RESEARCH PAPER

Thermal and kinetic behaviour of *Pongamia glabra* oil fatty amide

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ABSTRACT

N,*N*-bis(2-hydroxyl ethyl) *Pongamia glabra* oil fatty amide (HEPA) was synthesised by the aminolysis of pongamia oil. The structural elucidation of HEPA was carried out by FTIR, ¹H NMR and ¹³C NMR spectroscopy. Physicochemical studies were carried out by standard laboratory methods. Melting point of *pongamia glabra* oil and HEPA was measured through differential scanning calorimetry. Thermogravimetry/differential thermogravimetry analysis (TG/DTGA) was used to evaluate the thermal and kinetic behaviour of synthesised HEPA in nitrogen atmosphere under non-isothermal conditions with heating rates of 5, 10, 20, and 30 °C min⁻¹. The TG curves of polymers at four heating rates were approximately in the same shape which indicated that mass loss is independent of heating rate. Obtained TGA data were analysed by the means of model-free isoconversional methods using Flynn–Wall–Ozawa and Kissinger–Akahira–Sunoseon applications on the whole range of temperature, and were found to be consistent. It was found that at the end of the decomposition process, the value of activation energy increases.

KEYWORDS: pongamia oil, fatty amide, thermal degradation; kinetics

1. INTRODUCTION

Paint and coating are important materials for the protection of mild steel as well as decoration. Generally, coating materials are derived from petroleumbased product. Nowadays, vegetable oils are being considered as alternatives to petrochemicals products, and are also being used as raw materials in the

chemical industry. This has been possible thanks to the development of chemical modifications of triglycerides and its derivatives [1-3]. Plants are a most important renewable resource for example, lignin, starch, terpenes and oils. Plant oils are very useful for the preparation of polymers, they contain triglycerides including long alkyl chains which may also be unsaturated depending upon the fatty acids composition of the oil [4]. Various plant oils like linseed, soyabean, olive, Jatropha, pongamia, rubber seed oil, *Annona squamosa* have been used for the preparation of fatty amide diol and epoxy [5-10]. Their monomers require further modification by different acids and alcohol in the preparation of polyesteramide, polyetheramide, urethanes, *etc.* [11-14].

Pongamia glabra is also known as *Pongamia pinnata* or *Millettia pinnata*. *Pongamia glabra* seed oil one of the drying oil as well as non-edible oil was used for the preparation of monomers such as epoxy and fatty amide diols. Fatty amide diol is basic material for the preparation of polyesteramide, polyetheramide and urethane [12, 13, 15]. Fatty acid methyl ester of seed oils have been also used for biodiesel [16]. Vegetable-oil based materials are environmentally safe, non-toxic and biodegradable [17–19].

In this study, *Pongamia glabra* oil was converted to *N*,*N*-bis(2-hydroxyl ethyl) pongamia oil fatty amide HEPA) by the aminolysis reaction of pongamia oil and diethanolamine. The structure of HEPA was confirmed by FTIR, ¹H NMR, ¹³C NMR spectroscopy. In view of the potential applications of environmentally friendly materials, further studies to determine the thermal resistance and kinetics aspects involved in the thermal degradation of a HEPA were needed. In particular, *E* and *ln A* values were calculated by applying two model free methods to dynamic thermogravimetric data.

2. EXPERIMENTAL

2.1 Materials and methods

Pongamia glabra oil was extracted and characterised as reported previously [12], Diethanolamine (BDH Chemicals, Ltd Poole England), diethyl ether (Polyscience, Warrington, PA), sodium methoxide, sodium chloride, anhydrous sodium sulfate (Winlab, UK) were used as received.

FTIR spectra were obtained using Spectrum100 (PerkinElmer, USA) with a NaCl cell. ¹H NMR and ¹³C NMR spectra were recorded on a Jeol DPX400 MHz using deuterated chloroform (CDCl₃) as solvent and tetramethylsilane (TMS) as an internal standard. Thermal analysis was carried out by TGA/DSC1 (Mettler Toledo AG, Analytical CH-8603, Schwerzenbach, Switzerland). About 10.0 mg

of the sample was loaded into alumina (Al_2O_3) crucibles for TG/DTG. The TGA scanning mode ranges from ambient temperature to 800 °C with different dynamic heating rates at 5, 10, 20 and 30 °C min⁻¹ in nitrogen atmosphere with a gas flow of 20 mL min⁻¹. About 10.0 mg of sample was loaded into aluminium pan and an empty pan used as reference for DSC. The DSC ranges from -50 to 125 °C with heating rate at 10 °C min⁻¹ in nitrogen atmosphere with a gas flow 20 mL min⁻¹. The physico-chemical properties such as iodine value (ASTM D1959-97), hydroxyl value (ASTM D1957-86) and refractive index were obtained by standard methods.

2.2 Synthesis of *N*,*N*-bis(2-hydroxyl ethyl) *Pongamia glabra* oil fatty amide (HEPA)

HEPA was prepared as reported previously [5, 14]

3. RESULTS AND DISCUSSION

Scheme 1 represents the synthesis of HEPA and shows the characteristics absorption bands and peaks in FTIR and NMR spectra, respectively.



Scheme 1 Synthesis of HEPA.

3.1 Spectroscopic studies

FTIR spectrum of HEPA (Figure 1) shows the characteristic peak at 3357 cm⁻¹ for alcoholic OH group, asymmetric and symmetric CH₂ stretching at 2926 cm⁻¹ and 2842 cm⁻¹, while C–H stretching for unsaturation appears at 3005 cm⁻¹. The other stretching vibration band of carbonyl group of amide is observed at 1625 cm⁻¹ and C–N stretching at 1466 cm⁻¹.

¹H NMR spectra (Figure 2) reveals peaks at $\delta = 0.842 - 0.853$ ppm for terminal $-C\underline{\mathbf{H}}_3$, $\delta = 1.216 - 1.264$ for chain $-C\underline{\mathbf{H}}_2^-$, $\delta = 1.566$ ppm, for $-CO - CH_2 - C\underline{\mathbf{H}}_2 -$, $\delta = 1.962 - 1.978$ ppm, for $-C\underline{\mathbf{H}}_2$ - adjacent to chain unsaturation. Peak at $\delta = 2.323 - 2.361$ ppm is attributed to the $-C\underline{\mathbf{H}}_2$ - attached to amide carbonyl, $\delta = 3.448 - 3.492$ ppm for $-C\underline{\mathbf{H}}_2$ - attached to amide nitrogen,



Figure 1 FTIR spectrum of HEPA.



 $\delta = 3.721 - 3.760$ ppm for $-C\underline{H}_{2}$ - attached to hydroxyl groups, $\delta = 5.016$ ppm for $-O\underline{H}$ attached to $-CH_2$ and $\delta = 5.303 - 5.333$ ppm for $-C\underline{H} = C\underline{H}$ - of chain. ¹³C NMR spectra of HEPA (Figure 3) reveals peaks of $\underline{C}H_{2}$, and $-\underline{C}H_2$, of chain, at $\delta = 14.189$ and 22.745 ppm, respectively. Peaks at $\delta = 29.382 - 29.826$ ppm, attached to amide for -<u>C</u>H,carbonyl, $\delta = 50.608 - 52.283$ ppm for -<u>C</u>H₂attached to amide nitrogen, $\delta = 60.732 - 61.199$ ppm for $-\underline{C}H_2$ - attached to hydroxyl groups. The peak at $\delta = 129.786 - 130.031$ ppm is assigned for $-\underline{C}H = \underline{C}H$ of chain of fatty amide. The peak at $\delta = 175.664$ ppm is attributed to the carbonyl of fatty amide chain. The physico-chemical characteristics of HEPA such as the iodine value (48), hydroxyl value (8.2) and refractive index (1.473) were observed. Physicochemical properties changes from oil to HEPA showed the formation of HEPA. The DSC thermogram (Figure 4) of Pongamia glabra oil showed an endotherm, starting at -2.39 to 20.81 centred at -8.80, Similarly, the DSC thermogram of HEPA shows an endotherm from 12.51 to 28.68 centred at 21.22. These endothermic peaks may be correlated to the melting points.



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Figure 4 DSC thermogram of Pongamia oil and HEPA.

3.2 Thermal behaviour

The TGA curves of HEPA scanned at different heating rates (β) from room temperature to 800 °C, in nitrogen atmosphere, are shown in Figure 5a, while the corresponding DTG curves are shown in Figure 5b. HEPA showed good thermal stability with no weight loss observed up to 210 °C. The nonisothermal degradation of HEPA occurred two steps over temperature range 30-700 °C. The TGA curves showed a first thermal event in the range 250–325 °C, which corresponds to a weight loss of approximately 30% and it is attributed to the evaporation of alcohol loosely bound to the compound and the second thermal event occurring in the range 400-500 °C is attributed to further dehydration, dealkylation and breakdown of the long hydrocarbon chain of HEPA; temperatures higher than 500 °C correspond to the residual decomposition reactions [21]. The heating rate affects both the location of the TGA curve and the maximum decomposition rate. As can be seen in Figures 5a and 5b, there is a shift in conversion lines caused by various heating rates. At higher heating rates, individual conversions are reached at higher temperatures. The maximum of the decomposition rate is also slightly shifted towards higher temperatures. Thus, the temperature corresponding to the maximum reaction rate, T_{max} , for the first stage of the thermal degradation of HEPA was determined from the DTG curves as being 273.38 °C, 323.02 °C, 336.80 °C and

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340.15 °C for heating rates corresponding to 5.0, 10.0, 20.0 and 30.0 °C min⁻¹, respectively and for second stage 415.41 °C, 441.20 °C, 466.05 °C and 478.83 °C for heating rates corresponding to 5.0, 10.0, 20.0 and 30.0 °C min⁻¹. This fact can be a consequence of heat and mass transfer limitations delaying the sample decomposition [20].

3.3 Nonisothermal kinetics

The evolution of kinetic parameters with conversion extent may provide information on mechanistic changes during thermal degradation. In the present study, the apparent activation energy (E) and pre-exponential factor (*A*) for thermal decomposition HEPA were evaluated using two model free methods, Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS). These methods are well described and widely used in the literature, which provides reliable results. Therefore, these methods are selected for the kinetic analysis of the HEPA.

The FWO [22,23] represents an isoconversion method that determines activation energy from the weight loss *versus* temperature data obtained at different heating rates with equation:

$$ln\beta = -1.052(E/RT) + [ln(AE/R) - ln(g(\alpha)) - 5.33]$$
(1)

where β is the heating rate, *T* is the absolute temperature, *R*(8.314 J mol⁻¹ K⁻¹) is the gas constant, *E* is the apparent activation energy of degradation, and *A* the pre-exponential factor. The apparent activation energy is then obtained from the slope (-E/R) of the plot of *ln* β *versus* 1000/*T* for any level of conversion, independent of the $g(\alpha)$ model. This method gives a degradation profile that is dependence of the activation energy on conversion. After obtaining the activation energy from the slope of the fitted plot, the pre-exponential factor was also determined from the intercept of the plots at each conversion ratio.

The KAS [24,25] method also relates the isoconversion methods. The relation between temperature, at which the given conversion is reached, and the heating rate is described by the following equation:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\frac{AR}{Eg(\alpha)} - \frac{E}{RT}$$

For constant α , a plot of ln (β/T^2) *versus* 1000/*T* is a straight line whose slope is *E*/*RT*, and the intercept is ln *AR*/*Eg*(α).

In the present study, four data sets of (β, T) were used to evaluate apparent activation energy. The mean values of the apparent activation energy and pre-exponential factor were determined from the arithmetic average and the logarithmic average, respectively. According to the above equations, activation



Figure 5 (a) TGA thermograms and (b) DTG thermograms of HEPA for heating rates of 5, 10. 20 and 30 °C min⁻¹.



Figure 6 (a) FWO and (b) KAS plots various conversion of HEPA at 5, 10. 20 and 30 °C min⁻¹ heating rate.

energy and pre-exponential can be obtained by the plot of $\ln \beta$ versus 1000/T and ln (β/T^2) from 0.1 to 0.9 conversion by using FWO and KAS methods for the constant decomposition level of HEPA as shown in Figures 6a and 6b. The obtained activation energy and pre-exponential factors A from FWO and KAS calculations are tabulated in Table 1 and Figure 7. Figures 6a and 6b show a series of such lines created from the four curves in Figure 5a and 5b by plotting data at different conversion levels. Figures 6a and 6b show the linear dependence between heating rate and temperature, in the case of conversions ranging between 0.1 and 0.9 for the HEPA. The isoconversional plots are parallel straight lines that indicate a complex weight loss process with several mechanisms. The slope of the lines allows the activation energy to be calculated. The apparent activation energies of degradation process calculated from these plots are shown in Table 1 and Figure 7a. Figure 7a shows the relationship of activation energy values with the conversion extent as calculated by the FWO and KAS methods. Figure 7 shows the similar shape of the curves E versus α corresponding to the isoconversional methods which revealed that they agree with each other. The activation energy up to 60% conversion increases with advancing conversion and slightly decreases for conversion higher than 80% but after that a significant increase in *E* has been found. The results show that with increasing temperature, some strong bonds begin to break due to transition between the first and the second step in the mass loss with a gradually increases in its activation energy, which indicates that degradation becomes hard, for a high degree of conversion. The char formed protects the residual compounds to further degradation. The average activation energy values calculated from FWO and KAS methods were found to be 91.43 and 84.72 kJ mol⁻¹, respectively. The small differences of the activation energy value in both methods are observed due to different approximations of temperature. Hence, it can be concluded that

Conversion (%) –	$E (kJ mol^{-1})$		$\ln A (\mathrm{min}^{-1})$	
	FWO	KAS	FWO	KAS
10	50.29	43.60	5.04	7.65
20	53.06	45.73	4.65	7.21
30	68.37	60.98	6.45	9.38
40	95.68	89.17	10.55	14.10
50	110.94	104.96	12.75	16.57
60	113.26	107.24	12.84	16.68
70	106.27	99.65	11.29	14.95
80	103.81	96.73	10.38	13.93
90	121.24	114.50	12.36	16.15
Mean	91.43	84.72	9.59	12.95

Table 1 Activation energy values (E) and pre-exponential factor ($\ln A$) calculated by FWOand KAS methods for HEPA in an N₂ atmosphere



Figure 7 (a) Activation energy values calculated by the FWO and KAS methods and (b) Preexponential factor calculated by the FWO and KAS methods at varying degree of conversion.

the activation energy of nonisothermal decomposition of HEPA is reliable. It can be seen that the values of pre-exponential factor $\ln A$ regularly increase up to 60%, degree of conversion then decreases and lastly increases up to the end by both the FWO and KAS models (Figure 7b). These *A* values are the measure of the collision frequencies and the average values were found to be 9.59 and 12.95 min⁻¹, respectively. The average pre-exponential factors from the FWO method agree well with the KAS method.

4. CONCLUSIONS

Pongamia glabra oil based fatty amide diol is an eco-friendly coating material and is very useful in paint and coating technology. The approach provides an alternative method to utilise non edible seed oil. The melting points of *Pongamia glabra oil* and HEPA was –8.80 °C and 21.22 °C, respectively. HEPA decomposes in a two step process and kinetic parameters were measured using FWO and KAS methods which revealed that the calculated activation energy values were close to each other.

5. ACKNOWLEDGEMENT

This project was supported by King Saud University, Deanship of Scientific Research, College of Science – Research Center.

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