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DEVELOPMENT OF BIOBASED POLYMERS AND THEIR APPLICATIONS

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ABSTRACT

The innovation and implementation of biobased polymers aim to enhance sustainability and eco-friendliness in material production, addressing issues related to climate change and resource scarcity. A holistic evaluation of these materials' life cycles is crucial to fully assess their environmental impact. The use of vegetable oil-derived polymers as biomaterials has garnered significant interest for their potential to rival synthetic polymers in terms of physicochemical, thermal, and crystalline properties. In this research, we synthesized a novel green biopolymer using palm oil, castor oil, and soybean oil. We created polymeric nanocomposites from epoxidized vegetable oils and organically modified montmorillonite (OMMT) clay with diamino-diphenylmethane as the curing agent. These biopolymer nanocomposites underwent FT-IR, UV, XRD, TGA, and DTA analyses, revealing that optimal properties were obtained with OMMT loadings of 3 wt% and 7 wt%. All nanocomposites exhibited superior thermal properties compared to conventional polymers.

keywords: Epoxidized soyabean oil, castor oil, palm oil epoxy resins, DSC analysis, XRD, TEM analysis

1.Introduction

The ongoing environmental issues and the reduction of fossil resources have driven the search for sustainable alternatives. Biobased polymers from renewable sources have emerged as a prominent solution to these problems. These biopolymers, particularly those derived from vegetable oils, are appealing due to their plentiful supply, renewability, and biodegradability. Palm oil, castor oil, and soybean oil are among the vegetable oils extensively explored for polymer synthesis.

Epoxidized vegetable oils (EVOs) are especially advantageous because their oxirane rings allow for various chemical modifications, creating polymers with favourable properties. Adding nanofillers like organically modified montmorillonite (OMMT) clay to EVOs can significantly improve the mechanical, thermal, and barrier characteristics of the resulting nanocomposites. This research focuses on synthesizing and characterizing biopolymer nanocomposites from EVOs and OMMT clay, highlighting their potential biomedical applications.

2.Materials and Methods

Palm oil, castor oil, and soybean oil were sourced from local suppliers. Epoxidation was performed using performic acid, which was generated in situ from hydrogen peroxide and formic acid. Organically modified montmorillonite (OMMT) clay was acquired from Sigma-Aldrich. Diamino-diphenylmethane (DDM) served as the curing agent.

The functional group of the materials were recorded and analysed using FTIR spectra from the Fourier transform infrared spectrophotometer-SHIMADZU, Japan by employing KBr disc technique. The Thermogravimetric (TG) curves for the synthesized vegetable-based epoxy nanocomposites were recorded in TA instruments TGA Q50. Nearly 4 mg of the sample materials were taken in platinum pan and heated from ambient 50 to 800°C at 10°C/min. Inert nitrogen gas was supplied during the decomposition process.

3.Experimental

3.1 Preparation of OrganoMontmorillonite(OMMT) clay

Approximately 2.5 g of crude montmorillonite was suspended in 200 ml of 1M NaCl and stirred with a magnetic stirrer overnight (24 hours). The resulting clay slurry was left to stand for 2 hours to allow silica and other heavy impurities to settle, and the montmorillonite was decanted off. The suspension was filtered, and the filtrate was discarded. The strained sample was then air-dried. Around 3.7 g of the purified Na-montmorillonite clay was mixed with 100 ml of cetyltrimethylammonium bromide solution and stirred vigorously for 50 hours. The resulting white precipitate was isolated by filtration and washed several times with a hot water/ethanol (1:1) mixture until no bromide was detected in the filtrate by one drop of 0.1 N $AgNO_3$ solution. The cetyltrimethylammonium bromide ion-exchanged montmorillonite was then dried at 75°C.

3.2 Synthesis of Epoxidized Castor oil and Palm oil

Castor oil (45.9 g, 0.07 mol), glacial acetic acid (8.4 g, 0.14 mol), Amberlite (12.5 g), and toluene (20 g) were placed in a 500 mL four- neck round-bottom flask equipped with a mechanical stirrer, a thermometer sensor, and a reflux condenser. The mixtures were heated to a constant temperature of 55°C. Then, 30% H_2O_2 (28.4 g, 0.25 mol) was added slowly *via* a separating funnel and allowed to react at 55°C for 7 hours. The solution was subsequently filtered and washed with a saturated solution of Na_2CO_3 and distilled water. The toluene was removed by distillation under vacuum, and dried the product at 80°C for 2 hours. This procedure was followed for the epoxidation of palm oil also.

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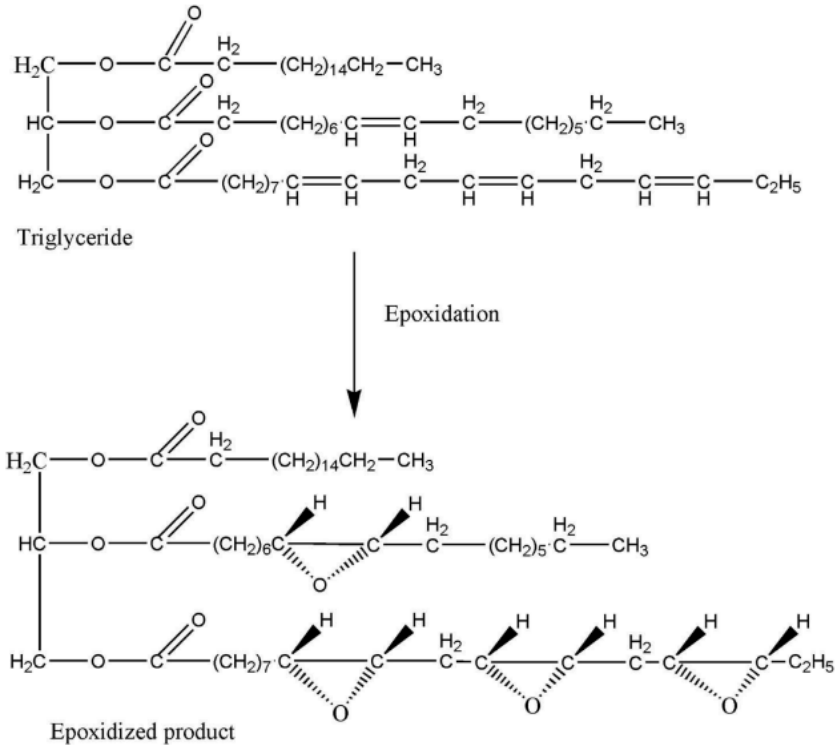

Fig.1 Epoxidation of Triglyceride vegetable oil

3.3 Preparation of Castor, Palm based epoxy matrix

The castor and palm-based epoxy matrix was prepared by mixing their respective epoxy resins with the base DGEBA resin in a 30/70 wt. % ratio, stirring vigorously at 60°C. The resulting homogeneous solution was combined with a stoichiometric amount of DDM at 90°C. The mixture was then degassed to remove trapped air bubbles and poured into a preheated mould. The casting was cured at 120°C for 3 hours, post-cured at 180°C for 2 hours, then removed from the mould and characterized.

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3.4Preparation of Castor and Palm based OMMT epoxy nanocomposites

The castor and palm-based epoxy matrix was blended with different concentrations of organophilic montmorillonite clay (1 wt.%, 3 wt.%, 5 wt.%, and 7 wt.% of the total resin mixture) at 70°C for 24 hours using a mechanical stirrer. A stoichiometric amount of the amine curing agent, corresponding to the epoxy equivalents, was then added. The mixture was degassed under vacuum to eliminate trapped air, cast into moulds, and cured at 120°C for 3 hours. The castings were post-cured at 180°C for 2 hours, then removed from the moulds, and characterized.

4.Results and Discussion

4.1FT-IR and UV-Vis Spectra

The FT-IR spectra of Na-MMT and OMMT, castor oil (CO) and epoxidized castor oil (ECO) are shown in Fig.1. The use of FTIR spectra is revealed the intercalation of long chain aliphatic amine in the Na-MMT with the appearance of transmittance peak at 2780 cm^{-1} due to N-CH_3 aliphatic stretching vibration. Coincidentally, appearance of a transmittance peak at 515 cm^{-1} demonstrated the presence of C-Cl and C-Br stretching vibrations. The presence of a broad band between 3200 and 3500 cm^{-1} assigned to the stretching vibration for intermolecular H bonds. The peak appearance in the region of 1010-1040 cm^{-1} corresponds to the presence of acetates.

Castor oil (CO) and palm oil (PO) are liquids at room temperature (25°C). After epoxidation, the former products ECO and EPO are semisolid indicating a conversion of all, or the majority, of alkenes into epoxide rings. The FT-IR spectra for CO and ECO are presented in Fig. 2. Characteristic absorption bands for C-H asymmetric stretching are observed at 2854.65 cm^{-1} and 2924 cm^{-1}, corresponding to CH_2 and CH_3 groups, respectively. The sharp peak at 1735.9 cm^{-1} indicates the presence of C=O in alkyl acids within CO. This peak is absent in ECO, confirming the disappearance of the C=O group due to epoxidation. A small peak at 856.39 cm^{-1} in ECO is attributed to the oxirane ring. The epoxy symmetric stretching band is centred at 1242.16 cm^{-1} in ECO. Additionally, during the epoxidation process, 10% of castor oil is converted into peroxides as a side product, indicated by the C-O-O-C stretching at 856.39 cm^{-1}

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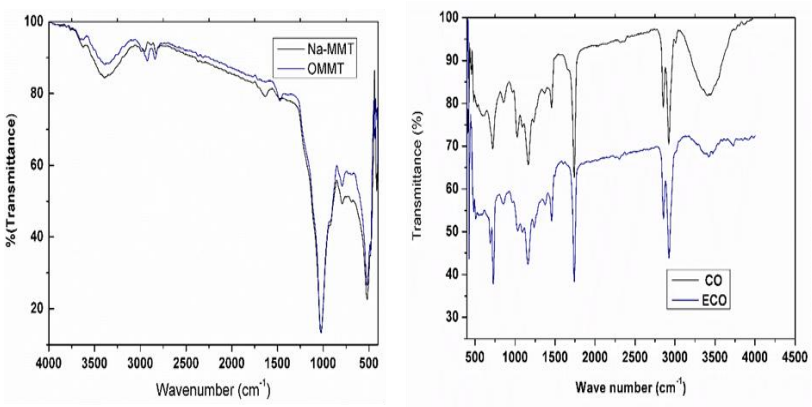

Fig.2 The FT-IR spectra of Na-MMT & OMMT, Castor oil (CO) & Epoxidized castor oil (ECO)

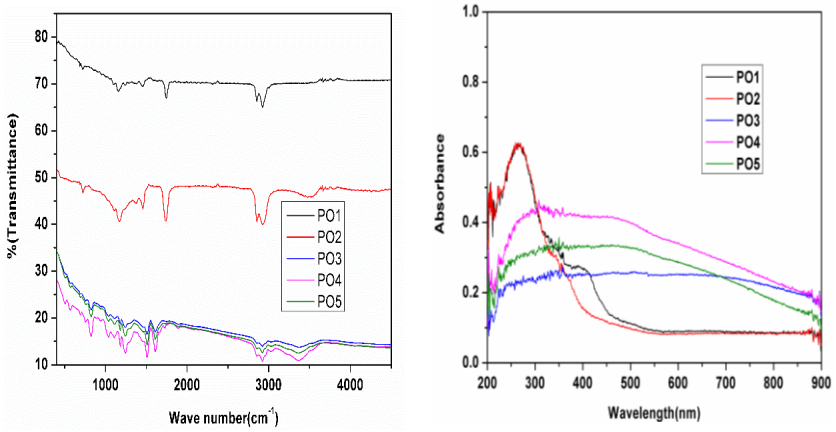

Fig.3 FT-IR & UV-Visible spectra for Palm-based epoxy matrix loaded with OMMT.PO1-0 wt.% OMMT, PO2-1 wt%, OMMT, PO3- 3 wt.% OMMT, PO4-5 wt.%OMMT and 7 wt.% OMMT.

In the FTIR spectrum (Fig. 3), the most notable absorption band appears at 850 cm^{-1}, corresponding to the oxirane ring in the synthesized product. The peaks at 1183 cm^{-1} and 1510−1615 cm^{-1} are attributed to the aromatic C−O and aromatic C=C stretching, respectively. The characteristic peaks for phenol C−O groups are observed at 1200−1250 cm^{-1}. Additionally, the FTIR spectrum confirmed that the starting epoxy resin did not contain OMMT, evidenced by the absence of the OH group. Regarding the UV-Vis spectrum, two key features are typically recorded. The first is λ_{max} at 250 nm, indicating the wavelength of maximal light absorbance due to the $\prod \rightarrow \prod^*$ transition. Another significant absorption is observed at 400 nm.

4.2 Thermal Analysis of Castor and Palm-based OMMT Epoxy nanocomposites:

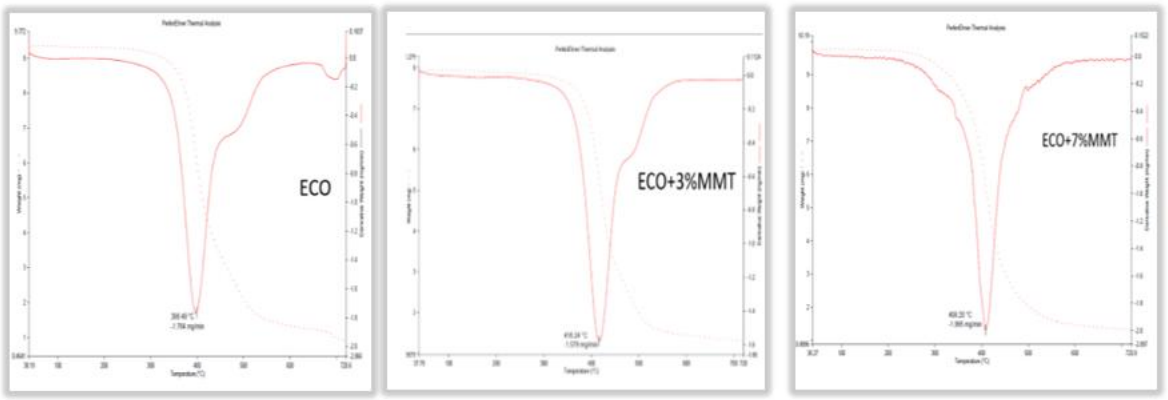

Fig.4 Differential thermogram for ECO, ECO+3%MMT and ECO+7%MMT

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The DTG curves for ECO, ECO+3%MMT, and ECO+7%MMT nanocomposites recorded at a heating rate of 20°C/min are shown in Fig.4.The two composites along with the basic epoxidized castor oil have excellent thermal stability. The char residue for ECO, ECO+3%MMT, and ECO+7%MMT is 22%, 21%, and 21% respectively. The basic ECO-based nanocomposites start to degrade (Ti) at 310°C thermally. The degradations reach a maximum (T_{max}) at 398.5°C and the decomposition ends (T_f) at 530^{0}C.For ECO+3%MMT and ECO+7%MMT decomposition starts at 350°C, 310°C respectively. For these two composites the maximum decomposition occurs at 416°C and 408 °C respectively and their decomposition ends at 530°C and 520°C respectively. Analysis of these indicate that there is a pronounced enhancement in T_{max} by introducing OMMT in the castor-based epoxy matrix.ECO+3%MMT shows effective in enhancing the thermal degradation behaviour.

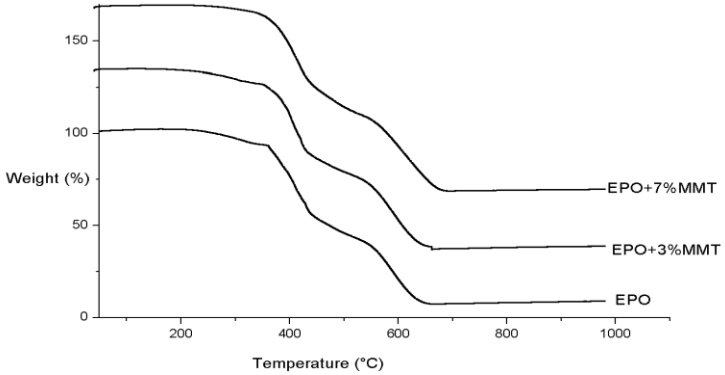

Fig.5 Thermogravimetric Analysis for EPO, EPO+3%MMT and ECO+7%MMT

The effects of EPO and OMMT contents on the thermal stabilities of the DGEBA/EPO and DGEBA/EPO/OMMT systems were studied using TGA at a heating rate of 20°C/min under a nitrogen atmosphere. Thermogravimetric analysis of the cured resin samples was conducted to assess their relative thermal stability. A typical TG trace is shown in Fig. 4. The initial decomposition temperature (Ti) and the temperature of the maximum rate of weight loss (T_{max}) were recorded from these traces, with the results summarized in Table 1. Additionally, the char yield at 980°C was determined. The highest char yield was observed in the 7% MMT-loaded biopolymer matrix, while the lowest value was found in the palm-based epoxy matrix without OMMT clay. The presence of silica particles in the biopolymer may account for this behavior. However, the initial decomposition temperatures were the same for all three polymer matrices.

Table1.Thermal behaviour of palm-based epoxy matrix with MMT

Material	T_i°C	T_{max}°C	Y_C %
EPO	380	570	40
EPO+ 3% OMMT	385	590	50
EPO+7% OMMT	385	595	55

4.3 Morphology and Structural Analysis of Castor and Palm-based OMMT epoxy nanocomposites

SEM and TEM Analysis

Scanning electron microscopy (SEM) has been extensively utilized in the study and analysis of biopolymer systems, providing detailed information about their structure, morphology, size, shape, and surface modifications. SEM has been crucial in examining biopolymers and biopolymer nanocomposites, revealing a relatively uniform dispersion of MMT layers, which indicates intercalation and exfoliation of the nanoparticle layers.Transmission electron microscopy (TEM) offers visualization of samples at the nanoscale. TEM analysis was conducted to gain further insights into MMT-loaded epoxidized biopolymer nanocomposites. SEM and TEM analyses suggest no phase separation between the silicate layers and the castor-based epoxy matrix. The particle shape and size are illustrated in Fig. 6, with nanoparticle diameters ranging from 100 to 300 nm.

The SEM and TEM images demonstrate that the shapes of MMT-loaded palm-based epoxy nanocomposites are predominantly spherical and cubical, with nanoparticle diameters ranging from 50 to 100 nm as shown in Fig. 7. The degree of uniform dispersion of MMT within the polymer matrix significantly influences its mechanical properties.

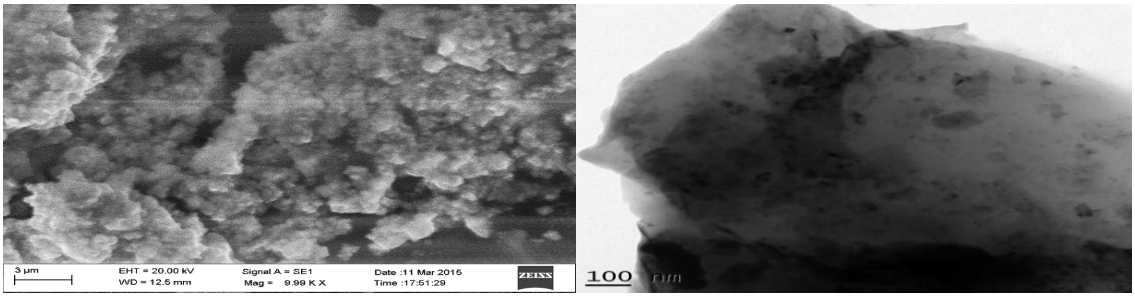

Fig.6 SEM and TEM images of OMMT-loaded castor-based epoxy nanocomposites

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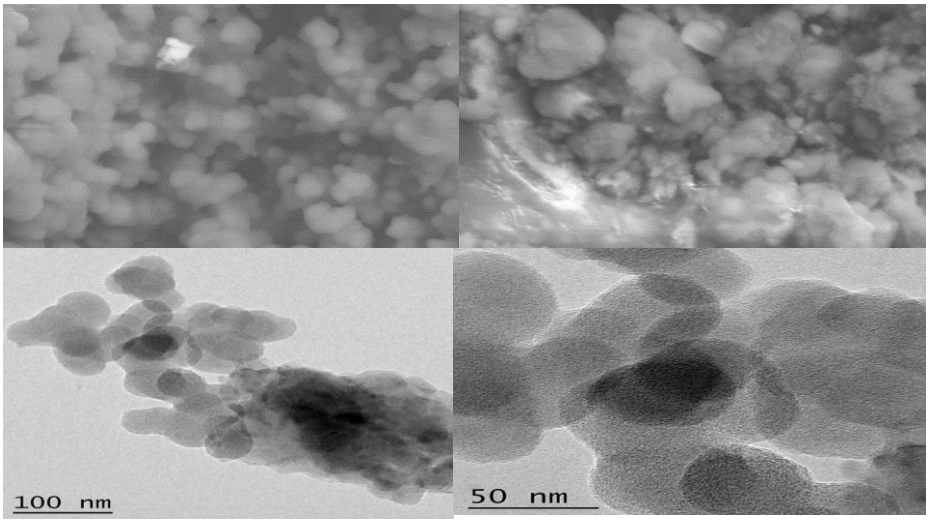

Fig.7 SEM and TEM images of OMMT-loaded palm-based epoxy nanocomposites

5. Conclusion

Castor-based and palm-based epoxy nanocomposites were synthesized using epoxidized castor oil, epoxidized palm oil, DGEBA, and OMMT clay. The presence of polar groups in the triglyceride-based matrix promoted the formation of an exfoliated structure within the nanocomposites. These rigid bio-based nanocomposites significantly enhanced material properties, including thermal stability. SEM and TEM analyses revealed a relatively uniform dispersion of MMT layers and a strong material interface. Castor and palm -based nanocomposites exhibited superior thermal properties compared to conventional polymers.

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References

[1] "Z. Wang, P.Gnanasekar, S.S. Nair, S. Yi, N. Yan, Curing Behavior and Thermomechanical Performance of Bioepoxy Resin Synthesized from Vanillyl Alcohol: Effects of the Curing Agent. Polymers, **13**,2891(2021)".

[2] "Rohani Mustapha, Abdul Razak Rahmat, Rohah Abdul Majid, Siti Noor Hidayah Mustapha, Vegetable oil-based epoxy resins and their composites with bio-based hardener: a short review, Polymer-Plastics Technology and Materials,2574-0881(2019)".

[3] "Rafael T. Alarcona , Caroline Gaglieria , Katie J. Lambb , Michael Northb , Gilbert Bannacha, Spectroscopic characterization and thermal behavior of baru nut and macaw palm vegetable oils and their epoxidized derivatives, Industrial Crops & Products, **154**,11258(2020)".

[4] "Andrea Anusic , Yannick Blob , Gernot Oreski , Katharina Resch-Fauster, High-performance thermoset with 100 % bio-based carbon content, Polymer Degradation and Stability,(2020).

[5] "Pawankumar Rai a,1 , Srishti Mehrotra a,c,1 , Smriti Priya b,c , Edgard Gnansounou d , Sandeep K. Sharma, Recent advances in the sustainable design and applications of biodegradable polymers, Bioresource Technology,**325**,124739(2021)".

[6] "M.V.Arcos-Hernandez, B. Laycock, S. Pratt, B.C. Donose, M.A.L.Nikolic, P. Luckman, A. Werker, P.A. Lant, Biodegradation in a soil environment of activated sludge derived polyhydroxyalkanoate (PHBV), Polym. Degrad. Stab., **97**,2301–2312(2012)".

[7] "R.Gheribi, Y.Habibi, K.Khwaldia,, Prickly pear peels as a valuable resource of added-value polysaccharide: study of structural, functional and film forming properties. Int. J. Biol. Macromol. **126**, 238–245".

[8] "Rida Tajau, Rosiah Rohani, Mek Zah Salleh, Physicochemical and Thermal Properties of Acrylated Palm Olein as a Promising Biopolymer, Journal of Polymers and the Environment,(2020)".

[9] "A.M.Salih, M. Ahmad, N.A. Ibrahim, K.Z. Mohd Dahlan, R.Tajau, M.H. Mahmood, W.M.Z Wan Yunus, Synthesis of radiation curable palm oil-based epoxy acrylate: NMR and FTIR spectroscopic investigations,. Molecules,**20**,14191–14211(2015)".

[10] "M.Y Cheong, T.L. Ooi, S.Ahmad, W.M.Z. Wan Yunus, D. Kuang, Synthesis and characterization of palm-based resin for UV coating, J Appl Polym. Sci., , **111**(5),2353–2361(2009)".

[11] " P.Li, S.Ma, J. Dai,X. Liu, Y. Jiang, S. Wang, J. Wei, J. Chen, J. Zhu J, Itaconic acid as a green alternative to acrylic acid for producing a soybean oil-based thermoset: synthesis and properties. ACS Sustain Chem Eng,,**5**(1),1228–1236(2017)".