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Effect of Oil Type and Fatty Acid Composition on Dynamic and Steady Shear Rheology of Vegetable Oils

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Abstract: In this study, effect of fatty acid composition on dynamic and steady shear rheology of oils was studied. For this aim, different types of vegetable oils (soybean, sunflower, olive, hazelnut, cottonseed and canola), were used. Rheological properties of oil samples were identified by rheometer (Thermo-Haake) at 25℃ and fatty acid composition of oils was determined by GC (Agilent 6890). Steady shear rheological properties of oil samples were measured at shear rate range of 0.1-100 s^{-1}. Viscosity of olive, hazelnut, cottonseed, canola, soybean and sunflower was 61.2 mPa.s, 59.7 mPa.s, 57.3 mPa.s, 53.5 mPa.s, 48.7 mPa.s and 48.2 mPa.s, respectively. There was a significant difference between viscosity of oils except soybean and sunflower. As a result it was seen that there was a correlation between viscosity and monounsaturated (R=0.89), polyunsaturated (R=-0.97) fatty acid composition of oils, separately. Equation was found to predict viscosity of the oils based on mono and polyunsaturation composition of oils. In addition the dynamic rheological properties of oils were also examined. G', G'' and tan δ (G''/G') values were measured at 0.3 Pa (in viscoelastic region) and 0.1-1 Hz. As a result of multiple regression analysis another equations were found between tan δ, viscosity and polyunsaturated fatty acids.

Key words: fatty acid, rheology, vegetable oils, viscosity

1 INTRODUCTION

Rheological analysis is a simple analysis that is applied to determine the flow behavior of liquid and semi-liquid foods. Rheological measurements play major role in describing heat transfer or in the design, evaluation and modeling of different food treatment[1)]. These measurements are also useful to determine behavioral and predictive information for various products and formulations in food industry[2)].

The fundamental parameter, obtained in the rheological study of liquid foods, is viscosity, used to characterize the fluid texture[3)]. Oil viscosity investigations have generally focused on the non-food application especially lubrication and biodiesel industry. These studies have tried to develop models, to the use of oils to substitute as diesel fuel[4)]. But rheological properties of oils are important in the view of nutrition and food process.

Viscosities of fatty acids and their mixtures are important in the design of process equipment for the oil and fatty acid industry. For example, viscosity is an essential parameter in estimating the efficiency of distillation columns for separation of fatty acids[5)]. Viscosity data are also required for the design of heat transfer equipment, process piping, reactors, stripping columns, deodorizers, liquid extractors, and other units for the oil industry[6)]. It was known that pressure losses increase and volume of flow decrease with increasing of viscosity. In other words for obtaining the same flow volume for liquids having high viscosity, the greater pumping pressure was required, which causes to increase the cost[7)]. It is also known that the higher viscosity of frying oils the greater oil content of fried foods[8)]. This would be explained by the fact that high viscosity can allow the oils to be accumulated more easily on the surface of fried foods and enter inside during the cooling period[9)]. Physical properties (including viscosity) of pure triglycerides or pure fatty acids have been evaluated in preceding studies[4)]. Viscosity increases with chain lengths of fatty acids and decreases with unsaturation[10)]. However natural vegetable oils are not composed of pure fatty acids or simple binary mixtures of fatty acids. They are complex mixtures of many fatty acids with different chain lengths.

The objective of this work was to evaluate the rheological properties (viscosity, shear stress, shear rate) of commercial edible oils (soybean, sunflower, olive, canola, hazelnut and cottonseed oils). The flow behaviors of six

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vegetable oils were investigated and correlated with their fatty acid composition.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

Oil samples were obtained from a local market from Kayseri in Turkey.

2.2 Determination of fatty acid composition of oils

100 mg of oil samples were saponified with 100 μL 2 mol/L KOH, and 3 mL *n*-hexane was added to the mixture. The mixture was vigorously shaken with a vortex (Nüve NM 110, Turkey) for 1 min, and then centrifuged at 2516 × g for 5 min at 25℃. 1 mL solution was put into GC vials and injection was started immediately. GC (Agilent 6890), equipped with a FID and a 100 m × 0.25 mm ID HP-88 column was used. Injection block temperature was set at 250℃. The oven temperature was kept at 103℃ for 1 min, then programmed from 103℃ to 170℃ at 6.5℃ / min, from 170℃ to 215℃ for 12 min at 2.75℃/min, finally, 230℃ for 5 min. The carrier gas was helium with a flow rate 2 mL/min; split rate was 1/50[11]. Two replications were applied for determination of fatty acid composition of oil samples.

2.3 Rheological measurements

2.3.1 Equipment

Rheological properties of oil samples were determined using a strain/stress controlled rheometer (Thermo-Haake, Rheostress 1, Germany) equipped with a temperature-control unit (Haake, Karlsruhe K15, Germany) and with a cone-plate configuration with a cone radius of 35 mm and a gap of 1.00 mm between the cone and plate.

2.3.2 Steady shear rheology

Measurements were carried out in the shear rate range of 0.1-100 s^{-1} at constant temperature (25℃). 0.85 mL oil sample was placed with micropipet between cone and plate and the measurement was started immediately. Total 30 data points were recorded at 10 s intervals during the shearing. Newtonian model was selected. Each measurement was replicated three times on the same sample with two repetitions. The flow curve, shear stress versus shear rate was plotted by increasing shear rate.

2.3.3 Dynamic shear rheology

Initially the viscoelastic region of each oil samples was determined by stress sweep test. For this aim measurements were obtained at 0.1-10 Hz frequency ranges. After that dynamic shear properties were obtained from frequency sweeps over the range of 0.628-6.283 rad/s at 0.3 Pa (within the range of linear viscoelasticity). Frequency sweep tests were performed at 25℃. Storage modulus (G'), loss modulus (G'') values were obtained from Data Analysis software of rheometer (version 2.96).

2.4 Statistical analysis

ANOVA (Analysis of variance), correlation, regression and multiple regression analysis were done by SPSS 17.0.1 programme[12].

3 RESULTS AND DISCUSSION

Fatty acid compositions of six different vegetable oils were analyzed as shown in Table 1. The percentage of total saturated and unsaturated fatty acids for all of the oils analyzed in this investigation ranged from 7.52% to 25.72% and from 72.05% to 91.18%, respectively. Especially, hazelnut, canola and sunflower oils contained very large amount of unsaturated fatty acids, relatively compared to the other oil samples. Degree of unsaturation of canola and hazelnut oils was sourced by mainly monounsaturation whereas sunflower oil unsaturation was caused by polyun-

Table 1 Fatty acid composition (%) of vegetable oil samples.

Fatty acid	Sunflower	Cotton	Canola	Olive	Hazelnut	Soybean
C14:0	0.08	0.72	0.06	–	–	0.07
C16:0	6.36	22.15	4.84	12.73	5.11	10.51
C16:1	0.11	0.55	0.21	0.14	0.15	0.13
C18:0	3.63	2.45	1.92	2.76	2.27	4.12
C18:1	29.30	19.50	62.27	69.95	77.25	23.41
C18:2	58.08	51.79	20.01	10.19	13.59	50.19
C18:3(n-6)	0.16	–	–	–	–	1.29
C20:0	0.70	0.27	0.33	0.31	0.14	1.40
C18:3(n-3)	0.25	0.21	6.17	0.14	0.19	4.29
C22:0	–	0.13	1.51	–	–	–
C24:0	–	–	0.34	–	–	–

saturation. Monounsaturated fatty acids, especially oleic acid ($C_{18:1}$), were the predominant component of hazelnut, olive and canola oils while sunflower, cotton and soybean oils were rich in linoleic acid ($C_{18:2}$). The presence of linolenic acid ($C_{18:3}$) was found as 4.29% and 6.17% in soybean and canola oils, respectively. Other vegetable oils have less amount of linolenic acid.

Steady shear measurements were applied at 25℃ to determine flow behaviour of vegetable oils. As it was seen in Fig. 1, shear stress is directly proportional to the shear rate which means that viscosity of oil samples do not change with shear rate. This type of flow is known as Newtonian flow. The characteristics of this type of flow were determined by the equation given below

$$\sigma = \eta\gamma$$

where σ is the shear stress (Pa), γ is the shear rate (s^{-1}), η is the viscosity (Pa.s). The viscosity of samples is equal to slope of shear stress vs. shear rate curve[13]. In this study, viscosity of each oil samples was found by this way. It was also reported in literature that vegetable oils showed Newtonian flow behaviour due to long chain molecule of oils[9]. However, viscosity values varied obviously depending on the type of oil samples in this study. As it was shown in Table 2, olive oil has highest viscosity, followed by hazelnut, canola and cottonseed oil. Soybean and sunflower oils have the same lowest viscosity. Shear rate vs shear stress curves for all oil type are shown in Fig. 1. The same sequence of vegetable oils was obtained in this figure.

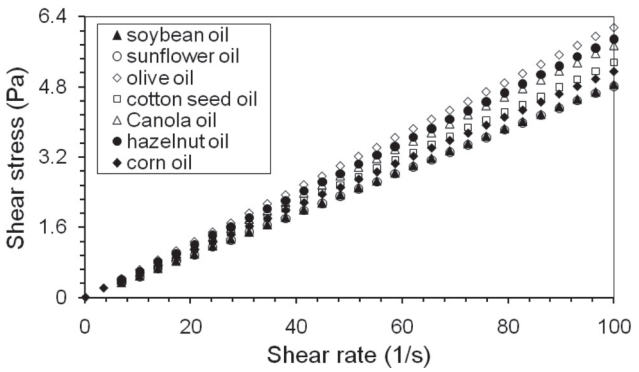


Fig. 1 Flow curves of the vegetable oils.

Highly positive correlation was observed between viscosity and total unsaturation (Table 3). When the viscosities of the vegetable oils were plotted against either monounsaturation (R = 0.89) (Fig. 2) or polyunsaturation (R = −0.97) (Fig. 3). After observation of correlation between unsaturation and viscosity values of oils, regression was applied to predict viscosity values of samples, based on polyunsaturated and monounsaturated composition of oils. As a result of regression the equation below was found (R = 0.875).

$$\eta = 0.06 - 0.004\ x/y \qquad \text{(Eq. 1)}$$

where η is the viscosity of the vegetable oils (Pa.s), x and y are percentage of polyunsaturated and monounsaturated fatty acid composition of oils, respectively.

Especially, a decrease in the oil viscosity was distinctly observed with increasing portion of polyunsaturated and a decreasing portion of monounsaturated fatty acids. This pointed out that the unsaturation level of vegetable oils mainly establishes the viscosity characteristics of them. Since each double bond with a *cis* configuration form results in a twist in the straight chain[14], the presence of

Table 2 Monounsaturated, polyunsaturated, saturated fatty acid composition (%) and viscosities of oil samples.

	Sunflower	Cotton	Canola	Olive	Hazelnut	Soybean
Viscosity (mPa.s)	48.20^{e}	53.50^{d}	57.30^{c}	61.20^{a}	59.70^{b}	48.70^{e}
Monounsaturated	29.41^{e}	20.05^{f}	62.48^{c}	70.09^{b}	77.40^{a}	23.54^{d}
Polyunsaturated	58.49^{a}	52.00^{b}	26.18^{c}	10.33^{e}	13.78^{d}	55.77^{ab}
Total unsaturated	87.90^{b}	72.05^{e}	88.66^{b}	80.42^{c}	91.18^{a}	79.31^{d}
Saturated	10.77^{d}	25.72^{a}	9.00^{e}	15.80^{c}	7.52^{f}	16.10^{b}

Values in the same line with different superscripts are significantly different ($p<0.05$).

Table 3 Correlation coefficients between viscosity and monounsaturated, polyunsaturated fatty acid compositions of oil samples.

	Polyunsaturated	Monounsaturated
Viscosity	0.886*	−0.966**
Significance (2-tailed)	0.019	0.002

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

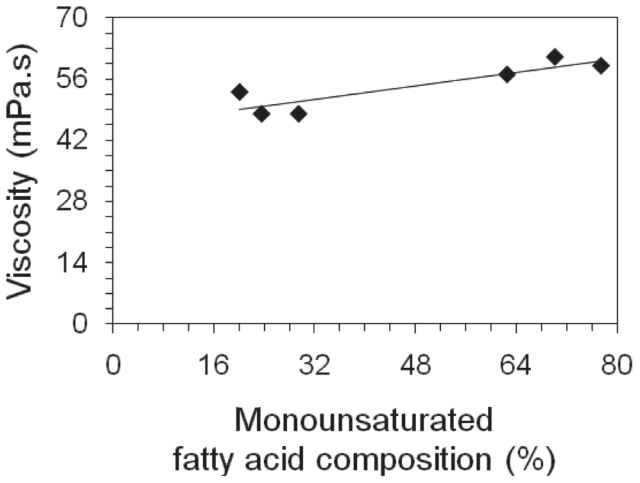


Fig. 2 Correlation between monounsaturated fatty acid composition and viscosity values of oil samples.

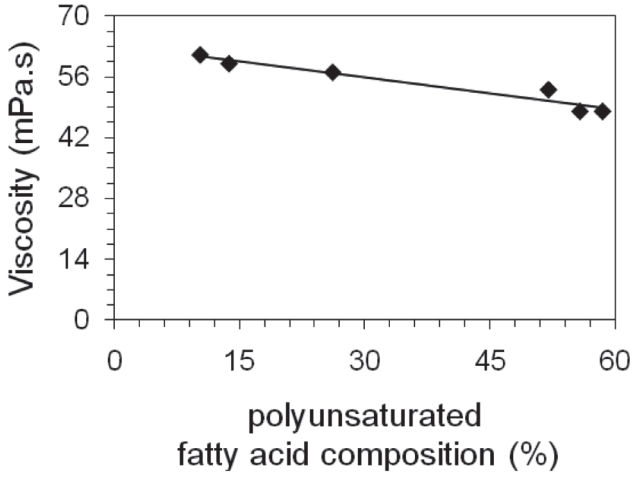


Fig. 3 Correlation between polyunsaturated fatty acid composition and viscosity values of oil samples.

double bond does not allow fatty acid molecules to pile closely together, consequently interfering with packing in the crystalline state. Thus, fatty acids with more double bonds do not have a rigid and fixed structure, being loosely packed and more fluid-like. Kim *et al.*[15] reported that any positive correlation was not observed between viscosity and total unsaturated fatty acids but highly positive correlations were observed between viscosities and ($C_{18:1}$) and ($C_{18:2}$). Existing of correlation between viscosity and these two fatty acids is interesting in which absence of correlation between viscosity and unsaturation. There is not in accordance between this study and our study in this view. Soybean and sunflower oils have the same less viscous structure because of their highly polyunsaturated composition compared to olive, hazelnut and canola oils. Kim *et al.*[15] found small viscosity values for vegetable oils rich in linoleic acid. There is accordance between ours and mentioned study. Although cottonseed oil possesses the similar linoleic acid composition, it has higher viscosity than soybean oil. It may be sourced two main reasons, soybean oil contains some amount of linolenic acid ($C_{18:3}$) and cottonseed oil has more amount of saturated fatty acid especially palmitic acid. Melting point of palmitic acid (62.9℃) is very higher[16] than the experiment temperature (25℃). Also molecular spatial interactions among alkylchain of triglicerides are very important. For example, although the melting point of free fatty acid form of palmitic acid is equal to 62.9℃, it differs in triglyceride molecules from 44℃ (in tripalmitoylglycerol at α position) to 77℃ (in 1-monopalmitoyl-glycerol at β position) according to its position in triglyceride molecules. Fatty acids may be located at different triglyceride positions in different oils. Ennouri *et al.*[17] observed low level of viscosity values in prickly pear seed oil at 60℃. They reported that this temperature was in the same range as the melting point of palmitic acid. Invisible aggregated palmitic acid particles occur because of this temperature difference. Smaller size particles of palmitic acid result in strength of resistance to flow and the increase of the viscosity[17]. For this reason cottonseed oil has higher viscosity values than soybean and sunflower oils. The crude oils contain free fatty acids from natural hydrolysis of the triacylglycerols (triglycerides). On the other hand, commercial oils were refined, so contain traces of free fatty acid. Ennouri *et al.*[17] have used crude pear seed oil in their study. There is a difference between the oil types.

On the other hand we found that olive and hazelnut oils which have the highest monounsaturation, have the more viscous structure than the others. Olive oil has the highest viscosity value followed by hazelnut oil. Kim *et al.*[15] found these two vegetable oils as the viscous oil but they sequenced them opposite of ours. Hazelnut oil has the highest monounsaturation but olive oil has higher saturated fatty acid (15.80%) than its (7.52%). Considering the melting point of the saturated fatty acids especially palmitic acid which were found in olive and hazelnut oil 12.73% and 5.11%, respectively, our findings may be accepted as meaningful. As described previously, because of high melting point of palmitic acid, it causes an aggregation and suspension and this aggregates resisted the flow and this may become the explanation of high viscosity of olive oil compared with the hazelnut oil. Geller and Goodrum[5] reported that viscosity of oil decreased by at least 25% for each 20℃ temperature increase. This might have resulted from the presence of saturated long-chain fatty acid residues in triacylglycerol molecules, because these fatty acids are solid at room temperature.

The dynamic rheological tests in this study were carried out at 0.3 Pa, determined as a result of stress sweep tests of all oil samples, in linear viscoelastic region. For a specific food viscoelastic properties are influenced by frequency, temperature and strain. For strain values within the linear

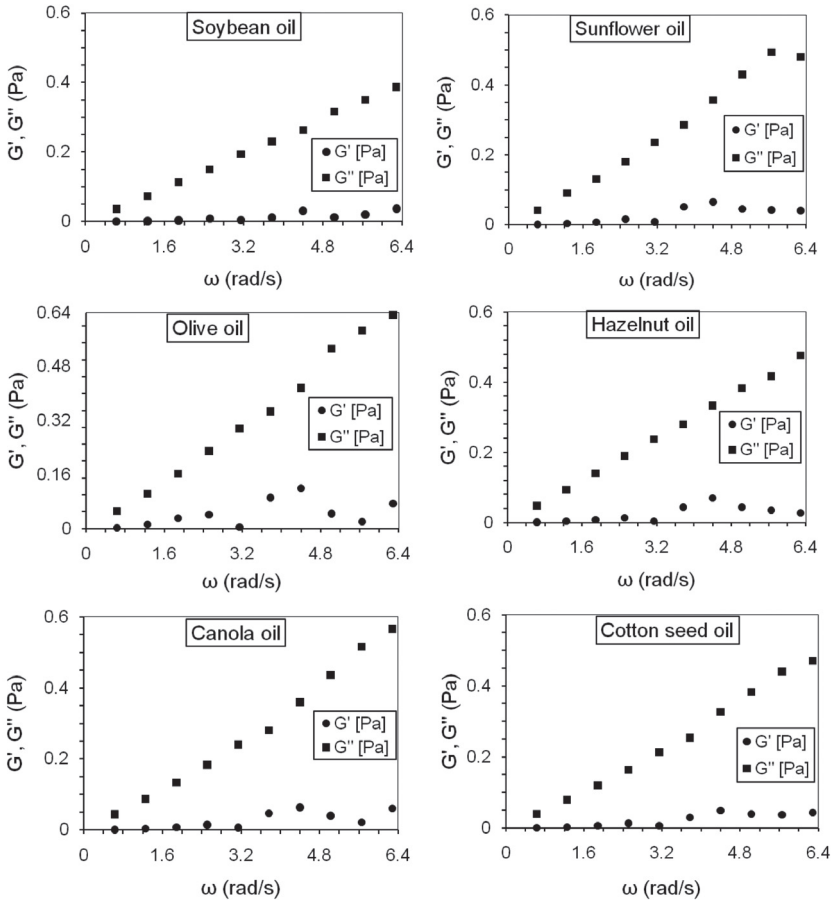


Fig. 4 Changes in the storage and the loss moduli with increasing angular frequency for vegetable oils.

Table 4 Storage modulus (G') and loss modulus (G") values of oil samples*

	Sunflower	Cotton	Canola	Olive	Hazelnut	Soybean
G' (mPa)	40[b]	42[b]	60[a]	75[a]	27[b]	37[b]
G" (mPa)	480[c]	470[c]	567[b]	633[a]	477[c]	387[d]

* These measurements were carried out at angular frequency of 6.283 rad/s. Values in the same line with different superscripts are significantly different ($p<0.05$).

viscoelastic region, these properties are independent of strain[13]. Figure 4 showed the elastic or storage modulus (G') and viscous or loss modulus (G") as a function of the angular frequency (ω) of the each vegetable oil. The storage modulus G' expresses the magnitude of energy that is stored in the material. G" is a measure of the energy that is lost during deformation. Therefore, for a perfectly elastic solid all the energy stored that is G" is zero. In contrast for a liquid with no elastic properties all the energy is dissipated as heat that is G' is zero[13]. As expected the values of G' for oil samples near to zero. Narine and Marangoni[18] observed a logarithmic linear relationship between elastic modulus G' and the solid fat content in their fat crystal studies. But Ennouri *et al.*[17] did not observe this relationship in prickly pear seed oil. They reported that the content of saturated fatty acid in these samples was significant but very low. So the values of dynamic parameters were very weak and did not permit more observation.

If G' is much greater than G", the material will behave more like a solid; that is, the deformations will be essentially elastic. However if G" is much greater than G', the energy used to deform the material is dissipated viscously and the materials behavior is like liquid-like[13]. In this study G" values were superior to G' for all vegetable oil samples. Sunflower, cotton, hazelnut, and soybean oils not significantly different each other, were found as significantly different from canola and olive (Table 4). All of them have viscous characteristics. As it was shown in Fig. 4, G" values increase with increasing of angular frequency. However G' values showed an irregular changes in all oil samples,

which might be resulted from liquid characteristics of oil samples. In addition commercial edible oils have no elasticity over their melting point. Olive oil has the greatest G" values on the other hand it has the greatest G' values compared with others (Table 4). Therefore, both dynamic rheological properties (G' and G") should be evaluated simultaneously during the investigation of them. For obtaining more accurate assessment loss tangent value is used in analysis. The loss tangent (tan δ) value of samples, stating directly the G"/G' ratio, is compared to illustrate the differences in the viscoelastic behavior of samples. Tan δ < 1 indicates elastic behavior while tan δ > 1 indicates viscous behavior. Figure 5 shows the tan δ values of oil samples as a function of frequency (f). As seen in Fig. 5 all of vegetable oil types have tan δ higher than 1. Olive oil which has the biggest viscosity level, has the lowest tan δ value while soybean oil which has the lowest viscosity level, has the biggest tan δ value for all frequency levels (Fig. 5). Tan δ values decreased by increasing of frequency.

Multiple regression analysis was applied to predict tan δ values of samples based on frequency, viscosity and polyunsaturated fatty acid composition of vegetable oils. According to multiple regression the below equation was obtained (R = 0.86).

$$\tan\delta = 49.962 - 8.762(f/\eta) + 0.587\,x \qquad \text{(Eq. 2)}$$

where f is frequency (Hz), η is viscosity (Pa.s) and x is percentage of polyunsaturated fatty acid composition of oils. If equation 1 was put into equation 2, equation 3 was obtained based on polyunsaturated, monounsaturated compositon and viscosity values of oils.

$$\tan\delta = 49.962 - 8.762[f/(0.06 - 0.004(x/y))] + 0.587\,x \qquad \text{(Eq. 3)}$$

where y is percentage of monounsaturated fatty acid composition of oils.

The corn oil sample was used for observation of the performance of the derived equations after determination of relationship between the fatty acid composition and η, tan δ values. The mono and polyunsaturated fatty acid composition of the corn oil were found as 28.89% and 56.54%, respectively. The viscosity of the oil was calculated as 52.2 mPa.s by using Eq. 1, which was found as 51.8 mPa.s by experimentally. It is seen that the predicted and experimental values were very close to each other. In addition, Eq. 2 or 3 was performed to predict tan δ values of the sample at different Hz (0.1, 0.2, 0.3 and 0.4). Figure 6 shows the relationship between the observed and predicted tan δ values, indicating that this equation was adequate for prediction of tan δ values. However there are also some limitations for this equation. These are;

- This study was carried out by refining vegetable oils. So this equation may not applicable for crude oils.
- The rheological measurements performed at 25℃. Therefore equations were notable at this temperature.
- The Eq. 2 or 3 was implemented for low frequency values (0.1 − 0.4 Hz).

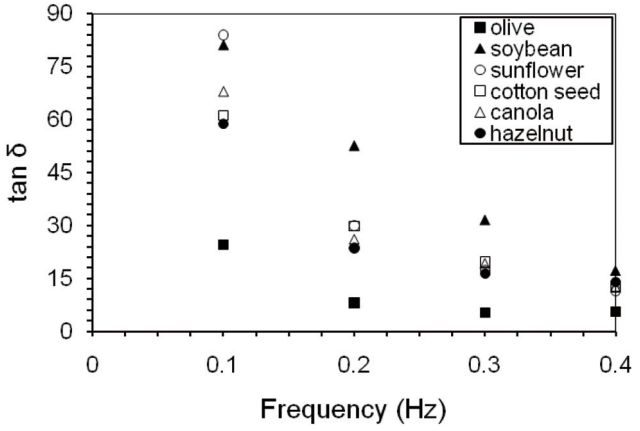


Fig. 5 Frequency dependence of mechanical loss tangent of vegetable oils

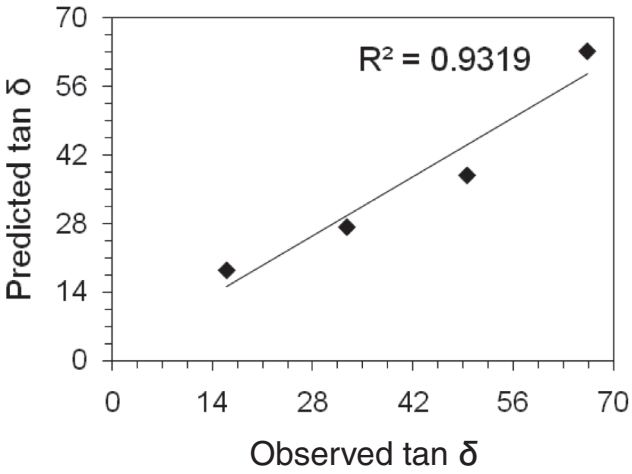


Fig. 6 Relationship between the observed and predicted tan δ (obtained from equation 2 or 3) values of the corn oil sample

4 CONCLUSION

In this study, the effects of fatty acid composition of oils on steady and dynamic rheological properties were examined. As a result of this study, it was found that the viscosity of oil samples may be predicted by using polyunsaturated and monounsaturated fatty acid composition. In addition dynamic mechanical parameter (tan δ) may also be predicted by using frequency, monounsaturated and polyunsaturated fatty acids compositions of oils. As a conclusion, according to results of this study, if the mono and polyunsaturated values of oil samples are known, the viscosity and tan δ values may be predicted without any rheo-

logical measurements by means of equations obtained in this study.

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