

Production of UV-Curable Palm Oil Resins/Oligomers Using Laboratory Scale and Pilot Scale Systems

(Penghasilan Resin/Oligomer Minyak Sawit Termatang UV Menggunakan Sistem Skala Makmal dan Skala Loji)

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ABSTRACT

In recent years, there are growing trends in using palm oil as raw materials in radiation curable resins production. In this study, the acrylated palm oil resins i.e. the EPOLA (epoxidized palm oil acrylate) and the POBUA (palm oil based urethane acrylate) were synthesized using two different systems, i.e. the 25 liter pilot scale reactor synthesis system and the 2 liter (L) laboratory scale reactor synthesis system through chemical processes known as acrylation and isocyanation. In this paper, the property of the acrylated resins which were produced by these two systems were evaluated and compared between each other. Their properties were characterized using the Fourier transform infrared (FTIR) spectrophotometer for functional group identification; the gel permeation chromatography (GPC) for molecular weight (Mw) determination, the Brookfield viscometer for viscosity measurements, the acid values (AV) and the oxirane oxygen contents (OOC) analysis. As a result, the production process for both the 2 L and 25 L reactor system were found to be time consuming and the main advantages for the 25 L reactor was its higher productivity as compared with the 2 L reactor system with the same synthesis process parameters i.e. the temperatures and the experimental methods. Besides that, the 25 L reactor synthesis process was found to be safe, easy to control and served unpolluted process to the environments. The final products, the acrylated palm oil resins were formulated into ultraviolet (UV) curable compounds before subjecting them under UV irradiation. As a result, the UV-curable palm oil resins showed potential uses as pressure sensitive adhesives, printing inks including overprint varnishes (OPV) and coatings.

Keywords: Acrylated palm oil resins; palm oil resins; UV-curable polymers/oligomers

ABSTRAK

Sejak kebelakangan ini, wujud satu arus perkembangan terhadap penggunaan minyak sawit sebagai bahan mentah dalam penghasilan resin termatang sinaran. Dalam kajian ini, resin minyak sawit terakrilat contohnya EPOLA (epoksida minyak sawit terakrilat) dan POBUA (uretana akrilat minyak sawit) telah disintesis menggunakan dua sistem yang berbeza iaitu sistem sintesis reaktor skala loji 25 liter dan sistem sintesis reaktor skala makmal 2 liter (L) melalui proses kimia yang dikenali sebagai pengakrilatan dan pengisosianatan. Dalam kajian ini, ciri-ciri resin terakrilat yang dihasilkan melalui dua sistem ini dinilai dan dibanding antara satu sama lain. Ciri-cirinya diselidiki menggunakan kaedah spektrofotometer transformasi Fourier inframerah (FTIR) untuk pencirian kumpulan berfungsi, kromatografi ketelapan gel (GPC) untuk pengukuran berat molekul, viskometer Brookfield untuk pengukuran viskositi di samping penilaian nilai asid (AV) dan kandungan oksigen oksirana (OOC) menggunakan kaedah titratan. Hasil kajian mendapati proses penghasilan untuk kedua-dua sistem iaitu skala 2 L dan skala 25 L menjimatkan masa dan juga didapati skala 25 L adalah lebih produktif dibandingkan dengan skala 2 L apabila ia diuji menggunakan parameter dan teknik amali yang sama. Selain itu, proses skala 25 L adalah didapati lebih selamat, mudah dikawal dan merupakan proses yang tidak mencemarkan persekitaran. Hasil produk akhir, iaitu resin minyak sawit terakrilat adalah diformulasikan kepada sebatian termatang ultralembayung (UV) sebelum didedahkan kepada sinaran UV. Hasil kajian menunjukkan resin minyak sawit termatang UV berpotensi digunakan sebagai bahan pelekat sensitif tekanan (PSA), dakwat percetakan termasuk varnis kemasan cetak dan penyalutan permukaan.

Kata kunci: Polimer/oligomer termatang UV; resin minyak sawit; resin minyak sawit terakrilat

INTRODUCTION

Commercialization of products from research and development (R&D) has become strong requirement for promoting new inventions to the relevant industry. It was

found that the work using a small 2 L laboratory scale production does not fulfilled these industrial needs. To fulfill the industrial needs, the Malaysian Nuclear Agency had initiated the installation of the 25 liter (L) pilot plant's

reactor synthesis at the Radiation Processing Technology Division (BTS), Malaysian Nuclear Agency, Malaysia. The process parameters from a 2 L of the laboratory scale synthesis must be upgraded to a higher capacity of 25 L bigger scale synthesis reactor to allow the fulfillment of the market's demands nowadays.

The establishment of this 25 L pilot plant's reactor synthesis will allow the promotion of these renewable and environment friendly palm oil resins to the relevant industry especially for those industries related to coatings including overprint varnishes (OPV), inks and adhesive areas. In addition, it is believed that, this synthesis process, i.e. the 25 L bigger scale synthesis reactor is safe, less time consuming, easy to control and more importantly served as a green or eco-friendly process to the environments. Besides that, it is our main goal to explore these local commodities such as palm oil resins as a possible replacement for the utilization of the petroleum based resins in the global market, which is becoming more expensive and diminishing.

In this work, the products that have been synthesized through a 2 L lab scale synthesis reactor and a 25 L bigger scale synthesis reactor will be evaluated and at the same time the products properties will be compared with each other. Finally, in this study, the palm oil resins will be formulated into UV-curable compounds for coatings and adhesives application. These products will also be tested for its acceptability in term of their hardness and tackiness.

An acrylic acid (AA) was used as a monomer, triethylamine (TEA) and 4-methoxyphenol (4-Mph) were utilized as a catalyst and an inhibitor for synthesizing the EPOLA. A diisocyanate compounds i.e. toluene 2,4-diisocyanate (TDI) and a hydroxyl terminated acrylates i.e. hydroxyl ethyl acrylate (HEA) were used as monomers to prepare POBUA resins. No solvent was used in this reaction. All chemicals employed in this synthesis process were purchased from Aldrich Chemical Co., USA. The pressure sensitive adhesive (PSA) formulations were mixtures of POBUA resin as an oligomer with isobornyl acrylate (ISBOA) (Aldrich Chemical) used as a monomer, acrylic acid used as an adhesive enhancer, hydroxyphenylketone (Doracure-1173) used as a catalyst (Ciba-Geigy Corporation, USA), nonylphenol monoethoxylate acrylate (M-111) (Toagosei Chemical Industry Co. Ltd., Japan) and 2(2-ethoxyethoxy) ethylacrylate (IRR-184) (Toagosei Chemical Industry Co. Ltd., Japan) as co-monoacrylate monomers. Figures 1 and 2 show the synthesis production systems which had been used in this study for synthesizing the palm oil resins. The coating formulations were mixtures of POBUA resins, trimethylolpropane triacrylate (TMPTA) (UCB Chemicals Sdn. Bhd., Malaysia) used as a crosslinker, 1,6-hexanediol diacrylate (HDDA) (Cytec Industries Inc., USA) used as diacrylate monomer and Doracure-1173 used as a catalyst. Chemical structure of monomers and photoinitiator used for the PSA and the coating formulations are shown in Figure 3.

MATERIALS AND METHODS

MATERIALS

An EPOP (epoxidised palm oil products) was purchased from Intermed Sdn. Bhd. (Kuala Lumpur, Malaysia) and used without further purification for producing the EPOLA.

METHODS

2 LITRES LABORATORY SCALE REACTION UNIT

The laboratory synthesis unit is a 2 L of reaction flask (Schott Duran). As shown in Figure 1, this unit was equipped with motor stirrer and condenser. The oil bath



FIGURE 1. The 2 L laboratory scale synthesis reactor

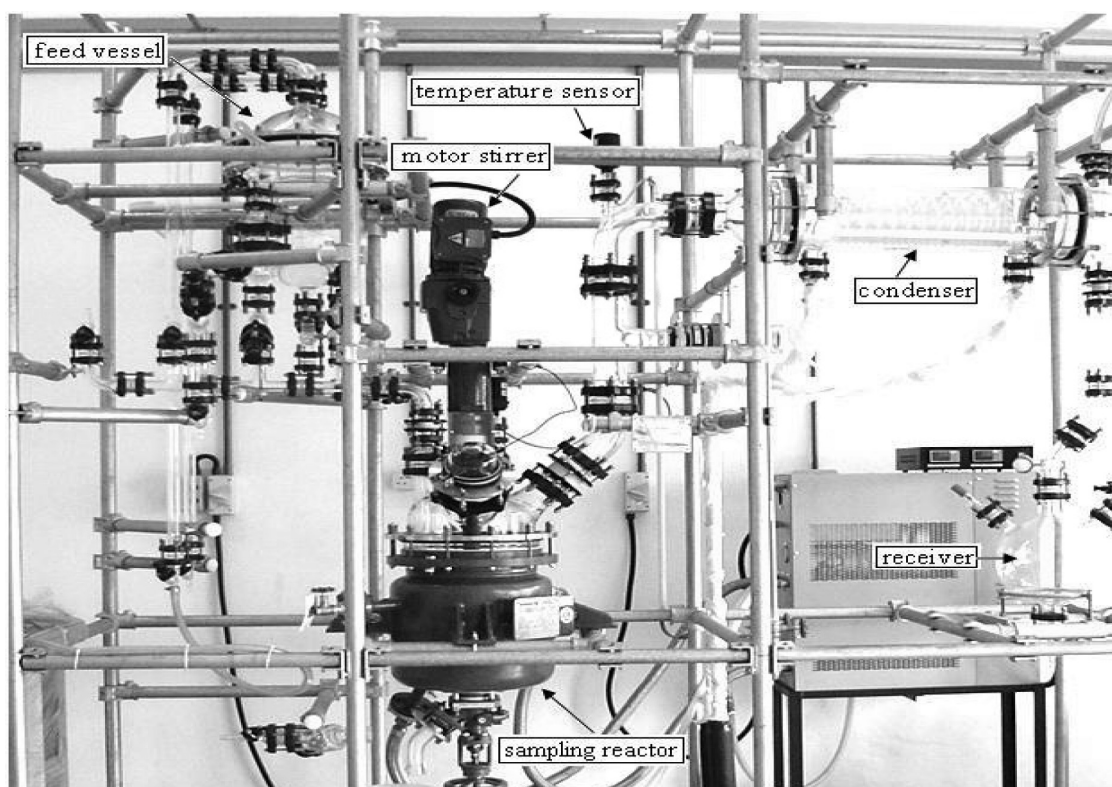


FIGURE 2. The 25 L pilot plant synthesis reactor

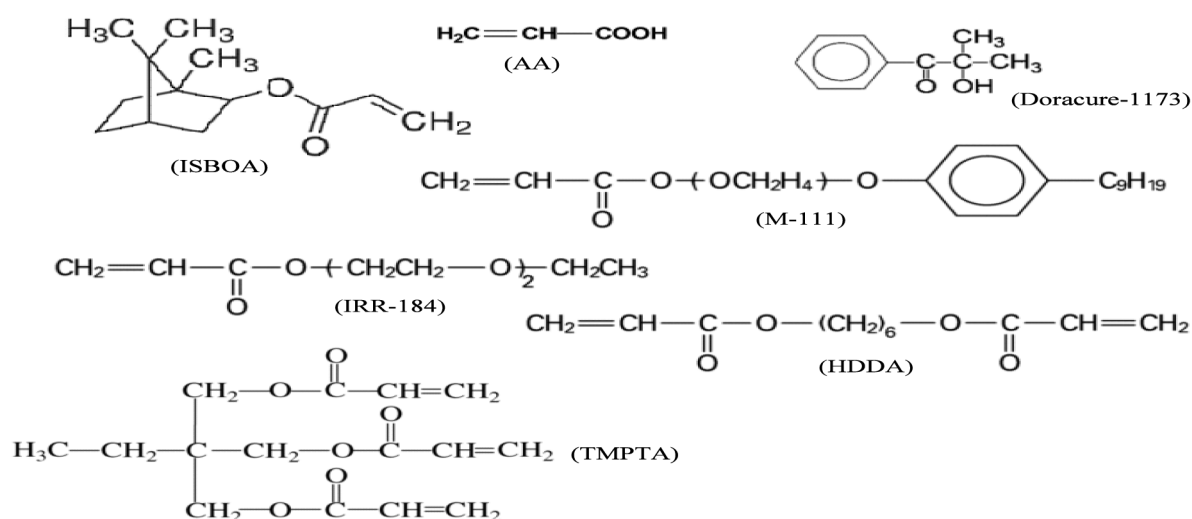


FIGURE 3. Molecular structure of the monomers and the photoinitiator

was manually assembled and attached to the unit during heating. For this system, about 1 kg of the feed material (raw material i.e. EPOP or EPOLA) was poured into the 2 L reaction flask to carry out the synthesis.

25 LITRES SYNTHESIS REACTOR UNIT

The QVF 25 L synthesis reactor unit was specially designed for the production of various palm oils based resins process/reaction. As shown in Figure 2, the unit consists

of a nominal 25 L reaction vessel (QVF borosilicate glass 3.3) with electrical heating oil bath as a synthesis reactor. The vessel was equipped with a motor stirrer, temperature sensor, feed vessel, receiver, condenser and sampling reactor. This 25 L synthesis reactor unit was connected to the cooling water system. For this system, about 20 kg of the feed material (raw material i.e. EPOP or EPOLA) was poured into the 25 L spherical sampling reactor to carry out the study.

SYNTHESIZING EPOLA AND POBUA PRODUCTS

In the production of EPOLA, an EPOP, an AA, a TEA and a 4-Mph for 1 kg and 20 kg for the 2 L and 25 L synthesis reactor, respectively, were mixed in a reaction synthesis unit. The reactor synthesis was heated to up to 110 to 120°C and the mixture was then stirred until the reaction was completed (Mohd Nor et al. 1990, 1992) which was confirmed by the standard methods.

Further, during the POBUA production, the reaction mixtures which consist of an EPOLA, a TDI, a HEA and a 4-mph (Mahmood et al. 1994) were heated at temperatures below 90°C using the 2 L and 25 L synthesis reactor, respectively. The reaction progress was monitored by the standard methods such as IR spectrophotometer (to ascertain the appearance of urethane peaks (-NH) and the disappearance of the hydroxyl peaks (-OH) until the reaction was completed.

STANDARD METHODS

For both products, i.e. EPOLA and POBUA, their physiochemical properties i.e. acid value (AV), oxirane oxygen content (OOC), molecular weights (MW), viscosities and Fourier transform infrared (FTIR) spectra were measured following the standard methods.

DETERMINATION OF ACID VALUE (AV)

The acid value (AV) was determined following the standard method of ASTM D0974. The AV value was calculated by using equation:

$$\begin{aligned} AV &= \text{mgKOH} / \text{g of resin} \\ &= 5.61 \times f \times v/w, \end{aligned} \quad (1)$$

where f is the factor (= 1), v is the volume of 0.1 N potassium hydroxide (KOH) and w is the weight of resin in gram.

DETERMINATION OF OXIRANE OXYGEN CONTENT (OOC)

The oxirane oxygen content (OOC) was determined following the standard method of AOCS Method Cd 9-57 (1963). The OOC was calculated using the following equation:

$$\text{OOC} = 1.6 \times N \times v/w \quad (2)$$

where N is a normality of hydrogen bromide (HBr), while v is a volume of HBr in mL and w is weight of resin in gram.

MOLECULAR WEIGHT (MW) ANALYSIS

Molecular weight of the raw material and the product's molecules were analyzed using Polymer Lab-50 GPC, at 40°C with 1 min/mL flow rate of Tetrahydrofuran's (THF) eluent, which is standardized by using Polystyrene standards. Approximately 0.02 g of sample was weighed

and solubilized in 10 mL of Tetrahydrofuran (THF, 99.9%, Merck). The above solutions were kept for 24 h before injected to the GPC system.

VISCOSITY MEASUREMENT

The viscosities of the products in liquid form were measured using Brookfield viscometer (Model VTDV-IIICP) at 25°C. About 5 g of sample was poured into wells-Brookfield cone and then the plate with grade 41 or 42 was selected for measuring viscosity.

FTIR SPECTROSCOPY ANALYSIS

Infra-red (IR) spectrum was obtained using FTIR spectroscopy (Perkin Elmer, Japan). The sample was placed on the readymade disc from a potassium bromide (KBr) for sampling. The IR spectrums were recorded at spectra in the range of 4000 cm^{-1} to 400 cm^{-1} .

UV CURING APPLICATIONS

The formulated resins were cured using UV irradiation by a medium pressure mercury vapour lamp of IST-UV Dryer (Switzerland) at the currents of 7.0 mA with the speeds of 20 m/min per pass for PSA and 10 m/min per pass for coating applications. The sample was coated to the polyethelene terephthalate (PTE) substrate and the glass substrate using a 20-30 μm thickness hand bar coater for the adhesive test and the coating test, respectively. The adhesive performances were tested using probe-type tackiness tester (Rhesca, Co. Ltd., Japan) for tackiness test. Meanwhile, the coating performances were tested using a Byk labotron pendulum hardness tester (Konig Method) in accordance with DIN 53157 for hardness test.

RESULTS AND DISCUSSION

THE REACTION SCHEME FOR THE PRODUCTION OF PALM OIL RESINS (EPOLA AND POBUA)

Figure 4 shows the synthesis reaction routes for the EPOLA and POBUA productions. Production of EPOLA was began/activated by the ring opening of oxirane oxygen group in the EPOP and at the same time the acrylate group reacted and attached into the opened epoxide ring (Figure 4). This process was known as acrylation. Further reaction was known as isocyanation whereby the hydroxyl group of the EPOLA reacted with the isocyanate group (-NCO) of the TDI before this reaction terminated with the HEA for production of the polyurethane acrylate resin, POBUA.

MONITORING THE EPOLA AND POBUA PRODUCTION IN THE 2 L LAB SCALE AND THE 25 L PILOT PLANT

Based on this study, all results (Figures 5 and 6) followed initial expectations where the acid values and oxirane oxygen contents decreased during the acrylation process. And, the molecular weight and the viscosity values of the

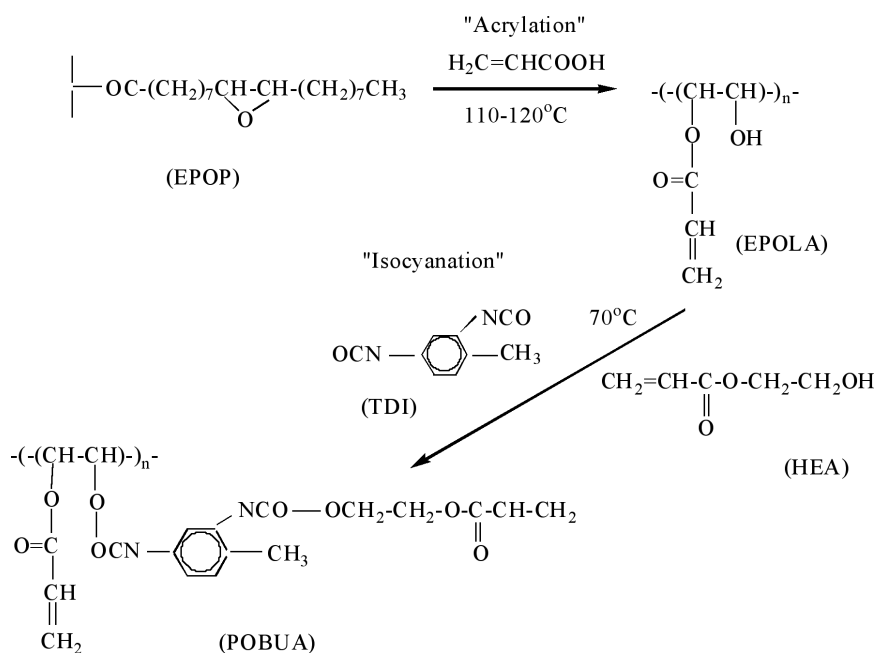


FIGURE 4. Synthesis routes for EPOLA and POBUA production

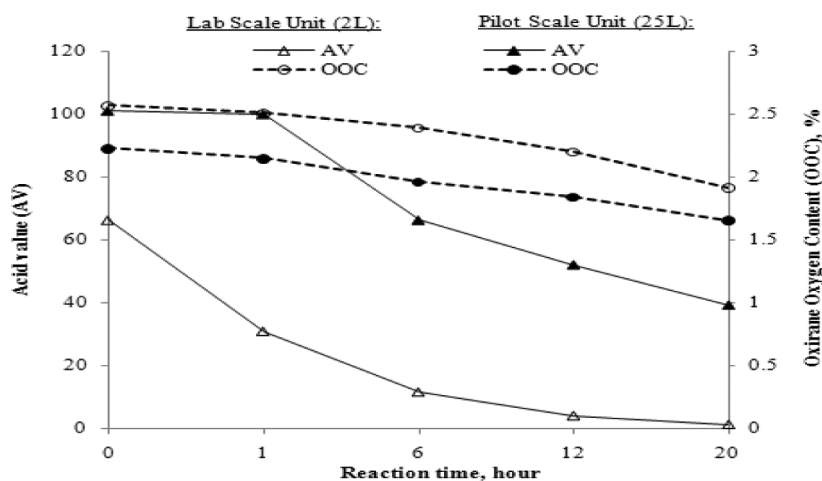


FIGURE 5. The AV and the OCC for EPOLA production

EPOLA increased and became higher after the reaction was completed. The reaction rate seemed to be dependent on the volume of the EPOP. At the end of the production time, the smaller volume of EPOP in the lab scale unit gives faster reaction process as shown by the lowest value of the AV which is approximately 1 compared with the 39 from the pilot plant unit. The fast reaction process could also be due to the bigger surface area of the smaller volume of EPOP (reactants in contact with the reaction surface of the reactor) in the 2 L unit as compared with the lower surface area of the bigger volume of EPOP in the 25 L unit. The MW and the viscosity of the products were increased upon the synthesis time, in accordance to the theory where the reaction was an exothermic which gives off heat to the surrounding i.e. flask or reactor during the synthesis thus promoting

self polymerization which at the final stage produced a big volume of product and thus making the molecular weight and viscosity become higher. The reaction time for both the 2 L and 25 L synthesis system was around 20 h, while their end products volume was around 1.2 kg and 23 kg, respectively. Also, the MW and the viscosity of the products are 3028 dalton and 291 centipoise (cps) for the 1.2 kg of EPOLA and 2410 dalton and 178 cps for the 23 kg of EPOLA.

Furthermore, the palm oil based urethane acrylate resin (POBUA) was also successfully produced using the 2 L and the 25 L reactor synthesis through established synthesis procedures of an isocyanation process (Mahmood et al. 1994) (Figure 4). The study showed that, the viscosities for both the 1 kg and 25 kg reactors were

found to be very slowly decreased upon synthesis time (Figure 7). On the other hand, in general, the product's MW for both the 2 L and 25 L synthesis scale reactor were found to be very slowly increased with time (Figure 7). The reaction time for both the 1 L and 25 L synthesis system were around 3 h, while their end products volume was around 1.1 kg and 22 kg, respectively. The MW and the viscosity of the products are 2201 dalton and 1166 cps for the 1.1 kg of POBUA and 4301 dalton and 1335 cps for the 21 kg of POBUA.

Other important techniques involved in monitoring the production of EPOLA and POBUA are the infrared (IR) spectra analysis. For the EPOLA production, the IR results, i.e. the presence of hydroxyl (-OH) absorption between 3440-3480 cm^{-1} , an absorption of acrylate groups at 1629, 1409, 987 and 814 cm^{-1} and the absence of the epoxide group at 834 cm^{-1} , strongly indicated that the product was an EPOLA (Figure 8). For the POBUA's production, the results, i.e. the appearance of -NH urethane group at 3300 to 3400 cm^{-1} and the absence of the free isocyanate groups between 2260

to 2274 cm^{-1} showed the reaction was completed and the POBUA resins was formed (Figure 8).

UV CURING APPLICATIONS

Figure 9 shows the photocleavage reaction of the Doracure-1173 photoinitiator after exposure to the UV light. This reaction generating the free radicals i.e. a benzoyl radical and a α -hydroxylalkyl radical which were capable of reacting with the acrylate double bond of the monomer and the oligomer/polymer (Decker et al. 2001). In the study for the coating test, it was found that the resins became dry film after passing through the UV lights (Table 1). On the other hand, for the PSA test, the resins became dry adhesive film but still reserved its tacky surface (Table 2). This represents that the formulated resins, which consist of the monomers and the POBUA were polymerized through their reactive radical's interaction after subjecting them to the UV light. The polymer networks generated upon UV curing are sketched in Figure 10.

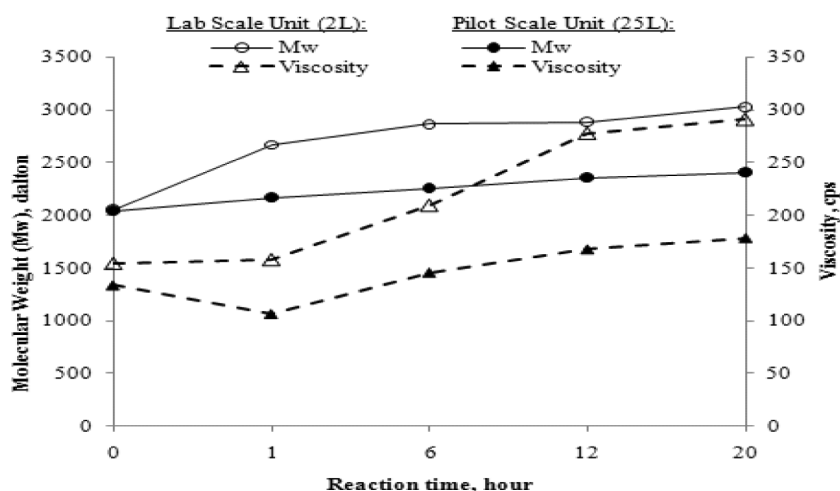


FIGURE 6. The molecular weight and the viscosity for EPOLA production

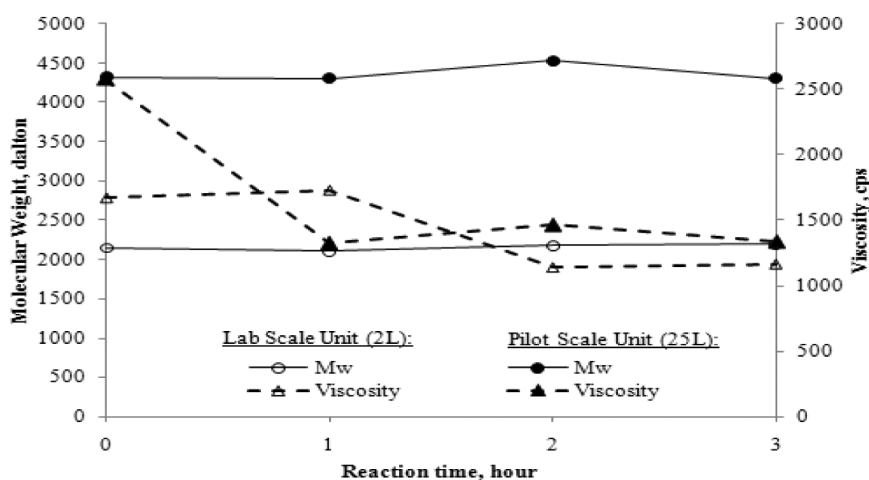


FIGURE 7. The molecular weight and the viscosity for POBUA production

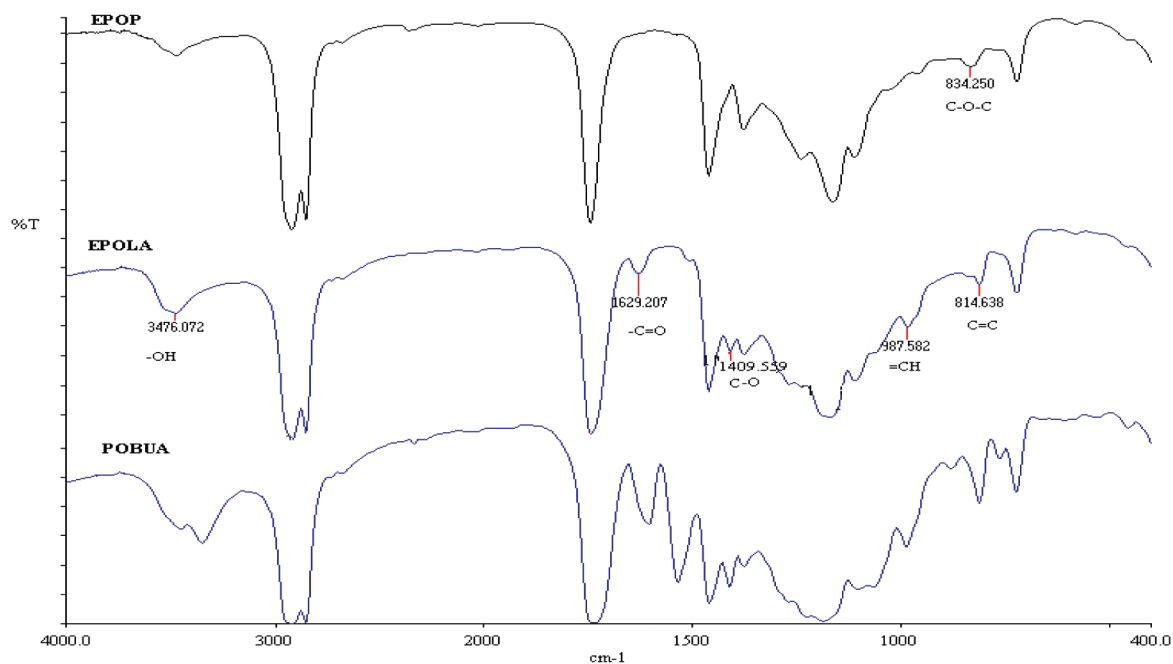


FIGURE 8. FTIR spectra of the EPOP, the EPOLA and the POBUA

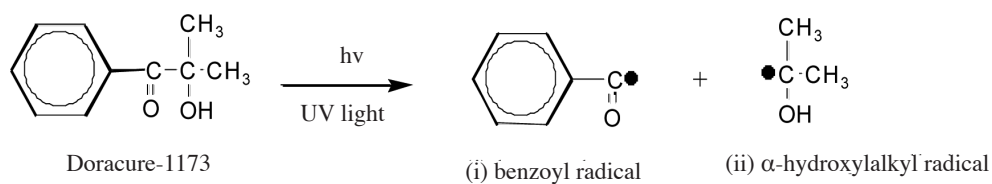


FIGURE 9. Photocleavage reaction of Doracure-1173

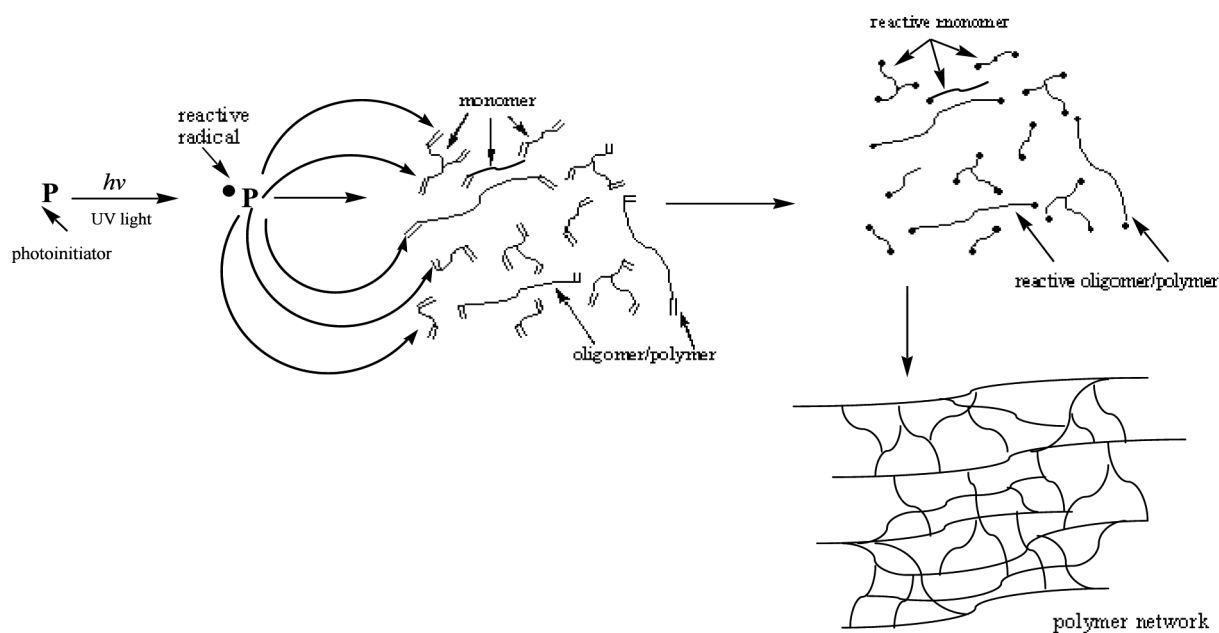


FIGURE 10. The structure model of UV light crosslink polymerization

TABLE 1. Coating performance

Sample formulation	(i) POBUA: 60% (ii) TMPTA: 20% (iii) HDDA: 20%	} Doracure-1173: 3% from total weight of sample
Bath scale	Lab (2 L) Pilot (25 L)	
Hardness	35% 39%	
UV curing performance:	UV Energy, Jcm ⁻²	
Conveyor speed: 10m/min per pass	3.15 3.15	
UV Energy: 0.21 Jcm ⁻² per pass		

TABLE 2. The pressure sensitive adhesives performance

Sample formulation	(i) POBUA : 42.5% (iii) IRR-184 : 17% (v) AA : 5% (ii) M-111 : 25.5% (iv) ISBOA : 10%			
	Doracure-1173: 5% from total weight of sample		Doracure-1173: 10% from total weight of sample	
Bath scale	Lab (2 L)	Pilot (25 L)	Lab (2L)	Pilot (25 L)
Tackiness (gf)	30	36	42	40
UV curing performance:	UV Energy, Jcm ⁻²			
Conveyor speed: 20m/min per pass	0.56	0.84	0.74	1.0
UV Energy: 0.093 Jcm ⁻² per pass				

Furthermore, the quality of this formulated polymer/polyurethane was then tested as coatings and PSA resins. Table 1 shows that, the coatings hardness values of 35% and 39% were found acceptable and presented similar properties for both synthesis systems and thus, these formulations were found suitable to be used in the related industrial applications. As for PSA (Table 2), the formulations must be modified in order to increase their tackiness performances for both systems, most importantly by utilizing IRR-153 acrylic oligomer (Mahmood et al. 2004) instead of IRR-184.

CONCLUSION

The study showed that this process could be utilized for up scaling the conventional 2 L laboratory scale reactor synthesis system to a 25 L pilot scale reactor synthesis system for the production of various palm oils based resins. The 25 L pilot plant served as a safe process, high productivity and less employee requirements (<2 workers per batch) production systems. The results obtained showed that the acrylated resins produced (i.e. the EPOLA and the POBUA) by this two systems has a potential to be used in UV applications.

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