Solid State Science and Technology, Vol. 25, No 2 (2017) 86-95
ISSN 0128-7389 | *http://journal.masshp.net*

SYNTHESIS AND PROPERTIES OF ACRYLATED EPOXIDIZED PALM OIL FOR UV CURED COATINGS

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ABSTRACT

Radiation curing technology using palm oil as a raw material has encountered increasing applications in recent years. An acrylated epoxidized palm oil (AEPO) was synthesized from epoxidized palm oil (EPO) using acrylic acid as a ring opening agent. FTIR and ^{1}H-NMR spectra were performed to confirm the formation of acrylate grafting on the fatty acid chain. The AEPO was mixed with four different amounts of photoinitiators using Irgacure 500. Glass substrate surfaces were coated with the resin formulations, subsequently cured under UV light and the coating adhesion were characterized. AEPO vinyl functional group appeared at 1624 cm^{-1}, CH_2=CH-COO and also at absorption band of 961cm^{-1}, =C-H. In ^{1}H NMR, the acrylate group CH=CH_2 introduced resonate around at δ5.8-6.5 ppm. The increased in viscosity of AEPO, 497.5 Cps was confirmed by appearance of peak at 3417cm^{-1} in FTIR. In the preparation of AEPO films in UV curing adhesive, AEPO 2wt% have the highest surface hardness. The AEPO 2wt% has the highest gel content whereas the AEPO 2.5wt% had the lowest gel content.

Keywords: acrylated epoxidized palm oil; UV curing; epoxidation

INTRODUCTION

Epoxidized molecules can be acrylated with acrylic acid or with acryloyl chloride. The inhibitor (to prevent polymerisation of the acrylic acid/acryloyl chloride), such as 4-methoxyphenol and small amounts of a catalyst, such as triethylamine are required during the reaction. The ring opening of the epoxide groups produce an acrylate unit, together with a hydroxyl group. The advantages of functional acrylates include their good adhesion to plastics, high cross-linking density, reactivity, chemical resistance, hardness and scratch resistance [1]. Therefore, crosslinking of acrylates monomers is needed in order to increase their thermo-mechanical stability. Moreover, functional acrylates can crosslink quickly either by radical or cationic polymerization. This UV curing technology offers many advantages like solvent-free polymerization, low energy

consumption, and rapid cure speeds which lead to shorter curing lines and hence reduced cost as well as the ability to cure these coatings on heat-sensitive materials like wood or wood-based materials. The use of palm oil as a starting material for cationically cured UV resins is one area which it was felt merited exploration. Acrylated epoxidized palm olein has been studied already to some extent by previous workers [2]. There have not been many studies about the exploitation of acrylated epoxidized palm oil and coating resin production. Hence, cured films coating resin were produced by ultra-violet curing technique and their properties were investigated.

METHODOLOGY

Preparation of Acrylated Epoxidized Palm Oil (AEPO)

A mixture of epoxidized palm oil, EPO (30g), acrylic acid (0.339 mol) and vinyltrimethoxysilane (0.1695 mol) containing 1% (w/w) of hydroquinone was stirred in round bottom reaction vessel which equipped with mechanical stirrer and nitrogen purging reaction at temperature of 80°C. The consumption of acrylic acid during acrylation process was monitored by determining the acid value (AV) and oxirane oxygen content (OOC) test. The value of OOC was determined using the standard hydrobromic acid in acetic acid method, AOCS Cd 9-57 by following Official Methods and recommended Practices of the American Oil Chemists' Society. Iodine value (IV) was determined on the product of epoxidation and acrylation using AOAC Official Method 993.20 using Wijs (Cyclohexane-Acetic Acid Solvent) Method.

Preparation of Acrylated Epoxidized Palm Oil (AEPO) films

Table 1 shows the formulations for each resin sample. The coating samples were all cured by exposing them to ultraviolet (UV) radiation under the irradiation by IST UV exposure machine from Fusion UV Systems. The films were characterized by using pencil hardness test, adhesion test and gel content.

Table 1: Formulations Mixtures in AEPO Films

Samples	AEPO (g)	Irgacure 500 (g)
AEPO 1.0wt%	5g	0.05
AEPO 1.5wt%	5g	0.075
AEPO 2.0wt%	5g	0.10
AEPO 2.5wt%	5g	0.125

RESULTS AND DISCUSSION

Synthesis of Acrylated Epoxidized Palm Oil

Figure 1 shows a schematic diagram of acrylation process of epoxidized palm oil. Epoxides resin reacted with carboxylic acid to form ester. Reaction took place between carboxyl group of acrylic acid and both the epoxy and hydroxyl group of epoxides.

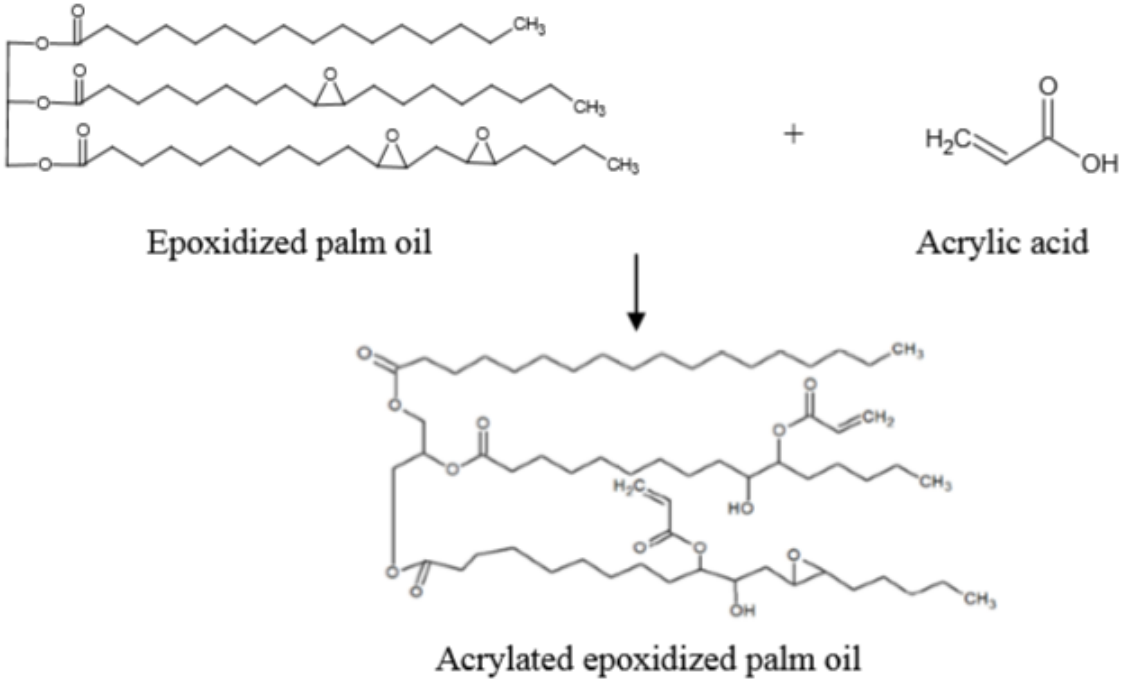

Figure 1: Schematic diagram of synthesis process of AEPO

The effect of oxygen oxirane content (OOC) on AEPO

The reduction in value of %OOC proved that there was opening of epoxide ring occurred during the acrylation process and also derivatisation of acrylates into the chemical structure of that fatty acid [2]. The OOC value was 0.88% which indicated that there was still remaining of epoxy group in the fatty acid backbone.

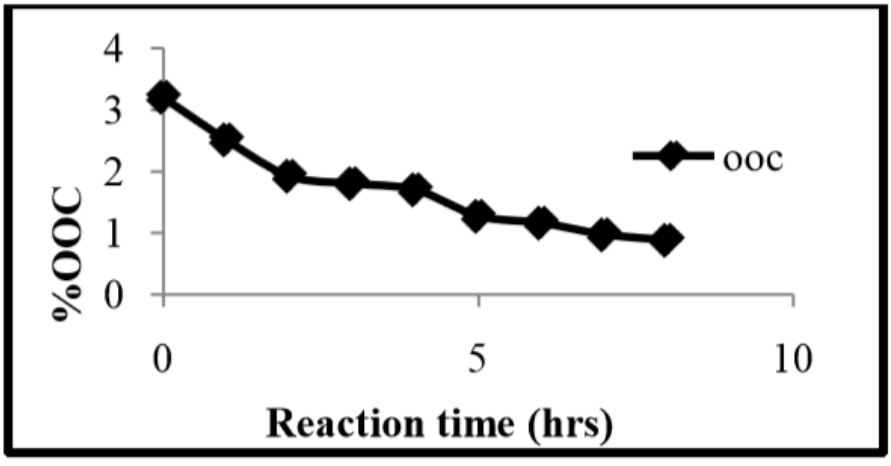

Figure 2: Graph of Oxirane Oxygen Content versus Reaction Time for AEPO

The effect of acid value on AEPO

The initial acid value of EPO was 1.55 mg KOH/g (Table 2). After addition of acrylic acid during preparation of AEPO, the number of acid value for the 1st hour increased to 83.79 mg KOH/g (Figure 3).

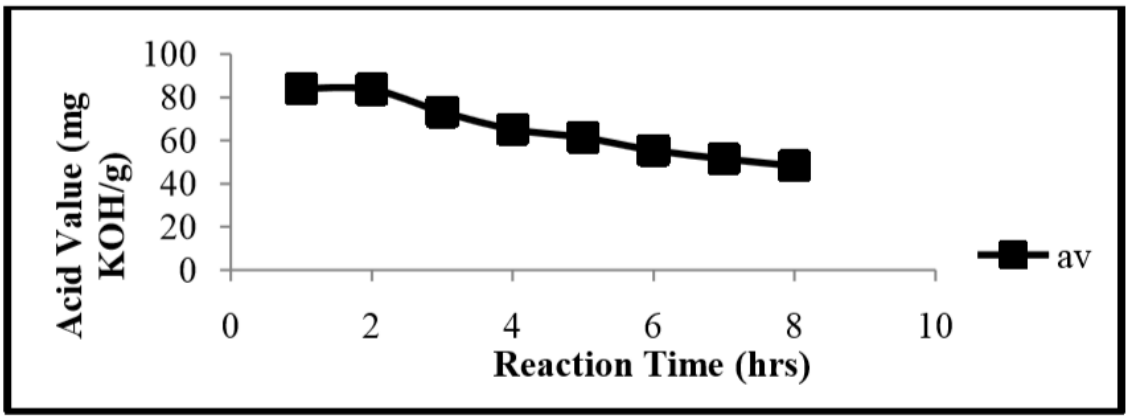

Figure 3: Graph Acid Value versus Reaction Time in Hours for AEPO

The initial acid value was high and will decreasing at prolonged reaction duration. The acid value of AEPO was about 48.25 mg KOH/g through 8 hours reaction time. Different acid value of EPO and AEPO was due to the higher concentration of reactive sites as well as higher possibility of epoxide groups and acrylic acid association. Table 2 summarised the properties of PO, EPO and AEPO respectively.

Table 2: Characteristics of PO, EPO and AEPO

Sample	Color	Viscosity (Cps)	OOC	IV	AV
PO	Yellow	72.00	0.05	60.98	0.03
EPO	Light yellow	117.0	3.20	9.49	1.55
AEPO	Dark brown	497.5	0.88	25.50	48.25

FTIR Analysis of AEPO

Observation on structural changed for both EPO and AEPO was done using FTIR spectroscopy. Based on the spectrum in Figure 4, a weak band representing hydroxyl groups can be observed at 3476 cm^{-1} in EPO. This might be due to the presence of acid residue during EPO preparation. The new bands which appears at 1624 cm^{-1} may attributed to the acrylate group CH_2=CH-COO and 961 cm^{-1} (=C-H) [3]. The other broad band which appear at 3417 cm^{-1} may be attributed to (OH) group showing the existence of hydroxyl group upon epoxy ring opening [4]. As in this study, the ring opening mechanism was done by acryloyl group from acrylic acid itself (CH_2=CH-COOH-). As epoxy ring was successfully opened, acryloyl group (CH_2=CH-CO-) joined the ring and simultaneously hydroxyl group (-OH) attached itself to the neighbouring carbon chain.

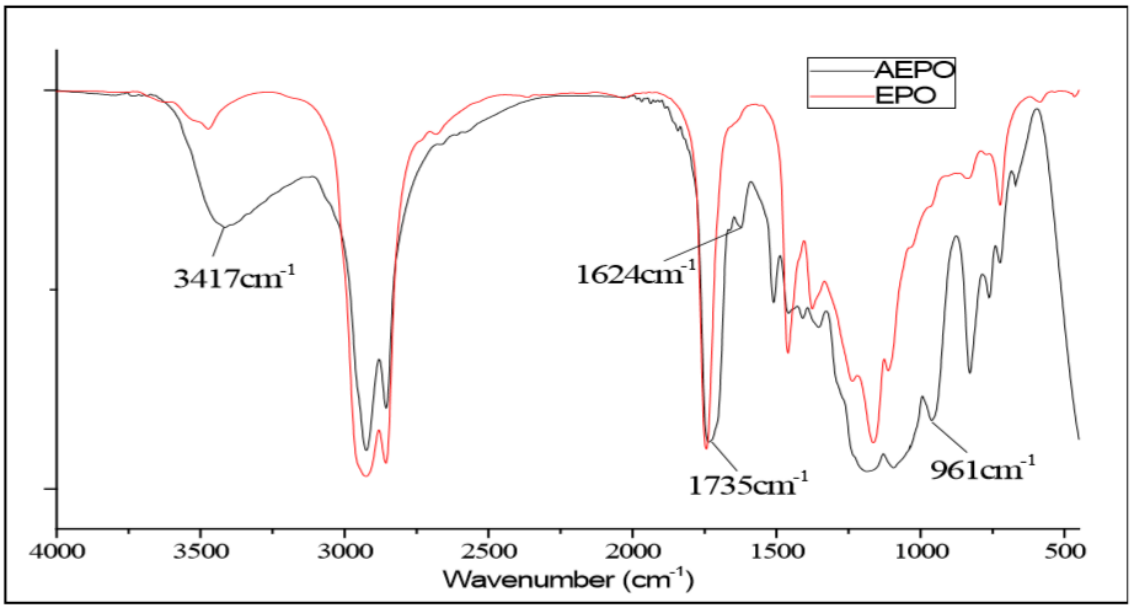

Figure 4: FTIR spectra of EPO and AEPO

^{1}H Nuclear Magnetic Resonance (NMR) Analysis for Molecular Structure Determination of Acrylated Epoxidized Palm Oil

After epoxidation, the chemical shift at δ 2.4 ppm, δ 2.5 ppm, δ 2.6 ppm, 3.5 and 3.6 ppm belonged to epoxy cyclic ring group, CH-O-CH, appeared corresponding to EPO as shown in Figure 5. Additional structural confirmation of AEPO was obtained from ^{1}H-NMR analysis as shown in Figure 6. Table 3 summarized the chemical shift for AEPO. The derivatised of acrylic acid of AEPO was detected at δ5.8-6.5 ppm indicated the appearance of acrylate C<u>H</u>=CH_2. Moreover, at δ4.4-4.0 ppm, the peaks were produced by methylene hydrogen atoms attached at the ester bond, (CH_2-O), while at δ5.3 ppm showed peak of proton CH group which was adjacent to CH_2 group, O-C<u>H</u>-CH_2 bonds [5].

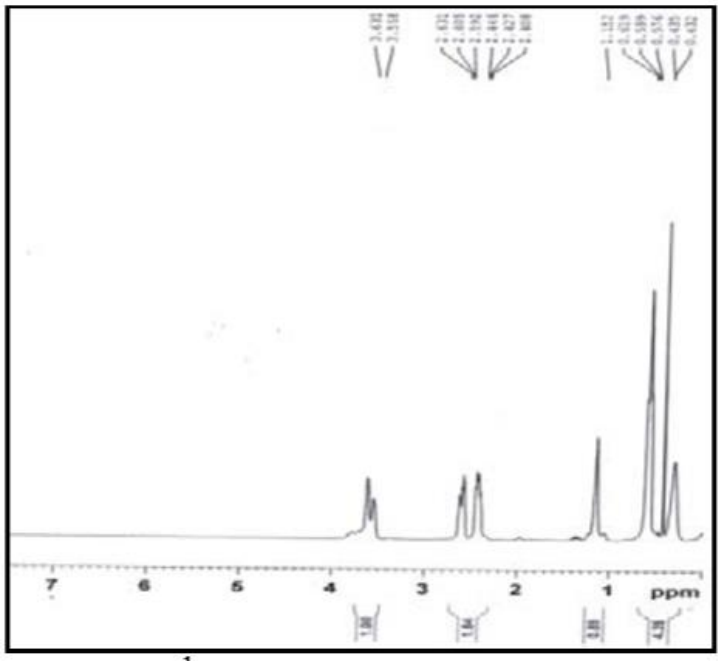

Figure 5: ^{1}H Nuclear Magnetic Resonance (NMR) Analysis of EPO

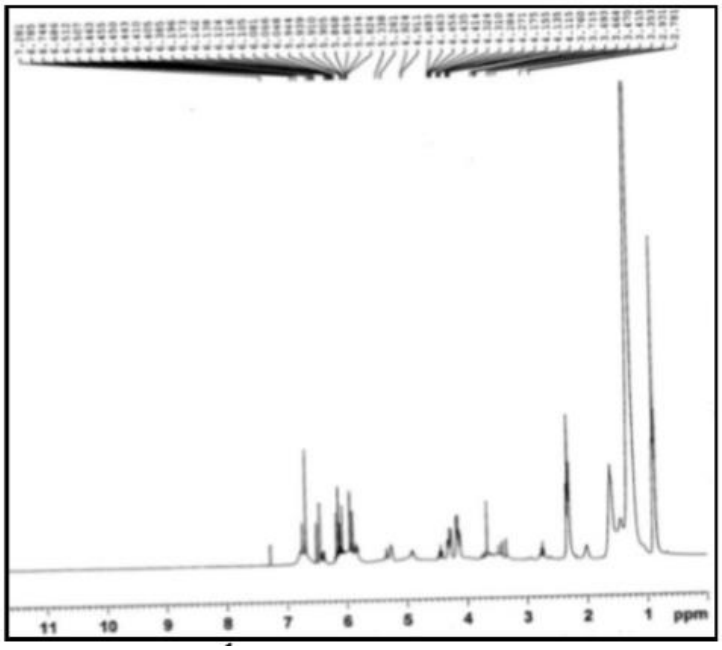

Figure 6: ^{1}H Nuclear Magnetic Resonance (NMR) Analysis of AEPO

Table 3: ^{1}H NMR Chemical Shift for AEPO

Chemical shift , dppm	Groups
0.9	$C\underline{H}_3$-$(CH_2)n$
1.3-1.2	$C\underline{H}_2$-$(CH_2)n$
1.6	$C\underline{H}_2$-CH
2.3	$C\underline{H}_2$-C=O(aliphatic methylene H)
4.4-4.0	$C\underline{H}_2$-O(methylene H at ester bond)
5.3	O-C$\underline{H}$-CH_2
6.5-5.7	$CH=CH_2$ (acrylate)

Determination of Surface Hardness on AEPO Films

Since aromatic segments do not exist in triglyceride systems, the hardness of the coating films only depends on their degree of cross-linking. The pencil hardness test was carried out by taking pencils of different grades (1B to 6B, F and 1H to 6H) according to ASTM D 3363-74. Table 4 showed the result of pencil hardness test on UV curable coating samples.

Table 4: Pencil Hardness Test on UV Curable Resin

Sample	Pencil Hardness
AEPO 1.0wt%	H
AEPO 1.5wt%	1H
AEPO 2.0wt%	2H
AEPO 2.5wt%	H

The increasing in the amount of Irgacure from 1 wt% to 2 wt% lead to increased in hardness properties. Sample AEPO 1wt% and AEPO 2.5wt% only passed the pencil hardness test up to H pencil grade while sample AEPO 2.0 wt% showed the highest value of hardness test, 2H. The performance of organic coating was related to its crosslink density that can be measured using gel content test. The chemical changed, that takes place in the structure of coating in the course of UV exposure tends to make it hard. According to [6], the tensile strength is almost constant as the photoinitiator increases up to 2.0%. Decreasing the photoinitiator concentration will reduce the crosslinking density and hence give a more loose structure. High value of hardness tends to have high tensile strength.

Determination of Adhesion on AEPO Films by Pull-off

Pull-off adhesion test was carried out to determine the adhesion strength between AEPO coating and glass substrate. Figure 7 gives information regarding the pull off adhesion for AEPO and AESO film coatings. The amount of photoinitiators used in formulation affecting the properties of polymer network. The increasing of photoinitiator from 1wt% to 2.5wt% in AEPO samples except for AEPO 1.5wt%

showed increasing in adhesion strength. AEPO 2.5wt% showed higher adhesion with 1.15MPa which indicated that the adhesion of interfacial base substrate and film was good.

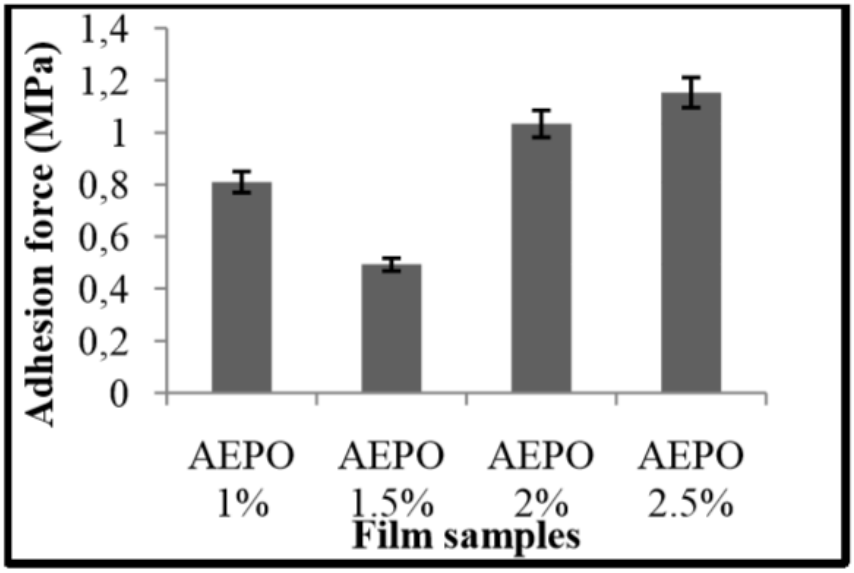

Figure 7: Graph of Pull-off Adhesion Test for AEPO Films

The study by [7] revealed that the adhesion of coating depended on the nature of substrates as well as on the coating formulations. However, when a curable oligomer is present, the formation of a three dimensional network grafted onto the substrate, having a covalent bond onto the substrate but this mechanism obviously does not apply to a glass surface and it explains why the adhesion of the resin was poor on it [3].

Determination of Gel Content on AEPO Films

According to [8], higher gel content indicated a higher density of crosslinks. The AEPO 2 wt% had the highest gel content whereas the AEPO 2.5 wt% had the lowest gel content (Figure 8). Gel content depends on the functionality of the monomer. The acrylate monomers contain C=C bonds, as the reactive site. If irgacure concentration is too high, the radical from photoinitiator can contribute to a high termination rate. A high termination rate can lead to poor physical properties like adhesion and tensile strength. AEPO 2 wt% has the highest crosslinked density compared to other samples. This observation indicates the higher cross-linking density compare to others, and is in good agreement with the results of the hardness. The cross-linking densities were increased which could be attributed to the increase of the deposited energy in the matrix resulted in a higher free radicals concentration [9].

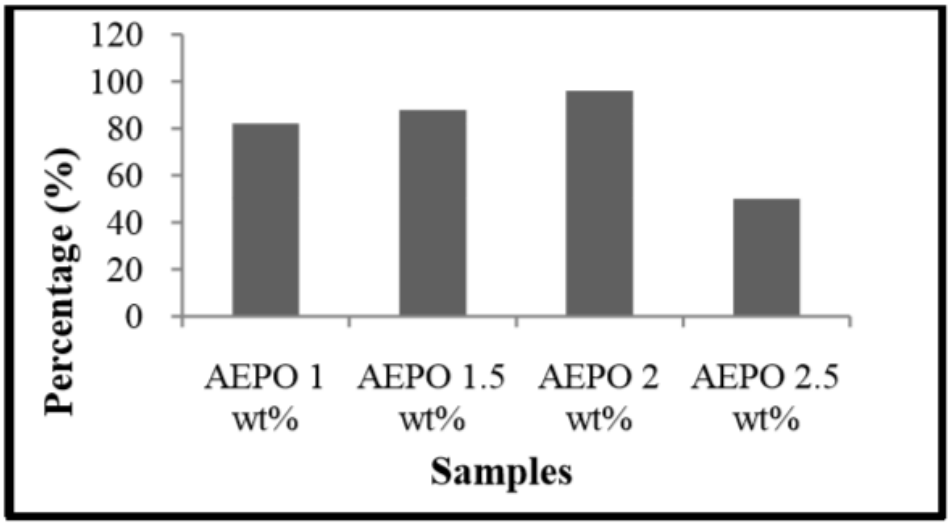

Figure 8: Graph of Gel Content Test for AEPO Films

CONCLUSION

As a conclusion, acrylated resin from epoxidised oil was successfully prepared. Introducing arylate group to epoxidised palm oil, EPO produced acrylate monomers having optimum oxirane oxygen content and acid value number which is highly reactive to UV curing. Acrylation process was found has increased the molecular weight and the viscosity of AEPO to give high crosslinked film and therefore due to unsaturated sites introduced, AEPO thus can react to form solid films quickly by UV radiation using radical photoinitiators.

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