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# Synthesis and Characterization of Acrylated Polyetheramide Based Coatings from *Albizia benth* Seed Oil

*C.O. Akintayo and E.T. Akintayo*

Depatment of Chemistry, University of Ado-Ekiti, P.M.B. 5663, Ado-Ekiti Ekiti-State, Nigeria

**Abstract:** Polyetheramide resin was synthesized through the condensation polymerization of N,N-bis(3-hydroxyl ethyl) Albizia benth oil fatty amide with bisphenol-A. The polyetheramide was modified by acrylation through the reaction of hydroxyl group on the polyetheramide with acryloyl chloride. Structural elucidation of these samples was carried out by FT-IR, $^{1}H$ NMR and $^{13}C$- NMR spectroscopic techniques. The physico-chemical /mechanical characteristics, chemical resistance as well as curing behaiviour of the samples were evaluated. Acrylation led to curing at lower temperature, (112°C - 120°C for acrylated Albizia benth oil polyetheramide as against 210°C - 250°C for the unmodified Albizia benth oil polyetheramide), improved physico-mechanical properties as well as improved resistance to chemicals.

**Key words:** Albizia benth oil · Polyetheramide · Acrylation · Coatings

## INTRODUCTION

Traditionally, triglyceride were used for the synthesis of value added polymeric resins which provide an opportunity to utilize ecofriendly and sustainable resources. Such oil based polymers are enjoying increasing production now especially as the petroleum based monomers decline because of spiraling prices and high rate of depletion of petroleum stock.

Vegetable oils such as linseed, pongamia, soybean and rubber seed have been used in the preparation of different low molecular weight polymers varying from alkyd [1], polyepoxides [2], polyesteramides [3-6] to polyurethanes [6-8]. Some of these oils are medicinal while others are edible. Due to their competitive use the oils are scarce and expensive. The use of renewable but non edible oils provide an opportunity to make value added products like polymeric resin for the paint and coating industry.

*Albizia benth* belong to the family minnosacea. It is widely planted and has reasonable oil yield, *ca* 40%. The oil is only used for curing leprosy. The use of the oil had been investigated in the preparation of chemically modified alkyd resin [9, 10]. In furtherance of our work on the industrial application of the *Albizia benth* seed oil, we are interested in preparing a new polymeric resin "Acrylated polyetheramide" from *Albizia benth* oil. Acrylic resins are used in the radiation curing industry as component in coatings and inks [11]. Coatings formed from it are highly flexible due to the flexibility of the aliphatic acrylic backbone [12-15] and they have improved adhesion,drying time and scratch hardness with good pigmemt wetting properties [16].

This work is aimed at using *Albizia benth* seed oil for the synthesis of a new class of ecofriendly industrial product, acrylated polyetheramides. Such resin prepared from other similar oils have been shown to have better physicomechanical/ chemical and end use properties than conventional alkyds [4-7].

## MATERIALS AND METHODS

**Collection of Samples:** Albizia benth seeds were collected from nearby farms and bushes in Ado-Ekiti, Nigeria. The seeds were milled on a C&N Junior laboratory mill size 5 (Christy and Norris Limited Engineers, Chemlsford, England).

**Extraction and Refining of Oil:** Albizia benth oil (ABO) were extracted using n-hexane in a Soxhlet apparatus and solvent removed on a rotavapour at 50°C. The crude oil were refined by agitating with 18M NaOH (1:30g/g) for 15min. The resultant mixture was then heated to 75 - 80°C to break the soap stock and neutral oil separated by centrifugation.

**Corresponding Author:** C.O. Akintayo, Department of Chemistry, University of Ado-Ekiti, P.M.B. 5663, Ado-Ekiti, Ekiti-State, Nigeria. Tel: +2348030659661, E-mail: temitopeakintayo@yahoo.com.

**Synthesis of Albizia Benth Oil Fatty Amide:** 0.32 mol of diethanolamine and 0.007mol of sodium methoxide were mixed in a four necked round bottom flask fitted with an electrical stirrer, thermometer and condenser and contents heated to 110°C while stirring. ABO (0.1mol) was then added dropwisely over a period of 60min. Progress of the reaction was monitored by TLC. On completion the reaction product was dissolved in diethyl ether, washed with 15% NaCl and dried over $Na_2SO_4$. The ethereal layer was filtered and evaporated in a vacuum evaporator to obtain the bis(2-hydroxyethyl) Albizia benth oil fatty amide (HEABOA).

**Synthesis of Albizia Benth Oil Polyetheramide (ABOPEtA):** Bis(2-hydroxyethyl) Albizia benth fatty amide (HEABOA) was first prepared as described above. Now 0.10mol of HEABOA and 0.07mol bisphenol were dissolved in 100ml of a mixture of xylene and butanone (1:1v/v) as solvent with dil.$H_2SO_4$ as a catalyst in a four necked round bottom flask equipped with Dean stark, $N_2$ inlet, thermometer and stirrer. The reaction mixture was heated to 180°C and allowed to reflux. Progress of reaction was monitored by TLC and hydroxyl value.

**Synthesis of Acrylated Albizia Benth Oil Polyetheramide:** 12.35g of Albizia benth oil polyetheramide (ABOPEtA), 4.72ml of triethethylamine and 14.06ml of tetrahydrofuran were charged into a 250ml round bottom flask equipped with a magnetic stirrer and reflux condenser. The reaction mixture was placed under nitrogen and cooled in an ice-bath. Then 14ml of acryloyl chloride in 40ml of tetrahydrofuran was added dropwisely over 1h keeping the ice around the flask. After complete addition of the acryloyl chloride, the reaction was allowed to continue at room temperature for 24h. The solution was filtered to remove the triethylamine chloride formed in the reaction. The filterate was precipitated in large volume of hexane and the precipitate re-solubilised in $CH_2Cl_2$ and solvent was removed over rotavapour.

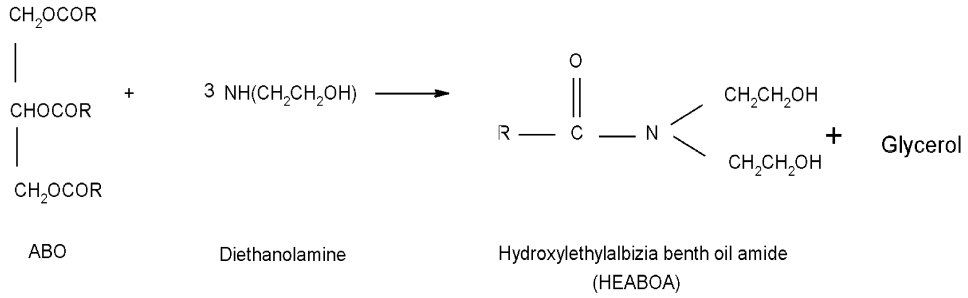
**Characterisation:** Samples were characterised by spectroscopic techniques such as FT-IR, $^1$H NMR and $^{13}$C NMR. FTIR spectra were recorded on Tensor 27 FTIR-H1026302 (Bruker Optik, GmBH, Germany) and $^1$H and $^{13}$C - NMR spectra obtained on a Bruker Avance - 400 (Bruker Instruments, Inc. Karlsruhe, Germany) Fourier transform spectrometer operating at 400.6 MHz. The gated decoupling pulse sequence was used with the following parameters, number of scans, 256; acquisition time, 1.366s; pulse width 10.3µs. Free induction decay FID was transformed and zero filled to 300K to give digital resolution of 2Hz/point. Thermal analysis was carried out by DSC 822$^e$ (Mettler Toledo GmBH, Giessen, Germany). Hydroxyl value (HV), Iodine value (IV), Saponification value (SV) and Refractive Index (RI) were determined according to standard procedures [17].

**Evaluation of Physico-Mechanical Characteristics:** Samples were thinned in toluene to a brushable consistency. The solutions prepared were applied by brush on clean mild steel panels of 15cmx 15cm for evaluating drying time, tin panels of the size 15x15cm for flexibility and adhesion, scratch hardness and impact resistance and glass panels of the size 15x15cm for water, alkali and solvent resistance. All coated panels were air dried for 48hr and sides protected by dipping them into molten wax before carrying out the above tests. The film characteristics were determined according to Indian standard specifications [18].

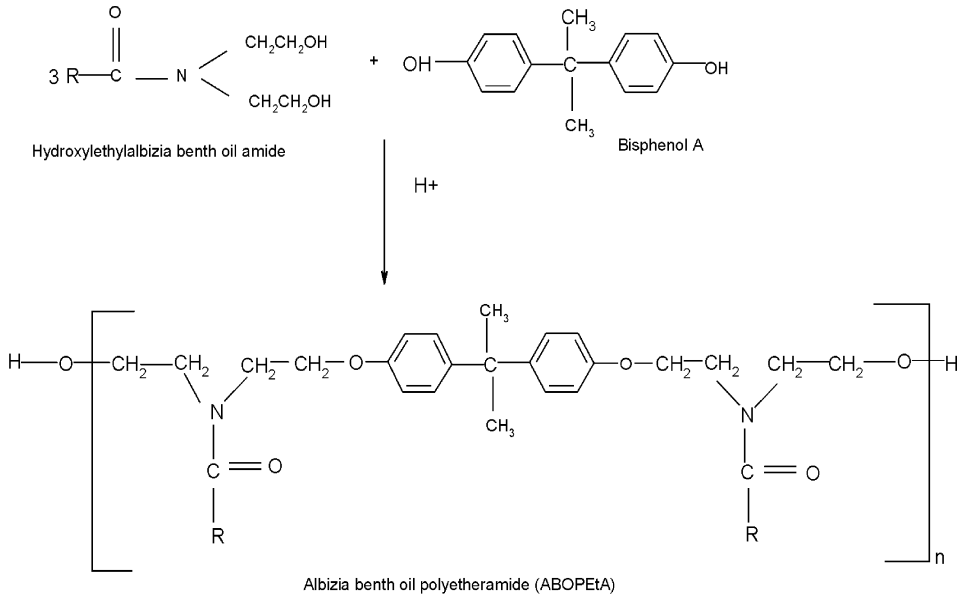
## RESULTS AND DISCUSSION

Reaction schemes 1, 2 and 3 illustrate the synthesis of hydroxylethyl *Albizia benth* oil amide (HEABOA), *Albizia benth* oil polyetheramide (ABOPEtA) and acrylated *Albizia benth* oil polyetheramide (AcrABOPEtA) respectively. The proposed reaction schemes for the ABOPEtA and AcrABOPEtA were confirmed by the presence of characteristic IR, $^1$H NMR and $^{13}$C NMR as shown in Figure 1-5.

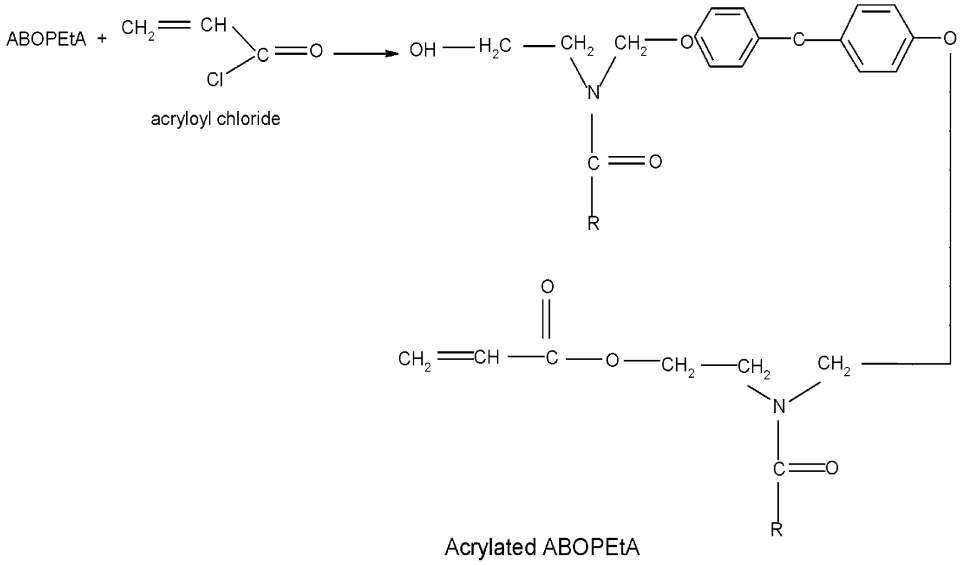
**Spectral Analysis of Acrylated Polyetheramides:** FT-IR spectra of ABOPEtA show characteristic bands for aryl alkyl ether (-C-O-C-) assymetrical stretching at 1247 - 1177cm$^{-1}$ and symetrical stretching at 1081cm$^{-1}$. A broad band appear at 3308cm$^{-1}$which is characteristic of alcoholic OH group. -$CH_2$ assymetric and symmetric stretching peaks appear at 2925 and 2854cm$^{-1}$ while the -$CH_2$ bending appears at 1464cm$^{-1}$. Band at 1612cm$^{-1}$ represent the stretching vibration of C=O of amide. The FT-IR spectra of the acrylated ABOPEtA showed that on acrylation, the characteristic hydroxyl group peak at 3308cm$^{-1}$ dissapeared. However presence of acrylate groups in the AcrABOPEtA gave rise to peaks 1638cm$^{-1}$ (C=C stretching vibrations), 1453 and 1407cm-1 (=$CH_2$ deformation), 1732cm$^{-1}$ (C=O stretching vibrations).




Scheme 1: Synthesis of HEABOA




Scheme 2: Synthesis of ABOPEtA




Scheme 3: Synrhesis of acrylated Albizia benth oil polyetheramide

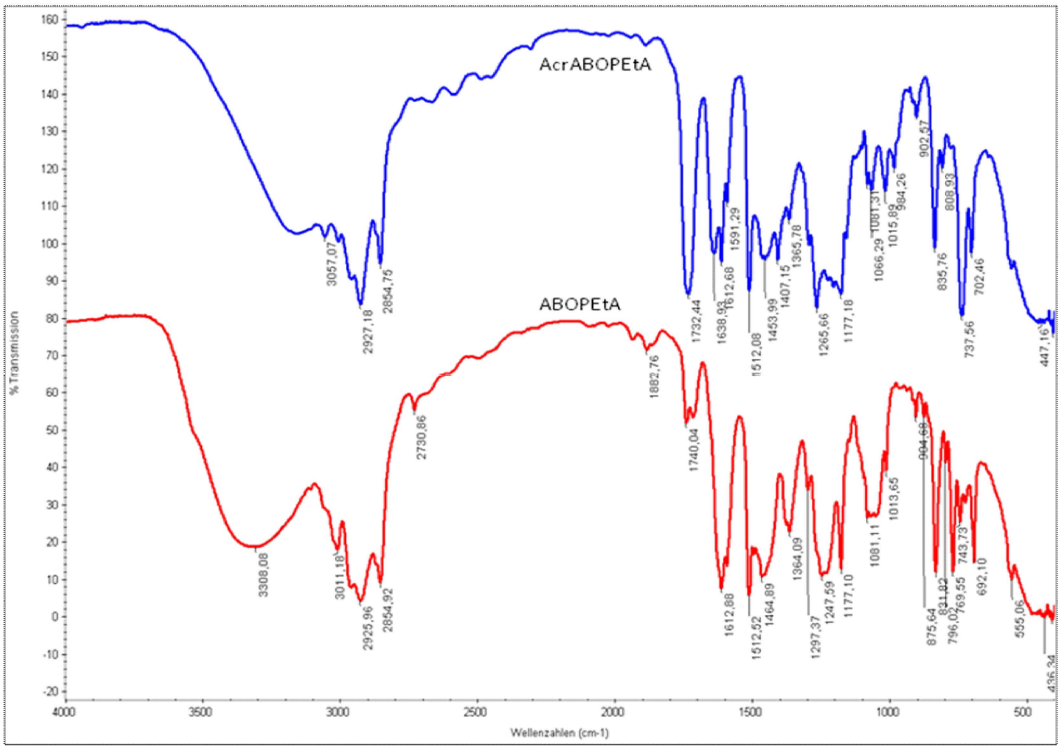



Fig. 1: FT-IR of Albizia benth oil polyetheramide (ABOPEtA) and acrylated Albizia benth oil polyetheramide (AcrABOPEtA).

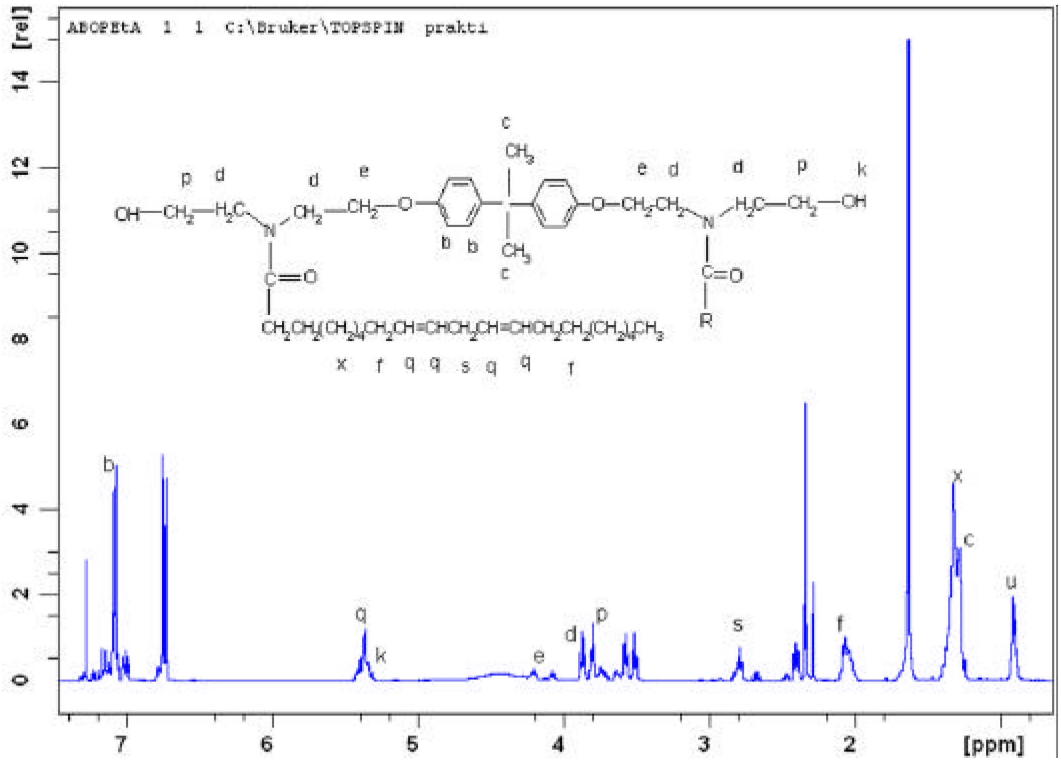



Fig. 2: $^{1}$H NMR of ABOPEtA

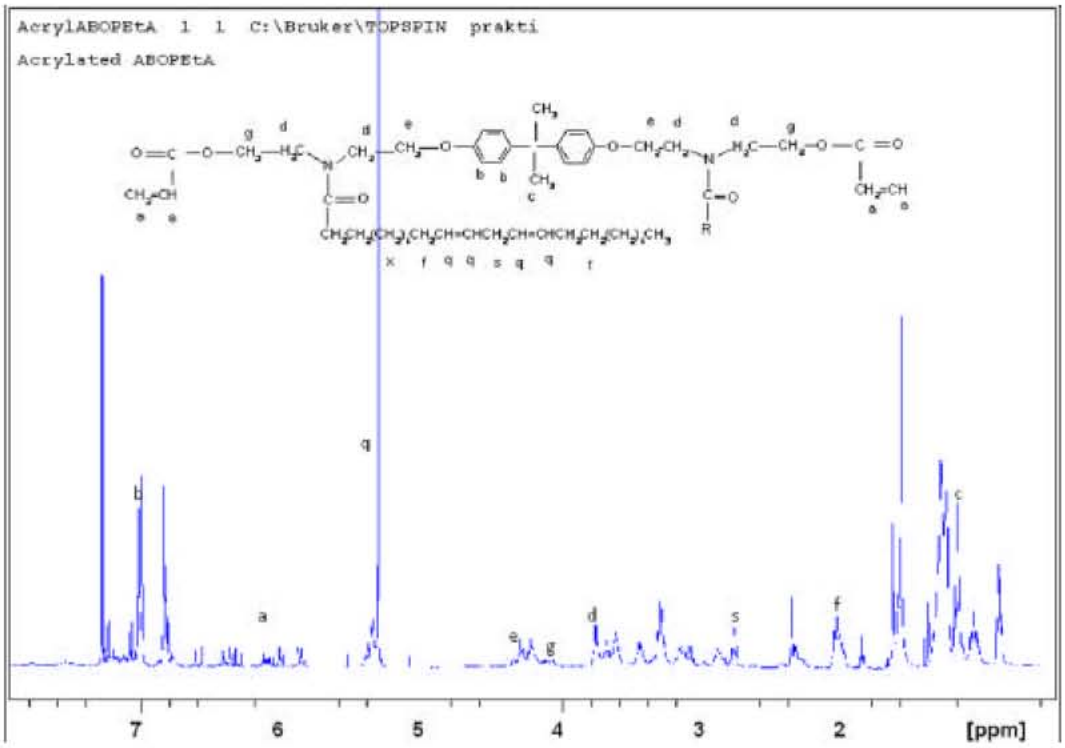



Fig. 3: $^{1}$H NMR of AcrABOPEtA

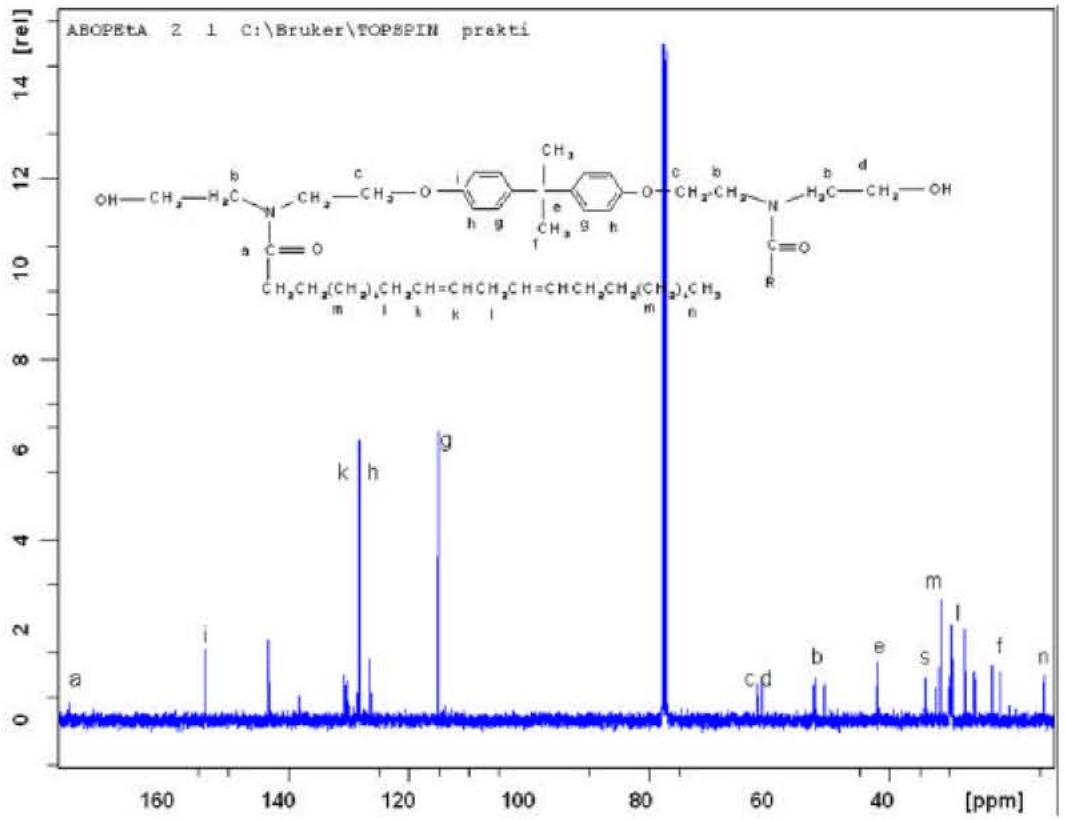



Fig. 4: $^{13}$C NMR of ABOPEtA

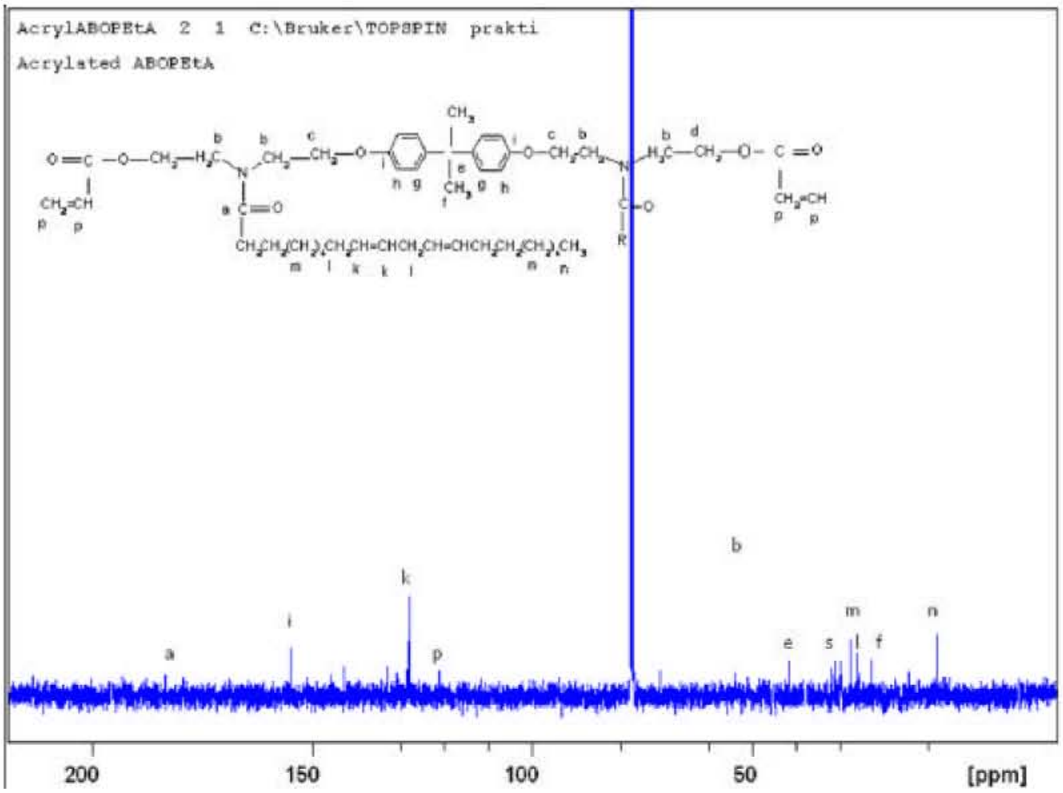



Fig. 5: $^{13}C$ NMR of AcrABOPEtA

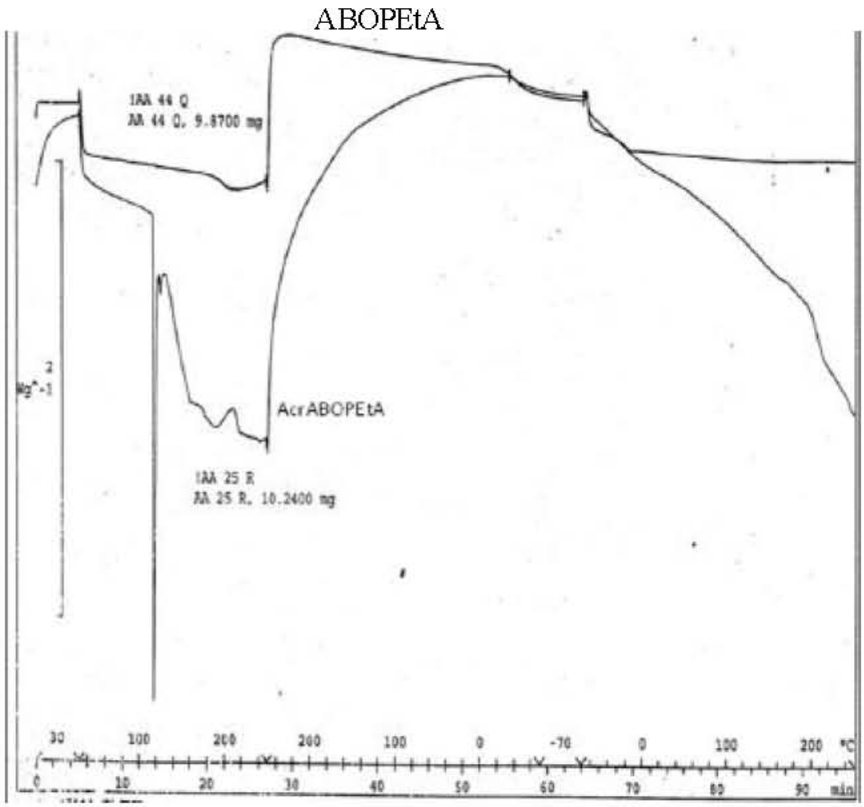



Fig. 6: DSC thermograms of ABOPEtA and AcrABOPEtA

Table 1: Physico - chemical properties of ABO, HEABOA, ABOPEtA and AcrABOPEtA

| | ABO | HEABOA | ABOPEtA | AcrABOPEtA |
|---|---|---|---|---|
| Acid Value (mgKOH/ g) | 8.12 | - | - | - |
| Hydroxyl Value (mgKOH/g) | 0.5 | 10.52 | 5.25 | 0.25 |
| Iodine Value (mg $I_2$/g) | 104.5 | 85.5 | 40.5 | 108.45 |
| Esterification Value | 182 | 165 | 162 | 315 |
| Specific Gravity | 0.915 | 0.923 | 0.935 | 0.945 |
| Refractive Index | 1.4725 | 1.4850 | 1.5225 | 1.5350 |

Table 2: Physico-mechanical properties of ABOPEtA and AcrABOPEtA

| | ABOPEtA | AcrABOPEtA |
|---|---|---|
| Surface dry (h) | Non - drying | 3h |
| Hard dry (h) | Non - drying | 14h |
| Impact Resistance (1 Kg load) | Fail | Pass |
| Flexibility and Adhesion (1/8inch mandrel) | Fail | Pass |
| Scratch hardness (Pencil Brand) | 6B | 2H |

Table 3: Chemical Resistance performance of ABOPEtA and AcrABOPEtA

| | ABOPEtA | AcrABOPEtA |
|---|---|---|
| Water Resistance | e | b |
| Xylene Resistance | f | b |
| NaOH (2%) Resistance | e | c |
| Hcl (2%) Resistance | e | d |

In the $^1$H NMR spectra of ABOPEtA, the protons of $CH_3$ attached to the Bisphenol-A appear at $\partial$ 1.28 ppm while aromatic protons appear at $\partial$= 7.17 - 6.99 ppm. The proton for -$CH_2$ of HEABOA forming ether linkages with Bisphenol- A appear at $\partial$= 4.20 -4.08ppm. The terminal -$CH_3$ and internal -$CH_2$ of the fatty amide chain appear at $\partial$= 0.91 and $\partial$= 1.32ppm respectively. The fatty acid double bond appear at $\partial$= 5.36 - 5.38ppm. In the $^1$H NMR spectra of AcrABOPEtA, the characteristic peaks for ABOPEtA are observed in addition to the acrylate vinyl protons which appear between $\partial$= 6.57-6.84ppm.

The $^{13}$C of ABOPEtA reveals peaks of -$CH_3$ (fatty amide chain) and -$CH_3$ of bisphenol-A at $\partial$ = 14.23 and 22.5 ppm respectively. The internal -$CH_2$ of fatty amide appear at $\partial$ = 30.11 -29.58 ppm while -$CH_2$ attached to amide carbonyl occur at $\partial$ = 128 - 126 and 115ppm. Peak at 130 - 126ppm is assigned to unsaturation of fatty amide chain of fatty acid. On acrylation of ABOPEtA, the acrylate carbon appear at $\partial$ = 122ppm.

**Differential Scanning Calorimetric Analysis:** The DSC thermograms of ABOPE$_t$A and AcrABOPE$_t$A is presented in Fig. 6. curing of ABOPE$_t$A starts at 210°C and ends at 250°C. However for AcrABOPEtA, curing starts at a much lower temperature, 112°C and extends to 120°C. This can be rationalised as being due to increase in molecular weight of the ABOPEtA on acrylation. With increase in molecular weight, fewer crosslinks are required to form coherent films. Hence the AcrABOPE$_t$A are able to achieve adequate curing rates when compared to the ordinary ABOPEtA. A small but broad exotherm is noticeable from 196°C - 216°C in the AcrABOPEtA and this may be attributed to the decomposition of the resin.

**Physico-Chemical Properties:** Physicochemical charateristics of the ABOPEtA and AcrABOPEtA are presented in Table 1. There is a decrease in hydroxyl value (HV) in the order HEABOA > ABOPEtA > AcrABOPEtA. The decrease in HV on going from HEABOA to ABOPEtA may be explained to be due to the reaction of some hydroxyl functional groups of HEABOA with Bisphenol-A to form ABOPEtA. A further decrease of HV on going from ABOPEtA to AcrABOPEtA may be explained to be due to the reaction of the hydroxyl group in ABOPEtA with acryloyl chloride to form AcrABOPEtA. This confirms that the acrylation took place by esterification reaction and not by grafting on to the unsaturation sites in the fatty acid chain. This observation was further confirmed by the increase in esterification value on going from ABOPEtA to AcrABOPEtA. The iodine value (IV) of ABO was 104. This decreased to 85.5 and 40.5 in HEABOA and ABOPEtA respectively. These decrease may be explained to be due to increase in molar mass on going from ABO to HEABOA and then ABOPEtA. However the IV of AcrABOPEtA increased sharply compared to that of AcrABOPEtA. This is due to the fact that the acrylate groups were succesfully attached at the hydroxyl site of the ABOPEtA and has therefore led to increase in unsaturation sites in the AcrABOPEtA compared to the ABOPEtA with unsaturation site mainly due to those in the fatty acid chain. The increase in specific gravity and refractive index in the order ABO< HEABOA < ABOPEtA < AcrABOPEtA correlates with increase in molar mass of these systems in that order.

**Physico-Mechanical Properties:** The ABOPEtA and AcrABOPEtA were applied on mild steel strips of standard size to evaluate their coating properties. Results in Table 2 reveal that while the ABOPEtA were non drying, the AcrABOPEtA became dry to touch in 3h and hard dry in 14h. The acrylate groups increased the molecular weight in AcrABOPEtA. With increase in molecular weight, fewer crosslinks are required to form coherent film and to reach the dry stage. The cured AcrABOPEtA passed both the impact resistance and flexibility tests that were failed by the ABOPEtA. The improved flexibility of AcrABOPEtA may be attributed to the flexible aliphatic acrylic moeity. Pencil hardness for cured AcrABOPEtA was good, 3H while that of the ABOPEtA was poor, 2B.

**Chemical Resistance:** The result of the chemical resistance tests is shown in Table 3. The result shows that acrylation of ABOPEtA led to improved chemical resistances.

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