Effect of frying on the rheological and chemical properties of palm oil and its blends

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Abstract The aim of this research was to determine the changes in the physicochemical properties of palm oil and its blends by FTIR and rheological measurements. Application of heat produces some chemical compounds as impurities and even toxic compounds in oils and fats that give absorbance at different region. FTIR spectra of pure palm olein shows an absorbance at 3002 cm^{-1} whereas other pure oils show maximum absorption at around 3007 cm^{-1} due to C-H stretching vibration of cis-double bond ($=\text{C-H}$). By blending of high unsaturated oils with palm olein, a clear shift of 3007 cm^{-1} band to 3005 cm^{-1} occurs. Viscosity of palm olein was found higher among all oils while it subsequently and substantially reduced by blending with other oils. Since it is a function of temperature, viscosity of pure oils and their blends decreases with the increase of temperature. The loss modulus (G''), for all oil blends before and after frying, in rheological experiment was found higher for all oils than the storage modulus (G'), therefore, the viscous property was found higher than elastic property of oils and blends. However, the critical stress for all oil blends was found higher than that of pure oils.

Keywords Palm olein · Oil blends · FTIR · Rheology

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Introduction

Vegetable oils are widely used in everyday food preparations. It provides us necessary vitamins, antioxidants and energy. It also works as a transporter of several vitamins to the body-cells (Kritchevsky 2008). Fats and oils are largely responsible for the pleasant creamy taste of foods; therefore, its physiological characteristic is important (Belitz et al. 2009). Frying causes oil to undergo a wide range of reactions, namely hydrolysis, oxidation, isomerization, and polymerization due to high temperature and absorption of water and oxygen (Go'mez-Alonso et al. 2003; Gloria and Aguilera 1998). The deteriorated oil has nutritional and toxicological implication on human health since the toxic substances may accumulate in oil through the food stuff fried in it; final products fried in deteriorated oil possess unpleasant taste, odor and texture (Tena et al. 2009). The oils upon repeated frying reach a certain stage that it can no longer be used and have to be discarded (Stevenson et al. 1984). Therefore, it is necessary to monitor the quality of oils after frying and to determine the functional, sensory, and nutritional quality changes through which it can be decided when the frying medium is no longer usable. Vegetable oils stability has been improved by blending with other oils and some of the blends were found better and stable than their original forms, specifically, on a study of palm oil and mustard oil blends (Chugh and Dhawan 2011). However, this oil blends are also subject to deterioration after a certain time of frying and storage. So this oil, on regular basis, should have to be checked to ensure its nutritional value and quality. In fact, chemical as well as physical properties are key factors in determining the application of oils and fats in food processing (Díaz Gamboa and Gioielli 2003). For this reason, the rapid, easy and fast IR spectroscopy has become an emerging technique for analyzing of edible oils due to its simple process of using (Yang et al. 2005). Moreover, the application of fourier transform infrared (FTIR) spectroscopy has been turned out to be a powerful technique in analyzing of

food, especially in oil and fats industries (Guillén and Cabo 2000). Besides, rheological measurements are useful since the behavioral and predictive information about different products and formulation can be determined by it (Wan Nik et al. 2005). The viscosity and flow are also important phenomenon though it has little influence in storage but it plays a significant role in frying of foods, since penetration of oil into the food stuff favoured by the viscosity of oil (Kim et al. 2010). Some literatures are available on rheology of different individual oils but, unfortunately, we have not found any record of such study on these aspects of different oil blends and comparison of results (Lioumbas et al. 2012; Santos et al. 2005; Wang and Briggs 2002). As blending of different oils are getting the attraction of many food industries nowadays, so this study will be a helpful for them to formulate their products.

The objective of this work was to speedy-evaluation of changes in the quality of the oil blends upon frying. Blending not only changes the chemical property of oil to some extent but also the saturation or unsaturation ratios of it, more specifically, the ratios of saturated and unsaturated fatty acids. Therefore, frying (or cooking) changes the quality of both the oils include in it and thus the physicochemical property of blends is a matter of interest for food industries.

Methodology

Oil samples

Pure and refined Palm oil as well as three other oil blenders were purchased from a local supermarket in Penang, Malaysia. Palm oil (PO) was blended with those three oils that are soybean (SO), sunflower (SF), canola (CO) to form a binary blend with each blender. However, another oil that is candlenut oil (Cnd) was extracted at lab by using supercritical CO₂ extraction. The extraction condition and characteristic of oil was reported earlier (Siddique et al. 2011). Blends were prepared by mixing of palm oil the oils from 10 % to 90 % w/w at 10 % interval. An electrical balance was used to weigh the two oils separately and the reading was taken near to 0.50 g. In a beaker the blend was stirred with the help of a magnetic stirrer for 30 min for a complete homogeneous mixture. The blends were covered with aluminum foil and were stores in the refrigerator below 4° C until the different tests were carried out.

Fish frying

Frying of fish was carried out by deep frying of 10 to 14 g of fish fillet (vacuum dried to reduce moisture) in 2.5 L of oil and their blends with the help of a deep fryer (FFA2001, Anvil, South Africa). At first oil was heated up to 200 °C and then the piece of fish was put into it. Frying was continued for 60 min

in three stages, 20 min for each frying time. Each time the piece of fish became yellowish red in colour and it stopped bubbling due to the cavity formed during demoiusturization. After frying oil samples were cooled to room temperature, sealed in a beaker and kept in refrigerator at -5 °C for further testing on it.

FTIR analysis

FTIR unit (AVATAR 360, Nicolet, U.S) was equipped with a deuterated triglycine sulphate (DTGS) as a detector and a KBr/Germanium as a beam splitter, interfaced to a computer operated under windows based and connected to OMNIC operating software system (E.S.P.5.1) was used for FTIR spectra acquisition. Automatic dehumidifier was used to diminish water vapor interface from the machine. A few drops of each sample were put onto the Attenuated Total reflectance (ATR) multibounce plate of crystal at controlled ambient temperature (25 °C).

All spectra were recorded from 4000 to 400 cm⁻¹ co-adding 32 interferograms with measurement accuracy in the frequency data at each measured point of 0.01 cm⁻¹, due to the laser internal reference of the instrument. To avoid high noise levels the spectra were collected at a resolution of 4 cm⁻¹ (Guillén and Cabo 2002). Each time this spectrum was subtracted from the background air spectrum. A new air spectrum was taken after every scan with sample (Rohman and Man 2010). The ATR plate was carefully cleaned with isopropanol and acetone and was dried with a soft tissue. The background spectrum of empty ATR plate was taken and it was verified by matching with the previous one. These spectra were recorded as absorbance values at each data point. After filling it with a sample it was assured that no air bubble was trapped onto the ATR in the sample. The software spectral library was used as reference to match the functional group of the spectra found for the samples.

Rheology

Rheological measurement was determined by using controlled-stressed AR 1000-N Rheometer (TA Instrument-UK) equipped with a temperature controller unit. The temperature was controlled by a Peltier system located in the base of the measurement geometry. The melted blend (80 °C) was applied on the base of the plate avoiding bubble formation and the superior plate was positioned on the sample surface using the auto-gap function of the rheometer software (1 mm).

Linear Viscoelastic Region (LVR) of the samples for temperature sweep step, frequency sweep step and temperature ramp were determined at 0 to 40 °C and at frequency of 1–100 Hz, shear stress of 1 Pas and shear rate of 0.1 to 500 S⁻¹ shear stress. A 4 cm cone plate (2 °) with a gap of 51 µm was used. About 1.5 mL of sample was loaded using a micropipette

on the rheometer plate for each run. As the shear and applied frequency could destroy the crystal network, after each run fresh sample was loaded. For temperature ramp, as the samples (oil blends) were crystallized at low temperature, with the automatic setup of temperature increase of 1 °C/min, data was recorded after the samples were melt. The storage modulus (G') and loss modulus (G'') were determined as a function of frequency within the LVR region for each sample.

Statistical analysis

The Microsoft Office Excel software was used to conduct the analysis. The frequency sweep graph of G' and G'' vs frequency as well as the standard deviation were plotted using MATLAB (version 7.11.0.548). All tests were conducted in triplicate, however the mean was considered and was reported.

Result and discussion

FTIR analysis

The importance of the IR spectroscopy in the identification of molecular structures originates from the possibility to assign some certain absorption bands related to the functional groups. In fats and oils, most of the peaks and shoulders are attributed to the functional groups (Bendini et al. 2007). Since triglycerides are the main component in oil and all types of oils consist of

Table 1 Evaluation of FTIR spectrum

1a. Region of hydrogen's stretching		
3009 cm ⁻¹	C-H stretching of <i>cis</i> double bond (=C-H)	
2922 cm ⁻¹ , 2855 cm ⁻¹	Symmetric and asymmetric stretching vibration of aliphatic CH ₂ group	
2962 cm ⁻¹ , 2872 cm ⁻¹	Symmetric and asymmetric stretching vibration shoulder of aliphatic CH ₃ group	
1b. Region of double bonds stretching		
1743 cm ⁻¹	Ester carbonyl functional group of the triglycerides	
1700 cm ⁻¹	Free fatty acids shoulder	
1654 cm ⁻¹	C=C stretching vibration of <i>cis</i> -olefins	
1c. Region of other bonds stretching		
1465 cm ⁻¹	Bending vibrations of the CH ₂ and CH ₃ aliphatic groups	
1418 cm ⁻¹	Rocking vibrations of CH bonds of <i>cis</i> -disubstituted olefins	
1397 cm ⁻¹	Bending in pale vibrations of CH <i>cis</i> -olefinic groups	
1377 cm ⁻¹	Bending vibrations of CH ₂ groups	
2. Fingerprint region		
1238 cm ⁻¹ , 1163 cm ⁻¹	Stretching vibration of the C-O ester groups	
723 cm ⁻¹	Overlapping of the CH ₂ rocking vibration and the out of plane vibration of <i>cis</i> -disubstituted olefins	

Guillén and Cabo 1997

almost same type of fatty acids therefore, the IR spectra shows typical characteristic absorption bands for all types of oils (Safar

Fig. 1 FTIR (Fourier transform infrared) Absorbance spectrum for the pure oils

Fig. 2 The shifting of band 3002 cm^{-1} to higher wave length in the oil blends due to blending with palm oil (high saturation)

et al. 1994). In this study the absorption spectra for pure oils found to show very identical results (Fig. 1) as well. The entire spectra obtained in this study for all oils and their blends apparently seem very identical due to their similar compositions. The oil blends after frying showed a slight difference in absorption bands and in its intensity at frequencies around at 3006 cm^{-1} , 2922 cm^{-1} , 1743 cm^{-1} , 1654 cm^{-1} and at 968 cm^{-1} . Table 1 indicates the functional groups at certain absorption.

FTIR spectra of palm olein and its blends show notable differences for the band at around 3006 cm^{-1} which is assigned to the C-H stretching vibration of the *cis*-double bond ($=\text{C-H}$). The exact position of the bands is a function

of oil composition and it shifts with the changes of fatty acids in oils (Vlachos et al. 2006). The values of frequency of non-oxidized blends vary from 3002 to 3007 cm^{-1} . For pure palm olein shows an absorbance at 3002 cm^{-1} whereas pure canola, sunflower, soybean and candlenut show maximum absorption in this region at around 3007 cm^{-1} . The observation is due to their composition, as palm olein contains a relatively higher amount of oleic acid while all other oils are rich in linoleic and linolenic acids. A similar result has been reported by Guillén and Cabo (1999) for oxidation of various edible oils (Guillén and Cabo 1999). With the blending of these high unsaturated oils in palm olein, a clear shift of 3007 cm^{-1} band to

Fig. 3 FTIR absorbance at 2922 cm^{-1} for 50:50 ratio of Plam oil with other blenders after frying (60 min)

3005 cm^{-1} occurs due to the reduced unsaturation in those blenders (Fig. 2). The absorption in this region for the oils varies for different oils and it also varies by a small proportion for blends upon mixing.

The absorption band at around 2922 cm^{-1} is due to the symmetric stretching vibration of the aliphatic groups. Pure palm olein and the rest of the oils give absorption at around 2922. cm^{-1} . However, the peak height for palm olein is higher than that of other oils due to the high values of saturated fatty acids. The 50:50 ratios of palm oil blends with other oils show a maximum absorbance at around 2922 cm^{-1} as well. After one hour of frying the blends of palm olein: canola oil shows a higher value of absorption than others (Fig. 3). This observation is consistent with the low IV (Iodine Value) in canola oil indicating the lost of mono unsaturated fatty acids in it. After being exposed to high temperature it lost some of those unsaturation and has comparatively lower IV. Since it has been showed that during a prolonged frying process, the fatty acid composition in oil undergoes modifications due to polymerization, as well as pyrolytic, hydrolytic and oxidative reactions also take place (Frankel 1998; Márquez-Ruiz and Dobarganes 2007). However, the researchers have stressed that the evaluation of the resistance to oxidation does not take into account the presence of natural antioxidants in oils (tocopherols and tocotrienols) nor the initial composition of fatty acids (Marco et al. 2007). The 2922 cm^{-1} and 2855 cm^{-1} bands are due to the symmetric stretching of CH_2 groups. It seems that the observation peak height for pure oils and blends of different ratios did not show any changes. It might be because of the main blender palm olein has higher saturation among the four other oils and upon blending with these oils, it essentially does not change the amount of fatty acids aliphatic methylene group, rather it affect on the changes of vinyl group.

The band, which appeared at approximately 1743 cm^{-1} is due to the ester carbonyl functional group of triglycerides. This frequency value remains practically unchanged for pure oils and its 50:50 blends after frying with an exception to palm olein: soybean 50:50 blend which shifted from 1743.78 cm^{-1} to a value of approximately 1742.34 cm^{-1} . It is also noted that the band at this region for 20:80 palm olein: soybean oil blend shows the similar characteristic which shifts by a small value to the low frequency level. This change could be associated with the overlapping of band ($\sim 1728 \text{ cm}^{-1}$) for the formation of aldehyde functional groups from oxidation and/or production of secondary oxidation products (Sanahuja et al. 2009). This observation is also in accordance with the result obtained from the peroxide value for blends in a previous study (Siddique et al. 2011). Moreover, these findings have been further consolidated by the results reported by Guillén and Cabo (2002).

At 1654 cm^{-1} region stretching vibration is due to *cis*-olefinic $\text{C}=\text{C}$ bonds. The intensity of the bands for pure oil

and their blend before and after frying apparently did not show any changes, but with close observation it shows a reducing trend of the peak height. Palm olein has a relatively lower absorbance with 0.041 whereas, other oils have approximately 0.045. After heating for one hour the 50:50 blends of PO: CO shows most reduced absorbance with 0.035 followed by PO: SF, PO: SO and PO: Cnd oil (i.e. 0.038, 0.039, and 0.042 respectively). However, all 20: 80 blends of palm oil with other oils after the same treatment show higher absorbance

Table 2 Viscosity of pure oil and their binary blends of different ratios at different temperature

Pure oils	Viscosity (cP)		
	23 °C	33 °C	43 °C
Palm olein	79.7	63.2	36.7
Soybean oil	61.1	38.6	29.3
Sunflower oil	62.0	44.0	30.3
Canola oil	67.1	53.1	32.4
Oil Blends			
Palm olein: Soybean oil			
10:90	60.8	42.5	30.1
20:80	62.1	44.1	30.6
30:70	63.9	44.5	33.7
40:60	68.1	46.6	32.6
50:50	69.1	46.6	32.9
60:40	71.7	48.4	33.9
70:30	72.8	49.4	34.7
80:20	75.1	50.2	37.5
90:10	76.6	52.0	34.7
Palm olein: Sunflower oil			
10:90	63.7	43.2	31.1
20:80	65.5	44.0	31.3
30:70	66.3	45.3	31.6
40:60	67.6	45.8	32.4
50:50	70.4	45.8	33.7
60:40	72.5	47.1	34.7
70:30	73.5	48.7	35.2
80:20	75.3	47.4	36.0
90:10	76.4	52.0	34.7
Palm olein: Canola oil			
10:90	66.5	45.6	32.9
20:80	68.3	46.1	32.6
30:70	69.9	46.3	33.4
40:60	70.4	46.1	33.9
50:50	71.5	48.9	35.5
60:40	72.8	50.0	35.0
70:30	74.0	49.7	35.2
80:20	76.6	51.0	35.7
90:10	77.4	52.3	35.7

than that of their 50:50 blends. This result might have been observed due to heat and oxidation that cause gradual changes of the *cis* fatty acids to *trans* fatty acids. Furthermore, This justification can be strengthened by the observation of absorbance band that appeared at approximately 968 cm^{-1} , which is related to the bending vibrations of CH group of isolated *trans*-olefins. This observation provides information of gradual *cis* to *trans* isomerization throughout this treatment process (Sanahuja et al. 2009; Tena et al. 2009). Moreover, Mishra and Sharma (2011) reported that repeated frying caused *trans* fatty acids to increase while the blended samples were within the acceptable range after few frying cycles. In this case, palm olein has the lowest absorption band (0.220) as well, where as Soybean oil shows the highest with 0.265 followed by sunflower and canola oil at (0.244 and 0.238, respectively) but candlenut oil does not give any band at this frequency. After one hour of heat treatment PO: SO shows a highest absorption with 0.250 while a minimum is observed for PO: Cnd oil (0.232). So, this observation supports the findings for changes in intensity of the bands at 1654 cm^{-1} . Additionally, these results are similar to those reported by Guillén and Cabo (1997; 2000) for other vegetable oils. Moreover, Enríquez-Fernández et al. (2011) also have reported that in terms of chemical properties PO:CO blends shows better results.

The production of free fatty acids could be quantified by chemical analytical methods; however no band was observed at 1700 cm^{-1} . Because of the fact that, in a mixture the compounds those are very low in proportion give very weak

bands, which are not detectable in the infrared spectrum (Guillén and Cabo 2002).

Rheology

The viscosity of the palm olein was found higher among these four vegetable oils used for blending, nevertheless viscosity of all oils and their blends decreased with the increase in temperature. The increase in temperature enhances the movements of the molecules and reduces intermolecular forces thus the layers of the liquid easily pass over one another and thus contribute in the reduction of viscosity (Siddique et al. 2010). This phenomenon also verified by the other researchers as oil viscosity depends on its molecular structure and decreases with the unsaturation of fatty acids while it increases with the increase of saturation of long chain fatty acids on TAG molecules (Kim et al. 2010; Geller and Goodrum 2000). It may be due to the π bonds that make the bonding more rigid, and thus rotation between C-C bonds becomes strenuous, moreover extended chain makes flow easier and reduces viscosity (Santos et al. 2005). This is probably because of less friction among the fatty acid chains. It was observed that viscosity decreases linearly with the increase of low viscous oil portion in the blends at 23 and 33 °C but at 43 °C viscosity of the blends decreases more with a slight deflection, especially for palm: soybean (PO:SO) oil blends. For a better perception, a table (Table 2) on viscosity of different blends (before frying) at various temperature is included which was

Fig. 4 Frequency sweep curve showing storage (G') and loss (G'') modulus at 20 °C for palm olein blends with other oils at 50:50 composition (before frying)

Table 3 Loss modulus (G'') and Storage modulus (G') behaviour of oil blends against the applied frequency as well as the Standard deviation of the measurements

PO:Cnd 50:50						
Fre (Hz)	G' (Mean)	STDEV	STD Err	G'' (Mean)	STDEV	STD Err
0.1	0.000139	1.53E-06	8.66E-07	0.0159	0.000153	8.83E-05
0.5	0.00016	3E-06	1.73E-06	0.0472	0.000115	6.64E-05
0.6	0.000183	4.51E-06	2.60E-06	0.0686	0.000153	8.83E-05
0.8	0.000179	4.73E-06	2.73E-06	0.0896	0.00123	2.76E-02
0.9	0.000299	3.21E-05	1.86E-05	0.097	0.049433	1.47E-03
3.3	0.00194	0.00476	2.75E-03	0.377	0.006018	1.45E-03
5.2	0.0137	0.000378	1.20E-04	0.699	0.345831	1.16E-05
7.6	0.017	0.000153	8.82E-05	2.26	0.03	1.73E-02
8.2	0.081	0.002827	1.16E-05	3.038	0.15454	1.20E-02
9.19	0.0917	0.046225	8.82E-04	4.055	0.523132	2.64E-01
20	0.0179	0.14458	1.45E-04	8.71	0.926812	8.19E-02
36	7.89	0.341223	1.97E-01	10.14	1.335902	1.23E-01
65	8.57	0.889119	5.13E-01	10.47	1.515333	4.16E-02
PO:CO 50:50						
0.1	0.000135	2.08E-06	1.20E-06	0.016	0.000557	3.22E-04
0.5	0.000142	1.53E-06	8.82E-07	0.0474	0.002062	3.33E-05
0.6	0.000175	1.15E-06	6.67E-07	0.0582	0.003620	2.08E-04
0.8	0.000323	1.43E-05	1.43E-05	0.0693	0.005050	8.83E-04
0.9	0.000589	2.11E-05	1.76E-05	0.08907	0.005563	1.16E-03
4.3	0.00194	1.53E-05	8.82E-06	0.779	0.056027	8.82E-04
5.8	0.0146	0.000208	1.20E-04	0.892	0.070644	8.82E-04
7.3	0.0168	0.000173	9.99E-05	2.28	0.163124	8.82E-03
8.2	0.142	0.001528	8.82E-04	4.55	0.858488	3.08E-02
9.19	1.24	0.392845	1.83E-01	6.82	0.391706	1.73E-02
10	4.26	1.220423	1.33E-01	7.41	0.524592	2.96E-02
50	25.51	1.617354	5.07E-01	15.22	1.558300	2.52E-02
69	29.34	2.634445	9.49E-01	28.91	1.926145	1.30E-01
PO:SF 50:50						
0.1	0.000016	0.00000156	9.02E-07	0.0170000	0.0002082	1.20E-04
0.5	0.000143	0.00000153	6.66E-07	0.0399000	0.0005568	2.03E-04
0.6	0.000173	0.00000115	6.67E-07	0.0547000	0.0011504	2.33E-04
0.8	0.000188	0.00000153	8.82E-07	0.0699300	0.0017088	2.82E-02
0.9	0.000255	0.00002646	1.53E-05	0.0899000	0.0020306	2.65E-03
4.3	0.001610	0.00020648	1.19E-04	0.6751000	0.0470779	1.45E-03
5.8	0.014500	0.0002082	1.20E-04	0.7550000	0.0650718	1.76E-03
7.3	0.016500	0.00015275	8.82E-05	2.3100000	0.0513160	2.96E-02
8.2	0.122000	0.01504400	1.45E-03	4.6100000	0.6117461	1.76E-02
9.19	0.170000	0.00321500	2.03E-03	6.7900000	0.6902174	1.15E-02
10	1.170000	0.27402200	8.35E-02	7.5400000	0.6415606	1.20E-02
50	9.240000	0.92684100	7.50E-02	9.7300000	1.2745326	1.86E-02
69	20.730000	1.13650000	2.32E-01	23.3100000	1.3963203	4.98E-02
79.9	28.220000	2.84640400	3.37E-01	40.4200000	3.7995658	7.31E-02
PO: SO 50:50)						
0.1	0.000136	1.528E-06	8.82E-07	0.0156	0.0003	1.73E-04
0.5	0.000155	1.528E-06	8.82E-07	0.0473	0.002944	1.15E-04
0.6	0.000418	3.732E-05	2.33E-05	0.0581	0.005339	4.91E-04
0.8	0.000642	8.679E-05	1.76E-06	0.0699	0.006668	2.96E-02

Table 3 (continued)

0.9	0.00102	0.0002185	3.76E-05	0.101	0.006067	2.40E-03
4.3	0.0131	0.0011082	2.73E-04	0.654	0.050406	1.45E-03
5.8	0.0173	0.0002646	1.53E-04	0.761	0.041384	1.45E-03
7.3	0.102	0.0179272	3.93E-03	2.35	0.406489	1.73E-02
8.2	0.159	0.0607033	1.45E-02	4.27	0.936162	3.21E-02
9.19	0.191	0.0873232	1.45E-03	5.61	0.53989	4.10E-02
10	1.42	0.452143	2.40E-02	7.36	0.642084	3.53E-02
50	1.46	1.15185	1.45E-02	11.49	0.882213	2.96E-02
69	20.47	2.2604719	2.69E-01	24.98	1.247157	1.19E-02

first appeared as a predecessor of this study (Siddique et al. 2010). This might be due to the presence of fat crystals that coalesce together and need more time for destruction while it increases the friction between the layers and results in the sharp increase in viscosity (Vaclavik and Christian 2003; Graef et al. 2008). One the probable explanation for this observation might be because at relatively low temperature there are fat crystals present in the oil samples. This crystals, with the increase of temperature disappear abruptly due to melting and thus cause a sudden decrease in viscosity.

From the rheology measurement of all oils and their blends before and after frying at high temperature shows the Newtonian behaviour. Viscosity of all the samples was constant against applied shear rate and the shear rate vs shear stress pass through the origin.

This phenomenon indicates that samples after being fried at high temperature retain its basic characteristics. Fully melted oils showed a weak viscoelastic liquid structure with loss modulus (G'') higher than the storage modulus (G') at all frequencies up to 10 Hz. The storage modulus (G') is an indication of the energy stored and recovered per cycle of sinusoidal deformation. It tells about the elastic nature of the substance while the loss modulus (G'') is a measure of the energy lost per cycle of sinusoidal deformation and is indicative of the viscosity of the substance (Ferry 1970). The higher G' tells about the solid like sample whereas higher G'' shows for viscous samples. The G'' is a measure of the energy lost during deformation, however, the value of G'' over G' means that the deformation energy of the material is dissipated viscously and the material behaves like 'liquid-like' (Rao 2007).

Accordingly, with higher G' value the samples show that the oils and their blends are less in elastic character than in a viscous liquid. It also represents the highly organized structure of the samples. G'' and G' for all pure oils and their respective blends show a linear increase with the increase of the frequency. Figure 4 depicts the changes in storage and loss modulus for oil blends of 50:50 ratio. Pure oils show a 'critical stress' at about 16 Hz at both 20 and 30 °C while in all blends, this phenomenon was found at about 16 and 25 Hz for 20 and 30 °C respectively. Oils at their pure state are showing low value of 'critical stress' and this value is high when they are

blended, suggests that the structure in blended oils are durable than in pure oils as critical stress tell about the destruction of the structure (Wan Nik et al. 2005). Besides, this is an effect of the onset of non-linear response of the matters at a certain frequency. This observation might be due to the relatively strong bonds of TAG molecules of different origins. Moreover, at a higher frequency both G' and G'' of the samples became gradually inconsistent, which might be because of the effect of higher applied shear the molecules in the samples behave incompatibly with other molecules. The standard deviation as well as the standard error of these measurements also support this finding of inconsistency of the sample behaviour at higher frequency (Table 3).

The oils and their blends, for temperature sweep test, show a gradual decrease in both G'' and G' value with the increase of temperature. It's worth mentioning that G' has always a lower value than G'' in temperature sweep test. This observation was similar to the findings of Yalchin et al. (2012), where the researchers have reported on the G' and G'' for pure vegetable oils. However, no crossover point was observed throughout this temperature range. This observation might be due to the destruction of the structure of the crystal network of the oils with the increase of the temperature that reduces the samples viscous property as well as the elastic property. Since all the oil samples are similar (vegetable oils) and no chemical modification was done on it, so the rheological measurement was also found similar for all samples and as a whole this experiment is able to provide valuable information about cooking oils. Therefore, Rheological measurements showed that the viscosity, G' and G'' are usable parameters as a probe to investigate the propensity of different oil blend samples to the thermal degradation.

Conclusion

Palm oil was found to be better against oxidation among other frying oils used in this study. This is a consequence of high saturation, which can be seen from the FTIR data, where palm oil shows band around at 3002 cm^{-1} and other oils show at 3007 cm^{-1} . Moreover, after frying for one hour the height of the absorption band at 2922 cm^{-1} tells about the increase of

saturation of these used oil, however, among other oil blends Palm: Canola 50:50 blend shows a better result to restrain the unsaturation against heat. The changes of *cis*- isomers to *trans*-isomers are less in palm oil than in Soybean, Sunflower and Canola oils. Therefore, the blends contained higher ratios of palm oil were found more stable of this *cis-trans* changes. The altering rate of *cis* to *trans* for 50:50 blends is lower for PO: Cnd followed by PO: SO, PO:SF and PO: CO. In physical properties, palm oil shows a higher viscosity than others which however, decreases with the temperature. This might be due to the presence of fat crystals that coalesces together and need heat for destruction. The rheology, in addition, tells that under the testing condition used for this study does not alter basic physical properties of cooking oil and it retains the Newtonian behavior; while G'' is higher than G' for both temperature sweep and frequency sweep tests. So oils and their blends show viscous property than the elastic property before and after heat treatment.

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References

- Belitz H-D, Grosch W, Schieberle P (2009) Edible fats and oils. Food Chem Springer-Verlag, Berlin, pp 640–669
- Bendini A, Cerretani L, Di Virgilio F, Belloni P, Bonoli-Carbognin M, Lercker G (2007) Preliminary evaluation of the application of the ftir spectroscopy to control the geographic origin and quality of virgin olive oils. J Food Quality 30:424–437
- Chugh B, Dhawan K (2011) Storage studies on mustard oil blends. J Food Sci Tech. doi:10.1007/s13197-011-0540-8
- Diáz Gamboa OW, Gioielli LA (2003) Consistencia de lípidios estructurados a partir de aceite de pescado y grasa de palmiste. Grasas y Aceites 54:122–129
- Enríquez- Fernández BE, Álvarez De La Cadena Y, Yañez L, Sosamoraes ME (2011) Comparison of the stability of palm olein and a palm olein/canola oil blend during deep-fat frying of chicken nuggets and French fries. Int J Food Sci Tech 46:1231–1237
- Ferry JD (1970) Viscoelastic properties of polymers. John Wiley & Sons Inc, New York, 217
- Frankel EN (1998) Lipid oxidation. The Oily Press, Dundee
- Geller B, Goodrum J (2000) Rheology of vegetable oil analogs and triglycerides. J Am Oil Chem Soc 77:111–114
- Gloria H, Aguilera JM (1998) Assessment of the quality of heated oils by differential scanning calorimetry. J Agri Food Chem 46:1363–1368
- Go'mez-Alonso S, Fregapane G, Salvador MD, Gordon MH (2003) Changes in phenolic composition and antioxidant activity of virgin olive oil during frying. J Agri Food Chem 51:667–672
- Graef VD, Goderis B, Puyvelde PV, Foubert I, Dewettinck K (2008) Development of a rheological method to characterize palm oil crystallizing under shear. Eur J Lipid Sci and Tech 110:521–529
- Guillén MD, Cabo N (2002) Fourier transform infrared spectra data versus peroxide and anisidine values to determine oxidative stability of edible oils. Food Chem 77:503–510
- Guillén MD, Cabo N (2000) Some of the most significant changes in the Fourier transform infrared spectra of edible oils under oxidative conditions. J Sci Food Agri 80:2028–2036
- Guillén MD, Cabo N (1997) Characterization of edible oils and lard by Fourier transform infrared spectroscopy. Relationships between composition and frequency of concrete bands in the fingerprint region. J Am Oil Chem Soc 74:1281–1286
- Guillén MD, Cabo N (1999) Usefulness of the frequency data of the Fourier transform infrared spectra to evaluate the degree of oxidation of edible oils. J Agri Food Chem 47:709–719
- Kim J, Kim DN, Lee SH, Yoo SH, Lee S (2010) Correlation of fatty acid composition of vegetable oils with rheological behaviour and oil uptake. Food Chem 118:398–402
- Kritchevsky D (2008) Fats and Oils in Human Health. In: Casimir CC, Min DB (eds) Food lipids Chemistry, nutrition, and biotechnology, 3rd edn. Taylor & Francis Group, LLC, Boca Raton
- Lioumbas JS, Ampatzidis C, Karapantsios TD (2012) Effect of potato deep-fat frying conditions on temperature dependence of olive oil and palm oil viscosity. J Food Eng 113(2):217–225
- Marco ED, Savaresea M et al (2007) Frying performance of a sunflower/palm oil blend in comparison with pure palm oil. Eur J Lipid Sci Tech 109:237–246
- Márquez-Ruiz G, Dobarganes C (1996) Short-chain fatty acids formation during thermoxidation and frying. J Sci Food Agri 70:120–126
- Mishra R, Sharma HK (2011) Effect of frying conditions on the physico-chemical properties of rice bran Oil and its belnded oils. J Food Sci Tech. doi:10.1007/s13197-011-0602-y
- Rao MA (2007) Rheology of fluid and semisolid foods principles and applications. Springer Science+Business Media, LLC, New York
- Rohman A, Man YBC (2010) Fourier transform infrared (FTIR) spectroscopy for analysis of extra virgin olive oil adulterated with palm oil. Food Res Int 43:886–892
- Safar M, Bertrand D, Robert P, Devaux M, Genot C (1994) Characterization of edible oils, butters and margarines by Fourier transform infrared spectroscopy with attenuated total reflectance. J Am Oil Chem Soc 71:371–377
- Sanahuja AB, Moya MSP, Perez SEM, Teruel NG, Carratala ML (2009) Classification of four almond cultivars using oil degradation parameters based on FTIR and GC data. J Am Oil Chem Soc 86:51–58
- Santos JCO, Santos IMG, Souza AG (2005) Effect of heating and cooling on rheological parameters of edible vegetable oils. J Food Eng 67:401–405
- Siddique BM, Ahmad A, Alkarkhi AFM, Ibrahim MH, Omar AKM (2011) Chemical composition and antioxidant properties of candlenut Oil extracted by supercritical CO₂. J Food Sci 76(4):C535–C542
- Siddique BM, Ahmad A, Ibrahim MH, Hena S, Rafatullah M, Mohd Omar AK (2010) Physico-chemical properties of blends of palm olein with other vegetable oils. Grasas y Aceites 61:423–429
- Stevenson SG, Vaisey-Genser M, Eskin NAM (1984) Quality control in the use of deep frying oils. J Am Oil Che Soc 61:1102–1108
- Tena N, Aparicio R, Garcí'a-González DL (2009) Thermal deterioration of virgin olive oil monitored by ATR-FTIR analysis of trans content. J Agri Food Chem 57:9997–10003
- Vaclavik VA, Christian EW (2003) Fat and Oil Products. In: Heldman DR (ed) Essentials of Food Science. Springer Science+Business Media, LLC, New York
- Vlachos N, Skopelitis Y, Psaroudaki M, Konstantinidou V, Chatzilazarou A, Tegou E (2006) Application of Fourier transform-infrared spectroscopy to edible oils. Anal Chim Acta 573–574:459–465
- Wan Nik WB, Ani FN, Masjuki HH, Eng Giap SG (2005) Rheology of bioedible oils according to several rheological models and its potential as hydraulic fluid. Ind Crops Prod 22:249–255
- Wang T, Briggs J (2002) Rheological and thermal properties of soybean oils with modified FA compositions. J Am Oil Chem Soc 79(8):831–836
- Yalchin H, Toker OS, Dogan M (2012) Effect of Oil type and fatty acid composition on dynamic and steady shear rheology of vegetable oils. J Oleo Sci 61(4):181–187
- Yang H, Irudayaraj J, Paradkar MM (2005) Discriminant analysis of edible oils and fats by FTIR, FT-NIR and FT-Raman spectroscopy. Food Chem 93:25–32