

Research Article

Albizia Benth Oil Maleinised Polyesteramides: Synthesis, Structure, and Characteristics

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Albizia benth oil (ABO) has been employed in the preparation of polyesteramide resin via the condensation of hydroxyethylamide derivatives of ABO fatty acids and phthalic anhydride. The maleinised Albizia benth oil polyesteramide was prepared, using maleinised hydroxyethylamide derivatives of ABO obtained by appending maleate half esters onto the hydroxyethylamide derivative of ABO and phthalic anhydride. Structural elucidation and characterisation of the products carried out revealed that maleic anhydride can successfully be used to modify polyesteramides, to improve its properties such as drying, flexibility, scratch hardness, impact resistance, chemical resistance, and lower curing temperature.

1. Introduction

Current interest in cheap and biodegradable polymeric materials has given impetus to the development of materials from readily available, renewable, inexpensive, and natural resources [1]. This interest is justified by the environmental advantages of these substances; zero net carbon and biodegradability. These polymers also constitute a new outlet for vegetable products [2].

In Nigeria, vegetable oil-dependent industries rely mostly on imported oils; oils such as linseed and soybean are very expensive. However, ABO is an agricultural byproduct, abundantly available in the country. It holds considerable promise as a source of unsaturated oil and suitable for the production of industrial chemical feedstocks.

A class of alkyd-resins polymers from ABO have earlier been prepared [3, 4]. Just like other commercially viable polymers are currently being investigated. This research is aimed at synthesizing, characterising and evaluating ABO polyesteramide, modified by maleinisation for improved film characteristics over the conventional alkyds. It is part of the ongoing investigation on the preparation of new polymeric materials from ABO. Results of possible application of Albizia benth seed oil outlined in this research could trigger an expansion albizia plant cultivation, a development that will improve income of peasant farmers. Similarly, many

industries will have cheaper raw materials to use, leading to inexpensive consumer items. Environmental friendly and biodegradable polymers, produced from the biobased chemical feedstock, will promote a cleaner environment.

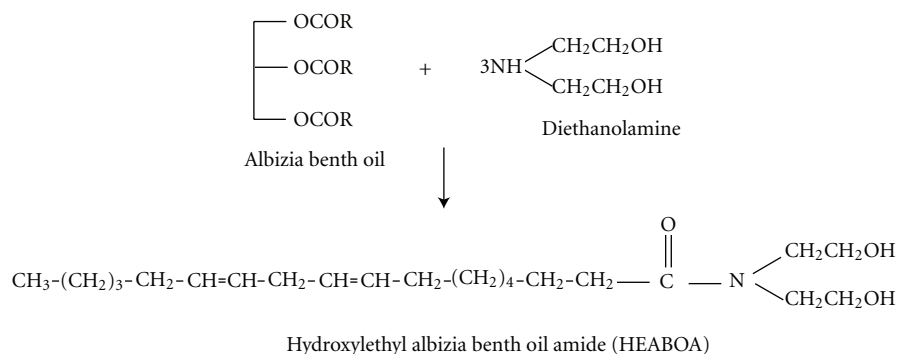
2. Experimental

2.1. 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, Chemsford, UK).

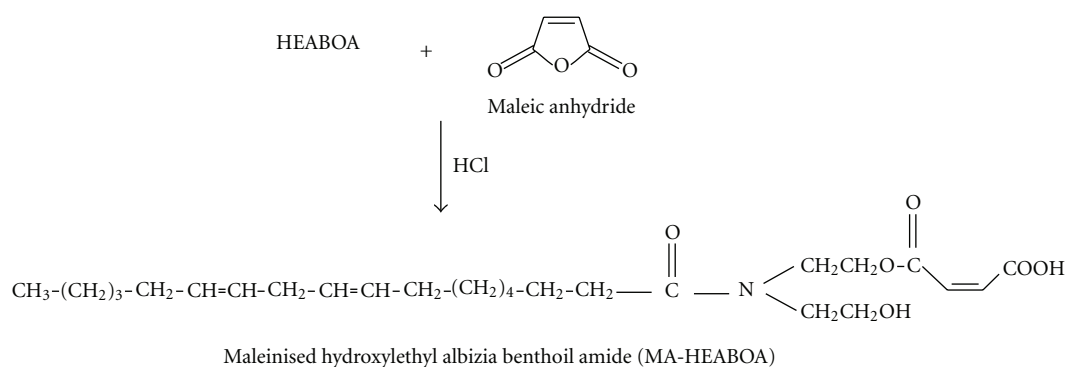
2.2. Extraction and Refining of Oil. Albizia benth oil (ABO) was extracted using n-hexane in a soxhlet apparatus and solvent removed on a rotavapour. The crude oils were refined by agitating with 18 M NaOH (1 : 30 g/g) for 15 min. The resultant mixture was then heated to 75–80°C to break the soap stock.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

2.3. Synthesis of Oil Derivatives

2.3.1. Synthesis of Hydroxyethyl Albizia Benth Oil Fatty Amide. 0.32 mol of diethanolamine and 0.007 mol of sodium methoxide were mixed in a four-necked round bottom



SCHEME 1



SCHEME 2

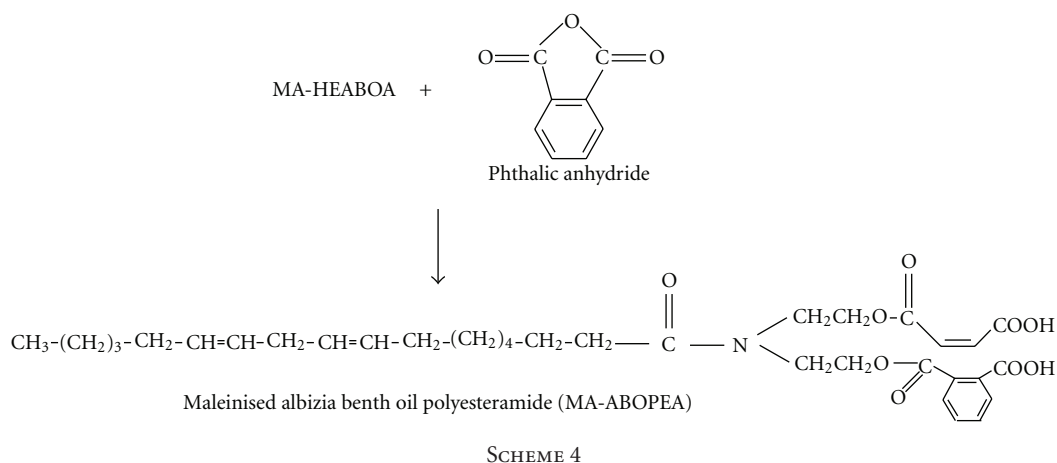
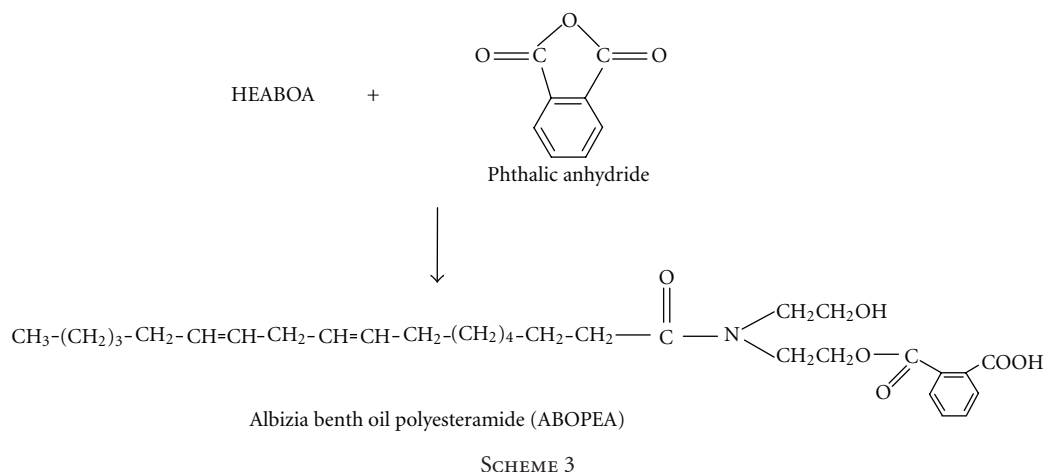
flask fitted with an electrical stirrer, thermometer, and condenser and contents heated to 110°C while stirring.

ABO (0.1 mol) was then added dropwisely over a period of 60 min. 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 Na₂SO₄. The ethereal layer was filtered and evaporated in a vacuum evaporator to obtain the bis (2-hydroxyethyl) Albizia benth oil fatty amide (HEABOA).

2.3.2. Synthesis of Maleinised Polyesteramide. 10 g of HEABOA prepared above was dissolved in 50 mL xylene: acetone mixture (3:1) in a four-necked flask fitted with nitrogen inlet gas, and mechanically stirred. The temperature of the system was brought to 100°C. Four drops of 1 N HCl were added to the mixture and 1.5 g of maleic anhydride dissolved in xylene:acetone (3:1) added dropwisely. The temperature of the reacting medium was raised to 145°C and reaction allowed to continue for 4 h to obtain the maleinised hydroxyethyl Albizia benth oil fatty amide (MA-HEABOA). 2.5 g of phthalic anhydride was added to the resulting product and the reaction allowed to continue for 6 h when acid value determination indicated complete reaction. Excess solvent was removed over rotary evaporator.

2.4. Characterisation. Samples were characterised by spectroscopic techniques such as FT-IR, ¹H NMR, and ¹³C NMR. FTIR spectra were recorded on Tensor 27 FTIR-H1026302 (Bruker Optik, GmbH, Germany) and ¹H and ¹³C—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, 1.366 s; pulse width 10.3 μs. Free induction decay FID was transformed and zero filled to 300 K to give digital resolution of 2 Hz/point. Thermal analysis was carried out by DSC 822° (Mettler Toledo GmbH, Giessen, Germany). Hydroxyl value (HV), Iodine value (IV), saponification value (SV), and refractive index (RI) were determined according to standard procedures [5].

For DSC analysis, approximately 10 mg of the resin sample was weighed into aluminium pans hermetically sealed into place. The sealed sample was initially kept at 30°C for 5 minutes and then heated to 250°C to erase its thermal history. To record the crystallization curve, the sample was cooled to −100°C and kept at the temperature for 5 minutes, after which the sample was heated to 250°C. Nitrogen was used for the cooling while both heating and cooling were done at the rate of 10°C/min.



2.5. Evaluation of Physicomechanical Characteristics. Samples were thinned in toluene to a brushable consistency. The solutions prepared were applied by brush on clean mild steel panels of $15\text{ cm} \times 15\text{ cm}$ for evaluating drying time, tin panels of the size $15 \times 15\text{ cm}$ for flexibility and adhesion, scratch hardness and impact resistance and glass panels of the size $15 \times 15\text{ cm}$ for water, alkali, and solvent resistance. All coated panels were air dried for 48 hr 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 [6].

3. Results and Discussion

The reaction schemes for the preparation of the hydroxylethyl Albizia benth oil amide (HEABOA), the maleinised HEABOA, Albizia benth oil polyesteramide (ABOPEA) and the maleinised ABOPEA are outlined in Schemes 1, 2, 3, and 4 respectively. The confirmation of the structures was carried out by FT-IR and NMR spectroscopic studies.

FT-IR spectrum of HEABOA (Figure 1) shows the characteristic absorption band at 3400 cm^{-1} for alcoholic OH. Asymmetric and symmetric CH_2 -absorption bands appear

at 2925 and 2854 cm^{-1} respectively. The amide carbonyl peak is observed at 1621 cm^{-1} . The $-\text{CH}_2$ bending is at 1466 cm^{-1} . The $\text{C}=\text{C}$ stretching band appear at 3008 cm^{-1} and the OH deformation is at 1049 cm^{-1} . In the FTIR of the MA-HEABOA, there is considerable reduction in the alcoholic OH band appearing at 3403 cm^{-1} compared to that observed in the HEABOA indicating that some of the hydroxyl groups may have reacted. The reaction of the maleic anhydride at the OH site is corroborated by the fact that the $\text{HC}=\text{CH}$ at 3008 cm^{-1} also appears in the FTIR of MA-HEABOA indicating that unsaturation was preserved during the maleinization reaction. The MA-HEABOA spectrum further shows the new ester and carboxylic acid carbonyl overlapping at 1735 cm^{-1} causing a broadening of the peak. The carbonyl of the amide appears at 1624 cm^{-1} . The $\text{C}-\text{O}-\text{C}$ ester stretching vibration appears at 1165 cm^{-1} and OH bending at 1073 cm^{-1} .

FTIR of the ABOPEA (Figure 2) presents peaks at 3009 , 2925 , and 2854 cm^{-1} assigned to the $\text{HC}=\text{CH}$, CH_2 asymmetric, and CH_2 symmetric stretching respectively. The amide and ester carbonyls appear at 1613 and 1731 cm^{-1} , respectively, and the $\text{C}-\text{O}-\text{C}$ asymmetric band appears at 1282 cm^{-1} . The $\text{C}-\text{O}$ stretching vibration is observed at

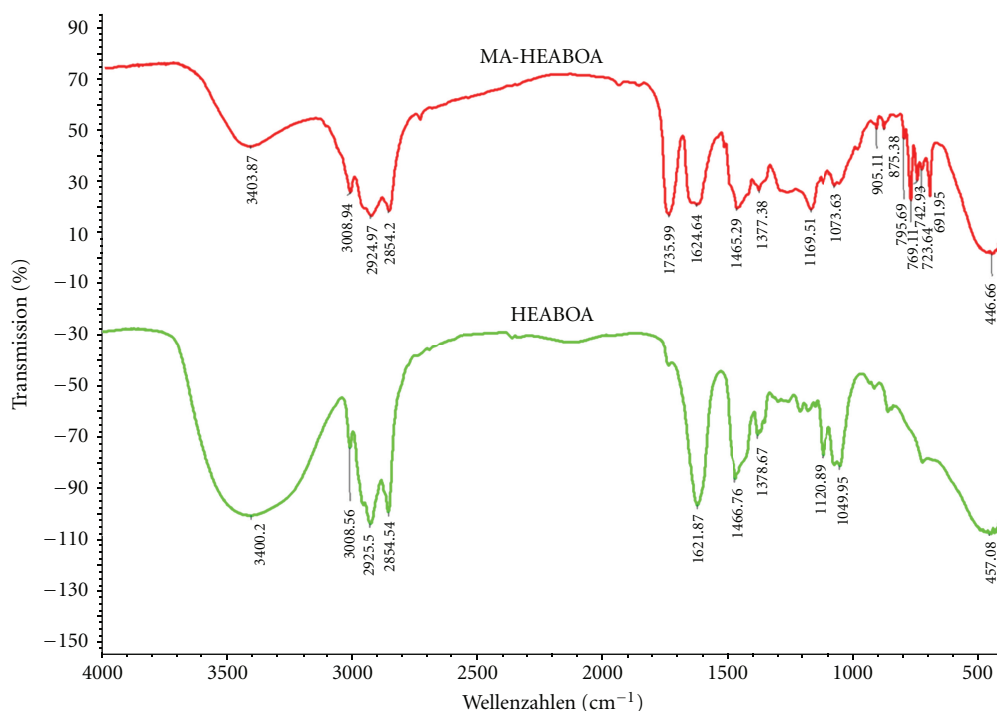


FIGURE 1: FT-IR of HEABOA and MA-HEABOA.

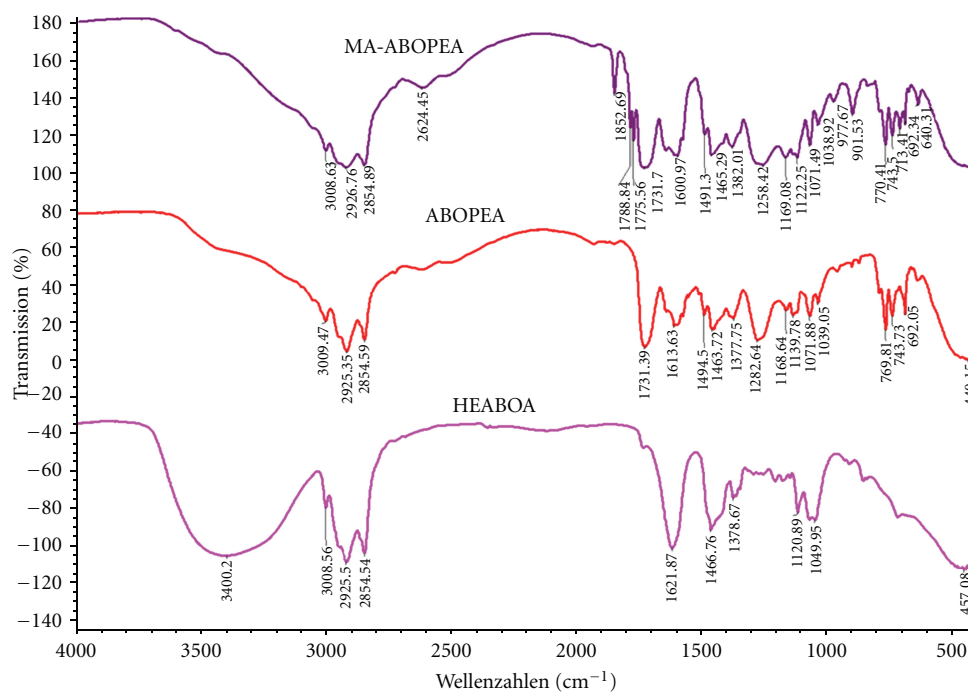
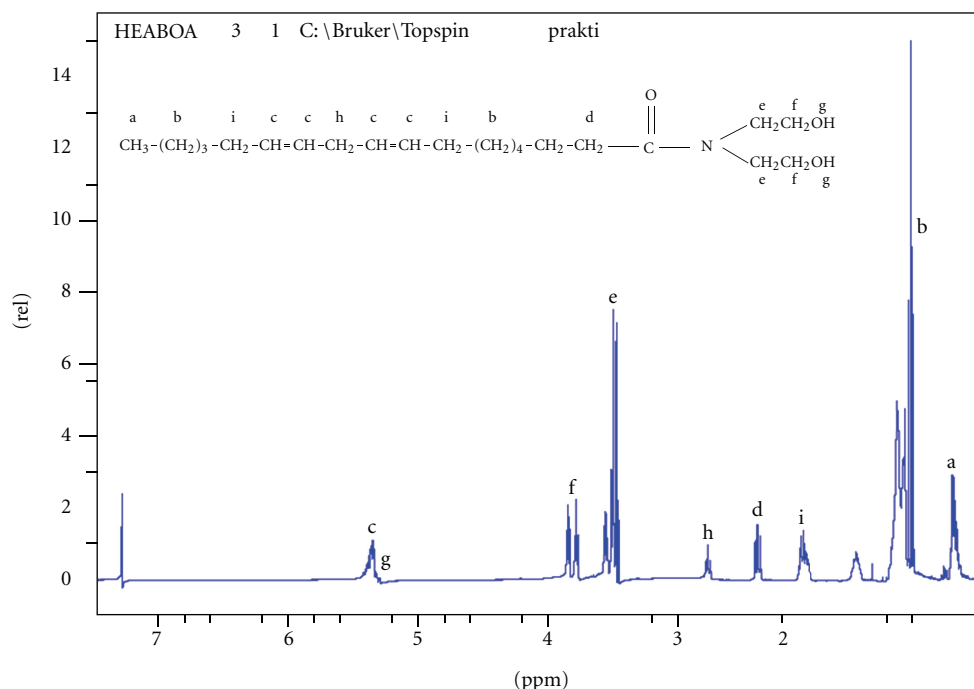
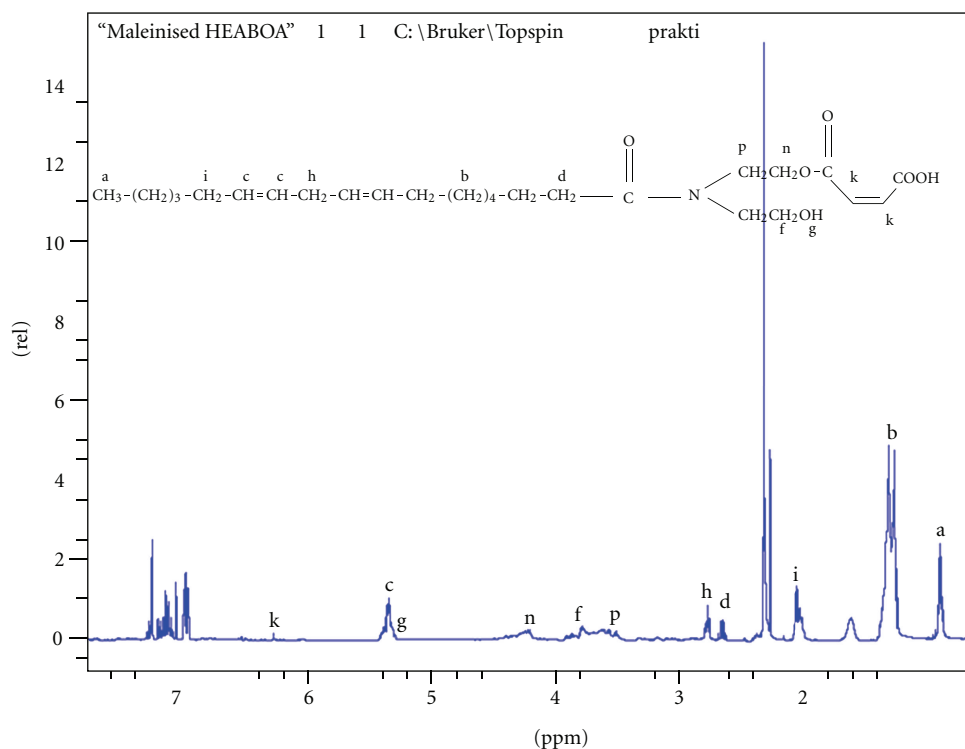


FIGURE 2: FT-IR of HEABOA, ABOPEA, and MA-ABOPEA.

1071 cm^{-1} . The absorption bands around $700\text{ to }770\text{ cm}^{-1}$ are due to the presence of C–H vibrations in the phthalic acid ring. There is a small hub around 3437 cm^{-1} which may be assigned to OH band. This OH band is suppressed and the suppression may be due to the presence of one terminal OH group in a large molecule of the ABOPEA.

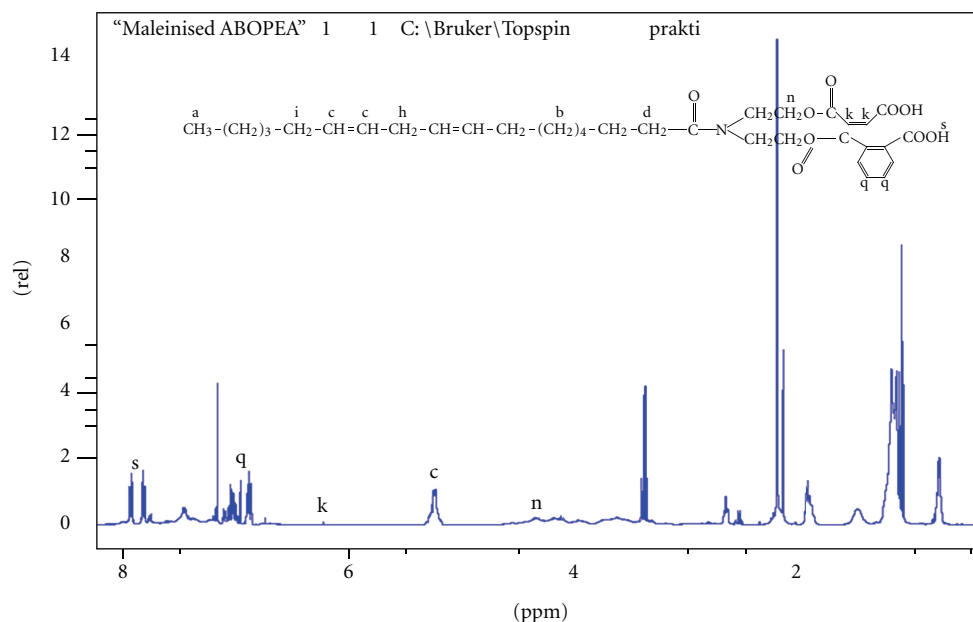
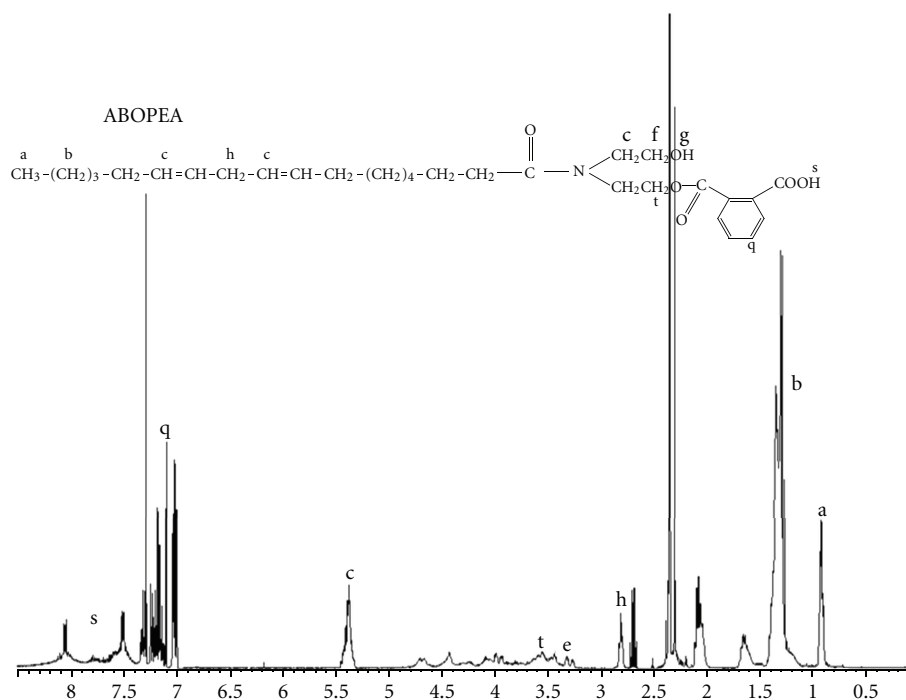
The FT-IR of MA-ABOPEA shows appearance of new peaks at $1852, 1788\text{--}1755\text{ cm}^{-1}$ which may be ascribed to the carbonyl of phthalic acid moiety as shown in Scheme 3 as well as carbonyl of some residual maleic anhydride. The broad unresolved band at 1600 cm^{-1} is assigned to aromatic C=C. The CH deformation bands at $699\text{--}770\text{ cm}^{-1}$ indicate

FIGURE 3: ^1H NMR of HEABOA.FIGURE 4: ^1H NMR of MA-HEABOA.

the presence of substituted benzene ring. All these corroborate the reaction of phthalic anhydride with MA-HEABOA to form MA-ABOPEA.

^1H NMR of the HEABOA and MA-HEABOA are presented in Figures 3 and 4, respectively. Figure 3 reveals proton

of terminal CH_3 at $\delta = 0.88$, chain CH_2 at $\delta = 1.28$ ppm, CH_2 adjacent to $\text{C}=\text{O}$ of amide at $\delta = 2.3\text{--}2.4$ ppm, CH_2 sandwiched between two $\text{C}=\text{C}$ at $\delta = 2.7\text{--}2.8$ ppm, $\text{CH}_2\text{--OH}$ at $\delta = 3.7\text{--}3.8$ ppm, and OH band overlapped with $\text{C}=\text{C}$ of fatty acid chain at $\delta = 5.3\text{--}5.4$ ppm. CH_2 adjacent to amide

FIGURE 5: ^1H NMR of MA-ABOPEA.FIGURE 6: ^1H NMR of ABOPEA.

nitrogen appear at $\delta = 3.4\text{--}3.5$ ppm. In the ^1H NMR of the MA-HEABOA, characteristic peak for CH_2OH at $\delta = 3.7\text{--}3.8$ ppm reduced considerably and maleate vinyl protons (HOOC-CH=CH-COO-) may be observed at $\delta = 6.3$ ppm while the methene signals $\text{HOOC-CH=CH-COO-CH}_2$ appear at $\delta = 4.2$ ppm.

The ^1H NMR of ABOPEA reveals a singlet peak for terminal CH_3 at $\delta = 0.92$ ppm (Figure 6). The peak at $\delta = 1.28$ ppm may be assigned to chain $-\text{CH}_2-$ stretching vibration. Peak at $\delta = 2.31$ ppm is assigned to $-\text{CH}_2-$ adjacent

to carboxyl group. CH_2 sandwiched between two C=C appears at $\delta = 2.8$ ppm and the $-\text{CH}_2-$ attached to carbonyl of phthalic acid appears at $\delta = 6.99\text{--}7.28$ ppm while carboxylic OH appears at $\delta = 7.49\text{--}8.05$ ppm. Figure 5 is the ^1H NMR of the MA-ABOPEA and it reveals the characteristic peaks in the MA-HEABOA, but with disappearance of the CH_2OH peak at $\delta = 3.7\text{--}3.8$ and appearance of ring protons at $\delta = 6.9\text{--}7.2$ ppm and carboxylic OH at $\delta = 7.8\text{--}8.0$. These spectra analysis support the structures of HEABOA, MA-HEABOA, ABOPEA, and MA-ABOPEA as proposed in Schemes 1–4.

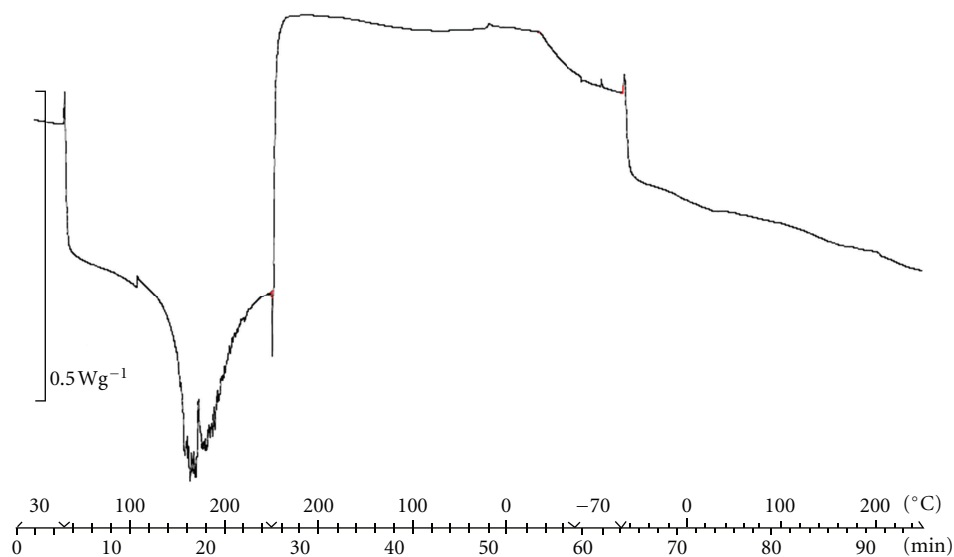


FIGURE 7: DSC thermogram of ABOPEA.

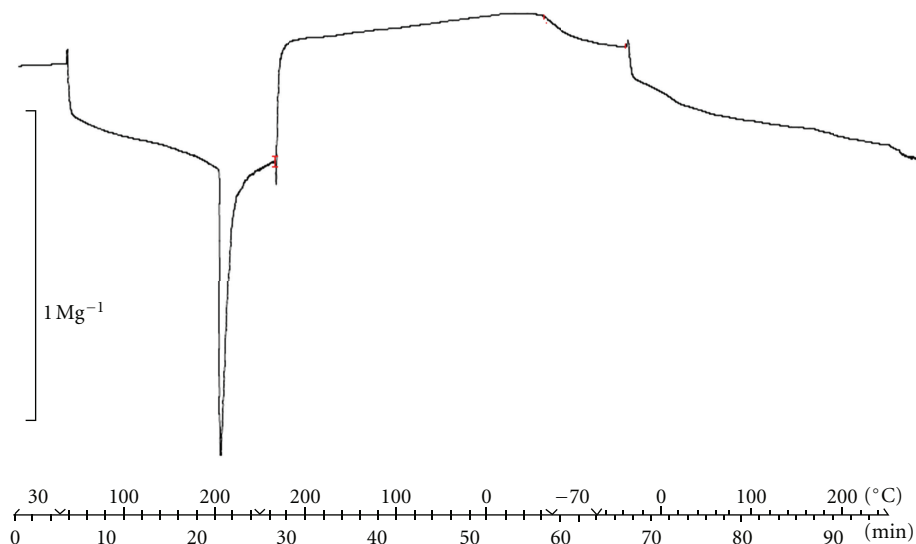


FIGURE 8: DSC thermogram of MA-ABOPEA.

4. Physicochemical Characteristics

Table 1 shows the physicochemical characteristics of the samples. The decrease in hydroxyl value (HV) of HEABOA in ABOPEA corroborates the reaction of phthalic anhydride with some hydroxyl groups of the HEABOA to form ABOPEA. In a similar manner, the decrease in HV of MA-HEABOA in MA-ABOPEA indicates the reaction of maleic anhydride with OH of HEABOA to form the half maleate as proposed in Scheme 2 and the much decrease in HV in MA-ABOPEA corroborates the reaction of the remaining hydroxyl groups in MA-HEABOA with phthalic anhydride to form the MA-HEABOA as proposed in Scheme 3.

Acid value (AV) determination for HEABOA was required to determine whether most fatty acids in the oil reacted with diethanolamine to form the diethanolamide.

The low acid value obtained (0.8) was a good indication of the fact that most of the acid, in form of methyl esters, reacted with diethanolamine. The higher acid value observed for ABOPEA, MA-HEABOA, MA-ABOPEA may be related to the presence of free carboxylic acid in these samples.

The decrease in iodine value (IV) and saponification value (SV) from oil to MA-ABOPEA may be attributed to progressive increase in molar mass and polymeric chain. The higher values of specific gravity (SG) and refractive index (RI) from oil to MA-ABOPEA may also be related to higher molecular mass of the samples.

5. Film Properties

Results of the film properties are presented in Table 2. Drying time of ABOPEA and MA-ABOPEA was recorded at an

TABLE 1: Fatty acid composition of ABO and physicochemical characteristics of ABO, HEABOA, MA-HEABOA, ABOPEA, and MA-ABOPEA.

| | ABO | HEABOA | MA-HEABOA | ABOPEA | MA-ABOPEA |
|---------------------------------|--------|--------|-----------|--------|-----------|
| Hydroxyl value (mg KOH\g) | 0.30 | 10.52 | 6.75 | 5.25 | 1.52 |
| Iodine value (mg iodine\g) | 104.5 | 85.5 | 90.2 | 60.3 | 82.5 |
| Saponification value (mg KOH\g) | 185.30 | 135 | 130 | 128 | 125 |
| Acid value (mg KOH\g) | 8.12 | 0.8 | 10.2 | 18.5 | 19.5 |
| Specific gravity (25°C) | 0.915 | 0.923 | 0.935 | 0.930 | 0.940 |
| Refractive index | 1.4735 | 1.4850 | 1.4925 | 1.4920 | 1.4950 |
| Palmitic (%) | 14.13 | | | | |
| Stearic (%) | 11.2 | | | | |
| Oleic (%) | 20.7 | | | | |
| Linoleic (%) | 47.9 | | | | |
| Linolenic (%) | 5.8 | | | | |

TABLE 2: Physicomechanical performance of ABOPEA and MA-ABOPEA.

| | ABOPEA | MA-ABOPEA |
|---------------------------------|--------|-----------|
| Drying time (min) at 110°C | 60 | 35 |
| Impact resistance (g) | 1000 | 1500 |
| Flexibility | Fail | Pass |
| Scratch hardness (Pencil Brand) | 4B | 2H |

elevated temperature (110°C) because the samples were non-drying and remained tacky for a long period of time at ambient conditions. Drying time (110°C) was 60 min for ABOPEA and 35 min for MA-ABOPEA. The maleate groups increased the molecular weight as well as introduced more unsaturation in the MA-ABOPEA. With increased unsaturation, crosslinks are easily formed and with increased molecular weight, fewer crosslinks are required to form coherent films and reach the dry stage.

Table 2 shows that MA-ABOPEA showed improved impact resistance over the ABOPEA. This may be explained to be due to the presence of the maleate group in the MA-ABOPEA. It made the resin to attain a reasonable larger chain length, along with desired crosslink density (due to the presence of higher unsaturation). Consequently, this resulted in a fine and dense structure with improved impact resistance. The MA-ABOPEA has better scratch hardness compared to the ABOPEA. While the ABOPEA failed the flexibility tests, the better flexibility of the MA-ABOPEA may be attributed to the presence of the maleate groups. Generally maleic anhydride is known to promote adhesion [7].

6. Chemical Resistance

The results of the anticorrosive properties of ABOPEA and MA-ABOPEA are presented in Table 3. The MA-ABOPEA are far superior to ABOPEA in anticorrosive ability. The MA-ABOPEA is unaffected in water, xylene, and NaCl (3.5 wt%) for 7 days and slightly loses gloss in HCl (2 wt%) after 7 days, and in NaOH (5 wt%) after 1 hr. The ABOPEA coatings

TABLE 3: Chemical resistance performance of ABOPEA and MA-ABOPEA.

| | ABOPEA | MA-ABOPEA |
|--------------------|--------|-----------|
| Water (7 days) | a | a |
| Xylene (7 days) | b | a |
| 5% NaOH (1 hr) | e | b |
| 2% HCl (7 days) | c | b |
| 3.5% NaCl (7 days) | b | a |

a: Unaffected; b: slight loss in gloss; c: loss in gloss; d: film partially removed; e: film completely removed.

however was completely removed in NaOH (5 wt%) after 1 hr, loses gloss considerably in HCl (2 wt%) after 7 days and slightly loses gloss in NaCl (3.5 wt%) and xylene after 7 days. The better corrosion resistance of MA-ABOPEA may be attributed to the presence of maleate half esters in them which provide the required degree of crosslinking density that helps in producing a most uniform and well-adhered coating on the surface of the substrate.

7. Differential Scanning Calorimetry (DSC)

The curing temperature range of ABOPEA and MA-ABOPEA was investigated by DSC. Results are presented in Figures 7 and 8. The curing of ABOPEA was found to start at 249°C while the curing temperature of MA-ABOPEA was much lower, 190°C. The decrease in the initial curing temperature can be attributed to the presence of maleate groups in the MA-ABOPEA which led to enhanced rate of crosslinking.

Acknowledgments

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