with respect to increasing concentration (Figure 4.5a). As well, increasing the concentration of PMHS interfered with the accurate quantification of the SAN internal standard

peak, which lay within  $50 \text{ cm}^{-1}$  of the PMHS peak. For this reason, as well as its lack of ideal behavior, PMHS was not chosen for further use as a candidate polymer in the chemical barcode system.

PMMA performed well, showing a positive slope in the lower concentrations, with a near linear alignment of low-error response averages (Figure 4.6a). However, the curve began to plateau at approximately  $20 \text{ mg/mL}$ , and beyond this concentration gave peak heights that were so high as to raise questions about the accuracy of the quantification, because the raw (non-normalized) peak height was higher than 70% absorbance (Blitz, 1998). Despite this observation, seven out of the ten concentration points preceding the plateau could be discerned with confidence from each other. The narrow bands of confidence reflected a high degree of IR-response reproducibility (Figure 4.10), and the peak heights in danger of inflated error also showed non-overlapping 95% confidence intervals, and thus a good deal of reproducibility compared to other candidate polymers. PMMA has been shown in previous research (Chapter 3) to give reproducible results in the presence of UV radiation and when left in solution, making it a possible candidate for use in further investigation into the chemical barcode system.

PPC exhibited a similar response curve to PMMA, but exhibited even lower error, better linearity of the response curve, and reached an apex at  $65 \text{ mg/mL}$  (Figure 4.7a). However, due to PPCs reported propensity for biodegradation (Du *et al.*, 2004) and proximity to the PMMA candidate peak (Chapter 3) in the IR spectrum, it was not chosen for further use. PPC, like PMMA gave an extremely strong response peak. It was found that concentrations beyond  $15 \text{ mg/mL}$  gave peak responses high enough to raise concerns about the associated error (Blitz, 1998). When associating PPC peak height to a given concentration, the 95% confidence error values were small enough to discern, with confidence, ten of the eleven concentration points assayed (Figure 4.10). Although quantification error has been previously shown in the literature to increase with peak height (Blitz, 1998), and has been reinforced within the previous chapter (Chapter 3, Figure 4), cases such as these where a given polymer shows a very strong peak may be

tolerated in producing concentration–response curves. When dealing with polymers such as PPC and PMMA which produce very strong peaks at maximum concentration, the definition of “narrow confidence intervals” is relative to the overall magnitude of the peak. For instance, a concentration response curve from PPC may have wider confidence intervals than those of the points of a polymer which produces a weak response, but because the range represents a smaller proportion of the overall span of potential peak heights, a greater number of concentrations are allowed, and are able to exist without overlap, not being bounded by narrow limits of peak heights (Figure 4.12). For this reason, although strongly-responding polymers such as PMMA and PPC are susceptible to quantitative error at high concentrations, the magnitude of the peak makes allowances for larger error in the absolute sense.

PSF’s concentration response relationship was poor, giving unpredictable results with increasing concentration. It lacked a sufficient upward trend, and the 95% confidence intervals were too wide to discern concentration ranges from each other. PSF’s candidate peak location in the spectrum contains much more background reflectance than most of the other polymers. For this reason, PSF’s concentration points showed higher error values, making it more difficult to effectively differentiate between concentration ranges. This fact, in concert with the low slope of the concentration-reflectance response curve demonstrated that PSF’s absorbance peak was relatively insensitive to increasing polymer concentration.

PVPK, like PSF, did not show sufficient sensitivity between concentration and reflectance response to allow it to be used in the chemical barcode system.

Of the seven polymers assessed, only three gave response curves appropriate for further use in the chemical barcode system, namely PMMA, PPC, and PCH. PPC and PCH, however have been determined in previous work (Chapter 3) to be unfit for use in an industrial setting due to their instability over time and in the presence of UV irradiation. In concert with these

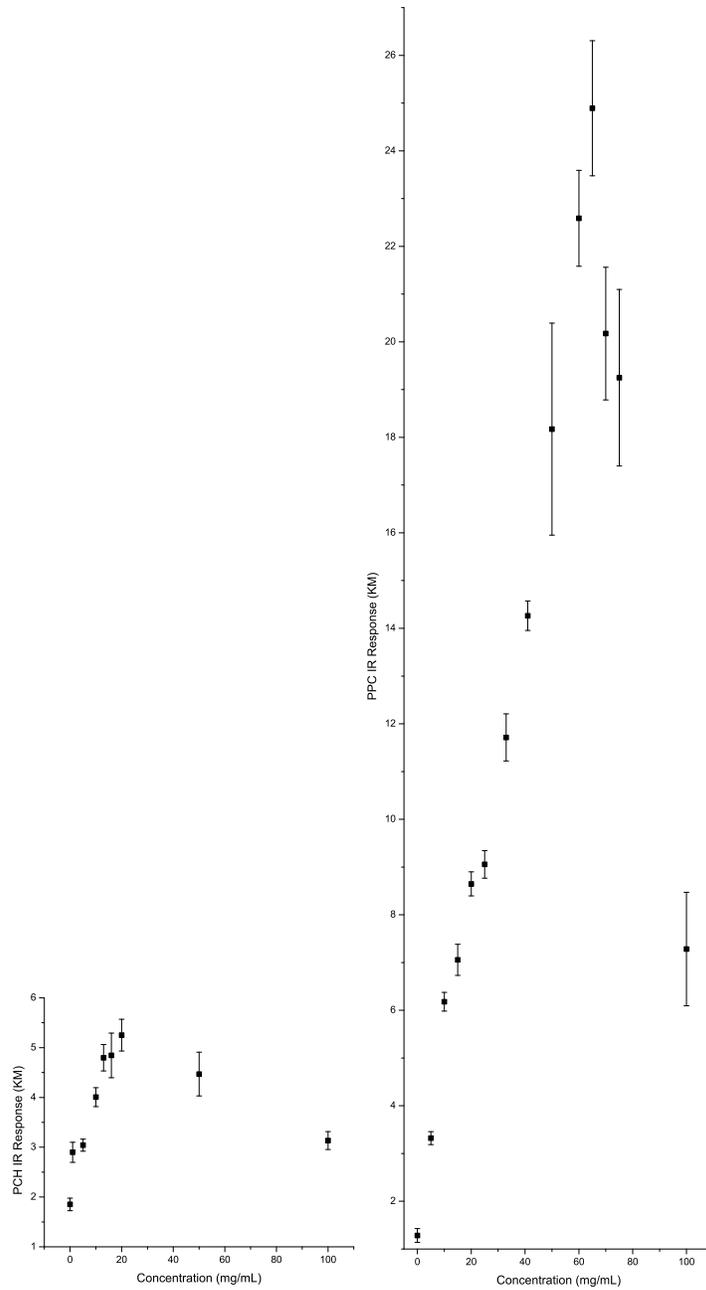


Figure 4.12: Proportional comparison of weak and strong responding polymer response curves and associated error. Despite high error at high PPC concentrations statistically discernible ranges can still be constructed due to the larger overall range of possible peak heights.

previous findings, these new data suggest that PMMA is the only candidate polymer which should be further used in the proposed system due to its stability and ideal IR response to increasing concentration.

The concentration points defined for PMMA show significant gaps in the concentration–response curve, suggesting the potential to introduce more concentration points to increase resolution. With the introduction of additional concentration points the potential resolution of the system may be further improved.

The means by which increasing polymer is added to the system may be responsible for some of the uncertainty observed in the experimental results. Polymers were applied to wood samples in solution, with the concentration of the solution being the independent variable and the IR reflectance response being the dependent variable. Considering that Kubelka-Munk theory is founded on the assumption of a material of infinite depth (Liang *et al.*, 1999), this may pose a problem since the depth of the film applied to wood was not only finite, but varied with changing polymer concentration. Although constant volumes of solution were added to sample slides, the amount of material left after evaporation, and therefore film depth, was proportional to the solution’s concentration. Also, film thicknesses within a single concentration sample set can vary due to varying wetting dynamics of different wood grains and the very high rate of evaporation of the application solvent (DCM) (Bormashenko *et al.*, 2006). In future studies investigating candidate peak heights with respect to polymer amounts, it would be wise to vary polymer proportions of a fixed polymer load, and therefore maintain a more consistent polymer depth to better satisfy the assumption of Kubelka-Munk, and ensure that the light’s path length is kept as close to constant as possible.

To achieve the best performance of a chemical barcode system, the responses collected from IR scans of candidate polymers should be based on the reflectance attributed to only coating polymers. Unfortunately, due to the minute depth of the polymer films, and the variation mentioned above, the

response curves collected in this study may reflect a gradually changing component of wood interference. IR spectra are additive (Skoog *et al.*, 1998), meaning that two different compounds eliciting a reflectance in the same wavenumber area will give an additive peak. Therefore when spectra are collected for various samples of different polymer concentrations, the increasing contribution from the polymer functionality may be supplemented by spectral contributions from a wood component active in at the same wavenumber, or bond energies attributed to the interaction between polymer and the wood surface. In addition, as polymer load increases (thus thickening the film covering the wood), contribution from the wood spectra may be progressively changed as potential contributions of wood-surface interactions are decreased due to increasing masking by pristine (uninfluenced) polymer mass. It has been reported that such interactions can effect as much as a  $33\text{ cm}^{-1}$  shift on carbonyl peaks (Kolling, 1999) of simple IR systems. The addition of this factor, which will vary in its spectral representation as the path length to the interfacial region progressively increases (with increasing polymer load), may contribute to the high level of error seen in some of the polymers which elicit a peak in spectral areas densely populated with wood-derived bond energies such as the carbonyl, phenolic, ether and alcohol functionalities within holocellulose and lignins.

This hypothesis is reinforced by the very ideal behavior of the SAN  $\text{C}\equiv\text{N}$  peak ( $2237\text{ cm}^{-1}$ ) with respect to increasing polymer load (Figure 4.2a). Existing in an area of the spectrum untouched by wood chemical moieties due to a lack of cyano groups in wood, SAN's candidate peak exhibits very narrow 95% confidence intervals, as well as a nearly linear trend through all concentrations assessed. This suggests that the functional similarity among many polymers to components of wood chemistry (carbonyl groups especially) creates a problem in obtaining the ideal polymer behavior necessary for the proposed chemical barcode system.

It may be possible to emulate the lack of wood polymer interference exhibited by SAN in other functionalities through further exploration of chemical priming steps (using an IR-opaque sub-coat), or perhaps introduction of a

blinding component into the polymer mixture itself. The most effective way to increase system resolution, however, is by introducing more candidate polymers, with functionalities active outside the areas of the spectrum populated by wood functionalities. Every additional candidate polymer which can be used will increase the possible number of solution permutations exponentially. Therefore, further efforts should be put into research and development of novel polymers with progressively increasing concentration responses.

## 4.5 Conclusion

This research was undertaken to investigate the possible use of seven polymers previously examined for stability (Chapter 3) for IR-responsiveness to increasing polymer concentration, and potential for use in a chemical barcode system. Of the seven polymers assayed, only three exhibited near-ideal concentration-response behavior. Of these three polymers (PMMA, PPC, and PCH), only one, PMMA, was previously found to be stable over time and in the presence of UV radiation. Other polymers were found to not behave with sufficient responsiveness to changing polymer concentration. The difference in polymer behavior is thought to be due to differing sensitivity to background IR influences from underlying wood, and the consequential differential seen with increasing polymer load. It has been concluded that PMMA is the only candidate polymer which should be further examined for use in the chemical barcode system.

## 4.6 References

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## Chapter 5

# An Innovative Method for Wood Product Tracking: Discussion and Conclusions

### 5.1 Discussion

#### 5.1.1 Significance of Results

Chain of custody is becoming increasingly complex in its requirements for accounting, credit management, and input categories (Chapter 1). However, all of these factors are reliant upon a necessary standard of input identification. Without methods of identification that can maintain and deliver the identity of specific products or batches, all of the efforts put into maintaining certified status beyond these critical points in the supply chain can be compromised (Nussbaum & Simula, 2005). Certification organizations and CoC systems are designed to allow organizations the flexibility to tailor CoC to their operation (Chapter 2). However, lack of guidance in the area of managing product identities through these critical points can lead to ineffectiveness or inefficiency in a CoC system. Critical points are steps of production, or steps within the supply chain where certified and uncertified products may come into contact, or be co-processed (Nussbaum & Simula, 2005). Complete segregation of these products is not yet a reality in the forestry industry, since most input suppliers and manufacturers either can-

not afford to do business in certified products alone, or require co-sourcing to meet product demands. As mentioned in Chapter 2, there needs to exist a means of identifying these products effectively from each other, as to maintain confidence in pure product CoC claims, and to ensure transparency of mixed-product processes (Fischer *et al.*, 2005).

Barcode labels have been utilized for these sorts of applications in the past. Conventional labels (adhesive or tag) can be developed to be robust, but are constantly at risk of coming loose, and effectively losing the identity of a log, or wood product, and any certified status that it may carry. Not only is this wasteful of labeling materials, but also detrimental to the suppliers and manufacturers who invest significantly in the certified status of their products, which can often be lost. Although this technology is inexpensive and easy to use, the 1-5% failure rate of the fasteners, issues with adhesive residues, and ease of tampering with labels (Dykstra *et al.*, 2003) can call into question the true utility of this simple method.

Nail-based labels are also used, but rather than being fastened to wood by an adhesive or fastener, they are equipped with nail-like extrusions which allow them to be directly fixed to a log or product. These metal or plastic tags remain attached to wood better, and take less time to apply than conventional tags. Being otherwise very similar to conventional tags, nail-based tags are often printed with barcodes, which can be used very efficiently to reference supporting data. However, these tags are difficult to remove, but must be to avoid damaging processing machinery, or interfering with treatment processes (Dykstra *et al.*, 2003).

Paint markings and the more complex chemical tracer paints have also been used to identify certified products in the supply chain, and in the forest. Although they are robust and extremely simple to apply and interpret, they can be misused easily or, for traditional paints, easily forged (Brack *et al.*, 2002). Chemical tracer paints are somewhat more difficult to interpret and forge, as they require specialist reagents or laboratory equipment to confirm their identity.

As well, in some forestry operations, but more commonly in retail and warehouse management operations, Radio Frequency Identification Tags (RFID) are being used to manage inventory flow. These radio-emitting chips offer many new and ideal properties to the landscape of inventory management, most importantly the potential to be integrated into products (not visible or removable), and not requiring a direct line of sight between the chip and the reader (Dykstra *et al.*, 2003). They can communicate very specific identifications, and are quite secure, but at the moment the balance between cost and functionality in the forest industry is askew. Any variety of RFID inexpensive enough to be used in the quantities required for log harvesting or primary processing would not only be relatively delicate, but also would have a very small broadcast range, meaning that the tag would be required to be aligned directly with a sensor (Roberti, 2006).

The forest industry is in need of system that blends the benefits of these sorts of methods, but omits the flaws. This thesis set out to do that, laying the foundations for a system which can be applied as easily as paint, is just as robust, and offers the identification specificity close to that of barcode systems. Using FTIR technology (DRIFT) in the development of this process may prove to allow the technical aspects of the barcode interpretation to translate easily into the industrial context using fibreoptic attachments to facilitate remote interpretation of chemical barcode. If such a technology were put into place, automated readers may be put into place to track products through all forms of certification “critical points”, in log yards, in the manufacture of co-processed batches, or in multi-component assembly lines.

The investigations described in Chapters 3 and 4 lay the groundwork for the development of an industrial system of this nature. Stability of the chemical species from which the system is built, and the responsiveness of the IR absorption with respect to the amount of polymer load is paramount to the accuracy of a chemical system like this. Of the seven polymers assayed, two were found to be sufficiently stable, and only one of these two was found to exhibit the concentration-response behaviors demanded by the ChemiCode

system. Polymers have been observed to be sensitive to both radical and ion producing stimuli, such as heat or UV irradiation, as well as hydrolysis, depending on the nature of the polymers being examined (Stevens, 1990). In a system to be utilized in the most extreme of weather conditions, enduring rain, extreme temperatures, submersion, and intense and prolonged sun exposure, it is imperative that the polymers being used exhibit maximum stability in the face of these factors, since they all have the potential to alter the IR absorbance response of the polymer systems, and thus must be protected against.

Error from these factors not only decreases the accuracy of the system, but also threatens to negatively impact the resolution of the overall system. In Chapter 4 the response ranges of polymers at different concentrations were analyzed, and used to develop calibration curves for polymers in the presence of the SAN internal standard. These response curves, however, can be negatively impacted if stability data show that the reading from a given concentration deviates into the response range of a different concentration over time. When error due to these effects forces the designer to set concentration points further apart, potential system resolution is decreased. At the conclusion of this work, the impacts of this degradation and its consequent effect on error ranges are available only for polymers at one concentration (25 mg/mL). The deeper insight into the polymers' behavior at this one concentration can offer guidance for further investigation into polymer age and elemental exposure, and its effect on calibration curve resolution. As reported in Chapter 3, error is also dependant on absorption peak intensity and thus on polymer concentration (for those polymers which exhibit a positive correlation between response and concentration). To understand the degree to which polymer exposure will affect readings at higher and lower concentrations, future research should include investigating representative concentrations at higher and lower polymer concentrations.

The foundational results taken from this study will allow thoughtful and effective development of a working prototype system in further works following this project. Insight into how polymer responses and stability be-

have on a wood medium will provide information germane to the design of such a system. Further quantitative works will be required to take into account many more factors, such as effects of Specular/Fresnel Reflectance in samples (glassy reflectance inflating diffuse IR reflectance), solution wetting dynamics, optimal peak intensity ranges, copolymer interactions, and influence of varying wood media. For this reason, a general understanding of the IR-spectral behavior of wood-polymer systems in the simplest context will provide the foundations required to design further candidates with the best outcomes. This proof of concept work not only provides evidence that DRIFT spectroscopy may be used for such quantitative application, but offers valuable insights in designing further experiments to prove feasibility of DRIFT as a quantitative measure. We have seen in this work that it is possible to superimpose spectral elements upon the IR spectrum of wood using the appropriate polymers, but further work will be able to determine to what specificity one can quantitatively differ these variables.

The potential system resolution presented in Chapter 4 is important to the context in which the proposed system will be used once fully developed. The specificity of a system determines how it can be used. In product identification, there are different levels at which a product can be marked. A means of product branding requires only one recognizable identifier (such as a logo, symbol, or color). A mass-produced label, stamp, paint or stencil could fulfill this role. Methods like this, which are traditionally seen in the form of paint logos, chisel marks, or branding hammers, don't offer any specificity in identification. They reference no supporting certificate or data, and can be very easily tampered with. To differentiate between product groups or specific products, batch labeling can be used. This blanket method can be done using more descriptive identification methods. Microtaggant tracers and chemical tracer paints are two examples of descriptive identifiers, which allow an organization a few different permutations for use within their system, but not enough to uniquely identify individual products (Dykstra *et al.*, 2003). The ChemiCode system, like a barcode or RFID, is intended to be a specific identification method, capable of differentiating products by

batch, date of production, wood source, or any other narrower descriptive criterion. Within a system as large and complex as a Chain of Custody scheme, there needs to be a great number of unique identifiers available to track products or batches. For this reason the ChemiCode system is being developed to accommodate this level of specificity.

The proposed system is intended for use in a highly specific context, and consequently will require several millions of unique IDs to be available through it. Using continuous values (absorbance peak intensity) to define discreet concentration categories, theoretically the potential number of chemical codes is limitless. However, in the non-ideal conditions that exist in real experimentation, the system is limited by the error imposed on IR concentration points, changes in response over time, responsiveness of polymer IR absorbances to changing polymer load, and break down of linear relationships at high polymer concentrations. At this time we can seek to optimize the potential number of identities that this system can produce by choosing polymers which display optimal stability (minimum error with respect to time) and maximum concentration responsiveness (minimal error between concentrations), as well as refining our methodologies to allow for higher-accuracy quantitative measurements of IR absorbance.

### **5.1.2 Strengths and Weaknesses of Reported Research**

This work contributes the first report of relationship between DRIFT absorbance intensity and polymer coating thickness on wood. With a great deal of work done in analysis of lignins and wood carbohydrates, a significant amount of information was taken from the literature about the background observed in IR scans of the candidate polymers on wood, and used to investigate the effects of light and age on polymer coatings, and the covered wood. As well, this research contributes to the understanding of how the wood IR spectrum can be modified using polymer coatings. Furthermore, integrating into these responses the changes caused by exposure to sun irradiation and aging adds a further dimensionality to our understanding of

the relationship between absorbances from specific functionalities and the amount of polymer from which they are derived.

One apparent weakness in the research thus far is the simplicity of the interpretation methodology for the IR spectra collected. Many more complex mathematical systems exist for interpretation of changes in IR spectra, such as Mahalanobis' generalized distance (Mark and Tunnell, 1985), K nearest neighbor (Kowalski and Bender, 1972), and soft modeling of class analogy (Sharaf *et al.*, 1986). These systems could have been used to assess changes in the IR spectrum with respect to changing polymer systems using a multi-factorial assessment, rather than basing all observations on a single wavenumber or functionality. As well, these sorts of methodologies could have been used to identify other areas of the spectrum affected by the progressive increase of polymer presence on the wood surface. Although these "chemometric" methodologies would have allowed a deeper insight into the dynamic between concentration and overall IR spectra, the multi-factorial nature of the assessment and the multi-factorial nature of the polymer mixtures to be used in prototype chemical barcodes would have made derivation of meaningful conclusions from future work nearly impossible. The system, as it is proposed, cannot be easily approached by traditional statistical methods, since it relies on so many variables, each of which can elicit effects over the entire spectrum. For this reason, the system limits spectral analysis to specific peaks.

Diversity of candidate polymers also proved to be an issue in the research performed. Although there is intention to include polymers which are not commercially available (but rather custom synthesized), in developing the ChemiCode system, significant obstacles were overcome in securing just the polymers used. Developing a list of polymers which were easily handled in standard conditions, were soluble in dichloromethane, and gave a strong candidate peak was a significant undertaking, even when using only commercially available polymers. Of the seven polymers experimented investigated, four contained a carbonyl functionality which contributed to a common candidate peak in the IR spectrum, which would have potentially indiscernible,

potentially synergistic peak interactions. Regardless of findings about stability and response, such chemical overlap would have prevented their use in concert due to these effects, which would inhibit the collection of meaningful, identifiable spectra.

### **5.1.3 Presentation of the Status of Relevant Working Hypotheses**

The proposed Chemical Barcode has been reinforced by the findings presented in Chapter 4. Being able to develop response curves for the polymers assayed that exhibit a positive slope and confidence intervals narrow enough to allow multiple concentration points suggests that the system could (in the future) allow use of other polymers to facilitate the construction of prototype polymer barcodes. The wood IR spectrum, however, is likely inflating the error of concentration point readings, and limiting the number of points allowable on calibration curves. As well, the feasibility of the system still rests upon whether the candidate polymers will behave in a similar fashion, with respect to concentration, when the barcode system includes additional polymers. If not in line with the calibration curves developed in this study, then polymers in multi-specific systems should behave in a consistent, progressive manner (forecastable) with respect to concentration, but independent of co-present polymers.

Although this research investigated single polymer systems and their behavior on a simple wood background, the concept will, in future, demand the increased complexity of multi-polymers systems, and be challenged by different wood backgrounds. Presented here is a proof-of-concept work, intended to demonstrate the possibility of modifying a minimally-varying wood surface spectra using IR-reactive polymer species. This research is meant to be a foundation, and it is imperative that it be built upon with further works investigating the IR spectral dynamics of multiple polymers on a diverse range of wood substrates.

#### 5.1.4 Research Insights and Significance in the Field of Study

The ChemiCode system proposed in this thesis is still in the early stages of research and development, but with continued work, this technology may address many of the common shortfalls that affect the materials tracking industry. Utilizing the ease of use and economics of a paint system, but being identifiable not by human sight, but by IR chemical absorbance, it could prove to be a simple, inexpensive and secure means of tracking wood products through the value chain or through a manufacturing line. With human labour becoming an ever-decreasing factor in the forest industry, this technology offers enormous potential for automation and integration into manufacturing process lines. Within this context, it could prove to streamline the supply chain, relieve significant CoC bottlenecks, and quicken production of certified products.

At this point seven candidate polymers have been assessed for suitability of use in the proposed system. Of the seven (eight, including SAN), only two were deemed appropriate. SAN, as an internal standard, and PMMA, as a barcode candidate (Table 5.1). Much more research must be dedicated to screening new polymers in a similar fashion until there exists a pool of suitable, co-usable polymers from which a functioning chemical barcode can be constructed. Once this has been developed, further work can go into the development of prototype chemical barcodes under the more strict methodologies of quantitative IR spectroscopy, and the investigation of polymer absorbance behaviors in mixed-polymer systems.

In addition, to develop increased resolution in the chemical barcode system, thus allowing more potential unique barcodes per polymer used, work may be done to address the issue of wood spectrum interference in the reading of chemical barcodes. This may be addressed through the application of an IR-opaque sub-coat to blot out the wood spectrum, or inclusion of such a component into the polymer mixtures.

Once a scientific foundation has been laid for this system, further research

Table 5.1: Summary of candidate polymer response with respect to aging techniques investigated.  $\checkmark$  denotes suitability in the given assay, while  $x$  denotes unsuitability

Polymer (peak $\lambda$ , $\text{cm}^{-1}$ )	Aging Assay	Concentration Response	Overall Suitability
CARB (2600)	$x$	$x$	$x$
PCH (1715)	$x$	$x$	$x$
PMHS (2166)	$x$	$x$	$x$
PMMA (1744)	$\checkmark$	$\checkmark$	$\checkmark$
PSF (1590)	$\checkmark$	$x$	$x$
PVPK (1700)	$x$	$x$	$x$
PPC (1770)	$x$	$\checkmark$	$x$

could also be carried out investigating novel application methods that suit the industrial environment in which the system may be used. Melt-spray technique or aqueous carrier suspensions could be investigated to increase the ease of handling of the polymers, and outfit the system with the improved safety and simplicity required by industrial users.

## 5.2 References

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