Novel phase change materials for thermal energy storage: Evaluation of tropical tree fruit oils

Gideon Lawer-Yolar, Benjamin Dawson-Andoh*, Emmanuel Atta-Obeng

Department of Forestry, West Virginia University, Morgantown, WV 26505, USA

A B S T R A C T

We report for the first time the evaluation of oils from the tropical forest tree, Allanblackia, shea butter and palm kernel oil as a potential phase change material for thermal energy storage based upon its thermo-physical and chemical properties. Differential Scanning Calorimetry showed that all the oils were polymorphic and hence exhibited multiple melting/freezing profile over a wide range. For both melting and freezing cycles, Allanblackia oil showed high latent heat of energy (80.53 J/g) with the highest melting point profile (34.74 °C) of all the oils. Thermo-gravimetric analysis showed that all the oil samples were thermally stable and did not degrade within the temperature of interest even though Allanblackia oil showed an increase in weight around 37 °C indicating oxidative instability. Chemical stability was confirmed by FTIR spectra. Of all the oils studied, Allanblackia exhibited a potential for use as a PCM for thermal energy storage if purified to improve oxidative stability.

1. Introduction

Many energy producing or consuming systems exhibit intermittent outputs. The peaks and valleys of such energy systems may be significantly reduced or smoothed out by coupling them to energy storage systems [1]. Long or short-term energy storage systems can be grouped into three: mechanical, electrical and thermal. The study reported here only focused on thermal energy storage (TES) using novel renewable and sustainable materials. Evaluation of these materials for TES were based on their physical and chemical properties only.

TES, also called heat and cold storage, is a physical process that enables heat or cold to be stored for later use [2]. Three types are recognized: sensible heat, latent heat and thermochemical heat storage. Sensible heat (SHS) involves the transfer of heat to the storage medium attended by an increase in temperature of the medium, i.e., a sensor can detect the temperature increase. The ratio of stored heat to temperature rise is called heat capacity of the storage medium. Examples of sensible heat storage materials are stones, brick and liquids (water). SHS uses the heat capacity of the storage medium and is accompanied by appreciable change in volume. Additionally, energy storage density is lower. In contrast, latent heat storage (LHS) occurs without a change in temperature of storage medium and requires materials that exhibit phase

changes (i.e. solid to solid; solid to liquid; liquid to solid; liquid to gas) upon heating or cooling making them excellent candidates. Phase change (PC) activity such as melting is usually accompanied by small volume changes (less than 10%) and high thermal energy storage density. In thermal chemical storage, energy is absorbed or released in the breaking and forming of molecular bonds in a completely reversible chemical reaction [3].

This study evaluated three novel renewable and sustainable materials as phase change materials (PCM) for use in LHS. When PCM are heated, they absorb heat (endothermic, enthalpy; heat of melting) and change from solid to liquid (i.e. they undergo a change in phase). However, their temperature stays constant. The reverse of this process is the release of absorbed latent heat at a constant temperature and change in phase (e.g. liquid to solid). This property of PCM allows them to be used in thermal energy storage applications such as solar energy (solar water heating) [4] where solar energy can be collected during the day and used in the night when the sun is no longer available.

Potential applications of PCM include LHS systems for solar engineering, solar water heating, space craft thermal control and thermal management for portable electronic equipment. In solar domestic hot water systems for residential housing, there is a mismatch between peak heating demand (evening and early morning) and availability of solar radiation (during the day). In this situation, thermal energy storage can be used to bridge the gap between the energy source (sun) and the application. This study evaluated three novel renewable and sustainable materials as phase change materials (PCM) for use in LHS.

* Corresponding author.
  E-mail address: bdawsona@wvu.edu (B. Dawson-Andoh).

In latent storage systems, PCM do not per se transfer or absorb heat from the medium. A heat exchanger is required for this function. However, this study did not address this aspect. Since this was a preliminary evaluation of novel materials as potential PCMs, the focus was on the physical/thermal and chemical properties of these materials. The energy involved in the phase transition of each material was determined using Differential Scanning Calorimetry (DSC). The thermal stability and reliability of these materials were determined via thermogravimetric analysis and DSC. A thermal recycler was used to recycle the phase change process a thousand (1000) cycles.

Physical and thermal properties of PCM dictate their use in thermal energy storage and include: (1) melting temperature in desired operating range, (2) high latent heat of fusion per unit volume, (3) high specific heat (high thermal conductivity in both the solid and liquid state), (4) small volume changes on transformation of phase, (5) congruent melting of PCM for a constant storage capacity of material for every freezing/melting cycle, (6) chemical stability, high nucleation to avoid super-cooling of liquid phase, (7) not degraded after several melting/freezing cycles, (8) non-corrosive, non-toxic, (9) non-flammable, readily available and (10) cheap [5].

Three main types of PCM are recognized: (i) organic, (ii) inorganic and (iii) eutectic mixtures. Organic PCM include saturated hydrocarbons (paraffin), alcohols, glycols, fatty acids and their esters. Inorganic PCM are salt hydrates (e.g. hydrated calcium chloride, $CaCl_2.6H_2O$; hydrated sodium sulfate, $Na_2SO_4.10H_2O$) [3]. Eutectic mixtures are not pure compounds but mixtures of two or more substances whose melting point are lower than that for any other mixtures of the same substances. They include naphthalene and benzoic acid mixture; aluminum chloride ($AlCl_3$) and sodium chloride (NaCl) mixture. Non-paraffin organic PCM evaluated so far are derived from fossil sources. The negative environmental footprint of such materials makes it paramount to seek sustainable and more environmentally compatible alternate materials as PCM. Consequently, this study evaluated three tree-based oils as potential PCM. They are oils from the tree species, Allanblackia species, shea butter and palm kernel.

Allanblackia spp. is an oil seed-bearing fruit tree found growing in the rainforest of West and East Africa sub-region. There are nine species of Allanblackia with an unknown species found in Fernando Po. The species of Allanblackia used in this study, *A. parviflora,* grows in West Africa from Sierra Leone to Ghana [6]. Allanblackia belongs to the *Guttiferae* family of the subfamily *Clusiodeae*. It is a medium sized tree that grows to a height of about 40 m with a cylindrical bowl and a diameter at breast height around 50 cm [7]. Oil production from a tree can be an average of about 12 kg/tree from a net seed weight of 35 kg. The oil of Allanblackia is a solid at room temperature and melts between 42–44 °C. There are on-going commercial operations to set-up *Allanblackia* spp. plantations in Ghana.

Allanblackia oil contains three major triglycerides: steari C-O leic-stearic (70%), steari C-O lei C-O leic (23%), and olei C-O lei C-O leic (4%) [8]. Shea butter is produced from the nuts of the shea butter tree (*Vitellaria paradoxa*) which grows primarily in the Savannah Woodland areas of West and Central Africa region. The fat content of shea butter is between 41–54 % [9].

Palm kernel oil is obtained from the oil palm (*Elaeis guineensis*) fruit nut. Oil palm trees originated from the tropical rainforest of West Africa and its fruit consists of an outer exocarp (outer skin) and the inner mesocarp (houses the pulp that contains the palm oil). At the center of the fruit is the endocarp (palm kernel nut which contains the palm kernel). Palm kernel nut is a by-product of palm oil extraction. The nut is cracked to produce the kernel from which the palm kernel oil is obtained. Palm kernel oil is saturated and semi-solid to solid at room temperature. Palm kernel oil crystallizes in the beta form at a temperature of 0–25 °C [10].

To the best of our knowledge, this is the first reported study of the evaluation of oils/fats derived from tropical/savannah woodland tree fruit oils for use as potential PCM in an LHS system. In this paper, only the results of oils/fats of Allanblackia, shea butter and palm oil are presented. Subsequent publications will report on the oil-derived fatty acids and their ester derivatives. This work illustrates alternate potential sustainable and renewable use of trees from tropical forest and savannah woodlands in Africa instead of current practice of converting trees to logs for use in the manufacture of wood and related products.

2. Experimental methods

2.1. Materials

Allanblackia spp. (*Allanblackia paviflora*) seeds (were obtained from Ghana); shea butter (Bulk Apothecary, Ohio, U.S.A.), palm kernel oil (Organic Creations, Oregon, U.S.A.), hexane (Fisher Scientific, NJ, U.S.A.

2.2. Methods

2.2.1. Processing of Allanblackia spp. seeds
Seeds of *Allanblackia* spp. were dried in an oven at 65 °C for 24 h. The seeds were then manually de-hulled and put in plastic bags and stored in the refrigerator until use.

2.2.1.1. Oil extraction from Allanblackia spp. seeds.
A full factorial design with two (2) factors and four (4) levels each was used in this study. The factors were mesh size and extraction time. The four levels of mesh size were: (0.25 mm; 0.5 mm; 1 mm; and 2 mm) and the extraction times were: (2 h; 4 h; 6 h; and 8 h). Five grams of ground material was used for each extraction.

De-hulled Allanblackia seeds were milled into fine particles using a coffee grinder (Mr. Coffee, USA) and passed through meshes of various sizes (0.25 mm, 0.5 mm, 1 mm and 2 mm). Five grams of ground seeds were placed in a cellulose extraction thimble and capped with a folded filter paper and placed in the extraction chamber of a Soxhlet extraction apparatus. Fifty ml of extraction solvent (hexane) was placed in a 250 ml capacity round bottom flask and connected to the extraction chamber. The extraction chamber was connected to a reflux system. The heating system of the extraction system was turned on and extraction was carried out according to ISO 659-1988E [11]. After extraction, the solvent containing the extracted material was transferred into the round bottom flask of a Buchi rotavapor, (model R-210/215) and the extraction solvent, hexane, recovered by vacuum distillation. The oil remaining in the extraction flask was recovered and dried over nitrogen gas. The resulting extract was placed in a desiccator to attain ambient room temperature conditions and weighed. The percentage yield was gravimetrically determined.

2.2.2. Chemical characterization of oils of Allanblackia spp., shea butter, and palm kernel
The functional group chemistry of extracted *Allanblackia* spp. oil, shea butter and palm kernel oil were characterized using Fourier Transform Infrared (FTIR) spectroscopy. The FTIR spectra of each oil was acquired using a Perkin Elmer Spectrum 100 spectroscopy instrument with Universal Sampling Accessory at a wave number range of 4000-650 cm^{-1}. Measurements were recorded in transmittance mode. The oil sample (about 0.1 ml) was placed on the diamond ATR probe aperture, and spectra were recorded at a resolution of 8 cm^{-1} using 4 scans under 1 min

against air as the background. FTIR measurements were recorded for samples before thermal cycling and after thermal cycling.

2.2.3. Thermo-physical characterization of oils

The enthalpies and phase change temperatures of the samples were determined by DSC. The instrument was calibrated with an indium standard. Measurements were taken under a nitrogen atmosphere using a heating/cooling/heating cycle at a heating rate of 5 °C/min, and the same rate for the cooling cycle. These measurements were made in triplicates and used to calculate the average melting and latent heat values. A Programmable Thermal Controller was used to determine the melting/solidification process for 1000 times to find the thermal reliability and stability of the samples after the thermal cycling. The samples were thermally cycled by heating from 0 °C to 50 °C at a rate of 1 °C/s and held for 30 s. They were then cooled from 50 °C to 0 °C at the same rate of 1 °C/s, and again held for 30 s. This process was repeated 999 times. This effect impacts the thermal energy storage of the samples as a PCM. The samples were also analyzed thermogravimetrically using a TGA instrument. The instrument was calibrated using calcium oxalate in a temperature range of 25–600 °C at a heating rate of 10 °C/min in a nitrogen/compressed air atmosphere [12].

3. Results and discussions

3.1. Oil yield from Allanblackia spp. seeds

The highest yield (70.4%) of Allanblackia spp. oil (Table 1) was produced by mesh size of 0.25 mm and a time of 4 h. This was higher than previously reported yield (67.59%) for Allanblackia floribunda seeds [13].

3.2. Differential scanning calorimetric analysis of oil samples

Oils from Allanblackia, shea butter and palm kernel are not pure compounds but consist of complex mixtures of triacylglycerol (TAG, 96–99 % of esters of glycerol and long chain fatty acids). Hence, they exhibit variable melting, crystallization temperature, heats of fusion and crystallization. These oils melted over a temperature range and exhibited multiple endotherms [14]. Freezing or crystallization of the oils followed the same pattern. DSC analysis showed that the melting and crystallization profile of these oils exhibited multiple values. They consisted of onset (T_o) and offset (T_f) temperatures, given by the points where the endotherm/exotherm curves meet the baseline when extrapolated. Various peak temperatures including the temperature of maximum difference in heat flow between T_o and T_f, were also

Table 1
Oil yield from Allanblackia spp. Seeds.

Sample Size (mm)	Time (hr)	Average oil yield (%)
2	8	62.07 ± 1.18
1	8	62.80 ± 1.45
0.5	8	65.68 ± 0.30
0.25	8	65.47 ± 4.85
2	6	60.74 ± 0.34
1	6	65.11 ± 0.81
0.5	6	66.68 ± 1.05
0.25	6	68.76 ± 0.44
2	4	61.24 ± 1.79
1	4	64.38 ± 0.75
0.5	4	62.08 ± 0.14
0.25	**4**	**70.36 ± 3.36**
2	2	60.14 ± 0.29
1	2	64.77 ± 1.14
0.5	2	65.47 ± 2.15
0.25	2	65.63 ± 5.36

determined. The temperature ranges of the melting and cooling profiles were determined by the difference T_o and T_f [15].

The DSC thermogram of Allanblackia spp. oil (Fig. 1, Allanblackia) exhibited a pattern which indicated heat release (exothermic) in the heating cycle at almost the same temperature range where freezing of the oil occurs during the cooling cycle. This phenomenon occurred before the melting process started. The exothermic heat of this process was 27.60 J/g at a temperature of 18.25 °C with an extrapolated temperature onto the baseline of 15.75 °C (which is the onset temperature T_o). The full temperature range at which this occurred was 11.53–22.08 °C. After this initial release of heat, the oil immediately exhibited heat absorption attended by melting of the oil at a peak temperature of 34.74 °C at B_1. The heat absorbed in the process was 80.53 J/g with an extrapolated temperature (T_o) of 30.50 °C and the temperature range of 22.66–38.87 °C. The initial release of heat (exothermic peak) in the Allanblackia spp. melting profile was due to the melting-re-crystallization or re-organization of the original fat crystals. Berger and Akehurst [16] reported that oil and fats do not exhibit specific melting and crystallization temperatures but show melting/crystallization profiles. The phenomenon whereby multiple melting/crystallization peak profiles occurs instead of a single peak is known as polymorphism. The latter observation strongly depends on the thermal history of the oil or fat [16]. Before the large peak from the re-organization effect, a small transition peak occurred as a shoulder peak to the larger melting-re-crystallization peak observed at A_1 (Allanblackia, Fig. 1). This shoulder peak overlapped with the main peak in the temperature range of 11.53–15.75 °C. After the melting process, the melted oil underwent a cooling cycle where the temperature was gradually reduced. Approximately within the same temperature range where the earlier heat was released, freezing or crystallization of the oil occurred in the range of 19.42-9.25 °C resulting in a freezing peak temperature of 17.02 °C at C_1. When extrapolated from the peak, the onset temperature was 19.16 °C and the heat released was 38.92 J/g. A small peak occurred in the cooling cycle as a shoulder after the offset temperature of 7.15 °C at C_2. Both the melting and freezing peaks were sharp. The melting process indicated a difference between the melting temperature peak for the main endothermic curve and the onset temperature T_o, to be about 4 °C. Similarly, the difference between the freezing temperature peak and the onset temperature for the main exothermic curve was about 2 °C. Since the temperature difference between the onset temperature and its melting temperature and, also the onset temperature and its freezing temperature were low, the heat absorbed and released respectively represented latent heat.

The DSC thermogram of shea butter oil showed both melting and freezing with a broad trace pattern (Shea, Fig. 1). Due to their polymorphic nature, the thermogram curves exhibited four transition temperature peaks in the heating profile. The main melting peak (A_3) overlapped with one of the transition peak (A_2). Two other transition peaks were separate small peaks (A_1 and A_4) that were not part of the main melting peak. The first transition peak (A_1) occurred before the major peak starts. A broad transition peak at A_4 again occurred after the offset temperature of the main endothermic curve. For the main curve in the heating process, the onset temperature for the main curve occurred at 4.27 °C and was associated with a melting peak temperature of 15.75 °C. The temperature difference was more than 11 °C with an unresolved overlapping transition peak occurring in the main peak. The heat absorbed in the process was 29.85 J/g, which was low compared to that of the Allanblackia spp. oil. Due to the nature of the curve, it was difficult to assign an absolute energy value since the curve was spread over a large temperature range. Therefore, this observation could not be described as latent heat energy. In the case of the freezing process, the energy obtained for the major peak was
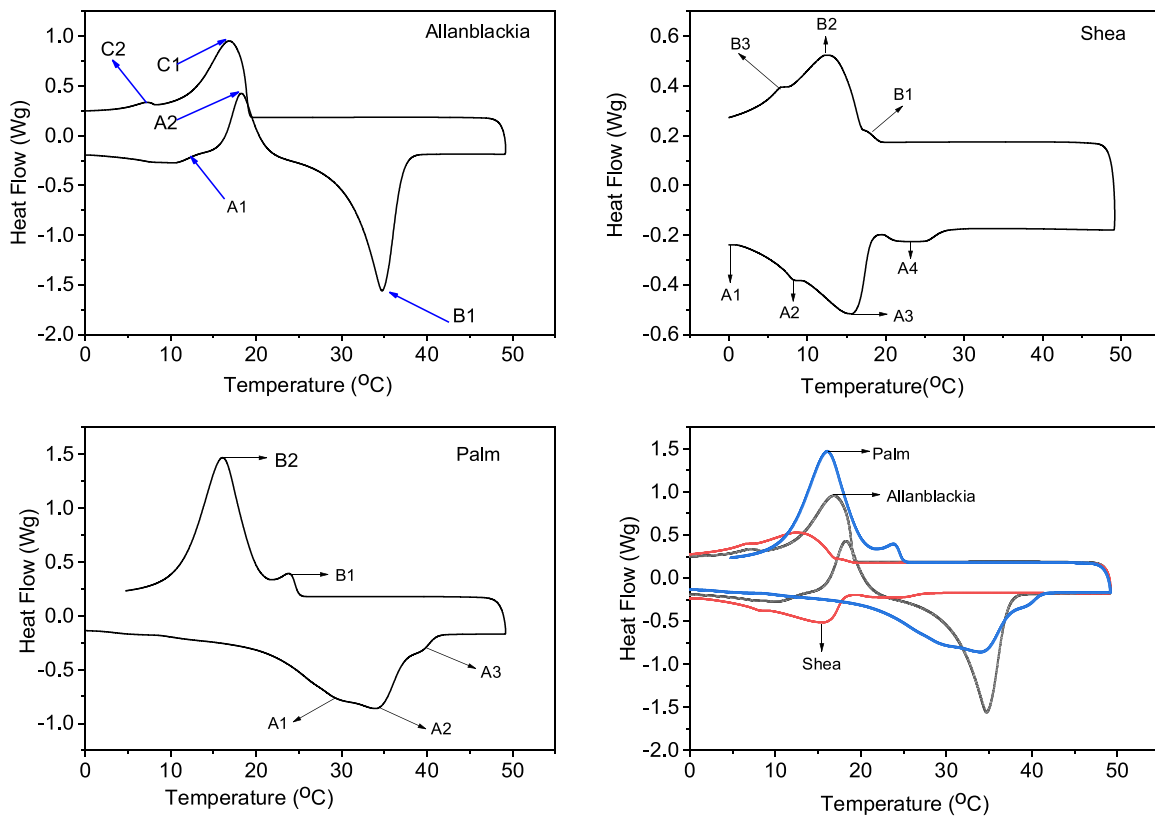
Fig. 1. The DSC thermogram of *Allanblackia* spp. oil, shea butter and palm kernel oil.

31.35 J/g. There were 3 peaks with 2 representing transition temperature peaks (i.e. B_1 and B_3). These 2 peaks were small and overlapped with the main peak. One transition peak appeared before the main peak at B_1, while the other after it at B_3. The energy was lower than that exhibited by *Allanblackia* spp. oil. Polymorphism effect also occurred for both melting and crystallization cycles. The onset temperature was 17.24 °C and the freezing peak temperature was at 13.10°C. The temperature difference between the onset temperature and the freezing peak temperature was about 4 °C which was far lower than the difference in the melting cycle. This difference was higher than that for the *Allanblackia* spp. oil freezing cycle (about 2 °C). In this instance, the heat released was latent heat of crystallization even though the magnitude was low compared to the heat released by *Allanblackia* spp. oil. Li and Ding [17] prepared a PCM from butanediol di-stearate and obtained an enthalpy value of 181.97 kJ/kg at a peak temperature of 51.81 °C with an onset temperature of 41.80 °C. Comparing the difference between the onset temperature and peak temperature, a value of 10.01 °C was obtained and this was still considered as latent heat energy. However, in comparison to the crystallization range 19.35-0.46 °C for shea butter, it was too high to be considered a latent heat. Further, the polymorphism effect is stronger than that of the *Allanblackia* spp. oil. For the purpose of this study, we considered latent heat temperature range to be 5 °C.

The palm kernel oil DSC thermogram (Palm, Fig. 1) exhibited a broad melting curve with the maximum melting point peak at 34.14 °C for peak A_2, and the onset temperature at 20.60 °C. The heat absorbed in the process was 94.12 J/g. The melting process exhibited a comparatively large difference of 13 °C between the onset temperature and the melting peak. The melting enthalpy could not be considered latent heat since latent heat absorption should be at a constant temperature or the temperature variation should be very small, but the temperature range of 14.07–41.43 °C

was too high. Two overlapping transition temperature peaks which occurred at A_1 and A_3, were all within the major melting peak. In the cooling cycle however, a small shoulder peak occurred at 23.85 °C just before freezing of the sample (Palm, Fig. 1). The freezing of the sample was very sharp with onset temperature at 20.32 °C and the freezing temperature at 16.10 °C.

The energy involved in this process was comparatively high (95.55 J/g). The endothermic (heating) cycle did not involve latent heat but the exothermic (freezing) cycle involved latent heat because the difference between the onset temperature and the freezing temperature was about 4 °C even though there was an overlapping shoulder peak before the major peak. The shoulder peak made the freezing process incongruent [5]. The crystallization for this sample was simpler and more reproducible than the melting because crystallization was influenced only by the chemical composition while the melting was affected by the initial crystalline state of the oil [18].

Comparing all the DSC thermograms of the three oils, *Allanblackia* spp. oil, had both melting and freezing cycles absorbing and releasing latent heats respectively as shown in Fig. 1 (combined thermograms). The enthalpies of melting and freezing were high, but not as high as those for palm kernel oil. They were higher than those for shea butter. Even though the palm kernel oil had the highest enthalpy values, its melting enthalpy was not a latent heat. The heating curve was broad and more polymorphic compared to that of the *Allanblackia* spp. oil. Only the freezing enthalpy was latent heat, but the melting enthalpy cannot be considered as latent heat but rather sensible heat energy. Shea butter oil has all the cycles exhibiting sensible heat instead of latent heat. Both the enthalpy of melting and freezing are not latent heats and the shape of the curve was broad. Shea butter oil had the lowest enthalpies of the three oils tested and the lowest melting temperatures. Palm kernel oil had the highest freezing enthalpy

which was sharp and represented latent heat (palm kernel and combined thermogram, Fig. 1). And, it exhibited a higher polymorphic effect (resulting in an incongruent freezing [5]), than the *Allanblackia* spp., whose major crystallization peak is non-polymorphic. The melting enthalpy of palm kernel oil, even though high, was too broad to be considered as latent heat (palm kernel and combined thermogram, Fig. 1). It was also polymorphic as compared to *Allanblackia* spp. oil.

Based on the thermal profile of the three oils produced by the DSC scans, *Allanblackia* spp. oil exhibited the greatest potential for use as a PCM for latent energy storage. However, the *Allanblackia* spp. oil thermal profile was not uniform since it released energy due to re-organization of the bonds before absorbing energy for melting. Even though palm kernel oil has large enthalpies in both the melting and freezing cycles, it was only the freezing cycle that released latent heat, while the melting cycle did not absorb latent heat but rather sensible heat because it was more polymorphic.

3.3. Thermogravimetric analysis of oil samples

Thermogravimetric analysis (TGA) method is a useful tool for measuring the thermal stability of a material and an important metric for the evaluation of the suitability of a material for use in thermal energy storage applications [12]. The thermal stabilities of *Allanblackia* spp., shea butter and palm kernel oils as investigated by TGA analysis are reported in Fig. 2.

Allanblackia spp. oil exhibited 5 different degradation steps (*Allanblackia*, Fig. 2). This observation confirmed that the oil was a mixture. The major component in the oil degraded at a temperature between 177.85 °C and 345.26 °C with a weight loss of 59.51%. The second degradation step was attended by a weight loss of 14.86% in the temperature range of 345.26–401.11 °C. The third, fourth, and fifth degradation steps were attended by weight loses of 13.01%, 9.69% and 2.88%. As earlier indicated by the thermogram, *Allanblackia* spp. oil was polymorphic and gave rise to multiple degradation temperatures in contrast to pure substances. Shea butter oil exhibited four different degradation steps (Shea, Fig. 2) reflecting multiple composition. This oil was polymorphic and exhibited multiple degradation temperatures. The major component of shea butter oil degraded at a temperature range of 219.51–349.79 °C with weight loss of 64.24%. The next degradation occurred at 349.79–407.56 °C with a weight loss of 12.36%. The third degradation occurred with weight loss of 11.02% at 407.56–467.60 °C. The final degradation occurred at 467.60–549.16 °C with a weight loss of 12.22%.

The degradation of palm kernel oil is presented in the TGA thermogram (Palm, Fig. 2). Palm kernel oil exhibited three levels of thermal degradation with polymorphic properties. The first degradation of palm kernel oil occurred at 226.31 to 315.80 °C with corresponding weight loss of 72.07%. The second degradation of this oil occurred from 315.80 to 426.82 °C with a weight loss of 21.77%. The final degradation of this oil occurred from 426.82 to 533.30 °C with a weight of 5.98%.

The overlaid TGA thermogram of the oils (combined thermogram, Fig. 2) showed that degradation level 1 of shea butter oil was faster than that of *Allanblackia* spp. oil. Also, the second
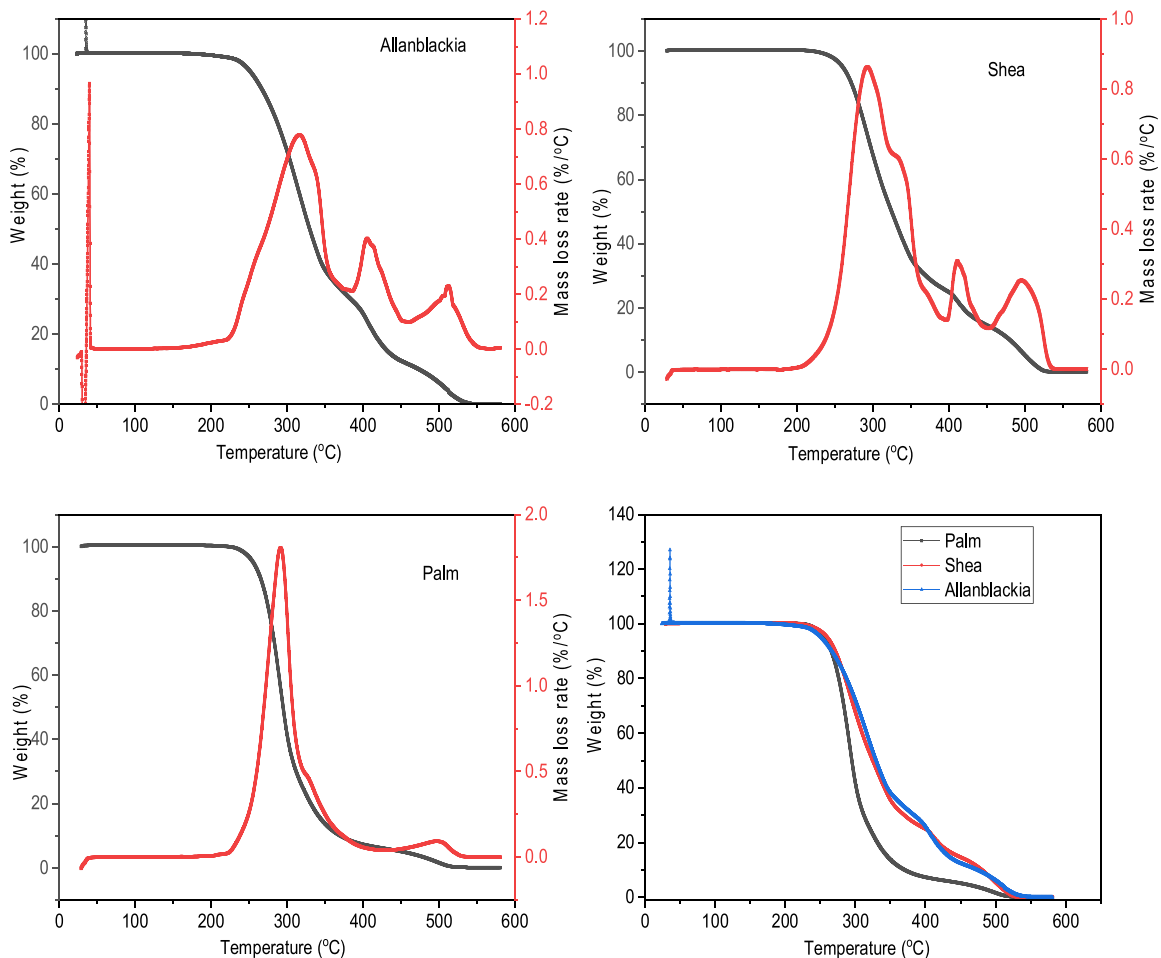

Fig. 2. The TGA thermogram of *Allanblackia* spp. oil, shea butter and palm kernel oil.

degradation level of *Allanblackia* spp. oil was minor and a little faster than that of shea butter oil confirming their respective weight loss values (*Allanblackia*, Fig. 2). The degradation at this stage between *Allanblackia* spp. and shea butter is comparable. Palm kernel oil showed a much faster rate of degradation with higher percentage weight loss than both *Allanblackia* spp. and shea butter in the first and second degradation levels with a total weight loss of 93.84%. It was speculated that the number of the chemical compounds in palm kernel oil may be less than *Allanblackia* spp. and shea butter oils. A peak observed for *Allanblackia* spp. oil at approximately 37 °C before degradation of the product might be due to the re-organization or re-crystallization of *Allanblackia* spp. oil components as observed in the DSC thermogram just before melting of the oil. This was unique for *Allanblackia* spp. oil as it was not exhibited by either shea butter or palm kernel oil. Edible oils (olive oil and milk fat) can take in oxygen during TGA with attendant increase in weight (due to oxidation) [19]. In TGA, oils are not stable at the temperatures where they gain weight. Shea butter and palm kernel oils did not exhibit any weight gain during melting and/or crystallization during TGA measurement. These oils therefore have oxidative stability within this temperature region. On the other hand, *Allanblackia* spp. oil showed a small sharp peak around 37 °C accompanied by weight gain. This could be ascribed to the effect of oxidative instability and re-organization of the chemical bonds before melting as described earlier. There was no thermal degradation within the melting/crystallization tempera-ture ranges of the oils. Consequently, within the melting/crystallization temperature ranges, all the oils were thermally stable and hence did not decompose or degrade at these temperature ranges.

3.4. FTIR spectroscopy of oil samples

A summary of key peaks in the FTIR spectra of all the oils is given in Table 2. FTIR spectra of *Allanblackia* spp. oil (Fig. 3) showed a medium shoulder peak at 3008 cm^{-1}. This peak was ascribed to a C—H stretching vibration of cis-double bond (=C). The intense peaks observed at 2921 cm^{-1} and 2852 cm^{-1} were due to asymmetric and symmetric stretching vibrations of aliphatic CH$_2$ groups respectively. The intense single band at 1744 cm^{-1} was due to the stretching vibration of the ester carbonyl functional group of the triglyceride oil. The small shoulder peak observed at 1641 cm^{-1} was also due to the C=C stretching vibration of cis olefins. The presence of the shoulder peak at 3008 cm^{-1} and, also the small peak at 1641 cm^{-1} indicated that *Allanblackia* spp. oil contained cis-olefenic carbons, and hence the oleic, linoleic and linolenic fatty acid groups might be present [20,21].

The sharp medium size peak at 1465 cm^{-1} was ascribed to the bending (scissoring) vibrations of the CH$_2$ and CH$_3$ aliphatic groups. The weak shoulder band at 1421 cm^{-1} was attributed to the bending (rocking) vibration of the cis (=C—H) group. The medium sharp 1377 cm^{-1} peak was due to the bending vibrations of CH$_3$ groups, while the medium size peak at 1240 cm^{-1} and the strong peak at 1159 cm^{-1} were due to the stretching vibrations of the C—O bond of the ester group as well as the bending vibration of the —CH$_2$ group. The various observed peaks at 1116 cm^{-1},

1097 cm^{-1} and 1026 cm^{-1}, were all due to the presence of the C—O stretching bond in the triglyceride of the *Allanblackia* spp. oil.

The peak at 721 cm^{-1} was due to the overlapping of the CH$_2$ rocking vibration and the out-of-plane vibrations of the cis-di-substituted olefins. The absence of a broad band beyond the 3000 cm^{-1} region indicated the absence of —OH group in the structure of *Allanblackia* spp. oil [20–22].

Shea butter oil showed a weak shoulder peak at 1421 cm^{-1} due to the bending (rocking) vibration of the cis olefinic group, while the peak at 1377 cm^{-1} was ascribed to bending vibration of the CH$_3$ group (Table 2). Also, shea butter showed a shoulder peak at 1240 cm^{-1} and a major peak at 1161 cm^{-1}. These were due to the stretching vibrations of the C—O ester bond. The observed peaks at 1117 cm^{-1}, 1103 cm^{-1}, are all due to the presence of the C—O stretching bond in the triglyceride of the shea butter oil. No hydroxyl group was observed beyond 3008 cm^{-1} for the shea butter just like the *Allanblackia* spp. However, overlapping CH$_2$ rocking vibration and the out of plane vibration (721 cm^{-1}) of the cis-di-substituted olefins were observed.

The FTIR spectra of palm kernel oil (Table 2) showed no shoulder peak at the 3008 cm^{-1} position as compared to the spectra of the other two oils. This was due to the absence of the cis olefinic C—H stretching vibration bond (=C—H). The asymmetric and symmetric stretching vibrations of the aliphatic CH$_2$ group were present at 2921 cm^{-1} and 2852 cm^{-1} as in the other oil samples. Also, palm kernel oil showed a small unresolved peak at 2953 cm^{-1} which was ascribed to asymmetric vibration of the aliphatic CH$_3$ group. A strong single carbonyl ester peak occurred at 1742 cm^{-1}, a little lower in wave number shift than for *Allanblackia* spp. and shea butter oil (1744 cm^{-1}) (Table 2). A small peak at 1641 cm^{-1} for *Allanblackia* spp., which was a minor peak in shea butter oil, was absent in palm kernel oil. This peak was attributed to olefinic C=C. The peak at 1466 cm^{-1} was due to the bending vibrations of the CH$_2$ and CH$_3$ aliphatic groups. The peaks at 1421 cm^{-1} and 1377 cm^{-1} were all like that in the other oils. The peak at 1240 cm^{-1} for both *Allanblackia* spp. and shea butter oil were ascribed to stretching vibrations of the C—O ester group shifted to 1229 cm^{-1} in palm kernel oil. Similarly, the C—O ester vibration peak at 1155 cm^{-1} was prominent for palm kernel oil and occurred at higher wave numbers in *Allanblackia* spp. (1159 cm^{-1}) and shea butter (1161 cm^{-1}) respectively. A double peak observed by both *Allanblackia* spp. (1116 cm^{-1}, 1097 cm^{-1}) and shea butter (1117 cm^{-1}, 1103 cm^{-1}) occurred as a single peak for palm kernel oil at 1111 cm^{-1}. These peaks were ascribed to C—O stretching vibrations. There were other peaks observed at 965 cm^{-1} and 888 cm^{-1}. The peak at 721 cm^{-1} was due to the overlapping of the CH$_2$ rocking vibration [22,23].

The absence of peaks around 3004-3008 cm^{-1} and 1640-1641 cm^{-1} in palm kernel oil confirmed the absence of cis-olefinic double bonds in palm kernel oil. Even though a small peak was observed around 2954 cm^{-1} for all the oils, palm kernel oil spectra was more discernable than that of *Allanblackia* spp. and shea butter (Fig. 3) and was due to an asymmetric vibration shoulder of the aliphatic CH$_3$ group. The absence of the double bond might have contributed to the increase the intensity of the peak for the palm kernel oil. The latter peaks around 1111 cm^{-1}, 1155 cm^{-1} and

Table 2
Summary of key peaks in the overlaid FTIR spectra of oil samples.

Sample	Allanblackia	Shea butter	Palm kernel oil
Peaks Observed/cm^{-1}	3008, 2921, 2852, 1744, 1465, 1421, 1377, 1260, 1240, 1159, 1116, 1097, 1026, 866, 803, 721	3008, 2922, 2853, 1744, 1465, 1421, 1377, 1240, 1161, 1117, 1103, 877, 721	2953, 2921, 2852, 1742, 1466, 1421, 1377, 1229, 1155, 1111, 965, 888, 721
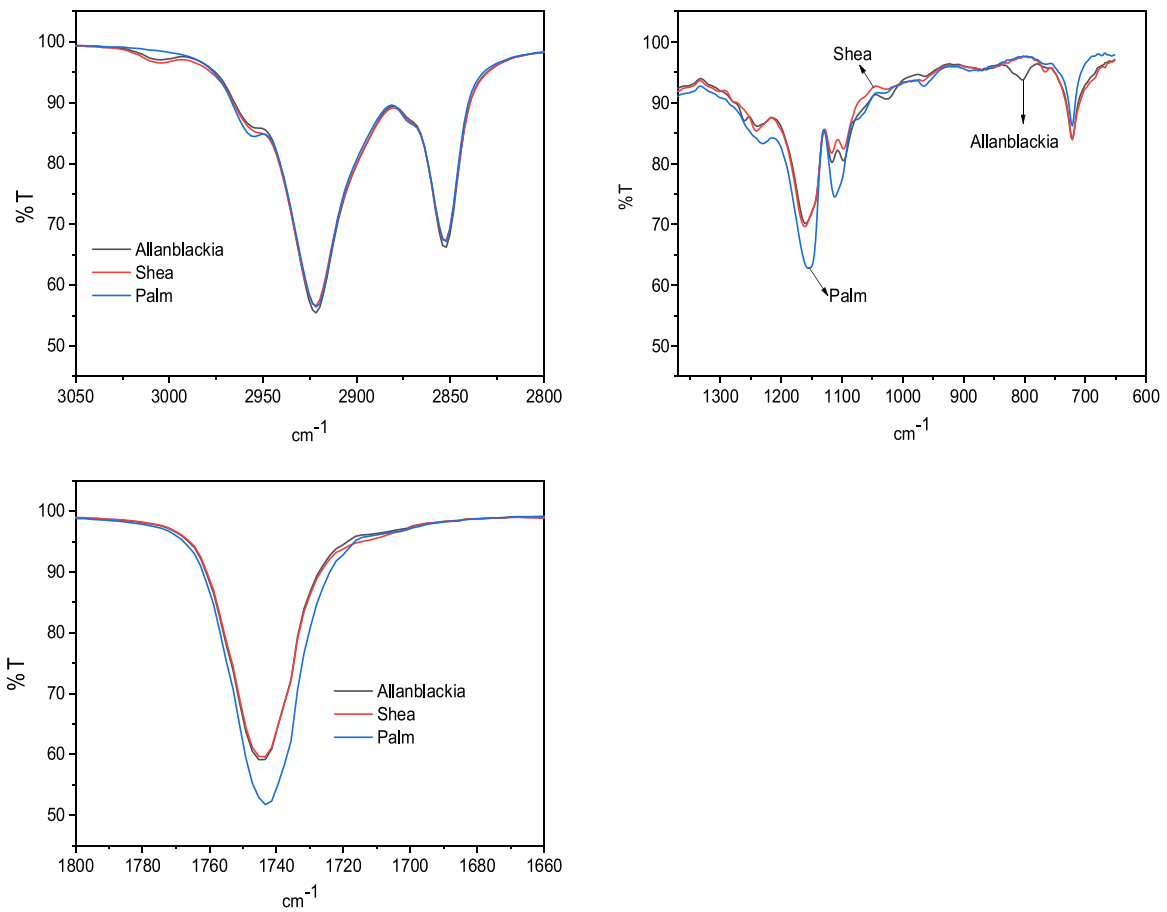
Fig. 3. Key peaks of the overlaid FTIR spectra of the three oils in the 2800 cm^{-1}-3051 cm^{-1} region, 700 cm^{-1} and 1371 cm^{-1} region, and at 1743 cm^{-1}.

1743 cm^{-1} (Fig. 3), all exhibited higher intensities than for *Allanblackia* spp. and shea butter.

Fatty acid profile of the oils is presented in Table 3. The fatty acids present in the oils and their combinations will greatly affect the melting and crystallization profile of the oil and hence their use as PCMs for energy storage. The major fatty acids present in *Allanblackia* spp. oil and shea butter were stearic and oleic acids. *Allanblackia* spp. oil contained more of stearic acid (45–58 %) than shea butter (20–50 %) while their oleic acid contents were comparable with *Allanblackia* spp. with a value of 40–51 % and 40–60 % for shea butter. Shea butter melting characteristics will be impacted by the presence of linoleic acid, which is unsaturated with a value of 3–11 % while *Allanblackia* spp. had less than 1% linoleic acid. Again, the palmitic acid (which is a saturated fatty acid with a lower molecular weight than stearic acid and oleic acid) content of shea butter was higher (2–9 %) than that of *Allanblackia*

spp. oil (<2%). Palm kernel oil had lauric acid as the major fatty acid present with appreciable amounts of oleic acid (10–23 %), myristic acid (14–20 %) and palmitic acid (7–11 %).

3.5. Thermo-physical and chemical characteristics of oils after thermal cycling

3.5.1. The DSC thermograms of oils after thermal cycling

All the samples were thermally cycled a thousand (1000) times to determine their thermal reliability as well as their chemical stability. Changes in their enthalpy values and the shape of the curves were determined via their DSC thermograms.

Changes in DSC thermogram of *Allanblackia* spp. oil after thermal cycling for a thousand times are shown in Fig. 4. The re-crystallization peak of the oil before its melting was not observed after thermal cycling. A small endothermic peak was observed

Table 3
Fatty acid characteristics of *Allanblackia* spp. oil, shea butter and palm kernel oil.

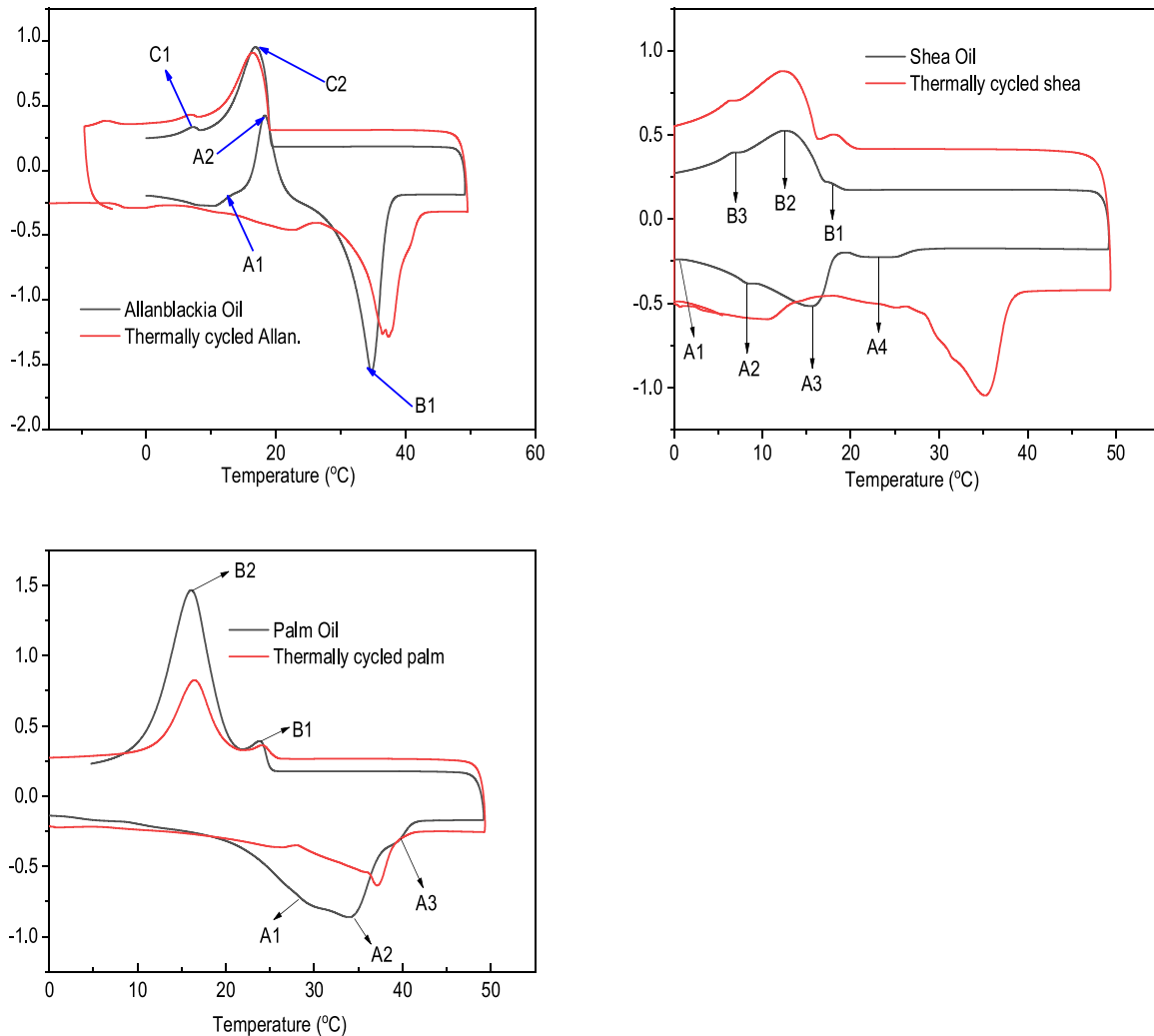| Fatty Acid (%)	Arachidic Acid (C20:0)	Stearic Acid (C18:0)	Oleic Acid (C18:1)	Linoleic Acid (C18:2)	Linolenic Acid (C18:3)	Palmitic Acid (C16:0)	Myristic Acid (C14:0)	Lauric Acid (C12:0)
Allanblackia Oil[a]	<1	45-58	40-51	<1	<1	<2	<1	<1
Shea Butter[b]	<1	20-50	40-60	3-11	<1	2-9	<1	<1
Palm Kernel Oil[c]	<1	1-3	10-23	<1	<1	7-11	14-20	41-55

[a] [8].
[b] [24].
[c] [25].

Fig. 4. Overlaid DSC thermogram for non- and thermally cycled oils.

before the major melting peak. The enthalpy value before thermal cycling was 80.53 J/g while that after thermal cycling, was reduced to 66.81 J/g, i.e., a reduction of 13.72 J/g. This is consistent with the work of Sharma et al. [26,27]. At the same time, the onset temperature before thermal cycling increased from 30.50 °C to 32.77 °C after thermal cycling. There was also a shift in the peaks toward a higher temperature for the thermally cycled oil to 37.37 °C from 34.74 °C (before thermal cycling). Additionally, the shape of the exothermic curve did not change much. However, enthalpy values dropped for the thermally cycled *Allanblackia* spp. oil (31.83 J/g) from the original value of 38.92 J/g.

Shea butter oil subjected to thermal cycling also exhibited changes in enthalpy values and shape of the curves (Fig. 4). A broad peak was observed in the range of -2.03 °C - 15.64 °C. This was absent or shown as a very small peak in the original sample. The major endothermic peak in the thermally cycled shea butter oil increased to 41.56 J/g from the value of 29.85 J/g. Again, this peak was broad due to the difference in the onset and peak temperature of 7.19 °C, and hence cannot be considered as latent energy. The crystallization curve did not exhibit much change in shape even though there was a large difference in enthalpy values. Before thermal cycling, the enthalpy value for the major peak was 31.35 J/g, and after thermal cycling increased to 48.21 J/g. The range was high and hence the peak was broad and again not suitable for latent heat considerations.

From the curves in Fig. 4, the melting curve for palm kernel oil exhibited a drop in enthalpy value after thermal cycling and it was still not a latent energy. The crystallization curve which was a latent heat before thermal cycling exhibited a drastic drop in enthalpy from 95.55 J/g to 35.35 J/g after thermal cycling. Such a large drop in enthalpy value was indicative of the instability of palm kernel oil.

3.5.2. TGA thermogram of thermally cycled oils

The TGA thermogram of *Allanblackia* spp. oil thermally cycled a thousand times differed from the non-thermally cycled oil (Table 4). Around 200–220 °C, all the samples began to lose weight. *Allanblackia* spp. oil showed a change in its TGA thermogram. The original oil sample exhibited 5 steps in its degradation while the thermally cycled oil gave 4 steps. Additionally, there was a drastic change in the degradation of the first step for *Allanblackia* spp. oil (Table 4). In the first degradation step, the original oil lost 59.51% of its weight in contrast to the thermally cycled oil sample (72.71%). For the non-thermally cycled *Allanblackia* spp. oil, extent of degradation in the first and second steps in the original *Allanblackia* spp. oil sample was like the first step of the thermally cycled oil. For shea butter, the same 4-step degradation in the non-thermally cycled oil was seen in the thermally cycled sample. Palm kernel oil exhibited the least change during thermal cycling. Even though there was a

Table 4
TGA profile of non- and thermally cycled oils.

Sample	Degradation Interval/°C	Step	Weight Loss/ %	State of Sample
Allanblackia	177.85-345.26	Step 1	59.51	Before Thermal Cycling
	345.26-401.11	Step 2	14.86	
	401.11-448.34	Step 3	13.01	
	448.34-516.10	Step 4	9.69	
	516.10-552.56	Step 5	2.88	
Shea Butter	219.51-349.79	Step 1	64.24	
	349.79-407.56	Step 2	12.36	
	407.56-467.60	Step 3	11.02	
	467.60-549.16	Step 4	12.22	
Palm Kernel Oil	226.31-315.80	Step 1	72.07	
	315.80-426.82	Step 2	21.77	
	426.82-533.30	Step 3	5.98	
TC Allanblackia	200.00-367.03	Step 1	72.71	After Thermal Cycling
	367.03-417.79	Step 2	8.24	
	417.79-499.63	Step 3	10.21	
	499.63-537.13	Step 4	8.19	
TC Shea Butter	220.00-355.73	Step 1	67.03	
	355.73-426.06	Step 2	13.52	
	426.06-496.99	Step 3	8.47	
	496.99-537.79	Step 4	11.51	
TC Palm Kernel Oil	225.00-330.33	Step 1	70.20	
	330.33-476.42	Step 2	25.99	
	476.42-526.64	Step 3	4.37	

degradation during thermal cycling process, there was no weight loss within the temperature of interest (i.e. the temperature at which the samples change phase). This is an indication that the samples did not degrade at the temperature of melting/crystallization (region of interest, for Allanblackia, melting: 30.50–34.74 °C, crystallization: 17.02–19.16 °C; shea butter, melting: 4.27–15.75 °C, crystallization: 13.10–17.24 °C; palm kernel oil, melting: 20.60–34.14 °C, crystallization: 16.10–20.32 °C).

Thus, in the region of interest (see above), there was no degradation or weight loss of the sample even though at higher temperatures, the TGA profile changed slightly. All the samples can be termed to be thermally stable and reliable within the region of interest.

3.5.3. Chemical stability of thermally cycled oils

FTIR spectra of shea butter and palm kernel oil exhibited no change after thermal cycling for 1000 times, an indication of the chemical stability of oils (spectra not shown). For Allanblackia, even though the peaks were the same, the intensities of the peaks for the thermally cycled oil within the range of 1404 and 758 cm^{-1} were reduced. The peaks did not disappear but were reduced after thermal cycling. The affected peaks in Allanblackia spp. occurred at 1261 cm^{-1}, 1116 cm^{-1}, 1098 cm^{-1}, 1023 cm^{-1} and 803-804 cm^{-1}. The peaks at 1116 cm^{-1}, 1098 cm^{-1} and 1023 cm^{-1} were all due to the C—O ester bond in the triglyceride. Since all the bonds were present but their intensities were reduced, the samples have not been degraded, but concentration has been affected.

4. Conclusions

The physical and chemical characteristics of fruit oils of three tropical/savannah woodland trees, Allanblackia spp. (A. parviflora), shea butter (V. paradoxa) and palm kernel oil (from the palm nut (Elaeis guineensis) fruit,) were determined to evaluate their use for potential thermal energy storage. The physico-chemical analytical methods included DSC, TGA and FTIR. DSC was used to determine whether the energy absorbed or released by the oils was high enough to be used for thermal energy storage, and, also whether it was latent heat energy. DSC determines both thermal energy storage properties and thermal reliability of the PCM. TGA was used to determine the thermal stability of oils. The FTIR spectroscopy was employed to characterize the functional groups of the oils before and after thermal cycles. Shea butter and palm kernel oils melt and/or crystallize over too wide a range of temperatures, exhibit polymorphism and therefore cannot be considered as candidates for PCM. In contrast, Allanblackia spp. oil exhibited melting and freezing cycles that was indicative of latent heats notwithstanding the decrease in latent heat after 1000 thermal cycles. The sudden increase in weight around the 37 °C point shown by TGA scans could be ascribed to oxidative instability. There was no degradation of Allanblackia spp. oils within the temperature of interest and confirmed its thermal stability in this temperature range. There was also a slight decrease in the FTIR peaks at 1260 cm^{-1}, 1116 cm^{-1}, 1097 cm^{-1}, 1023 cm^{-1} and 803 cm^{-1} which were attributed to C—O bonds in triglyceride. Most of these bonds were the C—O bond in the triglyceride of the oil, and due to the oxidative stability of the sample.

Of the oils evaluated in this study, Allanblackia spp. oil exhibited the potential for use as a PCM for latent energy storage. To increase oxidative stability, there is the need to further modify and or convert the oil to fatty acids and their corresponding esters.

Acknowledgements

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