



**SYNTHESIS AND CHARACTERIZATION OF BIOPOLYMER FROM  
VEGETABLE OIL VIA CATALYST FREE CLICK CHEMISTRY REACTIONS - A  
REVIEW**

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**Abstract**

The reviewed work addressed the shift in focus from conventional polymers to bio-based and renewable polymers. This chapter reviews the most important aspects of the application of click chemistry reactions in polymer science. The click chemistry approaches have revolutionized the polymer chemistry allowing the preparation of a wide range of functional polymers and complex macromolecules as well as facilitating the surface modification of diverse polymeric materials. Concisely, click chemistry encompasses a group of reactions that are fast, efficient, selective, tolerance to a variety of solvents and functionalities, and give high yields. “Click” reactions include several kinds of selective and orthogonal chemical ligations with high efficiency under mild reaction conditions. Different oils including grape, palm, sunflower, sesame, maize, olive etc are collected and have been used for analysis using conventional methods and further by FTNIR, FTIR. The collected spectral data from both NIR &IR are used for development of multivariate methods using unscrambler. This paper focuses on review of a work carried out by researchers in the field of production of biopolymers from different types of oil. This review paper contains the work of past researchers published between 2005 and 2015.

**I) Introduction**

The ever-increasing environmental concerns, as well as the dwindling in crude oil reserves and the rising cost of petroleum-derived commodity chemicals has led to the growing interest in polymeric materials from renewable origin.

Vegetable oils are perceived as one of the most important classes of renewable resources for the chemical industry in the synthesis of fine chemicals, monomers and polymers.

The use of vegetable oils as raw materials in the chemical industry has become more important year by year. In recent times, researchers have a new pathway to confront the current challenges of the society by using vegetable oils. The priorities of this way should be the human health and the protection of the Earth, maintaining the equilibrium between society, economy and environment.

Many researchers from around the World carried out studies on Polymer chemistry from vegetable oils and its applications in various areas in modern times. It is understood that vegetable oils can be easily used as a replacement to conventional petroleum products and fatty acids and so on.

## **II) Polymer Chemistry**

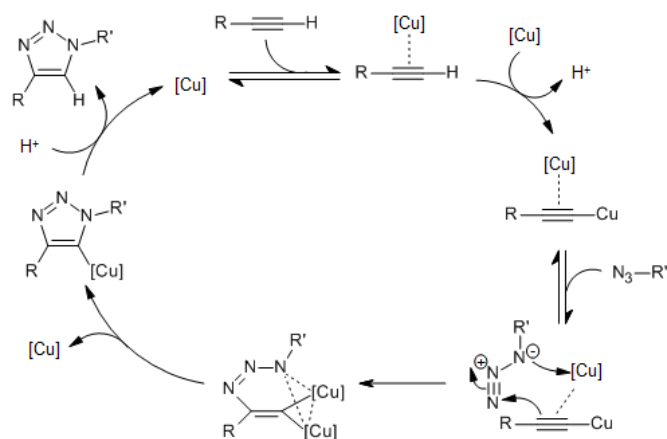
Polymer chemistry is a sub-discipline of chemistry that focuses on the chemical synthesis, structure, chemical and physical properties of polymers and macromolecules. The principles and methods used within polymer chemistry are also applicable through a wide range of other chemistry sub-disciplines like organic chemistry, analytical chemistry, and physical chemistry. Many materials have polymeric structures, from fully inorganic metals and ceramics to DNA and other biological molecules, however, polymer chemistry is typically referred to in the context of synthetic, organic compositions. Synthetic polymers are ubiquitous in commercial materials and products in everyday use, commonly referred to as plastics, and rubbers, and are major components of composite materials. Polymer chemistry can also be included in the broader fields of polymer science or even nanotechnology, both of which can be described as encompassing polymer physics and polymer engineering.

## **III) Click Chemistry**

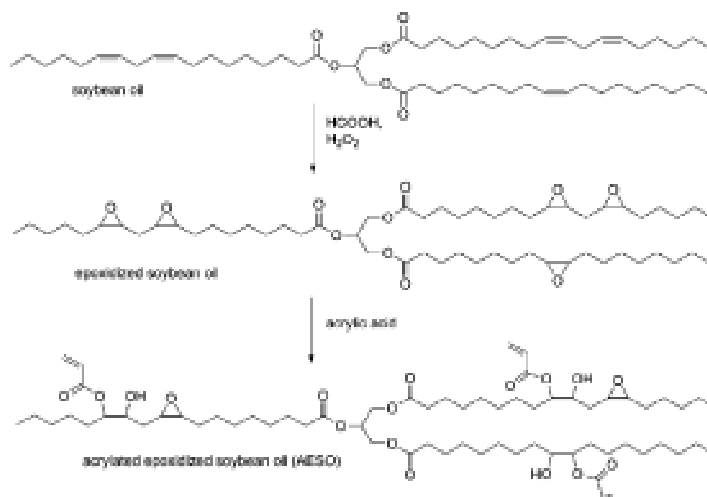
'Click chemistry' was defined by Sharpless and co-workers in 2001 (I) to describe a set of powerful, highly reliable and selective organic reactions which can be used for the rapid and facile synthesis of useful new compounds and combinatorial libraries. Each of these compounds is composed of small, modular sub-units stitched together through heteroatom linkages (C-X-C). Click chemistry reactions are simple, modular, stereo specific, very high yielding, wide in scope, can be conducted in benign/easily removable solvents, and generate side products which are easily removable by non-chromatographic methods. The primary driving force behind the development of click chemistry is the pharmaceutical industry's need

to generate very large combinatorial libraries of small-molecule (< 500 Dalton) compounds that can be screened as drug candidates. Click chemistry has the potential to accelerate the drug discovery process, as it makes each reaction in the multi-step synthesis of a small molecule fast, efficient and predictable.

Although there are several types of organic reactions that fit the definition of click chemistry, for modification of oligonucleotides, the relevant one is the copper (I)-catalyzed [3+2] cycloaddition reaction between alkynes and azides (1, 2). This reaction is extremely selective and regiospecific for conjugation reactions involving an oligo and a labeling moiety, as well as coupling reactions between two oligos. More detailed descriptions of specific click chemistry applications are provided in 'Click Chemistry Applications'.

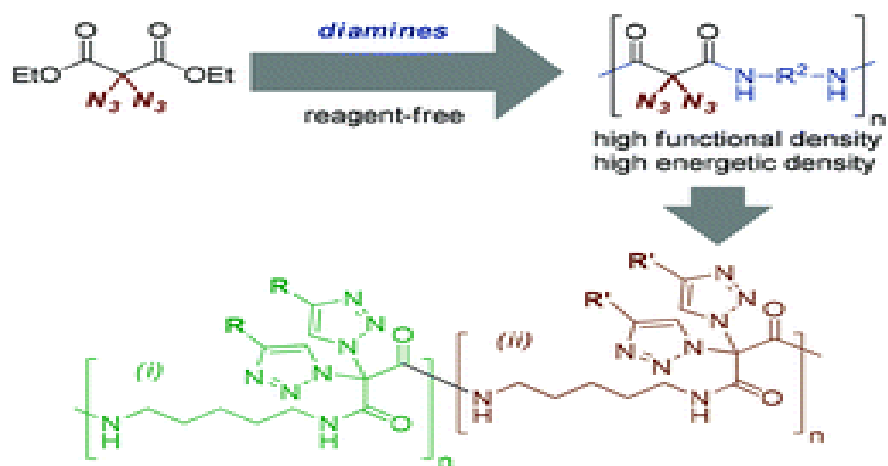


### (i) Synthesis of acrylatedepoxidised soybean oil



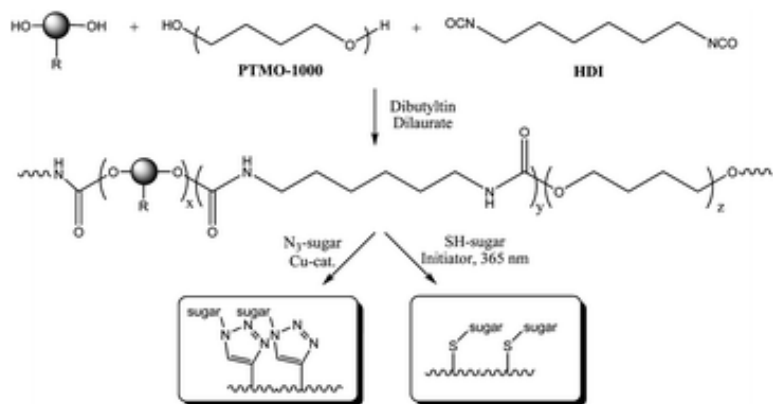
### (ii) Synthesis of polyamides

A diazidated malonate derivative was employed as a monomer for the reagent-free one-pot synthesis of several polyamides containing geminal diazido moieties within the polymer backbone. Using different diamines, azide-rich polyamides with diverse properties and sensitivities dependent on the structure of the diamine units were obtained. Postpolymerization CuAAC reactions of the geminal diazido units in the polymer backbone allowed for the introduction of additional functionalities, and the construction of densely functionalized polymeric structures.



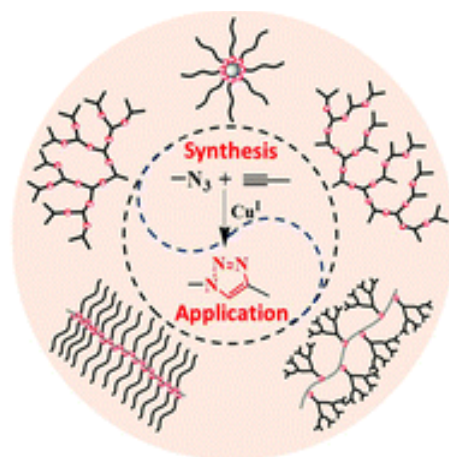
### (iii) Synthesis of polyurethanes

We report a facile synthetic route to prepare polyurethanes with pendant sugar-moieties in the side-chain of the polymer through incorporation of diverse chain extenders capable of undergoing copper catalyzed Huisgen 1, 3-dipolar cycloaddition or thiol-ene click reactions.



#### **(iv) Synthesis of poly azide alkynes**

The rapid development of efficient organic click coupling reactions has significantly facilitated the construction of synthetic polymers with sophisticated branched nanostructures. This Feature Article summarizes the recent progress in the application of efficient copper-catalyzed and copper-free azide–alkyne cycloaddition (CuAAC and CuFAAC) reactions in the syntheses of dendrimers, hyper branched polymers, star polymers, graft polymers, molecular brushes, and cyclic graft polymers. Literature reports on the interesting properties and functions of these polytriazole-based nanostructured polymers are also discussed to illustrate their potential applications as self-healing polymers, adhesives, polymer catalysts, opto-electronic polymer materials and polymer carriers for drug and imaging molecules.



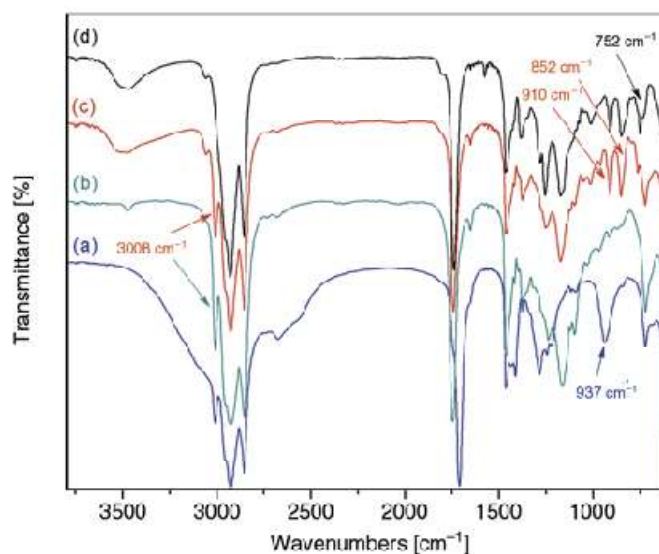
#### **IV) Materials and Methods**

The subject study highlighted the importance of using bio-based and renewal polymers rather than using conventional polymers. Its properties could be used in high end applications and combination of fatty acids in plant oil seeds was analyzed with the condition of unsaturation used the iodine value. This study reveals the fatty acid presence in plant seed oils and its applications in areas of thermosetting polymers.

A study has been carried out on the use of chemically modifying vegetable oil based green lubricants in place of petroleum lubricant usages in the evolving industrial sectors in order to avoid the impacts of petroleum based lubricants which is adversely affecting the environments all over the World. In addition to that sources of petroleum products are also depleting year by year which force us to look for alternative. Bioplasticizers, non-isocyanate polyurethanes, biofuel can easily be produced through chemically modified vegetable based lubricants, which is cost effective and environment friendly composition [I].

Glycidyl esters of epoxidized fatty acids derived from soybean oil (EGS) and linseed oil (EGL) have been synthesized to have higher oxirane content, more reactivity and lower viscosity than epoxidized soybean oil (ESO) or epoxidized linseed oil (ELO). The EGS and ESO, for comparison, were used neat and in blends with diglycidyl ether of bisphenol A (DGEBA). Thermosetting resins were fabricated with the epoxy monomers and either BF<sub>3</sub> catalyst or anhydride[V]. The curing behaviors, glass transition temperatures, crosslink densities and mechanical properties were tested. The results indicated that polymer glass transition temperatures were mostly a function of oxirane content with additional influence of glycidyl versus internal oxirane reactivity, pendant chain content, and chemical structure and presence of saturated components [VI]. Therefore, EGS that is derived from renewable sources has improved potential for fabrication of structural and structurally complex epoxy composites, e.g., by vacuum-assisted resin transfer molding [VII].

**(i) IR spectra of (a): mixed-FFA (b): soybean oil(c): glycidyl esters (d): EGS**



The main objective of this thesis was to develop new biobased polyurethanes from vegetable oil derivatives as renewable resources. To achieve this goal, the experimental work focused on exploiting the reactivity of unsaturated fatty acid compounds to prepare a set polyols for polyurethane synthesis by using different synthetic methodologies[XXIX]. The specific objectives were:

- i. To synthesize and characterize polyether polyols through the ionic coordinative catalyzed ring opening polymerization of epoxidized methyl oleate and the subsequent partial reduction of the pendant ester groups.

- ii. To synthesize lineal polyols by ADMET polymerization of 1, 3-di-10-undecenoxy-2-propanol.
- iii. To synthesize branched polyols by ATMET polymerization of glyceryltriundec-10-enoate.
- iv. To synthesize poly-2-oxazoline polyols by cationic ring opening polymerization of fatty acid derived 2-oxazolines and further thiol-ene click coupling of pendant double bonds with mercaptoethanol.
- v. To apply these polyols to the synthesis of thermosetting segmented and non segmented polyurethanes by using 4-4'-methylene-bis(phenylisocyanate) or L-lysine diisocyanate as coupling agents and 1, 3-propanediol as chain extender.

The need to rely less heavily on petroleum is a crucial step towards sustainability and is leading to a greater use of renewable materials, such as vegetable oils, for the development of polymers. In Particular, to prepare fatty acid-based monomers with polymerizable moieties capable of generating step-growth and chain-growth polymers with different properties depending on the structure of the initial monomers [V]. The diversity of monomers and polymers successfully synthesized and characterized in this dissertation, confirmed beyond any doubt the usefulness of vegetable oils as a source of original polymer materials.

All of these polymeric materials are attractive contributions to the growing realm of polymers from renewable resources and represent indisputable evidence that vegetable oils are promising precursors of innovative macromolecular materials with potential applications.

Palm oil-based alkyd resins were synthesized by alcoholysis and esterification reactions. Calcium oxide was used as a catalyst for the alcoholysis reaction between palm oil and glycerin. Esterification process was carried out by using phthalic anhydride and maleic anhydride. Physico-chemical properties of the resins such as density, viscosity, acid value, iodine value, saponification value, specific gravity, and moisture content were measured following ASTM and standard methods[XXX]. The structural confirmation and hydrogen density of the prepared resins were determined by Fourier transform infrared and proton nuclear magnetic resonance spectroscopy, respectively. Molecular weight of the resins was determined by using gel permeation chromatography.

The curing process involved heating at 140°C, without using any organic solvent in the presence of methyl ethyl ketone peroxide and cobalt-napthenate. ASTM methods were

followed to measure the gloss, hardness and chemical resistivity of the resins. Temperature behaviors were observed by differential scanning calorimetry and thermogravimetric analysis. Produced resins were found thermally stable (up to 300°C). The variations of the properties were noticed due to the types of anhydrides in terms of molecular weight, thermal and chemical resistivity of the resins, although the other properties were found close to each other.

Overall, the reported properties are found suitable for the materials to be used for surface coating applications.

Mechanically interlocked polymers can introduce new methods to engineer a polymer's physical properties. As macromolecular switches they contain a wide range of potential applications, such as developing "smart" materials with tunable mechanical properties. Moreover, preparation of poly[n]rotaxanes has been extremely demanding due to synthetic challenges. Here a polymer rotaxane containing a single mechanical bond shared between dibenzo[XXIV]crown and ammonium poly(methylacrylate) was prepared via dynamic host-guest interactions and CuAAC click chemistry. <sup>1</sup>H NMR has been used to show that polymer rotaxane retains general mechanical bond properties such as intramolecular rotation and translation, and reversibility. Photo-labile stoppers were used to increase efficiency of our synthetic route[XIII]. Photo-stoppered rotaxanes were synthesized and photo-protected to show via <sup>1</sup>H NMR that photo-labile stoppers could be used for rotaxane "lengthening". This technology can potentially be applied to improve yields of mechanically interlocked polymers.

This Chapter reviews the most important aspects of the application of click chemistry reactions in polymer science[XIII]. The click chemistry approaches have revolutionized the polymer chemistry allowing the preparation of a wide range of functional polymers and complex macromolecules as well as facilitating the surface modification of diverse polymeric materials. Concisely, click chemistry encompasses a group of reactions that are fast, efficient, selective, tolerance to a variety of solvents and functionalities, and give high yields. While several reactions fulfil these criteria, Cu-catalyzed azide/alkyne cycloaddition (CuAAC), the metal free alternatives such as Diels–Alder cycloaddition and thiol-based reactions are the most employed in the polymer field that eventually are contributing to the next generations of polymeric materials. Herein, the fundamentals of click chemistry and the main strategies



applied to the precise synthesis and modification of macromolecules are thoroughly examined with the aim to give an overview of the existing methodologies and enable the readers to select the most appropriate click reaction for a certain application. Besides, the most recent contributions and advances of click chemistry to current topics in polymer science will be briefly described.

Azide-alkyne Huisgen “click” chemistry provides new synthetic routes for making thermoplastic polytriazole polymers—without solvent or catalyst[XIII]. This method was used to polymerize three diesterdialkyne monomers with a lipid derived 18 carbon diazide to produce a series of polymers (labelled C18C18, C18C9, and C18C4 based on monomer chain lengths) free of residual solvent and catalyst. Three diesterdialkyne monomers were synthesized with ester chain lengths of 4, 9, and 18 carbons from renewable sources[XV]. Significant differences in thermal and mechanical properties were observed between C18C9 and the two other polymers. C18C9 presented a lower melting temperature, higher elongation at break, and reduced Young’s modulus compared to C18C4 and C18C18. This was due to the “odd-even” effect induced by the number of carbon atoms in the monomers which resulted in orientation of the ester linkages of C18C9 in the same direction, thereby reducing hydrogen bonding[XIX]. The thermoplastic polytriazoles presented are novel polymers derived from vegetable oil with favourable mechanical and thermal properties suitable for a large range of applications where no residual solvent or catalyst can be tolerated. Their added potential biocompatibility and biodegradability make them ideal for applications in the medical and pharmaceutical industries.

The continuous demand for novel hybrid materials in specific technological applications inspires people to develop new synthetic strategies in a modular and efficient way. In the recent years, extensive efforts have been devoted to using polyhedral oligomeric silsesquioxane (POSS) to construct multifunctional nanohybrids and nanocomposites with tunable hierarchical structures and unparalleled properties[XXI]. The shape-persistent nanostructure and diverse surface chemistry make those nanocaged materials ideal building blocks for such purposes. Functionalization of POSS cages are further facilitated by the introduction of “click” chemistry at the beginning of this century. “Click” reactions include several kinds of selective and orthogonal chemical ligations with high efficiency under mild reaction conditions [XVI]. The concept has generated real stimulus not

only in elegantly preparing materials of choice, but in making the leap from laboratory to industrial scale-up of POSS-based hybrid materials as well.

This study investigated the optimal reaction conditions for biodiesel production from sour sop (*Annonamuricata*) seeds. A high oil yield of 29.6% (w/w) could be obtained from sour sop seeds. Oil extracted from sour sop seeds was then converted into biodiesel through two-step transesterification process. A highest biodiesel yield of 97.02% was achieved under optimal

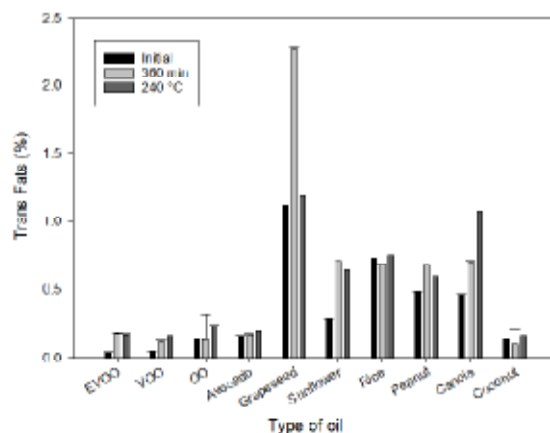
Acid-catalyzed esterification conditions (temperature: 65 °C, 1% H<sub>2</sub>SO<sub>4</sub>, reaction time: 90 min, and a methanol: oil molar ratio: 10:1) and optimal alkali-catalyzed transesterification conditions (temperature: 65 °C, reaction time: 30 min, 0.6% NaOH, and a methanol: oil molar ratio: 8:1). The properties of sour sop biodiesel were determined and most were found to meet the European standard EN 14214 and American Society for Testing and Materials standard D6751. This study suggests that sour sop seed oil is a promising biodiesel feedstock and that sour sop biodiesel is a viable alternative to petrodiesel [XXII-XXIV].

Biodiesel fuel (BDF) produced by alcoholysis of vegetable oils or fats is viewed as a promising renewable fuel source. Diminishing petroleum reserves and increasing environmental regulations have made the search for renewable fuel. Biodiesel is non-toxic and biodegradable produced from renewable sources and contributes a minimal amount of net green-house gases, such as CO<sub>2</sub>, SO<sub>2</sub> and NO emissions to the atmosphere. The main objective of the present study is to produce biodiesel from vegetable oils (edible and non-edible oil) and to use micro-emulsions with solvents ethanol and methanol following acid, alkali and fungal enzyme catalysis methods[XXXI,XXXII]. The best suited method of biodiesel production was ethanolic and alkali mediated transesterification process rather than methanolic and acidic transesterification. The maximum yield of biodiesel was obtained from *Rhizopusoryzae* lipase enzyme, ethanolic and alkali mediated transesterification followed by *Aspergillusniger*.

When cooking oils are exposed to heat, oil degradation occurs, and by-products are produced (free fatty acids, secondary products of oxidation, polar compounds). Some by-products of oil degradation have adverse effects on health. The smoke point of oil is believed to be correlated with the safety and stability under heat, although technical evidence to support this is limited. The aim of this study was to assess the correlation between oil's smoke point and other chemical characteristics associated with stability/safety when heating. Analysis was

undertaken in an ISO17025 accredited laboratory. Extra virgin olive oil (EVOO) and other common cooking oils were heated up to 240°C and exposed to 180°C for 6 hours, with samples assessed at various times, testing smoke point, oxidative stability, free fatty acids, polar compounds, fatty acid profiles and UV coefficients. EVOO yielded low levels of polar compounds and oxidative by products, in contrast to the high levels of by-products generated for oils such as canola oil. EVOO's fatty acid profile and natural antioxidant content allowed the oil to remain stable when heated (unlike oils with high levels of poly-unsaturated fats (PUFAs) which degraded more readily). This study reveals that, under the conditions used in the study, smoke point does not predict oil performance when heated. Oxidative stability and UV coefficients are better predictors when combined with total level of PUFAs. Of all the oils tested, EVOO was shown to be the oil that produced the lowest level of polar compounds after being heated closely followed by coconut oil

**(ii) Trans fats levels before and after heating trials**



Global demand for vegetable oils has recently increased, growing more than 5 percent a year for more than a decade, and is expected to continue to grow at that rate for the next decade.(IAPC 2011). This impacts not only the global economy, but also the atmosphere and ecosystems. Increasing demand for vegetable oils has traditionally translated into demand for more land to grow oil crops. Over the last decade much of that land has come at the expense of tropical forests, and this is particularly true for palm and soybean oil[XXVI]. This loss of tropical forest means a loss of precious biodiversity and ecosystem services (e.g., water cycle maintenance, potential sources of new medicines) and contributes to global climate change. Tropical deforestation accounts for about 15 percent of annual global carbon emissions.

**(iii) Vegetable oils are found in many cosmetic and cleaning products including soaps, shampoos, shaving creams, household cleaners, and paints.**



An increasing demand of fossil fuels has being a critical problem for us. The natural resources of fossil fuel are dwindling day by day. Biodiesel that may be called natural fuel may be a good source or substitute for fossil fuel in future. Biodiesel can be produced from non edible oil like *Jatropha curcas*, *Pongamia pinnata*, *Madhuca indica*, *Gossypium arboreum*, *Simarouba glauca* etc. and more. There is a best source as a raw material that is *Calophyllum inophyllum* (honne) oil for biodiesel production [XXXIII]. As it is an evergreen tree and grows along the coastal area. Our study is focused on the collection of seeds and oil extraction then proceed for biodiesel production with molar ratio 8:1, KOH were 1.2wt%, temperature 65°C, reaction time 90 minutes were used and testing of parameters as per ASTM 6751 standards. The physical properties like acid value, density, Calorific value, Flash point, Fire point and Moisture, Viscosity shows of *calophyllum methyl esters* were 0.702, 892 gm/cc, 37.18 MJ/Kg, 1760°C, 1820°C and 0.01%. The physico-chemical parameters showed that *Calophyllum* may works as a sustainable feedstock for biodiesel production that is equivalent to fossil fuel as per ASTM 6751.

Hydrogenated vegetable oils (HVOs) are increasingly finding application as a substitute for (semi)refined paraffin waxes; they offer good price economy, a wide range of melting points and a sustainable, renewable feedstock with consumer appeal.

Despite their positive credentials, HVOs display functional shortcomings that limit their use in applications originally developed around paraffin feedstocks [V]. Specifically, paraffin

exhibits excellent plasticity and cohesiveness, physical properties which are essential in e.g. paper coating and some candle-making processes, but are largely absent in HVOs. In order to overcome these significant limitations, Cargill has investigated the modification of HVOs using simple and affordable chemical processes transferable to existing food refinery infrastructure. The goal of this work is to achieve “paraffin-like” properties in the modified HVOs (including smooth and predictable crystallization behavior), while retaining the attractive features of HVOs described earlier.

Partial (trans) esterification of the HVOs with other lipid-derived species was the synthetic route selected as a basis for the chemical modifications investigated. Formation of the resulting complex lipid mixtures was monitored using gel permeation chromatography, and detailed chemical characterization was carried out using high temperature gas chromatography coupled with mass spectrometry.

Crystal morphology was studied using microscopy and XRD, while thermal properties such as melting profiles were assessed using conventional solid fat content measurement (NMR) and DSC. Mechanical properties such as flexural and compressive strength, hardness and brittleness were quantified using a TA.XT plus texture analyser. The melting temperatures of the modified HVOs ranged between 40 and 60 °C. The hardness values ranged from 4 times softer to 2 times harder than beeswax. Brittleness values could be reduced below that of beeswax. The products showed a high cohesiveness and several did not break under compression.

The application of these advanced scientific tools has revealed new understanding of the structure-performance relationships in complex lipid mixtures. Our study confirms that HVOs can be modified to substantially match the textural characteristics of paraffin and beeswax. The versatile nature of the modification and blending techniques used allow for a wide range of thermal and mechanical properties, which can thus be tailored to the application of interest. Finally, the scalability of the synthesis was successfully demonstrated on a refinery pilot plant unit.

Vegetable oils and their fatty acids (FAs) derivatives have become the most promising alternative solution to design performant bio-based polymers. The increasing success toward these renewable resources is explained by their wide availability, their low toxicity, as well as

their reactive sites opening up various possibilities of functionalization. However, considering the poor reactivity of the internal unsaturation of FAs through radical process, most currently available synthesis of monomers reported in literature are limited to polycondensation. Consequently, there is an important challenge in providing monomers from FAs suitable for radical polymerization to provide bio-based vinyl polymers. For instance, poly(alkyl)methacrylate (PMAs) have known a significant widespread since the beginning of the 20th century in various applications and more especially as viscosity modifier additives for mineral oils. However, except some patents reporting the synthesis of acrylic acid from glycerol, the majority of common PMAs are originated from petroleum resources. Therefore, the objective of our work is to synthesize monomers from fatty acids bearing reactive function through radical process and evaluates their resulting methacrylate polymers as viscosity modifiers in various oils such as mineral or vegetable oils.



Biodiesel is a fuel with various benefits over the conventional diesel fuel. It is derived from renewable resources, it has less emission to environment, it is biodegradable so has very limited toxicity and above all its production can be decentralized so that it could have a potential in helping rural economies. However, there are also some worth mentioning challenges associated with production of biodiesel. Among them repeatedly mentioned are the cost of feedstock and the choice of convenient technology for efficient production of the fuel from diverse feedstock types. There are four main routes by which raw vegetable oil and/or animal fat can be made suitable for use as substituent fuel in diesel engines without modification. These are direct use or blending of oils, micro-emulsion, thermal cracking or pyrolysis and transesterification reaction. Due to the quality of the fuel produced, the transesterification method is the most preferred way to produce biodiesel from diverse

feedstock types. Through this method, oils and fats (triglycerides) are converted to their alkylesters with reduced viscosity to near diesel fuel levels [XXVIII]. There are different techniques to carry out transesterification reaction for biodiesel production. Each technique has its own advantages and disadvantages as well as its own specifically convenient feedstock character. There are also some very important reaction conditions to be given due attention in each of this techniques for efficient production of biodiesel, such as molar ratio of alcohol to oil, type and amount of catalyst, reaction temperature, reaction time, reaction medium, type and relative amount of solvents, among others.

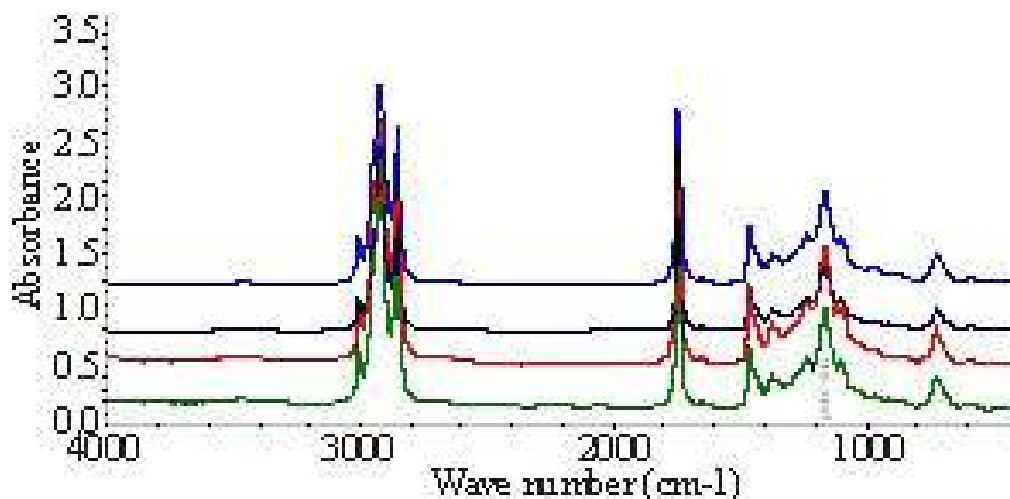
This review is meant to investigate the main transesterification techniques for biodiesel production in terms of their choice of feedstock character as well as their determinately required reaction conditions for efficient biodiesel production, so that to give an overview on their advantages and disadvantages.

Foss in Hillerød develops analytical instruments and in this project deals with the development of an analytical instrument for edible oils for rapid analysis purpose by replacing the time consuming conventional methods. In this project three parameters of edible oils i.e. Saponification number, Peroxide value & free fatty acids are chosen for the analysis [XXXIV].

Different oils including Rape, palm, sunflower, sesame, maize, olive etc are collected and have been used for analysis using conventional methods and further by FTNIR, FTIR. A GC/MS method was developed using capillary column and iontrap technology for analyzing of free fatty acid. The Free fatty acids chosen as a parameter for analysis includes C12, C14, C16, C18, and C18:1, C18:2, C18:3.

These Fatty acids are modeled by developing Partial Least Squares calibration curves. The collected spectral data from both NIR & IR are used for development of multivariate methods using unscrambler.

(iv) FTIR Spectra of oils



V) Conclusion

In the course of this review, new thermosetting polyurethanes from vegetable oils have been developed, showing that it is possible to exploit renewable resources to manufacture original and useful materials.

There has been rapid development in the field of click chemistry in recent years; this has provided a versatile toolbox of available reactions that can be combined with other synthetic and polymerization approaches to prepare a diverse range of polymeric materials with a variety of properties and applications. Without any doubt, the application of click strategies in the area of polymer chemistry will continue to facilitate the synthesis of macromolecules in a more efficient and simple manner alongside the design of unprecedented macromolecular structures. However, each of the reactions described previously present limitations, and reasonable efforts should be made to meet all the criteria of click chemistry, including using non-toxic reagents and carrying out aqueous or solvent-free reactions.

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