American Journal of Food Science and Technology, 2015, Vol. 3, No. 4, 97-102
Available online at http://pubs.sciepub.com/ajfst/3/4/1

DOI:10.12691/ajfst-3-4-1

Some Physicochemical Characteristics and Storage Stability of Crude Palm Oils (*Elaeis guineensis* Jacq)

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Received July 14, 2015; Revised July 30, 2015; Accepted August 05, 2015

Abstract Oils constitute one of the essential components of balanced diet as good source of energy. The chemical and physical properties of oils are amongst the most important properties that determine the quality and help to describe the present condition of oils. The physicochemical characteristics and storage stability of crude palm oils producer traditionally and industrially in Cameroon were investigated and compared to reference oil manufactured by a leading manufacturing industry. The mean physicochemical parameters of crude palm oils (CPO) before storage were: moisture content (1.15 and 0.25%), free fatty acid (6.49% and 9.44%), peroxide (4.86 meq/kg and 5.70 meq/kg) respectively for traditional and industrial oils, and melting point (33°C). All the physicochemical parameters determined were significantly ($p<0.001$) higher than those determined for reference. Storage stability of both oils under 30°C showed faster deterioration than when stored at 20°C. The mean free fatty acid values (oleic acid) obtained for both oils when exposed at 30°C and 20°C respectively throughout the period of study (3 months) were 11.08% and 8.03% for industrial oil and 16.50% and 15.19% for traditional oil. Similarly, the mean peroxide values were 10.36 and 9.34 meq/Kg for industrial oil and 11.33 and 10.19 meq/Kg. The physicochemical properties of the CPO indicated that it is edible, drying and suggested its suitability for industrial purposes as well as the nutritional potentials, which could serve as an alternative food ingredient for unsaturated vegetable oil.

Keywords: *crude palm oils, storage, traditional, industrial, physicochemical parameters*

Cite This Article: Goudoum Augustin, Makambeu Ndomche Anne, Abdou Bouba Armand, and Mbofung Carl Moses, "Some Physicochemical Characteristics and Storage Stability of Crude Palm Oils (*Elaeis guineensis* Jacq)." *American Journal of Food Science and Technology*, vol. 3, no. 4 (2015): 97-102 doi: 10.12691/ajfst-3-4-1.

1. Introduction

Fats and oils whether the source is animal, vegetable or marine in origin represent the highest source of energy per unit weight that man can consume. Apart from being a source of reserved energy, fats deposit insulates the body against loss of heat and protects vital organs against mechanical injury [6]. They are important food source for man, and are also extensively used for nutritional, cosmetic, drug dispersant in therapeutics and industrial purposes and are used for supplying essential fatty acids such as linoleic and arachidonic acids [23].

In Cameroon, palm oil (*Elaeis guineensis*) meets 80% of total edible oil needs and it is estimated that 30% of crude palm oil (CPO) production is provided by none industrial oil mills. The quality is associated with the method of processing. In Cameroon, there are three types of oil palm processors, traditional (mostly manual), semi-mechanized and mechanized processors [18]. To a larger extent, smallholder/traditional processor dominate the sector accounting about 80% [20]. Smallholder processors maintain low level of hygiene in the processing mills [16,21]. These have resulted to low quality of CPO. Authors have reported the physicochemical and microbiological properties of CPO processed traditionally to be of poor quality. The semi-mechanized processor share about 50% of smallholder characteristics. The major processing activities irrespective of kind of processing that could affect the quality of CPO produced include bruises during transportation, fermentation prior to threshing, clarification and storage [14,19].

However, the consumption of CPO can also be detrimental to human beings, as CPO contains some components which are likely to enhance numerous reactions (hydrolysis, oxidation, etc.) involved in the degradation of this product. Moreover, these degradation reactions can also be initiated and/or accentuated by poor transportation and storage conditions [27] of the product as it is generally the case among small holders. The most effective degradation process of CPO is acidification which was already mentioned by Desassis in 1957 [18].

Previous studies tend to demonstrate that, there was a problem with the consumption of CPO with respect to food safety. The effect of processing methods and storage time on some physicochemical parameters of Cameroonian CPO was assayed. Based on the determination of these physicochemical parameters studies by Ngando et al. [17], CPO from small holders' extraction sites was of lesser quality as compared to that from industrial oil mills regarding food safety. Considering the fact that about 30%

of Cameroon's national production of CPO is provided by small holders, one can assume that the quality of this product which is freely available in local markets is subject to doubt.

The present study aimed to assess the storage quality and stability (regarding food safety) of CPO available producer by traditional and industrial method, as well as the physicochemical characteristics. For this purpose, the physicochemical parameters were chosen: free fatty acid, deterioration of bleachability index, moisture content, peroxide value and melting point. We decided to use them for our study as they were routinely used worldwide for the assessment of the quality of cooking oils.

2. Materials and Mehods

The monitoring of physico-chemical characteristics of CPO was made at two different temperatures during three months for three different samples.

2.1. Sample Collection

The oil samples were collected from the tanks after delivery by a partnership instead. Three types of oil were used for testing:

- Industrial oil representing the one that was extracted using an industrial process, delivered by a local company (Sample 1);
- Artisanal oil that is the one generally produced by small producers. The extraction is mostly done traditionally with rudimentary equipment (Sample 2).
- Palm oil stored in a tank that is an imported industrial oil in Cameroon, which is the reference (Sample 3);

Samples of these oils were collected, filtered to rid them of any impurities and stored at 20°C in small galvanized tanks (diameter: 20 cm, high: 40 cm, thickness: 0.6 cm and total volume 10 liters).

2.2. Physico-chemical Analysis of Palm Oil

The three samples of palm oil were analyzed before storage to determine their baseline characteristics. The various parameters tested and monitored throughout the storage are as follows: free fatty acid (FFA); deterioration of bleachability index (DOBI); Moisture content; the melting point and the peroxide value.

2.3. Determination of Free Fatty Acid (FFA)

Estimation of the percentage free fatty acids as oleic acid was done, following the method of Pearson [22]. A mass of 2.5 grams of the sample was weighed into a conical flask, 50 mL of neutralizing solvent (ethyl alcohol) was carefully added to the weighed sample in the conical flask then the flask was placed on a hot plate at 40°C, swirled gently and titrated with standard potassium hydroxide (0.5M). Values were calculated using the formula:

$$\text{Free Fatty Acid} = 25.6 \times \text{Molarity of KOH} \times \text{Volume of KOH / mass of sample.}$$

Where 25.6 in the formular for FFA determination is equivalence factors (e) for palmitic acid; the predominant fatty acid in palm oil.

2.4. Deterioration of Bleachability Index

Deterioration of bleachability index (DOBI) was measured using the PORIM Test Methods (1995) [1]. About 0.1 g of oil was weighed and dissolved in up to 25 ml n-hexane (95%). The oil solution was placed in a 1cm cuvette and the absorbance reading was taken at 446 nm and 269 nm by using the spectrophotometer of mark PharmaSpec MODEL UV-1700. DOBI value is defined as the ratio of the spectrophotometric absorbance at 446 nm to 269 nm.

2.5. Determination of Moisture

The moisture content was determined using AFNOR [2] method. A mass of 10grams of thoroughly mixed POME sample was weighed into a known mass of clean Petri dish which had been previously dried and cooled in a desiccator. It was placed in the oven for four (4) hours, allowed to cool to room temperature in a desiccator for 45mins and further weighed. This was repeated till a constant weight was obtained. The moisture and volatile matter content was expressed in percentage by mass using the formula:

$$\% \text{ Moisture and Volatile content} = (\text{Mb} - \text{Md} / \text{Mb} - \text{M}) \times 100$$

Where M=Mass (g) of Petri dish
Mb = Mass (g) of Petri dish + sample
Md = Mass (g) of Petri dish + test sample after drying.

2.6. Determination of Melting Point

The melting point was determined using AOCSCc 3-25 [5] method. Capillary tubes were inserted into the blended oil samples to obtain a 10±2 mm long columns of oil sample, the capillary tubes were then sealed at one end using a Bunsen flame. The capillary tubes with the oil sample were kept in a refrigerator for three days during which the oil became solidified. With the help of a thread, the capillary tube with the sample was tie to a thermometer and inserted into a water bath at 30°C. The temperature at which the oil began to rise up in the tube was recorded as the melting point.

2.7. Peroxide Value Determination

The peroxide value was determined by titrating chloroform/glacial acetic acid/potassium iodide solution of the oil with an aqueous solution of sodium thiosulphate using starch as indicator [3]. About 10 g of oil was weighed into the 250 mL conical flask. A mixture of glacial acetic acid and trichloromethane chloroform (30 mL) was added in a ratio of 3: 2. 0.5 mL of saturated potassium iodide solution was also added. The mixture was properly shaken. 30 mL of water was added. The solution was filtrated with 0.01M sodium thiosulphate, while slowly adding the titrant with a continuous shaking until a yellow colour is shown. Approximately 5 mL of starch indicator was added to the titration process while shaking vigorously until a blue-black colour is discharged. A blank sample devoid of CPO was also analyzed using the same procedure. The peroxide value is expressed mathematically as follows:

Peroxide value (Meq Peroxide/kg) = (S – B) x M x 1000/Sample weight

Where S = Sample titrated

B = Blank

M = Molarity of sodium thiosulphate.

2.8. Statistical Analysis

The collected data were processed and analyzed with the XLSTAT software Version 2013. This software has permitted a variance analysis to compare the results obtained from the different treatments. Differences were considered significant from p< 0.05. The Beauvais-Pearson test was used to assess the degree of linear dependence amongst the various parameters assessed.

3. Result and Discussion

3.1. Physicochemical Characteristics of CPO Sample before Storage

The results of physicochemical properties before storage period of the three studied CPO oils obtained by different methods are presented in the Table 1.

Table 1. Physicochemical qualities of crude palm oil of three samples before storage.

	FFA (%)	DOBI	MIV(%)	MP (°C)	PV
Sample 1	6.49± 0.011^{a}	1.59± 0.005^{a}	1.15± 0,08^{a}	33± 0.5^{a}	4.86± 0.013^{a}
Sample 2	9.44± 0.023^{c}	2.47± 0.020^{b}	0.25± 0,023^{c}	33± 1^{a}	5.70± 0.015^{c}
Sample 3	4.46± 0.021^{b}	2.43± 0.010^{b}	0.12± 0,005^{b}	31± 0.5^{b}	2.52± 0.026^{b}

Averages followed by the same letter in the same column are not different significantly with P < 0.05 (Test of Duncan).
FFA : Free Fatty Acid ; DOBI : bleachability index ; MIV : moisture contents ; MP : melting point; PV : peroxide values

3.2. Evolution of the Free Fatty Acid during the Storage Period

Results of the shelf life of the CPO analyzed presented in Table 2 revealed variations in the different physicochemical properties study at two temperatures.

This table shows that the free fatty acid of CPO samples change significantly (p <0.001) during each month for all stored samples. For sample 1, the FFA increased from 6.49 to 11.08% and from 6.49 to 10.12%, respectively for 30°C and 20°C temperatures after three months of storage. For sample 2, the FFA pass from 9.42 to 16.50% and from 9.42 to 15.19% respectively for 30 ° C and 20°C. With regard to sample 3, the FFA increased from 4.46 to 9.58% at 30°C and 4.46 from 8.03% at 20°C.

Table 2. Storage stability of free fatty acid of three crude palm oils stored under different temperature

	Storage at 30°C			Storage at 20°C		
Storage period (month)	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 1**	**Sample 2**	**Sample 3**
0	6.49±0.011^{a}	9.42±0.023^{a}	4.46 ±0.021^{a}	6.49±0.011^{a}	9.42±0.023^{a}	4.46 ±0.021^{a}
1	8.93±0.013^{b}	12.05± 0.021^{b}	6.05±0.024^{b}	7.25±0.025^{b}	11.80±0.025^{b}	5.25±0.014^{b}
2	10.18±0.021^{c}	14.10±0.015^{c}	7.98±0.016^{c}	9.06±0.020^{c}	13.68±0.015^{c}	6.55±0.022^{c}
3	11.08 ±0.015^{d}	16.50±0.022^{d}	9.58 ±0.021^{d}	10.12±0.015^{d}	15.19±0.015^{d}	8.03±0.016^{d}

Averages followed by the same letter in the same column are not different significantly with P < 0.05 (Test of Duncan).

3.3. Evolution of the Deterioration of Bleach Ability Index Acid during the Storage Period

The Table 3, shows that the DOBI of CPO samples change significantly during each month for all stored samples (p <0.001) at 30 and 20°C.

Table 3. Storage stability of the DOBI of three crude palm oils stored under different temperature

	Storage at 30°C			Storage at 20°C		
Storage period (month)	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 1**	**Sample 2**	**Sample 3**
0	1.59±0.005^{a}	2.47±0.020^{a}	2.43±0.010^{a}	1.59±0.005^{a}	2.47±0.020^{a}	2.43±0.010^{a}
1	1.22±0.005^{b}	1.68 ±0.057^{b}	1.64±0.020^{b}	1.43±0.01^{b}	1.96±0.01^{b}	1.98±0.013^{b}
2	1.02±0.016^{c}	1.41±0.015^{c}	1.39±0.015^{c}	1.21±0.012^{c}	1.70±0.013^{c}	1.66±0.005^{c}
3	0.96±0.025^{c}	1.12±0.020^{d}	1.02±0.016^{d}	1.11±0.010^{d}	1.43±0.009^{d}	1.32±0.021^{d}

Averages followed by the same letter in the same column are not different significantly with P < 0.05 (Test of Duncan).

The CPO process industrially and traditionally exposed at 30°C for two month at, DOBI values decrease from 1.59 to 1.02 and 2.47 to 1.41 respectively and the values decrease to 0.96 and 1.12 respectively after three months. DOBI values for CPO process industrially stored at 20°C drop from 1.59 to 1.43 in the first month and to 1.11 in the third month. Similarly, the DOBI values for CPO process traditionally drop from 2.47 to 1.96 in the first month and recorded 1.43 in the third month. DOBI values between CPO stored at 30 and 20°C showed significant (p<0.001) difference.

3.4. Evolution of the Peroxide Index during the Storage Period

The Table 4, shows that the peroxide values of samples change significantly during each month for all stored samples (p <0.001) at 30 and 20°C.

The initial PV was seen to be higher in the CPO process industrially and traditionally compared with the reference (sample 3) at two temperatures. This showed the relative oxygen uptake by the three oils under study. At the beginning of the experiment a peroxide value (PV) for sample 2 exposed to ambiance temperature (30°C) was 5.70 meq/kg and after two months the value rose to 9.23 meq/kg and further to 11.33 meq/kg after three months.

Table 4. Storage stability of peroxide values of three crude palm oils stored under different temperature (meq/kg).

	Storage at 30°C			Storage at 20°C		
Storage period (month)	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 1**	**Sample 2**	**Sample 3**
0	4.86±0.013^{a}	5.70±0.015^{a}	2.52±0.026^{a}	4.86±0.013^{a}	5.70±0.015^{a}	2.52±0.026^{a}
1	6.32±0.021^{b}	7.14±0.015^{b}	3.70±0.024^{b}	5.54±0.037^{b}	6.75±0.016^{b}	3.85 ±0.022^{b}
2	8.24±0.033^{c}	9.23±0.032^{c}	5.69±0.011^{c}	7.39±0.021^{c}	8.12±0.023^{c}	5.28±0.025^{c}
3	10.36±0.03^{d}	11.33±0.015^{d}	8.20±0.030^{d}	9.34±0.020^{d}	10.19±0.26^{d}	7.02 ±0.012^{d}

Averages followed by the same letter in the same column are not different significantly with P < 0.05 (Test of Duncan).

The PV for CPO process industrially under the same condition as above rose from 4.86 meq/kg to 8.24 meq /kg and then recorded 10.36 meq/kg after three months. There is a significantly (p<0.001) higher difference between the three CPO.

PV for the CPO stored at 20°C did not show such a sharp increase after the first and second month of storage. During the first month, PV for sample 1 increased from 4.86 meq/kg to 5.54 meq/kg and increased further to 9.34 meq/kg two months later. That of sample 2 increased from 5.70 meq/kg to 6.75 meq/kg and in the next months recorded 10.19 meq/kg. Though there was a progressive increment in PV for the oils at the ambiance temperature up to three months of storage. The overall quality of the CPO samples assessed within this study was quite good regarding this parameter, as all the forty samples had PV below the 15 meq/kg maximal limit for cold pressed and virgin oils [8].

3.5. Evolution of the Melting Point during the Storage Period

The Table 5, shows that the melting point values of samples change significantly (p <0.01) during each month for all stored samples at 30 and 20°C.

Table 5. Storage evolution of meting point values of three crude palm oils stored under different temperature

	Storage at 30°C			Storage at 20°C		
Storage period (month)	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 1**	**Sample 2**	**Sample 3**
0	33.83±0.28^{a}	33.00±0.57^{a}	32.16±0.28^{a}	33.83±0.28^{a}	33.00±0.57^{a}	32.16±0.28^{a}
1	32.00±0.00^{b}	32.00±0.57^{b}	31.33±0.57^{b}	33.00±0.57^{b}	33.00±0.50^{a}	32.16±0.28^{a}
2	32.16±0.28^{b}	31.16±0.28^{c}	30.00±0.00^{c}	31.00±0.00^{c}	31.00±0.057^{b}	31.16±0.28^{b}
3	31.33±0.57^{c}	30.00±0.00^{d}	29.16±0.28^{d}	30.5±0.57^{c}	28.00±0.57^{c}	30.00± 0.00^{c}

Averages followed by the same letter in the same column are not different significantly with P < 0.05 (Test of Duncan).

The CPO process industrially and traditionally exposed at 30°C for two month at 30°C, melting point values decrease from 33.83 to 32.16°C and 33.00 to 31.16°C respectively and the values decrease to 31.33 and 30.00°C respectively after three months.

Melting point values for CPO process industrially stored at 20°C drop from 33.83 to 33.00 in the first month and to 30.50°C in the third month. Similarly, the Melting point values for CPO process traditionally drop from 33.00 to 31.00°C in the first two months and recorded 28.00°C in the third month. Melting point values between CPO stored at 30 and 20°C showed significant (p<0.01) difference.

3.6. Correlation between Physicochemical Parameters of Different Crude Palm Oils during the Storage

In the optic to better elucidated the physicochemical phenomena proceeding within the palm oil samples during storage a correlation was established between the various physicochemical parameters (Table 6).

Table 6. Correlation between differents physicochemical parameters of crude palm oils during the storage

correlations	**Sample 1**	**Sample 2**	**Sample 3**
DOBI/ FFA	-0.901**	-0.912**	-0.907**
DOBI/ PV	-0.933**	-0.942**	-0.920**
FAA / PV	0.978**	0.960**	0.972**
Melting Point/PV	-0.854**	-0.844**	-0.823**
Melting point/DOBI	0.884**	0.901**	0.889**
Melting point /FFA	0.837**	0.840**	0.830**

** Signification at P< 0.01.

According to the results of correlation, there is a significant correlation (P < 0.01) between the physicochemical parameters. The correlation between the DOBI, FFA and the peroxide index is very significant (P< 0.01), but negative (- 0.933), so the DOBI decreases while the peroxide index and acidity increase. On the other hand the peroxide index and FFA increase simultaneously during storage (0.978). These correlations show that the

physicochemical parameters decreased proportionally one to another.

4. Discussion

Sample 1 representing the industrial oil produced and delivered by a local company was a month old. This could explain the high FFA which is consecutive to the degradation. DOBI value of this oil also shows that the degradation is already started. The moisture of the sample 1 was 1.15%, which is higher than the norm of 0.3%. This may due to the fact that during storage, there is accumulation of water at the bottom of the storage tank due to the difference in density between water and oil. This accumulation of water could lead to an increase in the moisture content of the oil contained in the bottom of the storage tank. This increase in humidity can cause different damage occurring during storage of the oil. Sample 2, which is represented by oil traditionally produced by small holders, has a high levels of free fatty acid (9.44%) and peroxide indices (5.70). These values are higher than those of the reference (sample 1) that are respectively ≤ 5 and ≤ 3 for these two parameters.

This evolution of chemical parameters could be due to several factors such as the presence of water, the presence of oxygen, the presence of enzymes, the presence of heavy metals, microorganisms and high temperatures [6,13]. In the case of our analysis, a significant difference was observed between the values obtained at 30°C of the obtained at 20°C. The hydrolytic changes though not predominant, indicated that the formation of free fatty acids increased with increasing time of storage. The significantly ($p<0.001$) higher difference between the oils stored at 30°C and at 20°C may be due to the effect of sunlight and temperature differences as increase in temperature increases the rate of oxidation [6].

Many studies have pointed out the presence of a very active endogenous lipase in the mesocarp of the fruit of the oil palm [16,18]. This lipase is activated in the fruit at maturity upon wounding and/or bruising and is responsible for the hydrolysis of triglycerides and the liberation of FFA. In order to limit the action of the lipase, fresh fruit bunches (FFB) must be processed rapidly after harvest. This is the case in industrial oil mills where the harvested FFB are generally steam sterilized rapidly or at the very worst less than two days after harvest so as to inactivate the lipase, thus limiting subsequent FFA accumulation in the resultant CPO [13,18].

The decrease DOBI translate into lower carotenoid rate depends on the oxidation products. This decrease can be influenced by several factors. In fact, carotenoids are located within the internal membranes of chloroplasts which they are surrounded by a double membrane [11]. These carotenoids are fat-soluble, very sensitive to heat, but susceptible to enzymatic oxidation, chemical and photochemical [7,26]. During storage these carotenoids oxidize and gives rise to oxidation products [27]. These oxidation products are difficult to remove during refining. In addition, during refining, they polymerize under the action of high temperatures and make the dark refined oil [25,26]. A crude palm oil with low DOBI value (≤ 1.5) is difficult to refine because of the presence of oxidation products which are difficult to remove during refining [11]. This may cause instability of the color of palm olein obtained from palm oil degraded.

PV is used to assess the quality of cooking oils and fats through the measurement of the amount of lipid peroxides and hydroperoxides formed during the initial stages of oxidative degradation and thus, estimate to which extent spoilage of the oil has advanced. This parameter was chosen for our study as it is routinely used during food security controls to assess the quality of cooking oils. However, these peroxides are very unstable transitory products, and the determination of PV might not necessarily provide a correct estimate of the level of peroxidation, as it gives accurate information on the amount of peroxides and hydroperoxides but not on the secondary oxidation products. From another point of view, the overall low PV of CPO samples in our study is in the nature of things, as this oil is known to have a high oxidative stability. Thanks to its fatty acid composition with a balanced ratio of polyunsaturated/saturated fatty acids (51:49 w/w), CPO is less susceptible to oxidation and is widely used for frying of food [15]. Beside these visible harmful effects on the sensory quality of the oil, peroxidation also makes the oil dangerous for human health, as the free radicals generated by this process are proven to be carcinogenic [10,12,24].

Previous study has demonstrated that oil acidification and peroxidation processes are significantly enhanced by high moisture content of CPO samples at the outset [17]. Analyses showed there were no differences amongst samples for the three parameters assessed regarding the size of the market or information provided by the vendor on the origin, thus strongly suggesting that the CPO (randomly) sampled in our study were probably all processed by smallholders, as the control sample from an industrial oil mill had moisture content far below the 0.2% maximal limit.

Several factors could explain the decrease of the melting point. Indeed according Dandjouma et al. [9], changes at the melting temperature of the oils could be explained by the hydrolysis of triglycerides and the progressive oxidation observed during storage. The gradual hydrolysis of triglycerides materialized by an increase of the acid value of the oils, releases free fatty acids which are preferred substrates from oxidation. This oxidation leads firstly to saturated fatty acids a high melting point and on the other hand the fatty acid short chain low melting point fatty acids after cleavage at the unsaturations. Indeed, during storage, edible oils undergo physical and chemical changes under the influence of factors such as light, heat, trace metals and water. These changes give rise to secondary products called oxidation products.

5. Conclusion

The quality assessment of CPO produced by semi-mechanized and traditional processor in Cameroon showed that physicochemical parameters such as FFA, moisture content, DOBI and Peroxide value were high. The poor physicochemical properties are indications of poor handling and processing methods. This constraint can be addressed by further processing the oil. Removal of

moisture through further processing could increase the quality of the oil.

Prior to the study, the physicochemical characteristics of the oil largely conformed to codex standards. Depending on the mode of storage, the physicochemical properties changed significantly with storage time. The highest changing property was that of peroxide in oils exposed at 30°C. Oils kept in tightly sealed containers and stored at 20°C exhibited little change.

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