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SYNTHESIS OF BIO-BASED HYDROGEL FROM EPOXIDIZED PALM OIL CATALYZED BY FLUOROANTIMONIC ACID HEXAHYDRATE

(Sintesis Hidrogel Berasaskan Bio Daripada Minyak Sawit Terepoksidasi Bermangkinkan Asid Fluoroantimonik Heksahidrat)

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Abstract

An epoxidized palm oil-based hydrogel (HPEPO) was synthesized by using ring opening polymerization (ROP) in the presence of fluoroantimonic acid hexahydrate catalyst ($HSbF_6 \cdot 6H_2O$), followed by chemical hydrolysis catalyzed with sodium hydroxide (NaOH). The structural characterization and thermal property of synthesized hydrogel were studied. The successful ring opening of EPO was confirmed by disappearing of epoxy functional group at 833 cm^{-1} in the Fourier transform infrared (FTIR) spectrum. The formation of HPEPO was detected at 2500 cm^{-1} to 3400 cm^{-1} which represents the O-H stretching of carboxylic acid. Based on nuclear magnetic resonance (NMR), the disappearance of epoxy ring group at 2.8 – 3.0 ppm has indicated the completely reacted oxirane ring with the presence of peak at 3.7 ppm corresponded to hydroxyl group. Meanwhile, HPEPO exhibited low thermal stability by having melting temperature around 45 °C to 60 °C in Differential scanning calorimetry (DSC) and as showed by the great percentage of weight loss in thermogravimetric analysis (TGA) curve. However, the formation of char residue was slow, probably due to the formation of hydrogen linkages in hydrogel.

Keywords: hydrogel, epoxidized palm oil, ring opening polymerization, chemical hydrolysis

Abstrak

Hidrogel berasaskan minyak sawit terepoksidasi (HPEPO) telah disintesis menggunakan polimerisasi pembukaan cincin (ROP) dengan kehadiran asid fluoroantimonik heksahidrat ($HSbF_6.6H_2O$) sebagai pemangkin, diikuti dengan hidrolisis kimia yang dimangkinkan oleh natrium hidroksida (NaOH). Pencirian struktur dan sifat termal hidrogel yang disintesis telah dikaji. Kejayaan pembukaan cincin minyak sawit terepoksidasi (EPO) telah disahkan melalui kehilangan kumpulan berfungsi epoksi pada 833 cm^{-1} dalam spektrum Fourier inframerah (FTIR). Pembentukan HPEPO dikesan pada 2500 cm^{-1} hingga 3400 cm^{-1} yang mewakili regangan O-H daripada asid karboksilik. Merujuk kepada resonans magnetik nuklear, kehilangan cincin epoksi pada 2.8 – 3.0 ppm menunjukkan cincin oksiran telah bertindakbalas sepenuhnya dengan kewujudan puncak pada 3.7 ppm sepadan dengan kumpulan hidroksil. Sementara itu, HPEPO telah mempamerkan kestabilan haba yang rendah dengan mempunyai suhu lebur antara 45 °C to 60 °C daripada kalorimetri pengimbasan pembezaan (DSC) dan seperti yang ditunjukkan dalam kehilangan peratusan berat yang besar melalui lengkung analisis Termogravimetri (TGA). Walau bagaimanapun, pembentukan sisa arang didapati perlahan, berkemungkinan disebabkan oleh pembentukan ikatan hidrogen dalam hidrogel.

Kata kunci: hidrogel, minyak sawit terepoksidasi, polimerisasi pembukaan cincin, hidrolisis kimia

Introduction

Natural oil-based materials have been widely used in many industries due to environmental legislation and sustainability. They are used as precursors for many chemical materials such as alcohols (polyols), glycols, olefenic compounds, lubricants, plasticizers and stabilizer for polymers [1,2]. Researchers have successfully synthesized epoxidized natural oils from soybean oil [3], rubber seed oil [4], rapeseed oil [5] and linseed oil.

As one of the major producers of palm oil, Malaysia too has successfully developed epoxidized palm oil as starting materials for various industrial areas [6]. The production of macromonomer polyols through ring opening polymerization of EPO with Lewis acid in tetrahydrofuran [7] and with glycerol [8] has been reported. The benefit of EPO as a starting material is necessary to be explored progressively in order to expand the palm oil commercial value in various industrial areas. A research work completed by Ang et al. [9] have successfully synthesized polyol with high molecular weight and low hydroxyl functionality which is potentially to be used in wood adhesive applications. Clark and Hoong [7] have reported to derive macromonomer polyols from EPO by Lewis acid ring opening reactions in tetrahydrofuran (THF) solvent and reacted with MDI to furnish elastomeric polyurethanes.
This research has utilized EPO due to high reactivity of epoxy ring which can be subsequently converted into many products including polyols. An effort has been made to expand the use of EPO into new area such as hydrogel. Palm oil generally has the average 2.0 – 2.5 functionality as compared to ESO that has higher epoxy functionality. This drawback limits the use of palm oil polyol in the area that need longer molecular chain or higher molecular weight. However, the idea to introduce palm oil polyol with crosslinking network has brought the exploration of polyol into hydrogel.

Hydrogel, can be derived from many synthetic and natural polymers, possess high water absorption capacity and biocompatibility. These attractive properties contribute to wide applications such as in tissue engineering, pharmaceutical, and biomedical fields [10]. Liu et al. [11] have successfully synthesized epoxidized soybean oil (ESO) hydrogel via hydrolysis reaction.This study has adopted ring opening polymerization of EPO to prepare polymeric hydrogel in chemical hydrolysis reaction with the presence of sodium hydroxide (NaOH). The proposed reaction scheme is shown in Fig. 1. To date, no work has been done on the synthesis of hydrogel-based EPO.

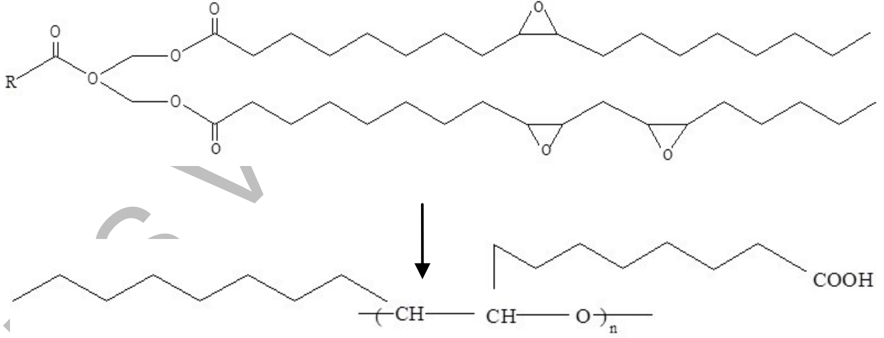

Figure 1. Scheme outlining the synthesis of HPEPO polymers

Materials and Methods

Materials

EPO with 2.7 – 2.9 % oxirane oxygen content (OOC), molecular weight of 1049 g/mol and iodine value of 0.58 eq/100 g value was supplied by Budi Oil (M) Sdn. Bhd. Fluoroantimonic acid hexahydrate catalyst ($HSbF_6{\cdot}6H_2O$) was purchased from Sigma Aldrich while methylene chloride, sodium hydroxide, hydrochloric acid and acetic acid were obtained from Qrec Chemical Co. Ltd.

Sample preparation: *Ring opening polymerization*

EPO was reacted with methylene chloride in the presence of fluoroantimonic acid hexahydrate as catalyst for 3 hours at room temperature to obtain polyol (PEPO) under nitrogen gas environment.

Hydrolysis reaction

PEPO was refluxed in sodium hydroxide for 24 hours before filtered and cooled down to room temperature. The obtained gel was precipitated with hydrochloric acid and washed with water for several times, then washed with acetic acid twice afterwards. The resulting hydrogel (HPEPO) was dried in the oven at 80 °C overnight and further dried in vacuum oven at 70 °C and the weight was measured for every 20 minutes until it reached a constant weight.

Characterization: *FTIR measurements*

Samples of the EPO, PEPO and HPEPO were analyzed using KBr plates. The IR spectra of these samples were recorded on Perkin Elmer IR spectrometer at room temperature with scanning range of 4000 to 400 cm^{-1} for 16 scans.

NMR measurements

The ^1H NMR spectrum for the EPO, PEPO and HPEPO samples were recorded quantitatively using a NMR spectrometer model of a Bruker Avance II 400 MHz UltraShield.

DSC measurements

The test was conducted using a DSC-6 Perkin-Elmer on PEPO Aand HPEPO. Samples were placed in the aluminium pan and were scanned from - 60 ^oC to 150 ^oC and the heating rate of 10 ^oC/min.

TGA measurements

A thermogravimetric analysis of the PEPO and HPEPO was carried out on TG (Mettler Toledo, TGA/SDTA851) under nitrogen atmosphere from 30 °C to 600 °C at heating rate of 10°C/min.

Results and Discussion

FTIR analysis

FTIR spectra of EPO, PEPO and HPEPO are presented in Fig. 2. The epoxy group of EPO at 833 cm^{-1} was disappeared in PEPO and HPEPO, indicated the ring opening reaction of epoxy was successfully achieved. Meanwhile, the ester carbonyl band of PEPO (1737 cm^{-1}) has shifted to the lower band in HPEPO (1710 cm^{-1}), implying the formation of strong hydrogen bonding of carboxylic acids dimers in HPEPO. Denisov et al. [12] found that hydrogen bonding and resonance have weaken the C:O bond, resulting in absorption at a lower frequency. Furthermore, a very broad peak observed at around 2500 cm^{-1} to 3400 cm^{-1} which represented the O-H stretching of carboxylic acid, supported the formation of HPEPO hydrogel.

NMR analysis

NMR was done to confirm the formation of polyol. Figures 3, 4 and 5 exhibit the ^{1}HNMR spectrum of EPO, PEPO and HPEPO respectively. From Fig. 3, the highest peak at 1.00 – 1.30 ppm belongs to the CH_2 proton in the fatty acid moiety. The presence of epoxy ring was detected by the peaks at 2.8-3.0 ppm. Meanwhile, the peaks that appeared at 2.7-2.9 ppm were corresponding to the proton adjacent to epoxy cyclic ring groups. Fig. 4 shows the ^{1}HNMR spectrum of PEPO produced. The proton peaks at epoxy cyclic ring group at 2.8-3.0 ppm disappeared and a new small signal at 3.7 ppm has emerged which indicated the presence hydroxyl group of the opened epoxy ring. Similarly, the spectrum of HPEPO in Fig. 5 has shown that there were no peaks from epoxy groups detected, indicating that the epoxy ring has completely reacted.

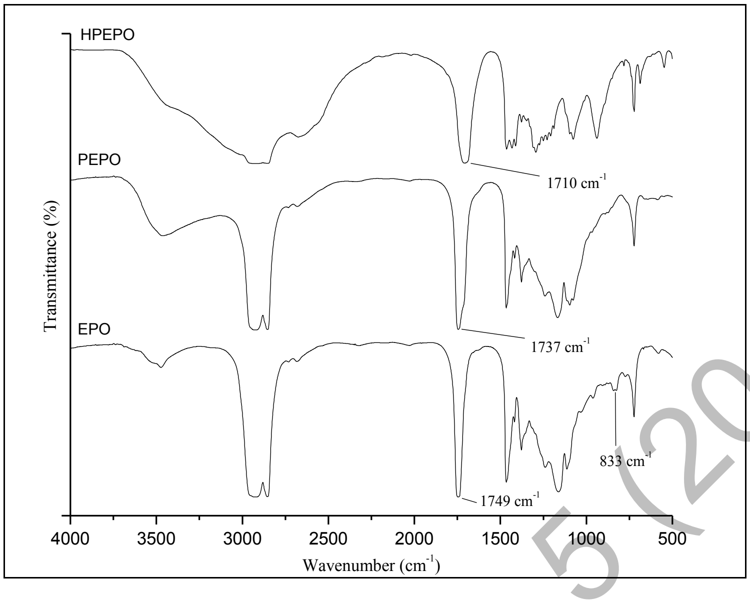

Figure 2. IR spectra for EPO, PEPO and HPEPO

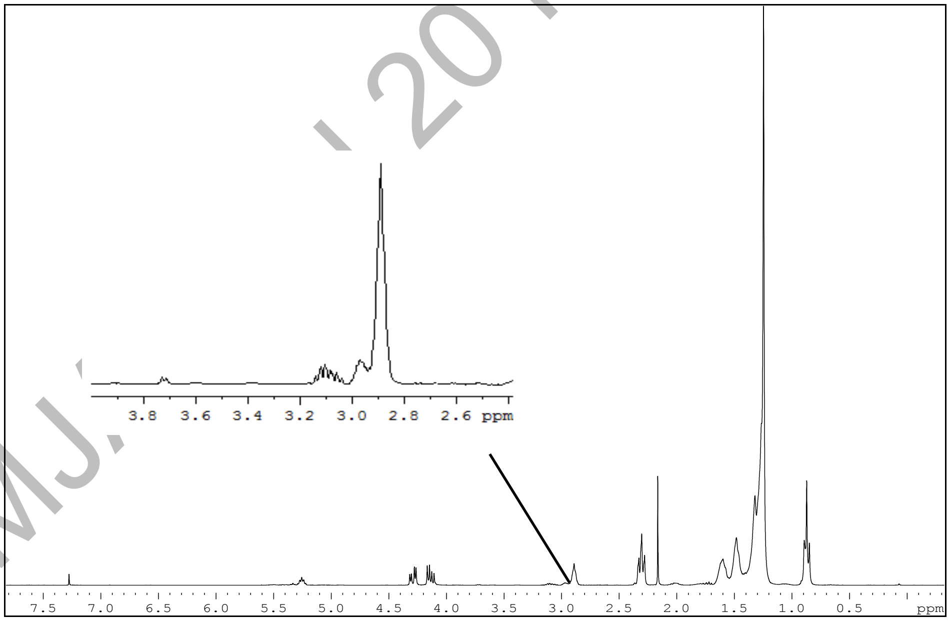

Figure 3. ^{1}HNMR spectra of EPO

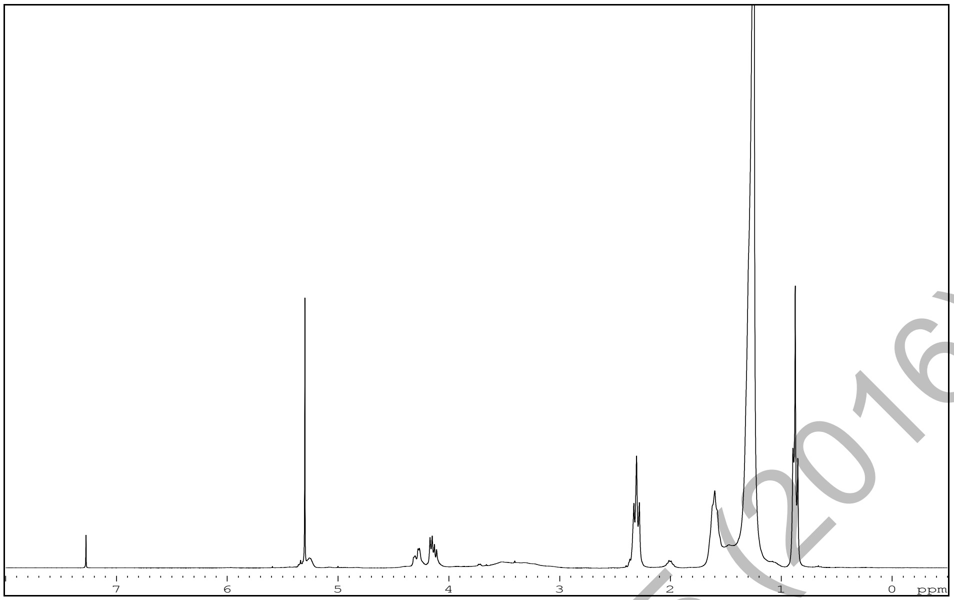

Figure 4. ^{1}HNMR spectra of PEPO

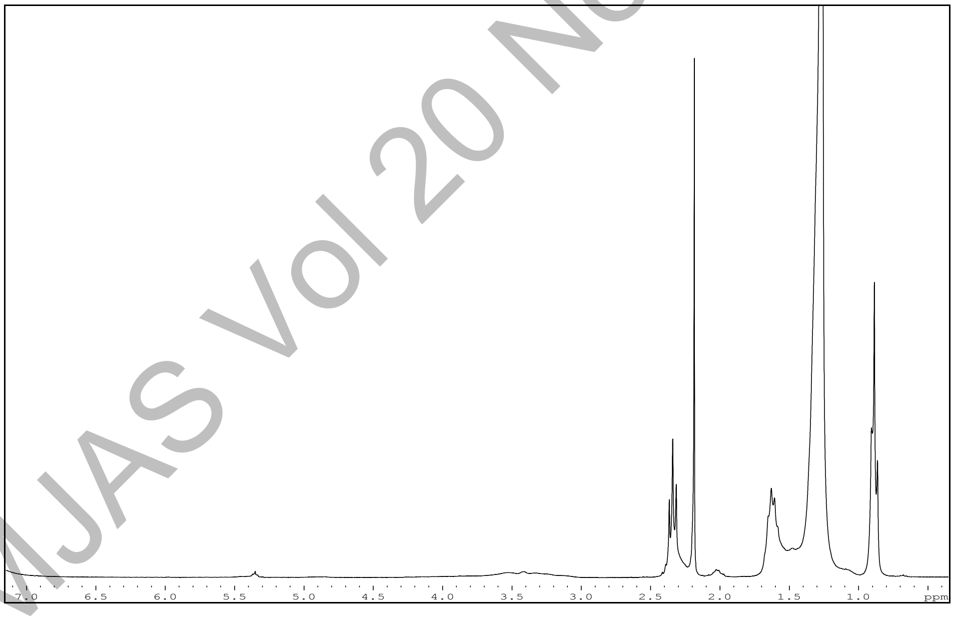

Figure 5. ^{1}HNMR spectra of HPEPO

Differential Scanning Calorimetry

Figure 6 shows the DSC thermograms of PEPO and HPEPO samples. Corresponding to an endothermic process, it can be seen that the DSC heating thermograms of the PEPO and HPEPO samples have shown positive peaks. From the graph, the melting temperature, T_m for PEPO was observed to be at 10 °C while HPEPO has higher in a range between 45 to 60 °C . As related to previous findings reported by Zhang et al.[13] and Rashmi et al. [14], bio-based polyols are typically have low melting temperature due the domain that consists of soft segments that crosslink to each other. According to Wang and Schuman [15], the composition of the polymer within the cross linked structure plays an important role in thermal behavior, with the inherently flexible structure of fatty acid chain in PEPO reducing the crosslink density to form a less compact crosslinked structure compared to HPEPO. As a result, a polymer with low crosslink network increased its free volume and reduced its viscosity, leading to the decrease in T_m.

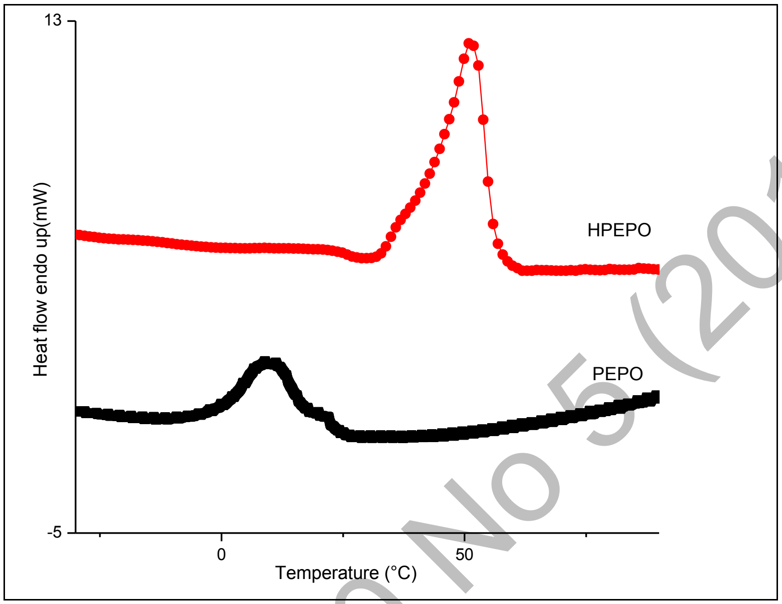

Figure 6. DSC thermograms of PEPO and HPEPO

Thermogravimetric analysis

Fig. 7 shows the TGA curves of PEPO and HPEPO. It can be seen both PEPO and HPEPO exhibited three degradation steps, related to the decomposition of polyunsaturated, monounsaturated and saturated fatty acids as both are palm oil based products, similar to most edible oils [16]. The decomposition in PEPO was not that obvious in the first region with a gradual reduction of weight loss at 5 wt%. On the contrary, HPEPO showed a sharp drop of plateau at about 40 wt%. This is thought due to the synthesis of HPEPO which involves hydrolysis reaction that caused the breakdown of ester linkage [17]. Furthermore, the release of volatile compounds such as hydrocarbon and carboxylic acid also contributes to the great weight loss of the sample [16]. In the second step, PEPO exhibited higher weight loss at 50 wt% compared to 40 wt% weight loss in HPEPO in the temperature ranges from 270 to 390 °C. As illustrated in Fig. 8, the weight loss fell sharply in PEPO as showed by a resolved peak of derivative TG (DTG) curve. In the third step, the char residue formed at above 400 °C, where about ca. 90 wt% and 95 wt% losses occurred in HPEPO and PEPO. However, the rate of degradation of HPEPO was slightly slower than PEPO, probably due to more hydrogen linkages that formed in the hydrogel apart from saturated fatty acids.

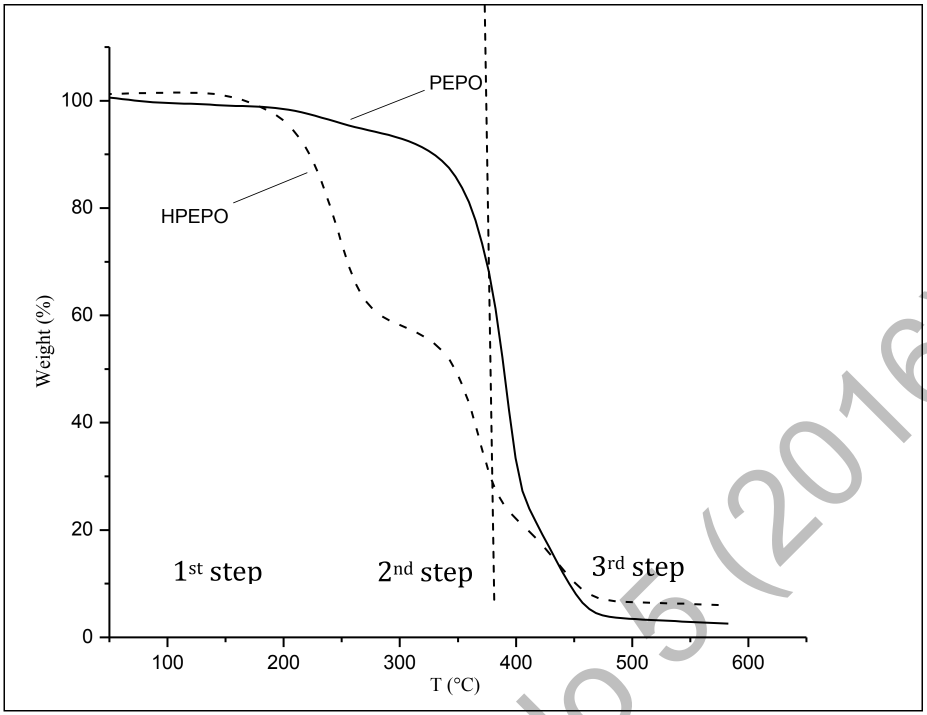

Figure 7. TGA thermogram of PEPO and HPEPO weight loss versus temperature

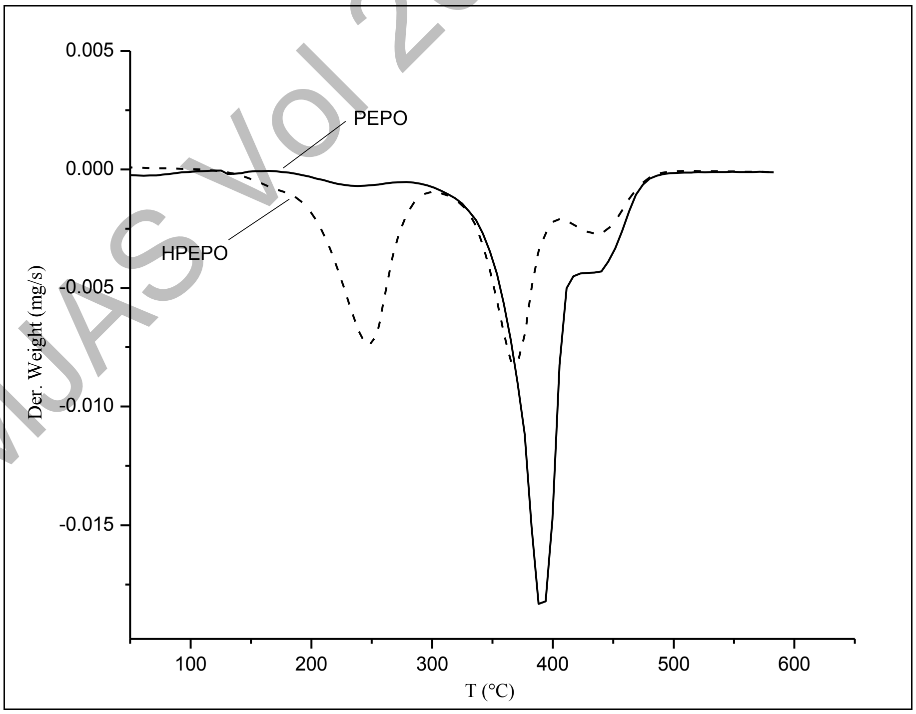

Figure 8. Derivative TG of PEPO and HPEPO versus temperature

Conclusion

The structural and thermal characteristics of epoxidized palm oil based hydrogel were studied. The epoxy ring in EPO had been successfully opened; evidently form the disappearance of 833 cm^{-1} epoxy characteristic band from FTIR spectrum. The formation of hydrogel HPEPO was confirmed with the detection of –OH stretching peaks of carboxylic acid at 2500 cm^{-1} to 3400 cm^{-1}, respectively. This is supported in NMR analysis where the disappearance of epoxy ring group at 2.8 – 3.0 ppm has indicated the completely reacted oxirane ring with the presence of peak at 3.7 ppm corresponded to hydroxyl group. Meanwhile, HPEPO exhibited melting temperature around 45 °C to 60 °C with low thermal stability in the first and the second degradation regions as showed by the great percentage of weight loss against PEPO. However, the formation of char residue was slower in HPEPO, probably due to hydrogen linkages that need higher temperature to be broken.

Acknowledgement

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