Journal of Mechanical Engineering *Vol SI 5(3), 50-60, 2018*

Spectroscopic Studies of Oils and Its Synthesized Bio-Polymer

*Nurulsaidatulsyida Sulong**
Faculty of Mechanical Engineering, Universiti Teknologi MARA,
Pasir Gudang Campus, Jalan Purnama,
81750 Masai, Johor, Malaysia.

Anika Zafiah Mohd Rus
Sustainable Polymer Engineering, Advanced Manufacturing and Material
Center (AMMC), Universiti Tun Hussein Onn Malaysia,
86400 Parit Raja, Batu Pahat, Johor, Malaysia.

Nik Normunira Mat Hassan
School of Engineering, KDU University College, 40150 Shah Alam,
Selangor, Malaysia.

Noraini Marsi
Department of Mechanical Engineering,
Faculty of Engineering Technology, University Tun Hussein Onn Malaysia,
86400 Parit Raja, Batu Pahat, Johor, Malaysia.

**saidatulsyida@johor.uitm.edu.my*

ABSTRACT

Nowadays, the development of alternatives to petroleum based - natural based polymeric materials were grow rapidly due to contemporary challenge attributable to environmental concerns and the effects of fluctuating oil prices.Triglycerides, the primary components of vegetable oils, are an abundant, renewable, and widely investigated as the alternative feedstock for polymeric materials [1], In this study, 3 types of cooking oil was used such as, Virgin Oil (VO), 'Popia' Oil (PO), and Mixed Oil (MO) for the synthesis of bio-monomer named as Virgin Oil Monomer (VOM), Popia Oil Monomer (POM) and Mixed Oil Monomer (MOM). These bio-monomers then converted to the bio-polymers named as Virgin Oil Polymer (VOP), Popia Oil Polymer (POP) and Mixed Oil Polymer (MOP). The spectroscopic properties of oils, bio-monomers and bio-polymers were tested using Fourier

---

ISSN 1823- 5514, eISSN 2550-164X
© 2018 Faculty of Mechanical Engineering,
Universiti Teknologi MARA (UiTM), Malaysia.

Received for review: 2017-05-10
Accepted for publication: 2017-06-16
Published: 2018-02-15

Transform Infrared Spectroscopy (FTIR). The characteristic peak 3010.65 cm^{-1} was attributed to the C–H stretching of VO, PO, and MO. The peaks at 3010.65 cm^{-1} disappear during the epoxidation process and new peak appear around 3330cm^{-1} – 3450 cm^{-1} in the VOM, MOM and POM attributed to the hydroxyl groups (O-H). For VOP, MOP, and POP, a strong 3330 cm^{-1} - 3345 cm^{-1} absorption band characteristic of the N–H group and an absorption band characteristic of the C=O group centered around 1700 cm^{-1} are present in all the FTIR spectra. Hence, its shows all types of oils were successfully converted to the bio-monomers and bio-polymers as refer to the absorption band in spectroscopic analysis.

Keywords: *FTIR, Oils, Bio-Polymer, Hydroxyl group, Epoxidation.*

Introduction

According to [2], vegetable oils are one of the cheapest and most abundant, annually renewable natural resources available in large quantities from various oil seeds. In general, human food or animal feed were produced from bulk of vegetable oils while another finds non-food uses, such as the production of soaps, lubricants, coatings and paints also come from vegetable oils based. While, according to [3], vegetable oil is one of the renewable fuels that become more attractive recently because of their environmental benefits and the fact that they are made from renewable resources.

In this study, vegetable oils were obtained from SMI's and fatty acid were chemically manipulated at the laboratory scale using less than 1L vegetable oils to convert to the bio-monomers. These bio-monomers were cross-linked with cross linking agent to produced bio-polymers. The Fourier Transform Infrared (FTIR) is used to determine the formation of OH group as the indication of bio-monomers conversion and determination of the urethane groups (-NH) and the carbonyl group as the polymerization process were totally take placed.

Fourier transform infrared (FTIR) spectroscopy is one of the instrument that can be used to characterize material by using infrared spectroscopy. FTIR can be used to structural analysis of oils, bio-monomoner and also bio-polymer. In Table 1, the absorption bands and the corresponding function/groups are assigned [4].

Table 1: Some representative IR absorption band values for fatty acids [4].

Absorption band (cm^{-1})	**Functionality**
3500	-OH functions corresponding to free gycerol and/or residual moisture
2930-2850	$-CH_2-$ groups (with an additional weak shoulder around 2960cm^{-1} reflecting the presence of terminal methyl groups)
1745	-COOH group
1160	C-O-C functions of the ester group
720	$-(CH_2)n-$ sequences of the aliphatic chains of the fatty acids
1650, 3010	Non-conjugated unsaturation of linoleic acid for linseed oil
990	Conjugated unsaturation of eleostearic acid chain for tung oil
970	*Trans* configuration of eleostearic acid chain for tung oil

Methodology

Materials

Three types of oils was collected which is one of the oils is natural oil that's come from vegetable oil and another two oils is waste cooking oils. 3 types of cooking oil was used such as, Virgin Oil (VO), 'Popia' Oil (PO), and Mixed Oil (MO) for the synthesis of bio-monomer. Waste cooking oils were taken from Small Medium Industries (SMI's) in Parit Raja, Batu Pahat, Johor. PO was taken from waste of cooking 'popia' crisp while MO was based on oil from cooking tapioca hot crisp.

Sample Preparation of Bio-Monomers

Virgin Oil (VO), 'Popia' Oil (PO), and Mixed Oil (MO) were chemically manipulated at laboratory scale using less than 1L of cooking oils.The catalyst was prepared to generate the epoxies from the unsaturated fatty compound to produced monomer, and second reaction is the acid-catalyst ring opening of the epoxies to form polyols or bio-monomer [5][6][7][8][9]. These bio-monomers were named based on the starting vegetable oils such as virgin oil monomer (VOM), 'popia' oil monomer (POM), and mixed oil monomer (MOM).

Sample Preparation of Bio-Polymers

Virgin oil monomer (VOM), 'popia' oil monomer (POM), and mixed oil monomer (MOM) were mixed with cross linking agent that is 4, 4'-Methylene Diphenyl Diisocyanate (MDI) and added with Toluene as the lubricant. The mixture stirred at 50°C at about 15 minute until the mixture become high viscous compound then the compound poured to the Teflon sheet at the room temperature for at least 12 hours until the disappearance of N=C=O groups as measured by Fourier Transform Infrared Spectroscopy (FTIR) [5][6][7][8][9].

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR stands for Fourier Transform Infrared. It is most useful for identifying chemicals either organic or inorganic materials. Oils, bio-monomers and bio-polymers were positioned flat on the crystal plate and clamped-down. When analyzed by infrared spectroscopy, materials produced a spectrum or fingerprint that identified the molecular composition of the materials.

Result and Discussion

Vegetable oils and its waste oils

Three types of cooking oil that were mixed oil (MO), 'popia' oil (PO) and virgin oil (VO) were tested by using Fourier Transform Infrared (FTIR). Figure 1 shows overlay spectra of three types of oils. These spectra show the typical characteristic absorption bands for common vegetable oils. The absorption peaks at 3010 cm^{-1} are due to C-H stretching vibration of the cis double bond (=CH). This peak also found by [10] which shows the C-H stretching vibration of the cis-double bond (=CH) for non-oxidized oil sample varies from 3009-3006 cm^{-1} while according to [11] shows the absorption peaks at 3006 cm^{-1} are due to the cis C=CH stretching. The prominent peak in the region 2900–2800 cm^{-1} is due to C-H stretching mode which is due to the symmetric and asymmetric stretching vibration. The C=O stretching is observable in the region 1800 cm^{-1}–1700 cm^{-1} which is 1744 cm^{-1} is refer to the ester carbonyl functional group of triglycerides.

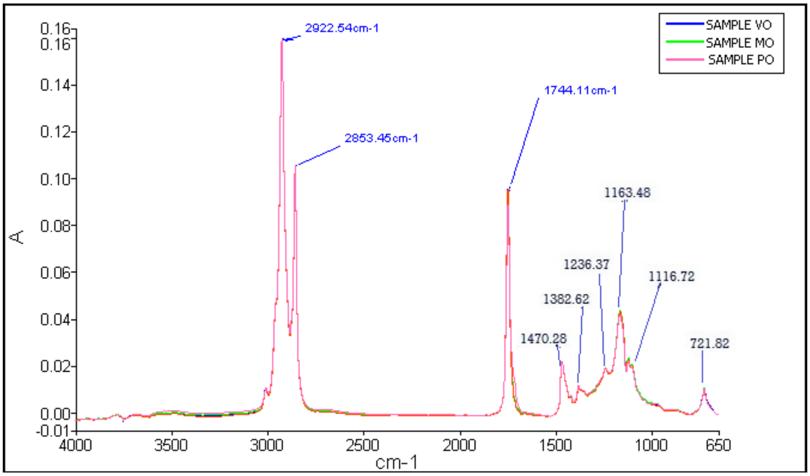

Figure 1: Overlay spectra of FTIR for Virgin Oil (VO), Mixed Oil (MO), and 'Popia' Oil (PO).

Bio-monomer conversion for vegetable and waste cooking oils

MO, PO, and VO were analyzed using FTIR to check whether these three type of oil were converted to MOM, POM, and VOM respectively. The FTIR spectra of MO, PO, and VO were overlay with MOM, POM, and VOM as shown in Figure 2 to Figure 4. The characteristic peak 3010.65 cm^{-1} was refered to the C–H stretching of VO, PO, and MO. The peaks at 3010.65 cm^{-1} disappear during the epoxidation process and new peak appear around 3330cm^{-1} – 3450 cm^{-1} in the VOM, MOM and POM attributed to the hydroxyl groups (O-H). The peak at 1744.11 cm^{-1} refer to ester carbonyl functional group (C=O) of triglycerides in the VO decrease to 1709.31cm^{-1} when become VOM which is dimerization weakens the C=O bond and lowers the stretching force constant, resulting in the lowering of the carbonyl frequency to about 1709.30cm^{-1}[12].

While, 1744.10cm^{-1} decrease to 1741.25cm^{-1} and 1744.04cm^{-1} to 1742.6804cm^{-1} for PO-POM and MO-MOM respectively which is the peak is very strong band of esters group (C=O) in range 1750cm^{-1}-1735 cm^{-1}. Another peak are same between oils and monomers but other peak spectra was appear at 1030cm^{-1}-1040 cm^{-1} which indicate C-O stretching absorptions, which in usually in fact appear in the range from 1300 cm^{-1} to 1000 cm^{-1} [12]. Two or more bands appear for the C-O stretching vibrations in esters in that range. Generally, the C-O stretch for the 'alcohol' part of ester may appear as a weaker band in the range from 1150 cm^{-1} to 1000 cm^{-1} [12].

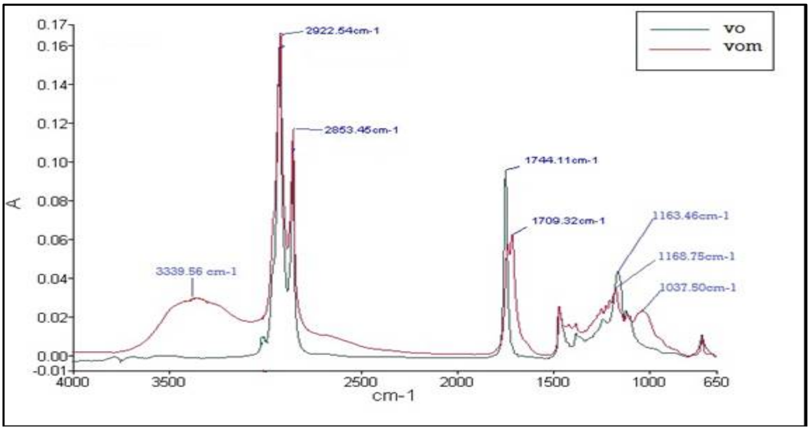

Figure 2: Overlay spectra of FTIR for Virgin Oil (VO) and it's monomer (VOM)

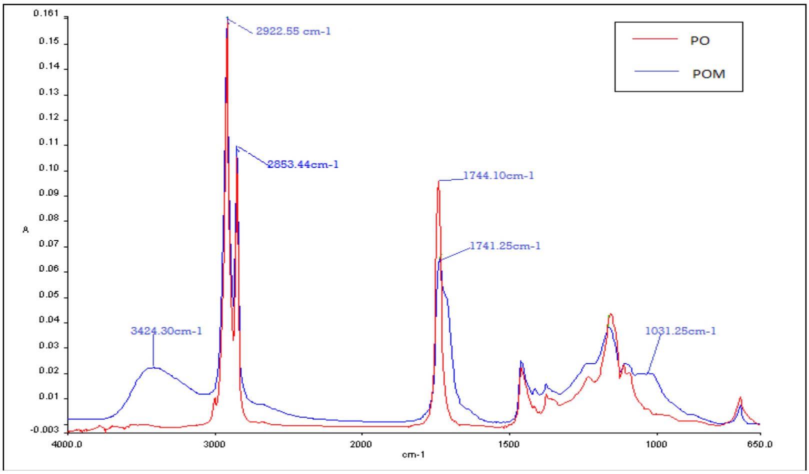

Figure 3: Overlay spectra of FTIR for 'Popia' Oil (PO) and it's monomer (POM)

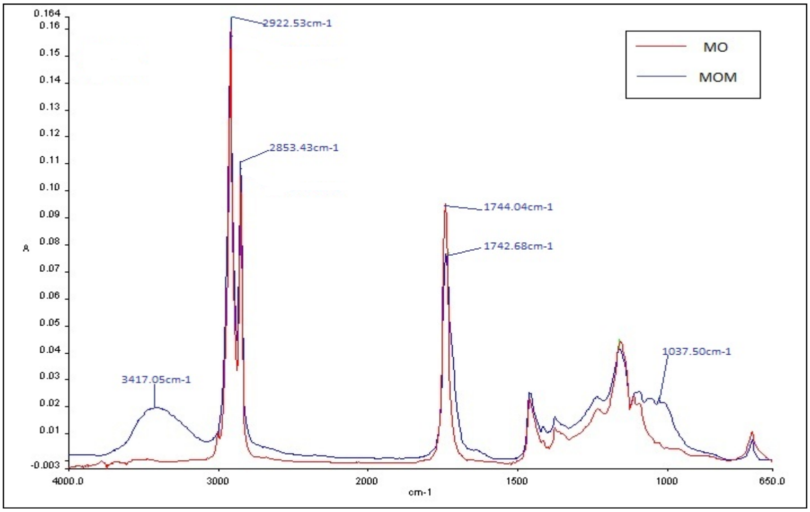

Figure 4: Overlay spectra of FTIR for Mixed Oil (MO) and it's monomer (MOM)

Conversion of bio-monomer to bio-polymer by crosslinking agent

From Figure 5 to Figure 7, it is noticed that the spectra of all the synthesized bio-polymers are similar and disappearance of stretching vibration band at 2270 cm^{-1} characteristic of isocyanate (-N=C=O) group of the MDI, which confirms that all of the isocyanate groups react during polymerization. New bands was observed in two principal vibration regions, the –N-H stretching vibration of urethane groups (-NH) at 3330cm^{-1} - 3345 cm^{-1}, which increase with the hard segment content and the carbonyl stretching vibration in the amide region (-C=O) at 1737cm^{-1} - 1702 cm^{-1} [13][14][15]. Other peak for VOP, POP, and MOP appear at 1640cm^{-1} – 1550cm^{-1} attribute to the N-H bending for primary and secondary amides [12]. In addition, the intensive absorption due to the ring C–C stretching of MDI is also observed at 1600cm^{-1}. The most easily interpretable bands in this system are the C=O stretching, whose frequencies and relative intensities are characteristic of hydrogen bond formation [13]. 1450 cm^{-1} – 1375 cm^{-1} is due to the CH_3 bending peaks and for the strong intensity absorptions near 1000 cm^{-1} – 1300 cm^{-1}, indicate ester group (C-O) [12].

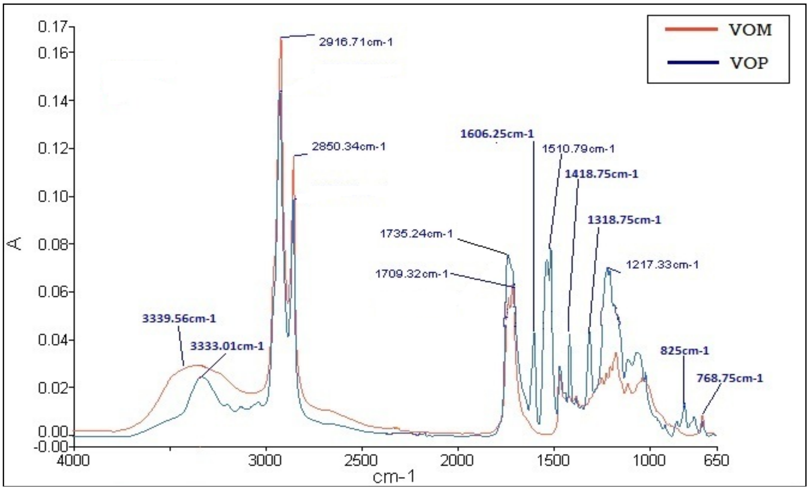

Figure 5: FTIR overlay spectras for Virgin Oil Monomer, VOM (▬) and Virgin Oil Polymer, VOP (▬)

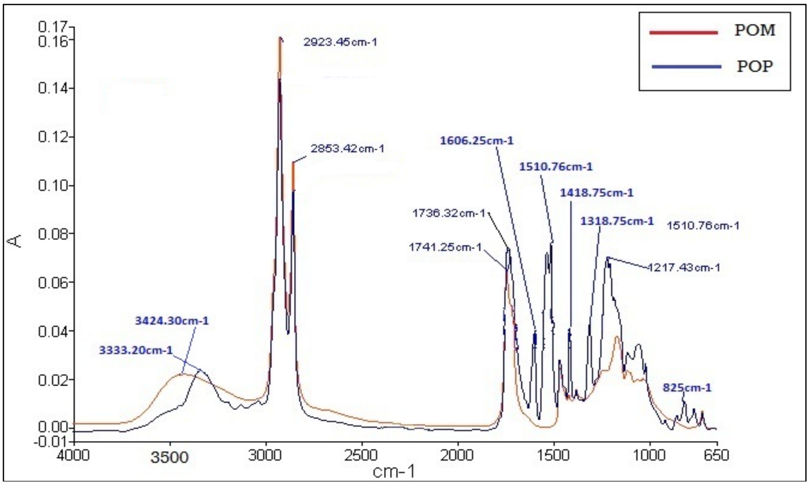

Figure 6: FTIR overlay spectras for Popia Oil Monomer, POM (▬) and Popia Oil Polymer, POP (▬)

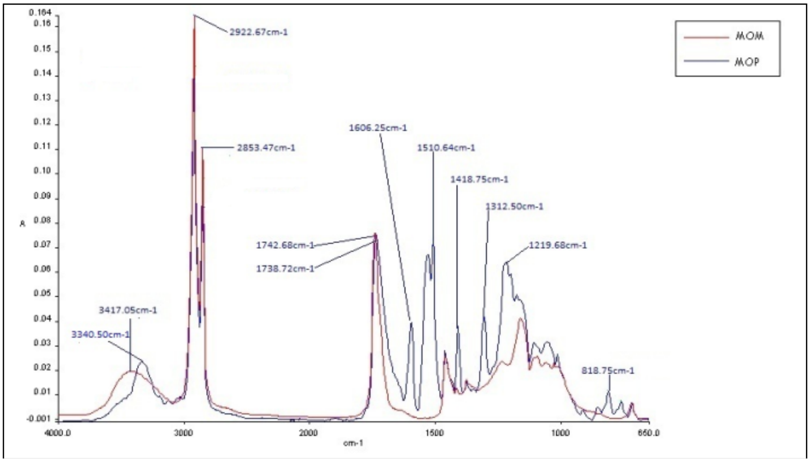

Figure 7: FTIR overlay spectras for Mixed Oil Monomer, MOM (▬) and Mixed Oil Polymer, MOP (▬)

Conclusion

As the conclusion, the hydroxyl functional group formation at around 3345-3450 cm^{-1} for bio-monomer and the NH group formation for bio-polymer were at 3330-3345 cm^{-1} was identified by means of FTIR spectroscopy. The hydroxyl functional group shows the oils were totally converted to the bio-monomer and NH funtional group shows the bio-monomer were totally converted to the bio-polymers. From the oils that were come from green plants were successfully produced bio-polymer for variety of application in daily life.

Acknowledgment

This research was supported by a grant 600-RMI/ST/FRGS 5/3/Fst (251/2010) from Research Management Institute (RMI) of Universiti Teknologi MARA (UiTM). The author also would like to acknowledge Head Principal Researcher of Sustainable Polymer Engineering, Advanced Materials and Manufacturing Center (SPEN, AMMC), Universiti Tun Hussein Onn Malaysia (UTHM), Johor for providing raw materials and facilities and Malaysian Government for supporting this research under Fundamental Research Grant Scheme, FRGS Vot 1481.

References

[1] C. Zhang, T. F. Garrison, S. A Madbouly, M. R. Kessler, "Recent advances in vegetable oil-based polymers and their composites", *Progress in Polymer Science*, 71, 91-143 (2017).

[2] D. D. Andjelkovic, M. Valverde, P. Henna, F. Li, R. C. Larock, R. C, "Novel Thermosets Prepared by Cationic Copolymerization of Various Vegetable Oils—Synthesis and Their Structure–Property Relationships", *Polymer,* 46, 9674–9685 (2005).

[3] A. Demirbas, "Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods", *Progress in Energy and Combustion Science,* 31, 466–487 (2005).

[4] F. S. Guner, Y. Yagci, A. T. Erciyes, "Polymers from triglyceride oils", *Progress in Polymer Science*, 31, 633–670 (2006).

[5] A. Z. Mohd Rus, 'Polymer from Renewable Materials", *Science Progress.* 93(3), 285-300 (2010).

[6] A. Z. Mohd Rus, "Degradation Studies of Polyurethanes Based On Vegetables Oils. Part I; Photodegradation", *Prog in Reaction Kinetic and Mechanism,* 33, 363-391(2008).

[7] A. Z. Mohd Rus, "Degradation Studies of Polyurethanes Based On Vegetable Oils. Part 2; Thermal Degradation and Materials Properties", *Prog React Kinet Mech,* 34, 1- 43 (2009).

[8] A. Z. Mohd Rus, "Effect of Titanium Dioxide on Material Properties for Renewable Rapeseed and Sunflower Polyurethane", *International Journal of Integrated Engineering,* 1(1).

[9] A. Z. Mohd Rus, "Material Properties of Novelty Polyurethane Based On Vegetable Oils".In: *The 11th International Conference on QiR (Quality in Research),* Depok, Indonesia (2009).

[10] N. Vlachos, Y. Skopelitis, M. Psaroudaki, V. Konstantinidou, A. Chatzilazarou, E. Tegou, "Application of Fourier transform-infrared spectroscopy to edible oils", *Analytica Chimica Acta,* 573–574, 459–465 (2006).

[11] M. A. Manaf, Y. C. Man, N. S. A. Hamid, A. Ismail, S. Z. A. Abidin, "Analysis of adulteration of virgin coconut oil by palm kernel olein using Fourier transforms infrared spectroscopy", *Journal of Food Lipids,* 14,111–121 (2007).

[12] L. D. Pavia, M. G. Lampman, S. G Kriz, "Introduction to Spectroscopy (2001). 3rd. United State of America: Thomson Learning, Inc.

[13] Y. Lua, R. C. Larock, “Soybean Oil-based, Aqueous Cationic Polyurethane Dispersions: Synthesis and Properties”, *Progress in Organic Coatings*, 69 (1), 31-37 (2010).

[14] M. A. Corcuera, L. Rueda, B. Fernandez d’Arlas, A. Arbelaiz, C. Marieta, I. Mondragon, A. Eceiza, “Microstructure and Properties of Polyurethanes derived from Castor Oil”, *Polymer Degradation and Stability*, 95, 2175-2184 (2010).

[15] S. S. Narine, X. Kong, L. Bouzidi, P. Sporns, “Physical Properties of Polyurethanes Produced from Polyols from Seed Oils: I. Elastomers”, *J Amer Oil Chem Soc,* 84, 55–63 (2007).