JCNaR
Journal of Chemical Natural Resources
Journal homepage: https://jcnar.usu.ac.id

# Synthesis of Cellulose Ether from Alkoxylyted Epoxide Methyl Esters Fatty Acids Rubber Seed Oil with Cellulose

Rayzki Ananta Keliat, Adil Ginting*
*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Medan, 20155, Indonesia*
*Corresponding Author: ginting.adil@yahoo.com

**ARTICLE INFO**
**Article history:**
Received 13 December 2022
Revised 23 January 2023
Accepted 14 February 2023
Available online 18 May 2023

E-ISSN: 2656-1492

**How to cite:**
Rayzki Ananta Keliat, Adil Ginting. Synthesis of Cellulose Ether from Alkoxylyted Epoxide Methyl Esters Fatty Acids Rubber Seed Oil with Cellulose. Journal of Chemical Natural Resources. 2023. 5(1):18-25.


https://doi.org/10.32734/jcnar.v5i1.11987

**ABSTRACT**

The alkoxylation reaction was carried out between the fatty acid methyl ester epoxide of rubber seed oil (RSO) and cellulose to produce cellulose ether. RSO was obtained from rubber seed by extraction method with n-hexane solvent followed by a purification process including a degumming stage, bleaching and neutralization. The RSO obtained was further dimetanolized with a NaOH catalyst producing a fatty acid methyl ester which is then epoxidized with a performance acid to give the epoxide compound. The resulting epoxide compound was reacted with cellulose in an isopropanol solvent, producing ether cellulose. RSO obtained as much as 46.75% with a free fatty acid content of 0,2184%, iodine amount, and unsaturated fatty acid content of 82,4%. The resulting ether cellulose was found to be vibrations in the area waves number of ($\bar{\upsilon}$) = 1118 $cm^{-1}$, which indicates the presence of C-O-C bonds from the ether, which can indicate that an etherification reaction has occurred in cellulose. This is also supported by the presence of vibrations at wave numbers ($\bar{\upsilon}$) = 1743 $cm^{-1}$, ($\bar{\upsilon}$) = 1165 $cm^{-1}$, ($\bar{\upsilon}$) = 1118 $cm^{-1}$, ($\bar{\upsilon}$) = 725 $cm^{-1}$, each of which shows the existence of a bond (C = O) from the ester, CH3 bond, C – O bond from the ester and bond to carbon ($CH_2$) n where n ≥ 4, which is not found in cellulose but is found in cellulose ether. It shows that an alkoxylation epoxide reaction of MEAL rubber seed oil with cellulose has occurred, which will produce cellulose ether.

**Keywords:** Alkoxylation, Cellulose, Epoxidation, Rubber Seed Oil

**ABSTRAK**

Reaksi alkoksilasi dilakukan antara asam lemak metil ester epoksida minyak biji karet dan selulosa untuk menghasilkan selulosa eter. Minyak biji karet diperoleh dari biji karet dengan metode ekstraksi dengan pelarut n-heksana yang dilanjutkan dengan proses pemurnian yang meliputi tahap deguming, bleaching dan netralisasi. Minyak biji karet yang diperoleh kemudian dimetanol dengan katalis NaOH untuk menghasilkan metil ester asam lemak yang kemudian diepoksidasi dengan performance acid untuk menghasilkan senyawa epoksida. Senyawa epoksida yang dihasilkan direaksikan dengan selulosa dalam pelarut isopropanol untuk menghasilkan selulosa eter. Didapatkan minyak biji karet murni sebanyak 46,75% dengan kadar asam lemak bebas 0,2184%, kadar yodium dan kadar asam lemak tak jenuh 82,4%. Vibrasi selulosa eter yang dihasilkan terdapat pada daerah bilangan gelombang ($\bar{\upsilon}$) = 1118 $cm^{-1}$ yang mengindikasikan adanya ikatan C-O-C dari eter yang dapat mengindikasikan telah terjadi reaksi eterifikasi pada selulosa. Hal ini juga didukung dengan adanya getaran pada bilangan gelombang ($\bar{\upsilon}$) = 1743 $cm^{-1}$, ($\bar{\upsilon}$) = 1165 $cm^{-1}$, ($\bar{\upsilon}$) = 1118 $cm^{-1}$, ($\bar{\upsilon}$) = 725 $cm^{-1}$, berturut-turut menunjukkan adanya ikatan (C=O) dari ester, ikatan CH3, ikatan C – O dari ester dan ikatan dengan karbon ($CH_2$) n dimana n ≥ 4, yang tidak terdapat dalam selulosa tetapi terdapat dalam selulosa eter. Hal ini menunjukkan telah terjadi reaksi alkoksilasi epoksida epoksida minyak biji karet MEAL dengan selulosa yang akan menghasilkan selulosa eter.

**Keyword:** Alkoksilasi, Epoksidasi, Minyak Biji Karet

## 1. Introduction

The use of renewable and sustainable bio-resources has positive effects on agriculture, the environment, industry and the economy. Since bio-based materials are widely applicable, such as packaging, tissue engineering and reinforcement of polymer composites, researchers have tried to replace petroleum-based materials with renewable ones. Researchers have studied natural resources such as starch and cellulose to search for new macromolecular materials because of their accessibility [1].

Cellulose is the most abundant organic compound polymer on earth. Production of cellulose from plants is predicted to reach 10-12 tons annually. Each plant is believed to contain at least 33% cellulose; wood contains about 50% cellulose, while cotton contains about 90% cellulose [2]. B-1-4 glycosidic bonds bond glucose units in cellulose, are the most common organic substances, and have intermolecular hydrogen bonds, resulting in a linear and rigid structure. Therefore, cellulose has attracted significant interest as an excellent reinforcement for biocomposites [3]. Due to its excellent mechanical properties, lightweight, and biodegradability, it is of interest not only for environmental reasons but also for high-performance admixtures, process advantages and low costs [4].

Indonesia is an agricultural country with a variety of biodiversity, including the rubber plant (*Hevea brasiliensis*). Until now, the production of rubber plants has only focused on the processing of latex and stems, while other products, such as seeds, have not received more attention. Rubber seed oil is a by-product of rubber plantations that can be used as a source of oil for biodiesel. Rubber seeds contain 40-50% oil by weight of the seeds. Rubber seed oil contains 17-21% oleic acid, 35-38% linoleic acid, 21-24% linolenic acid, 1% arachidic acid, 5-12% stearic acid, 9-12% palmitic acid, and 2-20% acid other free fats [5].

Chemical modification of starch, cellulose and other materials related to the insertion of alkyl chains has been studied to obtain hydrophobic materials. Some modifications of cellulose with the insertion of alkyl chains are the insertion of alkyl chains 8 and 12 [6], the insertion of alkyl laurate chains [7] and the insertion of alkyl chains 8 to 20 [8].

## 2. Materials and Methods

This research is an experiment in the Organic Chemistry Laboratory at FMIPA-USU Medan. The rubber seeds used were obtained from farmers in Binjai City, and the chemicals used, both reagents and organic solvents, were pa grade and made by E. Merck. The steps taken in its implementation follow the following procedure:

### *2.1. Extraction of Rubber Seed Oil*

Fruit rubber is separated from the skin. Then seed fruit rubber was cut small and dried. Then seed rubber that has been dry mashed with a blender and macerated with solvent–hexane for four days. After filtering, the filtrate obtained was dried with anhydrous $Na_2SO_4$ and then filtered. The filtrate obtained was evaporated using a rotary evaporator. The oil obtained was weighed and analyzed for its iodine number and fatty acid content.

### *2.2. Refining Rubber Seed Oil*

Rubber seed oil purification is carried out to remove impurities in the form of gum, reduce free fatty acid content and remove colour, which is carried out through the following stages:

1) Degumming and Bleaching

Oil seed rubber results extraction entered into the Erlenmeyer vacuum, adding Sour Phosphate as much as 0.02 % and bleaching earth as much as 2% of heavy oil and heating on temperature 110$^oC$ for 15 minutes in circumstances vacuum while stirred with a magnetic stirrer and then filtered with paper strain Whatman no. 42 with help pump vacuum. The obtained oil content was added n–hexane and $Na_2SO_4$ anhydrous and then purified. The filtrate obtained evaporated the solvent with a rotary evaporator. The obtained oil content was analyzed sour the fat.

2) Neutralization Process

Oil seed rubber results degumming entered into the Erlenmeyer vacuum And added solution NaOH 10% by stoichiometry from content sour fat-free. They were then stirred until homogeneous and heated at 50° C for 15 minutes in a circumstances vacuum. They were stirred with a magnetic stirrer and filtered with paper strain Whatman no. 42 with a helpful tool vacuum. The obtained oil was added with n–hexane, dried with $Na_2SO_4$

anhydrous, and Then filtered. The filtrate obtained evaporated the solvent with a rotary evaporator. The results obtained were weighed, and analyzed the iodine value and analyzed content sour fat-free.

*2.3. Preparation of Fatty Acid Methyl Esters from Rubber Seed Oil*

As much as 50 g of rubber seed oil was put into a two-neck flask and assembled reflux apparatus with a ball cooler. They were heated to a temperature of 50ºC. Then, 0.25 g of NaOH was added and dissolved in 15 ml of methanol through a dropper funnel and refluxed at 70 ° C for 45 minutes. Then the mixture was put into a separating funnel, cooled, and stood for ± 15 minutes until two layers were formed. The top layer was added 50 ml of n–hexane, washed three times with 15 ml of aquadest each, dried with anhydrous $Na_2SO_4$, and filtered. The filtrate obtained was evaporated with a rotary evaporator. The results obtained were analyzed by GC and FTIR spectroscopy.

*2.4. Manufacture epoxide Acid Methyl Esters Fat Oil Seed Rubber*

As much as 60 ml of formic acid 90%, and 30 ml of $H_2O_2$ 30%, were added via a funnel dropper while stirred. Furthermore, 2 ml of $H_2SO_4$ was added through a funnel dropper and stirred with a magnetic stirrer at 40 to 45ºC for 1 hour. Furthermore, 50 ml of acid methyl ester was added to fat seed rubber through a funnel dropper and maintained temperature warmup at 40 to 45ºC for 2 hours. The results obtained were entered into the funnel separately, and 50 ml of *n*–hexane was added to form two layers. Layer on. They then evaporated the solvent with a rotary evaporator. The results obtained in the analysis number the iodine and analyzed with FTIR spectroscopy.

*2.5. Preparation of Cellulose Ethers Through Alcocylation of Epoxide Methyl Ester Fatty Acid Rubber Seed Oil with Cellulose*

As much as 1 g of cellulose is put into the beaker glass. Then 20 ml of 10% NaOH was added and stirred with a magnetic stirrer for 1 hour at room temperature and filtered. The precipitate was put into a 2-neck flask, and 20 ml of isopropanol was added. Then, 6.48 g of methyl ester fatty acid epoxide of rubber seed oil was added through a dropper funnel while stirring and heated at 60° C for 5 hours while stirring with a magnetic stirrer. The mixture is cooled and neutralized with 90% acetic acid. Then 20 ml of acetone was added and filtered. The precipitate was washed with 80% acetone, as much as 50 ml, and then dried in the oven at 50ºC for one night. The results obtained were weighed and analyzed by FTIR spectroscopy.

*2.6 Analysis of Rubber Seed Oil and Synthesized Cellulose Ether*

Free fatty acid content was handled by acid-alkalimetry titration using 0.1 N NaOH standard solution (SNI 01-3555-1998), iodine number by iodometric titration using $Na_2S_2O_3$ solution using Wijs reagent, functional group analysis using FTIR spectroscopy and fatty acid composition by GC analysis.

## 3. Results and Discussion

*3.1. Oil Extraction and Refining*

The extracted rubber seed oil using n-hexane solvent obtained an oil content of 50.15%, a free fatty acid content of 5.7%, an iodine number of 112.095, and a dark yellow colour. For further research, the extracted rubber seed oil was then subjected to a purification process: Bleaching using bleaching earth, degumming using phosphoric acid and neutralization with 10% NaOH. The refining process results obtained an oil content of 46.75%, a free fatty acid content of 0.2184%, an iodine number of 108.9566 and a bright yellow oil.

*3.2. Preparation of Fatty Acid Methyl Esters of Rubber Seed Oil*

The fatty acid methyl esters of rubber seed oil were obtained from the methanolization of rubber seed oil using a NaOH catalyst. From 50 g of rubber seed oil reacted, 46 g of methyl ester was obtained. The results of gas chromatography analysis of the MEAL of rubber seed oil gave a chromatogram with a fatty acid composition consisting of $C_{16}$ = 8.885 %, $C_{18}$ = 8.448%, $C_{18:1}$ = 23.996 %, $C_{18:2}$ = 39.767 % and $C_{18:3}$ = 18.271 %. Furthermore, the results of the examination through FTIR analysis (Figure 1) provide the support that rubber seed oil contains unsaturated hydrocarbons where vibrations are found at wave number ($\bar{\upsilon}$) = 3001 cm -1, which indicates bonds (C=CH) $^{of}$ fatty acids unsaturated, ($\bar{\upsilon}$) = 1743 cm $^{-1}$ which indicates the (C=O) bond of the ester, ($\bar{\upsilon}$) = 1373 cm $^{-1}$ which indicates the presence of $CH_3$, ($\bar{\upsilon}$) = 1165 cm $^{-1}$ which indicates the presence of C– The O is from the ester and at ($\bar{\upsilon}$) = 725 cm $^{-1}$ is the bond on the carbon $(CH_2)n$ where $n \geq 4$ of the rubber seed oil fatty acid chain.

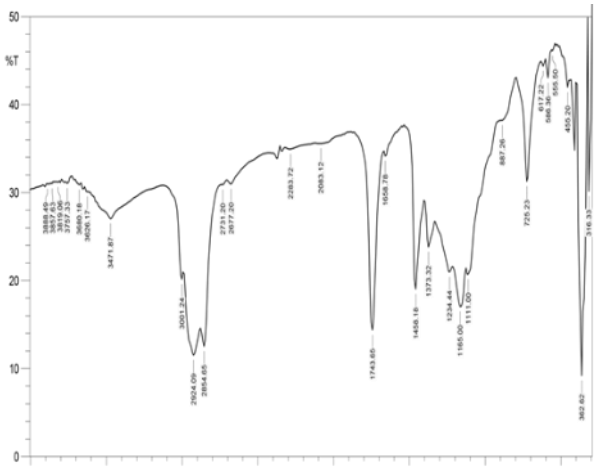


Figure 1. The FTIR spectrum of fatty acid methyl esters of rubber seed oil

*3.3. Epoxide Methyl Esters Fatty Acids Rubber Seed Oil*

The MEAL epoxide of rubber seed oil was obtained by reacting the unsaturated MEAL hydrocarbons with performic acid and a sulfuric acid catalyst (Figure 2). In this reaction, each π bond of the unsaturated fatty acid undergoes epoxidation to form an epoxide ring (oxirane).

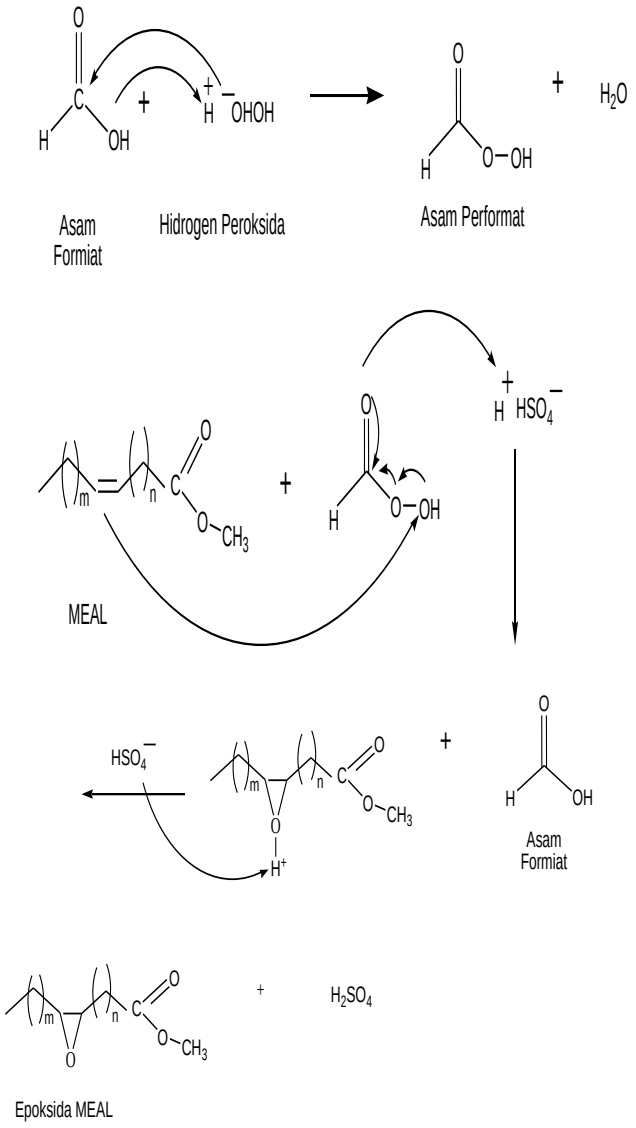


Figure 2. Epoxidation Reaction of methyl esters fatty acid of rubber seed oil

The occurrence of epoxidation reactions in the π bonds of unsaturated fatty acids can be seen from the difference in iodine numbers and FTIR spectra between the MEAL of rubber seed oil and the epoxide MEAL of rubber seed oil. The analysis results of determining the iodine number show a decrease in the iodine number, wherein rubber seed oil has an iodine number of 108.9566 to 10.6985. The FTIR spectroscopy analysis results found differences between the MEAL of rubber seed oil and the epoxide MEAL of rubber seed oil. In the FT-IR spectrum of epoxide MEAL, rubber seed oil (Figure 3), the loss of vibration at wave number ($\bar{\upsilon}$) = 3001 $cm^{-1}$, which shows the bond (C=CH) of unsaturated fatty acids proves that an epoxidation reaction has occurred in the π bonds of unsaturated fatty acids.

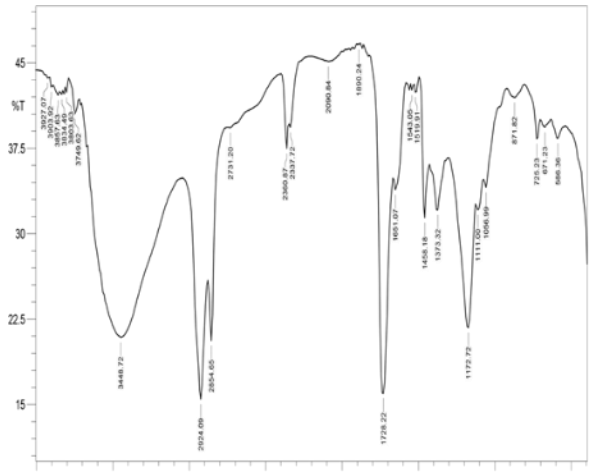


Figure 3. The FTIR spectrum methyl esters fatty acid epoxide of rubber seed oil

*3.4. Preparation of Cellulose Ethers from Alkoxylation of Epoxide Methyl Ester Fatty Acids of Rubber Seed Oil with Cellulose*

The cellulose ether results from alkylation and alkoxylation of the epoxide MEAL of rubber seed oil with cellulose where 1 g of cellulose used, 0.9386 g of cellulose ether was obtained. The alkalization process is carried out in the presence of the addition of NaOH, where the primary –OH on the C6 atom of cellulose reacts with NaOH to form Sodium Cellulose.

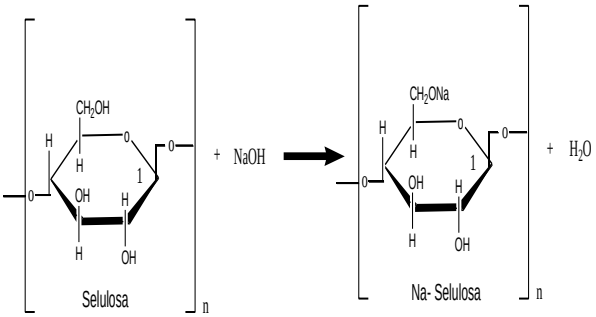


Figure 4. Alkalization of Cellulose

The alkoxylation process of the epoxide MEAL of rubber seed oil with sodium cellulose and isopropanol as a solvent will break the oxirane (epoxide) ring and continue with neutralization with acetic acid to produce cellulose ether compounds (Figure 4).

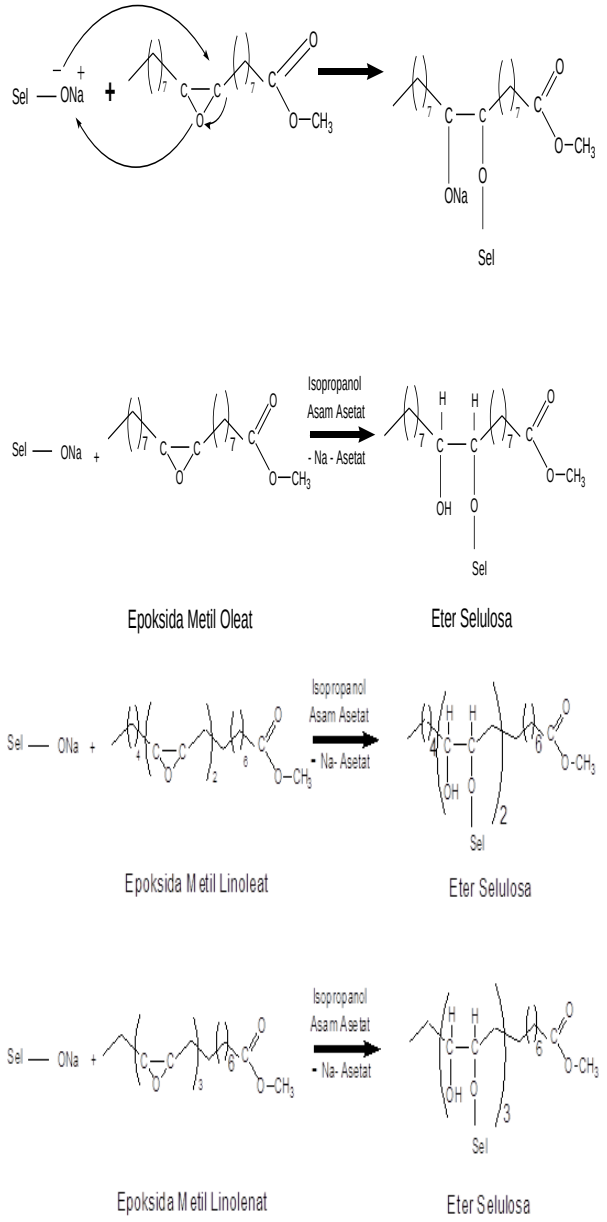


Figure 5. Alkoxylation Reaction Meal of Epoxide MEAL Rubber Seed Oil with Cellulose

The low nucleophilicity of the hydroxyl groups in cellulose can be increased by converting it into cellulose alkoxides which are more reactive than cellulose. Epoxides consisting of three rings containing oxygen are highly reactive. Hypothetically the cellulose alkoxy group will be bonded to the C atom of the epoxide ring, which is closer to the O atom than carbonyl and methoxy, which has a large electronegativity so that electrons will be attracted to the O atom, which causes the C atom to have a partial positive charge (Figure 5).

The formation of cellulose ether can be seen from the difference in the FT – IR spectra of cellulose and cellulose ether. In the FT – IR spectrum of cellulose (Figure 6), vibrations were found at wave number ($\bar{\upsilon}$) = 3348 cm $^{-1,}$ indicating the presence of hydroxyl groups (-OH) in cellulose, ($\bar{\upsilon}$) = 1635 cm $^{-1}$ indicating bonds (C=O ) of the aldehyde, ($\bar{\upsilon}$) = 1056 cm $^{-1}$ which indicates the presence of symmetrical C–O bonds in cellulose. In the FT – IR spectrum of cellulose ether (Figure 7), vibrations were found at wave number ($\bar{\upsilon}$) = 3425 cm $^{-1,}$ indicating the presence of hydroxyl groups (-OH), ($\bar{\upsilon}$) = 1651 cm $^{-1,}$ indicating bonds (C=O) of the aldehydes in cellulose. The appearance of vibrations at wave number ($\bar{\upsilon}$) = 1118 cm $^{-1}$ indicates the presence of COC bonds from the ether, indicating an etherification reaction in cellulose. This is also supported by the presence of vibrations at wave numbers ($\bar{\upsilon}$) = 1743 cm $^{-1}$, ($\bar{\upsilon}$) = 1165 cm $^{-1}$, ($\bar{\upsilon}$) = 1118 cm $^{-1}$, ($\bar{\upsilon}$) = 725 cm $^{-1,}$ which respectively indicate there is a (C=O) bond from the ester, a $CH_3$ bond, a C–O bond from the ester and a bond on the carbon $(CH_2)n$ where $n \geq 4$, which is not found in cellulose but is found in cellulose ether. This indicates

that there has been an alkoxylation reaction of the MEAL epoxide MEAL of rubber seed oil with cellulose which will produce cellulose ether.

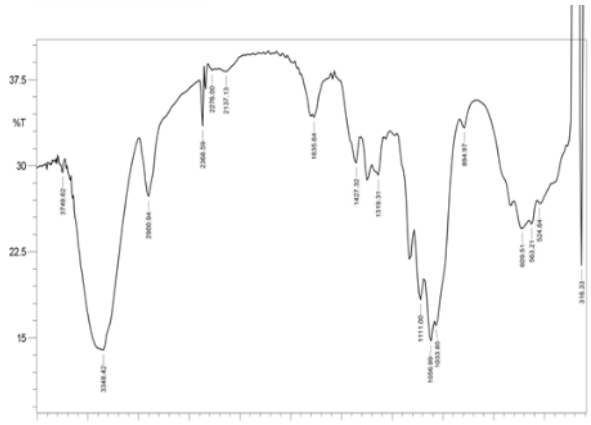


Figure 6. FT – IR Spectrum of Cellulose

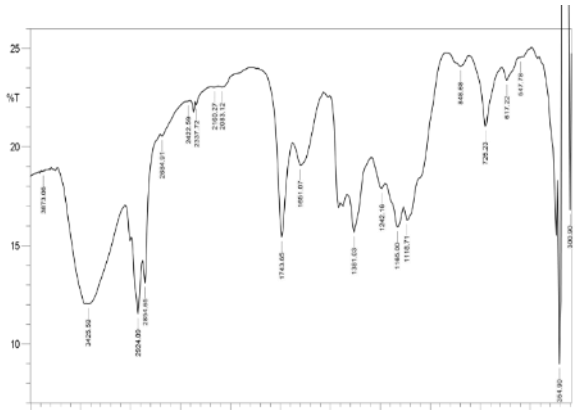


Figure 7. FT – IR Spectrum of Cellulose Ether

## 4. Conclusion

The cellulose ether compound's results were characterized by FTIR spectroscopy to prove that cellulose ether had been formed. The results of the FTIR spectrum of cellulose found vibrations in the region of wave number ($\bar{\upsilon}$) = 1118 $cm^{-1,}$ indicating the presence of C-O-C bonds from ether which could indicate that an etherification reaction had occurred in cellulose. This is also supported by the presence of vibrations at wave numbers ($\bar{\upsilon}$) = 1743 $cm^{-1}$, ($\bar{\upsilon}$) = 1165 $cm^{-1}$, ($\bar{\upsilon}$) = 1118 $cm^{-1}$, ($\bar{\upsilon}$) = 725 $cm^{-1}$, each of which shows the presence of bonds (C=O) from esters, CH3 bonds, C–O bonds from esters and bonds on carbon $(CH_2)n$ where $n \geq 4$, which is not found in cellulose but is found in cellulose ethers. This indicates that there has been an alkoxylation reaction of the MEAL epoxide MEAL of rubber seed oil with cellulose which will produce cellulose ether.

## 5. Acknowledgements

The authors thank the Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, for providing the facilities.

## 6. Conflict of Interest

Authors declare no conflicts of interest

## References

[1] Alessandro G and Mohamed NB, 2008. State-of-the-art in Monomers, Polymers and Composites from Renewable Resources. Edited by Mohamed NB and Alessandro Elsevier, Amsterdam.

[2] Granstrom M, 2009. Cellulose Derivate: Synthesis, Properties and Applications. Helsinki University. Publishing House. Helsinki

[3] Umemoto T, Ogita N, Noishiki Y, Nagatani H and Banzashi G, 2013. Cellulose Fibers and Process for Producing the same, CelluloseFiber Assembly and Cellulose - FiberComposite Material. US Patent US 20130338250A

[4] Kumar AP dan Singh RP, 2008. Biocomposites of Cellulose Reinforced Starch: Improvement of Properties by Photo–Induced Crosslinking. Elsevier Bioresource Technology
[5] Nurman S, Marlina, Saiful, 2016. Polyurethane Membrane from Rubber Seed Oil (Rubber Seed Oil) From Rubber Seed Oil With Hexamethylene – 1,6 Diisocyanate. Natural Journal. Vol. 16, No. 1, 2016.
[6] Purba, N. 2011. Analysis of Free Fatty Acids (ALB) from CPO Fresh, CPO Outspec, and CPO Blending at PTPN III Trade PKS Sei Mangkei. FMIPA. [Thesis]. Medan. University of Northern Sumatra
[7] Wen X, Wang H, Wang X, Liu C, 2017. Preparation and Characterization of Cellulose Laurate Ester by Catalyzed Transesterification. Elsevier. Carbohy thread polymers. 168 (2017). 247–254.
[8] Chen X, Zheng N, Wang Q, Liu L, Men F, 2107. Side-Chain Crystallization in Alkyl Substitute Cellulose Esters and Hydroxy propyl Cellulose Esters. Changchun Institute of China