Preliminary Investigation of Adhesive Bonds using IR-microscopy

PROJECTREPORT

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Contents

Abbreviations

SYP	Southern yellow pine
DF	Douglas fir
PF	Phenol formaldehyde
pMDI	polymeric diphenylmethane diisocanate
W	WIL-FIL Walnut Shell
M	Modal Spray Dark (alder bark)
CF	Corn flour
WF	Hard wheat flour
°C	degree Celsius
in.	inch
mm	millimeter
FT-IR	Fourier transform infrared spectroscopy
ATR	Attenuated total reflectance
TEM	Transmission electron microscopy
KBr	Potassium bromide
BaF_2	Barium fluoride
NaCl	Sodium chloride
KCl	Potassium chloride
CaF_2	Calcium fluoride
AgCl	Silver chloride
AgBr	Silver bromide
ZnS	Zinc sulfide
ZnSe	Zinc selenide
CsI	Caesium iodide
µm	micrometer
nm	Nanometer
mol/L	Molar concentration per liter

1. Introduction

The increasing use of wood as construction material, either as solid beams but even more as engineered wood products, improved the importance of research of the behavior different materials of wood and adhesives. Research, some already published and ongoing projects, is looking into ways to determine the behavior of adhesive bonds in wood. As the next step computer models are created to predict these results for different wood species and adhesive systems (Modzel, 2009).
The utilization of micro X-ray tomography (XTC), to quantify the microstructure of the bondline, used for this technique, is its disadvantage due to the necessity of access to specialized labs.

The focus of this preliminary investigation of adhesive bonds is conventional light microscope techniques and IR microscopy to characterize differences between wood cell material and the used adhesives.

The main goal of this research was to provide techniques for assessing adhesive penetration in wood. The specific tasks for were:

- Development of specimen preparation techniques for bonded specimens
- Assessment of the operational capabilities and limitations of the available equipment (cryo-ultra-microtome and FT-IR microscope)
- Creation of chemical maps for selected adhesive systems
- Comparison of chemical maps with epi-fluorescence microscopy

These objectives had to be accomplished during the authors six months stay at Oregon State University.

2. State of knowledge

2.1. Materials

2.1.1. Wood

Wood is distinguished in soft- and hardwood. Looking at a tree pit, the different parts could be seen on the cross cut form center to the outside. The center, also known as the pith, is surrounded by the heartwood which is surrounded by sapwood. The outer layers are known as bark, which can be distinguished in outer and inner bark. The main function of the outer bark is mechanical protection and limitation of water loss. Between the inner bark and sapwood is the cambium, responsible for a trees growth. Softwoods come from gymnosperms whereas hardwoods come from angiosperms. Another way to differentiate between softwood and hardwood is their difference in terms of component cells. Softwoods have a simple composure with only two different cell types. Hardwoods have a larger number of cell types, one of them is called vessel element, and a larger variability within these cell types. The cell wall of wood consists of cellulose, hemicellulose and lignin (Wiedenhoeft, 2010).

Table 1: composition of wooden cell walls - central European soft- and hardwoods in comparison (Lohmann, 2010)

substance	softwood	hardwood
cellulose	42 – 49 %	42 – 51 %
hemicellulose	24 – 30 %	27 – 40 %
lignin	25 – 30 %	18 – 24 %
extractives	2 – 9 %	1 – 10 %

Table 1 shows the distribution of cellulose, hemicellulose, lignin and extractives for softwood and hardwood in percent.

2.1.2. Adhesives

For engineered wood products, examples are glulam or plywood, adhesives are necessary. These adhesives are composed out of binders, pigments, extenders and fillers and excipients like hardeners (Niemz, 2005).

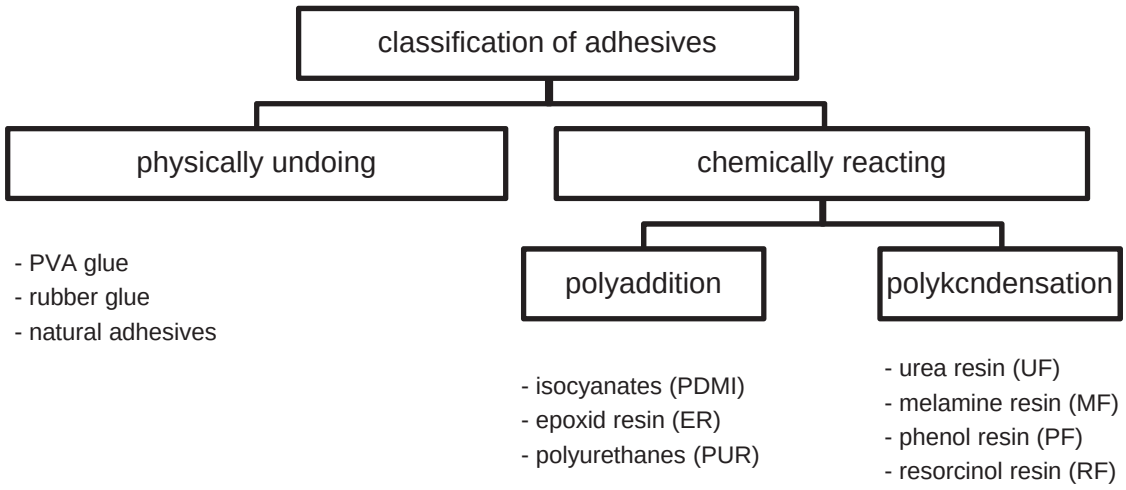

Figure 1: classification of adhesives (Dunky and Niemz, 2002)

Figure 1 shows the classification of adhesives. Adhesives systems are distinguished in physically undoing ones and chemically reacting adhesives. Fields of application for different resin systems can vary. Some adhesives are used as mixed systems, for example urea formaldehyde (UF) is often mixed with melamine formaldehyde (MF) to improve moisture resistance and is used for the production of plywood, particle board or also fiberboards like MDF (Niemz, 2005).

PVA-glue, rubber glue and all kinds of natural glues (e.g. animal, blood, casein or soybean based glues) cure due to release of solvents. Other glues within the group of physically undoing adhesives are hot melts, which are solid at room temperature and liquefy due to heat. The biggest disadvantage of natural resins compared to synthetic generated resins is their lack of moisture resistance which is why they are not used in commercial products (Pizzi, 2003).

Chemically reacting adhesives are distinguished in two types based on their curing properties, polyaddition and polycondensation. At polyaddition molecules connect each other with

the release of protons. Resins are isocyanates, epoxy resins or polyurethanes. Polymeric diphenylmethane diisocyanate (pMDI) adhesives are used in the forest products industry for the production of moisture resistant products. The properties of pMDI allows the creation of “formaldehyde free” panels (Niemz, 2005)

The curing process of polycondensation takes place due to the release of water in the adhesive which leads to the formation of macromolecules. Urea formaldehyde, melamine formaldehyde, phenol formaldehyde or resorcinol formaldehyde are often used in commercial applications. Also mixtures of these adhesives are common. MUF resins, a combination of melamine and urea formaldehyde, is used to improve moisture resistance of a product but on the other hand increases the price compared to pure urea formaldehyde (Niemz, 2005).

2.2. Methods

For this research project one of the most important things was sample preparation for data collection of wood – adhesive behavior using FT-IR spectroscope.

2.2.1. Microtomy

For sample preparation of thin sections for microscopic use, microtomy is an essential technique. Depending on the application different microtomes are available. On one hand with sledge microtomes for rather thicker sections and on the other hand ultra-microtomes for nanometer thin sections. During the process of sample preparation for this project, both techniques were tested and later on described in detail.

2.2.2. Microscopy

Epi-fluorescence microscopy and FT-IR microscopy were both worked with during this project. The same sections were used for data collection on the FT-IR microscope and afterwards comparing this information to pictures taken on a epi-fluorescence microscope.

3. Material and Methods

3.1. wood

Two softwood species were chosen for this project. Southern Yellow Pine and Douglas Fir as the two main softwood species used commercially within the USA.

3.2. adhesives

As adhesives for this research, a phenol formaldehyde resin and a pMDI resin were tested to see differences between those two at the examination with fluorescence and also FT-IR microscopy.

3.3. sample preparation

In this project were two different softwood species used for sample preparation. Pieces Southern Yellow Pine and Douglas fir sawn timber was cut on a circular saw in thin slices with focus on direction of grain. Afterwards these thin slices were planed on both sides and cut in length to fit the laboratory press. For bonding a phenol-formaldehyde (PF) resin and a pMDI resin were used.

Table 2: sample preparation - resin types and calculated spread rates

Adhesive	Solids content	Species	Adhesive Spread Rate (g/ft²)	Adhesive Spread Rate (mg/cm²)	Adhesive Spread Rate **per face** (g/m²)	Adhesive Spread Rate (g/m²)	Adhesive Solids Spread Rate (g/m²)	Adhesive Spread Rate (lb/1000ft²)	Solids Spread Rate (lb/1000ft²)	Press Temp. (°C)	Pressure (psi)	Press Time (min)
PF	0,433	SYP	25,7	27,7	138,4	276,8	119,8	56,7	25,0	180	100	8
		DF									100	
pMDI	1	SYP	11,3	12,2	61,0	122,1	122,1	25,0	25,0	180	100	8
		DF									100	

Table 2 gives an overview of different adhesives used for this research. PF stands for pure phenol-formaldehyde.
In the table above are also the measured solid contents for the adhesives and parameters regarding spread rates and the pressing process.
After the press small specimen were cut from the bonded blocks and prepared for sample embedding as shown in Figure 2.

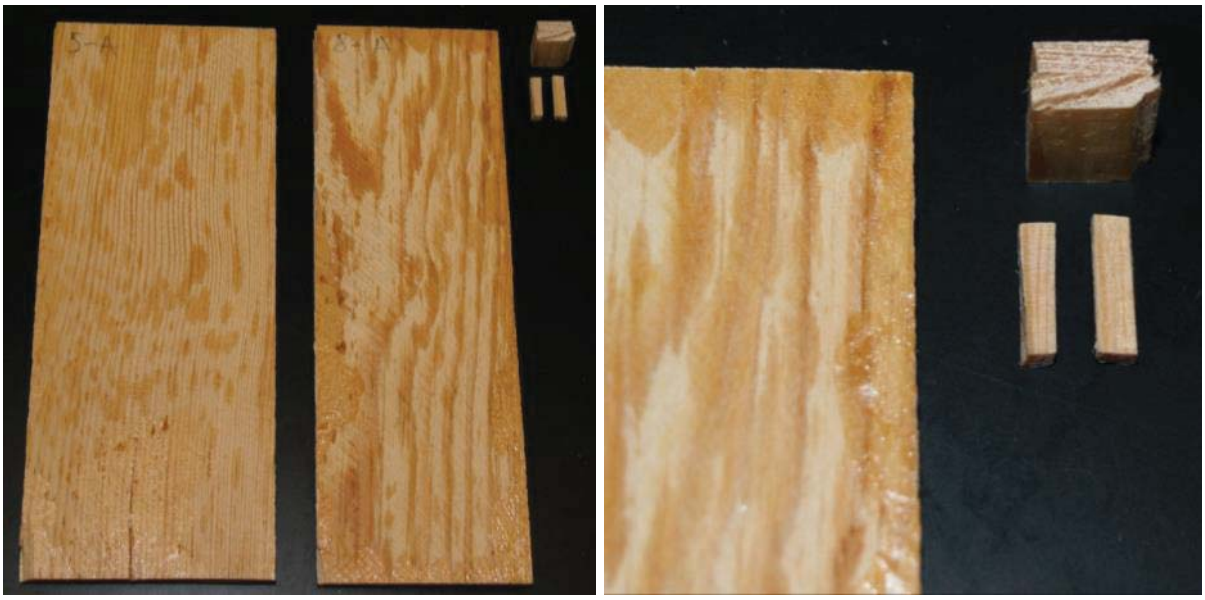

Figure 2: bonded wood slices and small specimen for embedding (Boehm, 2013)

The bonded blocks had a size of approximately 5 by 2 inch. Smaller blocks were cut form these blocks and in a next step, by using a razor blade, trimmed into much smaller (circa 2 by 2 mm) specimen. Main goal was to create small diameter specimen with a bond line in the sample for following sectioning.

3.4. sample embedding

To achieve thins sections, a thickness below 2 µm is usable for FTIR-microscopy, a specimen usually has to be supported in some kind of embedding material. The challenge while using FTIR-microscopy is the necessity of an embedding media which has no influence on the spectroscopy concerning chemical data quality. Therefore different materials were tested as embedding material for the bonded samples.

Useful embedding materials, according to literature, are potassium bromide (KBr), hexadecane, hexane, iso-octane and sucrose (figure 3). All of those materials were tested during sample preparation and microtoming but the successful sectioning was only with sucrose as and embedding media achived.

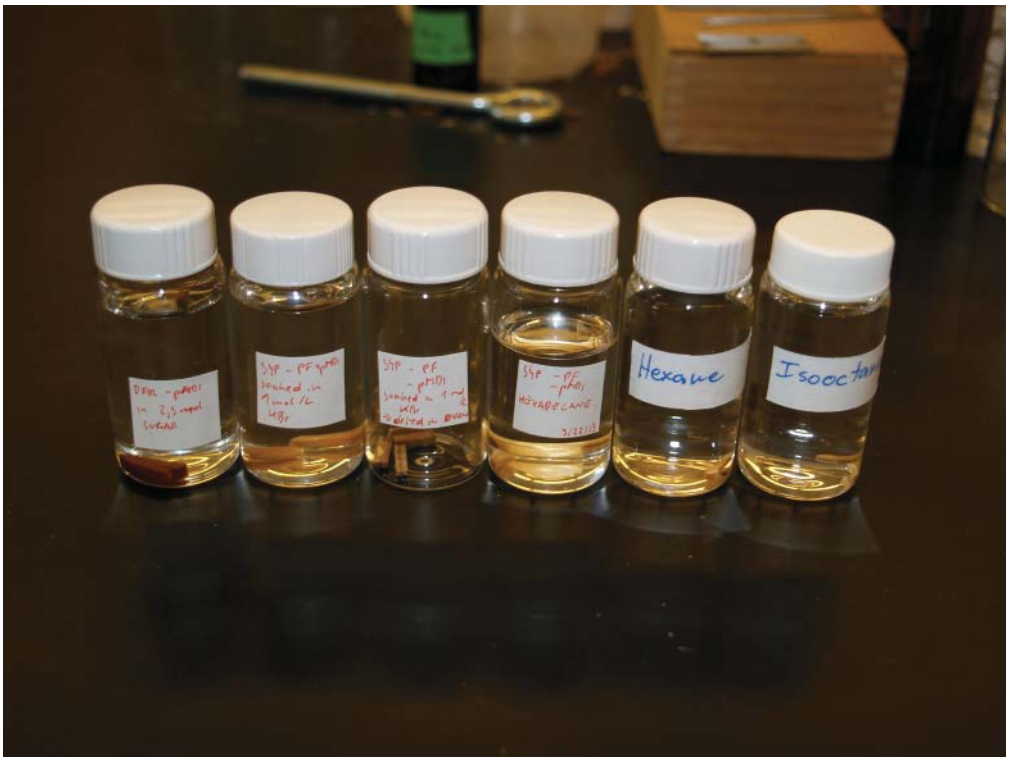

Figure 3: embedded specimens ready for sectioning (Boehm, 2013)

3.5. microtome techniques

For this project, thin sections of glued wood blocks were inevitable. Different microtome methods were tested to get suitable sections. These approaches are described in detail below.

3.5.1. sledge microtome

Sledge microtomes are a commonly and wide spread used technique to cut thin sections. Cutting sections from small wooden blocks is usually done on soaked specimen to reduce the required force and also the wear of the blade. For sectioning with sledge microtomes steel blades are often used. The limiting factors for sledge microtomes are on one hand the steel blades and especially the section thickness. The achievable thicknesses vary in the three directions, radial – tangential and cross. During experimenting with the sledge microtome, it was possible to get cross sections but the thickness of 20 µm and higher was not applicable for FTIR – microscopy.

Figure 4: sledge microtome with solid tungsten carbide knife (Boehm, 2013)

Figure 4 shows the sledge microtome used for the first sectioning attempts. Different knifes were tested (figure 4 & 5) but the section thickness was still at around 20 µm which didn't work with the FT-IR microscope.

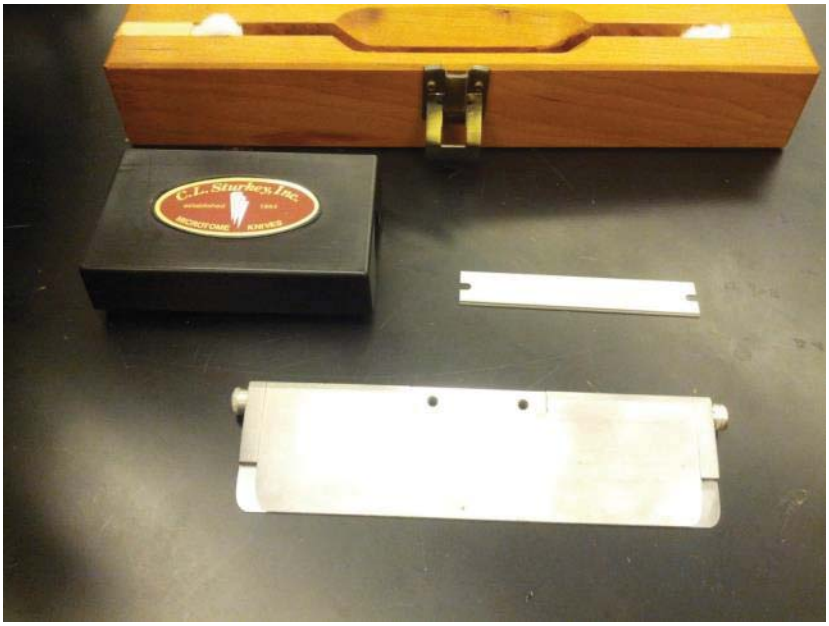

Figure 5: blade holder for disposable blades and blades (Boehm, 2013)

3.5.2. ultra microtome

A more advanced technique then sledge microtomes are ultra-microtomes. For this research a Leica EM UC7 ultra-microtome was available (figure 6). This type of microtome can, depending on available equipment, be operated either in room temperature or for cryosectioning at temperatures below 0°C. In progress of this project both techniques were tested to achieve thin sections.

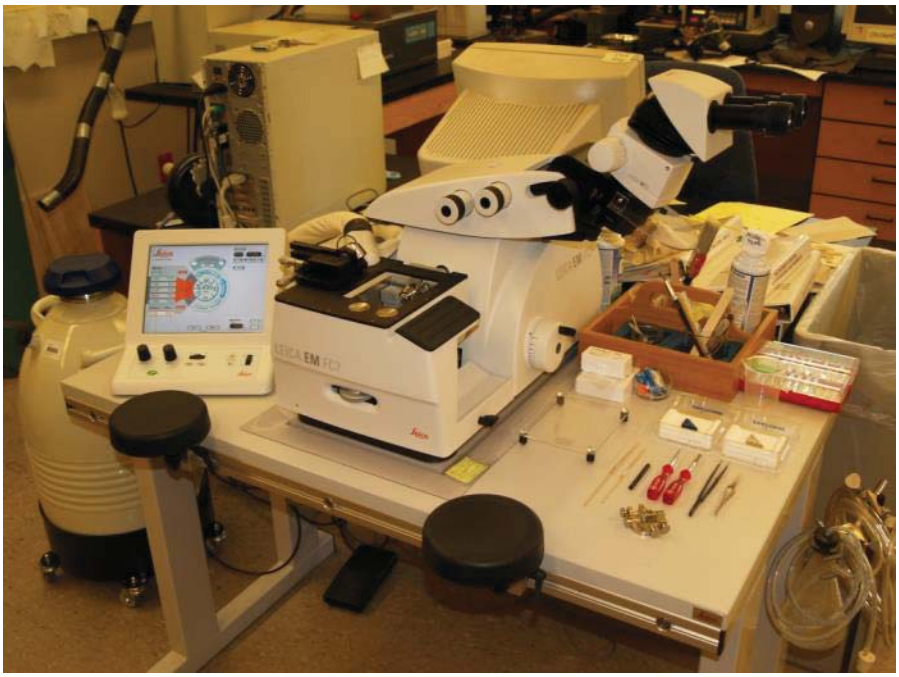

Figure 6: Leica EM UC7 ultra microtome (Boehm, 2013)

3.5.2.1. Sectioning at room temperature

The ultra-microtome used for this project was a Leica EM UC 7. The Leica EM UC 7 is equipped with a electronically controlled stage to move the trimming or the knife block in two separate axes. Moving directions are North – South and East – West and steps can be done in a range from 0.1 to 15 µm. Another feature is a full adjustable segment arc in which the specimen is inserted and fixed for sectioning. The microtome could be used in manual or full automated mode with variable cutting speeds. It is outfitted with several lights and a stereo microscope with different magnifications. All settings regarding section thickness, cutting speed, the cutting window and illumination are controlled via a touch screen control unit. For further is in the operating manual available.

For sectioning at room temperature glass knifes or diamond knifes can be used. For the purpose of this project both knife types were tested. The biggest advantage of glass knifes compared to diamond knifes, is their price, their biggest disadvantage is that they get dull quickly

depending on sectioning material. Glass knifes can be manufactured by the operator easily with using the Leica EM KMR3 knife. Diamond knifes on the other hand are expensive and very durable considering the edge. With diamond knifes thinner sections are possible compared to glass knifes. During the experiment it was possible to get sections with a thickness down to 1.5 – 2 µm.

3.5.2.2. Cryosectioning

For sections thinner than 1.5 – 2 µm working at lower temperatures was necessary. Therefore the Leica EM UC 7 ultra-microtome attachments were changed and a cryochamber, the EM FC 7 also from Leica, was installed. The cryochamber is cooled with liquid nitrogen and can be set at temperatures between -15°C and -185°C for cryosectioning. Another tool used for sectioning at low temperatures is the Leica EM CRION unit, an antistatic device.
The temperature levels as well as the intensity of the discharge from the antistatic device are adjusted through the same control unit as in room temperature mode. Additional available equipment for use at cryosectioning was a micromanipulator and a diamond trimming and also a diamond cutting knife from Diatome. Special accessories are provided in a separate case.

Operating in cryo mode glass and diamond knifes can be used but it seemed that glass knifes lost their sharp edge after a couple of cuts while with the diamond knife no change was recognized.

Before sectioning can start the ultra-microtome needs to be cooled down which takes between 30 and 60 minutes. The knife plate, a bracket for two knifes in which usually a trimming and a cutting knife are fixed in, is prepared and kept in the chamber to cool down with the chamber so all for cryosectioning necessary equipment has the same temperature. Another important part that needs to be inserted inside the cryo chamber is the cryo specimen holder where two different are available. Preset temperatures can be chosen from the control unit or otherwise specific temperatures can be assigned for the knife holder, the specimen arm and the chamber. During the cool down process of the microtome the prepared specimen was frozen in liquid nitrogen and when ready inserted in the ultra-microtome.
Before sectioning can start the specimen block needs to be trimmed in shape, therefore the trimming knife was used (see figure 7). The upper and lower side of the block should be parallel while the width of the section should decrease from the lower to the upper edge to decrease the cutting pressure while proceeding through the specimen block. As trimming is done the knife holder can be switched to the diamond cutting knife (figure 8) and sectioning

can start. Sectioning can be done in automatic mode with a preset section thickness and cutting speed or manual where speed and thickness can be adjusted for each section.

Figure 7: cryo diamond trimming knife (Boehm, 2013)

Figure 8: cryo diamond cutting knife (Boehm, 2013)

After sectioning, thicknesses of 250 nm and 500 nm with a bondline in the section were achieved, the thin sections needed to be stored before the inspection with fluorescence and FT-IR microscopy. For section storing different approaches were taken with microscope glass slides, crystal discs and TEM-grids.

3.6. microscope techniques

A epi-fluorescence microscope equipped with an digital camera was used for picture capturing of sections which were used beforehand on a FT-IR microscope to collect chemical data of the same section and area. The pictures were afterwards compared to the gathered chemical information.

3.6.1. fluorescence microscope

The fluorescence microscope used for this research was a Nikon Eclipse 400 with a mercury bulb as a light source and five different magnification lenses (4x, 10x, 20x, 40x and 60x). The microscope was further equipped with three different filters (UV, green and blue) and a digital camera to take pictures.

3.6.2. IR-microscope

A ThermoFischer Nicolet Continuum FT-IR microscope was used in combination with a Thermo Nicolet Nexus 470 FT IR bench as beam source for this research. The The FTIR microscope is outfitted with three different lenses, 10x, 15x and 32x and for the 15x and 32x lenses a detector. Another feature is a automated stage which allows collecting chemical maps. The microscope can be operated in reflectance and also transmission mode. Smallest achievable spot size is 5x5 µm, step size can be set to 1 µm. Apart from the microscope the bench offers the option to collect data from pellets and also an ATR FT-IR unit.

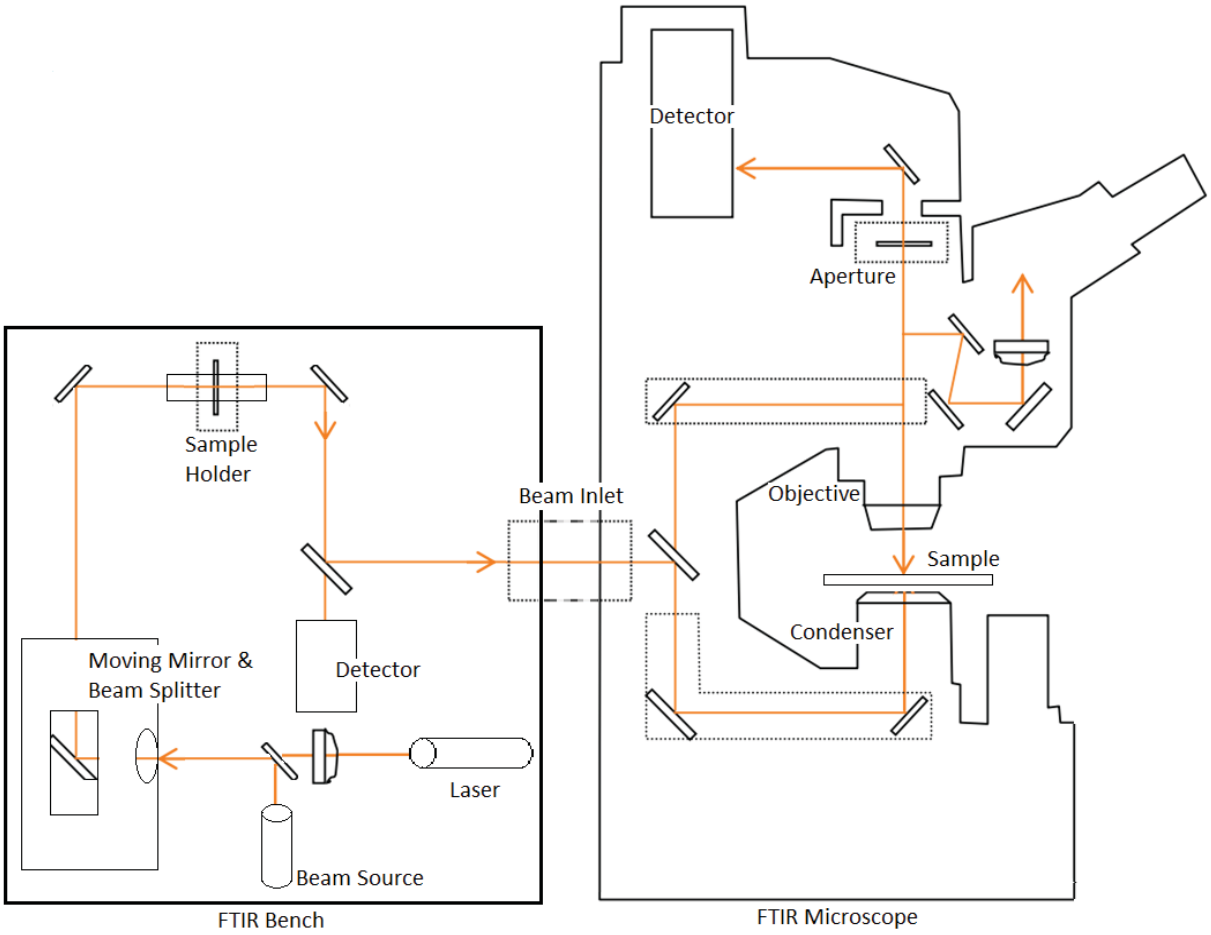

Figure 9: FT-IR microscope diagram (Adapted from Lin, Shan-Yang et al. Advanced drug delivery reviews 64.5 (2012): 461-478

Figure 9 shows a schematic setup of an FT-IR bench on the left and the FT-IR microscope on the right side. The microscope can be operated in transmission mode, where the beam transmits through the sample, gets collected in a condenser and then hits the detector, or in reflection mode, therefore a reflecting surface, placed below the specimen, is necessary.

On the FT-IR bench without a microscope, data can be collected from solids, powder samples and liquid samples. Powders are usually pressed into pellets, KBr is an often used material therefore, for the collection of chemical data. For solid specimen blocks the ATR-unit can be used. Limitations of the ATR-unit are spot size and the penetration depth into the sample.

4. Results and Discussion

4.1. Sample preparation and sectioning

After a few weeks of this project and the first test and trials it became clear that common known and used sectioning with sledge microtomes without embedding would not work to obtain satisfactory sections for FT-IR spectroscopy and data collection of area maps on such sections. Due to a rather low available amount of energy, limiting factors therefore is the standard setup of the equipment and also small aperture sizes for data collection, it was inevitable to reduce the section thickness below 2 µm. To achive this, a ultra-microtome is necessary. The first attempts were taken at room temperature using glass knifes but it was impossible to get sections, the only results were wood shavings. The next step was a diamond cutting knife instead of the glass knifes but even with this knife it was not possible to get sections. By equipping the ultra microtome with a cryo chamber and using diamond knifes and embedded specimens, it was possible to cut the first coherent sections with bondlines. The cryo chamber is cooled with liquid nitrogen and can reach working temperatures of -185 °C. Samples therefore were embedded and ahead of trimming and sectioning frozen in liquid nitrogen.
Sections with a thickness of 500 nm and 250 nm were achieved and stored on TEM grids for the following data collection on the FT-IR microscope.

4.2. Microscopy

Sections from Doulglas Fir and Southern Yellow Pine, both bonded with a sample of each adhesive, pMDI and PF, were collected on the ultra-microtome and stored on TEM-grids. Those sections were used for data collection using the ThermoFischer FT-IR microscope and also pictures were taken on the fluorescence microscope.

Due to a breakdown of the FT-IR bench, sample collection could not be finished within the timeframe and only a few area maps of sections were collected. These maps were only for trials and setup finding for data collection.

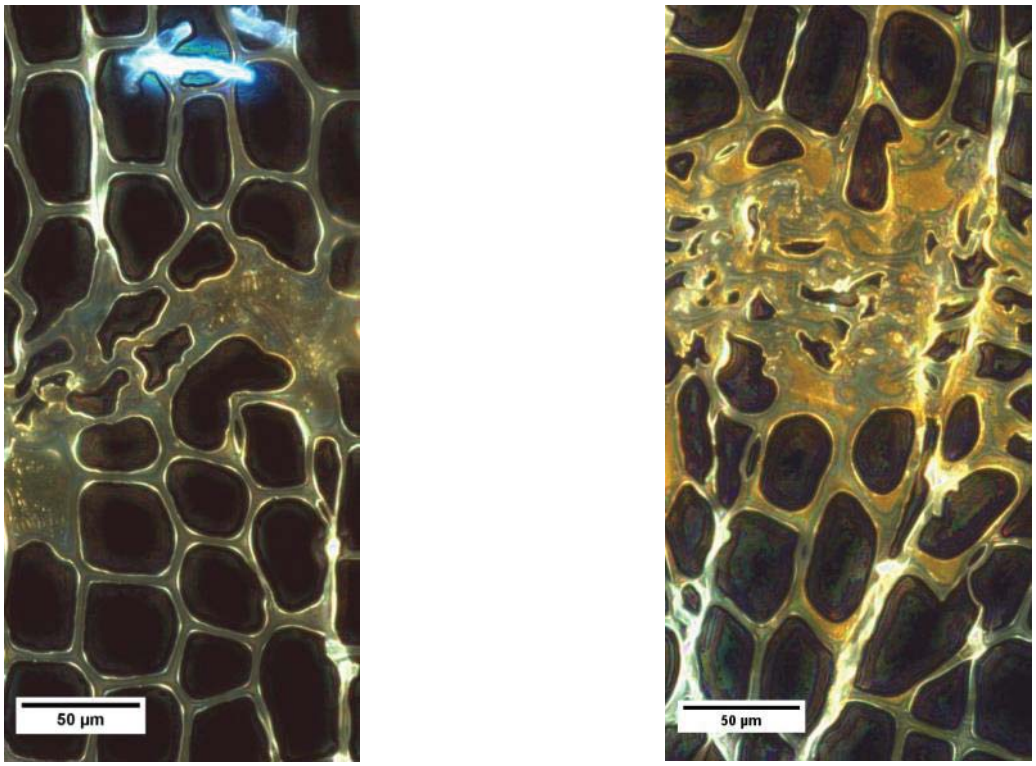

Figure 10: Photomicrographs of 250 nm thick Douglas-fir sections with pMDI bondline (left) and PF bondline (right), as viewed with UV filter set in fluorescence microscope (excitation wavelength 330 – 380)

Figure 10 shows stacked pictures from 250 nm thinn sections of Douglas Fir specimens. On the lefthand side, the picture shows a pMDI bondline. The resin is hardly visible , whereas the PF resin on the right side is cleary visible in the picture.

The comparison of pictures and collected data was not finished and is therefore not included in this report.

5. Conclusion

During my 6 month stay at Oregon State University and my work on this preliminary research it became obvious that sample preparation is the most important task using this technology and approach for data collection.

Sample preparation, embedding and sectioning required much effort to achieve satisfactory results. Trials with different embedding materials, different sectioning technologies and figuring out optimal settings as well as good solutions for sample storing required a lot of effort and time.

The following data collection on the FT-IR microscope was also time intensive but stopped with the breakdown of essential equipment.

Due to this breakdown not all of the earlier mentioned project tasks could be accomplished but important information regarding the entire sample preparation process for this purpose was collected.

The used technique requires a lot very sophisticated and expensive equipment with skilled people operating it. In my opinion the sample preparation can be optimized but due to the short timespan it wasn’t possible to figure it out.

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