SYNTHESIS OF UV-CURABLE HYPERBRANCHED URETHANE ACRYLATE FROM PALM OIL OLEIC ACID

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ABSTRACT

UV-curable hyperbranched urethane acrylate (HBPUA) from oleic acid of palm oil has been synthesized through a medium aided by p-toluene sulfonic acid as a catalyst. This mixture was then used as the core (HBP) and reacted with palm oil oleic acid to form the hyperbranched polyol (HBP-1). HBPUA was prepared by reacting HBP-1 resin with diisocyanate and hydroxyl-containing acrylate monomer with the presence of 0.1-2 wt% dibutyltin dilaurate as a catalyst. The reaction was confirmed by several analytical data i.e. hydroxyl value (OHV), Fourier Transform infrared (FTIR) spectroscopy, gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) spectroscopy analyses. The HBPUA was easily curable when subjected to ultraviolet (UV) radiation.

ABSTRAK

Uretana akrilat hipercabang (HBPUA) pematangan sinaran ultralembayung (UV) daripada asid oleik minyak sawit telah disintesis melalui tindak balas tiga langkah. Dipentaerithritol ditindakbalaskan dengan 2,2-bis (hidroksimetil) asid propionik dengan bantuan p-toluena asid sulfonik sebagai mangkin. Seterusnya campuran ini digunakan sebagai pengikat (HBP) dan ditindakbalaskan dengan asid oleik bagi menghasilkan poliol hipercabang (HBP-1). HBPUA disediakan melalui tindak balas HBP-1 dengan diisosianat dan monomer akrilat mengandungi hidroksil dengan kehadiran 0.1-2 wt% dibutiltin dilaurat sebagai mangkin. Tindak balas tersebut disahkan oleh beberapa data analisa seperti nilai hidroksil, spektroskopi inframerah Fourier Transform (FTIR), kromatografi penelapan gel (GPC) dan spektroskopi resonans magnet nukleus (NMR). HPBUA tersebut didapati dengan mudah mengalami pematangan apabila didedahkan kepada sinaran ultra-lembayung (UV).

Keywords: *UV radiation, hyperbranched polymers, oleic acid, urethane acrylate*

INTRODUCTION

UV-radiation curable coatings represent a class of coatings with no or little volatile organic compounds, VOCs. Its offer advantages such as instant drying, broad formulating range, reduced energy consumption, low space and low capital requirements for curing equipment compared to thermally cured coatings. The main components of UV curable formulations are oligomer, monomer and photoinitiator. Some of the commonly used acrylic monomers have strong odor, skin and eye inflamations (Holman, 1988). Most of the radiation curable resins available commercially are derived from synthetic raw materials. Only a few known acrylated oils are obtained from indigenous raw materials such as soybean, tung and linseed oils (Hilmi et al., 2003; Mek Zah et al., 1999). In recent years, there has been a trend in using vegetable oils as raw materials in resin production. The long fatty acids chains of vegetables oil impart desirable flexibility and toughness to otherwise brittle resin system such as epoxy, urethane and polyester (Hilmi et al., 2003; Mek Zah et al., 1999). Linear palm oil based urethane acrylate resin has been employed as the prepolymer in the free radical polymerization with encouraging results (Hilmi et al., 2003). However the curing speed and hardness of the cured films are considered low as compared to the commercial resins. The objective of the present work was to synthesize hyperbranched palm oil based urethane acrylate resin that has many advantages. Hyperbranched urethane acrylates exhibit very rapid curing rate and lower shrinkage than linear urethane acrylates. The cured films have excellent hardness, high chemical resistance, good scratch resistance, small amount of residual unsaturation and low extractables (Dzunuzovic et al., 2005; Yates et al., 2004).

Hyperbranced polymers are highly branched macromolecules and contain a large number of end-groups. Because of that, they exhibit properties significantly different from those of their linear homologues. They have high solubility and low viscosity compared to linear homologous. Except for the nature and structure of backbone, their properties are to a large extent dependent upon the number and nature of their terminal groups and they can be modified by chemical modification of terminal group. That leads to the possibility of designing the macromolecule with desired properties for any particular applications (Dzunuzovic et al., 2005; Gang Xu et al. 2004; Kishore et al., 2007; Yates et al., 2004).

Among all classes of acrylic oligomers, urethane acrylates have the highest mechanical strengths and chemicals resistant. Polyurethanes have many useful applications especially in the areas of elastomers, foams, coatings and adhesives. The mechanical properties and morphological structure of polyurethane depend mainly on the polyol structure, molar mass and its functionality and the molecular structure of the diisocyanate compounds (Badri et al., 2001; Yates et al., 2004). This paper presents synthesis and characterization of urethane acrylates based on hyperbranched polyester polyol from palm oil oleic acid.

MATERIALS AND METHODS

Materials

Dipentaerythritol (DPE), 2,2-bis (hydroxymethyl) propionic acid (DMPA), isophorone diisocyanate (IPDI), ρ-toluene sulfonic acid (PTSA) and dibutyltindilaurate (DBTDL) were obtained from Merck-Schuchardt Germany. 2-hydroxyethyl acrylate (2-HEA) and 2-hydroxy-2-methyl-phenyl-1-propanone (Darocur 1173) were obtained from Aldrich chemicals Co., USA and Ciba–geigy, Switzerland respectively. Trimethylolpropane triacrylate (TMPTA) was purchased from UCB Chemicals, Belgium and oleic acid (palm oil based) was obtained from Acid Chem Malaysia. All chemicals were used as received without further purification.

Synthesis of hyperbranched polyester polyol (HBP)

A five-neck round bottom flask equipped with a mechanical stirrer, nitrogen inlet, thermometer and dean-stark apparatus was used as the reactor. Hyperbranched polyester polyol (HBP) was synthesized by melt- polycondensation technique. DPE was used as the core molecule and DMPA as the chain extender. The reflux flask was connected to a condenser and the vacuum pump to withdraw the condensed water from the system. The synthesis procedure followed was derived from established methods described elsewhere in literatures (Badri et al., 2001; Bat et al., 2006; Dzunuzovic et al., 2005; Wyatt et al., 2006; Yates et al., 2004). The reaction was carried out at 140°C under nitrogen atmosphere in the presence of PTSA as the catalyst which was 0.4% of DMPA. The reaction was monitored periodically by checking the acid value and was stopped when the acid value reached below 10 mg KOH/g. The HBP was then reacted with the palm oil oleic acids (75%) at 190 -220°C. The HBP modified with oleic acid only is designated as hyperbranched resin-1 (HBP-1). The progress of the reaction was monitored by the determination of the hydroxyl values (OHV).

Synthesis of hyperbranched urethane acrylates (HBPUA)

The acrylate terminated urethane hyperbranched prepolymers/resins were prepared by carrying out the reaction in a 250 ml five necked flask equipped with a thermometer, dropping funnel, mechanical stirrer and nitrogen gas inlet. Required amount of IPDI with NCO: OH ratio of 9:1 was reacted with HBP-1 at 40-75 °C for 3 hours with the presence of 0.1-2.0% DBTDL as the catalyst. The NCO: OH ratio of 9:1 was selected based on our earlier work (Mohd Hilmi et al., 2003), which produces NCO terminated hyperbranched polyurethane (PU) prepolymers from HBP-1. 2-HEA was dropped into the flask with the same ratio of NCO. The synthesis procedure followed was derived from established methods described elsewhere in literatures suchs as by Holman (1988) and Lyman (1960). Dioxane was added to the flask in order to control the viscosity. The progress of the reaction was monitored by observing the consumption or disappearance of –N=C=O and –OH group at approximately 2250-2270 cm^{-1} and 3400-3500 cm^{-1} respectively (Mohd Hilmi et al., 2003; Silverstein et al., 1991).

UV curing of the resin

The prepolymers (HBPUA) were dissolved in acrylate monomers to reduce the viscosity and Darocur-1173 was used as a photoinitiator. The coating formulations were prepared at least one day prior to curing and were wrapped in a black paper. The formulated resins were coated on to glass plates using a manual bar coater (RDS 30, Japan), and cured using a 20 cm wide IST UV machine with the conditions of 8A current and 4 m/min conveyor speed giving energy per pass of approximately 0.18 J/cm^2.

Characterization of the resin

FTIR spectroscopy analysis was carried out using a spectrometer model Perkin Elmer Spectrum 2000. A drop of each sample was spread into a thin layer on the NaCl plate. The samples were scanned between 4000- 400 cm-^{1} wave numbers. The molecular weights (M_w) distributions were determined using Polymer Laboratories GPC, Model PL- GPC 50 plus and the viscosity of the synthesized resins were measured using a Brookfield Viscometer Model RVTDV-IICP. The ^{13}C-NMR spectra were recorded with a JEOLECP 400 MHz NMR using dimethylsulfoxide (DMSO-d_6) as a solvent. Standard method ASTM D4274-99 and MPOB Test Method c2.7: 2004 were used to determine hydroxyl values (OHV) and the acid values (AV) of the polyol.

Characterization of the cured resins

Determination of pendulum hardness

Labotron-BYK pendulum hardness tester was used to measure the Koenig pendulum hardness of the cured film in accordance with DIN 53157. It is the time taken for the pendulum to reduce its angle of swing from 6° to 3°. The films used for this method were 50 µm thick on a glass substrate. The result is expressed as percentage of pendulum hardness given by:

$$\text{Pendulum hardness (\%)} = \frac{\text{[(No. of oscillations for damping from } 6^{o} \text{ to } 3^{o} \text{ for sample)}}{\text{(No. of oscillations for damping from } 6^{o} \text{ to } 3^{o} \text{ for standard glass)]}} \times 100$$

Determination of gel contents of cured films

Film of certain quantity was weighed (W_1) in a SUS 304 stainless steel wire-mesh filter size #100 and then placed in a soxhlet extractor. Soxhlet extraction was carried out for at least 24 hours using acetone as a solvent. The residue was then taken out, vacuum dried and weighed until it approached a constant weight (W_2). The percentages of gels are calculated by the following equation:

$$\text{Gel content (\%)} = \frac{W2}{W1} \times 100\%$$

where W_1 mass of sample before extraction, g

W_2 mass of sample after extraction, g

RESULTS AND DISCUSSIONS

Synthesized of HBP Resin

Figure 1 illustrates the effect of reaction temperatures at 130-140°C and 140-150°C for 1 hour and 2 hours reaction times on the formation of HBP. At reaction temperature of 130-140°C, a broad absorption band at 3200-3600 cm^{-1} was observed which is a characteristic of hydroxyl groups of polyester polyol. At higher reaction temperature (140-150°C) the rate of hydroxylation and esterification decreased, where the OH peaks at this temperature were small and weak as compared to the more stronger and broader peaks resulted from the reaction temperature of 130-140°C. Two other absorption bands at 2943 and 2872 cm^{-1} indicated the presence of two types of - CH_x- groups as shown in Figure 1 as compared to Figure 2. An aliphatic methylene group, -CH_2- is identified by the absorption band at 1464 cm^{-1}. On the other hand, an absorption peak detected at 1371 cm^{-1} is an indication for aliphatic methyl group, (-CH_3-). The strong sharp peak at 1717 cm^{-1} corresponds to C=O stretching of the ester (Silverstein et al., 1991). A new absorption band is observed at 1240 cm^{-1}, which is another peak associated to the presence of ester (Bat et al., 2006).

Standard method ASTM D4274-99 was used to determine the hydroxyl values (OHV). Table 1 shows that at reaction temperature of 130-140 °C and reaction time of 1 hour the HBP produced has the highest OHV. Higher OHV might be able to give an indication that the reaction conversion is high due to high degree of hydroxylation and esterification. The higher the OHV, the higher number of OH group as the terminal group has been formed. Thus, optimum temperature and reaction time based on the targeted functional group formed in the HBP is 130-140°C and 1 hour of reaction time.

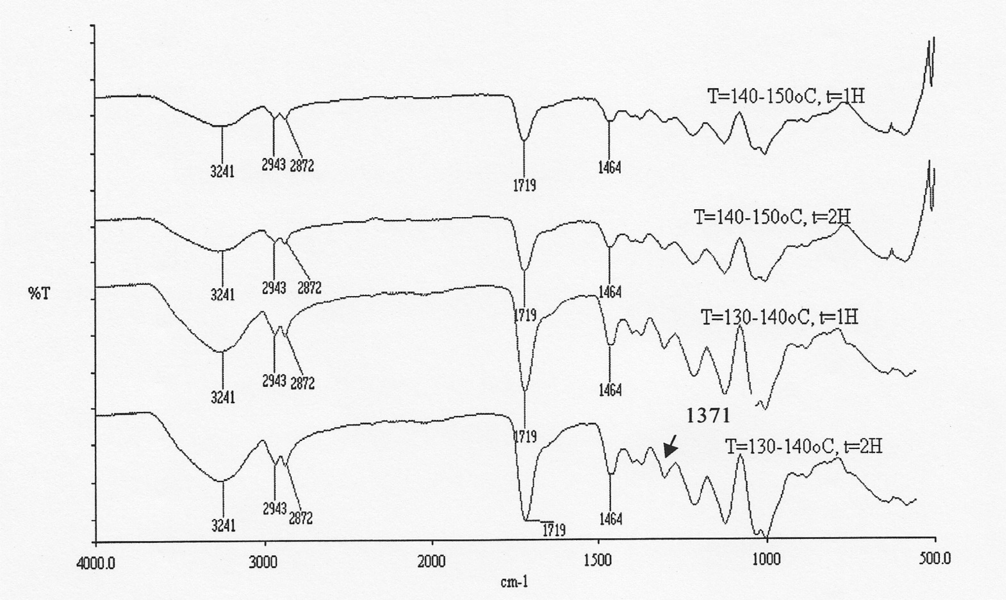

Figure 1 Effect of reaction temperature on the preparation of HBP indicated by the -OH stretching (3200- 3640 cm^{-1}) in the FTIR spectrum.

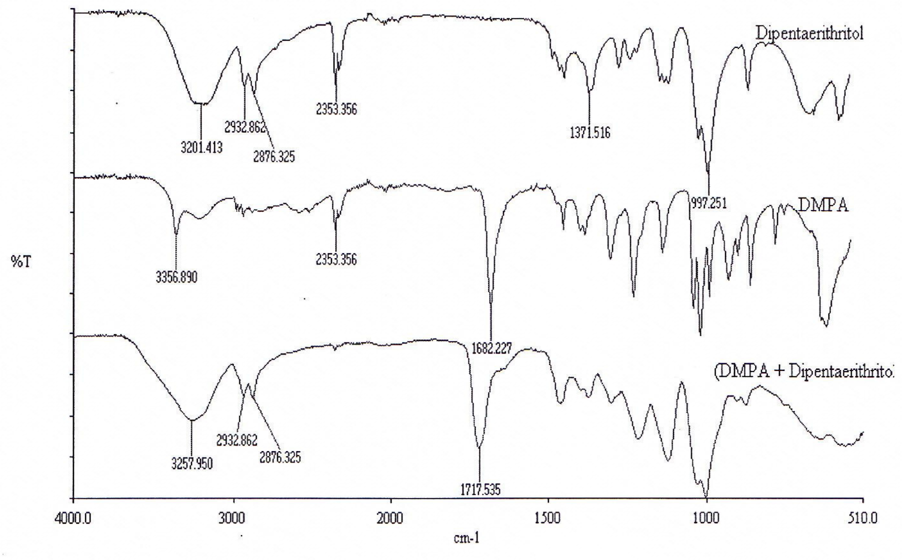

Figure 2 FTIR spectrum of dipentaerithritol, dimethylol propionic acid and HBP (T=130-140^{o}C, t=1 hour) as references.

Table 1: Effect of the reaction time and temperature to the hydroxyl value (OHV) of the HBP

Reaction time, hour	OHV, mg KOH/g	
	130-140 °C	140-150 °C
1	1255	1216
2	1172	1207

Figure 3 shows the ^{13}C-NMR spectrum of HBP. The absorption peak at δ174.75 ppm is assigned to the chemical shift of the carbon atoms in ester carbonyl (-C-$\underline{C}$O-O -). The presence of δ70.9 ppm peak is due to carbon atoms in methylene group attached to an oxygen and carbon atom (-C-$\underline{C}H_2$-O -). The presence of δ 65.43 ppm peak is assigned to the chemical shift of the carbon atoms in methylene group attached to hydroxyl group (-$\underline{C}H_2$-OH). The peak at δ39.5 ppm is assigned to carbon atoms attached to four carbon atoms (-C- $\underline{C}$-C-). These results confirmed the formation of hyperbranched polyester polyol resin (Dzunuzovic et al., 2005; Wyatt et al., 2006).

Synthesized of HBP-1 Resin

Figure 4 is the FTIR spectrum that illustrates the effect of reaction temperatures in the preparation of HBP-1. At the reaction temperature of 210-220 °C, a broad absorption band at 3200-3600 cm^{-1} is a characteristic of hydroxyl groups of polyester polyol was observed. Significant observation was made in identifying peak at 2936 cm^{-1} and 2843 cm^{-1} (-CH_2 -); 1744 cm^{-1} (-C=O-); 1468 cm^{-1} (-CH_2-, aliphatic) and 1240 cm^{-1} (-COO-, ester) to confirm the formation of HBP-1 resin.

Table 2 is data obtained from gel permeation chromatography analysis and determination of the OHV. The results show that at reaction temperature of 210-220 °C, HBP-1 resin has the highest hydroxyl value with high M_w and low viscosity. The higher the temperature of the reaction, the higher degree of hydroxylation and esterification. Low polydispersity index obtained justified the findings. The viscosity of hyperbranched polymers depends on the molar mass and intermolecular interactions, which then depend on the number and the nature of the end-groups (Dzunuzovic et al., 2005). One of the most interesting properties of hyperbranched polymers is their high M_w and low viscosity characteristic in comparison to linear analog (Yates et al., 2004). Therefore, the optimum temperature and reaction time for not only a cost-effective method but also the attractive chemical properties is 210-220°C.

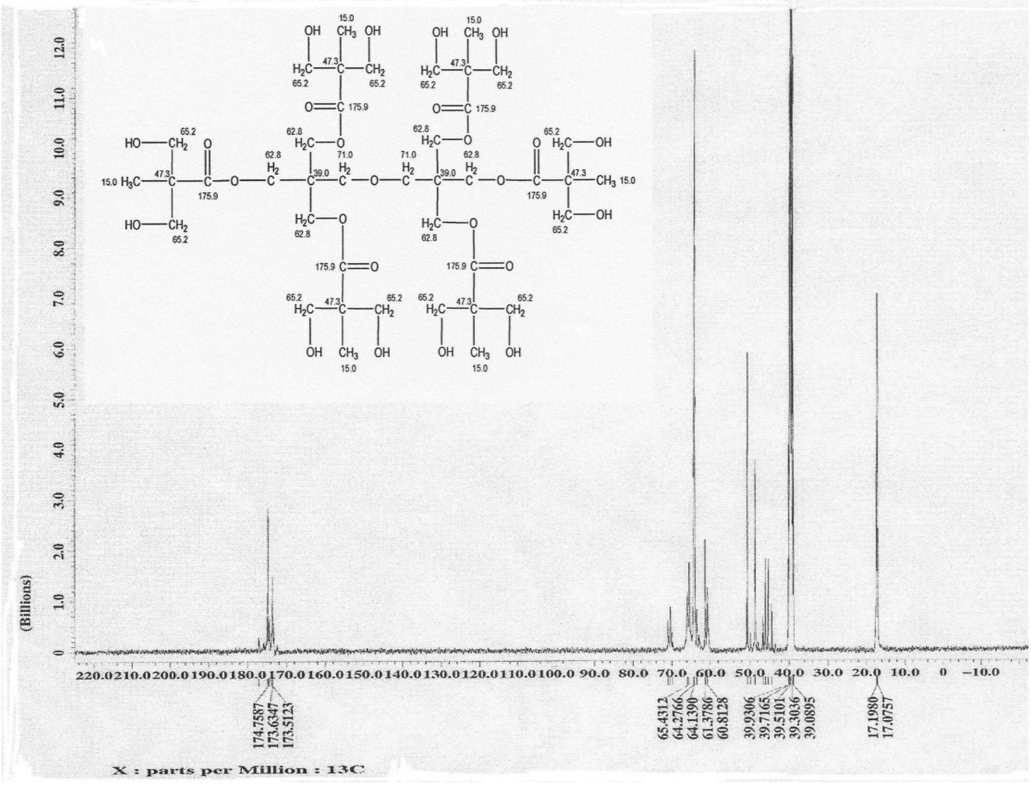

Figure 3 ^{13}C-NMR spectrum of HBP

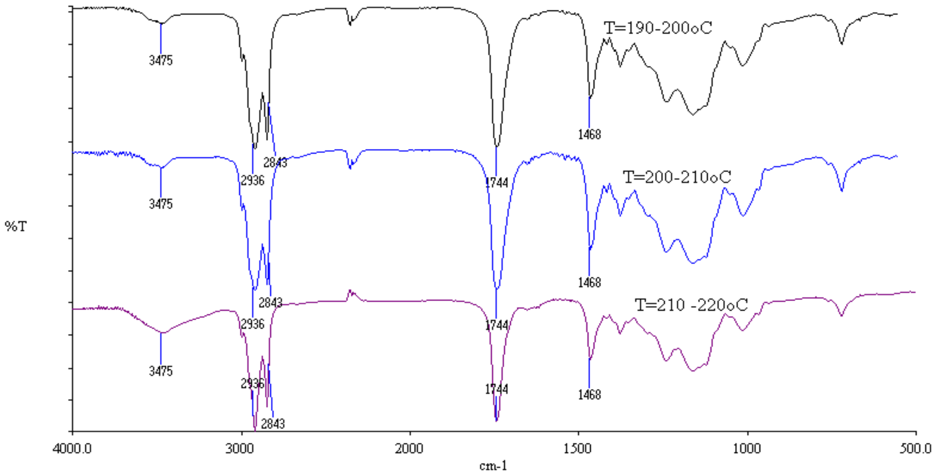

Figure 4 FTIR spectrum of HBP-1 at various reaction temperatures with reaction time, t of 10 hours.

Table 2 Effect of the reaction temperatures with reaction time, t of 10 hours on the M_w, viscosities and OHV of HBP-1 resin.

Reaction temperatures, °C	M_w	M_n	Polydispersity Index, PI= M_w/M_n	Viscosities at 25°C, mPa/s	OHV, mg KOH/g
190-200	20,997	5179	4.054	1615	350
200-210	24,591	8554	2.875	1377	610
210-220	40,755	13,692	2.976	680	700

Synthesis of hyperbranched urethane acrylates (HBPUA) resin

FTIR spectra of HPUA sample is shown in Figure 5. The absorption peaks at both 1562 cm^{-1} and 3300-3360 cm^{-1} indicated the -CN stretching vibrations and –NH- bending, - of –C-N-H group and a hydrogen bonded, secondary amine –NH stretching vibrations of urethane moiety (Silverstein et al., 1991). Peaks at 1635 and 810 cm^{-1} representing double bonds of acrylate groups (Hussin et al., 1990). This suggests that, both acrylate and amine groups have been successfully attached to HBP-1 resin in HBPUA samples.

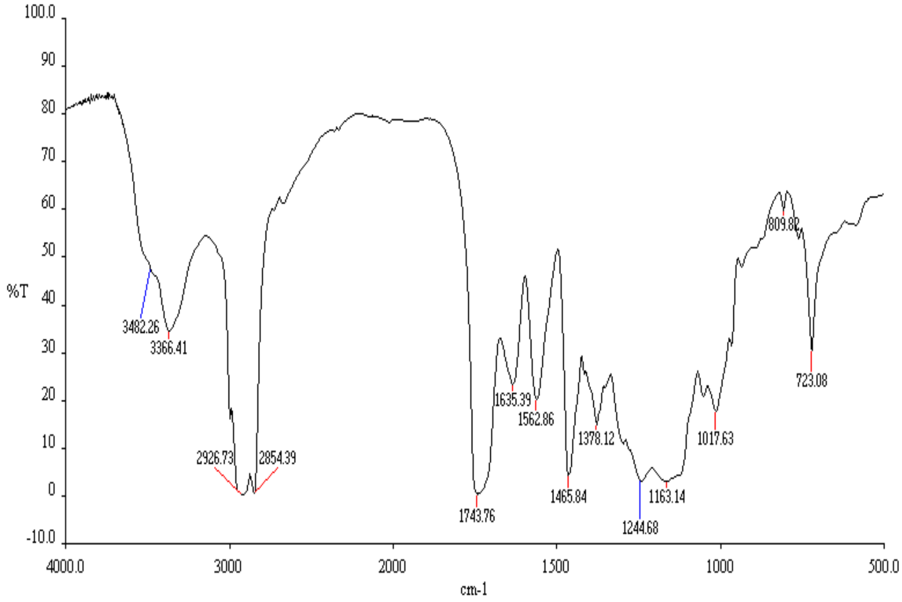

Figure 5: FTIR spectra of HPPUA

Characterization of the cured resins

UV cured film was obtained from formulations consisting of 40-70% HBPUA, 20-30 wt% TMPTA, other required mono/diacrylate monomers and 3-5 wt% Irgacure -1173 or other photoinitiators often used as synergists. The films require 0.18 - 0.54 J/cm^2 energy of the UV radiation in order to be cured and the gel content up to 85% with 40 - 60% pendulum hardness.

CONCLUSIONS

A hyperbranched polyurethane acrylate prepolymers/resins can be synthesized from palm oil oleic acid. The hyperbranching acrylate structures offer an advantage for various applications for coating industries such as wood coatings, printing inks, adhesives (PSA) etc. UV cured samples exhibited good cross-linking density or gel content with high pendulum hardness. The double bonds from unsaturated fatty acids contribute to curing with extra cross-linking by an oxidative mechanism.

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