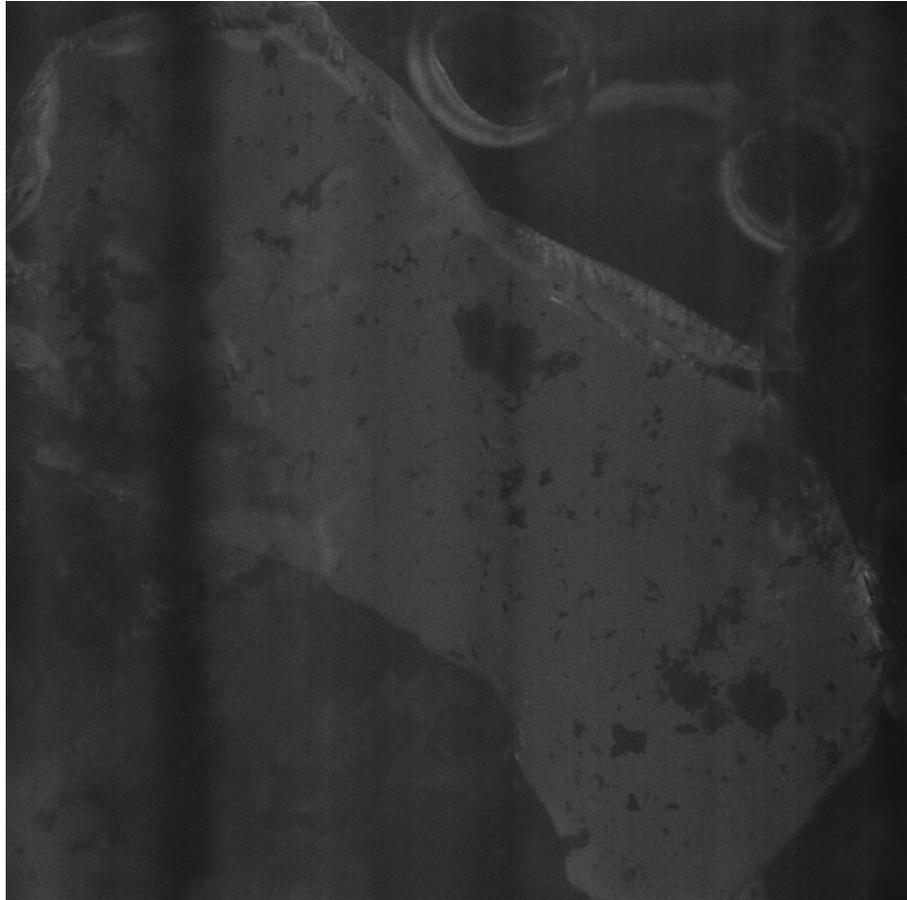




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# **A study of alternative Polyurethane films with Hemicellulose**

Preparation and characterization methods

Bachelor of Science Thesis

Maria Magnusson



BACHELOR'S THESIS 2017

# A study of alternative Polyurethane films with Hemicellulose

Preparation and Characterization methods

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UNIVERSITY OF TECHNOLOGY

Department of Chemistry and Chemical Engineering  
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CHALMERS UNIVERSITY OF TECHNOLOGY  
Gothenburg, Sweden 2017

A study of Polyurethane films with Hemicellulose  
Preparation and characterization methods  
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Cover: Fluorescence microscopy image of heterogeneous polyurethane film with arabinoxylan.

Study of Polyurethane films with arabinoxylan  
Preparation and characterization methods  
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## Abstract

Polyurethanes are important polymeric materials that are essential in day to day life in several different products and applications such as packaging materials, clothes and insulation. Polyurethanes are primarily made from crude oil and natural gas which neither is environmentally or economically beneficial which is why new green raw materials has grown in interest. This study will present insight and knowledge in the use of arabinoxylan in polyurethane film as an experiment to create a more environmentally friendly material. Analysis of the created films was carried out with FT-IR spectroscopy combined with differential scanning calorimetry as well as fluorescence microscopy to determine the interaction between the polymers and how arabinoxylan affect the material properties of polyurethane films. Different preparation method was examined and a procedure to prepare heterogeneous polyurethane films were established. The results from FT-IR showed that arabinoxylan interacted with the other polymers in the film and that urethane linkage was created. Different preparation methods to make homogeneous films with arabinoxylan was also examined. One homogeneous film was created and the FT-IR analysis of it indicated that arabinoxylan interacted with the other polymers to a greater extent than in the heterogeneous film with the same amount of arabinoxylan.

Keywords: Polyurethane, hemicellulose, arabinoxylan, green material.

## Sammanfattning

Polyuretaner är polymeriska material som är viktiga i flera vardagliga produkter och applikationer såsom i förpackningsmaterial, kläder, och isolering. Polyuretaner framställs huvudsakligen från råolja och naturgas vilket varken är miljövänligt eller ekonomiskt och har bidragit till att intresset för nya gröna råmaterial har ökat. Denna studie ger insikt och kunskap i användandet av hemicellulosan arabinoxylan i polyuretan filmer i ett försök att skapa ett mer hållbart material. Analys av de skapade filmerna utfördes med infraröd spektroskopi, differentiellscanning kalorimetri samt fluorescence mikroskopi för att bestämma interaktionen mellan polymererna samt undersöka hur arabinoxylan påverkar materialegenskaperna i filmerna. Olika preparationsmetoder undersöktes och en procedur för att skapa heterogena polyuretan filmer upprättades. Resultaten från IR-spektroskopin indikerade att arabinoxylan interagerade med de andra polymererna och att uretan-binding bildats. Olika preparationsmetoder för att skapa homogena polyuretan filmer undersöktes också. En homogen film skapades och resultat från IR-spektroskopin indikerade att arabinoxylan interagerat med de andra polymererna till högre grad än i den heterogena filmen med samma mängd arabinoxylan.

## Acknowledgements

Thank you to the department of Organic Chemistry for giving me the opportunity to perform this project and being able to use the equipment and material. I would like to thank the following people:

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Maria Magnusson, Gothenburg, June 2017

## Abbreviations

AX	Arabinoxylan
PU	Polyurethane
GPE	Glycerol propoxylate-block-ethoxylate
pMDI	Diphenylmethane 4,4'-diisocyanate
FITC	Fluorescein isothiocyanate
FT-IR	Fourier Transform Infrared Spectroscopy
DSC	Differential Scanning Calorimetry

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# 1

## Introduction

### 1.1 Background

Polyurethanes (PUs) are polymeric materials with several desirable properties, such as their toughness, chemical resistance and low filming temperature. Polyurethanes are widely used in different products such as clothes, insulation and automotive coatings, and are made from polyols and isocyanates. Since polyurethanes are found in various different applications they are often tailored to meet specific requirements and their properties can be altered selecting different polyols and isocyanates. Because a big quantity of polyols are available in industry, the choice of polyol often determines the material characteristics. Although process has been made searching for new precursors for polyurethanes, most polyols and isocyanates used in industry are petroleum based [1]. This causes both environmental and economical concerns which is why there is a growing interest in green chemistry and renewable raw materials.

An interesting material due to the demands for green chemistry is hemicellulose, which is biodegradable, renewable and non-toxic. Hemicellulose is a polymeric carbohydrate which occurs in plant material and is the second most abundant plant bio polymer on earth which also make it a promising material due to its ready availability and relatively low cost. Extracted hemicellulose has several potential applications and research is done within using hemicellulose to produce fuels, packaging materials and within the medicinal field [2]. Using hemicellulose in the production of polyurethane is one way to increase the use of renewable chemicals and possibly to discover new applications.

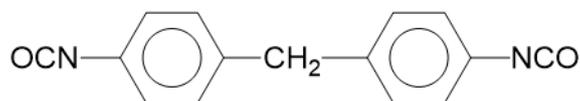
### 1.2 Purpose

The purpose of this thesis work was to create and characterize polyurethane films with focus on substituting one of the main components, polyol, against arabinoxylan to create a greener material. The aim was further to investigate how the different polymers bind, coordinates, and arrange themselves against each other to understand how different mixing ratios of polyol and arabinoxylan affect the material properties.

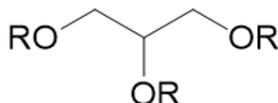
## 1.3 Theory

### 1.3.1 Polyurethane

Polyurethanes represents a big group of diverse materials. The reaction between isocyanate and hydroxyl groups from polyols was identified in the 19th century and the first polyurethane was made in 1937 by Otto Bayer and his coworkers at I.G. Farben in Germany [3]. The request for polyurethane is dominated by the increasing demand from industry in the eastern world, and polyurethane products accounted for 6 percent of the global consumption of plastics in 2012 [4]. The polyurethane market is based on different product types such as flexible- and rigid foams, coatings, adhesives and elastomers which are used in clothes, furniture and insulation among many other applications. Polyurethanes are classified as all polymers containing a urethane group (-NH-CO-O-) in their structure, and are made from reacting isocyanate with polyol. Isocyanates have NCO functional groups and polyols are alcohols containing multiple hydroxyl groups. The reaction is the extension of polyfunctional isocyanates and hydroxyl groups which result in a linear, branched or cross linked polymer. Isocyanates also reacts with water, which is how foams are produced [3]. Polyols are used to avoid stiffness and to provide flexibility in polyurethane formulations, and both isocyanate and polyol are primarily made from crude oil and natural gas [1]. In figure 1.1 and figure 1.2 the molecular structure of the diisocyanate and polyol used in the experiments are shown.



**Figure 1.1:** Showing the molecular structure of the diisocyanate, diphenylmethane 4,4'-diisocyanate



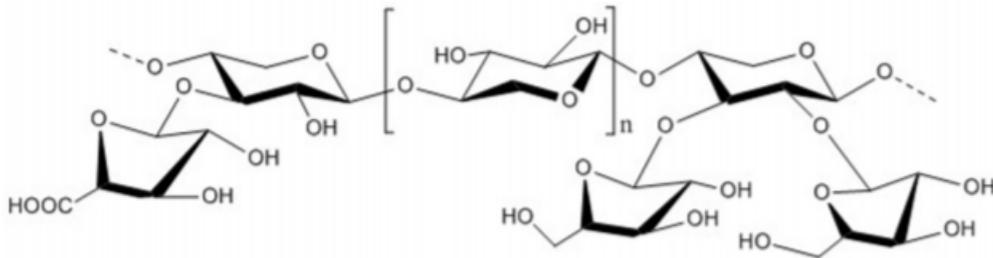
**Figure 1.2:** Showing the molecular structure of the polyol, glycerol propoxylate-block-ethoxylate

### 1.3.2 Hemicellulose

Hemicellulose is the second most abundant plant bio polymer on earth [5]. In plant cells, hemicellulose is concatenated with cellulose and lignin with hydrogen bonds respective covalent bonds [6]. Hemicellulose is an irregular hetero-polysaccharide with a branched structure which means that the polymer chain is built of a combination of different monomers [7,8]. There are four groups of hemicelluloses; xylanes, mannaners, mixed linkage-beta-glukanes and xyloglukanes [9].

### 1.3.3 Arabinoxylan

Arabinoxylan (AX) belong to the biggest group of hemicelluloses, the xylanes. AX is built of a backbone of beta-(1→4)-bound xylose units which are substituted with arabinose. The degree of substitution affect the water solubility and high degree of substitution increase solubility [10]. The side groups include small amounts of xylopyranose, galactopyranose, alfa-D-glucuronic acid or 4-O-methyl-alfa D glucuronic acid [6]. Arabinoxylane is the most abundant hemicellulose in annual plants [11].



**Figure 1.3:** Showing the molecular structure of arabinoxylan

# 2

## Experimental

### 2.1 Materials

Glycerol propoxylate-block-ethoxylate (GPE) and dibutyltin dilaurate (DBTDL) was purchased from Sigma-Aldrich. Diphenylmethane 4,4'-diisocyanate (pMDI) was obtained from Merck Millipore and polyether-modified-polysiloxane (TEGOSTAB B 8040) was obtained from Evonik. Acetone bought from Fisher Scientific Company was used as a medium to enable the reaction of other chemicals and did not take part in any chemical reaction. Fluorescein isothiocyanate (FITC) and pyridine was also purchased from Fisher Scientific Company. All materials were used as received without any alterations. Arabinoxylan previously extracted from barley husk was dried in desiccator and grounded to a fine powder before use.

### 2.2 Methods

In this section all experiments are presented. Firstly, procedures aiming to make PU films with AX are be presented, and later procedures aiming to make homogeneous PU films with AX. Homogeneous films were made in order to make it possible for the AX to dissolve in the film formation and blend properly with the other components. The procedures are presented in chronological order and are developed based on the results of the previous procedure. In table 2.1 the test schedule on which the experiments are based on is presented. Lastly the procedure of fluorescent labelling of AX is presented.

**Table 2.1:** Showing the test schedule and amount of chemicals for film experiments.

Sample	GPE:AX ratio	GPE	DBTL	TEGOSTAB B 8040	pMDI	AX
Reference	1:0	5 g	0.05 g	0.1 g	0.52 g	0 g
GPE:AX 9:1	9:1	4.5 g	0.05 g	0.1 g	1.34 g	0.5 g
GPE:AX 4:1	4:1	4.0 g	0.05 g	0.1 g	2.16 g	1.0 g
GPE:AX 2:1	2:1	3.25 g	0.05 g	0.1 g	3.39 g	1.75 g
GPE:AX 1:1	1:1	2.5 g	0.05 g	0.1 g	4.62 g	2.5 g

#### 2.2.1 Preparation of PU-GPE:AX films

Preparation of PU-GPE:AX films was carried out in two main procedures following studies in literature with some adjustments. Procedure 1 was prepared by following

a study of flexible starch-polyurethane films [12], and procedure 2 and 2.1 was established and determined after analyzing the results from the previous procedure. The amount of chemicals used for preparation of films is found in appendix (A).

### 2.2.1.1 Procedure 1

GPE, DBTL and TEGOSTAB B 8040 was added to a 250 mL round bottom flask and 30 g acetone was added with stirring. pMDI was added to an Erlenmeyer flask with 10 g of acetone. The solution in the round bottom flask was treated at heat and constant stirring until it reached the boiling point. The solution in the Erlenmeyer flask was then added and the reaction was allowed to stir under nitrogen for 15 minutes at 70°C. AX was then added and the solution was allowed to stir under nitrogen for another 15 minutes at 70°C. The solution was then cooled to ambient conditions and 2/5 of the solution was poured onto two 85 mm glass Petri dishes. The films were allowed to form upon drying at room temperature and was examined after 48h. The films were then removed and put in polystyrene Petri dishes to be stored until analysis.

### 2.2.1.2 Procedure 2

GPE, DBTL and TEGOSTAB B 8040 was added to an Erlenmeyer flask and 30 g acetone was added with stirring. pMDI was added to a 250 mL round bottom flask with 10 g of acetone. The solution in the Erlenmeyer flask was then slowly added to the round bottle flask under constant stirring at room temperature. 2/5 of the solution was then poured onto two 85 mm glass Petri dishes. AX was added to each Petri dish with stirring and the films were allowed to form upon drying at room temperature and was examined after 48h. The films were then removed and put in polystyrene Petri dishes to be stored until analysis.

### 2.2.1.3 Procedure 2.1

The films were made according to procedure 2 with the difference that 4/5 of the solution was poured onto two 85 mm glass Petri dishes and the films were examined after 2h.

## 2.2.2 Preparation of homogeneous PU-GPE:AX films

Preparation of homogeneous PU-GPE:AX films was carried out in three main procedures focusing on making films with a solution of AX dissolved in water instead of the AX powder. To prevent a reaction between water and pMDI, the water content need to be reduced which is why all procedures are focused on drying the solution of AX dissolved in water. An overview of the experiments are displayed in figure 2.1.

### 2.2.2.1 Procedure 1

AX and distilled water (20 mL) was added to a 250 mL one-necked round bottom flask. The dissolution of AX was carried out under nitrogen and constant stirring

## 2. Experimental

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at 80°C. The solution was then cooled to ambient conditions and GPE was added, and finally the sample was stored in desiccator for 48 h. Then, the dry weight mass was measured and the solution was used making films according to procedure 2.1, preparation of PU-GPE:AX films.

### 2.2.2.2 Procedure 1.1

The films were made according to procedure 1 with the difference that the solution was washed with acetone five times before the sample was stored in desiccator.

### 2.2.2.3 Procedure 2

AX and distilled water (20 mL) was added to a 250 mL one-necked round bottom flask. The dissolution of AX was carried out under nitrogen and constant stirring at 80°C. The solution was then cooled to ambient conditions and GPE was added, and finally the solution was freeze-dried. 30 g acetone, DBTL and TEGOSTAB B 8040 was then added. pMDI and 10 g acetone was added to a mortar and then the solution in the round bottom flask was added with stirring. The solution was then poured onto two 85 mm glass Petri dishes and the films were allowed to form upon drying at room temperature and was examined after 2h. The films were then removed and put in polystyrene Petri dishes to be stored until analysis.

### 2.2.2.4 Procedure 2.1

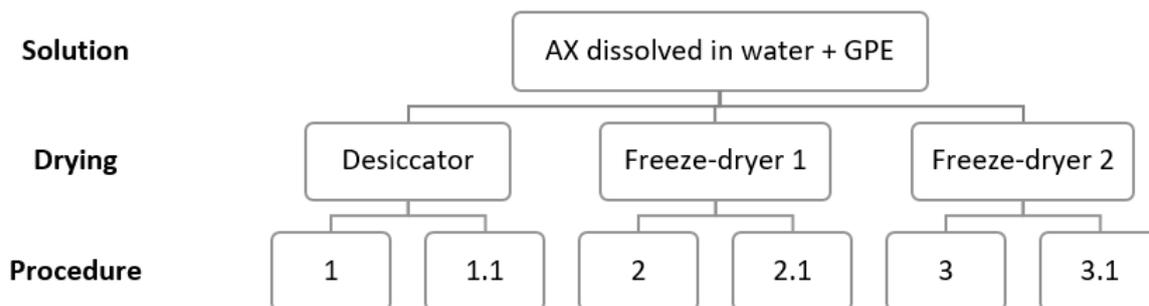
Films were made according to procedure 2 with the difference that the acetone was heated to 50°C before being added.

### 2.2.2.5 Procedure 3

AX and distilled water (20 mL) was added to a 250 mL one-necked round bottom flask. The dissolution of AX was carried out under nitrogen and constant stirring at 80°C. The solution was then cooled to ambient conditions and GPE was added, and finally the solution was freeze-dried with a different freeze-dryer than in procedure 2.. The freeze-dried solution was grounded to small flakes and then 30 g acetone, DBTL and TEGOSTAB B 8040 was added. pMDI and 10 g acetone was added to a mortar and then the solution in the round bottom flask was added with stirring. The solution was then poured onto two 85 mm glass Petri dishes and the films were allowed to form upon drying at room temperature and was examined after 2h. The films were then removed and put in polystyrene Petri dishes to be stored until analysis.

### 2.2.2.6 Procedure 3.1

Films were made according to procedure 3 with the difference that the freeze-dried solution was grounded to big flakes. The amount of chemicals used for preparation of films according to procedure 3.1 is found in appendix (A).



**Figure 2.1:** Showing an overview of the experiments preparing homogeneous PU-GPE:AX films.

### 2.2.3 Fluorescent labelling of AX

AX was labelled with fluorescein isothiocyanate (FITC) according to a method developed by Belder and Granath (1973)[13]. 1 g of AX was dissolved in 10 mL of dimethyl sulfoxide at constant stirring at 80°C. A few drops of pyridine was added and then 45 mg of FITC was added, followed by the addition of 20 mg of DBTL. The solution was treated under nitrogen and constant stirring for 2 h at 95°C. The solution was then cooled to ambient conditions, diluted with deionised water, dialyzed against deionised water in order to remove any excess FITC, and finally washed with ethanol. The fluorescent labelled AX was then dried in desiccator and stored in room temperature until films were made according to procedure 2.1, preparation of PU-GPE:AX films.

## 2.3 Analysis and Characterization

### 2.3.1 ATR-FTIR

Attenuated Total Reflection Fourier Transform Infrared, ATR-FTIR, was performed to determine functional groups and to examine how AX interacted with the other substances in the films. In this study a Perkin Elmer Frontier was used and three samples of each film was analyzed, chosen to represent different areas in the films. The samples were placed on the crystal and the FT-IR spectrum was then recorded in the range of 400-4000  $\text{cm}^{-1}$  using 8 scans per sample. KnowItAll Informatics System was used to study the spectra.

### 2.3.2 DSC

Differential Scanning Calorimetry, DSC, was performed to determine the glass transition temperature. In this study a Mettler DSC 820 was used and a temperature program of three intervals were performed with a ramp of 10°C/min from -100°C to 150°C. One sample was analyzed from each film and quantities of 6-10 mg sample was put in the DSC capsule. The glass transition temperature was determined from the inflection point on the curve representing the last interval.

### **2.3.3 Fluorescence microscopy**

Fluorescence microscopy was performed to determine if AX was successfully marked with FITC. In this study a Zeiss Axio Observer.Z1 microscope was used and images was taken with a iXon Ultra Andor camera with a five-fold magnification.

# 3

## Results and discussion

### 3.1 Preparation of PU-GPE:AX films

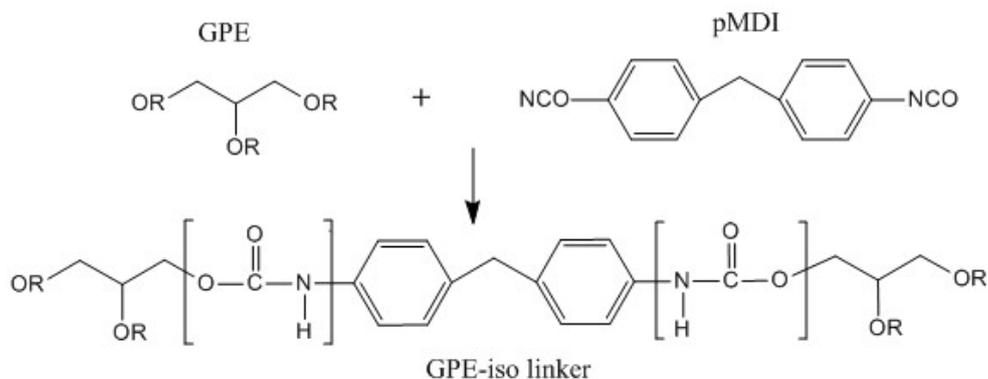
Procedure 1 was terminated after pMDI was added to the solution because a thick gel was formed which indicates that pMDI crosslinked to the acetone. To prevent this from happen again, the order of addition was changed in the following procedures. The films made according to procedure 2 was thin and hard to remove from the glass Petri dishes, indicating that the films were left to form for too long. Therefore more solution was poured onto the dishes in procedure 2.1. The films made according to procedure 2.1 were also examined after a shorter time to prevent all acetone from evaporating. Procedure 2.1 was used to make all films according to the test schedule, and the following results are presented for films made according to procedure 2.1. In figure 3.1 a picture of GPE:AX 4:1 made according to procedure 2.1 is shown. As seen in figure 3.1, the presented film is not homogeneous, and neither was the other films made according to procedure 2.1. AX has settled as a filler in the films, and there are areas with different content due to poor mixing of the components. The films are hard and inflexible and the stiffness of the films has a clear connection to the ratio of GPE:AX. The more AX that is added, the harder and brittle the films become. Pictures of the other films are displayed in appendix (B).



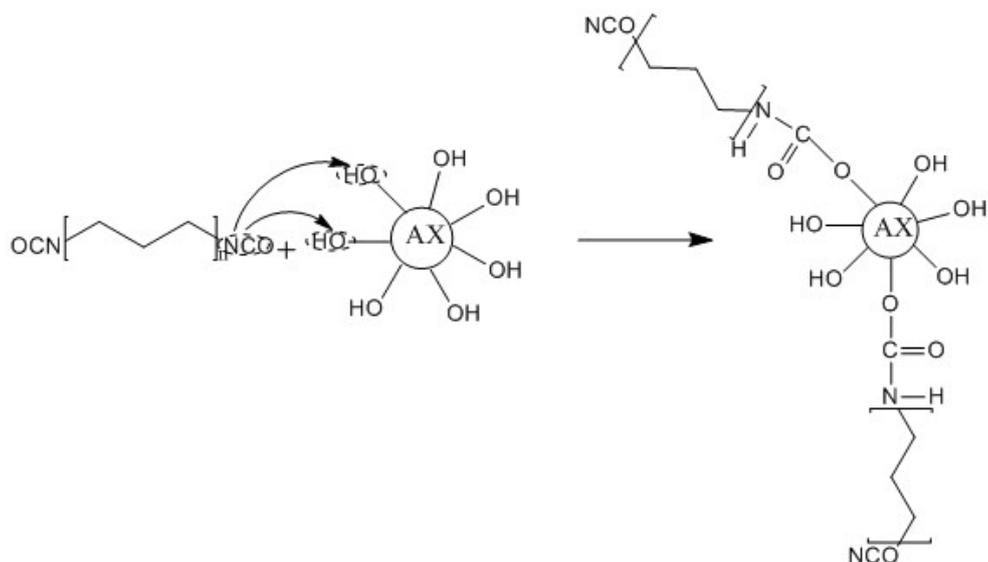
**Figure 3.1:** Showing GPE:AX 4:1 made according to procedure 2.1.

### 3.1.1 Synthesis of GPE-iso linker and PU-GPE:AX films

The schematic diagrams of synthesis of GPE-iso linker and reaction of AX and GPE-iso linker used for preparation of PU-GPE:AX films are shown in figure 3.2 and figure 3.3. The hydroxyl groups of GPE can easily react with diisocyanates, and in this reaction the hydrogen atoms from the hydroxyl groups from GPE covalent bond to the nitrogen atoms from pMDI. This reaction form carbamate (urethane) bonds, marked with brackets in figure 3.2, without producing any by-products. As seen in figure 3.4, characteristic peaks of -OH at 3300-3400  $\text{cm}^{-1}$  and peaks of NCO groups at 2200-2300  $\text{cm}^{-1}$  appear in the FT-IR spectra at same time. This indicates that GPE has not reacted fully with pMDI and that there are unreacted material. If the FT-IR spectra did not have these peaks it would indicate that the reaction between GPE and pMDI had reacted completely and that GPE-iso linker with NCO terminal had been produced.



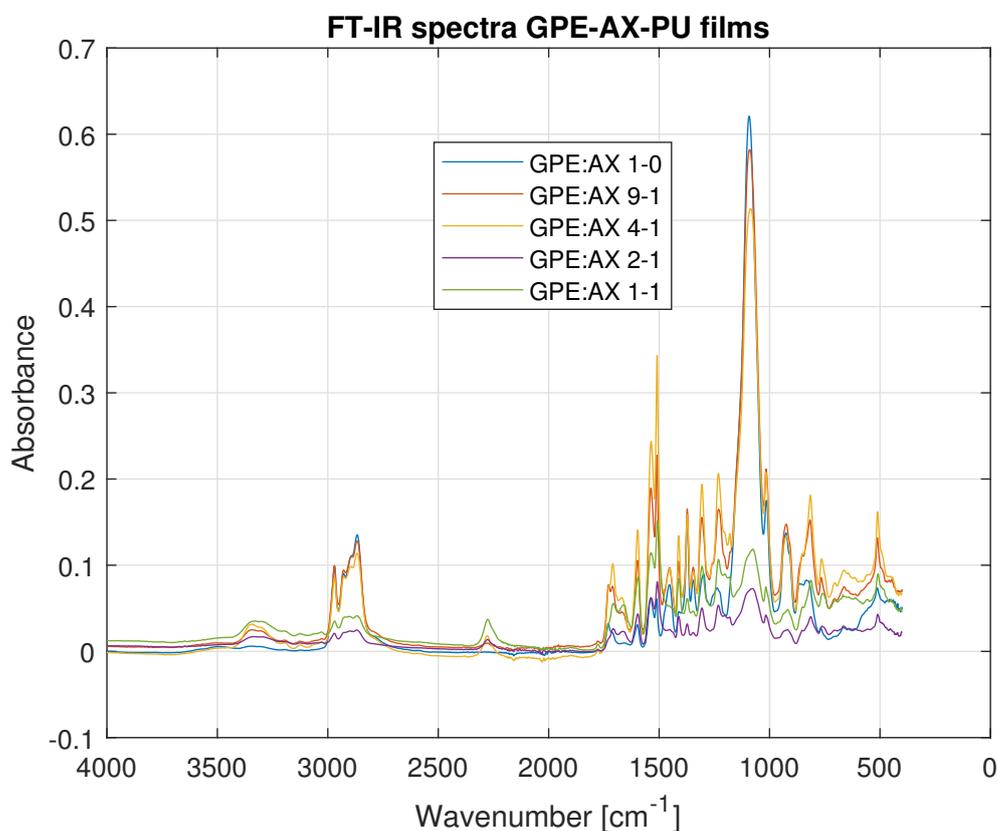
**Figure 3.2:** Showing illustration of synthesis of GPE-iso linker.



**Figure 3.3:** Showing the hypothetical reaction of AX and GPE-iso linker for preparation of GPE-AX-PU films.

### 3.1.2 IR absorption characteristics

The FT-IR spectra of PU films with arabinoxylan are presented in figure 3.4. The FT-IR spectrum of all samples indicates a strong peak for ether bonds at 1100  $\text{cm}^{-1}$  and a peak around 2900  $\text{cm}^{-1}$  indicating the presence of methyl groups. The spectrum of all samples also showed peaks at 1500  $\text{cm}^{-1}$  due to N-H stretching of amine groups and at 1700  $\text{cm}^{-1}$  due to C=O stretching of the newly formed carbamate groups. These new absorption peaks appear due to the attachment of NCO groups onto the GPE. The peaks are present in all samples but the intensity increase with the degree of substitution of GPE which supports the formulation of bonds between AX and pMDI and also GPE-iso linker. The FT-IR spectrum for GPE:AX 1:1 and GPE:AX 4:1 showed a characteristic peak around 2276  $\text{cm}^{-1}$  which can be assigned to nitrile stretch in unreacted isocyanate groups (NCO). Closeups of the mentioned peaks are found in appendix (C).



**Figure 3.4:** Showing the FT-IR spectra of PU-GPE:AX films made according to procedure 2.1.

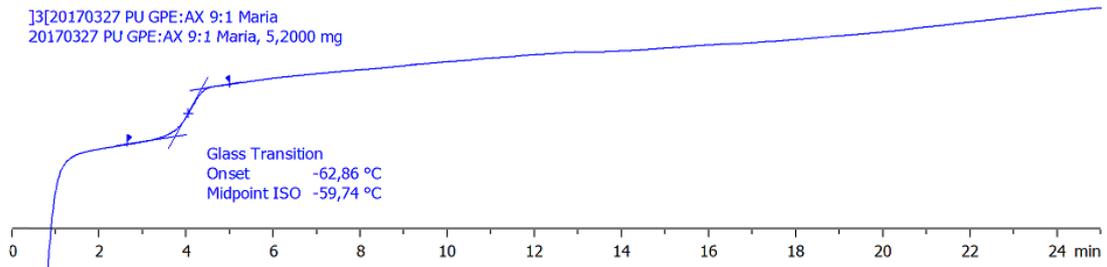
### 3.1.3 Phase-transition characteristics

DSC tests were made on all films and in figure 3.5 and 3.6 the DSC curves for GPE:AX 9:1 and GPE:AX 1:1 are displayed. DSC curves for the other films can be found in appendix together with a table displaying the glass temperatures. As can be seen in the figures, the samples exhibit relatively different curves, and the

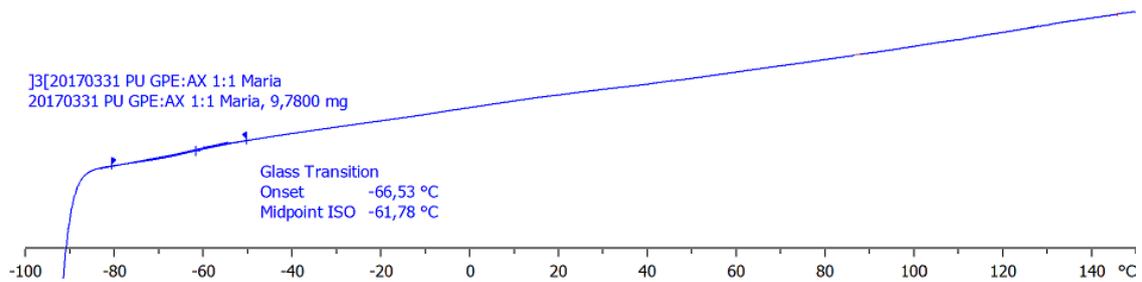
### 3. Results and discussion

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film containing 10 percent of AX (GPE:AX 9:1) has a steep curve compared to the film containing 50 percent AX (GPE:AX 1:1). The slope of the curve directly correlate to the amount of AX in the film, and gets less steep the more AX that is added. This together with the visual inspections that the films got harder and stiff by the addition of AX indicates that AX interacts with the other polymers and affect the intermolecular bonds. Yet, the glass transition temperatures of all samples are similar which confirms that it is hard to measure Tg on AX.



**Figure 3.5:** Showing the glass transition of GPE:AX 9:1



**Figure 3.6:** Showing the glass transition of GPE:AX 1:1

## 3.2 Preparation of homogeneous PU-GPE:AX films

In procedure 1, foam was produced instead of film which indicated that there was water left in the sample and that the hydroxyl groups of water had reacted with the nitrogen atoms from pMDI. Therefore the following procedures focused on eliminating the water content of the solution before it was mixed with pMDI, and in procedure 1.1 the sample was washed five times with acetone to do this. However, the acetone dissolved GPE and precipitated AX, and no film was made.

In procedure 2, the GPE-AX-solution was freeze dried to an oily consistency and inhomogeneous films were made. Procedure 2.1 focused on increasing the solubility of the freeze dried solution in acetone and therefore the acetone was heated. The films became inhomogeneous and got stuck hard to the glass Petri dishes which indicates that the polymers had interacted with the glass surface due to the higher temperature of the acetone.

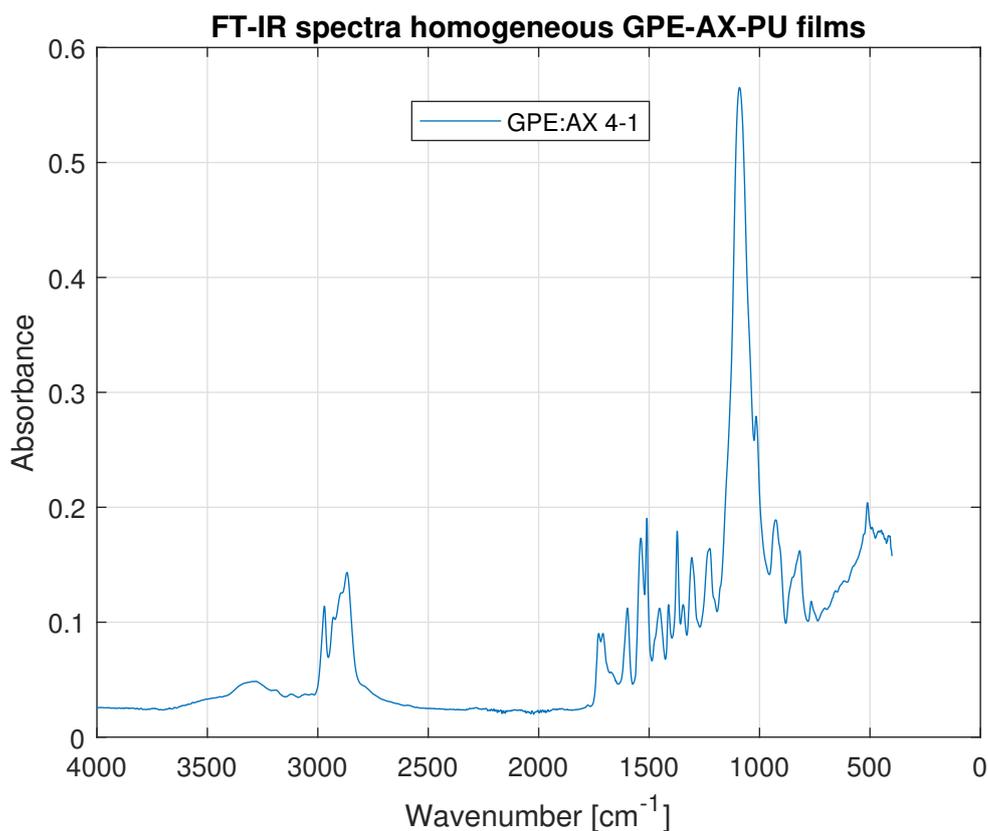
In procedure 3, the freeze-dried GPE-AX-solution had a consistency of cornflakes and near homogeneous films was made. The consistency of the freeze-dried solution and the freeze-dryer instrument is thus considered as an important aspect. In procedure 3.1 the affect of the particle size of the freeze-dried solution was investigated, and bigger cornflakes showed to be preferable. Procedure 3.1 was repeated to produce all films according to the test schedule, yet no more homogeneous films were made. Possible error sources to explain this is that the filming temperature and relative humidity had changed over the period of laboratory work, which might have affected the results. The following results are presented for the homogeneous film GPE:AX 4:1 made according to procedure 3.1. In figure 3.7 a picture of GPE:AX 4:1 made according to procedure 3.1 is shown. As seen in figure 3.7, the presented film is homogeneous. AX is dissolved in the film and the components has been properly mixed. The film is flexible and is easy to bend. Pictures of the other films are displayed in appendix (B).



**Figure 3.7:** Showing GPE:AX 4:1 made according to procedure 3.1

### 3.2.1 IR absorption characteristics

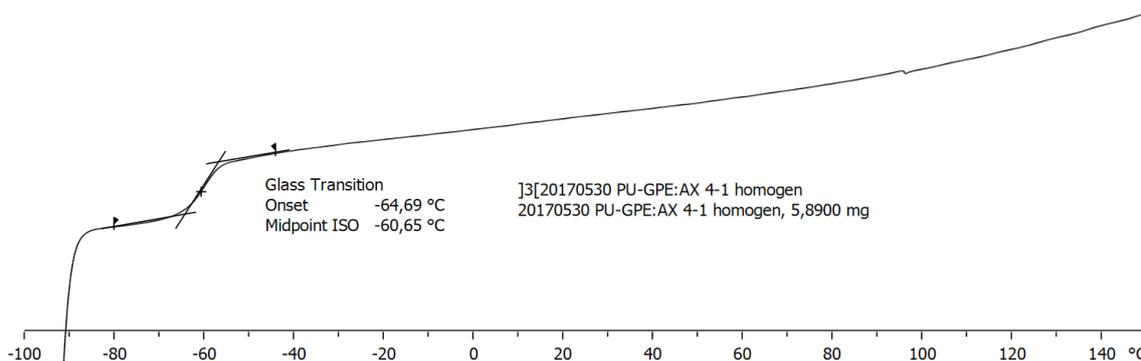
The FT-IR spectra of homogeneous PU film with arabinoxylan is presented in figure 3.8. The FT-IR spectra exhibit the same peaks as for the FT-IR spectra presented for the PU-GPE:AX films with the exception of the peak at 2200-2300  $\text{cm}^{-1}$  indicating unreacted isocyanate groups. The spectra does not have this peak which indicates that all pMDI has reacted and that GPE-iso linker with NCO terminal has been produced. This could also indicate that more AX interacts when being dissolved in the film. Closeups of mentioned peaks are found in appendix (C).



**Figure 3.8:** Showing the FT-IR spectra of homogeneous PU-GPE:AX 4:1 film.

### 3.2.2 Phase-transition characteristics

Figure 3.9 show the DSC curve of the homogeneous film. Comparing this curve with the DSC curve of the heterogeneous film with the same amount of AX (appendix (C)), there are one difference. The DSC curve for the heterogeneous film is less steep than the curve for the homogeneous film which contradicts the theory that the curve got less steep the more AX that is incorporated in the film since FT-IR indicated that more AX had interacted in the homogeneous film.



**Figure 3.9:** Showing the FT-IR spectra of homogeneous PU-GPE:AX 4:1 film.

### 3.3 Preparation of film with fluorescence labelled AX

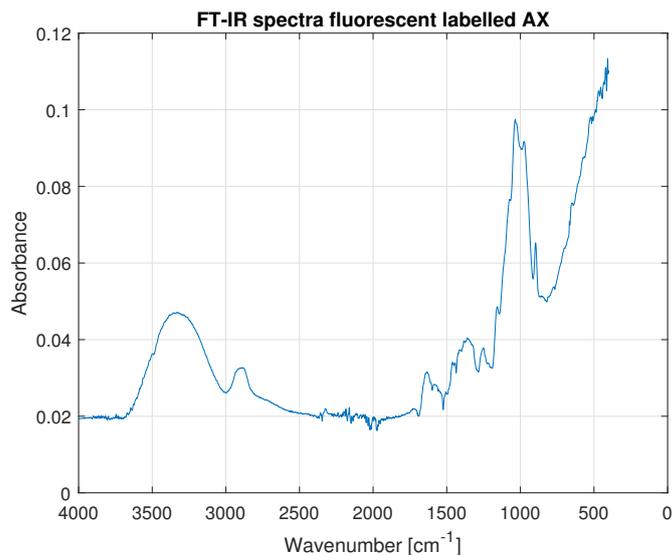
The film was made according to procedure 2.1 PU-GPE:AX films and became heterogeneous as can be seen in figure 3.10. Both the yellow and red segments are AX. The film is flexible and easy to bend compared to the heterogeneous film made with unmarked AX.



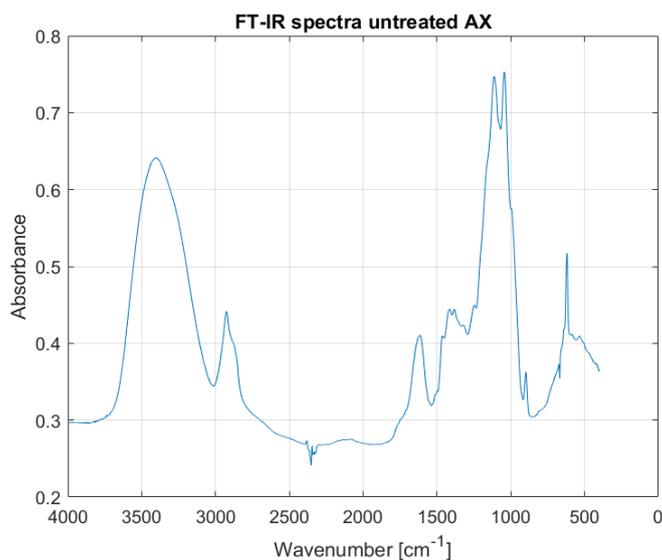
**Figure 3.10:** Showing GPE:AX 4:1 film made with FITC labelled AX

### 3.3.1 Synthesis of FITC-labelled AX

Hypothetically, AX and FITC will bind with urethane-linkage if the synthesis of FITC-labelled AX is successful. In figure 3.11 the FT-IR spectra of FITC-labelled AX is presented and in figure 3.12 the FT-IR spectra of untreated AX is presented. As can be seen in the figures there are a few differences, but it is had to determine only from this analysis if urethane-linkage has been created.



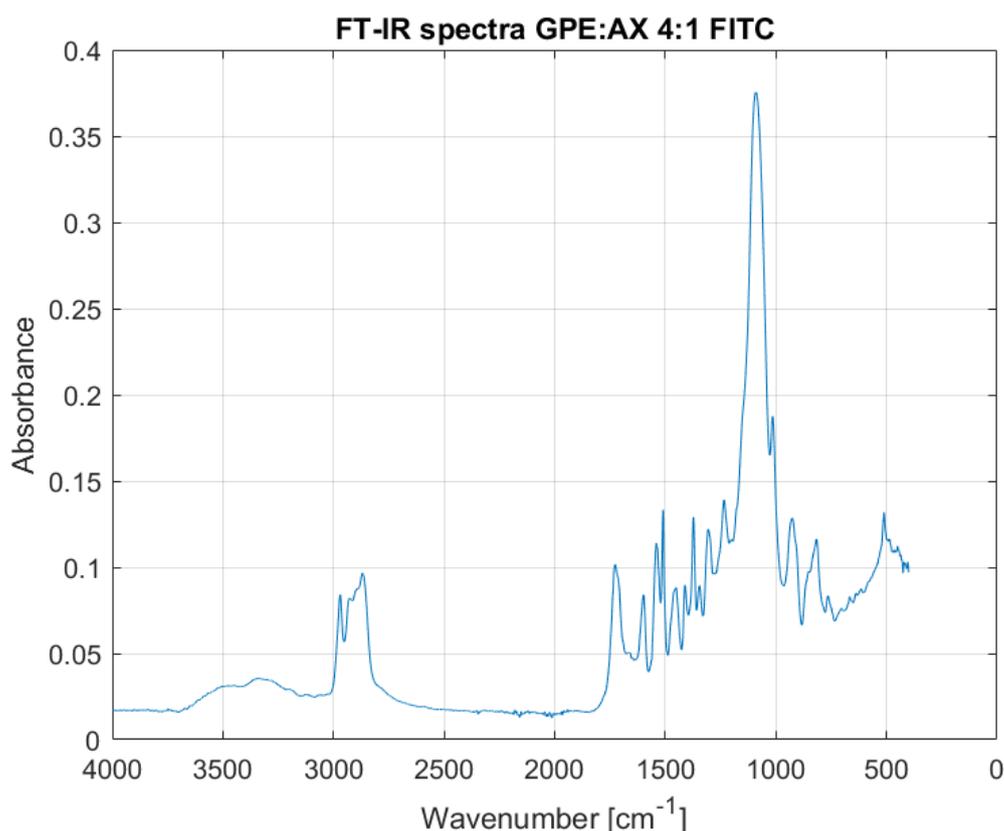
**Figure 3.11:** Showing the FT-IR spectra of PU-GPE:AX 4:1 film made with FITC-labelled AX.



**Figure 3.12:** Showing the FT-IR spectra of PU-GPE:AX 4:1 film made with FITC-labelled AX.

### 3.3.2 IR absorption characteristics

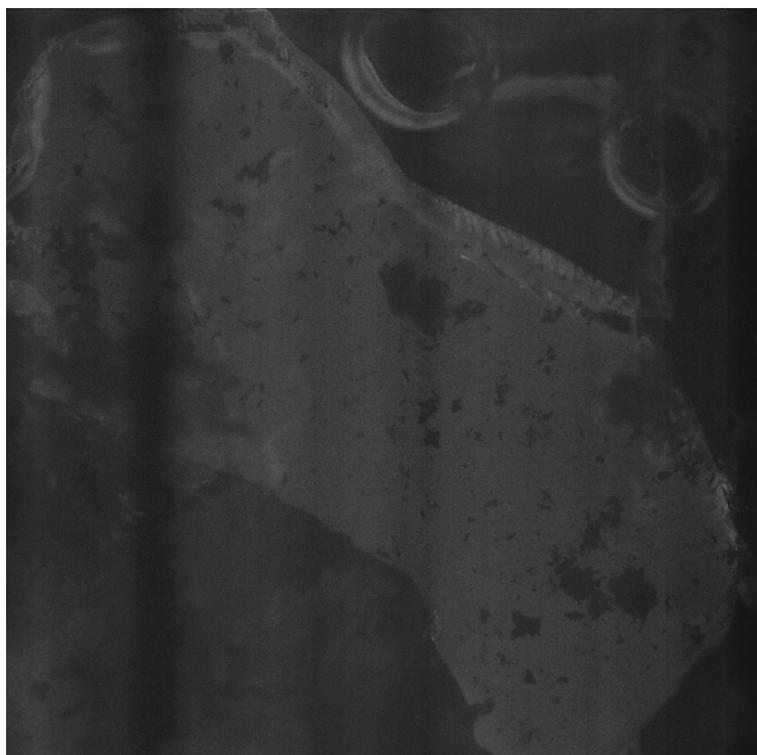
The FT-IR spectra of PU GPE:AX 4:1 film with FITC-labelled arabinoxylan is presented in figure 3.13. The FT-IR spectra exhibit the same peaks as for the FT-IR spectra presented for the PU-GPE:AX films with the exception of the peaks around 1500-1700  $\text{cm}^{-1}$  are more clear. As the FT-IR spectra for the homogeneous film also showed, no peak for unreacted isocyanate is present in the sample.



**Figure 3.13:** Showing the FT-IR spectra of PU-GPE:AX 4:1 film made with FITC-labelled AX.

### 3.3.3 Fluorescence microscopy

A fluorescence microscopy image of the film made with FITC-labelled AX is displayed in figure 3.14, and more pictures can be found in appendix (D). The image shows that the FITC-labelled AX is fluorescent which indicates that the fluorescent labelling was successful. The dark areas on the picture are due to the fact that the film was heterogeneous and that AX was not dissolved in the film. The circular forms in the upper right corner are due to air bubbles. On the fluorescent material, there are dark spots that are believed to be unmarked AX which indicates that the fluorescent labelling of AX was not completely accomplished.



**Figure 3.14:** Showing the FT-IR spectra of PU-GPE:AX 4:1 film made with FITC-labelled AX.

# 4

## Conclusion

The preparation of non homogeneous films with arabinoxylan went well and films were obtained. AX settled as a filler in the films and they were hard and inflexible due to the incorporation of AX. The FT-IR spectra indicated that AX interacted with the other compounds in the film. The more AX that was incorporated in the film, the bigger the peaks for carbamate groups was which indicates that AX form urethane-linkage with pMDI and GPE-iso linker.

To further analyze the polymer interactions in the films it was interesting to dissolve AX in water and produce homogeneous films. Preparing homogeneous polyurethane films with arabinoxylan has been shown to be a not optimized process where there are unclear instructions for obtaining a good result.

To further investigate the interactions in the films, AX was labelled with FITC to be studied with confocal laser microscopy. The confocal laser microscopy available was not installed and ready to use which is why such an analysis was not performed. The FITC-labelling of AX was examined with fluorescence microscopy and the result showed that the labelling was widely successful.

One objective of this study was to investigate how the different polymers interacted with one another. The results from the performed analysis did show some interesting results and a platform has been created were the filming parameters have been noted for further studies.

### 4.1 Future perspectives

Producing polyurethane films with AX is a complicated process that depend on several parameters. This study has shown that the preparation of homogeneous films where AX is dissolved in the material is a method that needs to be developed and optimized to be able to be used in a future perspective. After developing an optimized procedure the next step would be to produce films with different amount of AX and investigate the material properties.

Concerning the procedures, it would be interesting to perform the experiments in a controlled environment where temperature and relative humidity can be monitored to be able to eliminate possible errors. The particle size of the freeze-dried material used to produce the homogeneous film showed to be an important filming parameter and it would therefore be interesting to investigate how the particle size affect the filming in a controlled environment.

#### 4. Conclusion

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One important aspect that has not been an objective in this study but could be interesting in the future is to account for how much greener the material become substituting polyol against AX. This could increase the interest in using AX and positively influence the research done within the field.

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# A

## Appendix 1

**Table A.1:** Amount of chemicals used for preparation of films according to procedure 2.1, PU-GPE:AX films

Sample	GPE:AX ratio	GPE	DBTL	TEGOSTAB B 8040	pMDI	AX
Reference	1:0	4.9640 g	0.0562 g	0.1100 g	0.5167 g	0 g
GPE:AX 9:1	9:1	4.4211 g	0.0677 g	0.1287 g	1.3455 g	0.2047 g/ 0.2022 g
GPE:AX 4:1	4:1	3.9866 g	0.0518 g	0.1074 g	2.1602 g	0.4025 g/0.4237
GPE:AX 2:1	2:1	3.2474 g	0.0613 g	0.1159 g	3.5089 g	0.7060 g/0.7038 g
GPE:AX 1:1	1:1	2.5253 g	0.0522 g	0.1043 g	4.5964 g	1.0136 g/1.0764 g

**Table A.2:** Amount of chemicals used for preparation of films according to procedure 1 and 2, PU-GPE:AX films

Procedure	GPE:AX ratio	GPE	DBTL	TEGOSTAB B 8040	pMDI	AX
1	9:1	4.5250 g	0.0559 g	0.1237 g	1.3370 g	0.5027 g
2	9:1	4.4937 g	0.0613 g	0.1052 g	1.3538 g	0.1053 g/ 0.1000 g/ 0.1011 g

**Table A.3:** Amount of chemicals used for preparation of films according to procedure 3.1, homogeneous PU-GPE:AX films

Sample	GPE:AX ratio	GPE	DBTL	TEGOSTAB B 8040	pMDI	AX	Deionised water
GPE:AX 4:1	4:1	4.0235 g	0.0532 g	0.1149 g	2.1544 g	1.0012 g	20 ml

**Table A.4:** Amount of chemicals used for preparation of films according to procedure 1, 1.1, 2, 2.1 and 3, homogeneous PU-GPE:AX films.

Procedure	GPE:AX ratio	GPE	DBTL	TEGOSTAB B 8040	pMDI	AX	Deionised water
1	4:1	4.0672 g	0.0611 g	0.1121 g	2.2027 g	1.0165 g	20 ml
1.1	4:1	4.1245 g	0.0501 g	0.1243 g	2.1433 g	1.0001 g	20 ml
2	4:1	3.9952 g	0.0452 g	0.1054 g	2.1849 g	0.9878 g	20 ml
2.1	4:1	4.0054 g	0.0632 g	0.1198 g	2.1976 g	1.0299 g	20 ml
3	4:1	3.9896 g	0.0543 g	0.1010 g	2.1555 g	1.3266 g	20 ml

**Table A.5:** Showing the glass-transition temperature ( $T_g$ ) for PU-GPE:AX films.

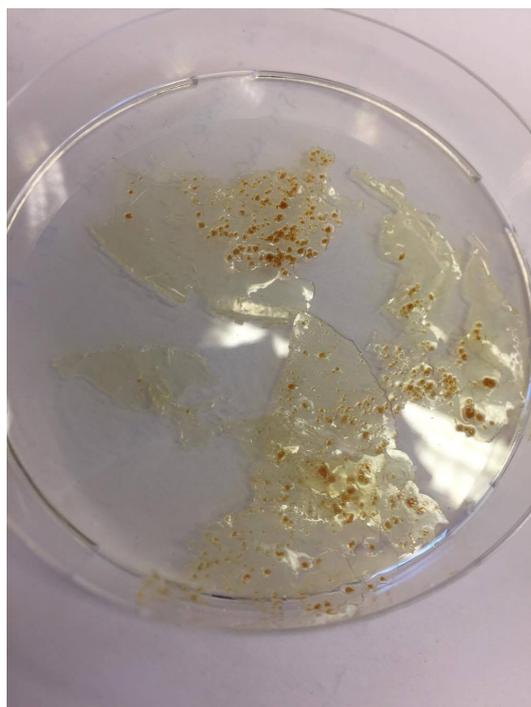
<b>Sample</b>	<b><math>T_g</math> (<math>^{\circ}\text{C}</math>)</b>
GPE:AX 1:0	-66.84
GPE:AX 9:1	-62.86
GPE:AX 4:1	-63.80
GPE:AX 2:1	-66.34
GPE:AX 1:1	-66.53

# B

## Appendix 2



**Figure B.1:** Showing GPE:AX 9:1 made according to procedure 1, PU-GPE:AX films.



**Figure B.2:** Showing GPE:AX 9:1 made according to procedure 2, PU-GPE:AX films.



**Figure B.3:** Showing GPE:AX 1:0 made according to procedure 2.1, PU-GPE:AX films.



**Figure B.4:** Showing GPE:AX 9:1 made according to procedure 2.1, PU-GPE:AX films.



**Figure B.5:** Showing GPE:AX 4:1 made according to procedure 2.1, PU-GPE:AX films.



**Figure B.6:** Showing GPE:AX 2:1 made according to procedure 2.1, PU-GPE:AX films.



**Figure B.7:** Showing GPE:AX 1:1 made according to procedure 2.1, PU-GPE:AX films.



**Figure B.8:** Showing GPE:AX 4:1 made according to procedure 1, homogeneous PU-GPE:AX films.



**Figure B.9:** Showing GPE:AX 4:1 made according to procedure 2, homogeneous PU-GPE:AX films.



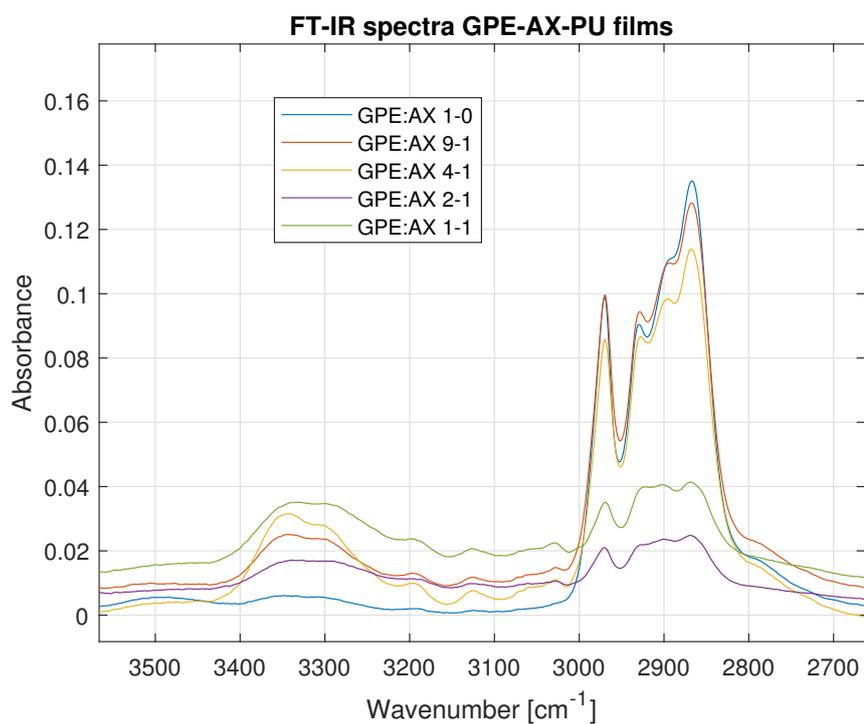
**Figure B.10:** Showing GPE:AX 4:1 made according to procedure 2.1, homogeneous PU-GPE:AX films.



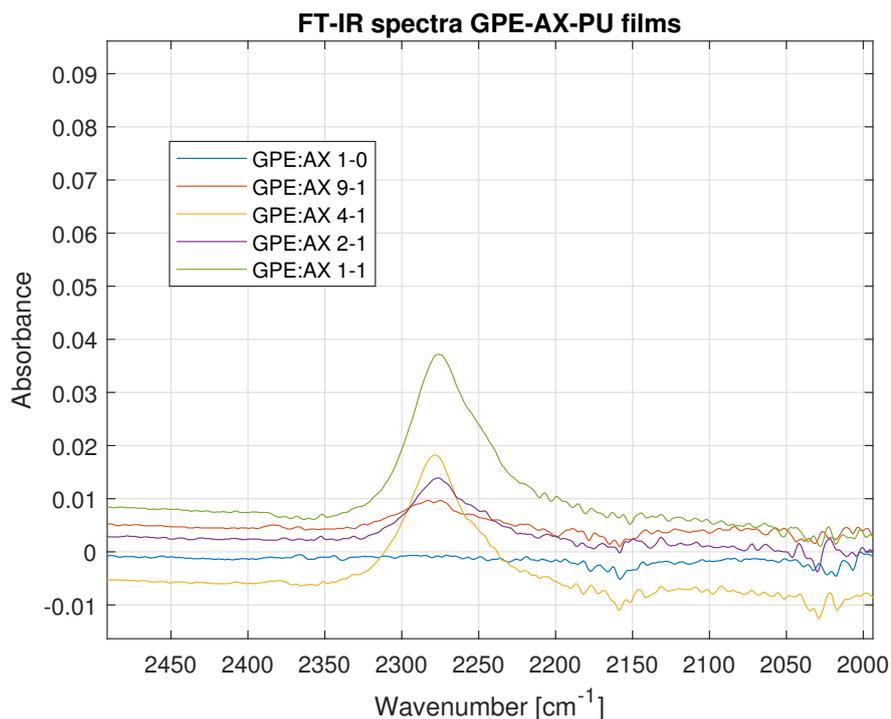
**Figure B.11:** Showing GPE:AX 4:1 made according to procedure 3, homogeneous PU-GPE:AX films.

# C

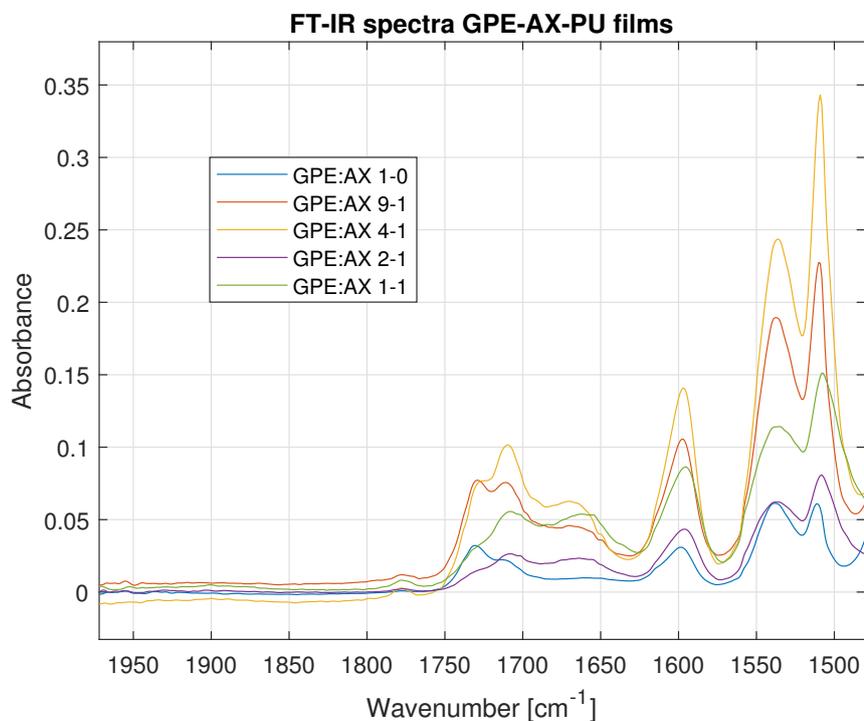
## Appendix 3



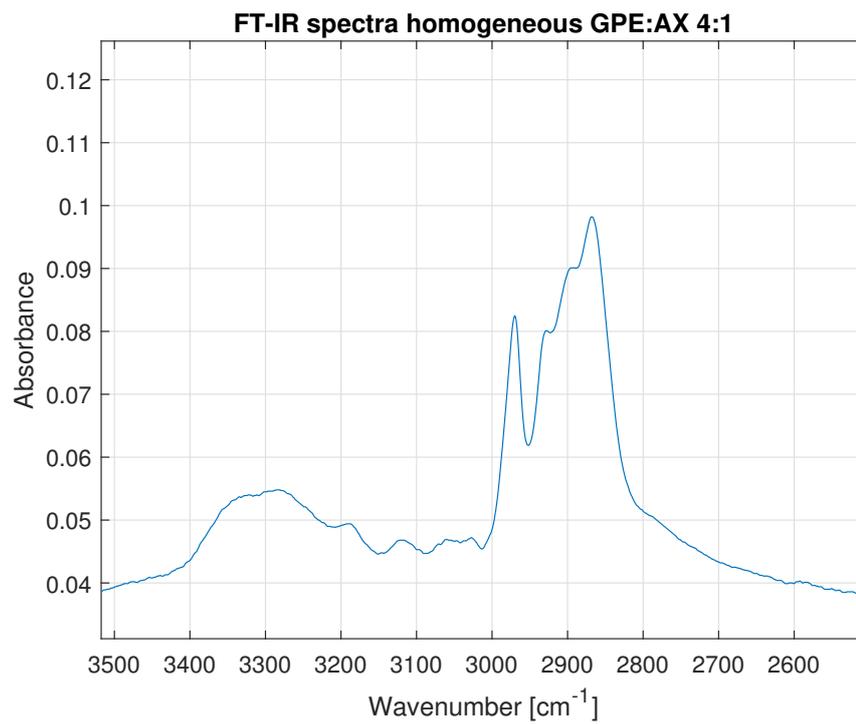
**Figure C.1:** Showing the FT-IR spectra of PU-GPE:AX films, a closer look at the peaks indicating the presence of OH- and methyl groups.



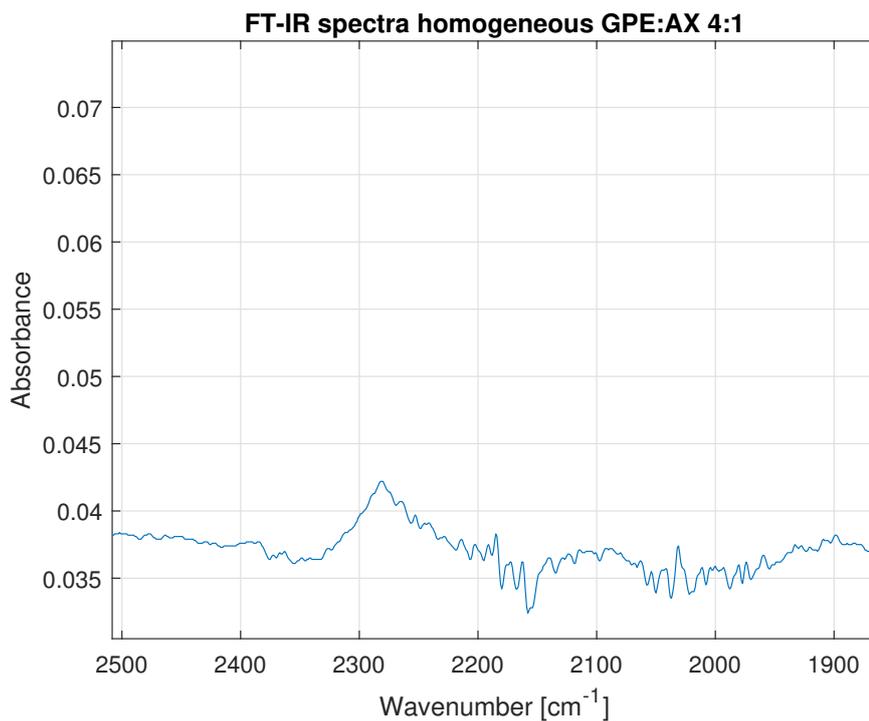
**Figure C.2:** Showing the FT-IR spectra of GPE-AX-PU films, a closer look at the peak indicating the presence of nitrile stretch of NCO groups.



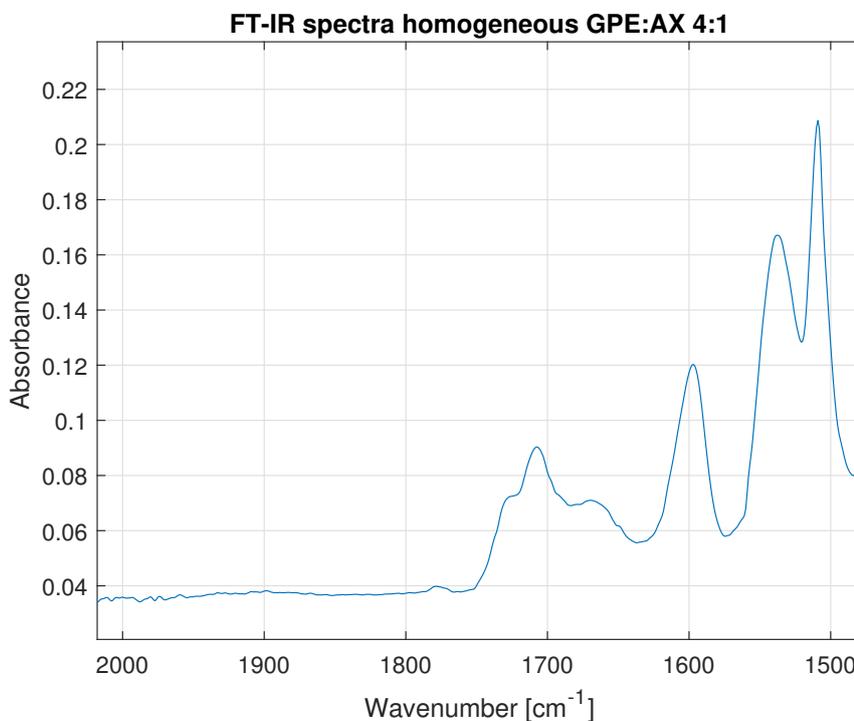
**Figure C.3:** Showing the FT-IR spectra of PU-GPE:AX films, a closer look at the peaks indicating the formation of carbamate bonds.



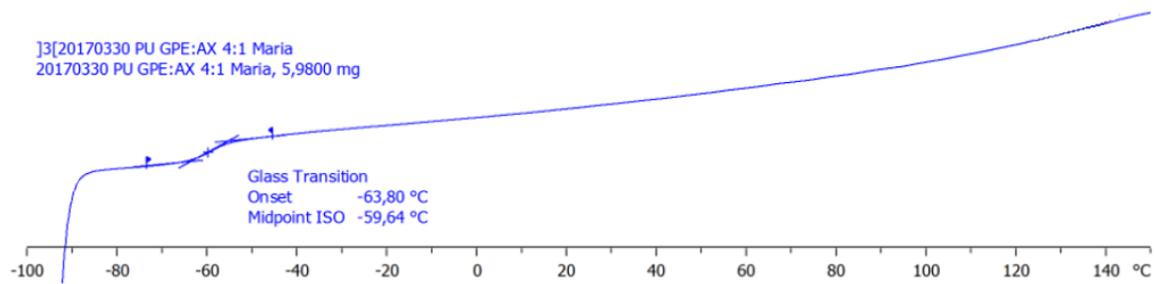
**Figure C.4:** Showing the FT-IR spectra of homogeneous PU-GPE:AX films, a closer look at the peaks indicating the presence of OH- and methyl groups.



**Figure C.5:** Showing the FT-IR spectra of homogeneous PU-GPE:AX films, a closer look at the area that does not have a strong characteristic peak for nitrile stretch of unreacted NCO groups.



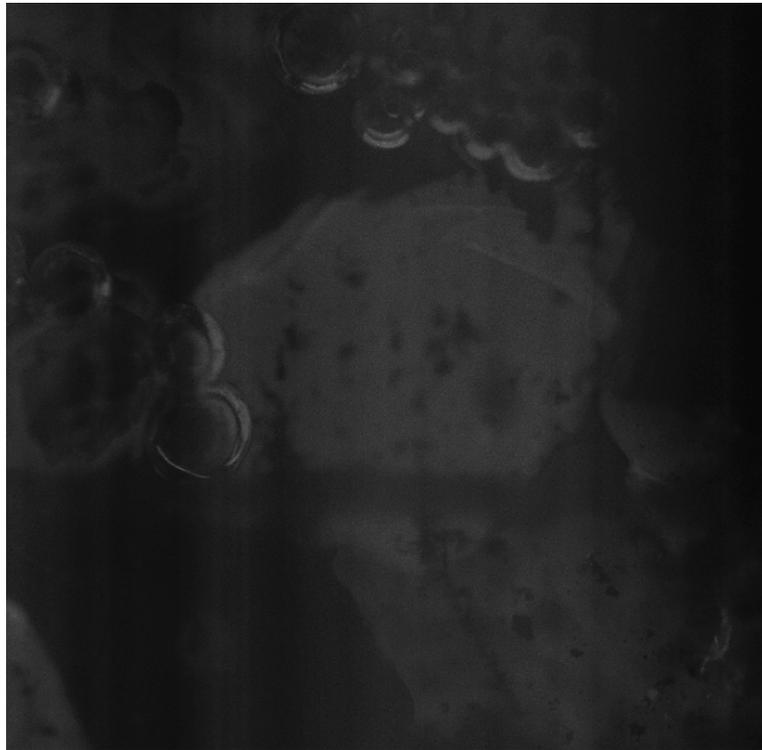
**Figure C.6:** Showing the FT-IR spectra of homogeneous PU-GPE:AX films, a closer look at the peaks indicating the formation of carbamate bonds.



**Figure C.7:** Showing the DSC curve of heterogeneous GPE:AX 4:1 film made according to procedure 2.1.

# D

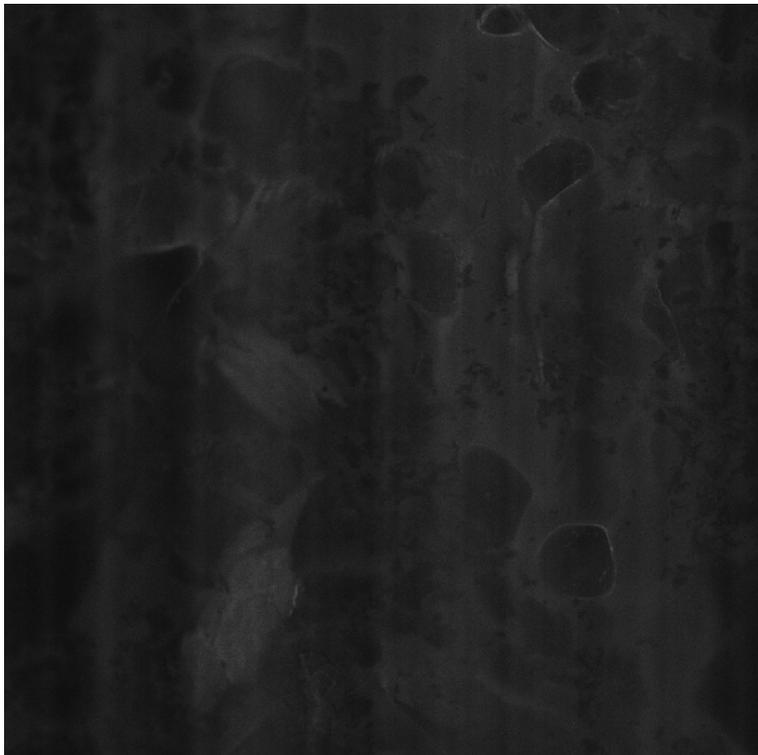
## Appendix 4



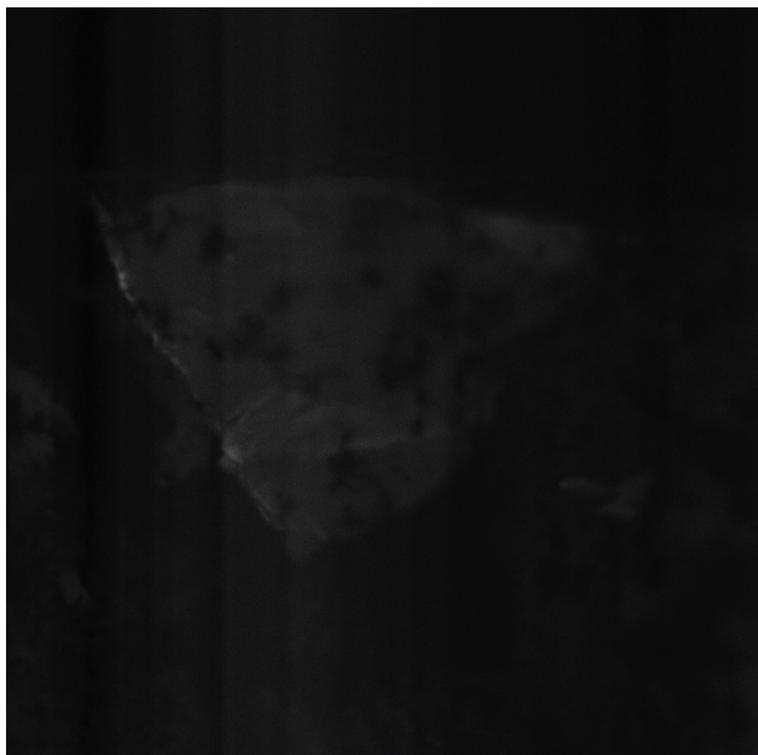
**Figure D.1:** Showing fluorescence microscopy images



**Figure D.2:** Showing fluorescence microscopy images



**Figure D.3:** Showing fluorescence microscopy images



**Figure D.4:** Showing fluorescence microscopy images