Development of specified risk material-based plywood adhesive with enhanced water resistivity

by

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A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

in

Chemical Engineering

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Abstract

Canadian plywood industry with its 2 billion square feet annual capacity [83] requires a large amount of adhesive materials to satisfy its needs. This forces plywood manufacturers to consider the utilization of agricultural bio-waste to create environmentally friendly adhesive materials with the properties similar to those commercially available in the market. Released in 2007, the Enhanced Feed Ban made available thousands of tonnes of Specified Risk Material (SRM) – tissues of cattle where abnormally folded proteins – prions that cause Bovine Spongiform Encephalopathy (BSE) disease, are the most likely to be concentrated. The recent studies show that if hydrolyzed according to the Canadian Food Inspection Agency protocol, prions get irreversibly broken down and SRM contains a sufficient amount of useful proteinaceous material. The purpose of this research was to develop an adhesive (glue) material with outstanding water resistive properties for potential application in plywood industry and to evaluate its performance.

Hydrolyzed SRM was chemically modified by esterification reaction with alcohol. The degree of esterification and other characteristics were evaluated with size exclusion high performance liquid chromatography (SEC-HPLC), sodium dodecyl sulphate poly-(acrylamide) gel electrophoresis (SDS-PAGE), Fourier transform infrared spectroscopy (FTIR), contact angle measurement, and qualitative

calculation of free carboxylic groups. The modified SRM appeared to have better water resistant properties that the original SRM.

The modified SRM was further crosslinked with glutaraldehyde and further evaluated with Fourier transform infrared spectroscopy (FTIR). The adhesive properties of crosslinked esterified SRM were evaluated in accordance with the American Standard of Testing Materials (ASTM) standard technique – lap shear stress evaluation of an adhesive bonded joint using the Instron MTS 810 equipment.

Overall, this study has showed that the chemical modification of SRM by esterification improves water resistance of hydrolyzed SRM. The adhesive material developed by crosslinking of chemically modified SRM with glutaraldehyde performed well and passed the standard requirements by ASTM showing that the pressing temperature is the crucial factor in the application of SRM-based adhesive of the evaluated formulation.

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Chapter 1. Introduction

The agricultural sector in Canada provides a large amount of opportunities for waste material recycling programs. Some of them were already implemented (biogas plants), some are still being developed and evaluated. Growth of the amount of cases of Bovine Spongiform Encephalopathy worldwide about a decade ago resulted in the introduction of Canadian Enhanced Feed Ban (2007). This resulted in the exclusion of rendered tissues of animals with potentially highest concentration of misfolded proteins - prions (Specified Risk Material (SRM)) from any application as animal feed, fertilizers, and pet food. According to the Canadian Food Inspection Agency protocol, rendered SRM can be landfilled or hydrolysed (thermal or alkaline hydrolysis) at a high economical cost and significant environmental concerns [1-4]. Incineration is another method of SRM disposal.

The problem emerges from the amount of SRM being landfilled annually in Canada, US, and European countries. The price of handling and landfilling SRM varies from $75 up to $200 per tonne [17]. Until recent time, all the SRM has been a subject to landfilling which resulted in the sufficient economic losses for the agricultural sector and emerged environmental concerns due to a large amount of SRM landfilled (over 300,000 tonnes) annually [17]. Since 2010, the Canadian Government has been supporting multiple initiatives when over $300 million has

been pledged for different SRM programs and research projects; however, a vast majority of these investment has been dedicated to the research in bio- and medical related fields and investigation of the BSE disease. Although, a large amount of money is being invested, the problem of utilization of SRM left unsolved. It is only within the last few years SRM material has been studied and characterized in terms of development of valuable materials. There has been a broad spectrum of characterization experiments (such as size exclusion high performance liquid chromatography (SEC-HPLC), sodium dodecyl sulphate poly (acrylamide) gel electrophoresis (SDS-PAGE), Fourier transform infrared spectroscopy, etc.) indicating that SRM can potentially provide a valuable proteinaceous material that can be utilized for various application. Some concepts have been tested showing that hydrolyzed SRM can be potentially used for the development of thermosetting plastics, biocomposites, and adhesive material for wood oriented strand board (OSB) and plywood [5-7].

The main objectives of the present project were:

- Develop a technology platform to convert SRM into marketable adhesive for plywood manufacturing application
- Develop and evaluate the properties of SRM-based adhesive with enhanced water resistivity

- To optimize the conditions of adhesive formulation
- Evaluate the performance of adhesive material for potential application for plywood manufacturing in compliance with ASTM D4690-12 standard
- Evaluate potential marketability of SRM-based adhesive material for torrefied wood pellets production

The following strategies had been developed before the research was started and have been tested as the research progressed:

- Proteinaceous material recovered from hydrolyzed SRM can be used as a base material for the wood adhesive development
- If SRM goes through chemical modification, resulting in substitution of hydrophilic carboxylic acid functional groups with less hydrophilic ester bonds, the water resistivity of SRM will be improved
- If chemically modified SRM crosslinked with glutaraldehyde, it will result in the formation of three dimensional thermosetting polymer that can be used as an adhesive
- If water resistivity of SRM is improved, glutaraldehyde does not need to be pre-polymerized if used as a crosslinking agent with chemically modified SRM to obtain a water resistant material

- If SRM-based polymer is used as a hot-melt adhesive, pressing temperature affects the adhesion strength

With all the above mentioned taken in consideration, in-detailed research has been carried out and the properties of modified SRM and SRM-based adhesive were exclusively studied.

In Chapter 2, an in-depth review was done on the problem of BSE and SRM, approved procedures and protocols of handling and utilization, and an Enhanced Feed Ban. Also in Chapter 2, there exists a wide overview of recently published papers on thermal hydrolysis protocols, peptides recovery procedure and the characterization experiments that have been carried out on the recovered from SRM peptides. There was also a review done on the plywood manufacturing process and the mechanisms of adhesion that takes place in the process with a general overview of adhesive materials. More in-detail insight has been taken at the academic articles about the development of protein-based adhesives.

Chapter 3 is dedicated to the chemical modification of peptides recovered from SRM which has been studied within this research. The esterification of carboxylic acid groups has been attempted to improve the water resistant properties of hydrolyzed SRM. Chapter 3 provides a deep scientific insight in the mechanism of the reactions that potentially take place and gives and explanation of why this

particular type of modification has been attempted in the research. The chapter contains the entire description of the experiment as well as the detailed description and results of characterization experiments that have been carried out on the modified material: size exclusion high performance liquid chromatography (SEC-HPLC), sodium dodecyl sulphate poly (acrylamide) gel electrophoresis, Fourier transform infrared spectroscopy, contact angle measurement, and pH titration

The procedure on formulation of a plywood adhesive by crosslinking modified SRM with glutaraldehyde and the results of lap shear stress test are presented in Chapter 4. Chemically modified SRM has been crosslinked with glutaraldehyde at different concentrations and the adhesive properties of each formulation have been tested on the MTS Intron 810 unit in compliance with ASTM D4690-12 standard. The results have been reported in MPa units for both dry and soaked conditions.

A brief market evaluation and economical assessment of torrefied wood pellets market are presented in Chapter 5 to assess a potential marketability of SRM-based adhesive as a binder for torrefied wood pellets manufacturing. This chapter includes some price estimations for direct conversion of SRM into binder.

Finally, Chapter 6 gives an outlook on the research that has been carried out, conclusions and result achieved, and gives an overview of suggestions for future work.

Chapter 2. Literature review

2.1 Livestock sector in Canada and in Alberta

Canada has one of the largest agricultural sectors in the world. According to the reported *Overview of the Canadian Agriculture and Agri-Food System 2015*, Canada is the fifth-largest exporter of agriculture and agri-food products in the world with its $46.0 billion export sales and the sixth-largest importer with $34.3 billion total sales in 2013. The amount of investments being spent mostly by the federal government are estimated to be around $643 million in 2013-2014[8]. According to the *Canadian Agriculture Outlook Highlights 2015* report, the total cash income in 2015 was as high as $13 billion (mostly from the record cattle receipts) [9].

The livestock sector of the Canadian agriculture has one of the highest contributions to the total income. The livestock population in Canada is as large as over 13 million heads (as of July, 2015) [10] with 4.9 million heads farmed in Alberta [11].

2.2 Specified Risk Material

However, the large number of farms and a huge herd population results in multiple issues related to managing diseases that can occur among the cattle and, which is more problematic, handling the "bi-products" of such diseases.

One of the largest health issues of a ruminant animal is a Bovine Spongiform Encephalopathy (BSE) – a progressive fatal disease potentially caused by abnormal or misfolded proteins called BSE prions. There have been 19 cases reported in Canada, 14 of them were diagnosed in Alberta with the last case reported in 2015[12, 13].

The biggest issue with BSE is handling and utilization of so called Specified Risk Material (SRM). The Canadian Food Inspection Agency defines SRM as the brain, skull, eyes (with nerves attached to brain), trigeminal ganglia, tonsils, spinal cord, and dorsal root ganglia (nerves attached to the spinal cord), of cattle aged 30 months or older; and the distal ileum of cattle of all ages [14]. Canada is on the list of countries with controlled BSE status (countries that have at least one BSE case confirmed within the last 10 years) [15].

In 2007, the Canadian government has released an Enhanced Feed Ban. This has been done to decrease the spread of BSE among the cattle. According to the enhanced feed ban, all Specified Risk Material has to be removed and processed in

compliance with the approved protocol. The enhanced feed ban is intended to insure that all the SRM is excluded from any application in human food, pet food, animal feed, and fertilizers [16].

Previously, SRM used to be sold as a meat and bone meal after a rendering process. However, due to the enhanced feed ban, SRM became subject to rendering with further lipid recovery, while the rest of the fractions (protein and ash) have to be landfilled or incinerated. The amount of SRM needs to utilized through the landfilling or incineration can be as large as 300,000 tonnes a year. The utilization of such a huge amount of SRM imposes significant economic stress on farms and causes environmental concerns, especially the large landfills that can potentially contaminate soil and water [5].

Although, the government of Canada has already pledged over $300 million on BSE study, almost all of these funding has been spent on the BSE study and the search for cure for BSE [7]. There has been no reported research done on potential valorization and characterization of SRM until the past decade, when the first results in development of value-added products from SRM have been released.

2.3 Recovery and Characterization of SRM

Starting 2010, the Canadian federal government has pledged over $300 million on BSE-related research. However, almost all of these funding has been invested in BSE treatment and a search for cure for this disease [7].

It is only in 2013 the first reported results on characterization and potential value of specified risk material development have been published [17, 18]. According to Tizazu Mekonnen's report, two types of hydrolysis were carried out: alkaline and thermal. The alkaline hydrolysis is not considered in-detail in this thesis report due to high extend of protein break-down resulting in shorter chain peptides in the hydrolyzed material.

Thermal hydrolysis was carried out at 180^{o} C and a pressure of 174 psi with a load of 1000g of SRM and 1000 g of water (SRM:water 1:1 (w:w) ratio) in a 5L hydrolysis reactor (Parr Instrument, Moline, IL, USA) [17]. Thermal hydrolysis was followed by the protein recovery (Figure 1) including following steps: SRM, Thermal hydrolysis, centrifugation of solubilized protein, collection and vacuum filtration of supernatant, hexane extraction, hydrolyzed protein [18].

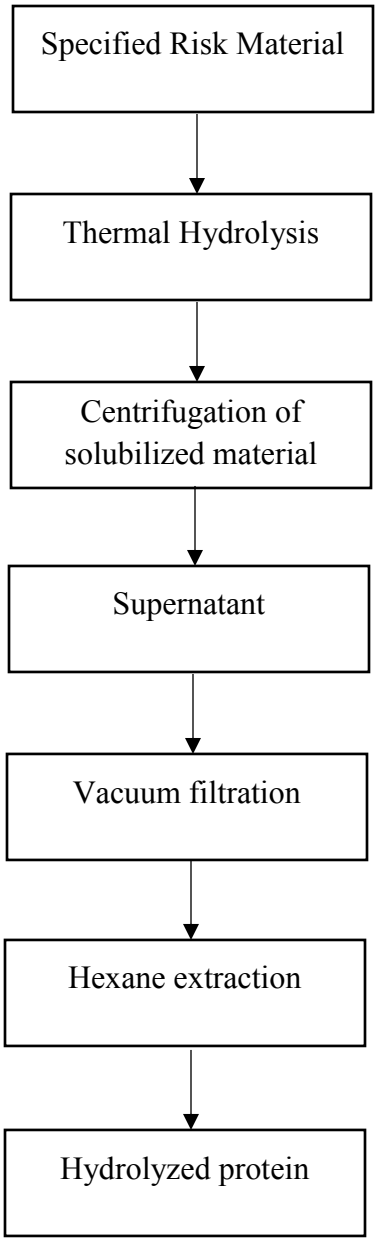


Figure 1: Peptides recovery from SRM feedstock [17]

2.3.1 Molecular weight distribution and amino acid quantification of SRM

SDS-PAGE was done on proteinaceous material dissolved and centrifuged in Milli-Q water according the protocol developed by Shagger [19]. The SDS-PAGE

analysis has been done to evaluate the degree of separation of proteins in hydrolyzed SRM compared to the raw feedstock.

Figure 2 shows the result of SDS-PAGE done on SRM, thermally hydrolyzed, and alkali hydrolyzed SRM.

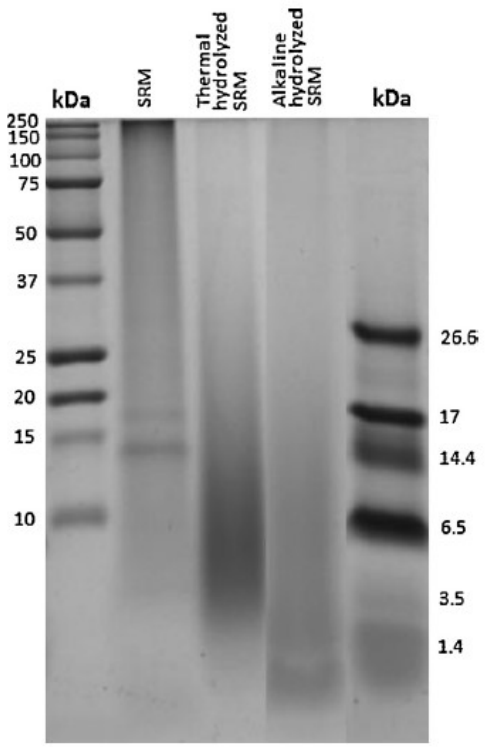


Figure 2: SDS-PAGE of SRM at 50% solvent concentration [17]. Reproduced with the permission of Process Biochemistry, Elsevier ©

The figure shows that unhydrolized SRM has a broad distribution of molecular weights with two clear bands slightly above and below 15 kDA mark. Thermally and alkali hydrolyzed SRM have the higher concentration of molecules in a low molecular weight area due to the cleavage of peptides in the hydrolysis process [17].

The SEC-HPLC analysis has been conducted on a standard meat and bone meal (MBM) sample to eliminate the potential contamination of separation columns with prions that can be presented in SRM. MBM sample has been then compared to SRM hydrolyzed at different concentration. The MBM sample can be characterized by the molecular weight exceeding 250 kDa. As the concentration of water in the hydrolyzed samples increases, the degree of protein cleavage increases resulting in proteinaceous material with 6.5 kDa molecular weight on average[17],[18].

Quantification of free and total amino acids in thermally hydrolyzed SRM has been done as well [18].

2.3.2 Development of SRM-based materials

There have been several attempts to develop value-added materials from hydrolyzed SRM. Also, there have been results reported on the successful proof of concept on development of SRM-based adhesives, biocomposites, and thermosetting plastics [20-24].

In the biocomposites development, the calculated amount of hydrolyzed SRM has been used as a curing agent for epoxy resin [23]. In this study, two types of natural fibers were used as reinforcing fiber mats: oriented chopped strand mat (CSM) and woven roving (WR). The composite material was made by application of layers of

the fiber on the pre-polymerized SRM with epoxy resin. The following properties of the obtained materials were tested: thermal analysis, mechanical properties, and water absorption test.

2.4 Adhesion forces and adhesive materials

There is a wide range of adhesive materials being used in plywood industry. Each type of adhesive has its own advantages and disadvantages based on the conditions of its formulation and application. The most common types of adhesives are phenol-formaldehyde (PF), epoxy resin-based, and polyurethane adhesives. Figure 3 shows various types of adhesive materials [25-28].

Although phenol-formaldehyde adhesives have been used widely in plywood industry and showed outstanding results, there has been raised a concern due to formaldehyde usage for adhesive formulation as formaldehyde has been confirmed to a human carcinogen [29], [30].

Before the adhesion process is explained, an adhesive material needs to be defined. Adhesive (material) can be defined as non-metal, liquid or solid material which can be used to join to adherents by means of adhesive and cohesive forces [26]. Adhesive-bonding is a materially joined process in which surface-to-surface joining of two similar or dissimilar materials are bonded together via the application of an adhesive [25], [26].

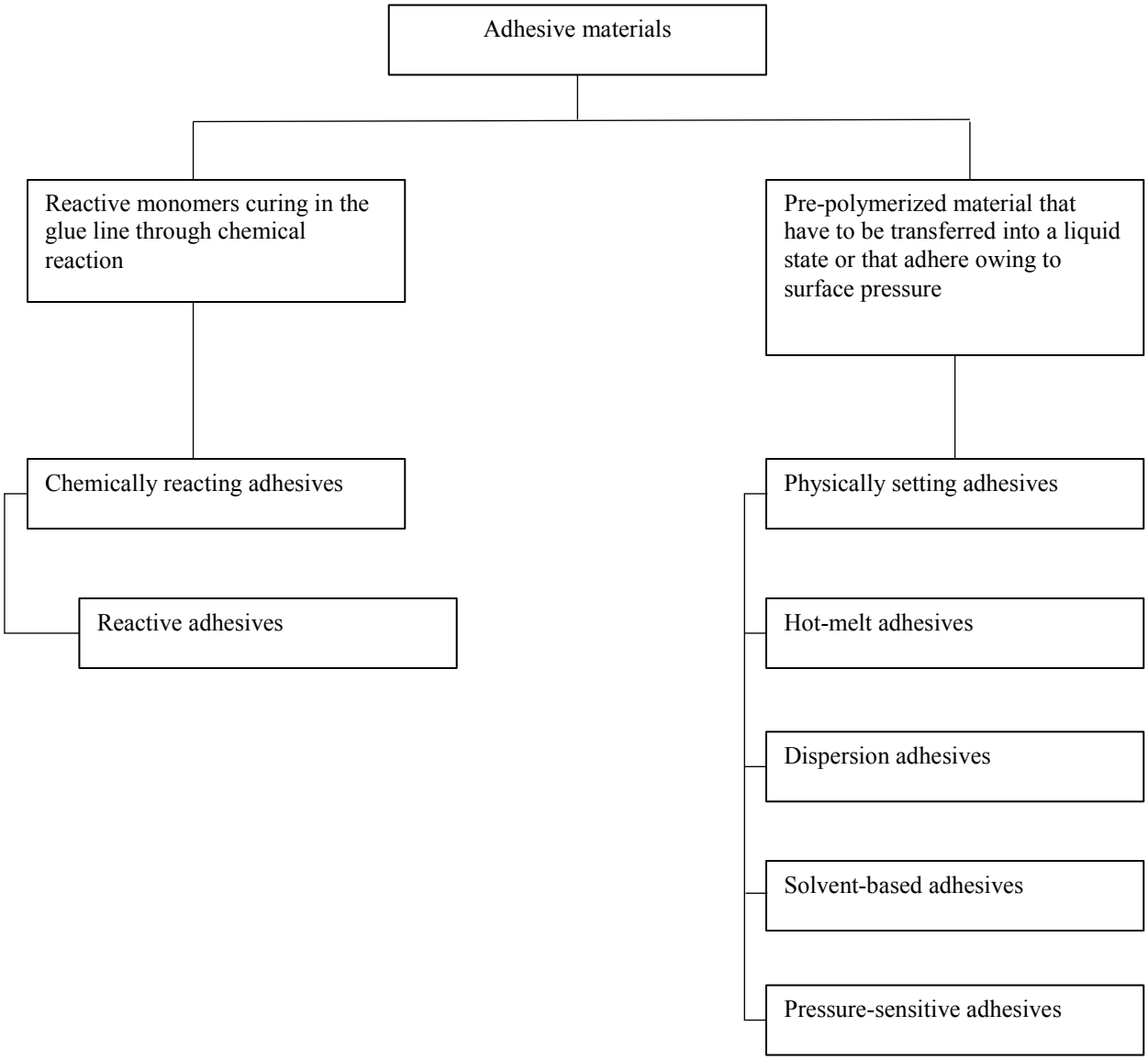


Figure 3: Types of adhesive materials [26]. Reproduced by permission of Wiley Books, John Wiley and Sons ©

The type of adhesive that has been created during my research is the hot melt adhesive. As all the protein-based adhesives, hot melt adhesives are the most commonly used adhesive materials in plywood industry. This type of adhesive materials becomes highly reactive when melted in the temperature range 120°-240°C and applied immediately to adherents. The chemical reaction takes place between adhesive and adherents results in a bonded joint formation.

However, the adhesion process is a very complicated phenomenon that cannot be completely explained even today. There have been multiple theories developed on the adhesion forces [30], [31]. The common idea of all these theories is that the total adhesive force is a contribution of different types of bonds: physical, hydrogen, and chemical [26].

Despite the large contribution of chemical bonds formed during the chemical reaction between an adhesive and a wood surface, there is a large contribution of so-called physical bonds caused by interactions between dipole moments. They are: Keesom, Debye, and London forces. Keesom interaction is the interaction between permanent dipoles caused by the shift in electron distribution due to the electronegativity of a bond or a molecule.

Another type of physical interaction occurs between permanent dipole and induced dipole. Induced dipole occurs as a counter dipole in the molecules without a

permanent dipole when brought to a very close distance. These counter dipoles are able to interact with permanent dipoles resulting in the occurrence of an attractive forces (Debye force) as well as with each other (London dispersion forces). It needs to be mentioned that London dispersion force is the only temperature independent physical contribution to an adhesion [31], [32].

The contribution of chemical reactions is the highest and plays a primary role in adhesion. However, it will be discussed further when particular reactions taking place between the adhesive and wood will be discussed.

Another important aspect of adhesion is wetting. Wetting phenomenon (refer to Figure 4) is described by the ability of a droplet to form a contact angle on a surface [26].

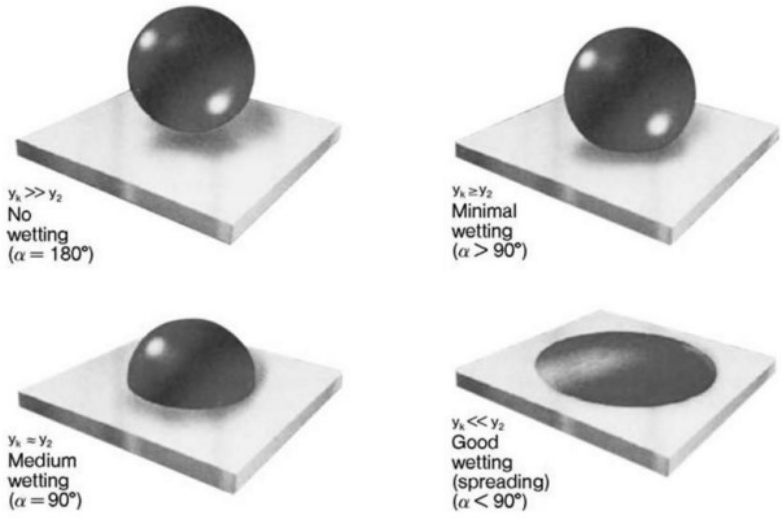


Figure 4: Wetting phenomena and contact angle formation [25]. Reproduced by permission of Wiley Books, John Wiley and Sons ©

This ability is related to the surface energy of a surface, droplet, and a media and the surface energies at the interfaces. The relationship of the surface energies is given in the Equation 1 [25]:

$$\gamma_{23} \cdot cos\theta = \gamma_{13} - \gamma_{12} \quad (1)$$

Where γ_{23} is the surface tension at the droplet-media interface, γ_{13} – surface tension of the surface – droplet interface, γ_{12} – surface tension at the surface-media interface. The wetting phenomenon only takes place when the contact angle formed is below or equal to 90º. This means that wetting can only occur when the surface tension in the surface-droplet interface is higher than the one of the surface-media [31], [32].

2.4.1 SRM-based adhesive materials

There have been a few reported attempts on the wood adhesive formulation using the protein recovered from hydrolyzed SRM. In the first case, an adhesive material with potential application for oriented strand board (OSB) composite material development. In the second case, an adhesive for plywood manufacture has been developed and its performance has been tested [20], [21].

Both reports indicated a good adhesive performance under dry conditions; however, soaked shear stress experiments resulted in failure die to a poor water resistance of the adhesive material.

Thus, the research carried out had two main purposes:

- Develop and evaluated and adhesive material with low environmental and health impact by substituting toxic components with less- or non-toxic
- Improve water resistivity of hydrolyzed SRM in order to develop a water resistive adhesive material

2.4.1.1 SRM-based adhesive for oriented strand board (OSB)

According to Canadian Standards Association (CSA) oriented strand board (OSB) is a wood material composed of rectangular shaped wood strands arranged in layers at a certain angle in layers to arrange a strong and stiff mat [33].

In the OSB manufacturing process, the strands or wafers are dried at given conditions and the resin is sprayed on each strand after the drying is over. Then, the resin covered strands are formed in layers and heat and pressure is applied to form a board. The key point of the experiment was to develop a substitute to the existing resins that contain isocyanates or formaldehyde [20].

In this research, the protein has been recovered and purified from specified risk material according the protocol mentioned previously in this chapter.

The adhesive material was formulated by dissolving hydrolyzed SRM in distilled water and mixing with the crosslinking agent (MDI) at various concentrations. Then, pre-conditioned wood strands with the moisture content 2% were covered with the water repellent wax and the adhesive and the pressure of 5,000 kPa has been applied at an ambient temperature of 204°C [20].

Due to high reactivity of isocyanate with an active hydrogen containing functional groups in amino acids (amines, carboxylic acids, hydroxyl, etc.) the adhesion took place and the OSB board has been formed. Figure 5 shows potential chemical reactions between protein and wood cellulose and isocyanate [20].

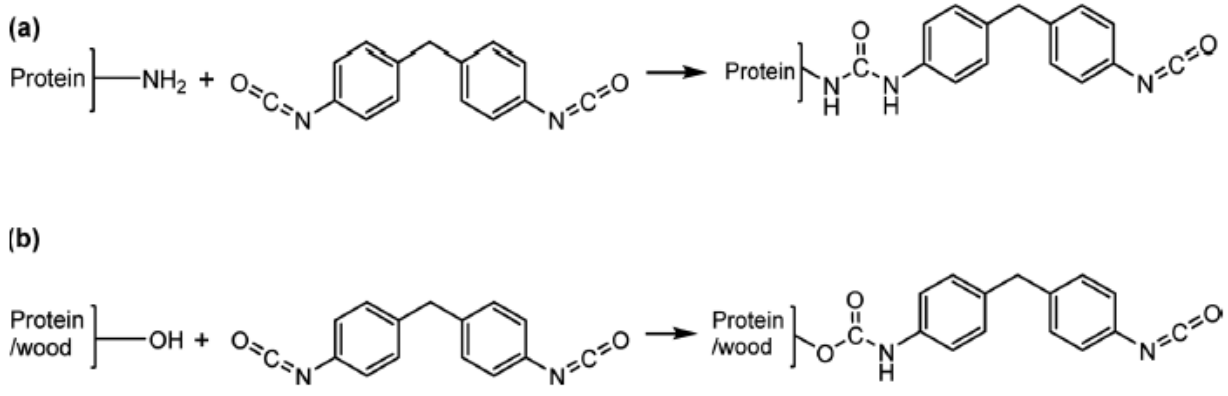


Figure 5: Reactions of (a) amino group in protein and (b) hydroxyl group in cellulose with isocyanate [20]. Reproduced by permission of Macromolecular Materials and Engineering, John Wiley and Sons ©

The OSB has been tested according the CSA standard on the following:

- Mechanical performance
- Thickness swell test
- Density profile

The mechanical performance and thickness swell test indicated that the performance of the board was reduced as the concentration of hydrolyzed protein in the adhesive was increased. In thickness swell test up to 102% increase in thickness has been observed [20].

This result was explained by the reaction of polar functional groups (i.e. carboxylic acid) of hydrolyzed SRM with water, resulting in lower water resistance.

2.4.1.2 SRM-based adhesive for plywood

The similar result has been obtained and reported in plywood adhesive experiment [21]. The development of a plywood adhesive is the primary topic of the proposed thesis work, hence more attention was dedicated to the abovementioned report.

In this experiment, protein material recovered after hydrolysis at various temperatures has been reacted with a pre-polymerized mixture of glutaraldehyde and resorcinol resin. The ratios of mixture and other experiment conditions were varied according Taguchi experimental design [21].

The experiments have been carried out in compliance with ASTM D4690-12 and ASTM D2339-98 standards [34], [35]. The specimens were prepared from a birch veneer of 1 mm thickness cut into rectangles of dimensions 50 mm X 20 mm and preconditioned in the moisture chamber to get 10-12% moisture content. After that, the area of 20 mm X 20 mm on each specimen has been coated with the adhesive and the joined pieces were glued to each other at the hot press at 140^{o}C and 3.5 MPa [21], [35].

The strength of the adhesive material was tested by measuring the amount of force required to apply to make the specimen undergo an adhesive failure in accordance with ASTM D2339-98 and ASTM D1189-03 standards [35], [36]. Dry and wet shear strengths have been evaluated for all types of the adhesive.

The results of the lap shear stress test (Figure 6) show that the dry shear strength of an adhesive passed the standard requirement of 2.344 MPa [20], [34]. However, the soaked shear stress results (Figure 7) clearly show that the soaked shear stress does not meet the standard requirements [20], [34].

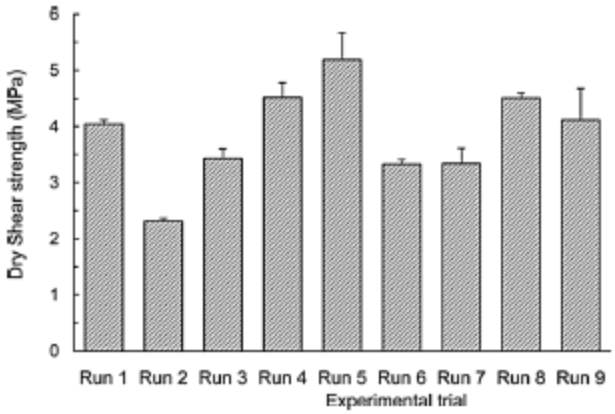


Figure 6: Dry shear stress of the protein extract crosslinked with resorcinol-glutaraldehyde pre-polymer [20]. Reproduced by permission of Macromolecular Materials and Engineering, John Wiley and Sons ©

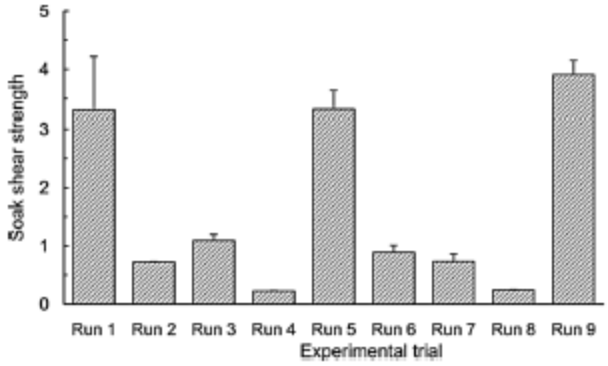


Figure 7: Soak shear stress of the protein extract crosslinked with resorcinol-glutaraldehyde pre-polymer [20]. Reproduced by permission of Macromolecular Materials and Engineering, John Wiley and Sons ©

The formulations 1, 5, and 9 (only 220 ^{o}C hydrolysate was used) were concluded to meet the standard requirement due to higher concentration of glutaraldehyde-resorcinol resin concentration, so that highly reactive and hydrophilic groups in the amino acids were mostly consumed during the polymerization [20].

There exists a proposed relation between the reductions in the soaked shear stress test results with the increase in the hydrolyzed SRM amount added into the

adhesive. Also, excessive amount of protein resulted in a high viscosity adhesive that probably decreases the wetting ability and, as a result, penetration of the adhesive into wood. The concentration of crosslinking agent has also been shown as the primary factor of the enhanced shear strength [20].

Overall, the conclusion was made that, although, adhesive shows good results in dry conditions, its application should be limited to dry condition use only as the soaked shear stress results proved that the adhesive does not meet the standard [20].

Thus, further research has been continued in order to resolve the main issue raised by the described research – high water solubility.

2.4.2 Protein-based adhesive materials

The idea of protein-based adhesive materials for wood applications is not a new one. There is evidence of the research approached in this area in early 1900s' with the one of the first published results in 1923 [37]. However, there has been a long period when scientists left this research behind and it is only a recent growth of environmental concerns, regarding the substitution of toxic chemicals from industry with eco-friendly materials, has brought the development of environmentally friendly adhesives to the top of the research areas. There have been several studies carried out recently on the development of a protein-based

material using multiple various feedstocks, such as: soy protein [37], [41], animal blood [38], meat and bone meal [39], bio solids and mustard [40].

When developing a protein-based wood adhesive, it is important to keep in mind that the performance depends on several parameters: particle size, nature of surface, protein structure, pH, and viscosity of protein. Processing parameters can also affect the final adhesive performance [37]. Although, most of the parameters only depend on the nature of protein, it needs to be mentioned that proteins are generally extremely soluble in water and chemical modification is required to unfold and denature the protein molecule as well as to decrease its reactivity with water [37].

Thermal hydrolysis was studied, characterized, and described previously [17-20]. Chemical modifications of proteins will be described further in this report. In most cases, soy-protein based adhesive with good water resistant properties have been prepared by crosslinking of protein isolate with formaldehyde-based resins or with other organic resins [38], [41].

Similar results have been observed when the protein extracted from meat and bone meal has been evaluated in terms of adhesive strength and water resistance [39]. An attempt to improve the water resistance has been done by crosslinking proteinaceous material with glutaraldehyde to create a three-dimensional branched

polymer with improved water resistance. The results indicate that the crosslinked material has a better water resistivity than the original denatured protein mixture (Figure 8) [39].

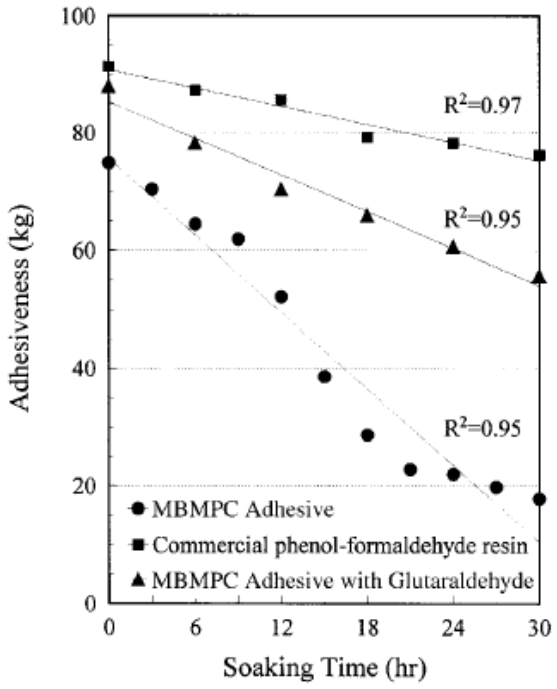


Figure 8: Effect of crosslinking agent on Meat and Bone Meal Protein Concentrate adhesive performance [39]. Reproduced by permission of Journal of the American Oil Chemists' Society, Springer ©

The new studies show that not only animal- or plant-based proteins can be used as an adhesive material, but almost all the biopolymers are good sources of proteinaceous material that can find an application in adhesive development [40], [42]. Return activated sludge (RAS) obtained from bio solid wastes has been evaluated

in terms of adhesive strength [40]. The adhesion strength of RAS was found to be compatible to other bio-based proteins having the same water resistance issue. Another study suggested an application of polysaccharides derived from microorganisms as a resource for wood adhesive [42]. In this research, the adhesive has been prepared from the extracellular microbial polysaccharide with a peak molecular weight of 500 kDa by dissolving the polysaccharide material in water at 33% (w:w) concentration and the shear strength measured after setting the specimens at 23% and 53% relative humidity (Figure 9).

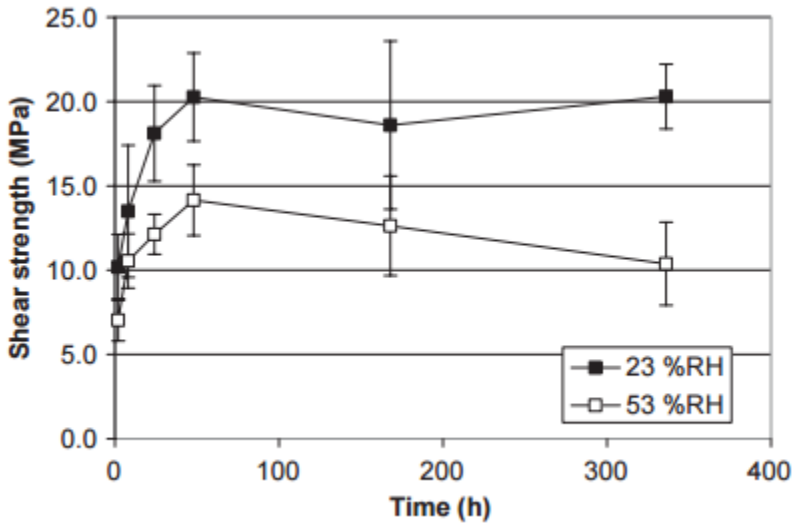


Figure 9: Time effect on shear strength of microbial polysaccharide – based adhesive at different relative humidity (RH) [42], [82]. Reproduced by permission of International Journal of Adhesion and Adhesives, Elsevier ©

2.5 Water resistance improvement through chemical modification of peptides

Water solubility of protein-based adhesives has been the most significant factor limiting wide commercial application of this type of adhesives. There has been a wide range studies targeting the improvement of water resistance of proteins [43-51]. Blending with phenol-formaldehyde (PF) and urea-formaldehyde (UF) resin has been considered as one of the best options [38]. Although, the results of this type of blending have indicated a significant improvement in water resistivity, there is a tendency on substitution of formaldehyde containing chemicals due its carcinogen nature.

Among the most recent types of chemical modifications of protein, the crosslinking with epichlorohydrin resin (PAE). PAE resin contains active azetidinium functional groups that are able to react with carboxyl groups of a protein resulting in a less water soluble material [44], [51]. Figure 10 shows that in case of soy protein-based adhesive the addition of PAE significantly affects wet shear strength of an adhesive.

Co-reactant ⇒	*Without PAE*		*With PAE*	
Soy product	*Dry*	*Wet*	*Dry*	*Wet*
Flour, 30% of 90 PDI	5.0 ± 1.2	0.3 ± 0.2	6.6 ± 1.3	2.2 ± 0.2
Arcon SM, 20%	8.2 ± 0.2	1.8 ± 0.2	≥ 8[a]	3.8 ± 0.3
Commercial isolate, 15%	7.2 ± 1.3	3.0 ± 0.4	7.6 ± 0.8	5.0 ± 0.3
Laboratory isolate, 30%	4.6 ± 0.4	1.1 ± 0.5	7.2 ± 0.5	3.2 ± 0.2

Figure 10: Shear strength values (MPa) for soy protein-based adhesives [44]. Reproduced by permission of American Chemical Society ©

A recently new study has been carried out in 2015, showing the positive effect of the reaction of soy protein with ethylene glycol of different molecular weight (ethylene glycol, diethylene glycol, 400-, 2000-, and 10,000 Dalton ethylene glycol) [48]. The study shows that hydrophilicity of a protein-poly (ethylene glycol) matrix increases with the increased molecular weight of ethylene glycol.

Soy protein has been a popular topic on water resistivity studies. So, another research carried out in 2015 has proposed that the water resistivity of a protein can be improved by reacting it with undecylenic acid (UA) [47].

The proposed reaction of soy protein isolate and undecylenic acid is shown in Figure 11.

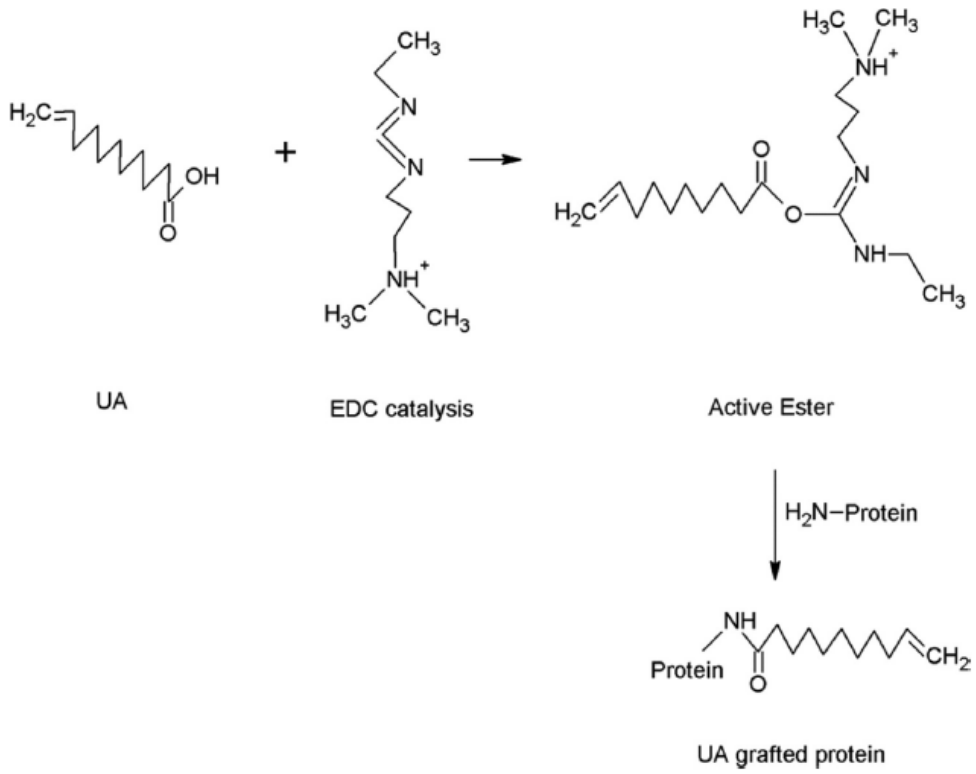


Figure 11: Schematic representation of amidation mechanism between undecylenic acid and soy protein isolate [47]. Reproduced by permission of Industrial Crops and Products, Elsevier ©

This type of modification has resulted in a better water resistance (Figure 12). The proposed explanation to it was the replacement of amino groups of protein with aliphatic chains of undecylenic acid. Since undecylenic acid is non-water-soluble, it prevented the water molecules from penetrating the crosslinked protein-UA molecules, improving its hydrophobicity. The modification could potentially result in the decrease in the amount of hollow cavities between protein and wood [47].

UA	Dry strength (MPa)	WCF	Wet strength (MPa)
0%	5.991 ± 0.788	100%	2.038 ± 0.177^{C}
3%	5.243 ± 0.724	100%	2.748 ± 0.314^{B}
5%	6.103 ± 0.635	100%	2.701 ± 0.106^{B}
7%	5.940 ± 0.827	100%	2.880 ± 0.079^{B}
10%	6.671 ± 0.580	100%	3.296 ± 0.243^{A}

Figure 12: Dry and wet shear strength of a protein-based adhesive modified with undecylenic acid at different concentrations [47]. Reproduced by permission of Industrial Crops and Products, Elsevier ©

There are another two types of chemical modification of proteins that have been considered in more detail in this report due to their significance for the proposed research.

First, esterification of peptides with alcohol. This type of chemical modification has been reported multiple times through the second half of 20th century resulting in an improved water resistive material [50], [52-53].

Second, chemical crosslinking of proteins with glutaraldehyde, which results in formation of a branched three-dimensional thermosetting polymer [54-59].

It is important to mention that all the described experiments and development of protein-based wood adhesives have been carried out with animal- or plant-based proteinaceous material. SRM-based protein has never been reported to be chemically modified and only since 2014 it has been reported to be evaluated as a wood adhesive.

This makes the development of SRM-based wood adhesive, involving chemical modification of protein obtained from SRM, a unique experiment. At the same time, it gives a significant freedom in the approach to be taken in chemical modification of the material evaluated.

In this thesis work, the following steps have been done to create SRM-based adhesive:

- Esterification of peptides with alcohol. The reasons for carrying out this particular type of modification include the following: there are large number of reports on the improvement in water resistance of esterified protein; the mechanism of esterification reaction is well studied; the reaction is easy to set up, it needs only HCl acid as a catalyst; the reaction can be done at room temperature; it is easy to characterize the reaction product and conclude whether the esterification took place.
- Crosslinking with glutaraldehyde. Glutaraldehyde has been reported as a known and well-studied crosslinking agent. Multiple papers and reports suggest glutaraldehyde as a crosslinking agent for proteins. As been mentioned before, one of the primary goals of the SRM-based adhesive development is to find a substitute to formaldehyde component in adhesives. Since formaldehyde containing adhesives are reported to be

highly hydrophobic, glutaraldehyde is a reasonable substitution to use instead because the reaction mechanism is expected to be similar and glutaraldehyde is known as non-carcinogenic, less hazardous for health material than formaldehyde. In addition, the reaction mechanism of protein crosslinking has been studied in depth in many published articles [54-59].

2.5.1 Esterification of peptides with alcohols

Esterification of proteins with alcohol takes place at the carboxylic functional group (Figure 13) [50].

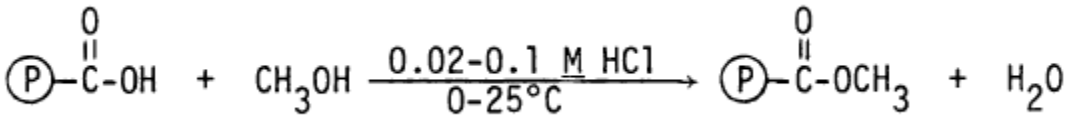


Figure 13: Esterification of protein with methanol (HCl catalyst) [50]. Reproduced by permission of American Chemical Society ©

This reaction has been utilized in the SRM-based adhesive development as the method of chemical modification with the hypothesis that it will result in decrease in hydrophobicity due to the conversion of highly hydrophilic carboxylic acid groups into less hydrophilic ester linkages. It has been proven that esterification of protein leads to the blockage of carboxyl groups, resulting in net positive charge of the molecule, thus making it more basic and raising its isoionic point [53], [60].

The results of the solubility experiments of the esterified proteins generally indicate a decrease in water solubility of the resulting product. So, Figure 14 shows the results of such an experiment when β-lactoglobulin has been esterified with methyl- and ethyl alcohol [53].

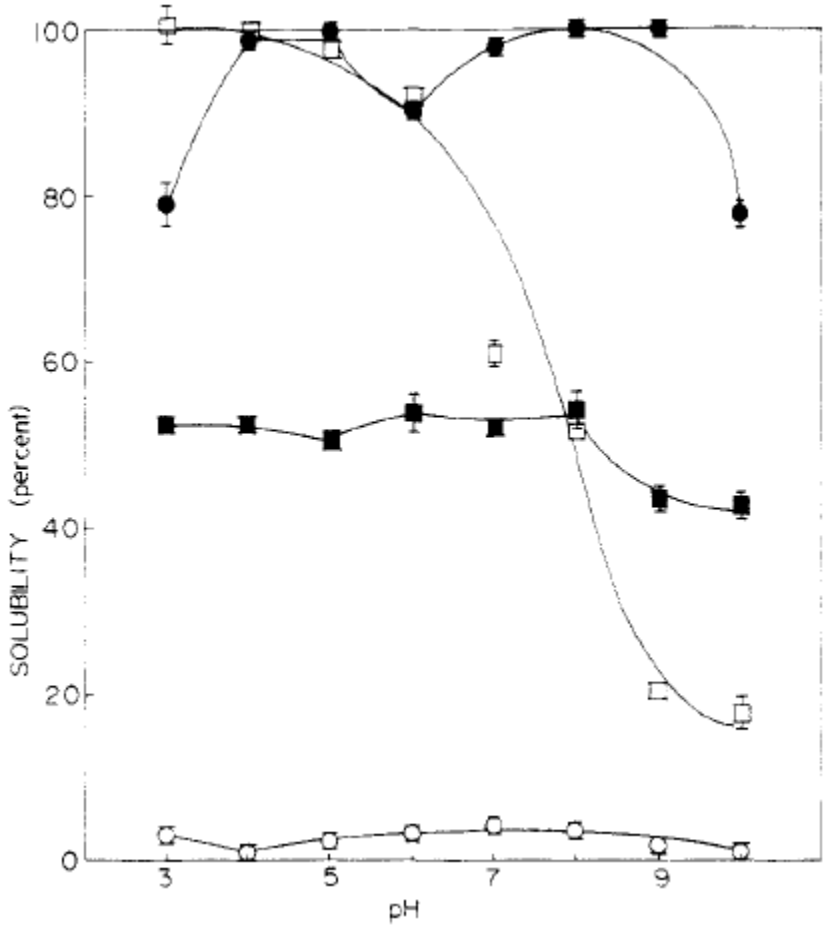


Figure 14: Water solubility at different pH of methyl esterified (o) and native state (•) β-lactoglobulin [53]. Reproduced by permission of American Chemical Society ©

Another experiment reports approximately 83% of carboxyl groups has been blocked after esterification of β-lactoglobulin with methanol (1% w:w) [61].

In general, esterification reaction involves three steps. First is the mixing of reactants, protein and alcohol. The second step is the reaction itself occurring at room temperature and lower for the period of 24 hours up to 12 days. The last step is the esterified product recovery [52].

Methanol has been found to be the most reactive alcohol resulting in the highest degree of esterification [52-53], [61].

Also, two different factors affecting the water solubility of esterified protein are discussed. First, the decrease in isoelectric point towards the alkaline pH, and the second is the replacing of carboxylic groups with hydrophobic ester bonds. The first one improves water solubility, and the second one contributes to increased hydrophobicity of the esterified protein. The final solubility depends on the balance of these two contributions. The second effect is more efficient in case of higher alcohols (ethanol, propanol), while the first one is more evident in the reaction with methanol [52].

2.5.2 Crosslinking of peptides with glutaraldehyde

Crosslinking is a very important process in adhesive formulation and adhesion taking place. During crosslinking two molecular components join together by a covalent bond [45]. Glutaraldehyde has been known as a crosslinking agent for years and can be considered as a less toxic substitute for formaldehyde and multiple

articles report the development of protein-based adhesives with enhanced properties due to crosslinking with glutaraldehyde [54-59].

Figure 15 shows possible reactions that take place between glutaraldehyde and protein. Glutaraldehyde polymerizes through a Schiff base and the resulting polymer can couple two amino groups in protein [45].

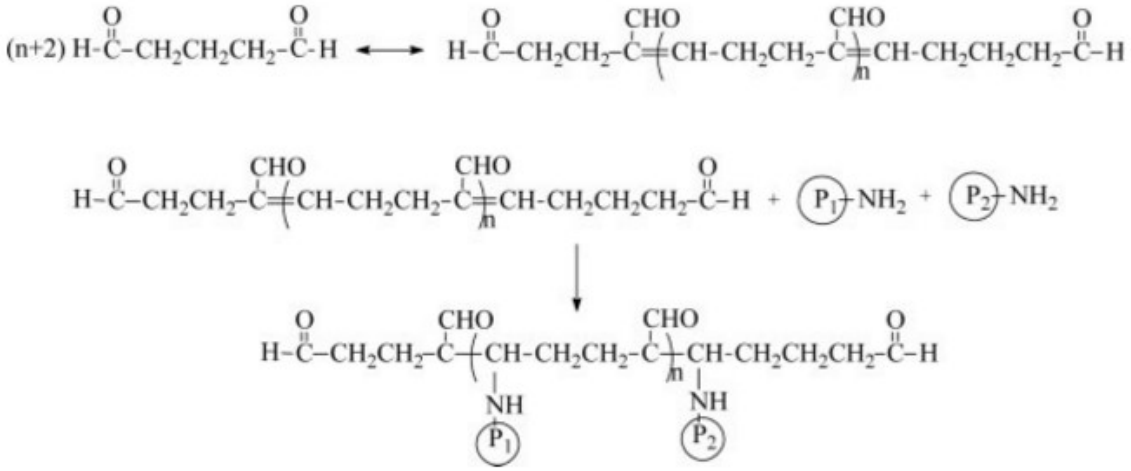


Figure 15: Reactions between protein and glutaraldehyde [45]. Reproduced by permission of Journal of Applied Polymer Science, John Wiley and Sons ©

It has also been reported an improvement in shear stress of glutaraldehyde crosslinked soy protein adhesive (Figure 16) for dry, wet, and soaked shear stress tests.

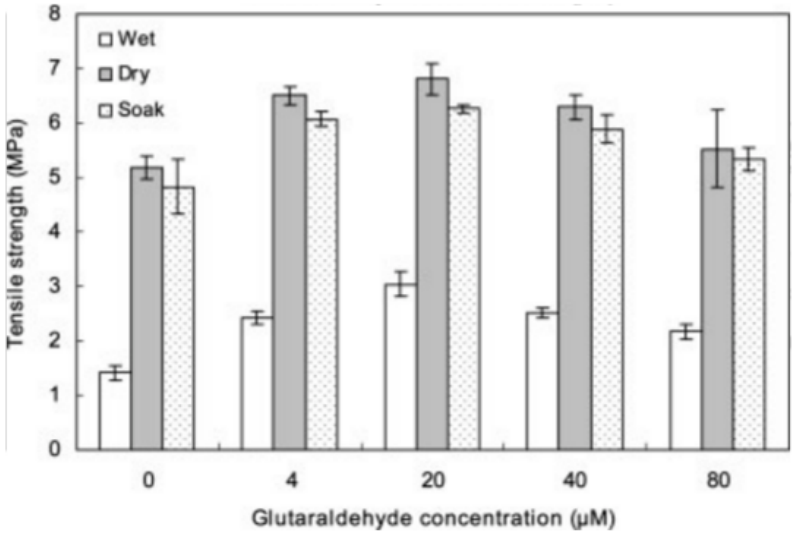


Figure 16: Effect of glutaraldehyde concentration on shear stress [45]. Reproduced by permission of Journal of Applied Polymer Science, John Wiley and Sons ©

Some articles, however, reported the formation of either soluble or insoluble product at different pH values. These pH values were different for different types of proteins [54].

Polyacrylamide gel electrophoresis experiments carried out on albumin to compare the effect of crosslinking with formaldehyde and glutaraldehyde showed that glutaraldehyde treated serum albumin does not migrate into the gel, if added at the same concentration as formaldehyde, due to a highly branched matrix formation (Figure 17). To overcome this, lower concentrations of glutaraldehyde should be added [62].

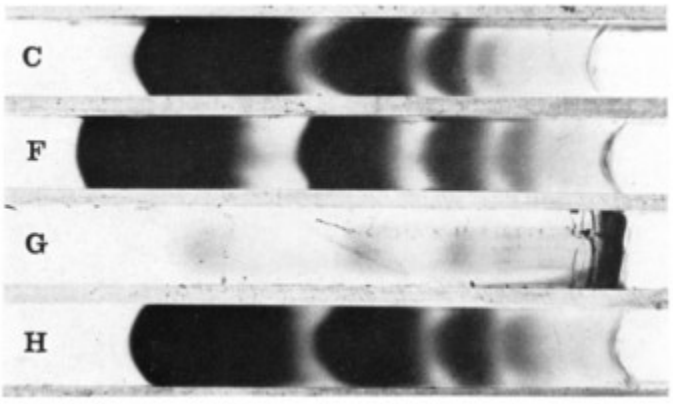


Figure 17: Effect of serum albumin (C) crosslinking with formaldehyde (F) and glutaraldehyde (G) [62]. Reproduced by permission of Histochemistry, Springer©

Chapter 3. Chemical modification of thermally hydrolysed SRM.

As described previously, the main issue of SRM-based plywood adhesive development was high hydrophilicity of adhesive material and, as a result, inability to pass the soaked lap shear stress test.

Previously, for plywood adhesive development, glutaraldehyde pre-polymerized with resorcinol was used [20], [21]. Although, its dry shear strength was relatively high, the results of soaked shear strength indicated that further work had to be done to improve the water resistivity of the adhesive material.

Since there exists no previous reports found on any type of chemical modification, there were a wide range of different types of chemicals to start with to enhance water resistance of SRM-based peptides.

For this research, the initial step in chemical modification was chosen to be esterification reaction with alcohol. The choice was made based on several reasons:

- Esterification of peptides was known for many years [53]
- The reaction mechanism is relatively simple
- The reaction can be carried out at room temperature and normal conditions

- Various types of alcohols can be used to compare the properties of the final products
- The improvement in hydrophobicity has been proven and the results have been reported [43]

3.1 Methodology

The hypothesis for approaching chemical modification of thermally hydrolyzed SRM was to partially substitute highly hydrophilic carboxylic functional groups with less hydrophilic ester bonds thus decreasing overall hydrophilicity of the material [61]. Figure 18 shows the simplified version of anticipated esterification reaction that potentially takes place at the carboxylic acid terminus of the peptide molecule.

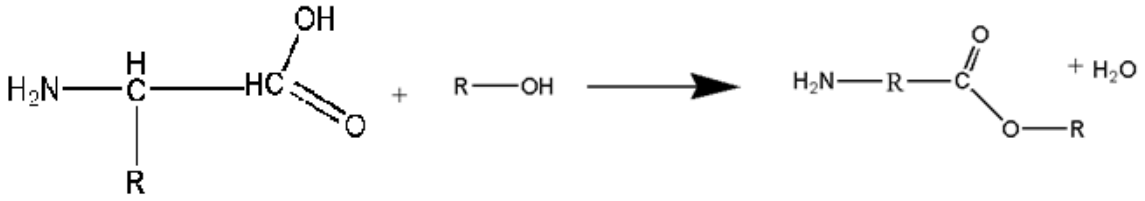


Figure 18: Esterification reaction mechanism of amino acid with alcohol

Thermally hydrolyzed SRM was recovered according the CFIA approved protocol: 1,000 g of raw SRM was mixed with 1,000 mL Milli-Q water and hydrolyzed in the reactor at 180 °C and 1,200 kPa for 40 minutes. After the hydrolysis, another

10,000 mL Miili-Q water was added to the hydrolysate and the full amount 10,000 mL was centrifuged at 7,000 rpm (6,500 x g) JLA-8.1000 rotor. The insoluble solid material was removed after the centrifugation through vacuum filtration using #4 filter paper (20-25 μm).

The liquid residue was thoroughly washed with n-hexane in ratio 1:2 to remove any dissolved lipid particles. Hexane-washed thermally hydrolyzed SRM was further freeze-dried for 7 days and thermally hydrolyzed SRM in a form of a yellow-brownish powder was collected.

Chemical modification of thermally hydrolyzed SRM was attempted [53], [64]. To optimize, thermally hydrolyzed SRM was mixed with methanol in different ratios (w:v): 1:10, 1:20, 1:50, and 1:100. For chemical modification and characterization purposes this report only describes SRM esterified with methanol, however, the formulations of adhesive was done within the research team with different types of modified SRM: methanol-, ethanol-, and propanol esterified thermally hydrolyzed specified risk material.

Thermally hydrolyzed SRM was suspended in methanol at the ratios described above and stirred for 24 hours at room temperature. HCl (0.05 M) was added and used as catalyst. After 24 hours the pH of the mixture was adjusted to 5.5 with ammonia solution [63].

The resulting mixture was vacuum-filtered to recover the insoluble particles. The solid residues were dried in a fume hood at room temperature. Dissolved SRM (reacted and unreacted) was recovered from the filtrate by using the rotary evaporator to remove methanol. Unreacted solids were dissolved in Milli-Q water and freeze-dried. Chemically modified thermally hydrolyzed SRM was evaluated further to determine whether the esterification reaction took place. To determine the degree of esterification, there was done **pH titration** of thermally hydrolyzed SRM and chemically modified SRM [66]. 0.33 g of modified SRM was dissolved in 50 mL Milli-Q water. The pH of the solution was adjusted to 7.0 with 0.1 M NaOH. The amount of HCl (0.1 M) was measured to bring the pH from 6 to 3 [66]. All samples were done in triplicates. **Water solubility** was evaluated by measuring the absorbance at 280 nm [67]. The method is based on the determination of three amino acids – tryptophan, tyrosine, phenylalanine which have non polar side chains. Thermally hydrolyzed SRM and methylated SRM samples were diluted to 0.1% and stirred at room temperature for 1 hour. The resulting solution was further centrifuged at 10,000 g for 15 minutes and supernatant liquid was collected. The absorbance at 280 nm was taken to determine water solubility [67].

High performance liquid chromatography (**HPLC**), Sodium-Dodecyl Sulfate poly-(acrylamide) gel electrophoresis (**SDS-PAGE**) analysis were carried out to determine whether any change in molecular weight took place.

SDS-PAGE analysis was carried out according the protocol developed by H. Schagger (2006) [67]. Separating gel (10%) was prepared by adding 3.5 mL Milli-Q water, 1.5 mL Glycerol, 5 mL of 3M tris-HCl (pH 8.5), 5.0 mL of 40% acrylamide solution, 14 μL of 10% ammonium persulfate, and 14 μL TEMED. Stacking gel (4%) was prepared by using 3.9 mL Milli-Q water, 1.55 mL of 3M Tris (pH 8.5), 0.8 mL of 40% acrylamide solution, 14 μL of 10% ammonium persulfate, and 14 μL TEMED. Cathode buffer (10x) composition: 121.1 g Tris Base, 179.2 g Tricine, 800 mL Milli-Q water pH 8.3, 50 mL 20% SDS, all adjusted to 1 L with MQ-water. Anode buffer (10x): 242 g Tris Base to 700 mL MQ-water, pH adjusted to 8.9 with HCl, and adjusted to 1 L with MQ water. 3M Tris – CL/SDS, pH 8.45 was prepared by using 182 g Tris Base in 300 mL MQ-water, pH adjusted to 8.45 with HCl, adjusted to 500 mL with MQ-water, and 1.5 g SDS added. Standards diluted 1:20 in Tris-Ticine sample buffer (MQ-water 4.0 mL, 2.0 mL 0.5M Tris-HCl pH 6.8, Glycerol 2.4 mL, 10% SDS 1.0 mL, β-mercaptoethanol 0.2 mL, 0.5% Coomassie G-250 0.4 mL), heated up to 95 ^{o}C for 5 min, then 5 μL/well of a sample was added. The electrophoresis experiment was started at 30 V until the peptides entered the stacking gel, then increased to 100 V.

Gels after electrophoresis were placed in a fixative solution for 30 min after the experiment and were stained for 1 hour in a staining solution Coomassie G-250.

The distaining was done in a distaining solution (40% Acetic acid) for 3 x 15 minutes washes [67].

For size exclusion chromatography – high performance liquid chromatography (**SEC-HPLC**) analysis, the samples were diluted in a mobile phase containing 0.15 M Na_2HPO_4 (adjusted to pH 9 with 0.1 M NaOH) in HPLC-grade water containing 5% acetonitrile, and filtered using 22 μm filter paper. The components were analyzed by UV detector at 210 nm, two separation columns (Superdex 200 10/300 GL and Superdex Peptide 10/300 GL) for different molecular weight range were used in series, and the elution rate was 0.5 mL/min [17].

Fourier transform infrared spectroscopy (**FTIR**) was carried out in nanoFAB using diffuse reflectance infrared Fourier transform spectroscopy device Nicolette 8700 (ThermoScientofic). The samples diluted in KBr were analyzed at near infrared frequency.

Finally, **contact angle** formed by a water droplet on a pelletized SRM was evaluated to determine the change in hydrophobicity after the esterification reaction. To measure contact angle, FTA-2000 equipment was used at nanoFab

3.2 Characterization of esterified SRM. Results and discussions

3.2.1 pH titration

The idea of pH titration is based on the isoelectric point concept [63]. At pH 7.0 peptides are in zwitter-ionic form, as shown in Figure 19.

Thermally hydrolyzed SRM had a pH around 5.7 units, and the pH of methylated SRM was at approximately 4.2 - 4.6 units. In order to bring peptides into a zwitter-ionic form, 0.1 M NaOH has been added to bring the pH to 7.0.

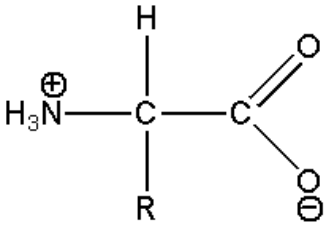


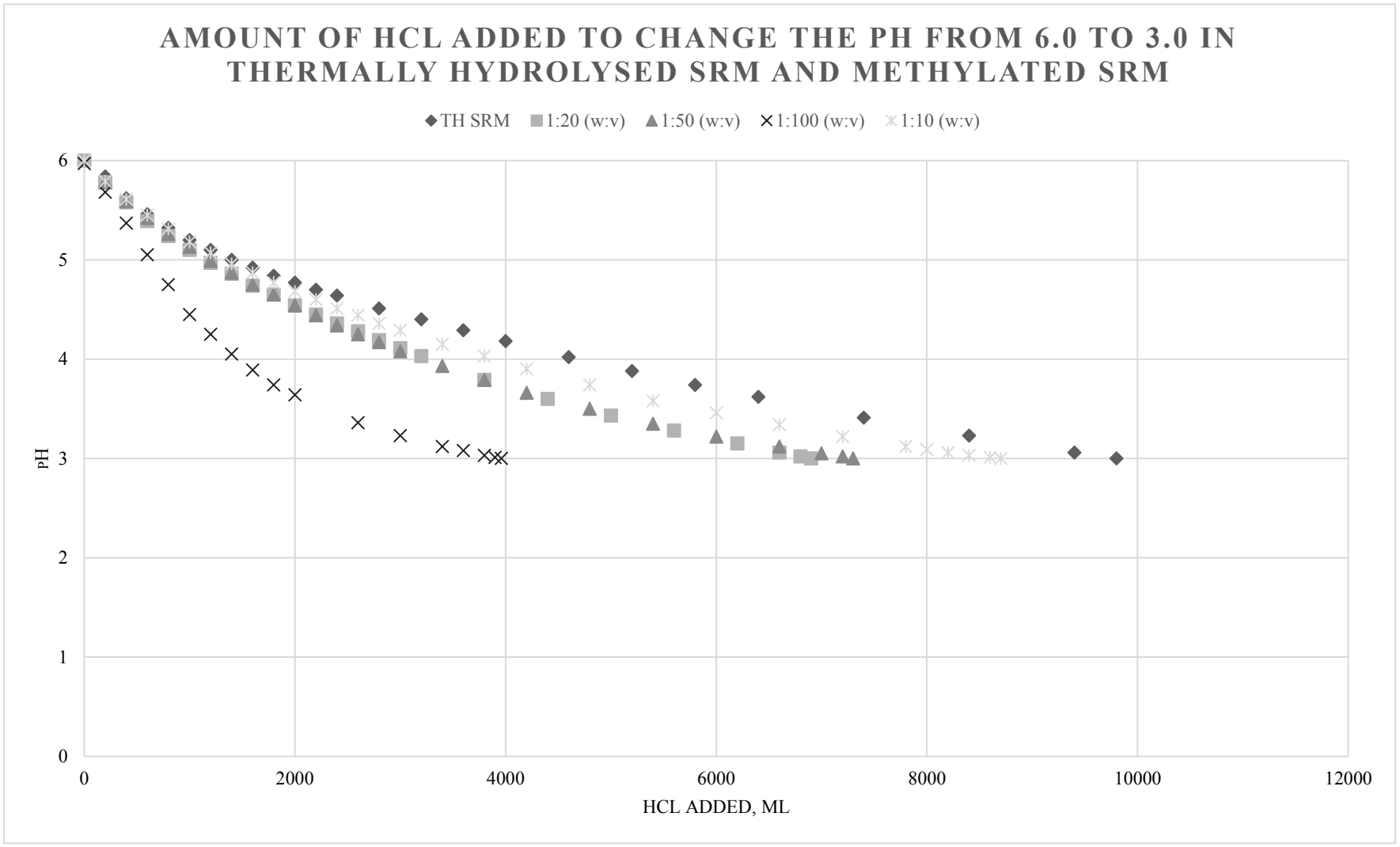
Figure 19: Zwitter-ionic form of a peptide molecule

Then, 0.1 M HCl has been added and the amount of acid added was measured. It is assumed that the amount of acid added depends on the amount of ionized carboxylic acid groups presented in the evaluated material [63].

After, the amount of acid required to bring the pH from 6.0 to 3.0 was measured for methylated SRM collected from the esterification reaction at various concentration and based on the results obtained, the degree of esterification was determined and the amount of carboxylic acid groups was estimated. Graph 1

shows how the amount of acid required to change the pH from 6.0 to 3.0 changes for various samples of methylated SRM, based on SRM:alcohol concentration during the esterification reaction.

The data have been summarized in Table 1. It is obviously that the degree of esterification increases with increasing ratio of mixing SRM in alcohol. However, the yield gets reduced as the larger amount of SRM gets dissolved in alcohol. Overall, an assumption can be made based on the results of pH titration that the esterification reaction took place.



Graph 1: Amount of HCl required to change the pH from 6.0 to 3.0

SRM	CH_3OH	Reaction time, hr	Yeld, %	Degree of Esterification, %	-COOH, mmol/g SRM
10 g	100 mL	24	~ 46.7	~ 11 ± 2.0%	1.321
10 g	200 mL	24	~ 37.5	~ 27.6 ± 6.0%	1.076
10 g	500 mL	24	~ 21.7	~ 25.7 ± 1.0%	1.104
10 g	1,000 mL	24	~ 8.2	~ 59.3 ± 0.5%	0.603

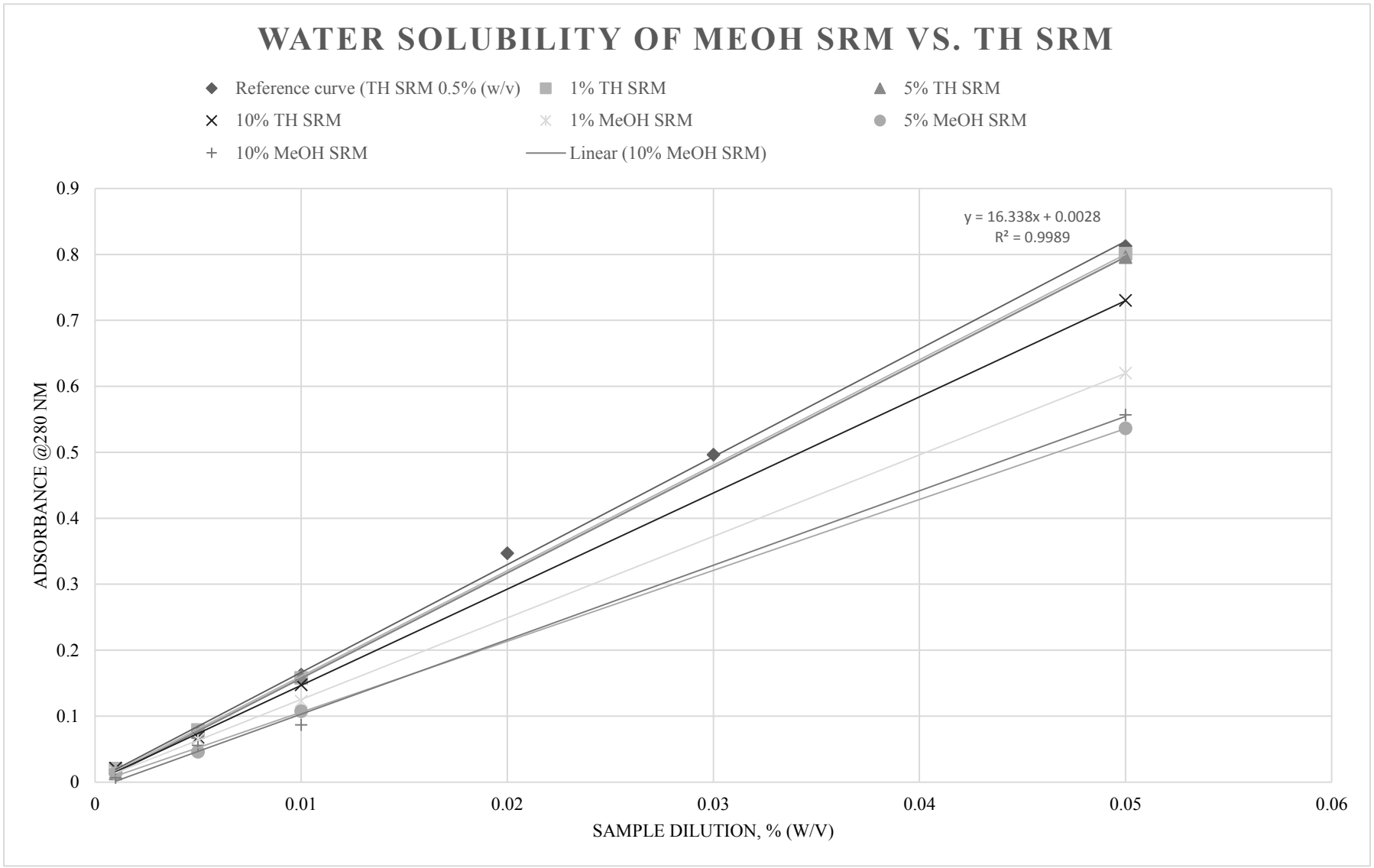
Table 1: Results of pH titration of thermally hydrolyzed and methylated SRM

3.2.2 Solubility test

Another test was carried out to determine whether esterification reaction took place and resulted in the improvement of water resistance of SRM material. In this experiment supernatant liquid has been evaluated after dissolving samples in water. Thermally hydrolyzed SRM was compared to thermally hydrolyzed SRM after the esterification reaction.

After stirring for 1 hour the samples were centrifuged at 10,000 g for 10 minutes and the absorbance of supernatant liquid was taken at 280 nm as described previously [67]. All the samples were done in triplicates.

The results are presented in Graph 2. There were prepared six experiments (each one done in triplicate (three samples per experiment)): three samples with thermally hydrolyzed SRM at 1% w:v, 5% w:v, and 10% w:v, and three samples with methylated SRM at the same concentrations as thermally hydrolyzed SRM. Each sample was further diluted to 0.05%, 0.01%, and 0.005% with Milli-Q water. The absorbance was taken at the spectrophotometer at 280 nm.



Graph 2: Comparison of water solubility of thermally hydrolysed SRM and SRM esterified with alcohol

As Graph 2 shows, the absorbance of thermally hydrolyzed SRM sample is always higher than the absorbance of methylated SRM sample at the same concentration and dilution rate. Higher absorbance indicates higher water solubility as more dissolved molecules are represented in the supernatant liquid of the sample. For a less soluble material, there is a lower amount of molecules dissolved in the liquid, thus the absorbance is lower.

The results of water solubility test are summarized in Table 2.

	Adsorption @ 280 nm (0.05% dilution)	
Concentration	**TH SRM**	**MeOH SRM**
1% (10 g/L)	0.801	0.620
5% (50 g/L)	0.796	0.536
10% (100 g/L)	0.730	0.557

Table 2: Absorbance @ 280 nm of thermally hydrolyzed SRM vs. methylated SRM of different concentration at 0.05% dilution

3.2.3 Contact angle measurement

The contact angle determination experiment was done at nanoFAB facility at the University of Alberta using Contact Angle FTA-2000.

To carry out this experiment, thermally hydrolyzed SRM and methylated SRM samples were pelletized, to form pellets 3 mm in diameter.

A water droplet was placed on each pellet and pictures of the contact formation were taken with the frequency of 1 picture per 0.3 seconds. The resulting contact angles were compared at 0.0 s, 1.0 s, 2.0 s, 3.0 s, 15.0 s, and 30 s.

The formation of a contact angle on the surface of thermally hydrolyzed SRM is shown in Figure 20.

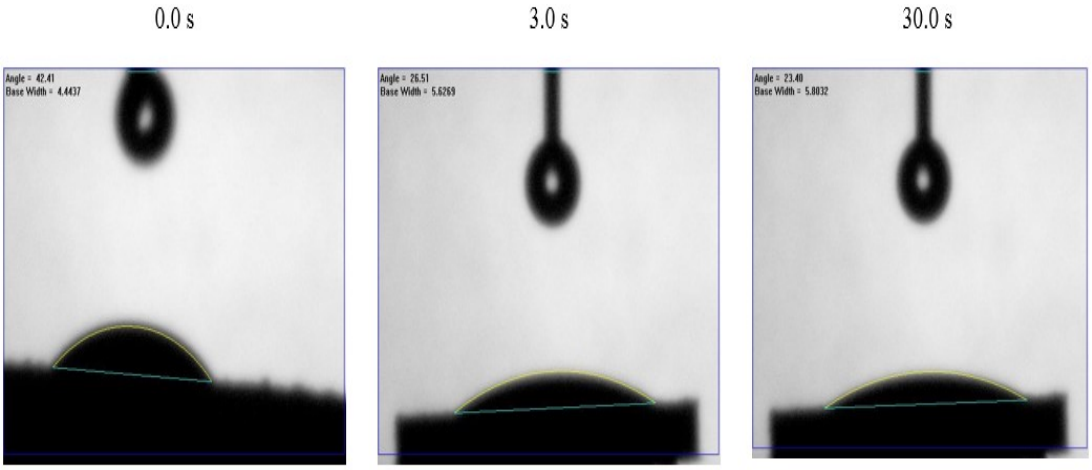


Figure 20: Formation of a contact angle on thermally hydrolyzed SRM surface

At the initial moment, when the water droplet touched the surface, the contact angle 42.41° was formed. However, after three seconds it dropped down to 26.51°. After 30 seconds, a 23.40° contact angle was formed.

The different picture was observed for methylated SRM surface. At the initial moment the water droplet has formed the contact angle 39.27° which indicated more hydrophilic surface (Figure 21) [31]. However, after three seconds the value of a contact angle was 33.43° and after thirty seconds it only reduced to 29.08°.

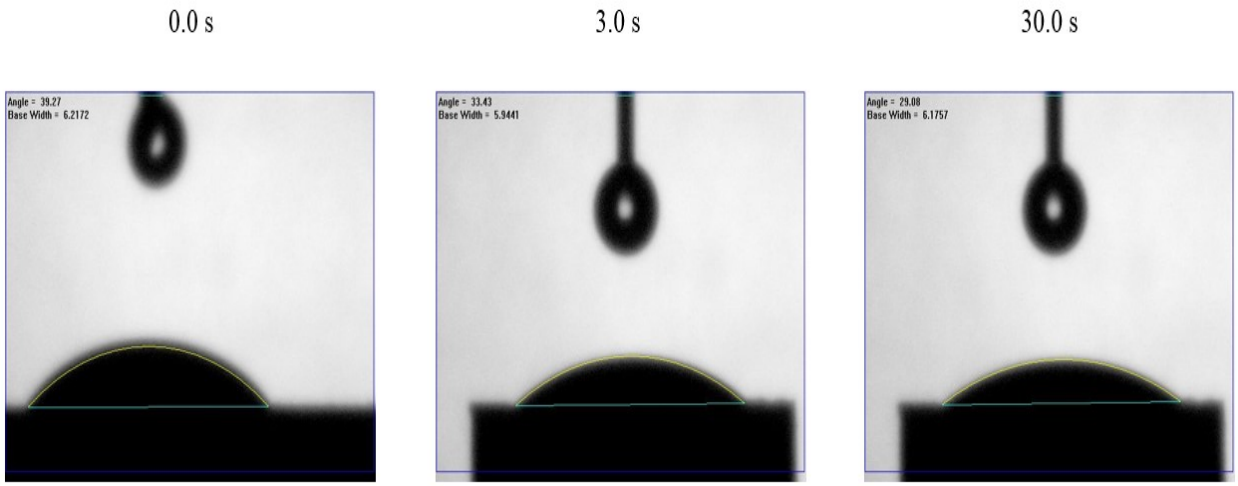


Figure 21: Formation of a contact angle on esterified with methanol SRM surface

Finalized results are represented in Table 3. The results indicate that at the initial moment, the contact angle on thermally hydrolyzed SRM surface is higher than that on the esterified SRM surface, which results in thermally hydrolyzed SRM to be more hydrophobic material (which is opposite to what has been expected).

Time, s	Angle, ^{o}	
	Thermally hydrolyzed SRM	SRM esterified with methanol
0.0	42.4	39.3
1.0	37.5	35.3
2.0	28.7	35.1
3.0	26.5	33.4
15.0	25.7	33.5
30.0	23.4	29.1

Table 3: Contact angle formation on thermally hydrolyzed SRM surface and methylated SRM surface

However, change in contact angle values with time show that the contact angle on methylated SRM reduces slower than the contact angle on thermally hydrolyzed SRM, which means that this material has a lower water absorbance property.

Also, needs to be mentioned, that the initial contact angle values can be incorrect due to poor quality of the pellets prepared for the experiments, when the pelletized layer is damaged and has powder material instead of a film [31], [32].

3.2.4 Fourier transform infrared spectroscopy (FTIR) analysis

FTIR analysis was carried out in order to determine whether the new bonding type of functional groups have been emerged after the esterification reaction. The analysis was done at nanoFAB using THERMOSCIENTIFIC DRIFTS analyzer. The samples were prepared by diluting thermally hydrolyzed SRM or methylated SRM in KBr salt and evaluated at near-infrared frequency light.

Thermally hydrolyzed SRM can be characterized by the presence of peptide bond appearing when two or more amino acids form a peptide, as well as O-H, N-H, S-H stretching signals emerging from different amino acid side chain groups in the range of 3000-3500 cm^{-1}. Also, C-H stretching can be determined around 2850 - 3000 cm^{-1} from the alkane chain of the molecule (Figure 6, 7 in Appendix). In methylated ester the peaks were expected to be emerged for C=O and C-O ester bonds at 1650-1750 cm^{-1} and 1000-1300 cm^{-1} respectively, however, due to complex nature of the material, it is impossible to detect the emerge of new peaks.

Figure 22 shows both spectra for thermally hydrolyzed SRM and methylated SRM.

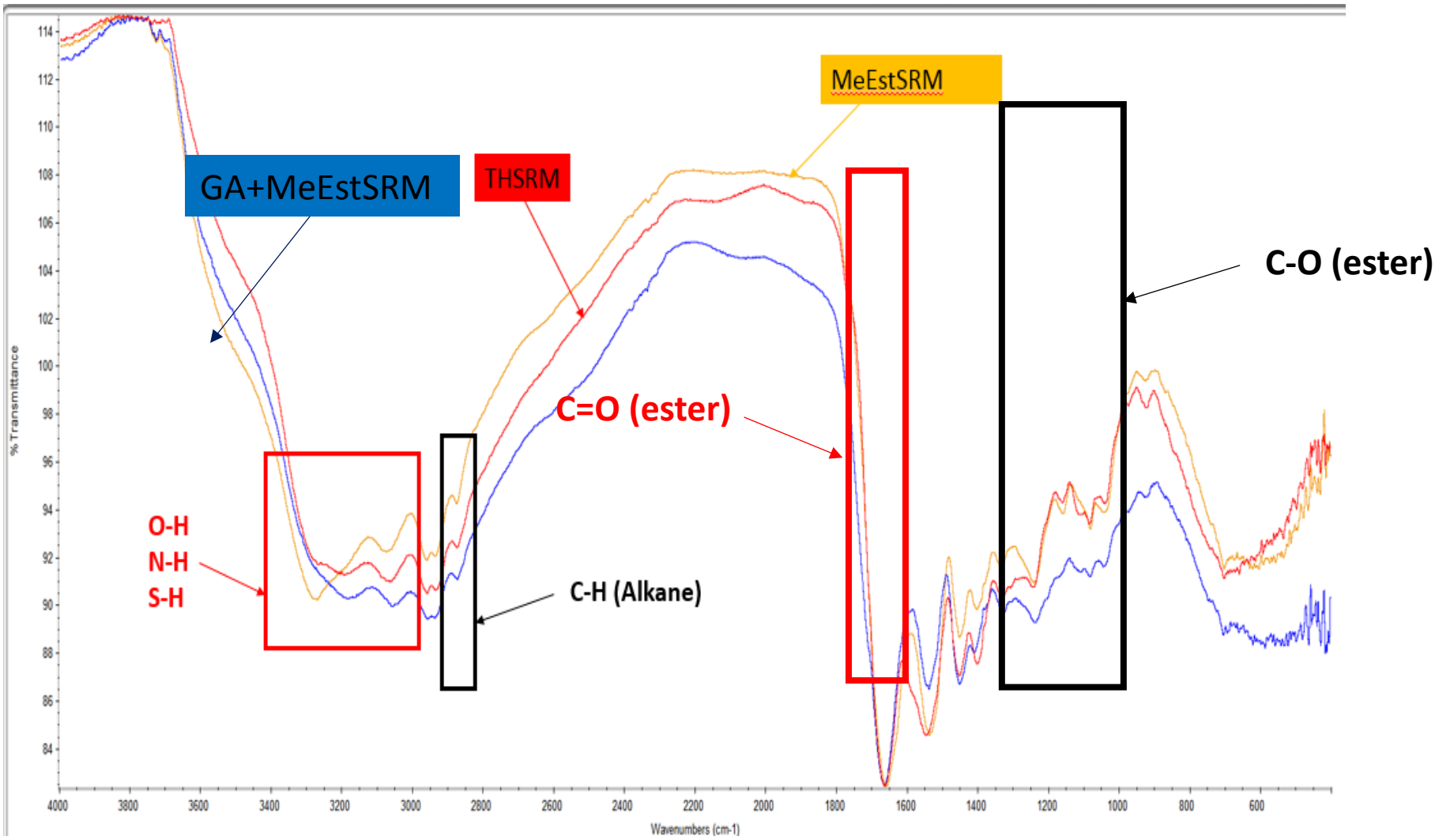


Figure 22: FTIR spectra of thermally hydrolyzed SRM and methylated SRM

As was found before, thermally hydrolyzed SRM is a proteinaceous material consists of peptides that are randomly formed during the breakdown of protein molecules during the thermal hydrolysis. As a result, each batch of hydrolysis results in the release of peptides with various lengths, also consisting of different amino acids [17]. Because of this random composition, each sample of thermally hydrolyzed SRM is somewhat different from one another. This results in a spectrum with multiple peaks corresponding to numerous functional groups from side chains of amino acids presented in the sample. Thermally hydrolyzed SRM is not a pure one-component material, thus the amount of different bonds is so large that all the peaks look overlapping, resulting in very wide peak ranges as it can be observed in Figure 22.

After the modification with alcohol, for instance, the new bonds, if they are formed, cannot be clearly observed, because even if the new peak is emerge, it appears to be overlapped with the already existing ones.

As a conclusion, FTIR could not be used as a reliable evidence of the esterification reaction taken place.

3.2.5 High performance liquid chromatography (HPLC) analysis

To determine if the esterification reaction resulted in any changes in molecular weight distribution, size exclusion high performance liquid chromatography analysis was carried out.

The analyzed samples were: standard mix of proteins of different molecular weight, thermally hydrolyzed SRM, and SRM esterified at different concentrations: 10% (w:v), 5% (w:v), 2% (w:v), and 1% (w:v). Figure 22' shows the results of the HPLC analyses.

The results of HPLC indicate that the original thermally hydrolyzed sample has the largest peak emerging at around 90 units, followed by the peaks in a lower molecular weight range at 105-135 units. The picture changes for the methylated samples significantly. In the range of 105-135 units elusion time the peaks become weaker for 10% sample (10 g thermally hydrolyzed SRM in 100 mL methanol). The peaks tend to disappear as the concentration of thermally hydrolyzed SRM in the esterification reaction becomes lower.

Also, there is an obvious shift in the largest peak can be observed from 90 minutes to around 80 minutes.

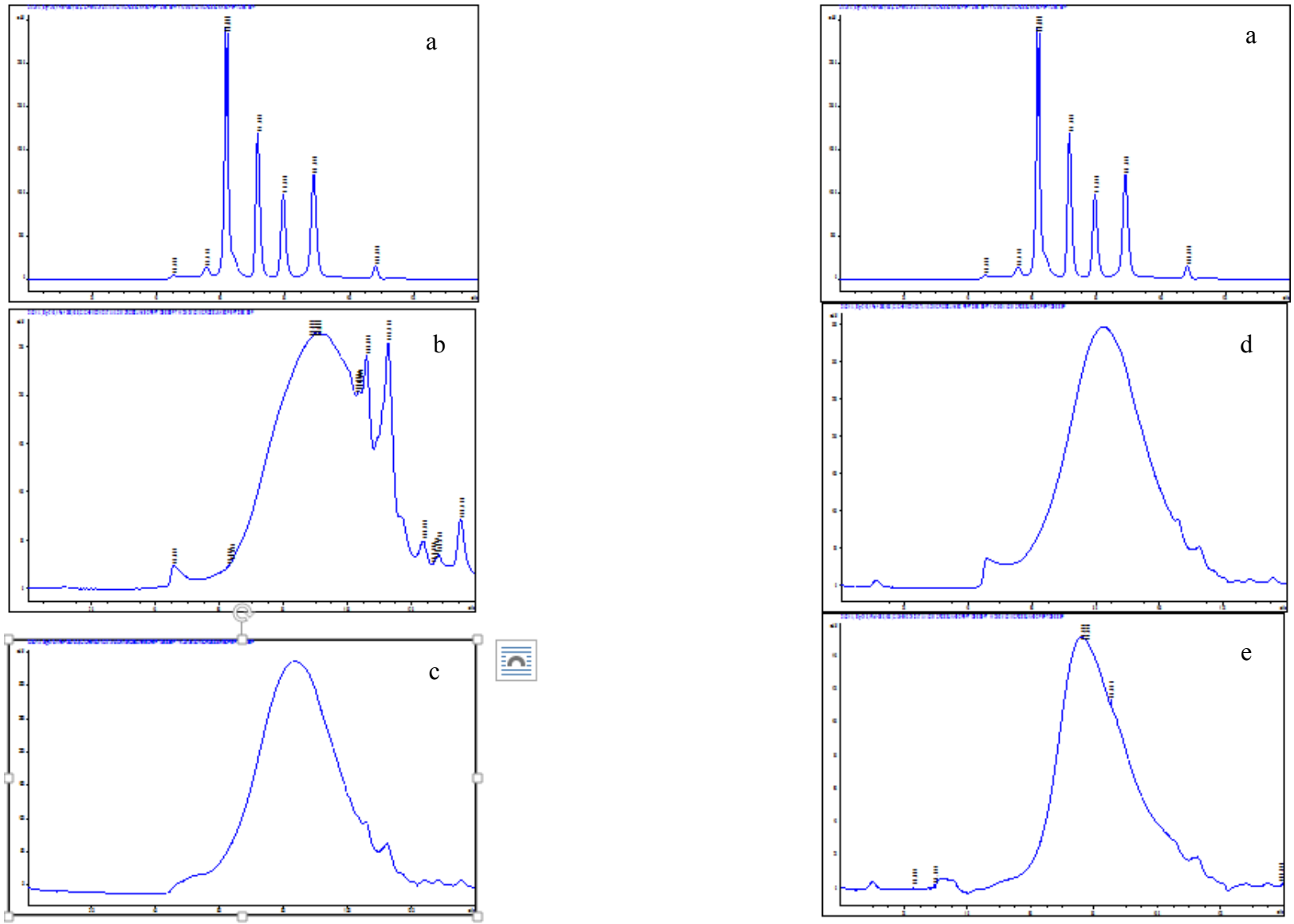


Figure 22': HPLC chromatograms: a. standard sample; b. thermally hydrolysed SRM; c-e. methylated SRM (10%, 5%, 2% w:v);

The chromatograms presented in Figures 23-28 potentially can be an indication of change in the molecular weight of thermally hydrolyzed SRM due to the formation of ester bonds and substitution of carboxylic functional groups with ester bond, however, the changes can also occur due to purification of SRM (Figure 18).

3.2.6 Sodium dodecyl sulfate poly-(acrylamide) gel electrophoresis (SDS-PAGE)

Another experiment for determination, if any molecular weight change took place, was SDS-PAGE.

The result of SDS-PAGE of thermally hydrolyzed SRM can be found in Figure 23.

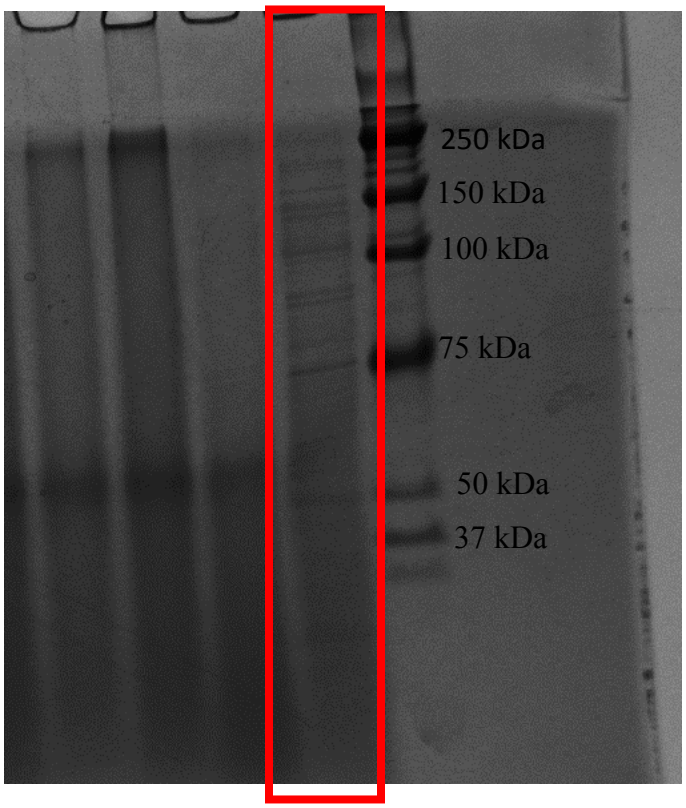


Figure 23: SDS-PAGE of thermally hydrolyzed SRM

As previously discussed, thermally hydrolyzed SRM is not a pure one-component material [17]. Thus, the SDS-PAGE results in a many separation bands with each corresponding to a particular molecular weight. The large amount of bands can be explained by the formation of peptides of a distribution of chain lengths.

The SDS-PAGE results for esterified SRM are shown in Figure 24. There are some differences in comparison with thermally hydrolyzed SRM results. Firstly, the new band emerged around 250 kDa molecular weight band, and there are no more visible bands can be observed as it was for thermally hydrolyzed SRM.

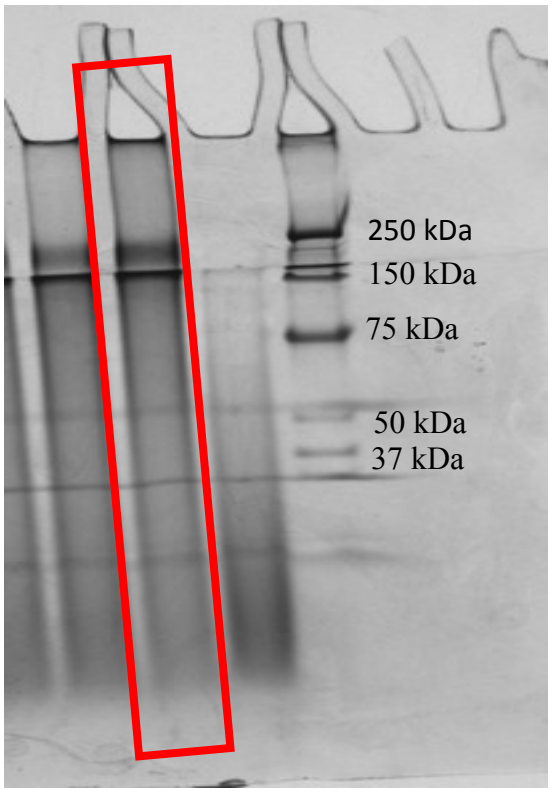


Figure 24: SDS-PAGE of esterified SRM

However, the appearance of a new band can be argued as the concentration of the sample was too high that resulted in poor separation of the molecules of various molecular weight.

Although, SDS-PAGE analysis shows some evidence of the molecular weight change, it cannot be used for decision making without other characterization analyses.

Chapter 4. Formulation of modified SRM-based adhesive

In previously done work on the development of SRM-based wood adhesive, the effect of crosslinking of SRM with glutaraldehyde was evaluated [20], [21].

Thermally hydrolyzed SRM was used as a hardening component, and the crosslinking agent was developed by mixing glutaraldehyde with resorcinol at different ratios [20]. The result showed that the adhesive material worked good in dry conditions; however, it did not survive any contact with water [17], [18], [20-21].

The rationale of this research was to make an adhesive with good water resistant properties by using glutaraldehyde as a pure component without chemical modifications, since it was reported as crosslinking agent used in adhesive industry [25-27], [54].

However, it was assumed that if thermally hydrolyzed SRM is modified so, that its water resistance is improved. Then, the wood adhesive will also have good water resistivity [50], [52].

4.1 Crosslinking of esterified SRM with glutaraldehyde

It was assumed that crosslinking of esterified SRM with glutaraldehyde takes place at the amine terminal end group of the peptide molecule with the formation of imine bond (Figure 25) [45], [54].

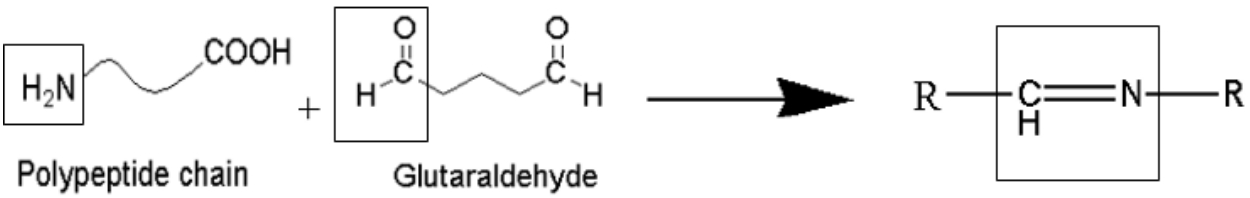


Figure 25: Reaction of aldehyde group with amine group of peptide with formation of imine bond

To react methylated SRM with glutaraldehyde, there was prepared 5 samples. Each sample contained 1 g of methylated SRM (5% w:v). Glutaraldehyde (50% water solution, Fischer Scientific) was added into each sample in the amount of: 0.1 mL, 0.2 mL, 0.5 mL, 1.0 mL, and 2 mL. One sample was used as the control and did not contain any glutaraldehyde.

The samples were stirred for two hours at room temperature. After two hours in samples that contained 0.5 mL of Glutaraldehyde and more white precipitate was observed. In the samples with 0.1 mL and 0.2 mL of glutaraldehyde, no visible changes were noticed and they visually looked exactly like the control sample without glutaraldehyde added.

Furthermore, characterization experiments were done to determine whether any changes took place after the crosslinking reaction.

4.1.1 Contact angle measurement

The contact angle determination was done similarly to the determination of contact angle described in Chapter 3. The crosslinked esterified SRM was freeze-dried to

obtain solid material that was further pelletized to form solid pellets 3 mm in diameter.

The results of contact angle determination are represented in Figure 26. The contact angle at the initial moment was 40.67^{o} and it went down to 28.73^{o} at 30.0 s.

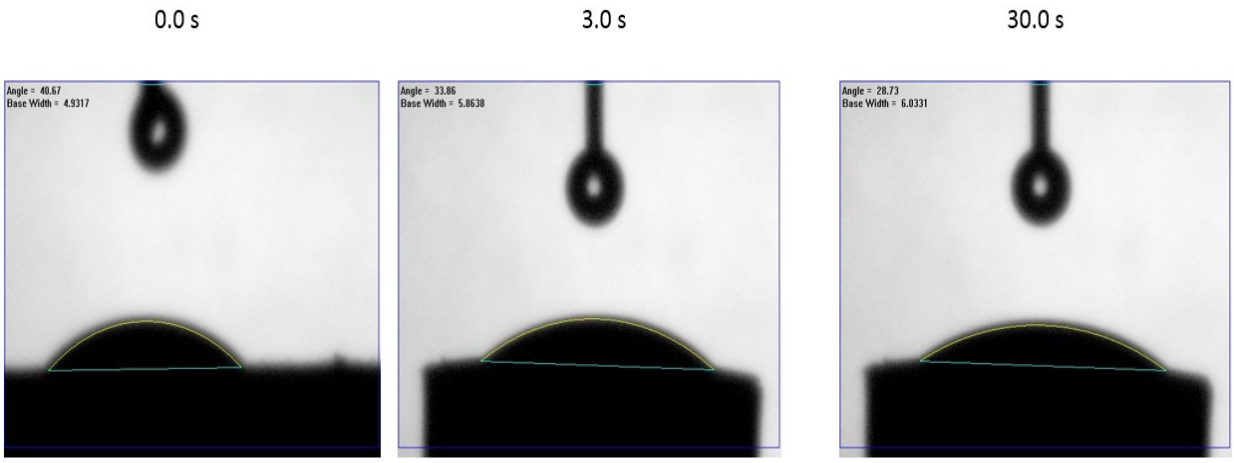


Figure 26: Formation of a contact angle on esterified SRM crosslinked with glutaraldehyde

Table 4 shows the contact angle measurement results for all three types of materials: thermally hydrolyzed SRM, methylated SRM, and methylated SRM crosslinked with glutaraldehyde.

Time, s	Angle, [o]		
	THSRM [a]	MeEstSRM [b]	GA_MeEstSRM [c]
0.0	42.4	39.3	40.67
1.0	37.5	35.3	34.7
2.0	28.7	35.1	33.9
3.0	26.5	33.4	33.9
15.0	25.68	33.5	32.2
30.0	23.4	29.1	28.73

Table 4: Contact angle values for: a. thermally hydrolyzed SRM, b. methyl-ester of thermally hydrolyzed SRM, c. methyl-ester of thermally hydrolyzed SRM crosslinked with glutaraldehyde

The results showed that the contact angle at the initial moment is higher for glutaraldehyde crosslinked methyl-ester than for methyl-ester before the crosslinking, but due to a low quality of pellets it cannot be considered as a correct result, since it indicated that glutaraldehyde crosslinked methyl-ester is more hydrophilic than thermally hydrolyzed SRM.

However, it needs to be mentioned, that in 30 second range the decrease in contact angle is still lower than the one of thermally hydrolyzed SRM one.

4.1.2 SEC-HPLC

HPLC tests were done in accordance with the protocol described in Chapter 3 for samples prepared as described in Section 4.1

As previously stated, each HPLC sample needs to be filtered before injected into column. Apparently, the crosslinking reaction between methylated SRM and glutaraldehyde results in the formation of insoluble crosslinked material which cannot be properly analyzed using molecular weight distribution techniques.

The HPLC results did not give any evidence of the crosslinking reaction taking place (Figure 27).

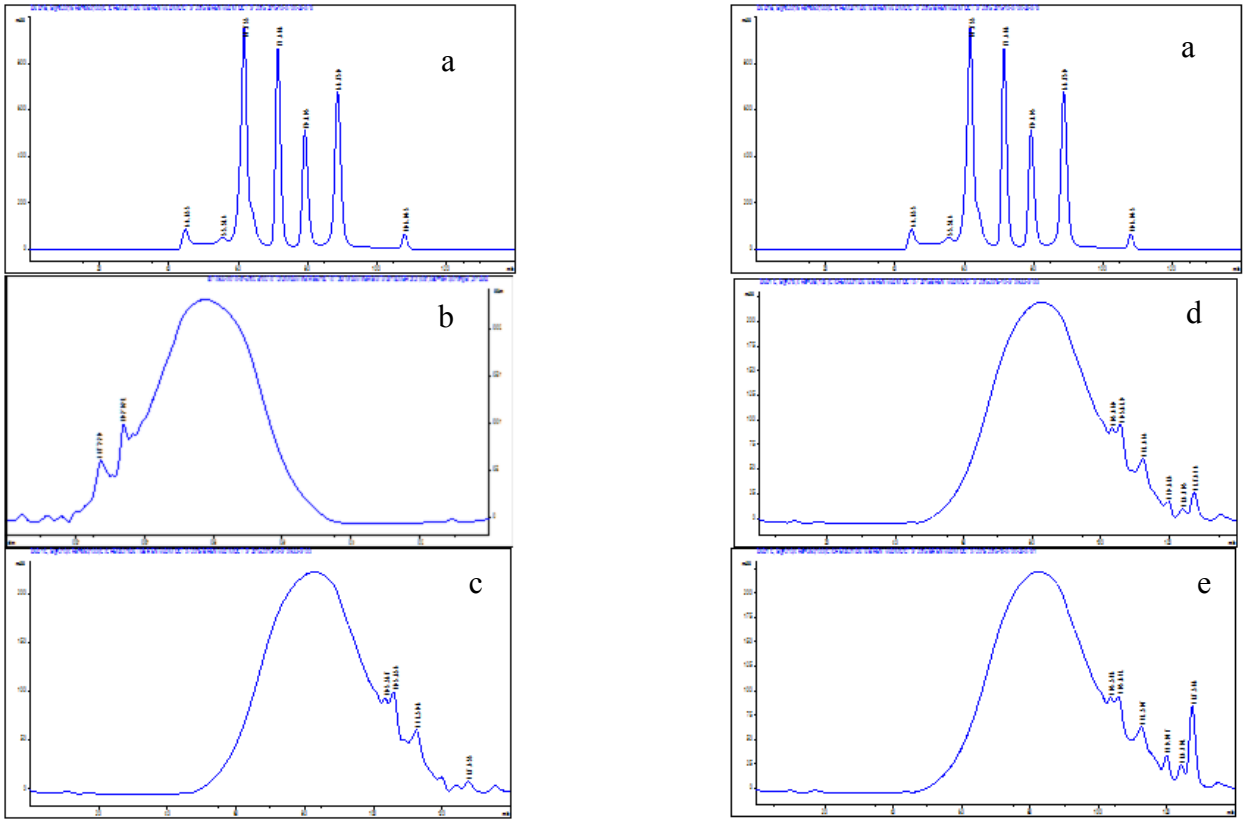


Figure 27: SEC-HPLC results of 5% methylated SRM: a. standard sample; b. 0.2 mL glutaraldehyde added; c. 0.5 ml Glutaraldehyde added; d. 1.0 mL glutaraldehyde added; e. 2.0 mL glutaraldehyde added

Obviously, all the chromatograms look identical, which indicates that the product of the reaction did not pass through the filter in the form of solution. SEC-HPLC test was not informative for the determination of the evidence of crosslinking reaction.

4.1.3 SDS-PAGE

Similarly to SEC-HPLC, sodium dodecyl sulfate poly-(acrylamide) gel electrophoresis did not result in any visual evidence of the crosslinking reaction taking place between methylated SRM and glutaraldehyde (Figure 27').

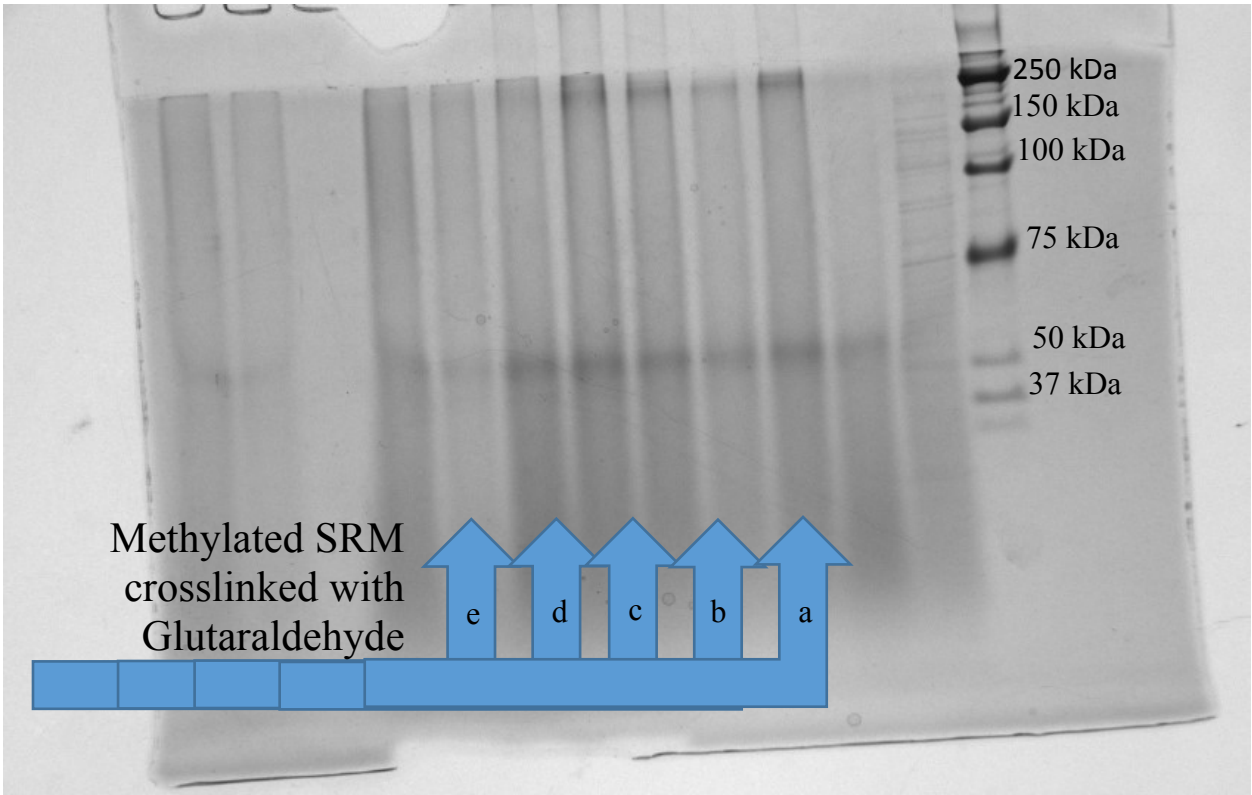


Figure 27': SDS-PAGE of methylated SRM (5%w:v in water) crosslinked with the given amount of glutaraldehyde: a. 0.1 mL, b. 0.2 mL, c. 0.5 mL, d. 1.0 mL, e. 2.0 mL

As mentioned before, the insoluble product of crosslinking could not be properly analyzed using SDS-PAGE technique. The similar issue was previously reported in literature [62]. However, there are darker areas appear on top of the stacking gel that could correspond to the presence of a high molecular weight molecules which

could be also a result of the esterification reaction but not the crosslinking with glutaraldehyde.

4.1.4 FTIR

The crosslinking reaction was expected to take place at the amine terminus of the peptide with the aldehyde group of glutaraldehyde with the formation of imine bonds. According to the literature, the imine bond peak emerges in the range of 1690-1640 cm^{-1} [69]. However, it is the same area where ester C=O stretching can be observe and the results of FTIR done on methylated SRM show the presence of this peak (Figure 28).

Thus, FTIR experiment did not show any evidence of neither esterification nor crosslinking reaction taking place due to a large amount of various peaks presented in the original thermally hydrolyzed SRM sample. Both, esterification with alcohol and crosslinking with glutaraldehyde either did not introduce any new type of bond, or, if introduced, the new peaks overlapped with the already existing peaks.

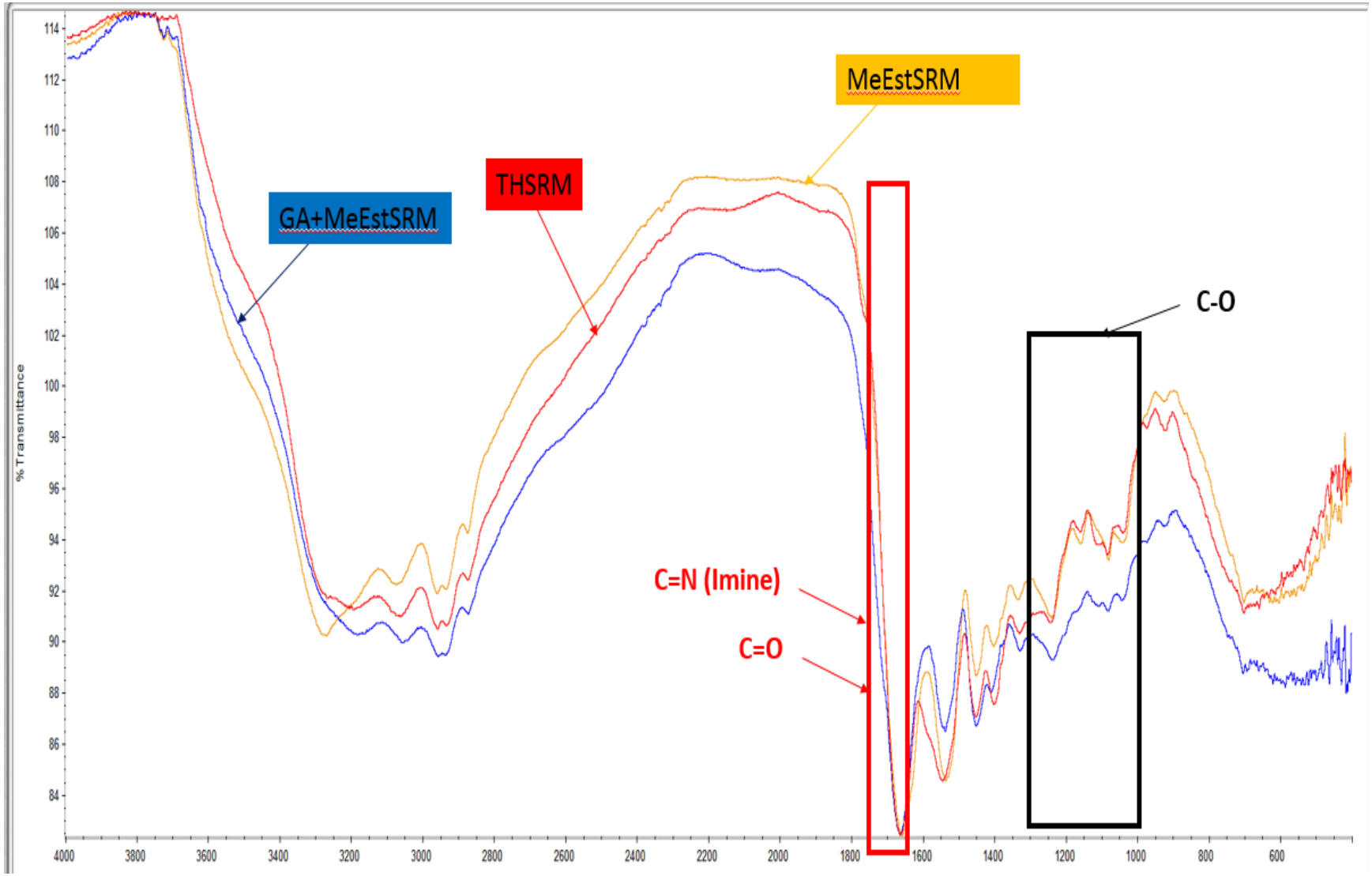


Figure 28: FTIR of methyl ester of SRM crosslinked with glutaraldehyde

4.2 Formulation of the adhesive material and preparation of test specimens

As previously mentioned, protein-based adhesives used in the wood industry are hot-melt adhesives in essence (see Figure 9 in Appendix) [26]. Hot-melt adhesives are adhesive materials consisting of two components: resin and a hardener [25]. In case of SRM-based adhesive, the peptides purified from hydrolysate is the hardening component, while glutaraldehyde is "resin" even though it is not a resin in its nature.

The SRM-based adhesive material was prepared by mixing the water solution of esterified SRM with glutaraldehyde. The concentrations of water-SRM solution and crosslinking ratios were studied and the results are given in the next sections of this report. The reaction of esterified SRM with glutaraldehyde resulted in the formation of a crosslinked partially insoluble thermoplastic solid material that was applied to the wood veneer samples. The application of an adhesive material to the adherent surface is called "coating" [25].

After the coating, the specimens were placed in a hot press where at a given temperature and pressure the adhesive material melts and the reaction between the active functional groups of an adhesive and wood cellulose or lignin is triggered as shown in Figure 40.

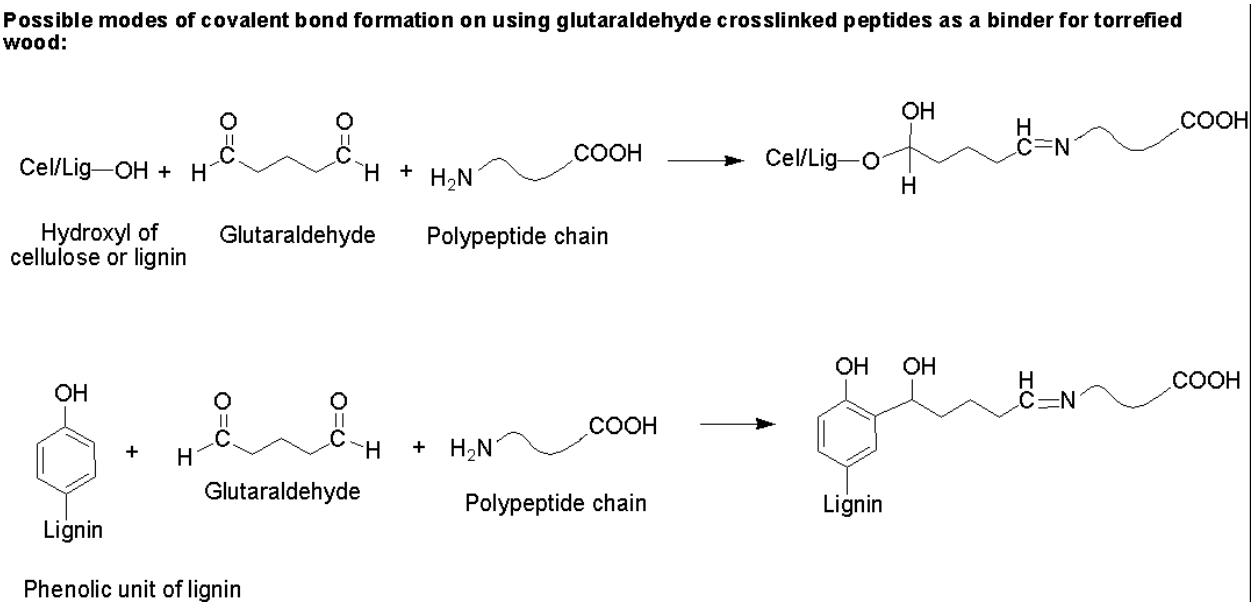


Figure 29: Possible reactions between glutaraldehyde crosslinked peptides and cellulose or lignin in the wood

The formation of bonds showed in Figure 40 takes place while specimen cools down – the curing process [26]. After the curing the specimen is considered prepared for the test of the bonded joint strength.

4.2.1 Formulation of the SRM-based adhesive

Chemically modified SRM (esterified) was dissolved in water at room temperature to form a dark-brown semi-transparent liquid. Glutaraldehyde (50% water solution) was added to the water solution of SRM and stirred at room temperature in a fume hood. When the reaction took place, a white solid precipitate appeared in the form of a solid powder and the mixture changed the color to a bright brown liquid, no transparency has been observed.

In further sections there will be described conditions of the adhesive material formulation that have been evaluated.

4.2.2 Preparation of test specimens

Preparation of test specimens was done according the standard procedure described in ASTM D906-98 [70]. Wood veneer (birch) 1.6 mm thickness was purchased at Winsor Plywood, Edmonton, AB.

The selected veneer was cut into specimens with the dimensions: 50 x 20 mm and conditioned at the moisture chamber to reach 12% moisture content. The adhesive prepared was applied on the area of 20 x 20 mm on each specimen according to the experiment requirements in the amount of 2.5 mg (solid content) per 1 cm^2 [21]. The assembled specimens were further hot pressed at 120 ^oC (if other not specified) and 3.5 MPa pressure to follow the protocol on the optimized parameters developed previously [21], [70]. After hot pressing all the specimens are required to be conditioned in accordance with the standard requirements. For dry shear stress experiment all the samples have to be conditioned for 7 days in a moisture chamber at 50 % relative humidity [70]. For soaked shear stress experiment, all the samples after hot pressing have to be soaked in the water at room temperature for 48 hours and after that conditioned for 7 days in a moisture chamber at 50%

relative humidity [70]. After conditioning all the samples are to be tested to measure lap shear strength of the adhesive bonded joint.

To meet standard requirements, the average reported adhesion strength in MPa should be higher than that given in the standard and shown in Table 5 [34].

Test	Test requirement (minimum)
Dry shear strength at 24 ^{o}C	2.344 MPa (340 psi)
48-hour soaked	1.930 MPa (280 psi)

Table 5: Lap shear strength test requirements [34]

To be considered for commercialization, the developed adhesive has to meet both requirements.

4.3 Lap shear strength test of the SRM-based adhesive for plywood

Lap shear strength test is an internationally accept standard procedure on the determination of the strength of an adhesive material [25-26].

In this test, the sample is fixed tightly by the jaws of the grips and the tensile force is applied. The test described in this report, was done in compliance with ASTM

D4690-12 and D906-98 [34], [70]. The sample has to be perfectly aligned with the grips directly above each other, as shown in Figure 41 [25].

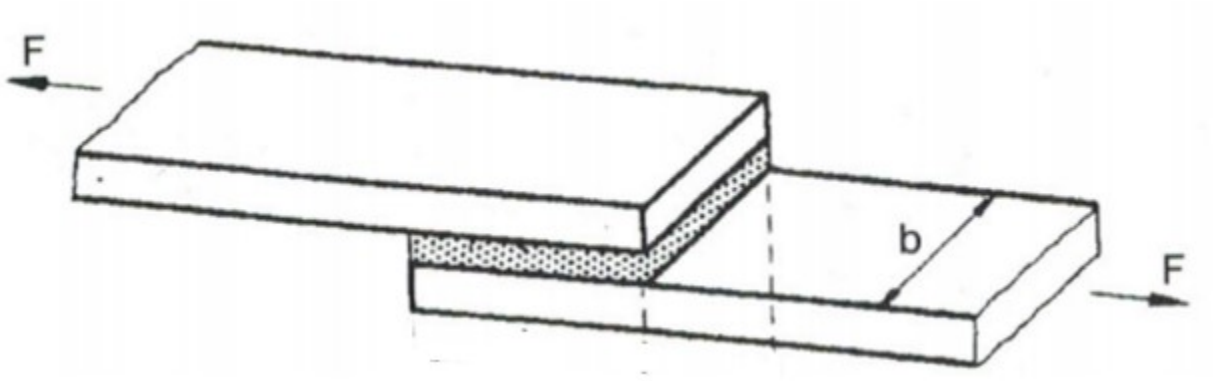


Figure 30: Lap shear strength test specimen with the tensile force applied [26]. Reproduced by permission of Wiley Books, John Wiley and Sons ©

When the tensile force is applied, the sample begins to bend in the glued area creating a momentum of a rotational motion (Figure 42). This momentum at each instance has two components: normal stress (σ) and shear stress (τ).

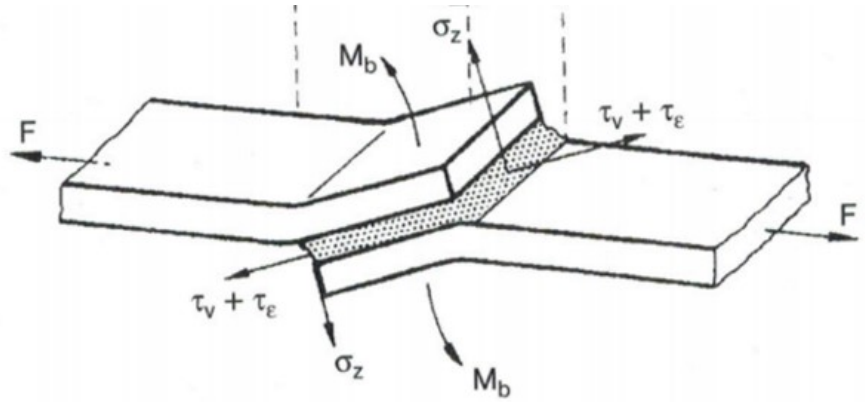


Figure 31: Types of stress emerging during the lap shear strength test [26]. Reproduced by permission of Wiley Books, John Wiley and Sons ©

Shear stress, however, has two components: τ_ε caused by the extension of wood, and τ_v occurs due to the displacement of adherents [25].

Eventually, at the certain point of time, one of three types of failure happens [25-27]:

- Adhesive or interfacial failure, when the bond breaks at the interface between the adhesive and the adherent
- Cohesive failure of the adhesive, when the break point located inside the adhesive layer
- Cohesive failure of wood, when the adhesion forces are stronger than cohesive force of wood, the wood adherent breaks before the bonded joint (never the case in this report)

According the ASTM D906-98(2004), the load rate applied to the specimen has to be in the range of 4535 to 7560 g/s (600 to 1000 lb./min) [70]. To fit in this range, the crosshead speed of 1 mm/min was used in the experiments descried further.

The recorded load (kN) is the converted into MPa – standard unit to be reported by dividing the load by the glued area [34].

For each experiment there were prepared seven samples, however, the standard recommended amount is at least five samples per each experiment [34-36].

Lap shear stress test was carried out at the Mechanical Engineering facility of the University of Alberta on Material Testing System – MTS INSTRON 800 with 10 kN load cell.

4.4 Lap shear strength experiments and results

4.4.1 Evaluation of the effect of reaction time on adhesion strength

According to the literature [24-26], adhesive can keep its adhesive properties only for a given amount of time, which varies for different time of adhesives. This amount of time is called the "pot life time" [24]. The first experiment carried out was the determination of a pot life time – what is the minimum time required to get the strongest adhesive properties and how the adhesive strength changes with time.

From previously carried out experiment, it was found that the visual precipitation while crosslinking SRM (water solution) with glutaraldehyde occurs at the SRM:glutaraldehyde ratio around 7:1 - 8:1 (w:w). Thus, it was decided to start the experiment of the effect of time on the adhesion strength with the crosslinking ratio 7:1 (methylated SRM : glutaraldehyde). However, the effect of crosslinking ratio on the adhesion strength was also evaluated and the results are reported in the following sections.

For each experiment there were prepared two sets of samples (7 in each set). One was used for dry shear strength experiment, another one was used for soak shear strength experiment.

In some cases, in soak shear strength tests, the samples delaminated (separated) before the adhesive strength was measured. Although, the standard suggests that these samples can be excluded from the average shear strength estimation, for the purpose of this report they were included because they affect the average lap shear strength. Equation 1 shows how the reported average lap shear strength was calculated:

$$\tau = \frac{\tau_1 + \tau_2 + \tau_3 + \tau_4 + \tau_5 + \tau_6 + \tau_7}{7} \quad (1)$$

Where, τ_i is the adhesion strength (MPa) of the i^{th} specimen.

In time evaluation experiment, methylated SRM was dissolved in Milli-Q water and glutaraldehyde was added in 7:1 ratio (SRM:glutaraldehyde) to make the total solid content 20%. The effect of solid content was also evaluated in the following experiments, however, 20% has been chosen as the optimal for the convenience of the coating process. Hot pressing temperature was 120 ^{o}C (393 K) - minimum recommended for protein-based hot-melt adhesives [24].

The results of dry shear and soaked lap shear strength tests are shown in Graph 3.

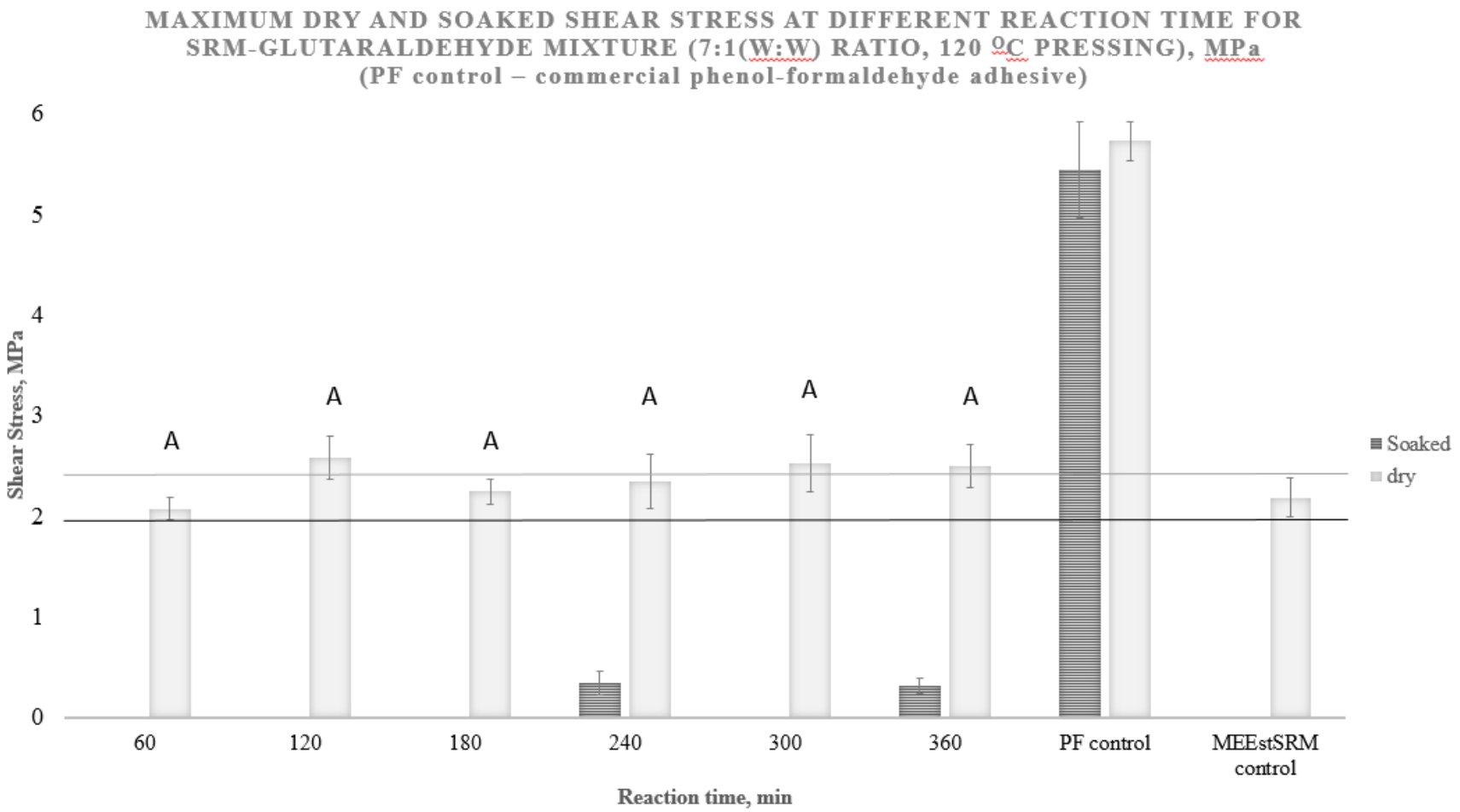
As shows Graph 3, the first time when the adhesive is strong enough to pass the standard requirement is 120 minutes. As shown in previous experiments, 30 minutes, 60 minutes, and 90 minutes were not enough for the crosslinking reaction to take place.

There were two reaction times that resulted in the adhesive where the average amount exceeded the standard value – 120 minutes and 360 minutes. It was decided to continue the experiments with 120 minutes reaction time from the processing point of view, because the amount of samples passed the standard value was the same for 120 minutes and 360 minutes: five out of seven. In both 120 and 360 minutes, there were two samples that had a lap shear strength below the standard.

However, almost all the samples were found delaminated after conditioning after 48-hour soaking. There were 2 samples not delaminated in 240 and 360 minutes reaction time formulations, but it did not meet the standard requirement of at least five samples has to be measurable to consider the experiment complete.

As the control comparison there was used commercially available phenol-formaldehyde resin (PF control) and methylated SRM without crosslinking with glutaraldehyde. As it can be seen in Graphs 3, PF control has a lap shear strength around 5.5 MPa for both dry and soaked shear strength experiments. Methylated

SRM samples completely delaminated after the first 24 hours of soaking and the dry shear strength samples did not pass the standard recommendation with five samples out seven showing the result below the standard value.



Graph 3: Effect of the reaction time on lap shear strength

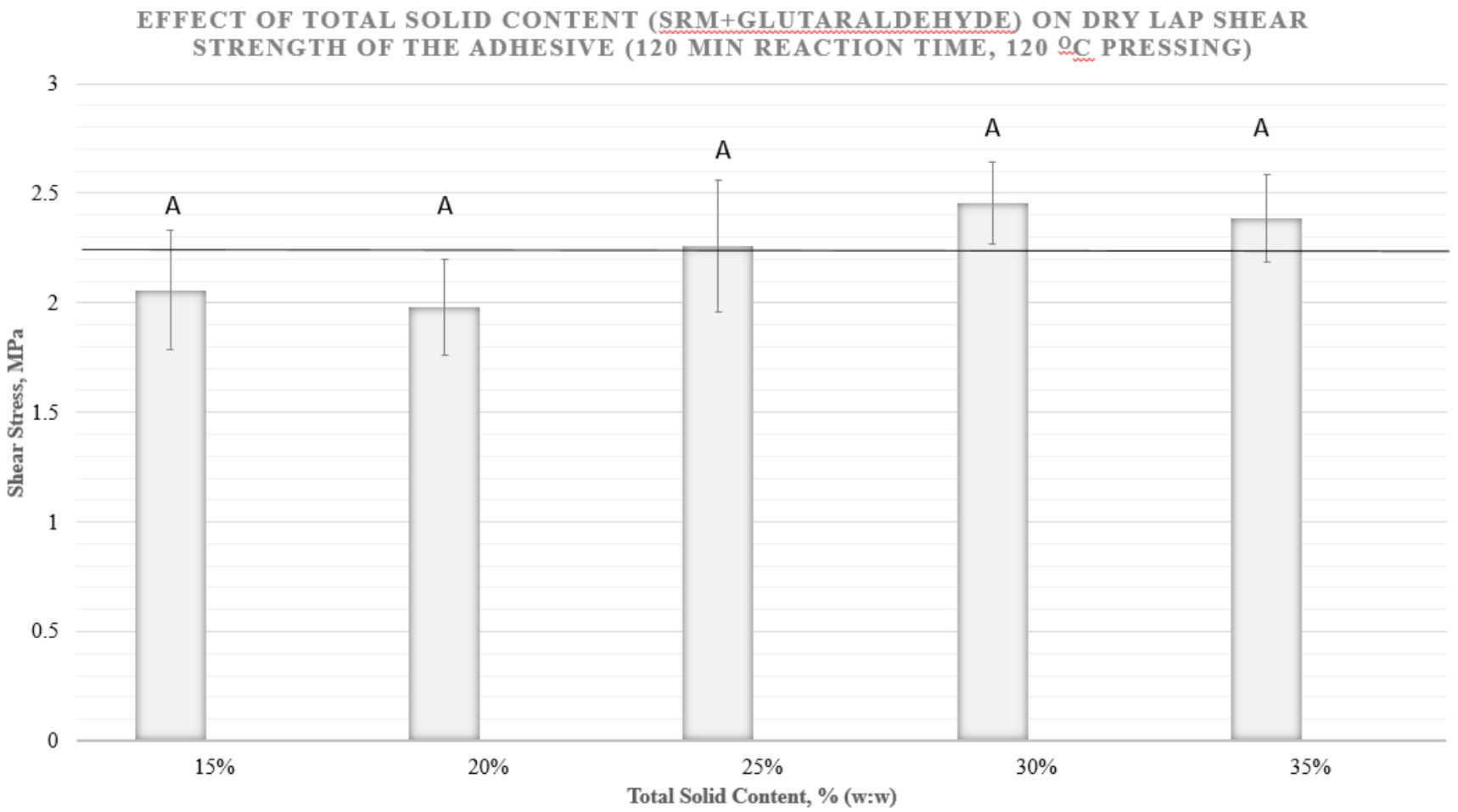
4.4.2 Evaluation of the effect of solid content on lap shear strength

The evaluation of solid content was done to determine the optimal formulation for the coating process. In this experiment, methylated SRM was crosslinked with glutaraldehyde (50% water solution) and Milli-Q water was added to make the total solid content (methylated SRM + glutaraldehyde) 15%, 20%, 25%, 30%, and 35%.

Graph 4 shows the results of lap shear strength of SRM-based adhesive at different solid content. The samples were prepared by hot pressing at 120 ^{o}C and pressure 3.5 MPa per sample.

From this graph, it appears that 30% total solid content has the highest lap shear strength with five out of seven samples exceeded the standard value. Similar results were reached by 35% total solid content specimens but this formulation was not suitable for proper coating due to an extremely high viscosity and poor wettability of the material.

The results of soaked shear stress samples are not shown for this experiment as almost all the samples delaminated after soaking.



Graph 4: Effect of total solid content on lap shear strength

4.4.3 Evaluation of the effect of crosslinking ratio (SRM:glutaraldehyde) on lap shear strength

So far, all the samples were prepared using the adhesive formulation with 7:1 ratio of the esterified SRM to glutaraldehyde.

The next experiment was done to evaluate the effect of crosslinking ratio between esterified SRM and glutaraldehyde.

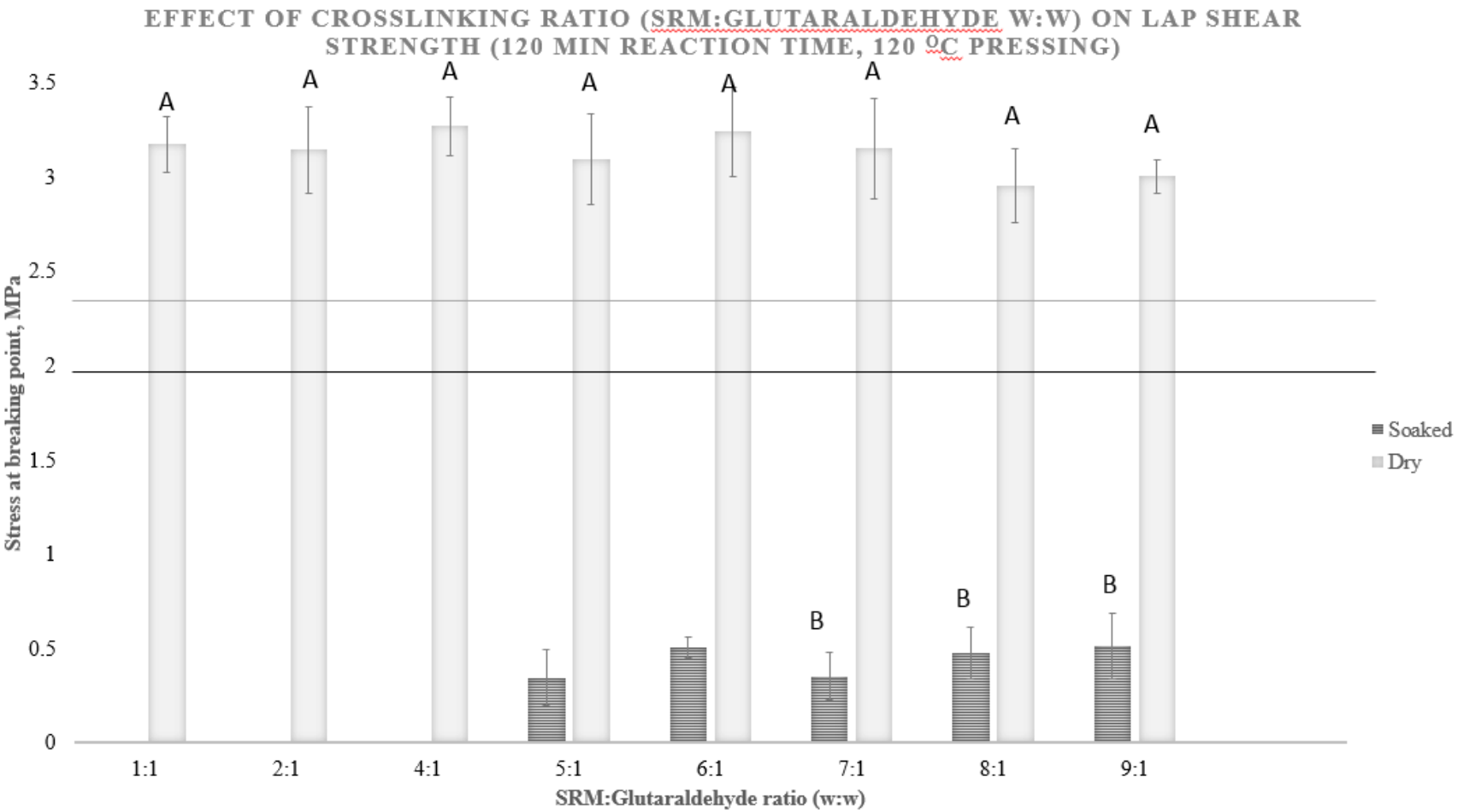
The adhesive was prepared by mixing esterified SRM (water solution) with glutaraldehyde (50% water solution) at various ratios (methylated SRM:glutaraldehyde): 1:1, 2:1, 4:1, 5:1, 6:1, 7:1, 8:1, 9:1 (w:w, dry weight basis).

The adhesive was applied to the pre-conditioned veneer specimens (2.5 g (solid) per cm^2) and hot pressed at 120 ^oC and 3.5 MPa per sample.

Graph 5 shows the results of dry lap shear strength and soak lap shear strength experiments. The result of dry lap shear strength experiment shows that there is no significant difference between the considered ratios. However, soak lap shear strength test showed that the samples with the ratios 1:1, 2:1, 4:1 did not survive the soaking at all and delaminated after soaking of during the conditioning in the moisture chamber.

The ratios 5:1 and 7:1 had lower average lap shear strength than those for 6:1, 8:1, and 9:1, however, they are not significantly different. Also, for 6:1 crosslinking ratio, all the samples were measurable after the soaking in water and 8:1 crosslinking ratio had the largest lap shear strength result out of all the samples tested which resulted in a large error bar.

Overall, it has been proven that the crosslinking ratio (methylated SRM:glutaraldehyde) affects lap shear strength, especially for soak lap shear strength experiment.



Graph 5: Effect of crosslinking ratio (SRM:Glutaraldehyde) on lap shear strength of the adhesive

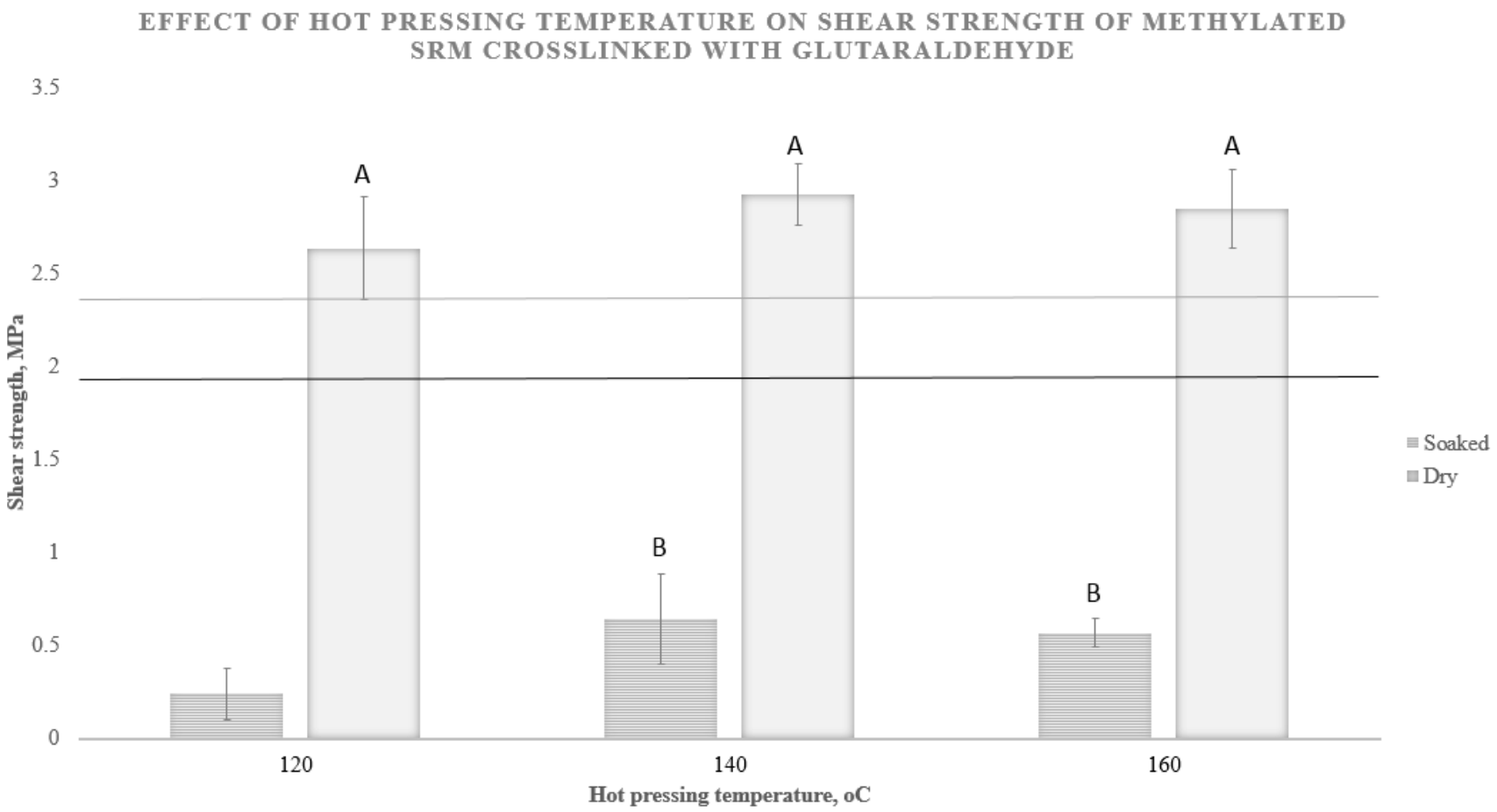
4.4.4 Evaluation of the effect of hot pressing temperature on lap shear strength

So far, all the specimens were prepared by hot pressing at 120 ^{o}C. In this experiment the samples have been prepared by crosslinking glutaraldehyde with methylated SRM to make a 30% solid content adhesive material with crosslinking ratio 8:1 (SRM:glutaraldehyde).

The hot pressing temperature was varied to evaluate its effect on lap shear strength of the adhesive. The temperatures considered were: 120 ^{o}C, 140 ^{o}C, and 160 ^{o}C.

Hot pressing temperature appeared to have no, or very insignificant effect on dry lap shear strength test results (Graph 6). However, it has a significant effect on soak shear strength of the adhesive. Hot pressing temperature 120 ^{o}C showed the worst result, while 140 ^{o}C, and 160 ^{o}C showed significantly higher lap shear strength results. Although, 140 ^{o}C hot pressing temperature has a higher average shear strength, two out of seven samples have delaminated during the experiment, which resulted in a wide error bar. Opposite, 160 ^{o}C hot pressing temperature has resulted in all seven samples were able to be measured and successfully survived 48-hour soaking in water and 7 days conditioning in a moisture chamber after.

The literature recommended hot pressing temperature for hot-melt adhesives to be up to 240 ^{o}C [24], thus, it has been decided to repeat this experiment for 140 ^{o}C, 160 ^{o}C, and 180 ^{o}C.



Graph 6: Effect of hot pressing temperature on lap shear strength

4.4.5 Evaluation of the effect of esterification with different alcohols on the lap shear strength

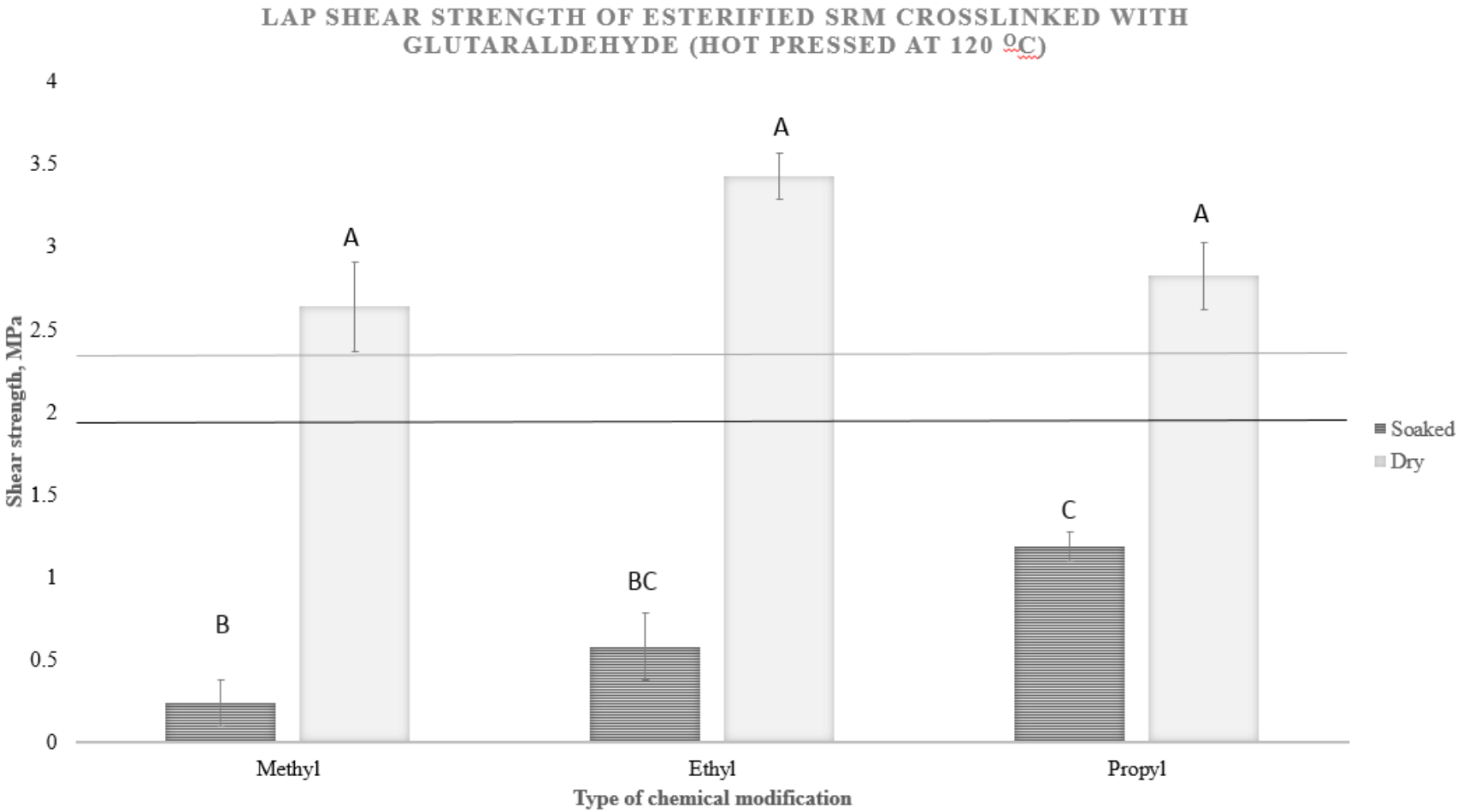
All the experiments previously reported were performed with methylated SRM only. This material was used for characterization and proof of concept purposes.

However, it was important to look at the effect of the esterification of SRM with different alcohols: ethanol and propanol, for instance, and assess the ethyl- and propyl- esters of SRM.

For the evaluation of ethyl- and propyl esters of SRM on lap shear strength a 30% solid content adhesive was prepared with the crosslinking ratio 8:1. Each sample contained 2.5 mg solid per cm^2 of glued area. The hot pressing temperature was 120 ^oC and pressure 3.5 MPa per sample.

Dry lap shear strength experiment showed that ethyl-ester of SRM had a slightly higher average shear strength if crosslinked with glutaraldehyde than methyl- or propyl- esters of SRM crosslinked with glutaraldehyde (Graph 7)

However, the soak lap shear strength test showed a significant increase in used propylated SRM, with approximately 1.2 MPa which is almost four times higher than the result of methylated SRM at the same conditions.



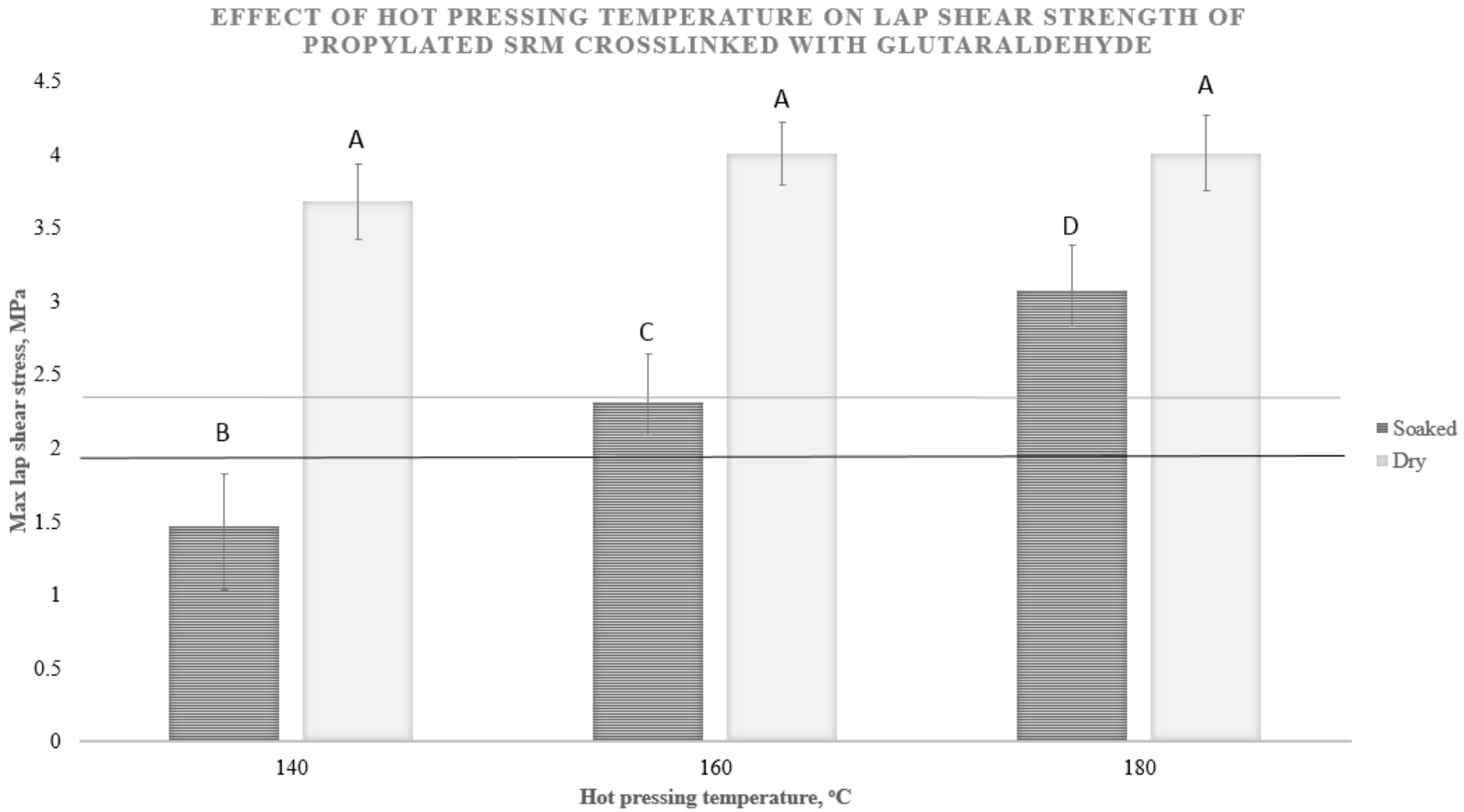
Graph 7: Effect of the esterification with different alcohols on lap shear strength

Taking in consideration the results of the experiments described in sections 4.4.4 and 4.4.5, it was decided to repeat these experiments using propylated SRM and compare the lap shear strength results for 140 ^{o}C, 160 ^{o}C, and 180 ^{o}C hot temperatures.

4.4.6 Evaluation of the effect of various hot pressing temperatures on lap shear strength of propylated SRM crosslinked with glutaraldehyde

In this experiment, the effect of hot temperature change on lap shear strength of SRN-based wood adhesive prepared by crosslinking of esterified with propanol SRM and glutaraldehyde was evaluated. Propyl-ester: glutaraldehyde ratio was 8:1, 30% total solid content, mixing time was 120 minutes, mixing temperature – room temperature. The adhesive has been applied to veneer specimens in the amount of 2.5 mg per cm^2, equilibrated for 15 minutes, and then taken to the hot pressing station.

The most important results were collected after running soaked lap shear stress experiment (Graph 8). The results have clearly indicated that the propylated SRM crosslinked with glutaraldehyde used as an adhesive for plywood, can survive soaking in water for 48 hours and passes the standard value of 1.93 MPa on the lap shear strength test after.



Graph 8: Effect of hot pressing temperature on lap shear strength of propyl-ester of SRM crosslinked with glutaraldehyde

Chapter 5. Torrefied Wood Pellets: Overview*

5.1 Definition of torrefied wood biomass

Torrefaction is a thermal treatment of wood biomass in the temperature range of 200°C to 300°C and in the absence of oxygen. The reasons for carrying out torrefaction of wood is to breakdown the wood components, which alleviates several issues with wood biomass:

- Low calorific value
- High moisture content
- Low energy density
- Non homogeneous nature
- Low combustion efficiency (smoke)
- Poor grindability
- High hygroscopy
- High organic content (volatiles)

The torrefaction process can address most of these problems to varying extents, resulting in production of a biomass with improved properties [71], [75].

Torrefied biomass has some outstanding properties that make it more useful as an energy resource. Torrefied wood can be co-fired with coal, has a high carbon

content resulting in a high syngas production, it is easy to store, and is more homogeneous than wood biomass before torrefaction [72].

However, the usage of torrefied wood biomass has some limitations due to its low density (lower than the biomass before torrefaction) and a requirement of a binder to densify the torrefied material. Another major issue is the extreme explosibility of the dust of the torrefied material, which can be potentially mitigated through the use of a binder [72], [75].

5.2 Energy consumption of the pelletisation process

As noted before, the grinding of a torrefied wood biomass consumes significantly less energy compared to that of non-torrefied wood. Specifically, one study suggests that the energy consumption for grinding of torrefied wood has 5-6 times less energy consumption (Figure 43) [72].

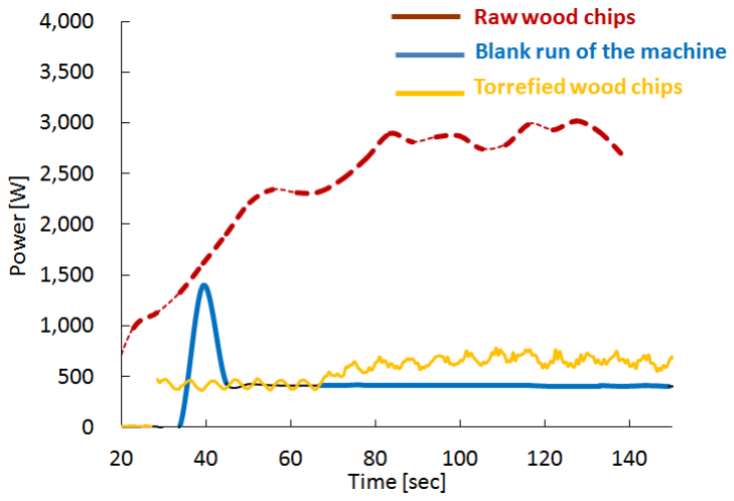


Figure 32: Grinding process power rate for torrefied wood vs. raw wood (Bahman Ghiasi, 2015)

A similar situation is observed for the pelletisation process (Figure 44). Although, the pelletisation process of torrefied wood material is still energy intensive, the energy consumption of this process can be minimized through the application of a binder.

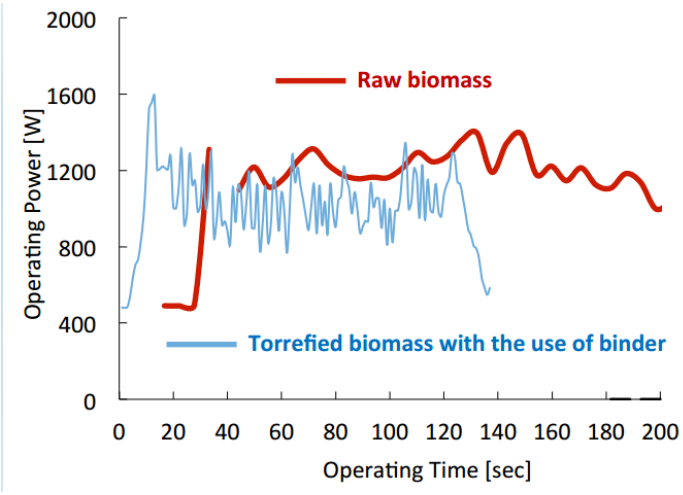


Figure 33: Power rate of the pelletisation process of the raw wood vs. torrefied wood (Bahman Ghiasi, 2015)

Table 6 shows the results of test runs of the grinding and pelletisation processes of torrefied wood biomass and raw wood chips. Note that the energy consumption in the case of torrefied wood is approximately two times lower in case of pelletisation and more than seven times lower in the case of grinding than the results for the raw wood [72].

	Torrefied wood	Raw wood
Grinding, kJ/kg	39.1	291.9
Pelletisation, kJ/kg	461.1	756.9

Table 6: Energy consumption for torrefied wood processing vs. raw wood (Bahman Ghiasi, 2015)

The figures above clearly indicate that the torrefied wood biomass has a greater potential to become a valuable energy resource. However, there are issues still associated with using torrefied wood biomass. One approach to address these issues would be to develop a cheap and environmentally friendly binder.

5.3 Canadian Wood Pellet Market Assessment

5.3.1 Wood pellets from raw wood

The European Union is the largest wood pellet market in the world in terms of production, import, and export of wood pellets, with a total consumption of 17,100,000 tonnes a year in 2014 [73]. Although, the Canadian market is not as big as the European one, new government policies and a focus on environmental issues is predicted to result in steady growth of the Canadian wood pellet market. In 2012, the number of plants producing wood pellets in Canada has increased to 39 at the total production of 3,400,000 tonnes [73], [76].

As indicated in Table 7, British Columbia is the Canadian province with the highest wood pellet production, followed by Quebec and New Brunswick.

However, there has been a decrease in pellet production due to the current market situation and closure of uncompetitive plants in Ontario, British Columbia, and Newfoundland [76].

	Capacity, tonnes			
Province	2011	2012	2013	#
BC	1,882,640	2,097,000	2,017,000	61.3%
QC	600,000	625,000	625,000	19.0%
NB	142,000	182,000	202,000	6.1%
NS	150,000	160,000	168,000	5.1%
AB	135,000	145,000	150,000	4.6%
ON	15,000	95,000	80,000	2.9%
SK	0	0	15,000	0.5%
NL	63,000	63,000	13,000	0.4%
MB	0	5,000	5,000	0.2%
Total	2,987,640	3,372,000	3,290,000	

Table 7: Pellet capacity by province

5.3.2 Torrefied Wood Pellets Market

Because of the outstanding properties of torrefied wood (increased heating value, improved water resistivity, etc.) the interest in torrefied biomass has dramatically increased within the last few years.

Several initiatives are ongoing, that involve universities, research institutes, funding agencies, and industry to evaluate the performance of torrefied wood biomass and assess potential risks related to the torrefied wood applications. Although a developed market for torrefied wood pellets yet not exist in Canada, some estimations of the future market size can be calculated based on data available through industry-related sources [76].

5.3.3 Current Torrefied wood pellets producers

According to a 2015 report entitled "*Status overview of torrefaction technologies*", there is only one facility in Canada producing torrefied wood pellets on an industrial scale – AIREX (Becancour, QC) with a capacity of 16,000 tonnes a year. All the pellets produced are being supplied at the local power station.

Another two AIREX facilities are in the pilot stage (Rouyn-Noranda (QC) and Trois-Rivieres (QC), but information on their capacity cannot be estimated.

Another facility in Nova Scotia will only be attempted for construction by the Bio Energy Development & Production Company [74]

5.3.4 Estimated Torrefied Wood Pellet Market Size

According to targets of the federal government regarding the planned decrease in coal consumption in Canada, it is expected that 30% co-firing will be attained by 2020, which corresponds to an estimated consumption of 11 million tonnes of torrefied wood pellets [76]

Table 8 shows estimated torrefied wood pellet consumption in Canada based on 30% co-firing with coal.

	Estimated theoretical consumption of torrefied wood pellets, tonnes/year (based on 6.2 MWh/tonne)
2016	6,800,586
2017	7,934,017
2018	9,067,448
2019	10,200,879
2020	11,334,310
2021	12,467,741
2022	13,601,172
2023	14,734,603
2024	15,868,034
2025	17,001,465

Table 8: Estimation of theoretical market for torrefied wood pellets at 30% co-firing (Melin, 2012)

In the most optimistic scenario torrefied wood pellet market can be as large as coal market with over 41 million tonne consumed in 2014 [77]

For instance, in 2016, the consumption of torrefied wood pellets is predicted to be 6,800,856 tonnes of pellets. In this scenario, when the amount of binder required is only 1% of total torrefied wood pellets mass, it will require about 150,000 tonnes of SRM in 2016. In 2025 this number can reach more than 374,000 tonnes.

5.4 SRM-based binder for torrefied wood pellets

Specified Risk Material (SRM) is the cattle tissues with potentially highest concentration of prions – harmful protein that causes Bovine Spongiform Encephalopathy (BSE). In 2007 the federal government has released an Enhanced Feed Ban excluding any SRM usage in animal feed, pet food, and fertilizers production.

According to the Canadian Food Inspection Agency, SRM processing requires hydrolysis in compliance with an approved protocol (minimum 180^{o}C, at least 174 psi) followed by the utilization through landfilling. This has been done at high economical expenses, when the price of SRM utilization varied $70-$200 per tonne, and environmental risk.

However, the recent experiments indicate that the amount of the proteinaceous material, such as polypeptides, that can be recovered from the hydrolyzed SRM is approximately 35% of a dry weight of SRM [17].

Polypeptides can be used as a building material for multiple valuable products, such as: thermosetting plastics, flocculants, biocomposites, and adhesive materials. This brings us to an idea that, if crosslinked with a proper agent or a resin, peptides recovered from hydrolyzed SRM can form a cheap and environmentally friendly binder.

In the research carried out in the lab, SRM has been hydrolyzed at 180^{o}C and the peptides have been recovered. These polypeptides have been modified through the esterification reaction to improve the water resistance and further crosslinked to obtain an adhesive material.

According to the lab tests of the adhesive strength, the best crosslinking agent was found – Kymene resin which is a Polyaminopolyamide-Epichlorohydrin (PAE) resin in its nature.

5.5 Price estimation of an SRM-based binder for torrefied wood pellets

The price estimations presented in this chapter are based on the following assumptions:

- According to Sylvain Bertrand[1] the price range of torrefied wood pellets is $225-$275 per tonne and the price of binder is $200-$1000 per tonne
- The price of resin used for binder formulation is within the range of $500-$771.62 per tonne
- Cost of electric energy has been estimated based on the results presented in Table 1 of this report and current Alberta tariffs
- The price of torrefied wood is considered within the range of $100-$250 per tonne
- The purchase price of raw SRM is considered $0/tonne

For this report, we have considered two approaches. In the first approach, the breakeven price of raw SRM conversion into a binder has been estimated as one of the steps in torrefied wood pellets production (Section 5.5.1). In the second approach, the breakeven price of raw SRM conversion into a binder has been considered as a step in the binder production process only (Section 5.5.2).

1. Sylvain Bertrand – CEO at AIREX Energie Inc. AIREX is the only company, producing torrefied wood pellets in Canada on commercial scale.

5.5.1 Price estimation based on torrefied wood pellets production process

In Table 9, we see the results for the most pessimistic scenario, when the market price of torrefied wood pellets is low ($225/tonne) and the prices for torrefied wood ($220/tonne) and resin ($771.62/tonne) are high.

For 1 tonne of torrefied wood pellets			
	1% binder in pellets (w:w)	2% binder in pellets (w:w)	3% binder in pellets (w:w)
Amount of binder needed, kg	10	20	30
Amount of Resin needed, kg	2.3	4.6	6.9
Amount of torrefied wood needed, kg	990	980	970
Amount of Hydrolyzed SRM needed, kg	7.7	15.4	23.1
Amount of raw SRM needed, kg	22	44	66
Price of resin ($/1 tonne of pellets)	$1.77	$3.55	$5.32
Price of torrefied wood ($/1 tonne of pellets)	$207.90	$205.80	$203.70
Price of raw SRM ($/1 tonne of pellets)	$0.00	$0.00	$0.00
Price of pelletization process ($/1 tonne of pellets)	$6.21		
Price of SRM processing ($/1 tonne of pellets)	**$9.11**	**$7.34**	**$5.56**
Price of SRM processing, $/1 tonne of raw SRM	**$414.27**	**$166.80**	**$84.31**

Table 9: Cost estimations of raw SRM conversion into a binder based on the market price of torrefied wood pellets

The amount of binder was based on 1 tonne (1000 kg of pellets). So, 1% of 1000 kg is 10 kg.

The amount of resin needed was calculated as 23% (w: w) of the total amount of binder. This number (23%) is the best formulation of the adhesive. The amount of hydrolyzed SRM required was then estimated by subtraction of the amount of resin from the amount of binder. Similarly, the amount of torrefied wood was calculated (1000 kg of torrefied wood minus the amount of binder).

To calculate the amount of raw SRM, the amount of hydrolyzed SRM has been divided by 0.35 (assuming that the average yield of useful peptides from raw SRM is 35%). Price of resin $1.77 per tonne of torrefied wood pellets was estimated from $771.62/tonne of resin recalculated for the amount of resin needed. Similarly, price of torrefied wood feedstock was derived from $225/tonne adjusted to the amount of torrefied wood needed for 1 tonne of torrefied wood pellets.

Price of the pelletization process was calculated based on the tariff price ($0.04286/kWh + fixed $0.313/day). The amount of energy consumed was estimated from Table 6.

Price of SRM conversion into binder was calculated as: Price of 1 tonne of torrefied wood pellets – Price of resin (per tonne of torrefied wood pellets) – Price

of torrefied wood (per tonne of torrefied wood pellets) – Price of electric energy (per tonne of torrefied wood pellets) – raw SRM purchase (assumed $0)

This means that, for example, if 1 tonne of torrefied wood pellets contains 1% of a binder (10 kg), then the breakeven price of processing raw SRM required to produce 10 kg of binder is $9.11 (per 22 kg of raw SRM) or $414.24 per tonne of raw SRM.

5.5.2 Price estimation based on binder production process

The results of theoretical estimations are presented in Table 10. For this cost estimation the following pessimistic scenario was considered: the resin used in our system was priced at $771.62/tonne, while the competitor's commercially available price was considered at $200/tonne.

For 1 tonne of a binder	
Amount of resin required, kg	230
Amount of Hydrolyzed SRM required, kg	770
Amount of non-Hydrolyzed SRM required, kg	2,200
Price of Resin, $/1 tonne of a binder	$177.47
Price of raw SRM, $/1 tonne of a binder	$0.00
Price of processing SRM into a binder, $/1 tonne of a binder	**$22.53**
Price of processing SRM into a binder, $/1 tonne of raw SRM	**$10.24**

Table 10: Theoretical cost estimations of raw SRM conversion into a binder based on the market price of binder ($200/tonne)

This means that if the market price of the binder available is $200/tonne, then the cost of raw SRM conversion into a binder cannot exceed $10.24/tonne, however, Table 11 indicates that the cost of raw SRM conversion can be increased if the market price of binder becomes higher (i.e. $1000/tonne)

For 1 tonne of a binder	
Amount of resin required, kg	230
Amount of Hydrolyzed SRM required, kg	770
Amount of non-Hydrolyzed SRM required, kg	2,200
Price of Resin, $/1 tonne of a binder	$177.47
Price of raw SRM, $/1 tonne of a binder	$0.00
Price of processing SRM into a binder, $/1 tonne of a binder	**$822.53**
Price of processing SRM into a binder, $/1 tonne of raw SRM	**$373.88**

Table 11: Theoretical cost estimations of raw SRM conversion into a binder based on the market price of binder ($1000/tonne)

It should be noted that the most pessimistic scenario when the torrefied wood price is high and the price of torrefied wood pellets is low (or the price of resin is high but the price of binder is low) will never happen in real life due the linkage of the price of a feedstock to the price of final product.

Price estimations for different scenarios are presented in the Appendix to this report.

5.6 Conclusion

According to the rapidly growing interest for torrefied wood pellets, its potential market size can be as huge as coal market, particularly if a suitable binder can be identified that addresses major problems currently associated with torrefied wood pellets. This means that the solution for torrefied wood pellets binder issue becomes a primary task for the industry. Formulation of a cheap and environmentally friendly binder could potentially lead to rapid development of the torrefied wood pellets market, and increase profitability for producers of torrefied wood pellets.

As shown in the theoretical calculations in this report, Specified Risk Material (SRM) can be considered as a primary source for the new type of binder for torrefied wood pellets. However, a large volume of research and optimization needs to be done to bring the cost of SRM conversion to its minimum.

Chapter 6. Conclusion and future work

Eventually, an adhesive formulation was developed and it was able to pass all the ASTM requirements. And it was propylated SRM crosslinked with glutaraldehyde in the ratio of 8:1(w:w) with the total solid content 30%, coated on a wood veneer 1.6 mm thickness and hot pressed at 160 ^{o}C or higher.

The strategies that were proposed at the beginning of the experimental work were shown to be effective. Firstly, SRM can be used as a wood adhesive if crosslinked with glutaraldehyde. Water resistivity of the SRM can be improved by chemical modification through esterification reaction with alcohols. The higher the molecular weight of alcohol – the better the water resistance.

As the experimental data showed, the most significant factors affecting the water resistance were: crosslinking ratio and hot pressing temperature.

The crosslinking ratio depends on the amount of glutaraldehyde that can react with amine groups available in SRM. However, because it is impossible to calculate or experimentally determine the equivalent molecular weight of SRM, the mixing ratio with glutaraldehyde had to be found experimentally in terms of weight by weight ratio.

However, one of the most important parameters affecting the lap shear strength of the adhesive was the hot-pressing temperature. Similar results were found in reported literature [81]. The effect of hot pressing temperature can be explained mainly by completeness of evaporation of moisture from veneer samples [81].

Also, SRM-based adhesive is a hot melt adhesive in nature, which means that its reactivity with cellulose and lignin in the wood is enhanced by temperature, due to a better penetration of the adhesive in molten state into the surface roughness, forming more entanglements and resulting in forming a thermoset with higher dimensional stability and cohesive strength [25-26].

The future work for this research should concentrate on a large scale experiments, such as making a real-life size plywood boards, using the best formulations from this report, and testing its strength. Potentially, it might result in commercialization of the SRM-based adhesive.

Another experiment to be carried out using glutaraldehyde-crosslinked SRB-based adhesive is a wet lap shear strength test. Unlike the soak lap shear strength test, wet shear strength test only involves 48-hour soaking of the specimens with the strength testing of a wet samples without conditioning in a moisture chamber.

Also, it is strongly suggested to look into the formulation of the SRM-based adhesive using SRM obtained after the hydrolysis at 200 ^{o}C, 220 ^{o}C, and 240 ^{o}C.

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Appendcies

Appendix A

Cattle and Calves on Farms in Alberta										
January 1										
('000 Head)	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016p**
Bulls, 1 year plus	101.3	100.9	97.0	93.6	90.0	89.2	86.4	89.4	89.0	90.0
Beef cows	1,988.7	1,965.1	1,808.6	1,672.0	1,607.4	1,595.4	1,595.9	1,594.0	1,553.0	1,564.8
Milk cows	81.4	81.3	81.2	81.1	81.0	80.9	80.8	80.7	77.4	77.9
Heifers: dairy replacement	35.9	35.8	36.7	37.4	38.4	38.7	38.6	38.7	38.5	39.5
Heifers: beef replacement	253.7	247.1	213.5	204.9	219.3	218.3	225.6	224.1	213.6	224.8
Heifers: slaughter	644.2	645.5	594.2	636.8	575.5	625.5	619.5	615.3	580.0	575.5
Steers, 1 year plus	663.3	658.9	641.5	699.0	662.6	730.5	711.8	728.2	682.0	666.0
Calves, under 1 year	1,911.5	1,795.4	1,872.3	1,695.2	1,580.8	1,596.5	1,701.4	1,704.6	1,671.5	1,686.5
TOTAL	**5,680.0**	**5,530.0**	**5,345.0**	**5,120.0**	**4,855.0**	**4,975.0**	**5,060.0**	**5,075.0**	**4,905.0**	**4,925.0**
Total as % of Canada	**40.2**	**40.2**	**41.0**	**40.4**	**39.9**	**40.6**	**41.1**	**41.5**	**41.1**	**41.2**
July 1										
('000 Head)	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015r**
Bulls, 1 year plus	105.0	107.6	104.2	98.3	95.9	91.0	91.7	91.2	91.2	88.7
Beef cows	2,025.0	2,039.4	1,921.8	1,740.3	1,637.7	1,596.1	1,585.9	1,600.3	1,579.1	1,509.1
Milk cows	82.0	80.9	80.8	80.7	80.6	80.5	80.6	80.2	79.9	76.4
Heifers: dairy replacement	38.0	38.0	39.1	39.5	40.3	41.4	40.5	40.1	38.8	36.8
Heifers: beef replacement	278.0	285.4	269.8	254.2	254.6	275.4	262.0	261.3	252.1	248.1
Heifers: slaughter	812.0	838.7	757.3	801.0	739.6	753.7	756.4	776.6	764.6	724.6
Steers, 1 year plus	888.0	982.6	850.2	907.7	841.3	891.0	886.0	911.5	905.5	939.5
Calves, under 1 year	2,072.0	1,977.4	1,946.8	1,803.3	1,735.0	1,725.9	1,756.9	1,773.8	1,743.8	1,676.8
TOTAL	**6,300.0**	**6,350.0**	**5,970.0**	**5,725.0**	**5,425.0**	**5,455.0**	**5,460.0**	**5,535.0**	**5,455.0**	**5,300.0**
Total as % of Canada	**39.4**	**40.5**	**40.0**	**40.0**	**39.6**	**40.3**	**40.4**	**40.9**	**41.0**	**40.7**
Note: Data Subject to Revision **Sources:** Statistics Canada, Alberta Agriculture and Forestry										

Table 1: Total cattle and calves on all farms – Alberta, 2015[83]. Reproduced by permission of Government of Alberta

Appendix B

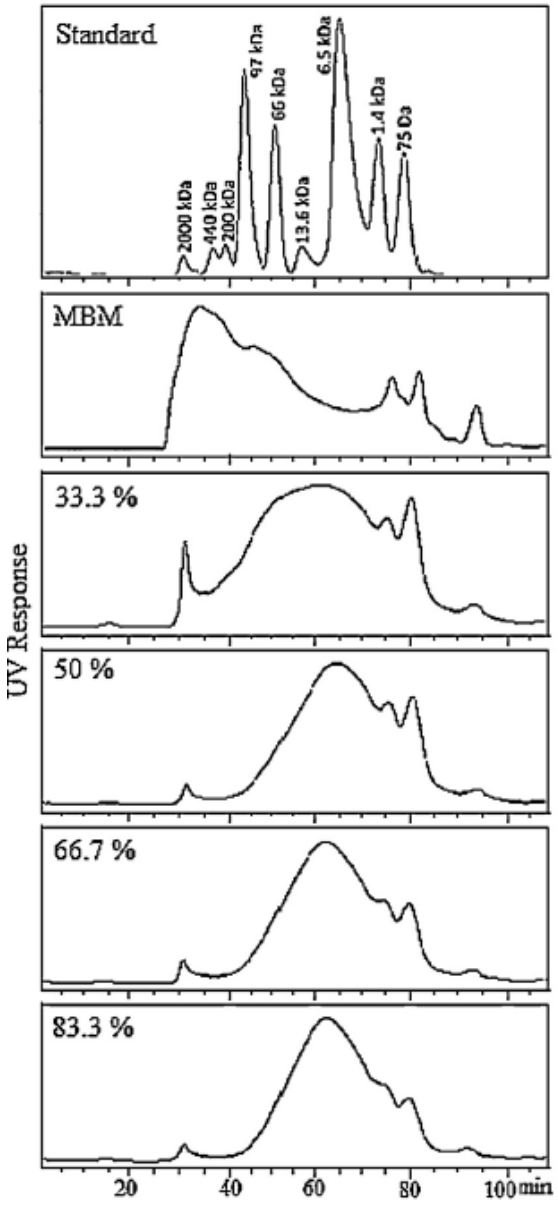

Figure 1: SEC-HPLC of thermally hydrolyzed SRM at 33.3%, 50%, 66.7%, and 83.3% concentration of water to the total mass [17]. Reproduced with the permission of Process Biochemistry, Elsevier ©

Temperature (°C)	Free amino acids (mg g^{-1}) in dry weight of the hydrolyzed SRM protein				
	180	200	220	240	260
Aspartic acid	1.17 ± 0.01^{a}	1.89 ± 0.01^{b}	1.55 ± 0.03^{a}	-	-
Glutamic acid	0.10 ± 0.02	-	-	-	-
Serine	0.84 ± 0.08^{a}	0.85 ± 0.00^{a}	-	-	-
Histidine	0.58 ± 0.02^{a}	0.77 ± 0.00^{b}	1.60 ± 0.01^{c}	-	-
Glycine	6.64 ± 0.01^{a}	8.47 ± 0.02^{b}	21.33 ± 0.08^{c}	23.02 ± 0.07^{c}	10.81 ± 0.01^{d}
Arginine	1.71 ± 0.30^{a}	1.80 ± 0.00^{a}	2.74 ± 0.01^{b}	0.01 ± 0.00^{c}	0.01 ± 0.00^{c}
Alanine	7.01 ± 1.20^{a}	7.11 ± 0.10^{a}	12.38 ± 0.13^{b}	23.43 ± 0.02^{c}	12.67 ± 0.01^{d}
Tyrosine	0.65 ± 0.11^{a}	0.62 ± 0.00^{a}	1.09 ± 0.01^{b}	1.55 ± 0.00^{c}	0.66 ± 0.00^{a}
Valine	1.00 ± 0.17^{a}	0.87 ± 0.00^{a}	2.21 ± 0.02^{b}	3.76 ± 0.02^{c}	2.23 ± 0.02^{b}
Methionine	0.86 ± 0.15^{a}	0.82 ± 0.01^{a}	1.41 ± 0.01^{b}	1.30 ± 0.06^{c}	-
Phenyalalanine	0.50 ± 0.09^{a}	0.55 ± 0.00^{a}	1.21 ± 0.0^{b}	1.87 ± 0.00^{c}	0.68 ± 0.01^{d}
Isoleucine	0.40 ± 0.07^{a}	0.37 ± 0.00^{a}	0.82 ± 0.02^{b}	1.79 ± 0.01^{c}	0.78 ± 0.02^{b}
Leucine	1.00 ± 0.17^{a}	1.05 ± 0.00^{a}	2.34 ± 0.02^{b}	3.74 ± 0.00^{c}	1.41 ± 0.00^{d}
Lysine	1.88 ± 0.30^{a}	1.74 ± 0.01^{a}	2.88 ± 0.01^{b}	6.30 ± 0.04^{c}	5.39 ± 0.03^{d}
Total	24.34 ± 2.53^{a}	26.91 ± 0.15^{a}	51.56 ± 0.26^{b}	66.73 ± 0.18^{c}	34.61 ± 0.12^{d}

Value – mean ± standard deviation
a-dMeans with the same superscript letters within a row are not significantly different at $P < 0.05$ level.

Figure 2: Free amino acids profile of hydrolyzed SRM [17]. Reproduced with the permission of Process Biochemistry, Elsevier ©

	MBM	SRM hydrolysis temperature (°C)				
		180	200	220	240	260
Aspartatic acid	61.9 ± 0.8^{a}	23.7 ± 1.8^{b}	21.4 ± 0.4^{b}	24.9 ± 0.8^{b}	-	-
Glutamic acid	119.4 ± 1.1^{a}	113.9 ± 6.9^{a}	102.4 ± 1.6^{b}	93.3 ± 2.0^{b}	138.3 ± 1.3^{c}	151.6 ± 3.4^{d}
Serine	31.5 ± 0.3^{a}	9.9 ± 0.6^{b}	8.1 ± 0.2^{b}	7.8 ± 0.2^{b}	-	-
Histidine	18.4 ± 0.2^{a}	11.8 ± 0.6^{b}	11.6 ± 0.3^{b}	10.3 ± 0.2^{b}	7.1 ± 0.1^{b}	0.5 ± 0.1^{c}
Glycine	136.1 ± 3.8^{a}	108.2 ± 6.5^{b}	108.4 ± 2.0^{b}	102.7 ± 1.6^{c}	101.3 ± 0.9^{c}	64.0 ± 1.6^{d}
Threonine	24.9 ± 0.2^{a}	7.8 ± 0.5^{b}	6.8 ± 0.1^{c}	5.3 ± 0.1^{d}	-	-
Arginine	66.4 ± 3.3^{a}	38.2 ± 2.0^{b}	39.2 ± 0.6^{b}	40.8 ± 1.1^{b}	1.1 ± 1.9^{c}	-
Alanine	72.3 ± 0.6^{a}	68.6 ± 4.2^{a}	67.8 ± 1.1^{a}	60.0 ± 1.0^{b}	54.3 ± 0.4^{c}	46.4 ± 1.1^{d}
Tyrosine	22.3 ± 0.3^{a}	19.0 ± 1.0^{a}	22.8 ± 0.4^{a}	19.0 ± 1.8^{a}	26.5 ± 0.1^{a}	24.5 ± 2.0^{a}
Valine	29.1 ± 1.1^{a}	32.6 ± 1.9^{a}	32.2 ± 0.6^{a}	27.5 ± 0.5^{a}	30.9 ± 0.5^{a}	23.4 ± 0.7^{b}
Methionine	15.3 ± 5.1^{a}	11.2 ± 0.5^{a}	8.2 ± 3.5^{b}	7.6 ± 2.1^{b}	8.3 ± 0.8^{b}	4.8 ± 0.3^{c}
Phenylalanine	22.4 ± 3.2^{a}	25.5 ± 1.5^{a}	25.0 ± 0.4^{a}	21.6 ± 0.4^{a}	20.4 ± 1.4^{a}	17.2 ± 2.3^{a}
Isoleucine	21.3 ± 0.2^{a}	22.0 ± 1.3^{a}	21.7 ± 0.5^{a}	18.6 ± 0.4^{a}	18.0 ± 0.2^{a}	11.9 ± 0.3^{b}
Leucine	38.9 ± 0.2^{a}	47.1 ± 2.8^{b}	45.3 ± 0.8^{b}	39.8 ± 0.8^{a}	35.4 ± 0.3^{a}	21.2 ± 0.6^{c}
Lysine	36.5 ± 2.5^{a}	33.7 ± 3.2^{a}	32.2 ± 0.4^{a}	29.0 ± 1.0^{a}	24.4 ± 1.6^{b}	13.9 ± 1.2^{c}
Total	716.7 ± 16.4^{a}	573.2 ± 33.1^{b}	553.1 ± 23.5^{b}	508.2 ± 9.9^{c}	466.7 ± 4.15^{d}	373.4 ± 9.4^{e}

Value – mean ± standard deviation (n = 3).
[a-e] Means with the same superscript letters within a row are not significantly different at $P < 0.05$ level.

Figure 3: Total amino acid profile of hydrolyzed SRM [17]. Reproduced with the permission of Process Biochemistry, Elsevier ©

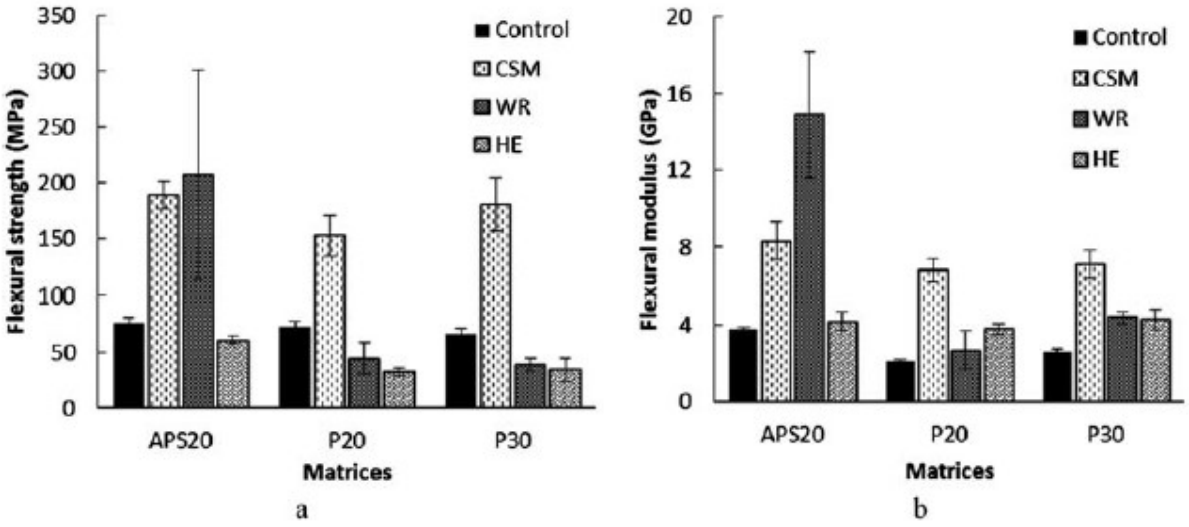

Figure 4: Flexural strength and flexural modulus of composites reinforced with CSM, WR, and HE fibers [23]. Reproduced from an open access article.

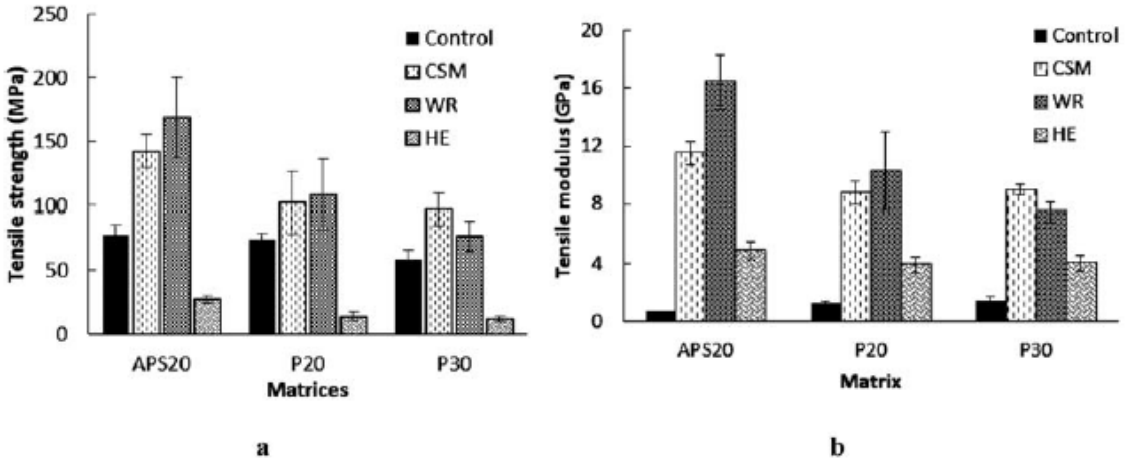

Figure 4: Tensile strength and tensile modulus of composites reinforced with CSM, WR, and HE fibers [23]. Reproduced from an open access article.

Forces	Physical bonds			Hydrogen bridge bonds	Chemical bonds	
	Permanent dipoles	Induced dipoles	Dispersion forces		Covalent	Ionic
Range (nm)		0.3–0.5		0.3–0.5	0.1–0.2	
Bonding energy (kJ mol^{-1})	<20 (Keesom energy)	<2 (Debye energy)	0.1–40 (London energy)	<50	60–700	600–1000
Mathematically calculated adhesion forces (MPa)	200–1750	35–300	60–360	500	17500	5000; 30
Strength of the assemblies as measured experimentally (MPa)	15–25					

Table 1: Types of interactions in interfaces [26]. Reproduced with the permission of Wiley Books, Joh Wiley and Sons ©

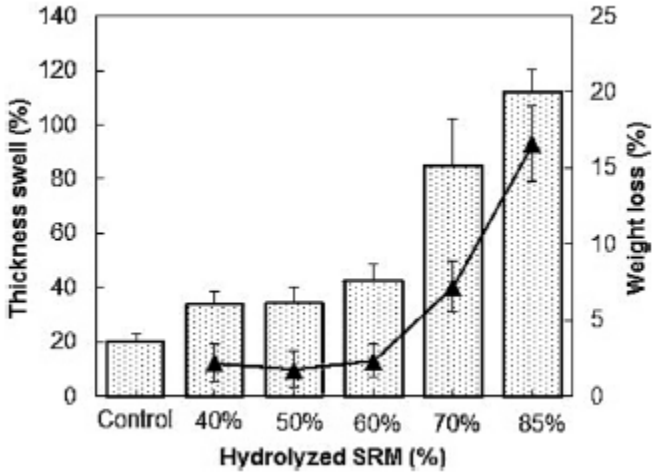

Figure 5: Thickness swell of OSB panels using MDI crosslinked with hydrolyzed protein [20]. Reproduced by permission of Macromolecular Materials and Engineering, John Wiley and Sons ©

Factors	Level 1	Level 2	Level 3
Protein conc. DWB [wt.-%]	20	30	40
Glutaraldehyde–resorcinol resin conc. DWB [wt.-%]	10	25	40
Mole ratio	1:2	1:1	1:0.5
SRM hydrolysis temp. [°C]	180	200	220

Table 2: Components and their concentrations in plywood adhesive [21]. Reproduced by permission of Macromolecular Materials and Engineering, John Wiley and Sons ©

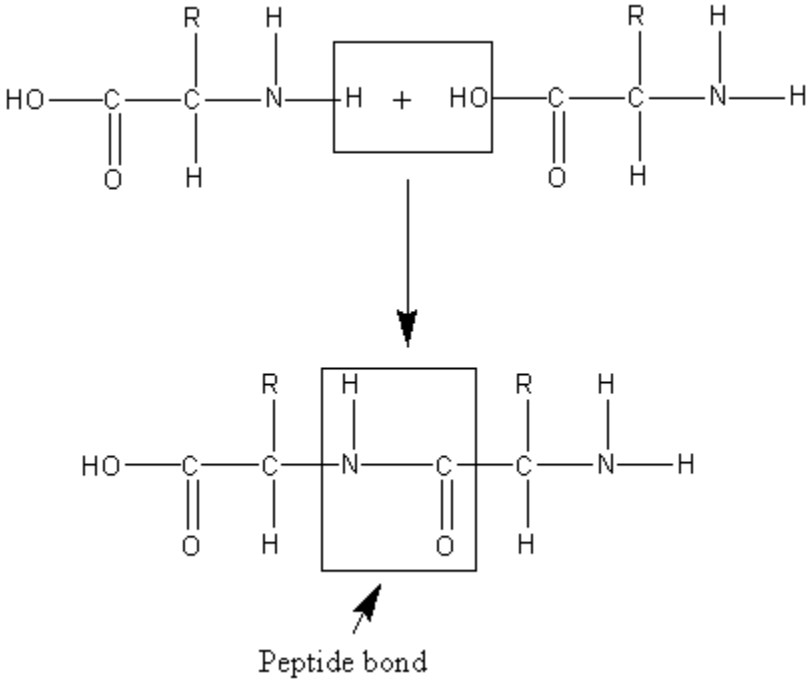

Figure 6: Peptide bond formation mechanism

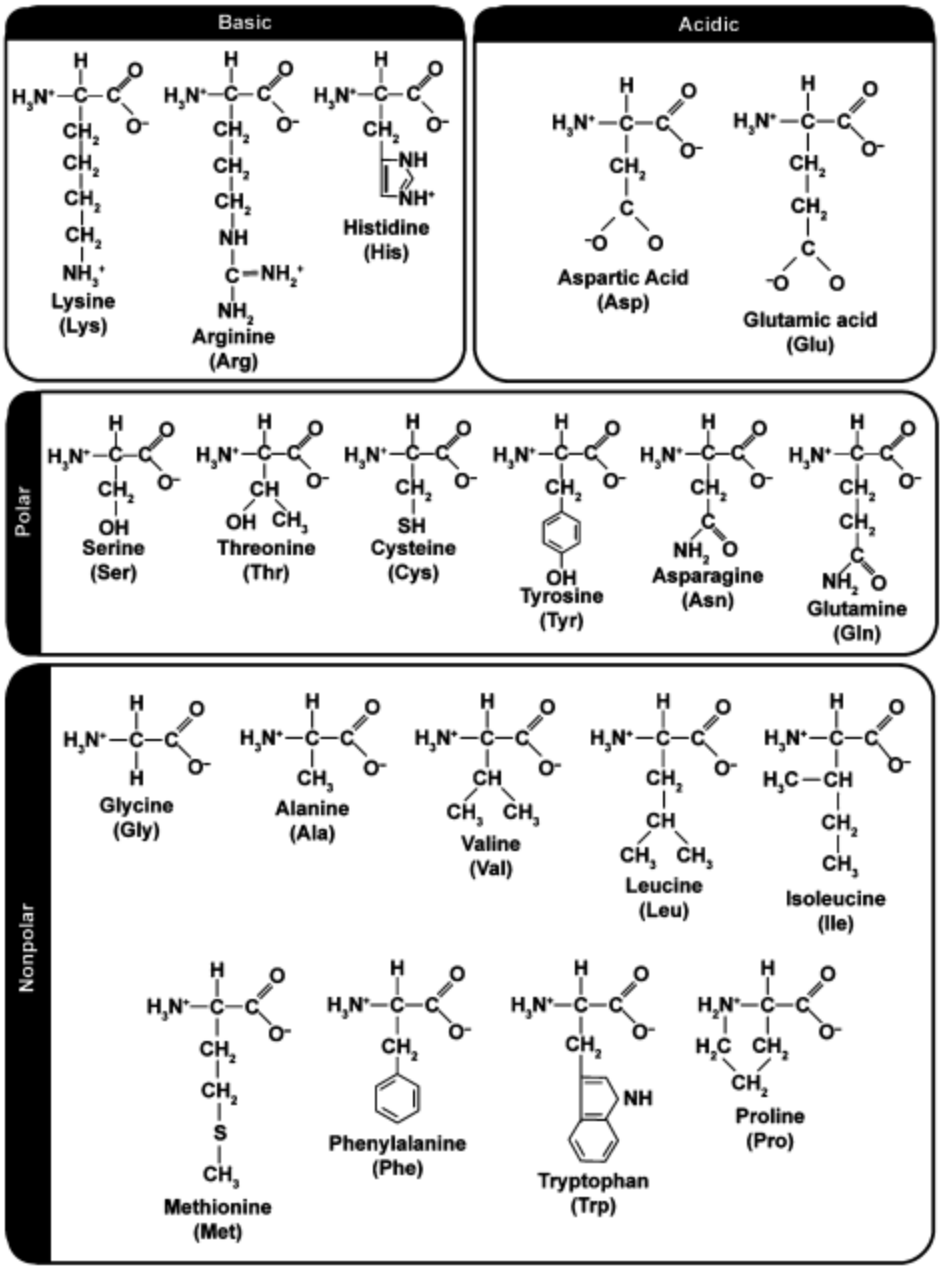

Figure 7: Amino acid side chains [44]. Reproduced by permission of American Chemical Society ©

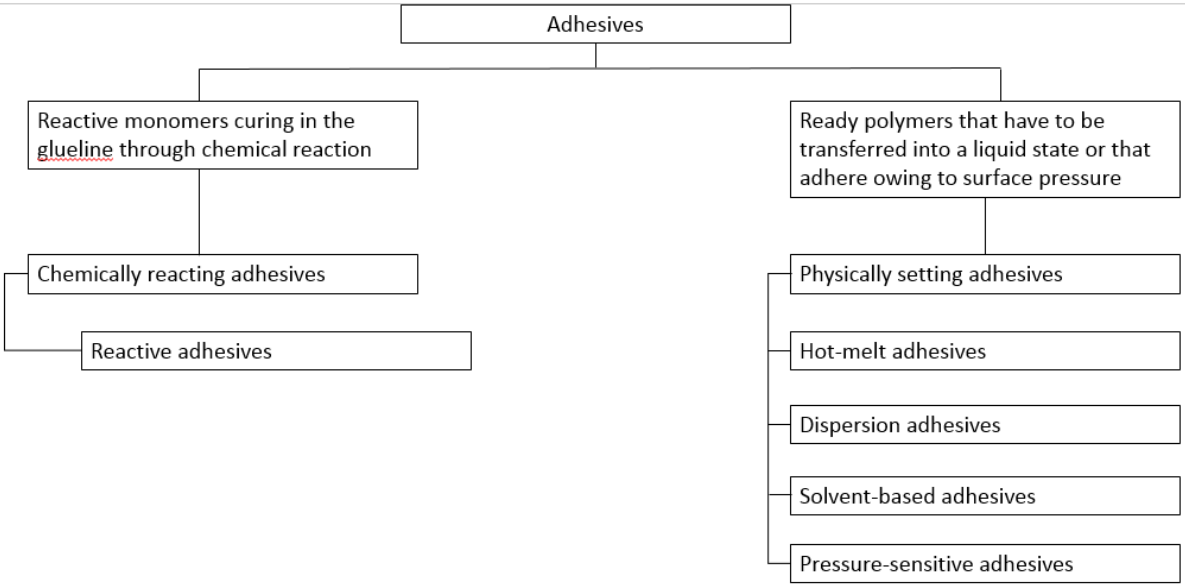

Figure 8: Adhesive materials classification according to the type of curing [26]

Appendix C

In Chapter 5 a pessimistic scenario has been considered, when the purchase price of torrefied wood and resin is the highest possible and the price at which pellets are sold is relatively low.

However, the opposite scenario is also possible. In this Appendix various scenarios have been considered.

1. Resin and torrefied wood has been purchased at the lowest price, $500/tonne and $100/tonne respectively, and pellets have been sold at the highest estimated price of $275/tonne:

For 1 tonne of torrefied wood pellets			
	1%	2%	3%
Amount of binder needed, kg	10	20	30
Amount of Resin needed, kg	2.3	4.6	6.9
Amount of torrefied wood needed, kg	990	980	970
Amount of Hydrolyzed SRM needed, kg	7.7	15.4	23.1
Amount of raw SRM needed, kg	22	44	66
Price of resin ($/1 tonne of pellets)	$1.15	$2.30	$3.45
Price of torrefied wood ($/1 tonne of pellets)	$99.00	$98.00	$97.00
Price of raw SRM ($/1 tonne of pellets)	$0.00	$0.00	$0.00
Price of pelletization process ($/1 tonne of pellets)	$6.21		
Price of SRM processing ($/1 tonne of pellets)	**$168.64**	**$167.49**	**$166.34**
Price of processing SRM to pellets, $/1 tonne of raw SRM	**$7,665.39**	**$3,806.56**	**$2,520.28**

Table C1: Optimistic case, when the resin and torrefied wood is cheap and the torrefied pellets price is high

In this case, the amount of money the manufacturer can spend on conversion of SRM into a binder goes up to $7,665.39 per tonne of raw SRM. However, this amount is only a breakeven price of SRM

processing, which means that if the amount spent on SRM processing is less than $7,665.39 per tonne, the difference becomes a profit.

2. It is important to mention that all the cases considered assume that raw SRM has been obtained for free. However, the raw SRM price has a significant impact on the breakeven price of SRM processing. Consider exactly the same case, but assume that now we have to buy raw SRM at $100/tonne.

For 1 tonne of torrefied wood pellets			
	1%	2%	3%
Amount of binder needed, kg	10	20	30
Amount of Resin needed, kg	2.3	4.6	6.9
Amount of torrefied wood needed, kg	990	980	970
Amount of Hydrolyzed SRM needed, kg	7.7	15.4	23.1
Amount of raw SRM needed, kg	22	44	66
Price of resin ($/1 tonne of pellets)	$1.15	$2.30	$3.45
Price of torrefied wood ($/1 tonne of pellets)	$99.00	$98.00	$97.00
Price of raw SRM ($/1 tonne of pellets)	$100.00	$100.00	$100.00
Price of pelletization process ($/1 tonne of pellets)	$6.21		
Price of SRM processing ($/1 tonne of pellets)	**$68.64**	**$67.49**	**$66.34**
Price of processing SRM to pellets, $/1 tonne of raw SRM	**$3,119.94**	**$1,533.83**	**$1,005.13**

Table C2: Optimistic case, when the resin and torrefied wood is cheap and the torrefied pellets price is high and the raw SRM purchase price is $100/tonne

It is obviously that the breakeven price of raw SRM conversion is approximately two times lower once the raw SRM price goes up from \$0/tonne to \$100/tonne. For the most pessimistic scenario from the Chapter 3.1 the breakeven price becomes negative once the price of raw SRM goes up to \$100/tonne. This means that with those resin, torrefied wood prices, and raw SRM purchase price the SRM conversion into a binder will never give a profit.

Production of a binder for torrefied wood pellets

In Chapter 5.4 there have been considered the most pessimistic and the most optimistic scenarios for SRM conversion into a binder process. However, those estimations have been done with an assumption of a purchase price of raw SRM at \$0/tonne. If, for the worst case scenario the purchase price of raw SRM becomes \$100/tonne, then the following results are obtained:

For 1 tonne of a binder	
Amount of resin required, kg	230.00
Amount of Hydrolyzed SRM required, kg	770.00
Amount of non-Hydrolyzed SRM required, kg	2,200.00
Price of Resin, $/1 tonne of a binder	$177.47
Price of raw SRM, $/1 tonne of a binder	$100.00
Price of processing SRM into a binder, $/1 tonne of a binder	**-$77.47**
Price of processing SRM into a binder, $/1 tonne of raw SRM	**-$35.21**

Table C3: The breakeven price of raw SRM conversion into a binder when the resin price is high ($771/tonne) and the competitors' price of the binder is low, assuming the SRM purchase price $100/tonne

Table C clearly shows that if the price of resin is high and the price of manufactured binder is low, the expenses of the SRM conversion into a binder process become higher than the income.

Similarly, for the best market scenario, if the raw SRM purchase price goes as high as $200/tonne, the breakeven price of 1 tonne of SRM processing decreases only to $311 (Table C4)

For 1 tonne **of a binder**	
Amount of resin required, kg	230.00
Amount of Hydrolyzed SRM required, kg	770.00
Amount of non-Hydrolyzed SRM required, kg	2,200.00
Price of Resin, $/1 tonne of a binder	$115.00
Price of raw SRM, $/1 tonne of a binder	$200.00
Price of processing SRM into a binder, $/1 tonne of a binder	**$685.00**
Price of processing SRM into a binder, $/1 tonne of raw SRM	**$311.36**

Table C4: The breakeven price of raw SRM conversion into a binder when the resin price is low ($771/tonne) and the competitors' price of the binder is low, assuming the SRM purchase price of raw SRM is $200/tonne

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