Synthesis and Characterization of Photocrosslinkable Acrylic Prepolymers from Waste Palm Frying Oil

Munirah Onn[a,c], Haikal Mustafa[b], Hairul Amiza Azman[c], Zuliahani Ahmad[d], Mat Uzir Wahit [a,*]

[a]Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310,Johor Bahru, Johor, Malaysia
[b]Faculty of Chemical Engineering, UiTM Cawangan Johor, Kampus Pasir Gudang, 81750, Masai, Johor, Malaysia
[c]Faculty of Applied Sciences, UiTM Cawangan Johor, Kampus Pasir Gudang, 81750, Masai, Johor, Malaysia
[d]Faculty of Applied Sciences, UiTM Cawangan Perlis, Kampus Arau, 02600, Arau, Perlis, Malaysia
 r-uzir@utm.my

Worsening environmental issues are a result of an increase in the generation of waste palm frying oil (WPFO) and its improper disposal. Due to the enormous volume of WPFO produced by household use and the food industry, new technologies for its reuse in the creation of goods with high economic value are being developed. The use of renewable resources such as WPFO in the polymer industry offers environmental and economic advantages. Deterioration in cooking oil after the frying process is reflected by the decrease in iodine value and increase in free fatty acid (FFA) and acid value. A decrease in iodine value shows a decrease in the content of fatty acids with double bonds and it indicates oxidation of the oil, thus, modification of oil through enzymatic acidolysis is conducted to enlarge unsaturated sites that permit chemical modification. The double bonds and active methylene act as functional sites for the introduction of acrylic polymers. Thus, this research involves adding chemical groups that can polymerize by using WPFO as the precursor. The acrylation process was conducted with the mole ratio of 1:1 (WPFO: acrylic acid) in five neck reactor vessels with nitrogen inlet at 80 ºC for 6 h After the purification process, WPFO acrylic prepolymer was blended with tri-functionality reactive diluents and photoinitiator to become photocrosslinkable acrylic films. The film was cured under UV LED light with 85 % light intensity for 5 min. From the characterization result, WPFO can be considered as a potential waste that can be used as a renewable polymer precursor to replace those that are currently derived from petroleum hydrocarbons thus saving crude oil usage.

1. Introduction

Palm oil (Elaeis guineensis) originates from Southeast Asia and Equatorial Africa and is currently the world's leading vegetable oil, with yearly consumption and production of around 45.3 million tonnes, accounting for nearly 60 % of worldwide vegetable oil commerce on the worldwide market, and it is projected that by 2020, global demand for palm oil would have doubled (Begum et al., 2019). Glycerol and fatty acid molecules are joined together by hydrocarbon bonds in the structure of palm oil molecules. These chemical combinations result in the formation of glycerides, which give rise to many distinctive chains known as di-glycerides and triglycerides for fatty acid chains with two and three, respectively. Saturated and unsaturated fatty acids are typically balanced in palm oil's chemical structure. Oleic acid C18:1 typically predominates among unsaturated fatty acids, while palmitic acid C16 often dominates among saturated fatty acids. The primary and secondary oxidation compounds formed as a result of the very unstable and vigorous reaction of the unsaturated fatty acid chain with oxygen and other substrates had an impact on the viscosity behaviour of the palm oil (Zulhanafi et al., 2021). One of the best techniques for preparing food is deep frying, where materials used to make deep-fried food are submerged in hot oil at temperatures as high as 180 ºC. The hydrolysis, oxidation, and polymerization reactions that result from heating the oil to such high temperatures affect its composition, which alters the oil's flavour and stability (Habarakada et al., 2021). Today, one of the most significant oils used for frying food is palm oil. The oil produces high-quality and delicious dishes, is accessible in large quantities, has a high level of

oxidative stability, and is reasonably inexpensive (Matthäus, 2007). As soon as atmospheric oxygen combines with lipids and other organic molecules in oil, structural breakdown in the oil result in lowering food quality and endangering human health (Zahir et al., 2017).

To prevent climate change and an energy shortfall, the growing environmental concerns and the depletion of petroleum supplies have prompted a quest for alternative replacement of petroleum-based raw materials by renewable resources like waste palm frying oil (WPFO) as a precursor is the essential step towards achieving a more sustainable and environmentally friendly future (Moshood at al., 2022). Without competition from food uses, WPFO is a substantial biomass resource. However, triglyceride sources in WPFO may include pollutants, moisture, and high free fatty acids (FFA). These contaminants may obstruct the polymerization process and have an impact on the final polymer's uniformity and quality. To solve these problems, appropriate purification and characterisation techniques are required (Mannu et al., 2020). The allylic carbons, double bonds ester group, and carbons next to the ester group are among the triglyceride's active sites that can undergo chemical reactions. Using the same synthetic methods employed in the manufacture of polymers based on petrochemicals, these active sites can be exploited to insert polymerizable groups on the triglyceride. The crucial stage is to increase molecular weight and crosslink density and integrate chemical functionalities that are known to give polymer networks rigidity (Khot et al., 2001).

Photocrosslinkable or ultraviolet (UV) curable films are coatings that undergo a chemical reaction and crosslinking when exposed to UV light. In-depth research has been done on light-induced curing in polymer coating systems because it protects the environment, uses less energy, and can cure materials quickly even at ambient temperature. One of the most efficient ways to create spatial crosslinked polymers quickly is to expose a multifunctional monomer or oligomer to UV light while it is combined with an initiator. Due to its environmentally friendly method and exceptional qualities, such as high glossiness, hardness, chemical resistance, and scratch resistance generated by high crosslink density from acrylate groups, UV-curing technology has been suggested as an alternative to conventional solvent-borne coatings (Jančovičová et al., 2013). The exploration of WPFO as a new potential sustainable polymer precursor in the polymer sector represents the research gap in this work. Therefore, the objective of this study was to synthesize the acrylic prepolymers from WPFO and produce photocrosslinkable UV LED (Light Emitting Diodes) acrylic coatings. The photocrosslinkable polymer coatings were prepared by the inclusion of 4-isobutylphenyl-4'-methylphenyliodonium hexafluorophosphate (Irgacure 250) as a cationic photoinitiator and trifunctional acrylate reactive monomer. The outcome was evaluated by free fatty acid (FFA) and iodine titration test, pH, viscosity, fourier transformed infrared spectra (FTIR) and atomic force microscopy (AFM). The study presents a new approach to polymer synthesis by modifying WPFO through enzymatic acidolysis to increase unsaturated sites, allowing the introduction of acrylic polymers thus offering a cutting-edge and greener substitute for customary solvent-borne coatings. This innovative approach also offers a way to create polymer materials that are thereby contributing to waste management and environmental preservation.

2. Methodology

2.1 Materials

The main raw material is SAJI brand cooking oil which was used to fry the dish up to three times and the sediment left in WPFO such as breading or crumbs was discarded using filter paper Whatman #41. Analytical grade acrylic acid (99 %) contains 200 ppm monomethyl ether hydroquinone as an inhibitor, trimethylolpropane triacrylate (TMPTA) contains monomethyl ether hydroquinone as an inhibitor, triacylglycerol acylhydrolase enzyme from *Candida rugosa* lipase catalyst, boron trifluoride etherate ($BF_3 \cdot Et_2O$) for synthesis, technical grade oleic acid (90 %) were supplied by Sigma Aldrich Sdn Bhd. Reagent-grade acetic acid glacial (CH_3COOH), cyclohexane (≥99 %), and hexane (95 %) solvents were supplied from Chemiz Sdn Bhd. The sodium hydrogen carbonate ($NaHCO_3$), potassium hydroxide (KOH), potassium iodide (≥99 %), and phenolphthalein solution 1 % in ethanol, Wijs solution were supplied by Merck (M) Sdn. Bhd. The activated carbon from coconut shell (ACCS) with mesh size (8x30) was purchased from My Filter. Irgacure 250 photoinitiator was supplied by BASF. Analysis grade sodium thiosulfate pentahydrate ($Na_2S_2O_3$, ≥99.5 %), starch, and isopropyl alcohol (IPA, >99.8 %) solvent were purchased from Merck. All chemicals were used without further purification.

2.2 Synthesis and Curing Preparation of Acrylated Waste Palm Frying Oil (AWPFO)

For WPFO treatment, 10 % (g/v) ACCS was mixed with 200 mL WPFO and the FFA titration followed pH test was conducted. In a typical (enzymatic acidolysis) reaction with mild nitrogen gas inlet, 100 mL of WPFO and 3 g of enzyme lipase catalyst was added to a four-neck 500 mL round reactor vessel with a cooling condenser and using a high-speed mechanical stirrer (500 rpm). 25 mL of oleic acid was added slowly using a dropping funnel at 40 ºC for 4 h and iodine test titration was conducted before and after the reaction to identify the enhancement of double bond content in WPFO. Next, by using formulation 1:1 mol, the WPFO solution was

added with acrylic acid and stirred continuously at 80 ºC for another 6 h and the polymerization was quenched by using an ice cube. The produced AWPFO was washed with 5 % aqueous NaHCO₃ solutions to remove unreacted catalyst (which can be recycled) until the pH approaches 7. Hexane solvent was added for purification to extract unreacted monomers and the solution was separated in a vacuum evaporator at 80 ºC at a speed of 0.5 m/s to remove the solvent. To be protected from photooxidation, AWPFO was blended using a magnetic stirrer with 35 % TMPTA and 3 % Irgacure 250 in an amber glass bottle. The solution was applied to the Teflon mould and Polymethyl methacrylate (PMMA) panel and undergo curing under UV LED at 5 min with 85 % light intensity at the temperature of 35 ºC and the cured film was used for characterization.

2.3 Analysis and characterization

The surface area and pore size of the ACCS were conducted using Micromeritics Tristar II with degassing temperature at 250 ºC for 4 h under a continuous flow of nitrogen gas. Viscosity was done by using Brookfield digital viscometer (model DV-11+) and referring to ASTM D2983 as the standard method and density was measured by dividing the mass of the sample by volume of the sample. The pH analysis was observed using a pH meter by applying ASTM E70 as the standard method. By using FTIR in the range of 550–4000 cm^{-1} with a 4 cm^{-1} resolution, the functional groups were recorded using a Varian 4100 FTIR Excalibur Series. Iodine value is the relative degree of unsaturation in oil components and the iodine titration method was done by complying with ASTM D1959 where a 2 g sample was mixed homogenously with 15 mL of cyclohexane, 15 mL CH₃COOH, 25 mL of Wijs solution. For 30 min, the mixture was sealed and kept at room temperature in a dark environment and after that, the solution was added with 3 drops of starch and the mixture was titrated against 0.1 N Na₂S₂O₃ solution. The calculation of iodine value was depicted in Eq(1) below:

$$Iodine\ value = (A - S) \times N \times 126.9\ g/mol \div M \tag{1}$$

Where :
A : volume of Na₂S₂O₃ solution used (mL)
S : initial Na₂S₂O₃ solution reading (mL)
N : the normality of the Na₂S₂O₃ solution (0.1 N)
M : mass of the oil sample (g)

For the coating surface imaging and roughness measurement, AFM using JPK Nanowizard (R) 3 via tapping mode and the primary beam was rostered over the 10 µm x 10 µm area of the sample surface with tip velocity of 6.7 µm/s and overscan time 0.166 s. The FFA%, 5 g of sample was mixed with 50 mL IPA in a conical flask and 1 mL phenolphthalein indicator was added and titrated with 0.1 N KOH solution until the mixture changed from colourless to pink colour. The volume of KOH solution used to neutralize the FFA in the sample was recorded and the calculation of FFA was depicted in Eq(2) below:

$$FFA\% = (V - B) \times N \times 56.1\ g/mol \div m \tag{2}$$

Where :
V : volume of KOH solution used (mL)
B : Initial KOH solution reading (mL)
N : the normality of the KOH solution (0.1 N)
m : mass of the WPFO sample (g)

3. Results and Discussion

The synthesis started with the purification of WPFO. To discard the contamination and reduce the FFA value, the WPFO was first filtered by using the Whatman #41 and the pH was identified below ≤5. The WPFO will be purified with 0.1 mol NaHCO₃ solution until the pH neutralizes. The incoming ACCS was tested out with the Brunauer-Emmett-Teller test (BET) to ensure it has pleasant adsorption capacity and performance. From the results, a sizable amount of surface area is accessible for adsorption, as indicated by the specific surface area result of 708.9 m^2/g. Additionally, mesopores, which are bigger than micropores but smaller than macropores, may be present, as indicated by the reported pore size of 20.9 Å. Activated carbon materials frequently exhibit this mesoporous structure and large surface area combination. From Table 1 below, the contact with activated carbon has reduced the FFA value by only 27 %. The wider range of results might be due to the high evaporation rate of isopropyl alcohol that might affect the results. It has been reported that ACCS was able to reduce FFA by 45 % as indicated by Fajriati et al. (2023). The acrylation reaction can be hampered by the presence of high FFA % in WPFO. High FFA % concentrations might result in undesirable side effects such as saponification or esterification, which can lower the yield of the desired results (Susilowati et al., 2019). As for viscosity, the change in pure cooking oil and WPFO is quite significant. During frying, the oil may undergo polymerization and

oxidation processes due to repeated heating and air exposure. Larger molecular chains are created during polymerization, which might make the oil more viscous. Increased viscosity can also be caused by oxidation reactions because they produce oxidative by-products such as fatty acids and other polar substances (Siddique et al., 2015).

Table 1: Results of density, viscosity, FFA and iodine value.

Parameters	Density (kg/m³)	Viscosity (cP, 25 ºC)	Iodine (gI$_2$/100 g)	FFA (mg KOH/g)
Pure palm frying oil	900	60	60±0.2	0.3±0.02
WPFO	930	75	54±0.5	1.44±0.08
Purified WPFO	930	75	54±0.5	1.04±0.05
High oleic WPFO	925	74	90±0.8	-
AWPFO	935	79	-	-

The iodine value reflects the degree of the double bond in the triglyceride. The iodine value was tested before and after the enzymatic acidolysis process whereas from the results, the iodine value was reduced after repeat frying due to lipid oxidation which result in the breaking of the double bonds in pure oil and produced reactive compounds. According to Lin and Huey (2009), cis–9–octadecenoic acid can be added to oils to increase the unsaturated fatty acid content of the pure oil and provide functionality and extensive crosslinking processes. As outlined by Zaharudin (2019) from the result, oleic acid content increased by a total of 57 % (v/v) after the enzymatic acidolysis reaction using WPFO, proving their viability as a substrate for the formation of structured lipids. When there is enough enzyme present, oleic acid is more likely to be incorporated into triglycerides at the sn-1 and sn-3 positions. Additionally, it should be remembered that the catalyst used which is enzyme from *Candida rugosa* lipase is a non-stereoselective lipase that is responsible for acyl migration from the sn-2 position of triglycerides. The enzyme load of 30 % (w/w), with a maximum iodine value of 164 gI$_2$/100 g, was chosen as the ideal enzyme loading (Zaharudin et al., 2019). As depicted in Table 1, the lowest value of iodine is WPFO and it indicates a low degree of unsaturation which means a higher oxidation rate occurs during frying. After addition with oleic acid, the increase in iodine value with 36 gI$_2$/100 g indicates the enhancement site for double bond. Due to this, enzymatic acidolysis has been favoured as a method for modifying WPFO that are rich in high-value polyunsaturated fatty acids. The process of acrylation includes adding acrylic acid to the double bonds in fatty acid chains thus adding extra double bonds to WPFO might give more places for acrylic (CH$_2$=CHCOOH) functionalities. Because of this, the high oleic WPFO can act as a useful precursor in the production of acrylate goods or acrylate-based polymers. Those with more acrylic groups per molecule offer more crosslinking-reactive sites for UV curing. As there are more sites accessible for the crosslinking reaction to take place, curing can proceed more quickly and effectively. The cationic type of trifunctionality reactive monomers and photoinitiators were added in AWPFO to provide the necessary chemical reactivity for polymerization to occur and initiate the polymerization reaction by generating reactive species. When these reactive species interact with the reactive monomers, crosslinks are created which enables the efficient curing of UV-curable materials using UV LED light sources.
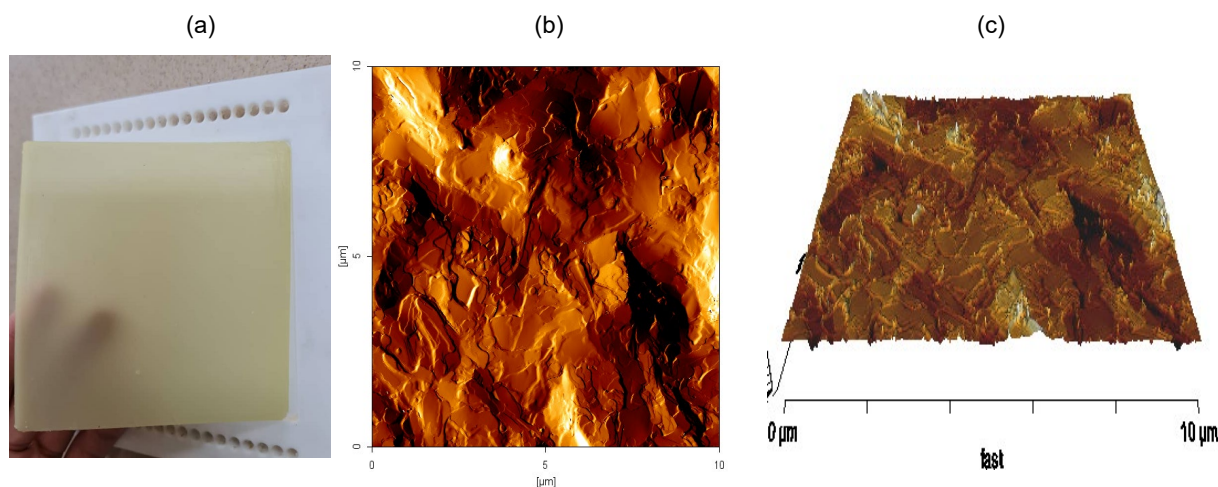
(a)　　　　　　　　　　　　　(b)　　　　　　　　　　　　　(c)

Figure 1: (a) 2 mm thickness AWPFO coating on Teflon mold (b) Surface topography analysis of AWPFO (c) Surface topography analysis of AWPFO in 3D

The combination of the AWPFO with these monomers and photoinitiator creates a hard curable coating as shown in Figure 1(a) above. After 5 min of exposure to UV LED (model Honle LED cube 100), the solution turns into a hard solid yellowish coating and the combination shows homogeneity with a matte smooth finishing coating. In areas where the visual component is not crucial, matte coatings are frequently used. The surface morphology is supported by results 1(b) and 1(c) from AFM analysis which provided results on the AWPFO surface topography imaging with nanometre (nm) scale resolution, surface roughness and surface defects. From the result, the average surface roughness (Ra), root mean square roughness (Rq), and peak to valley roughness (Rt) of the film depicted 0.0201 nm, 0.0277 nm, 0.339 nm respectively and it indicates that the surface roughness of the AWPFO surface is relatively low. A lower roughness rating is typically preferable in coating applications since it denotes a smoother surface. Smoother surfaces typically exhibit superior aesthetic appeal, improved coating adherence, and a lower likelihood of coating flaws.
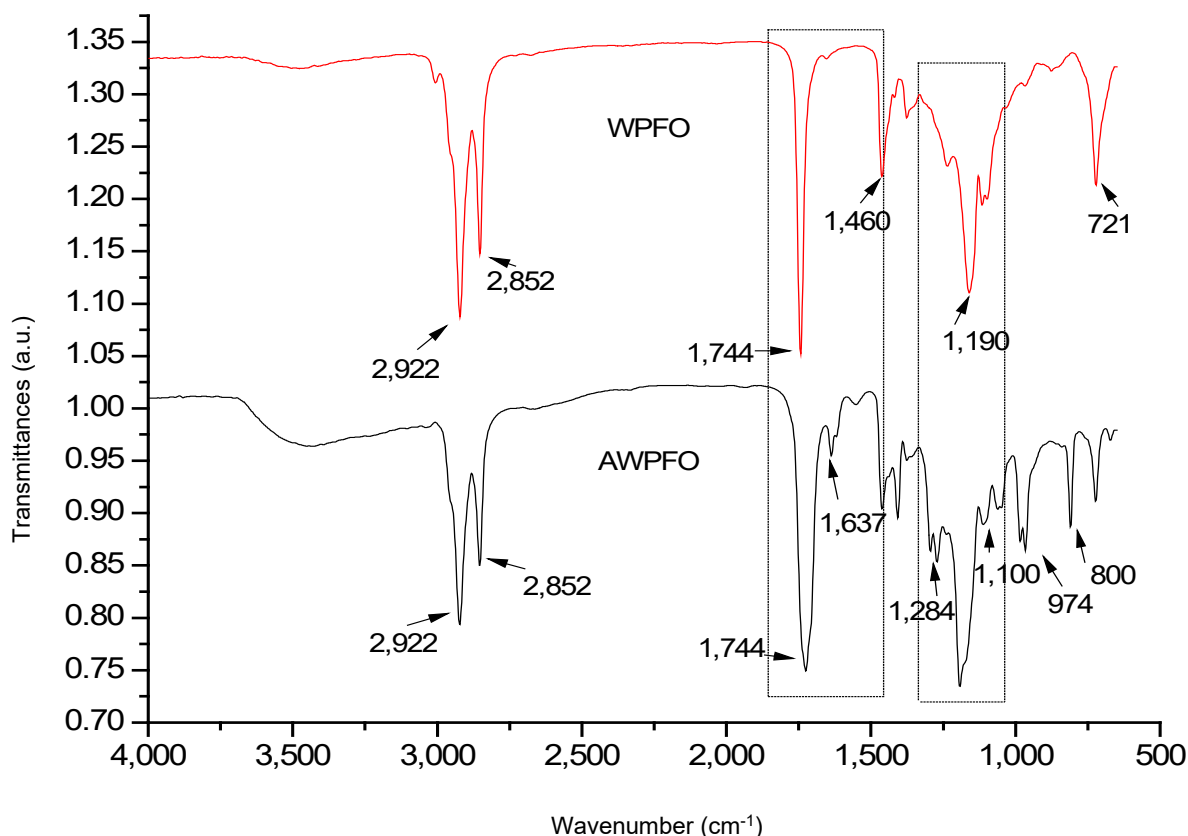

Figure 2: FTIR spectra of WPFO and AWPFO (transmittance vs wavenumber)

In this study, the effects change of acrylation process of WPFO on chemical structures were examined in Figure 2 via FTIR. The functional groups present in the WPFO and AWPFO with the peaks from 4,000 cm^{-1} to 500 cm^{-1} represent C-H stretching vibrations from the aliphatic chains of fatty acids (2,922 cm^{-1} and 2,852 cm^{-1}), carbonyl (C=O) stretching vibration from ester group present in triglycerides (1,744 cm^{-1}), C-H bending vibrations (1,460 cm^{-1} and 800 cm^{-1}), and =C-H out-of-plane bending vibrations of cis double bonds (720 cm^{-1}) (Awogbemi et al., 2019). The peak which confirmed the occurrence of acrylic group is C=C stretching vibration from the acrylate functional group at 1,637 cm^{-1} and 974 cm^{-1} (C=CH_2) vinyl group. The significant difference is at wavelength 1,744 cm^{-1} which depict C-H bending vibrations and C-O-C stretching vibration whereas in AWPFO, the peak is longer and wider, and it is an indicator of the ester groups resulting from the acrylation reaction (Kasetaite et al., 2018). These FTIR results prove the incorporation of acrylate functional groups into the unsaturated fatty acids present in the WPFO molecular structure. Peak positions in the FTIR spectrum have changed as a result of the addition of acrylate functional groups. The peak shifts may result from modifications to the atoms' electrical surroundings, binding strengths, or bond lengths. These modifications may have an impact on the molecules' vibrational modes and cause peak positions to alter.

4. Conclusions and Future Directions

The UV-curing technology used in this study has successfully cured the AWPFO thus it offers an environmentally friendly alternative to conventional solvent-borne coatings. Through FTIR analysis, it was verified that acrylate functional groups had been incorporated into the molecular structure of WPFO. Producing photocrosslinkable materials with characteristics identical to those of currently used chemicals is a major challenge for the bio-renewable sector. Further optimization of the acrylation process can be conducted to improve the yield and quality of AWPFO. Concerning the synthesis, fine-tuning the reaction conditions, such as enzyme loading, temperature, and reaction time, can lead to better results.

Acknowledgments

References

Awogbemi O., Onuh E. I., Komolafe C. A., 2019, Thermal degradation and spectroscopic study of neat palm oil, waste palm oil, and waste palm oil methyl ester, IOP Conference Series: Earth and Environmental Science, 331(1), 012032.

Begum H., Alam A. S. A. F., Awang A. H., 2019, Sustainability of Malaysian oil palm: A critical review, International Journal of Environment and Sustainable Development, 18(4), 409.

Habarakada A., Perumpuli P. A. B. N., Thathsaranee W. T. V., Wanninaika I. P., 2021, Physical, chemical, and nutritional quality parameters of three different types of oil: Determination of their reusability in deep frying, Food Research, 5(5), 226–235.

Jančovičová V., Mikula M., Havlínová B., Jakubíková Z., 2013, Influence of UV-curing conditions on polymerization kinetics and gloss of urethane acrylate coatings, Progress in Organic Coatings, 76(2-3), 432–438.

Kasetaite S., De la Flor S., Serra A., Ostrauskaite J., 2018, Effect of selected thiols on cross-linking of acrylated epoxidized soybean oil and properties of resulting polymers, Polymers, 10(4), 439.

Khot S. N., Lascala J. J., Can E., Morye S. S., Williams G. I., Palmese G. R., Wool R. P., 2001, Development and application of triglyceride-based polymers and composites, Journal of Applied Polymer Science, 82(3), 703–723.

Lin S. W., Huey S. M., 2009, High oleic enhancement of palm olein via enzymatic interesterification, Journal of Oleo Science, 58(11), 549–555.

Liu Y., Sotelo-Boyás R., Murata K., Minowa T., Sakanishi K., 2012, Production of bio-hydrogenated diesel by hydrotreatment of high acid value waste cooking oil over ruthenium catalyst supported on al-polyoxocation-pillared montmorillonite, Catalysts, 2(1), 171–190.

Matthäus B., 2007, Use of palm oil for frying in comparison with other high-stability oils, European Journal of Lipid Science and Technology, 109(4), 400–409.

Moshood T. D., Nawanir G., Mahmud F., Mohamad F., Ahmad M. H., Abdul G, A., 2022, Sustainability of biodegradable plastics: new problem or solution to solve the global plastic pollution? Current Research in Green and Sustainable Chemistry, 100273 (5), 1-18.

Sikiru Y. A., David A. O., Aderemi O. M., George A. U., 2019, Waste frying oil as a feedstock for biodiesel production, Petroleum Chemicals - Recent Insight, 79433, 1-20.

Susilowati E., Hasan A., Syarif A., 2019, Free fatty acid reduction in a waste cooking oil as a raw material for biodiesel with activated coal ash adsorbent, Journal of Physics: Conference Series, 1167, 012035.

Siddique B. M., Muhamad I. I., Ahmad A., Ayob A., Ibrahim M. H., Ak M. O., 2015, Effect of frying on the rheological and chemical properties of palm oil and its blends, Journal of food science and technology, 52(3), 1444–1452.

Zaharudin N. A., Rashid R., Mohamed Esivan S. M., Othman N., Idris A., 2018, Oleic acid enhancement in used frying palm oil via enzymatic acidolysis, Malaysian Journal of Analytical Sciences, 22(4), 633-641.

Zahir E., Saeed R., Hameed M. A., Yousuf A., 2017, Study of physicochemical properties of edible oil and evaluation of frying oil quality by Fourier transform-infrared (FT-IR) spectroscopy. Arabian Journal of Chemistry, 2(10), S3870-S3876.

Zulhanafi P., Chong W. W. F., Abdul H., Syahrullail, S., 2021, The effect of saturated and unsaturated fatty acid composition in bio-based lubricant to the tribological performances using four-ball tribotester, Journal of Oil Palm Research, 33 (4) 653-667.