

**Synthesis and characterization of fish-oil-based epoxy resin and its
blending with epoxidized sunflower oil.**

A Dissertation submitted to

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It is my pleasure to forward the dissertation entitled "Synthesis and characterization of fish-oil-based epoxy resin and its blending with epoxidized sunflower oil." submitted by Jintu Daring, student of B.Sc. 6th Semester of our College for the partial fulfillment of B.Sc. Degree in Chemistry (Core) under Dibrugarh University, Assam. Jintu Daring Carried out the investigation under my constant supervision and guidance. The results enter incorporated in this dissertation have not been submitted to any university or institute for any purpose. The dissertation is in my opinion worthy of consideration for the paper DSE 603 of Chemistry core in accordance with the regulations of Dibrugarh University, Dibrugarh.



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With regards



Jintu Daring

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Synthesis and characterization of fish-oil-based epoxy resin and its blending with oxidized sunflower oil.

Abstract:

Fish oil and sunflower oil based thermosetting polymer was synthesized from waste-derived fish oil. The oil first oxidized to form epoxides followed by crosslinking with polyamidoamine based crosslinker and citric acid modified cellulose. Synthesized products were characterized by FTIR and ¹H NMR spectroscopy.

Keywords: *Bio-based-epoxy, fish oil, sunflower oil*

1. Introduction:

Recently, in the synthesis of polymer, the substitution of petroleum-based raw materials with renewable raw materials has attained worldwide consideration due to necessities for sustainability, resolutions for ecological problems and depletion of fossil fuels. Among the various types of renewable raw materials, fish oil and vegetable oils are excellent raw materials for new monomers and polymers due to their easily availability, environmental, and social advantages¹.

Epoxy resins are a thermosetting synthetic polymer which are basically composed of two substances known as resin and hardener. The main purpose of epoxy is to be used as an adhesive due to its high durability. Epoxy resin adhesive forms an excellent bonding agent. The bonding of the resin can be developed to yield several different products, each with its own unique application. Epoxies are typically used to fabricate high-performance composites with superior mechanical properties, resistance to corrosive liquids, and environments. Epoxies are also used to achieve good electrical properties, good performance at high temperature, and good adhesion to the substrate².

Vegetable oils are esters formed by glycerin and different fatty acids containing from 8 to 24 carbon atoms and between 0 and 7 carbon-carbon double bonds, depending on the plant type and climatic conditions of growing³. Moreover, various chemical modifications can be performed on vegetable oils, yielding functionalized vegetable oils (FVOs) that can be used to obtain diverse products. The interest on epoxidized vegetable oils has been increasing in the last years due to their use as renewable and sustainable lubricants, plasticizers or as intermediate to produce a wide range of chemicals. Epoxidized soybean oil is a bio-based product derived from the epoxidation of soybean oil with hydrogen peroxide and either acetic or formic acid obtained by converting the double bonds into epoxy groups, which is non-toxic and of higher chemical reactivity. They can be converted by different kinds of reactions with co-monomers and/or initiators. Three-dimensional structure that comes from the directing cross-linking of ESO and hardeners forms material with high stability, superior mechanical properties and high chemical resistance, which make the products versatile among a variety of materials. In addition, the chemical modification of ESO has gained more and more attention in recent years.

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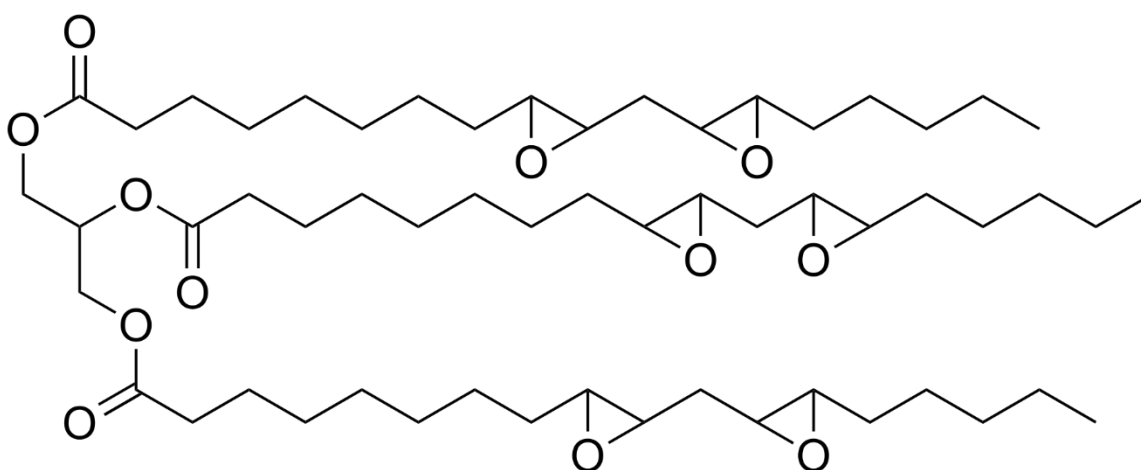


Fig.1: Epoxidized linoleina major component of epoxidized sunflower oil.

Fish oil is biodegradable, and is readily available as a byproduct in the production of fish meal. Typically, fish oil has a triglyceride structure with a high percentage of polyunsaturated ν -3 fatty acid side chains, which can contain as many as 5 to 6 non-conjugated carbon-carbon double bonds per ester side chain. These double bonds in the fatty acid chains of the fish oil triglyceride have cis-stereochemistry⁴. which can be easily converted to corresponding epoxy resins.

Nevertheless, in the field of bio-based polymer, very little work has been performed in fish oil-based polymers in comparison to vegetable oil-based polymer. Therefore, in this work, we have used fish oil and soybean oil as raw material for the synthesis of epoxy resin. Currently, fish oil is used industrially to produce protective coatings, lubricants, sealants, inks, animal feeds and surfactants⁵. Fish processing generates large amounts of waste that is presently used to produce low cost fertilizers or dumped at sea⁶ With approximately 50 wt.% of the total catch being discarded as waste, there is a large amount of material available for use as a feedstock for bio-polymer synthesis. With increasing production in the aquaculture industry to meet the growing demands of a growing population, the amount of waste produced will also increase. This waste will need to be disposed of, at a cost to the industry. The amount of recoverable oil from this waste varies considerably depending on the species, season, and tissue present in the waste material, but can account for up to 50% of the waste material. By utilizing this material for the production of bio-polymers, it does not compete with food production or use large amounts of land space.

As the bio-economy slowly gains interest to the researchers and in industries, the focus is shifting to the synthesis of bio-based epoxy resin extracted from inexpensive and renewable natural resources, such as lignin, vegetable oil, waste derived fish oil, rosin, sugars, furan, and itaconic acid. Recent bio-based materials showed similar or improved properties than commercial petroleum-based product.

Within this investigation, fish oil based thermosetting polymer is synthesized from waste-derived fish oil with the oil first oxidized to form epoxidized fish oil followed by crosslinking with polyamido amine based crosslinker.

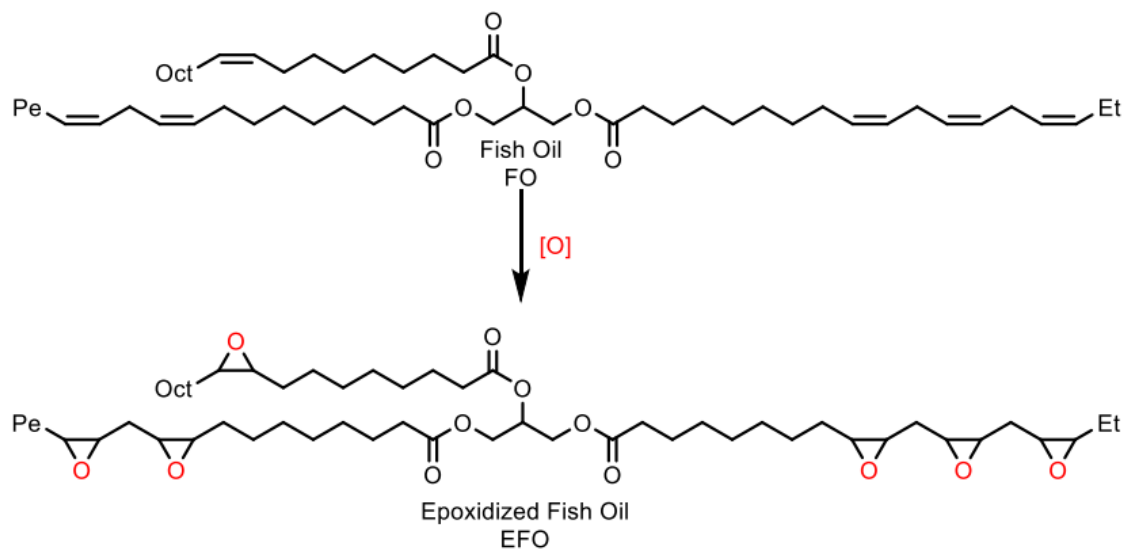


Fig.2: Epoxidation reaction of fish oil.

Polymers ranging from soft crosslinked gel to hard thermosetting plastics have been obtained. ¹H NMR, FTIR, differential scanning calorimetry (DSC), and TGA have been used to characterize the structures and physical properties of the fish oil-based polymers. The results indicate that the products are typical thermosetting polymers with densely crosslinked structures. These polymer materials have densities of approximately 1000 kg/m³, which appear to be independent of their compositions. The structure of the bulk polymer is composed of 40–85 wt% of crosslinked polymer networks plasticized by 15–60 wt% of unreacted free oil.

Cellulose is a linear biopolymer found naturally in plant cells such as wood and cotton. It is the world's most abundant polymer in nature and possesses properties such as good biocompatibility, low cost, low density, high strength, and good mechanical properties. By

mechanical or chemical treatment, the cellulose fibers can be converted into cellulose nanofibers (CNFs) or cellulose nanocrystals (CNCs) that possess outstanding properties compared with the original cellulosic fiber but also when compared with other materials normally used as reinforcements in composite materials such as Kevlar or steel wires⁷

The cellulose molecule contains three different kinds of AGU: a reducing end group that contains a free hemiacetal or aldehyde at the C1 position, a non-reducing end group with a free hydroxyl group at the C4 position, and internal glucose rings joined at the C1 and the C4 positions. The internal glucose units are predominant due to the long chain lengths. Each internal AGU has three hydroxyl groups. The hydroxyl group at the C6 position is a primary alcohol, while the hydroxyl groups at the C2 and C3 positions are secondary alcohols. These hydroxyl groups are all possible sites for chemical modification of cellulose where the hydroxyl group at the C6 position is the most reactive.

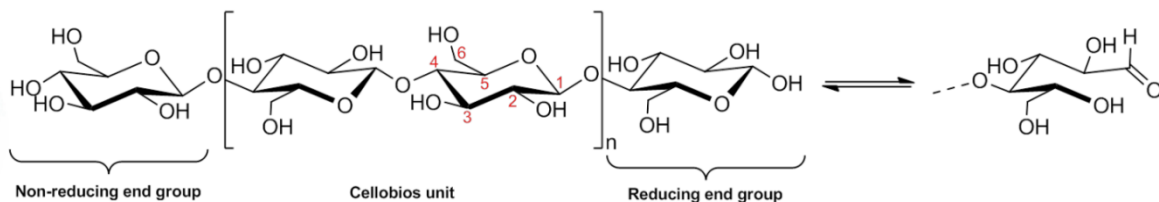


Fig.3: The molecular structure of a cellulose polymer where the cellobios is the smallest repeating unit in the polymer. The reducing end group can be either a free hemiacetal or an aldehyde.

1.1. Literature review:

J. Wisniak et al (1970) epoxidized anchovy oil of iodine value 188.8 in situ, with preformed peracetic acid, or using a mixed strategy, to determine a kinetic model for the reaction and the optimization of double bond conversion to oxirane rings. In the range of the operating

variables, epoxidation and ring opening may be described by a pseudo-first-order reaction, and use of a mixed strategy allows a 92.2% conversion of the double bonds with a final oxirane number of 8.5 and iodine number of 19.4. Optimal conditions correspond to an in situ process at 70° C. with partially preformed peracetic acid and fast addition of the oil, using 6.16 moles of 41 weight % hydrogen peroxide and 0.5 mole of acetic acid, per mole of ethylenic unsaturation, in the presence of 10 weight % dry basis of resin catalyst Dowex 50W-12X, 50/100-mesh. Thermal stability of the epoxidized oil compares favorably with that of commercial PVC plasticizers⁸

K. Rehman et al (2014) used fish oil for preparation of bio gels using polymer hydrogel and fish oil and found effective as vehicles for transdermal drug delivery. They found that fish oil bigels offer better thermal stability and higher drug permeation than hydrogel formulations alone. The addition of fish oil proved to be beneficial as it allowed bigels to offer higher cumulative drug permeation and drug flux, which may be due to the omega-3 fatty acids. The oleogel-hydrogel proportion of 10:90 was proven to be the best combination for bigels in this study showing higher release and good mechanical properties⁹.

C. Chang et al (2017) developed a process for the production of epoxides with a terminal oxirane group from soybean oil. Optimized reaction parameters were obtained using response surface method (RSM) based on a Box-Behnken experimental design. The model predicted by RSM indicated that the molar ratio of EPCH to soap, CTAB loading, and reaction time were highly significant to epoxidation yield. An epoxidation yield of 94.26%, which was obtained under optimal reaction conditions, was very close to the predicted yield¹⁰

D. Piccolo et al (2018) studied the effects of microwave irradiation on the process of epoxidation of soybean oil. A rigorous comparison was performed between the products obtained by conventional and microwave heating, using two batch reactors with the same

geometry but different heating sources. The epoxidation of the oil was performed by reaction with peracetic acid generated in situ by reaction between hydrogen peroxide (HP) and acetic acid. Acetic acid and HP 35 wt% were used instead of the commonly used formic acid and HP 60 wt% to reduce the risk of detonation and corrosion. The MW heating showed a strong beneficial effect on the selectivity and especially on the rate of the process, reducing the time required by about 50%¹¹

2. Objective:

The objectives of this study are:

1. Extraction of oil from fish
2. Epoxidation of the extracted fish oil
3. Epoxidation of sunflower oil.
4. Curing of epoxidized fish oil to produce thermosetting polymer
5. Synthesis of citric acid modified nanocellulose
6. Synthesis of copolymer of sunflower oil and fish oil cured with citric acid modified nanocellulose and polyamidoamine.
7. Characterization of the synthesized polymers /copolymers by FTIR and NMR spectroscopy.

3. Materials

Acetic Acid glacial (RANKEM), Sodium Hydroxide (RANKEM), Hydrogen Peroxide (RANKEM), Sodium Bicarbonate (RANKEM), Sulphuric Acid (RANKEM), Citric Acid, Cellulose were used as received without further purification.

4. Experimental:

4.1. Extraction of Fish oil:

The extraction process was done using ultrasonic extraction unit¹². This apparatus consists of 500 ml. extraction beaker, ultrasonic bath and ultrasonic generator. The ultrasonic bath has frequency of 25 kHz. The extraction beaker was immersed in the ultrasonic bath. Ethanol was used as solvent during the extraction process. Extraction process was initially done in the absence of ultrasonic wave. For example, 10 g of dried fish was mixed with 300 mL of ethanol and placed in a 500 mL. beaker. The beaker was left for 20 min at ambient condition without sonication. After that, the sample was filtered to remove the powder and evaporated by using rotary evaporator to get oil. The amount of extracted oil was recorded.

4.2 Synthesis of epoxidized sunflower oil:

Sunflower oil was epoxidized through in-situ method in the presence of glacial acetic acid and hydrogen peroxide as reported earlier by Kim et al and Sahoo et al. Epoxidation of oil was performed in a 3-necked flask equipped with a magnetic stirrer and thermometer. The flask with 79 g of linseed oil was placed in water bath, and first 30 g of acetic acid and 19.75 g of Seralite resin were added followed by stirring for 30 minutes. After this, 113 g of hydrogen peroxide (H₂O₂) was added drop-wise through the dropping funnel and stirred for 6 hours at 500 rpm. Subsequently, the epoxidized oil layer was separated through separating funnel, washed with 2 wt% Na₂CO₃ solution, and then with distilled water. The epoxidized oil later dried using MgSO₄ followed by filtration and dried overnight at 60°C under high vacuum.

4.3 Epoxidized Fish Oil

Prepared following a previously reported method,⁹ with modification of the reaction time, solvent, and equivalents of reagents. Waste-derived fish oil (3.00 g) and CH₃COOH (0.45 g,

7.6 mmol) was dissolved in heptane (0.65 g) and heated in an oil bath to the reaction temperature. An acidified hydrogen peroxide solution (2.60 g, 23 mmol H₂O₂, 30% wt/wt; 0.026 g conc. H₂SO₄) was added dropwise to the reaction over 1 h. Upon complete addition, the reaction was stirred for 12 h at the desired temperature. The reaction mixture was cooled to 0 °C, dissolved in 5 mL CH₂Cl₂, and washed with deionized water (3 organic phase was dried over anhydrous MgSO₄ and the solvent removed under reduced pressure to give a clear, colourless oil (1.66 g).



Fig.4: Experimental setup for epoxidation of fish oil.



Fig.5: Synthesized epoxidized fish oil.

4.4. Curing of epoxy resins:

To prepare cured epoxy resin, epoxidized fish oil and mixture of epoxidized fish oil and sunflower oil was dissolved in tetrahydrofuran. Then, amine curing agent, polyamidoamine, was added to the mixture. The mixture was casted into molds and cured by heating at 80 C for 3 h and 150 C for 3hrs.

4.5. Preparation of CAC/epoxy resin composites:

To prepare CAC/epoxy resin composite, CAC was mixed with fish oil/sunflower oil or mixture of both with contents of 5, 7,10,15 and 20 wt% with magnetic stirring at roomtemperature for 3 h. Then, amine curing agent, polyamidoamine, was added to the mixture¹³.The mixture was casted into molds and cured by heating at 80 C for 3 h and 150 C for 3hrs. Pure epoxy resin and unmodified cellulose/epoxy resin composites were also prepared.

5. Measurements

Fourier transform infrared (FT-IR) spectra of the samples are recorded on Nicolet Impact 410 FT-IR spectrometer over a frequency range of 4000–500 cm^{-1} .¹H NMR spectra were recorded using a Bruker DPX300 NMR machine.

6. RESULTS AND DISCUSSION:

6.1 ¹H NMR analysis:

The ¹H NMR spectrum for FO, Figure 6, contains a triplet at 0.87 ppm that corresponds to the terminal methyl group for all fatty acids except ω -3 fatty acids, which appear at 0.97 ppm. Peaks from 1.24 to 1.32 ppm correspond to protons of the methylene groups. A peak at 1.61

ppm represents the proton on the carbon β to the carbonyl group for all fatty acids except DHA. The peak centered on 2.02 ppm corresponds to the protons on the allylic carbons. Peaks from 2.28 to 2.31 ppm correspond to the protons on the carbon β to the carbonyl group for all fatty acids except for DHA, which appears as a small peak at 2.38 ppm. Peaks around 2.80 ppm correspond to protons on allylic carbons between two double bonds, which shifts upfield after epoxidation. Peaks from 4.11 to 4.30 ppm and 5.25 ppm represent the protons in the glycerol chain of the triglyceride, on the methylene and methine carbons, respectively. The peaks around 5.32 ppm correspond to the olefinic protons. The ^1H NMR spectrum for EFO shows new peaks from 2.80 to 3.19 ppm, which corresponds to the formation of the epoxide.

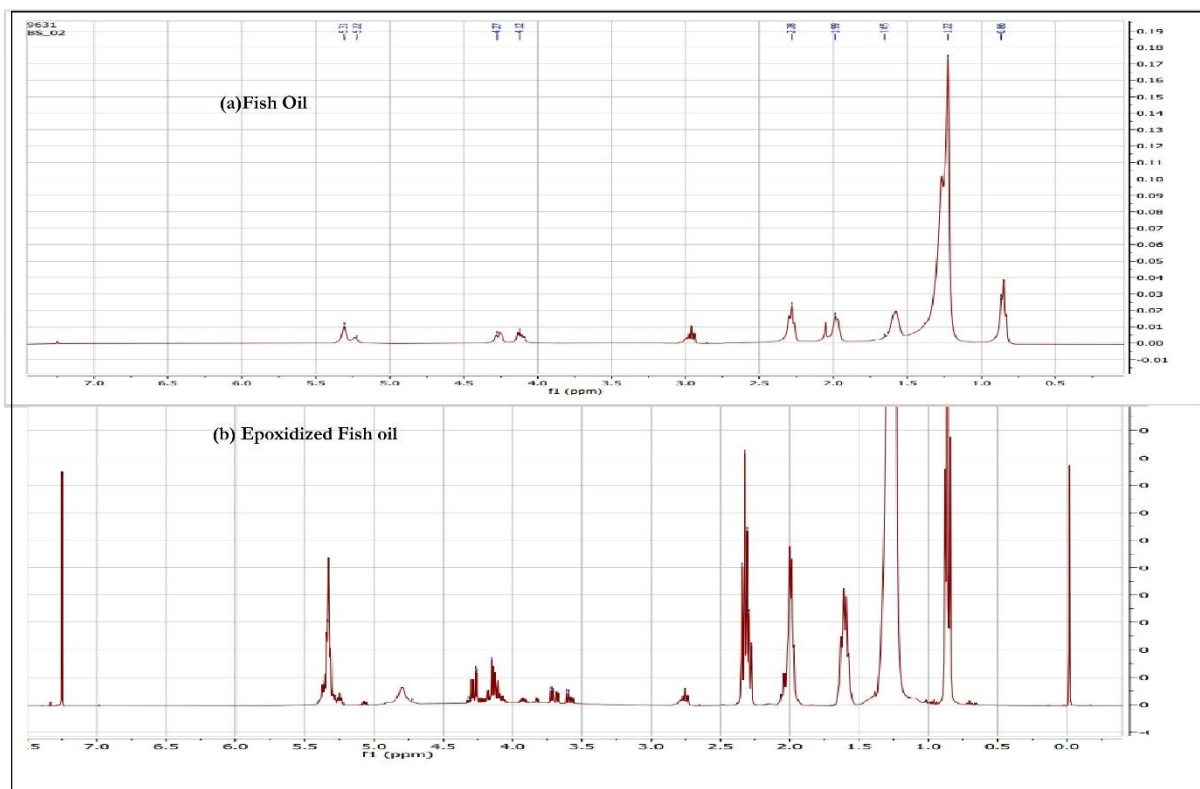


Fig. 6: ^1H NMR spectra of epoxidized fish oil (a) and fish oil (b).

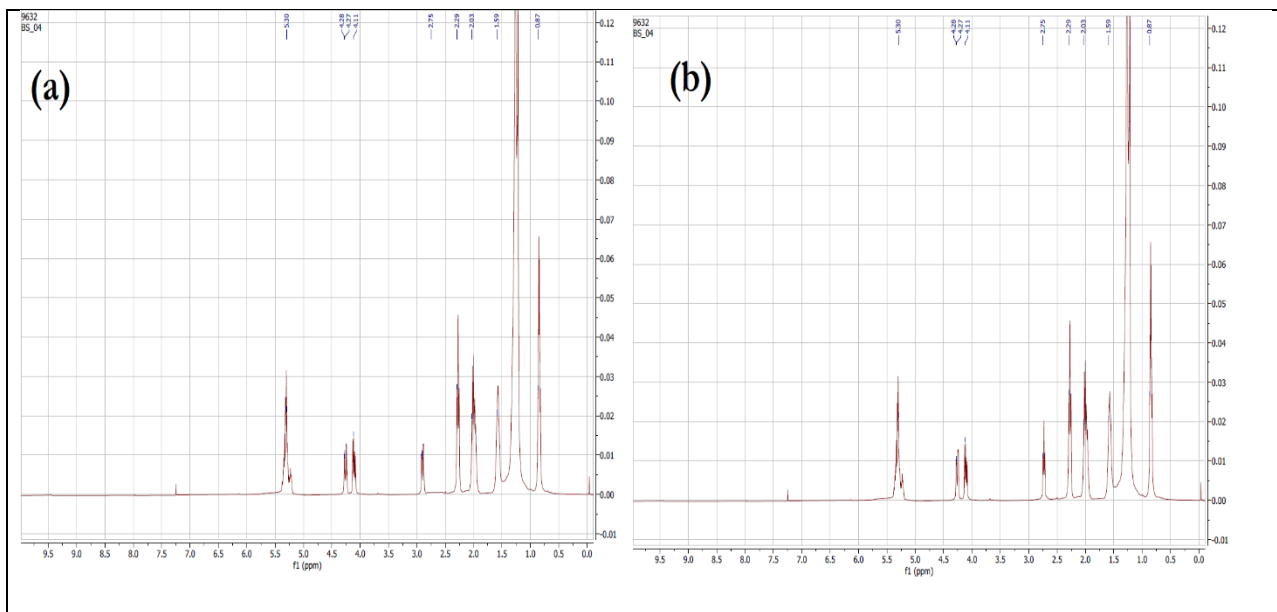


Fig. 7: ¹H NMR spectra of epoxidized sunflower oil (a) and sunflower oil (b)

6.2. FT-IR study:

Representative spectra for FO and EFO are shown in Figure 8. The spectrum for FO showed a characteristic band at 3009 cm⁻¹ from the double bonds, which did not appear in the spectrum for EFO. The spectrum for EFO showed a characteristic band at 825 cm⁻¹ from the epoxide group, that was not present in the FO spectrum. Bands at 1743 cm⁻¹ and 1158 cm⁻¹, due to the ester group and bands at 1462 cm⁻¹ and 1377 cm⁻¹, due to the methyl groups, were present in both spectra.

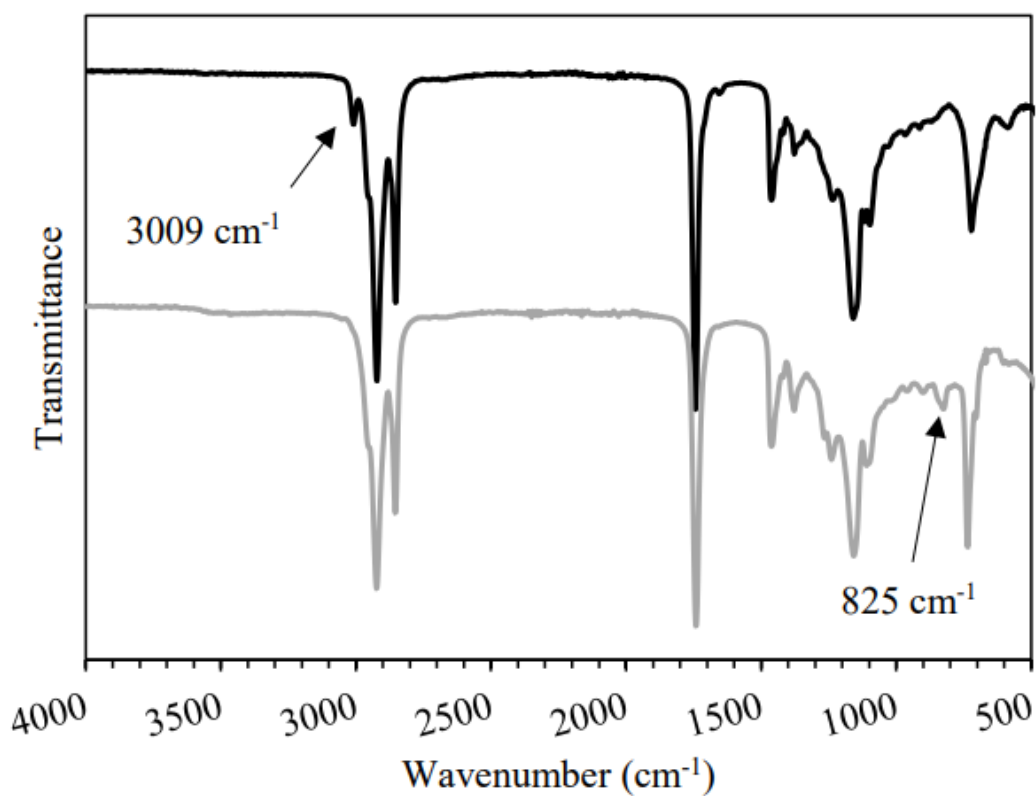


Fig.8: (a)FTIR spectra of fish oil(a) and epoxidized fish oil(b).

The surface modification of cellulose was confirmed by ATR-IR. Compared with the characteristic spectrum of cellulose, CAC and fibrillated CAC showed a new absorption peaks around 1720 cm⁻¹ assigned to -COO stretching vibration

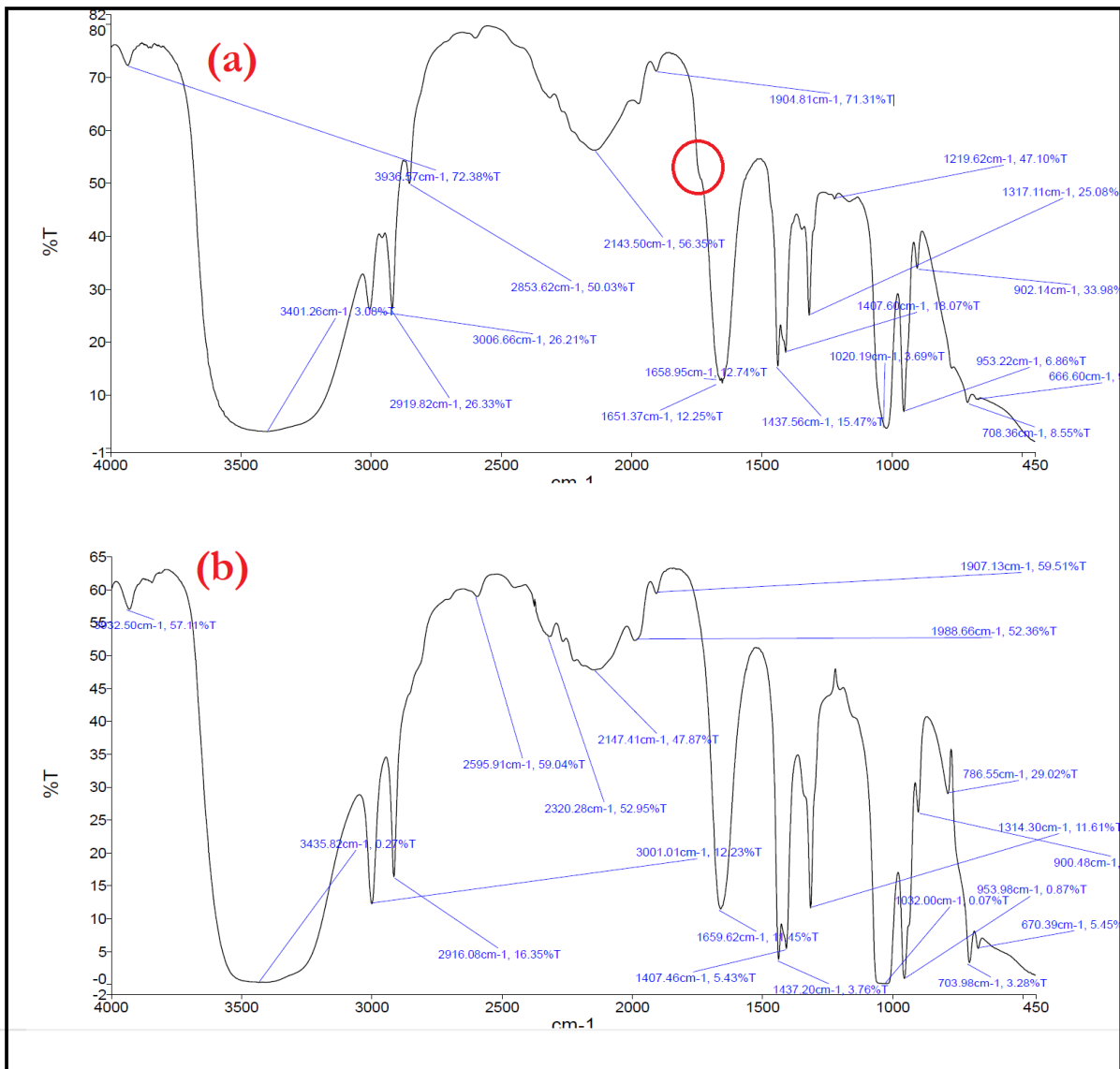


Fig.9:(a) FT-IR spectra of citric acid modified cellulose(b)FT-IR spectra of unmodified Cellulose.

7. Conclusion:

Fish oil was extracted from fish waste. Fish oil based thermosetting polymer was synthesized from waste-derived fish oil with the oil first oxidized to form epoxidized fish oil followed by crosslinking with polyamido amine based crosslinker. Synthesized products were characterized by FTIR and ¹H NMR spectroscopy.

8. References:

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