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SURFACE TENSION AND HYDROPEROXIDE CONTENT OF VEGETABLE OILS: EFFECT OF REPEATED DEEP FRYING

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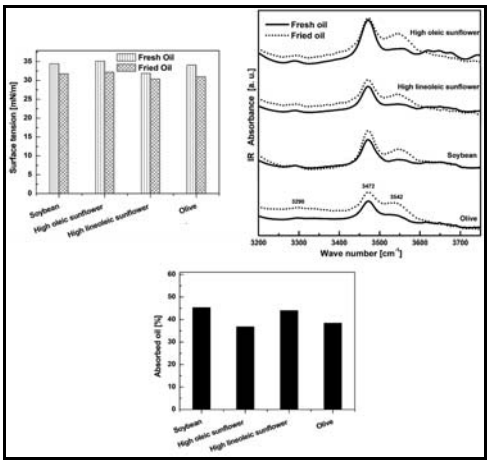
In this study, dried potato chips have been repeatedly fried using four vegetable cooking oils of different types. The influence the deep-frying process on the surface tension and hydroperoxide content of the used oils was investigated by pendant drop method and Fourier transformation infrared (FTIR) spectroscopy, respectively. The oil surface tension was also analyzed into its polar and dispersive components using contact angle measurements of the oil drop on Teflon (PTFE) dispersive surface. It is found that both the percentage of the oil absorption (OA) and its degree of oxidation decrease with decreasing its surface tension. Among the studied oils, the high linoleic sunflower oil (SF2) shows the lowest value of surface tension, the minimum change in the hydroperoxide content, and the lowest rate of oil absorption. The results in this report show that surface tension can be used as a simple gauge for exploring the effect of repeated deep-frying process on quality of vegetable oils.



INTRODUCTION

Sunflower, soybean and olive oils are among vegetable oils, which are frequently used for food processing including frying. Frying food is a complicated process starting from heat transfer to removing moisture from the fried food and finally oil up taken inside the foods texture.[1-5] The vegetable oil structure consists of glycerin bounded with three linked fatty acids. These fatty acids reflect the chemical and physical properties of the mother oil including the length of the fatty acid hydrocarbon chain and the number of unsaturated double bounds existed on the fatty acids backbone. During food processing, the frying oil is subjected to both heat and moisture contained in oil and in raw food ingredient. These conditions likely provoke two most worrying issues.

The first is nutrition issue, which is, the amount of up taken oil that replaced the moisture in the food texture.[1-5] However, fried food with high oil content is unfavorable because it is one of main causes of obesity, high blood pressure and heart disease. Consequently, considerable efforts from scientific community have been devoted to control oil absorption in foods. The percentage of absorbed oil into the fried material depends on several factors such as oil type, frying conditions, and material properties and its pretreatments.

The second is related the oxidation of the oil itself, which leads to form peroxides in oil of two types one that bounded to the backbone of the fatty

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acid, and the other is free unbounded peroxides.[6-8] On repeating frying process, this might lead the formation of unhealthy products, which in turn can penetrate into the fried food.

Physicochemical properties of cooking oil such as its color, density, viscosity, moisture content, peroxide value and surface/interfacial tension can be highly influenced by repetitive frying process. Hence, they are frequently used to determine the cooking oil quality and influence of various thermal treatments including frying process on its properties.[1-3] Among them, surface and interfacial tensions are the most exciting, because they play a vital role in the oil absorption during frying process.[1-9] For example; Kalogianni *et al*., have studied the influence of repeated frying on the viscosity, density and dynamic interfacial tension of palm and olive oil.[10] They found that the time-dependence of interfacial tension is different in the two oil types when they are fried. They linked the observed difference to the different degradation compounds formed in each oil type during frying. More recently, Sahasrabudhe *et al.*, have investigated the impact of oil degradation during frying on surface tension and wettability of canola oil.[11] They found that the surface tension decreases linearly as a function of temperature. However, they did not observed any significant effect of surrounding medium and oil quality on the surface tension, while they observed the quality of oil significantly affects the oil wettability. These findings contradicts the results obtained previously by Dana *et al.*[12] Therefore, there is still a need for more experimental work in this field using standard techniques.

Moreover, surface tension is the physical property that is summing up the overall degree of hydrophobicity of the oil, which results from the hydrophobicity of hydrocarbon chain of fatty acids and the hydrophilicity of the unsaturated double bounds of the fatty acid and the polar ester group of fatty acid with glycerin.[9] The hydrophilicity of the oil is also affected by formed peroxides during production, storing, and during reusing for frying the processed food. Therefore, oil surface tension changes during frying process are highly interconnected to the peroxides formation.

Among various methods,[2,11-16] the Pendant drop technique is very attractive for measuring the surface and interfacial tensions of frying oils.[11,13-16] On the other side, Fourier Transform Infrared FTIR spectroscopy proved to be a very attractive technique for simply and effectively studying the influence of this process on the content and nature of peroxides in the frying oils.[7,17-21] Using this technique, it has been demonstrated that the influence of thermal heating time on the oxidation of edible oils can be simply estimated by monitoring the changes in the FTIR bands due to the bounded and unbounded peroxides. Therefore, combining of both surface tension measurements and FTIR spectroscopy to evaluate the quality of the repeatedly frying oils is a very interesting. This is because such a combination can afford a valuable information about the impact of the hydroperoxide formation on the surface tension. To the best of our knowledge such an approach has not yet been reported.

In this study, the influence of repeated deep-frying of dried potato chips on the surface tension of four vegetable oils of different brands, which are usually used for preparing of fried food dishes, is reported. These are correlated with the corresponding changes in hydroperoxide content that evaluated using FTIR measurements. In addition, the influence of the frying process on the wettability of the studied oils is also investigated.

EXPERMENTAL

1. Studied oil

Four trademark vegetable oils of different kinds, which are frequently used in local kitchen for food cooking processes, including frying, were tested. They were purchased from local shops, and their fatty acids content that was marked by the manufacturer in grams (g) in one tablespoon (15-mL) servings is summarized in Table 1.

Table 1

Fatty acids content in grams (g) in one tablespoon (15-mL) servings of studied oils

Fat (1Tbsp) fat/tbsp.	Saturated Fat (g)	Monounsaturated Fat (g)	Polyunsaturated Fat (g)
High oleic sunflower (SF1)	2 g	11 g	2 g
High linoleic sunflower (SF2)	1.2 g	2.6 g	6.2 g
Soybean (Sb)	2.1 g	3.2 g	7.9 g
Olive (Ol)	2 g	10 g	1.5 g

2. Frying process

Dried potato chips of nearly similar shape and weight were purchased from local shop. These chips were used to study the effect of frying process on the surface tension of the oils. Prior to frying process, same quantity of each oil was heated in the frying pan at 160°C for ten seconds, cooled to laboratory temperature and its surface tension in the air was measured. At the same laboratory conditions, this procedure was consecutively repeated for ten times for each of the studied oils. The measured values of surface energy (γ) are plotted in Fig. 1. It can be observed the value of γ becomes almost stable after eighth heating and cooling cycles (N = 8). Based on this experiment, the potato chips were fried in same quantity of oil at 160°C for ten seconds. Then frying oils samples were cooled to laboratory temperature and the fried chips also cooled to laboratory temperature on the filter papers. This was repeated eight times (N = 8) for each of studied oil. The used dried potato chips in this study were similar in porosity, weight and volume. Therefore, the percentage of absorbed oil (OA) inside of potato chips after frying process could be estimated by using the following equation:[4]

$$OA\ [\%] = [(W_f - W_0)/W_0] \times 100 \quad (1)$$

where: W_0, W_f is the weight of potato chip before and after frying.

3. Surface and interfacial tension

The influence of frying process on the surface/interfacial tension and contact angle of the oil was determined using a goniometer (OCA 15 plus, SCA 20, Data Physics Instrument GmbH, Germany). Syringe heating device (SHD) was used in order to control the temperature of oil droplet during measurements. All measurements were carried out at temperature of (25 ±1)°C. The surface and interfacial tension of each oil with air and water respectively, were measured using pendant drop method. A droplet of 5 μL in size was dropped onto the surface of a locally commercial available Teflon flat sample, and the contact angle (CA) was measured. The measured values of CA and the surface energy value of the Teflon substrate (25.93 ± 0.2) mN/m were used to analyze the surface tension (δ) of each oil before and after the frying process into its polar and dispersive components. The value of surface energy of Teflon substrate was determined from analyzing the CA values of the Teflon substrate with double distilled water, extrapure ethylene glycol and methylene iodide (99%) using Owens, Wendt, Rabel and Kalble (OWRK) method.[22] The used ethylene glycol and methylene iodide were purchased from PROLABO and Sigma-Aldrich, respectively.

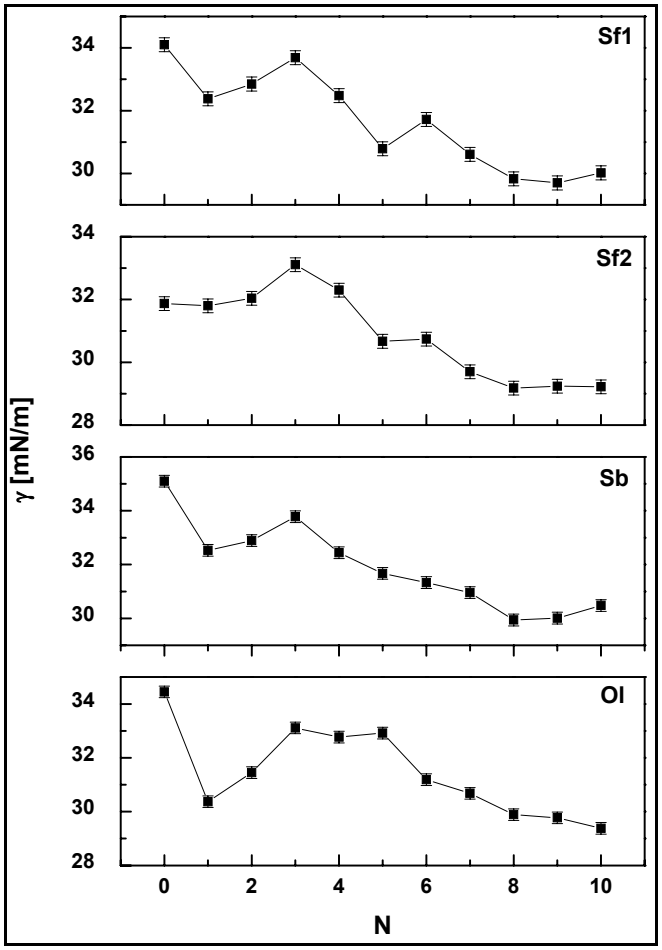

Fig. 1 – Variation of surface tension (γ) of the studied oils as a function of thermal heating cycle (N). The time, and the temperature of heating in each cycle is 10 S and 160°C, respectively.

All measurements were replicated 5 times at the same conditions for each sample and the mean value ± standard deviation (SD) that obtained using a suitable software program, were reported.

4. FTIR measurements

FTIR study was carried out using similar procedures described in details elsewhere.[7] FTIR spectra of each repeatedly fried oil were recorded using FTIR Nicolet 6700 instrument, equipped with DTGS detector, KBr beam splitter and OMNIC operating system software (Version 7.3, Thermo Nicolet,USA). The spectra were taken in the range is 4000 to 400 cm^{-1}, with a resolution of 4 cm^{-1} at 64 scans using a liquid cell. All oil samples were inserted by syringe between two newly polished KBr windows. In order to boost the absorption of peroxide bands, the path-length of the beam was increased by placing Teflon thin layer (0.091 mm) spacer between KBr windows in accordance with Beer-Lambert law.

RESULTS AND DISCUSION

The measured values of the surface tension (γ) for each of the four studied oils measured in the air using pendant drop method; before (fresh), and after 8 consecutively repeated frying cyclic (fried) are depicted in Fig. 2. The value of γ for each sample is the mean of five consecutive measurements. The surface tension value (31.9 ± 0.38) mN/m for un-fried (fresh) sunflower oil (Sf2) sample is lower than that of sunflower oil (Sf1), soybean (Sb) and olive (Ol) by around 3.2 ± 0.34 mN/m, 2.6 ± 0.39 mN/m and 2.2 ± 0.36 mN/m respectively. After frying, the surface tension decreases in all studied cases.

Fig. 3 shows the variation of surface tension as a function of the repeated frying cycles (N=8), and the percentage of the absorbed oils (OA) after each frying cycle, of the studied oils. The observable general trend of behavior from these plots is that values of OA are inversely proportional to the γ values. The observed fluctuation in both γ and OA values as a function of the repeated frying cycles, can be attributed to the changes in the surface active degradation products, formed as oil degrades during heating and cooling cycles.[11] However, there is a need for further research effort to deeply understand these changes and their impact on the oil uptake and quality.

FTIR proved to be a very useful technique to study the influence of thermal treatment on the nature of chemical bonding of cooking oils.[7,16-20] In particular, it has been established that the change in the relative intensity of IR band due to O-H stretching modes of the peroxide groups can be simply used as an indicator for monitoring of the cooking oils oxidation process.[7] Herein, FTIR spectra of the study oils were recorded in the spectral rang 3200-3750 cm^{-1} and used to investigate the influence of frying process on the content and nature of the hydroperoxide. The FTIR spectra of the studied oils before (fresh) and after frying process (fried) are shown in Fig. 4. The strong and broad IR band in the range 3390-3606 cm^{-1} with maximum at ~3472 cm^{-1}, was deconvoluted into three peak-components using a Gaussian fitting method. Fig. 5 shows the fitting results of this band for olive (Ol) sample before and after frying process. The weak peak at ~ 3432 cm^{-1} is the O-H stretching of alcohol associated group,[19,20] whereas the two strong peaks at around 3472 cm^{-1} and 3542 cm^{-1}, are assigned to the bounded and unbounded hydroperoxide groups respectively.[7] The integrated intensity of these two peaks changes noticeably, after frying process [Fig. 5(ii)]. The content of bound and unbounded hydroperoxide is estimated from the ratio: integrated area of each peak component / integrated area of the total band.

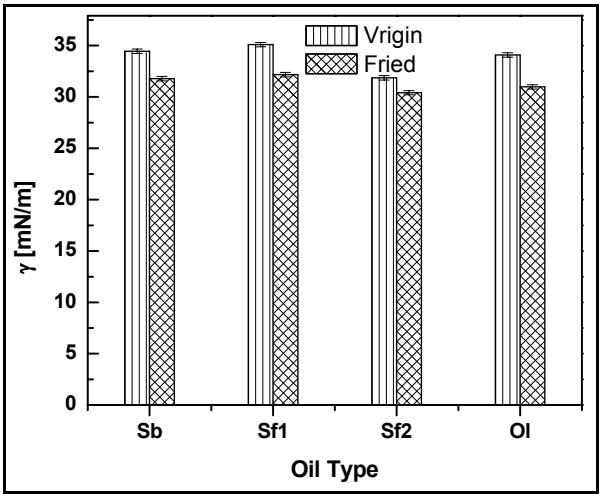

Fig. 2 – Measured values of the surface tension (γ) for each of the four studied oils; before (fresh), and after 8 consecutively repeated frying cycles (fried). The frying time and the frying temperature of each cycle were 10 s and 160°C, respectively.

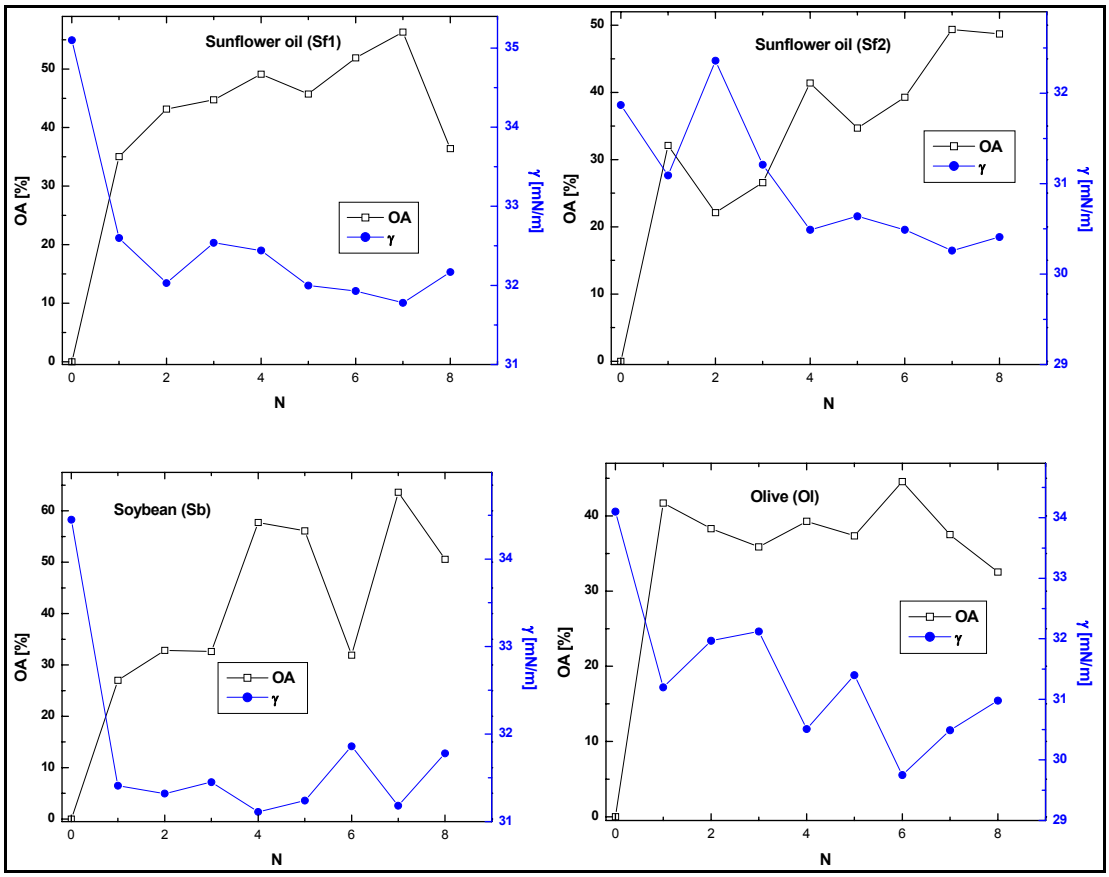

Fig. 3 – Variation of surface tension of the studied oils (γ) as a function of the repeated frying cycles (N=8), and the percentage of the absorbed oils (OA) after each cycle.

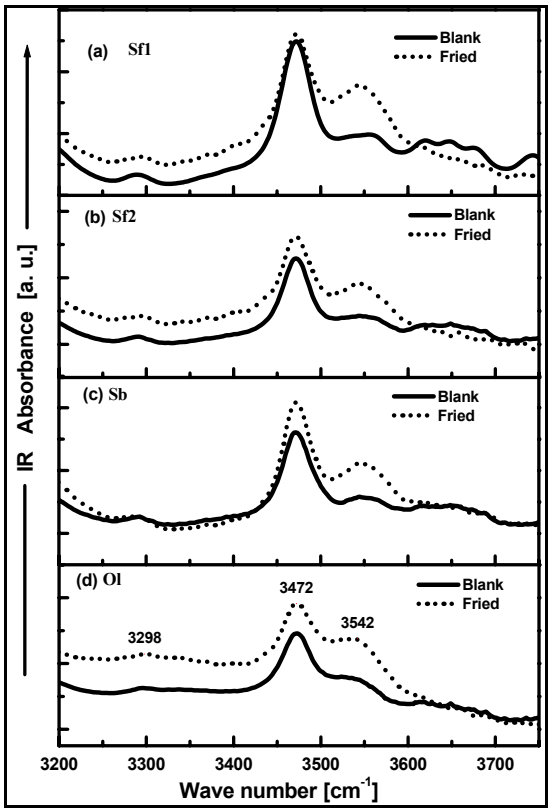

Fig. 4 – FTIR spectra of the studied oils before (fresh) and after frying process (fried).

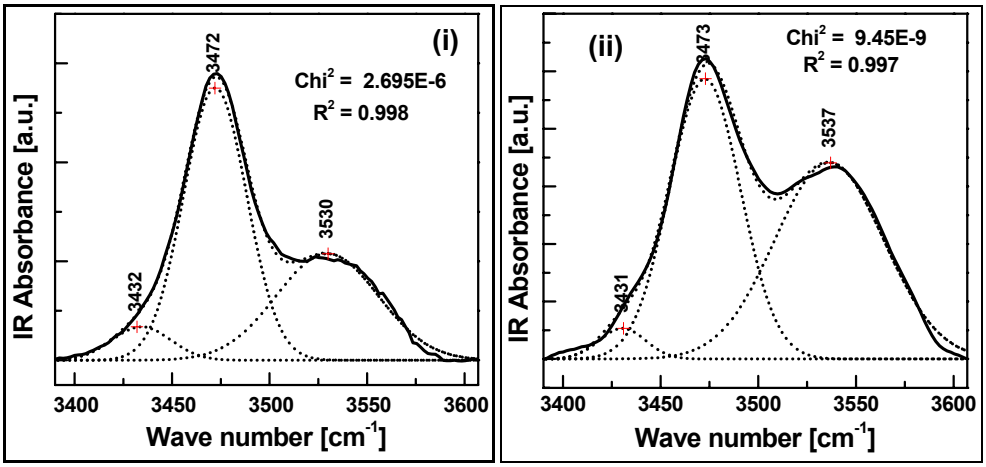

Fig. 5 – FTIR spectra of hydroperoxide bands for olive (Ol) sample (solid lines): (i) before and (ii) after frying process. The dotted lines show the best Gaussian line shape fit of these bands.

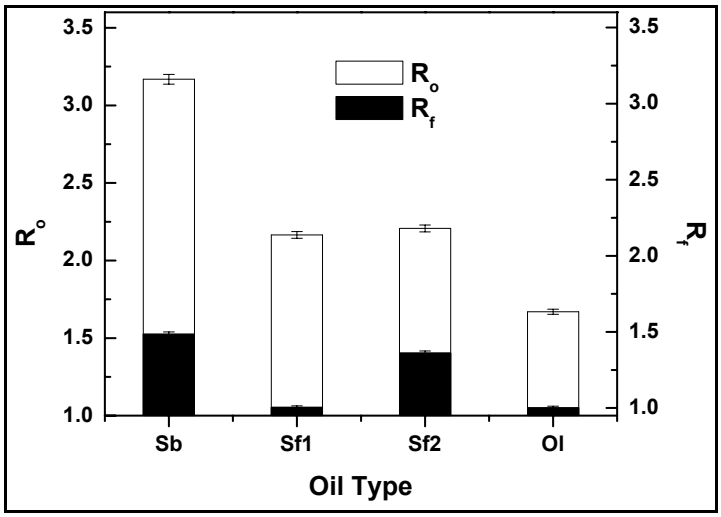

Fig. 6 – Variation of the ratio of bounded hydroperoxide content to unbounded hydroperoxide content of the studied oils; before (R_0) and after (R_f) frying process.

Fig. 6 shows the influence of frying process on the ratios R_o and R_f of the studied oils, where R_o and R_f are the ratio of bounded hydroperoxide content to the ratio of unbounded hydroperoxide content before and after frying process respectively. For all studied oils, this ratio decreases after frying process. This indicates that the content of unbounded hydroperoxide increases and it is attributed to the induced thermal oxidation effects. In addition, it is seen from Fig.4 that the relative area of the weak peak at around 3432 cm^{-1}, due to the stretching mode of O-H in alcohols, decreases after frying process due to induced-thermal oxidation. This is in a very good agreement with the existed literature, where it has been observed that the intensity of this peak decreases after thermal heating process of edible oils due to thermal oxidation during frying process.[7] The percentage change in the content of unbounded hydroperoxide (R) of the four oils due to frying process was estimated using the relation; $R= (R_o-R_f/R_o)\times100$. Fig. 7 depicts value of R, as well as the change in the surface tension value ($\Delta\gamma$) for the studied oils with $\Delta\gamma = \gamma_o - \gamma_f$, where γ_o and γ_f are the surface tension of the oil before and frying process respectively. It is observed that the sunflower oil (Sf2) sample has the lowest values for both R and $\Delta\gamma$. This in its turn indicates that this sample has better oxidation resistance against the frying process than the other used oils. This can be ascribed to the difference in the chemical composition of each of the studied oil, and especially its content of fatty acids as it can be seen from Table 1. It is clear from the table that the Sf2 sample has the lowest value of saturated fats among the studied oils.

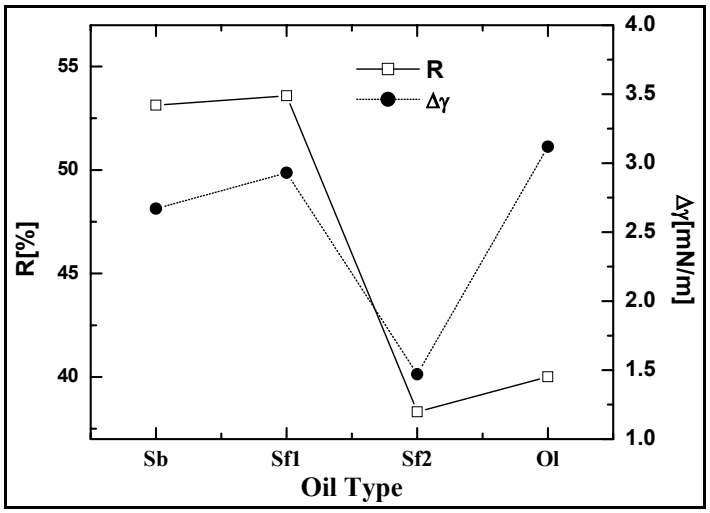

Fig. 7 – Variation of both the content percentage of unbounded hydroperoxide (R) and the change in the surface tension value (Δγ) for the studied oils due to frying process.

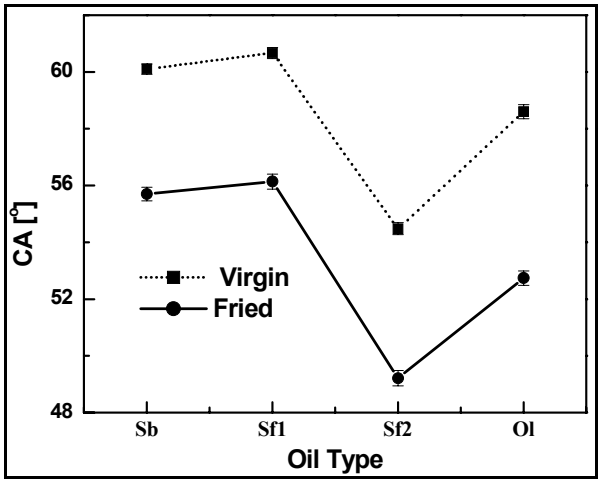

Fig. 8 – Variation of the contact angle (CA) of the studied oils before (fresh), and after 8 repeated frying cycles.

Moreover, the mean value of the absorbed oil percentage over the whole frying cyclic <OA>, was calculated from the data in Fig. 3. It is found to be around 45.3%, 36.8 %, 44.0 %, and 38.4 % for Sf1, Sf2, Sb and Ol, respectively. The standard error (SD) in <OA> value is found to be around 2.6 %, 3.5%, 5% and 1.3 % respectively. It can be also seen from Fig.2 that among the studied oils, the sunflower oils Sf1 and Sf2 samples have the highest and the lowest values of γ respectively. These indicate that the value of γ of the fresh oil can be used as an indicator for identifying its absorption quality; as the value of surface tension γ increases, the amount of the absorbed oil due the frying process decreases.

In addition to the surface tension, the oil absorption process is related to many other factors; the most important are the chemical composition of the oil and the porosity of fried material and its physical properties. Since in our present case the used dried potato chips have nearly the same porosity, size and weight, the observed difference in the oil absorption can be attributed to the difference in chemical composition of the studied oils, especially the content of saturated. Moreover, FTIR results were also assisted by analyzing the surface tension of the studied oils into their polar and dispersive components using contact angle measurements of oil droplet on a Teflon substrate.[23]

Fig. 8 shows the static contact angle (CA) of the studied oils before (fresh) and after 8 repeated frying cycles. It can be seen that the fresh sunflower sample Sf2 has the lowest value of CA among the studied oils. The value of CA decreases after frying and shows similar trend of behavior of its value before frying process. This well agrees with previously reported results.[11,24-26]

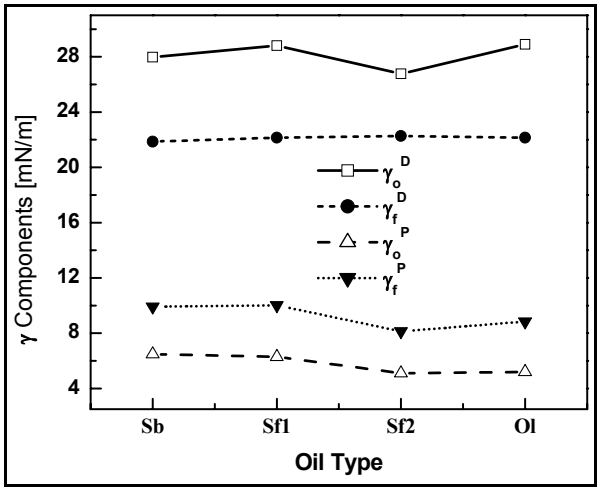

Fig. 9 – Variation of surface tension (γ) components for the studied oils; the polar components before and after frying are indexed as γ_o^P and γ_f^P respectively, while their corresponding dispersive components are indexed as γ_o^D and γ_f^D respectively.

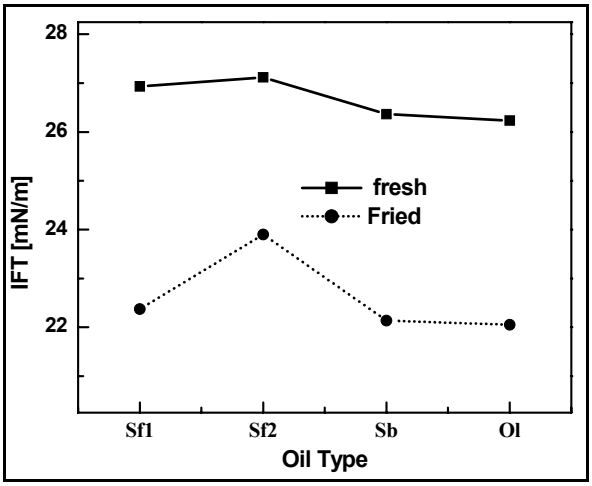

Fig. 10 – Interfacial tension (IFT) of the studied oils against water; before (fresh) and after the frying process (fried).

Using the measured values of CA and the surface energy value of used Teflon substrate (25.93 mN/m), the surface tension (γ) of each oil before and after the frying process is analyzed into its polar and dispersive components using SCA 20 software. The calculated values of polar and dispersive components of each of the studied oils; before (γ_o^P and γ_f^P) and after frying process (γ_o^D and γ_f^D) are respectively plotted in Fig. 9. Although oils are non-polar in nature, but it has been observed that the presence of fatty acids in its composition leads to a residual polarity. The value of this polarity depends on the methods of surface tension analysis.[26] It can be observed that the Sf2 sample, which among the studied oils has the lowest fatty acid content (Table 1), has also the lowest value of polar component γ_o^P. After frying, the value of dispersive component decreases, whereas the value of polar component increases in all cases. This can be attributed to the presence of surface active degradation products, formed as oil degrades during heating (frying) and cooling cycles.[11] Furthermore, it can be observed than the maximum and the minimum changes in the γ components are attained for Sf1 and Sf2 samples respectively. This is in a good agreement with our above FTIR results and surface tension measurements using pendant drop method. Since all kinds of vegetable oils are mainly composed from glycerides, which are three ester of fatty acid with glycerin. Therefore, the overall hydrophobicity of the oil is greatly depends on its structure, the hydrophobic fatty acid from one side and the hydrophilic ester groups and the double bounds from another side. These double bounds are epoxidized during heating and post-cooling process in the presence of the oxygen. Since the number of double bounds differs for different type of oils, the results in this report show that surface tension, which greatly depends on the total polarity

of the oil can be used as a simple technique to evaluate the quality of repeatedly fried oil.

Moreover, the interfacial tension (IFT) of the studied oils in water before and after the frying process is also measured using the pendant drop methods, and the results are depicted in Fig. 10. The value of IFT increases after the frying process, which refers to an enhancement of oil residual polarity, and as well coincides with our results above.

CONCLUSION

The influence of repeated frying of dried potato chips on the surface tension of four branded vegetable cooking oils of different kind is investigated. It is demonstrated that both the percentage of the oil absorption (OA) and its degree of oxidation decrease with decreasing its surface tension. These are found to well correlate with surface and oil/water interfacial tensions measurements using contact angle and pendant drop techniques. The results in this report show that surface tension can be used as a simple gauge for quality assessment of vegetable oil used for food frying process.

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