

# Synthesis pathways for bio-renewable thermosets form vegetable oils

Reena S. Vaidya<sup>1</sup>, Gajanan N Chaudhari<sup>2</sup>, Nitin Raut<sup>3</sup>

<sup>1</sup> Shri Shiivaji Science College, Dept. of Chemistry, SGB Amravati University, Amravati, India  
reenanraut@gmail.com @email.com

<sup>2</sup> Shri Shiivaji Science College, Dept. of Chemistry, SGB Amravati University, Amravati, India  
author2@email.com

<sup>3</sup> Faculty of Engineering, Sohar University, Sohar, Sultanate of Oman  
drnitinraut@gmail.com

**Abstract:** Biobased thermosets are synthesized from vegetable oil by addition polymerization or copolymerization with the petroleum based monomers. The double bond in the triglycerides of vegetable oils can be functionalized by different techniques and treated effectively to yields thermoset with desired properties. The thermomechanical properties of these thermosets can be controlled by a proper control of the structure and choice of suitable comonomers. This study takes into account the various techniques which are commercially employed for functionalization of the double bond and subsequently synthesize the thermoset.

**Keywords:** epoxidation, biocomposites, thermosets, acrylation, maleinization.

## 1. Introduction

Natural polymers in the form of cotton, wool, silk and leather are extensively used in our day to day life. Vulcanized natural rubber was amongst the first synthetic polymer derived from natural polymeric materials. Along with the use of petroleum products there has been an exponential growth in the use of petroleum based synthetic polymer. The evolution started in the beginning of the 20th century since the synthesis of completely synthetic phenol formaldehyde resin. The last two decades have shifted the focus from petroleum based polymers and plastic to synthetic polymers and composites from renewable sources and this has become of great interest to researchers and scientists. The use of starch, cellulose, lignin, lipids and proteins has re-energized and rebooted the polymer industry (Gandinei, 2008, Lligadas, 2013).

This is not only because of the renewability of the sources, but also because of the depleting fossil fuel reserve. Also environmental sustainability and economics govern the choice between petroleum and bio-based polymers and composites. The environmental pollution and non-biodegradability of the petroleum based polymers and composites are of serious concerns and efforts are concentrated on reducing or partially or completely replacing them with bio based polymers and bio-composites (Miyagawa, 2005).

Bio-composites consist of matrix structure reinforced partly or completely with nonrenewable fibers. These bio-composites are used in construction, automobile and electronic industries. Bio-composites are preferred over polymers because of their mechanical and thermal

properties. These are normally strong and stiff and retain their properties over a wide range of temperatures. Their utilizable life span and density coupled with economical maintenance make them an obvious choice over metals. These composites are classified as thermoplastic and thermosets. Thermoplastics composites which are a combination of plastics and short fibres normally find applications in the automobile industries in door panels and dashboards (Vaidya et al., 2012). Resins filled with long fibers, termed as thermosets are extensive employed in renewable energy and marine applications.

As compared to the first generation bio-composites, today they are economical due to emerging and innovation processing technologies. Therefore the applicability and sustainability has increased rapidly.

These thermoset can be synthesized from a wide range of plant and vegetable oils which are ester of different fatty acids commonly called triglycerides. Because of the presence of the multiple carbon-carbon double bonds in the fatty acid chain they can be transformed with hydroxyl, carboxyl, amine and epoxy groups and can be cross linked to produce rigid polymers. These are cross linked with synthetic groups or cross linkers in the form of isocyanates, amines, polyols and poly-carboxylic acids. Present day research is focused to find a biological source for the isocyanate crosslinker. The choice of the plant and vegetable oils depends on the geographic location and the native crops are given preference. Plant or vegetable oils which are used as a renewable source are soybean, linseed, rapeseed and sunflower.

Different reaction pathways are employed for modifying the triglycerides in order to achieve desired properties and functional performance in the resulting thermoset. Oil

modifies unsaturated polyester s can be strengthen by introducing urethane in the polymer matrix. The presence of urethane in the resulting bio-composite makes it suitable and easy to engineer the application of these biocomposites to a variety of structural applications. Numerable variation and combination in the unsaturated oil based polyester reinforced by urethane and wide variations in the composition of isocyanate results in different type of thermosetting resins for a broad range of application.

## 2. Thermoset from vegetable

Vegetable oil consists of a mixture of triacylglycerol where in one molecule of glycerol is attached to three different fatty acid groups as in Fig. 1. The nature and number of carbon atoms in the fatty acids chain differs and hence these triacylglycerol are of different varieties (Chaudhary, et al., 2012). During the seed development the synthesis of glycerolipid and fatty acid take place simultaneously. 95 % of the weight of the Triacylglycerol or triglycerides is the weight of the fatty acid and these fatty acids determine the contents and chemical compositions of the vegetable oil which in turn depends on the plant oil and geographical location (Montero, 2011).The number of carbon atoms in the fatty acid chain is between 14 to 22.The number of carbon- carbon double bond is from 0 to 3 for each molecule of fatty acid. The fatty acids in castor oil are characterized by an additional hydroxyl functional group. Similarly, vernonia oil and licania oil have epoxide and ketone functional groups. The presence of these additional functional groups increases the versatility and chemical reactivity of the fatty acids and the triglycerides. , vernonia oil and licania oil have additional functional groups hydroxyl, epoxide and ketone. The degree of unsaturation also varies depending on the triple carbon –carbon bond. The fatty acids compositions and content depends on the season, growth conditions and purification methods, as summarized in table 1.

Table 1 Fatty Acid Composition of Different Plant Oils (Wool and Sun, 2005).

Fatty Acid	Oil					
	1	2	3	4	5	6
Palmitic 16:0	5.50	11.0	44.4	3.00	1.50	6.00
Stearic 18:0	3.5	4	4.1	1	0.5	4
Oleic 18:1	19.1	23.4	39.3	13.2	5	42
Linoleic 18:2	15.3	53.2	10	13.2	4	47
Linolenic 18:3	56.6	7.8	0.4	9	0.5	1
Gadoleic 20:1	–	–	–	9	–	–
Erucic 22:1	–	–	–	49.2	–	–
Ricinoleic 18:1	–	–	–	–	87.5	–

\*1.Linseed                      2.Soybean                      3.Palm  
4.Rapeseed                    5.Castor                        6.Sunflower  
\*\*Fatty Acid Composition (X:Y, where X is the number of carbon atoms and Y is the number of double bonds) %

Biocomposites and thermosets in general are synthesized mainly from soybean oil because of higher supply, low cost and the composition, mainly the unsaturated fatty acid content. As seen from table 3 the percentage of unsaturated fatty acids in soybean oil is nearly 80 to 85. The percentage of saturated fatty acid ranges from 20 to 25 percent with (palmitic and stearic acid) whereas the unsaturated content, linoleic acid constitutes 55 percent and 25 percent is oleic acid. It is estimated that there 4.6 carbon-carbon double bond per mole of soybean oil and the avg. molecular weight is 874 g/mol (Petrovic, 2010).The presence of the highly reactive epoxy and hydroxyl group in triacylglycerol of the vegetable oil facilitates the conversion of the carbon-carbon double bond (Del Rio et al., 2010). The process technologies for petroleum based polymers could be suitably applied to process biopolymers and biocomposites (Wool and Sun, 2005).

A number of synthetic reaction paths could be followed to functionalize the glycerides of vegetable oils which may subsequently polymerized by ring opening, polycondensation or free radical polymerization (Wool and Sun,2005). The vegetable oil triacylglycerol can be reformed to unsaturated sites or glycerol sites or both.

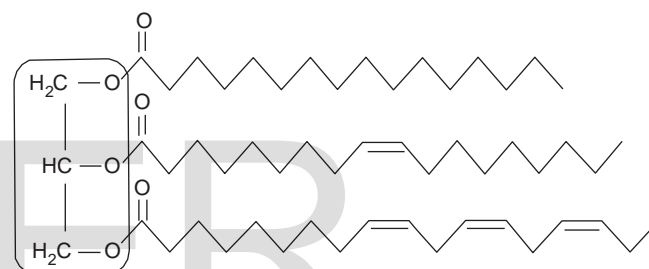


Fig. Triglyceride molecule

The epoxy or maleate modified unsaturated carbon of the triglycerides can be polymerized by the ring opening polymerization whereas the hydroxylated unsaturated carbon glyceride cab be polymerized by the polycondensation. Free radical polymerization of the acrylated modified triglyceride form the epoxy functional group can be done. Additionally the hydroxylated glycerides can be converted to maleate half ester and ester triglycerides. Amidation or glycerolizes of the monoglyceride in the vegetable oil glyceride could be done. This can be subsequently polymerized by the polycondensation method.

The hydroxyl groups of the vegetable oil monoglyceride are maleanised with maleic anhydride and the resulting maleanised unsaturated fatty acid is polymerized by free radical polymerization. Alternatively saturated maleanised monoglyceride can also be produced for subsequent free radical polymerization.

The conversion rate for the epoxidation of the plant oil makes it economically feasible to be the first choice in its industrial application with the annual production being 160.59 million metric tons.

## 3. Synthesis routes

The fatty acid content of the plant oil can be converted and modified to industrially used biocomposites and polymers by

the three different routes. These are shown in figure.....As shown these plant oils can be directly polymerized, chemically modified or producing intermediate chemicals used to produce monomers.

### 3.1 Direct Polymerization

Free radical or cationic polymerization of vegetable oils can be employed to break the double bonds of the fatty acid. The polymerization of linseed or tung oil has been reported and is used for the synthesis of polymers and composites.

The triacylglycerol or the double bonds in plant oil reacts with atmospheric oxygen and undergoes oxy-polymerization as shown in Fig. 2. Initially the double bond of the methylene group of the triacylglycerol is dehydrogenated which then undergoes radical polymerization and produces crosslinking groups in the form of alkyl, ether or peroxy groups ( Mallegol et al., 2000, Meier et al., 2007, Gonon et al., 2001).

Plant oils with high iodine values can be cationically polymerized initiated by the presence boron trifluoride diethyl etherate (Meier, 2007). Some vegetable oils can be modified by styrene, divinylbenzene, norbornadiene, or dicyclopentadiene using methyl oleate based trifluoride diethyl etherate initiator (Ronda et al., 2011). This rate of this homogeneous cationic copolymerization can be increased by using microwave irradiation which mobilizes and increases the reactivity of the reaction of the internal double bonds.

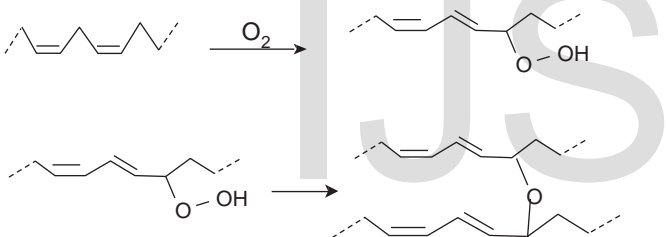


Fig. 2. Oxidative polymerization of triglycerides

### 3.2 Chemical Transformation

The triacylglycerol's of the plant oil can be chemically altered or transformed by reactions of the ester group or the alkene group along the aliphatic chains and the hydroxyl groups (Gandini, 2008). The ester groups can be very easily hydrolyzed or transesterified to produce biocomposites or intermediates for further polymerization. The ester or alkene groups can be functionalized by a number of reaction routes and pathways as described below.

### 3.3 Epoxidation of Triglycerides

In the past few years the requirement of temperature and light resistant polymers and composites has grown substantially. The vegetable oil based polymers have exhibited improved thermal and light resistant properties in a variety of applications (Petrovic, 2010).

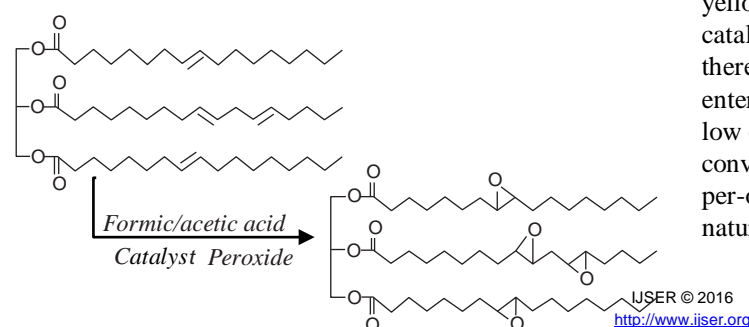


Fig. 3 The process of Epoxidation

The alkene in the triacylglycerol of the vegetable oil on reaction with an organic peroxy acid produces cyclic ethers composed of three elements in the ether ring as seen in Fig.3. Such cyclic ether is called as epoxide. Amongst the vegetable oil linseed oil due its high linoleic acid content and availability is epoxidized on a large extent. Epoxidized linseed and soybean oil is available commercially (Wool and Sun, 2005) because the oxirane ring can be further chemically transformed to synthesize thermoset by polymerization with anhydride or amine compounds (Stemmelen, 2011). Apart from the conventional epoxidation methods, it can also be achieved by acid ion exchange resins (AIER), enzymes and acid catalysts.

### 3.4 Conventional Chemical Treatment

The conventional process for epoxidation is most widely used for large scale commercial productions. The epoxidation of this plant oil is achieved by reaction with peracids which are produced onsite by treating carboxylic acid with concentrated sulfuric acid. The epoxidation kinetics of cotton seed oil with hydrogen peroxide in the presence of various inorganic acids was studied by Dind et al; 2008. Carboxylic acid was found to be an effective oxygen carrier as compared to formic acid. Sulfuric acid was reported to highly efficient and effective in catalyzing the epoxidation (Wool and Sun, 2005).

Meyer et al: 2008 reported a conversion of 83 percent for the epoxidation of soybean oil under atmospheric pressure and 500 C in approximately 600 minutes. Soybean oil was epoxidized by peroxyacetic acid catalyzed by sulphuric acid. (Seniha, 2006). The sulfuric acid epoxidation of soybean, sunflower, corn and jatropa oil in presence of peroxyacetic acid was reported by Cai et al., 2008. Soybean oil is reported to give the highest reaction conversion as compared to sunflower, corn, jatropa.

The epoxidation of mhau oil was investigated by Dind et al. 2008, in an attempt to optimize the process. The effect of catalyst, temperature, reactants concentration and mixing speed was investigated. The epoxidation was catalyzed by sulphuric and nitric acid in presence of hydrogen peroxide and glacial acetic acid. The epoxidation increased the economy values of mhau oil. As with other plant oils the sulphuric acid was found to be effective as a catalyst as compared to other inorganic acids.

### 3.5 Acid Ion Exchange Resin (AIER) Method

The peroxy acid synthesized from the reaction between hydrogen peroxide and formic acid or acetic acid enters the active sites of an acid ion exchange resin in the form of small yellowish organic polymer beads. In the AIER method the catalyst (AIER) active sites are filled up by the per-oxy acid, therefore the triglyceride when loaded into the reactor cannot enter the AIER because of the gel type structure leading to low oxirane degradation (Gonon, 2001). The AIER catalyzed conversion of the unsaturated fatty acid to oxirane ring using per-oxyformic or per-oxyacetic acid varies with the type and nature of the plant oil.

The kinetic studies on AIER epoxidation of soybean oil in toluene exhibit that AIER epoxidation is more efficient and advantageous than the conventional epoxidation method because of selectivity and suppression of the side reaction (Petrovic et al.). Per-oxyformic acid is comparably far more efficient than per-oxyacetic acid (Gandini, 2008). The conversion of double bonds to oxirane groups and the reaction time was minimized for the AIER (Amberlite IR-120) epoxidation of karanja oil in presence of per-oxy acetic acid (hydrogen peroxide and acetic acid) at an optimum epoxidation temperature of 55 to 65<sup>0</sup> C., molar ration of acetic acid and hydrogen peroxide to oil as 0.5 and 1.5 respectively (Stemmelen, 2011)

### 3.6 Enzymatic Method

The unsaturated and saturated fatty acids of the plant oils are converted into per-oxy acid in the presence of hydrogen peroxide and lipase. This enzymatically synthesized per-oxy acid is the actual expoxidizing agent whereas the carboxylic acid just acts as an oxygen carrier. The unsaturated per-oxyacid's can also undergo self-epoxidation by the reaction (Fig. 4) to produce per-oxyoleic acid and epoxy stearic acid.

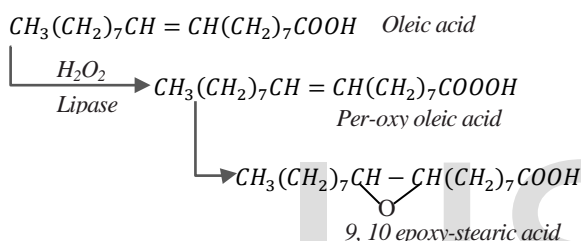


Fig. 4 Self epoxidation-conversion of oleic acid to epoxy-stearic acid

The lipase helps in converting these unsaturated fatty acids to unsaturated per-oxyacid by per-hydrolysis which is subsequently epoxidized by self-epoxidation in the absence of a catalyst (Rusch, 1997). The epoxidized peroxy acids produced also acts as expoxidizing agent (Fig. 5)

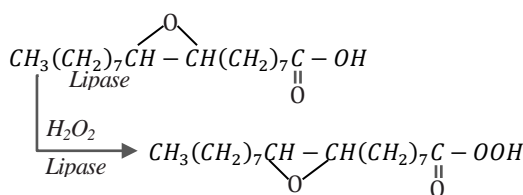


Fig. 5 Epoxidized peroxy fatty acid

Per-oxy acids are also produced by the lipase catalyzed per-hydrolysis of the carboxylic acid alkyl esters as in Fig. 6.

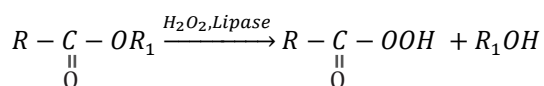


Fig. 6 Production of peroxy acid from esters

Similarly the glycerides also undergo enzymatic per-hydrolysis. The selectivity, yield and conversion of epoxidation can be improved by using enzyme catalyst. This increases the safety aspect of the in-situ epoxidation process. This can be achieved by adding lipase step wise which proves to be a very good alternative to chemical treatment.

However, the low stability of the lipase under the reaction conditions significantly limits the enzymatic epoxidation process. In enzymatic epoxidation the enzymatic efficiency is reduced at elevated temperatures and hydrogen peroxide concentrations (Piazza, 2005).Candida Antarctica B lipase which is most prominently used in these epoxidation is found to be stable above 50<sup>0</sup>C but does not favour epoxidation due to the decomposition of hydrogen peroxide.

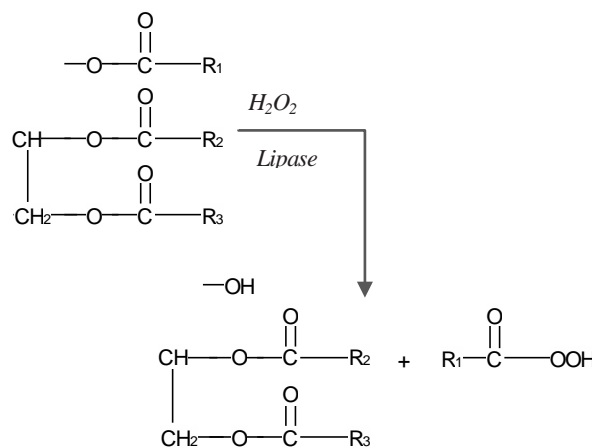


Fig. Enzyme catalysed perhydrolysis

Under circertain reaction conditions, lipase catalyst seems to offer excellent stability and reusability for epoxidation. (Puig, 2006). Shangde Sun et al. (2011) investigated the immobilized Candida Antarctica B lipase epoxidation of Sapindus mukorossi seed oil in presence of per-oxystearic acid(hydrogen peroxide and stearic acid) and reported the epoxidation was favored by enzymatic load and the activity of the enzymes reduce significantly at higher temperatures. Warwel et al., 2001, reported a selective epoxidation of lipase based catalytic epoxidation of different plant oils and the conversion in many case exceeded 92 percent (14-32).

Conversion as high as 99 percent are reported for the Candida Antarctica B lipase epoxidation of sunflower oil methyl esters in the presence of hydrogen peroxide and in the absence of alkanoyl group.

### 3.7 Metal Catalyst Method

The mineral acid catalyzed per-acid epoxidation process have several disadvantages, such as low selectivity of the catalyst, need of advanced separation processes and environmental and health safety. This can be substantially overcome by replacing the mineral acid catalyst with a metal catalyst. Metal catalyst such as titanium, molybdenum, tungsten is extensively used in the epoxidation of vegetable oils. These metals catalyst improve the oxirane content thereby enhancing the epoxidation efficiency. Researches on using metal catalyst (Titanium on amorphous silica) for epoxidation with hydrogen peroxide show increased conversions and yields (Frankl and Pryde, 2014). Ashish et al., 2014 reported 100 percent conversion of the unsaturated fatty acid of canola oil employing sulfated SnO<sub>2</sub> catalyst in a reaction time of 960 minutes.

### 3.8 Acrylation of Epoxidized Oils

The vegetable oil triglycerides on epoxidation can be

acrylated (Fig. 7) to produce thermally resistant thermoset. The acrylation can be achieved by using acrylic acid and epoxidized vegetable oil (Hodakowski, 1978). The acrylated triglycerides thus obtained can undergo addition polymerization. Acrylic acid itself acts as a catalyst however the higher conversion rates could be achieved by additionally catalyzing the reaction with tertiary amines or organometallic catalyst. The reaction schematic is as shown in Fig.7. Habib and Bajpai, 2011 acrylated epoxidized soybean oil catalyzed by trimethylamine and inhibited by hydroquinone. The unreacted acrylic acid is recovered by extraction with water or petroleum ether. The use of organometallic catalysts is quite common during the acrylation process.

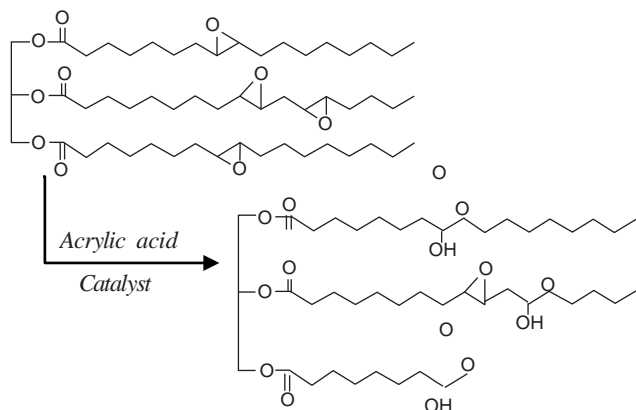


Fig. 7 Acrylation of epoxidized triglyceride oil

### 3.9 Maleinization of Acrylated Epoxidized Oils

The maleinization of the acrylated epoxidized oil can be carried out by reacting the acrylated epoxidized oils with maleic anhydride (Wool et al., 2009). This maleinization reaction introduces more double bonds in the triglycerides. The maleinization reaction must be properly controlled otherwise there will be an increase in the viscosity, which may gelate the oligomer thus produced. Typically maleinization could be followed by curing with styrene.

### 3.10 Hydroxylation of Triglycerides

Hydroxylation is one of the chief reaction pathways for functionalization of the triglycerides (Zlatanovic et al., 2004). Polyols can be synthesized by breaking the double bond of the fatty acid in triglycerides and replacing it with a hydroxyl group.

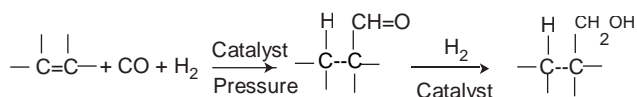


Fig. 8 Hydroformylation-creating primary hydroxyl group

These polyols are of great importance as they are used as initiators in the manufacture of polymeric polyols. The hydroxyl groups occur in some natural oils such as castor oil. These polyols are produced by the reaction of epoxidized triglycerides. Treating the epoxidized triglycerides with hydrochloric or hydrobromic acid will open the epoxidized triglyceride ring for further hydroxylation. Alternatively, this can also be achieved by acid catalyzed reaction in presence of methanol to produce methoxylated polyol (Fig. 8).

Catalytic hydrogenation can also be done to open the ring in order to introduce the hydroxyl groups.

## 4. Conclusion

The carbon double bond in a triglyceride can be functionalized by a variety of techniques. However, careful selection of the epoxidation process and subsequent preparation of thermosets depend on the properties desired in the final thermoset. The degree of epoxidation and the amount of epoxide present influence the properties of resulting product during the acrylation process. The acid values of the epoxidized oil are also important parameter. The polyol formation and subsequent polymerization depends on the type of acid used in the ring opening mechanism. Therefore, optimum choice of the epoxidation techniques will yield thermosets of desired value and application.

## Acknowledgement

The authors wish to thank Department of Chemistry at Shri Shivaji College of Science, Amravati, Maharashtra, India for providing the facilities and infrastructure for conducting the research studies. Also, the help and cooperation rendered by the University Department of Chemical Technology, Amravati, Maharashtra, India is highly appreciated.

## References

- [1] Alzina, C., A. Mija, L. Vincent, and N. Sbirrazuoli. 2012. Effects of incorporation of organically modified montmorillonite on the reaction mechanism of epoxy/amine cure. *J. Phys. Chem B* 116: 5786–5794.
- [2] Asish, K., R. Somidi, V. Rajesh, V. Sharma and A.K. Dalai. 2014. Synthesis of Epoxidized Canola Oil Using a Sulfated-SnO<sub>2</sub> Catalyst *Ind. Eng. Chem. Res.*, 2014, 53 (49), pp 18668–18677 *Ind. Eng. Chem. Res.*, 2014, 53 (49), pp 18668–18677
- [3] Cai, C., H. Dai, R. Chen, C. Su, X. Xu, S. Zhang and L. Yang. 2008, Studies on the kinetics of in situ epoxidation of vegetable oil, *European Journal of Lipid Science and Technology*. vol.110, no.4, pp.341-346.
- [4] Chaudhary, G.N., R.S. Vaidya, N.B. Raut and G.B. Shinde. 2012. Green fiber biocomposites, *International Journal of Biotechnology, Chemical & Environmental Engineering (IJBCEE)*, Vol.1, (3), December 2012
- [5] Dinda, S., A.V. Patwardhan, V. Goud and N.C. Pradhan. 2008. Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalyzed by liquid inorganic acids. *Bioresource Technology* 99, 3737–3744
- [6] Frankel, E.N., and E.H. Pryde. 1977. Catalytic hydroformylation and hydrocarboxylation of unsaturated fatty compounds. *J Am Oil Chem Soc.*; 54:874A-83A.
- [7] Gandini, A. 2008. Polymers from renewable resources: a challenge for the future of macromolecular materials. *Macromolecules*, 41 (24):9491-504.
- [8] Gonon, L., J. Lemaire, J. Gardette and J. Malle. 2001. Long-term behaviour of oil-based varnishes and paints. Influence of film thickness on the photo oxidation. *Polym. Degrad. Stab.* 72:191-7.
- [9] Hodakowski, L.E., C.L. Osborn, E.B. Harris and E. Brucey. 2011. Polymerizable epoxide-modified

- compositions. U.S. Patent US4119640, 1978. Firdous Habib and Madhu Bajpai, synthesis and characterization of acrylated epoxidized soybean oil for UV cured coatings, chemistry & chemical technology Vol. 5, No. 3, 2011
- [10] Klaus, M., and S. Warwell. 2005. Lipase-catalysed preparation of peroxy acids and their use for epoxidation. *J. Mol. Catal. A: Chem.* 1997, 117, 311–319 Piazza GJ, Foglia TA. Preparation of fatty amide polyols via epoxidation of vegetable oil amides by oat seed peroxygenase. *J Am Oil Chem Soc.* 2005; 82(7):481-5.
- [11] Mallegol, J., J. Lemaire, J.L. Gardette, 2000. Drier influence on the curing of linseed oil. *Prog. Org. Coat.* 0; 39(2-4):107-13.
- [12] Meier, M, J. Metzger and U Schubert. 2007. Plant oil renewable resources as green alternatives in polymer science. *Chem Soc. Rev*; 36 (11):1788.
- [13] Petrovic, Z.S. 2010. Polymers from biological oils. *Contemp. Mater* 2010; 1(1):39-50.
- [14] Ronda, J.C., G.Lligadas, M. Galia and V. Cadiz. 2011. Vegetable oils as platform chemicals for polymer synthesis. *Eur. J Lipid Sci. Technol.*; 113(1):46-58.
- [15] Rosana, C., S. Schneider I, R.S. Luciano, T.B. Bitencourt II, M. Nascimento II and M. Nunes. 2009. Chemo-enzymatic epoxidation of sunflower oil methyl esters'. *Braz. Chem. Soc.* vol. 20 no. 8 Sao Paulo.
- [16] Seniha, G.F, Y. Yagci and E. Tuncer, 2006. Polymers from triglyceride oils. *Prog. Polym Sci.* 2006; 31(7):633-70.
- [17] Stemmelen, M., F. Pessel, V., Lapinte, S. Caillol, J.P. Habas and J.J. Robi. 2011. A fully biobased epoxy resin from vegetable oils: from the synthesis of the precursors by thiol-ene reaction to the study of the final material. *J Polym Sci., Part A: Polym Chem*, 49(11):2434-44.
- [18] Sun, S., L. Shan, Y. Liu, Q. Jin, Y. Song and X. Wang, Solvent-free enzymatic synthesis of feruloylated diacylglycerols and kinetic study. *Journal of Molecular Catalysis B: Enzymatic*, Volume 57, Issues 1–4, May 2009, Pages 104–108.
- [19] Vaidya, R.S., G.N. Chaudhary, N.B. Raut, G.B. Shinde and N.G. Deshmukh. 2012. Synthesis of Biocomposites from Natural Oils- a Review. *International Conference on Environmental, Biomedical and Biotechnology IPCBEE vol. 41*
- [20] Wool, R.P. and X.S. Sun. *Bio-based polymers and composites*, 2009 Elsevier Science & Technology Books; 2005. Lu Y, Larock RC. Novel polymeric materials from vegetable oils and vinyl monomers: preparation, properties, and applications. *Chem. Sus. Chem*; 2(2):136-47.
- [21] Zlatanovic, A., Lava, C., Zhang, W., Petrovic, Z.S., 2004. Effect of structure on properties of polyols and polyurethanes based on different vegetable oils. *J. Polym. Sci., Part B: Polym Phys J Polym Sci. Part B: Polym Phys* .42, 809