Experimental investigation of electro-rheological properties of modeled vegetable oils

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Abstract Vegetable oil becomes polarized on oxidation and polymerization resulting in the formation of peroxide, triglycerides, etc. The quality and reusable state were investigated for sunflower, sesame, rice bran oil and model oil with the addition of oleic acid (2, 4 and 6 %) and antioxidants (citric and tert-Butyl hydroquinone-TBHQ). Excessive reclaims of cooking oil produce toxic by-products due to chemical breakdown that induce the production of polar compounds in oil. To determine the consumable fitness, variations of dielectric constant are observed at different temperatures (29 to 70 °C) and frequencies (1 to 10⁷Hz) for the cooking oil. Physical parameters, such as viscosity and density associated with the saturated and unsaturated fatty acid, are also measured at different temperatures to determine the quality of oil. Dielectric constant and viscosity are correlated and analyzed using a newly developed equation with high correlation constant ($R^2=0.998$) for oil added with citric acid. Oil added with 2–4 % of oleic acid is observed to have high determination coefficient ($R^2>0.92$). A lowest correlation ($R^2=0.6–0.7$) was observed for the oil added with TBHQ. The present study also states that addition of TBHQ to oil does not impede oxidation reaction. Besides, even the shelf life of the oil could not be enhanced and may produce adverse effects in human health.

Keywords Vegetable oil · Model oil · Citric acid · TBHQ · Dielectric constant · Viscosity · Density

Introduction

Oil is an indispensable cooking ingredient, which when subjected to high temperatures and repeated heating, degrades to produce peroxides, free fatty acids, polar monomers, dimers, trimers and oligomers. These chemical changes undergone by the oil have a direct effect on the health of the consumer. Moreover the content of polar compounds in frying oil has been associated with endothelial dysfunction and hypertension (Williams et al. 1999; Soriguer et al. 2003).

The chemical and a few non-chemical methods, which have been used so far to test the grade of cooking oil, have been proven extensively. Traditional methods include: sensory evaluation method, column chromatography, chemical system and infrared detection method (Augustin et al. 1987; Al-Kahtani 1991). These chemical methods have disadvantages like time-consuming, extensive use of chemical reagents that causes pollution, lack of in-situ advantage, costly and minimal elemental information given for most samples. Electro-rheological properties, on the other hand, have several notable advantages over traditional chemical methods. Dielectric constants quantify the polar compounds; viscosity exhibits the saturated free fatty acids accurately and instantaneously (Velasco et al. 2004). Hence electro-rheological properties of oil are estimated for determining oil quality.

Relation between TPC values and viscosity for oil was studied by early researchers and was observed that they were linearly correlated (Al-Kahtani 1991; El-Shami et al. 1992). The maximum suggested levels for polar compounds present in frying or cooking fats and oil is 25/100 g of oil or 25 % (Pace et al. 1968; Risman and Bengtsson 1971; El-Shami et al.

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1992). Dillip Kumar et al. (2013) have suggested that electrical properties may be used as indicators of condition and quality of edible oil. The changes in physical and chemical properties partially depend on the unsaturation degree of the fatty acids, as well as on the temperature to which they are heated (Velasco et al. 2004; Quiles et al. 2006; Kim et al. 2010). The dielectric constant is generally influenced by temperature, moisture levels, electrical frequency and thickness of oil sample. The rate-of-change of the dielectric constant will depend on the physical properties of the oil that affects the settling rate of the contaminants, such as density and viscosity. It has been observed that the change in the dielectric constant of oil provides the simplest method for assessing their deterioration (Fritsch 1981). Augustin et al. (1987) have reported the existence of highly significant correlation between the dielectric constant of oil and the polar components present in it. Further, the dielectric constant of different fresh fats has been found to be different. Both observations regarding dielectric constant of oil are manifestations of behaviour of polar molecules in a viscous media. More polar compounds such as triglycerides, polymers and peroxides are formed from the hydrolysis, oxidation, or polymerization processes resulting in higher dielectric constants in frying fats (Choe and Min 2007; Hampikyan et al. 2011).

Quantification of TPC and polymers is used as a conventional method in the study of thermal degradation and antioxidant efficiency. In the past, there were few data about the effects of antioxidant activity in oil employed in industry because they were presumed to be safe since they occur in foods and have been used for centuries (Rubalya and Neelamegam 2012). Adding natural and synthetic antioxidants in foods have received special attention as they inhibit biological harmful oxidation reactions in oil (Pokorny et al. 2001). As a consequence, antioxidant compounds are now-a-days of more and more interest in oil industries. Antioxidant inhibits the functioning of chain reaction involved in oil. By eliminating or keeping the amount of free radicals to a minimum quantity, it can avoid oxidation of oil and peroxide formation (Rubalya and Neelamegam 2012).

During frying process, a wide variety of chemical reactions result in the formation of compounds with high molecular weight and polarity. The repeated use of oil at high temperatures results in several oxidative, polymerization and thermal degradation reactions leading to changes in their physical, chemical, nutritional and sensory properties (Kochhar 2000; Warner and Gehring 2009).

Possibilities to enhance the stability during the frying process include the use of modeled oil with different fatty acid composition, such as high oleic contents or by adding natural and synthetic antioxidants. Therefore, attempts have been made to assess the quality of the oil and their modeled variants based on easily measurable physical properties like viscosity, dielectric constant and density. The influence of temperature

and frequency on the polar compounds in oil is studied using dielectric constant, conductivity and resistivity. Variation of viscosity with temperature is experimental and correlated with empirical equations for better fit. Novel equation relating viscosity and dielectric constant was correlated and observed to signpost high determination coefficient.

Materials and methods

Popular branded rice bran oil (*Oryza sativa*), sesame oil (*Sesamum indicum*) and sunflower oil (*Helianthus annuus*) were bought from a local grocery store in Tiruchirappalli District, Tamil Nadu, India. For this study, pure oil consisting of three samples and their modeled mixtures with stabilizing agents and antioxidants (Oleic acid, Citric acid and TBHQ were purchased from Sigma Aldrich Chemicals India Private Ltd.) were taken for analysis. Oleic acid was added in proportions 2, 4, 6 to 100 ml of rice bran oil, sesame oil and sunflower oil and thereby, nine samples were prepared. Antioxidants namely citric acid and Tertiary Butyl Hydroquinone (TBHQ) were added at a concentration of 1 mg/L of oil consisting of 6 samples. These 18 samples were kept in dark bottles with a paper wrapped around them to offer protection from external atmospheric conditions and thereby ambient temperature was maintained.

Dielectric constant measurement

Dielectric constant of the oil was measured by the capacitive method using DCK-001 (Mittal Enterprises, New Delhi, India) at 2 MHz. Dielectric constant from 1 Hz to 10 MHz was measured in accordance with the standard of IEC 61620. All dielectric measurements follow ISO 9001:2000.

Viscosity measurement

Kinematic viscosities (ν) of oil were measured using redwood viscometer (manufactured by Associated Instrument Manufacturers, India Private Limited, New Delhi, India). The observation was made thrice and the average value was taken for further calculations.

Density measurement

Density of the oil was precisely measured using a pycnometer with an accuracy of ± 0.2 kg m⁻³ in accordance with the ASTM (American Society for Testing and Materials) standard method D891-09.

Statistical analysis

The independent parameter temperature and dependent parameter dielectric constant were fitted with Arrhenius equation and analysed using SPSS (version 12) as illustrated in Table 1. Empirical equation relating viscosity to dielectric constant was correlated and correlation coefficient R^2 was observed between 0.811 and 0.993 with 2–6 % of accuracy as shown in Table 2. Five different models were used in the study of variation of flow properties of sample with temperature. Andrade, Walther and Wright ASTM have been used for this purpose. Tables 3, 4 and 5 list out the values of constants A, B and C, along with the correlation coefficient and standard error estimate (SEE) using least square approximation. The R^2 value and SEE were computed using graph pad software.

Result and discussion

The electrical property-dielectric constant of oil and model oil decreases with increase in temperature as illustrated in Fig. 1. When thermal energy of oil increases dielectric constant decreases, due to the presence of unsaturated fatty acids and decrease in force of attraction between the polar compounds (Dilip Kumar et al. 2013). It is observed that ϵ_r value of Fig. 1a for rice bran oil is less and almost remains to be constant with the increase in temperature as the electrostatic charges in the oil are less. Drastic variation is observed when oleic (Monounsaturated fatty acid) acid is added to the rice bran

oil. 2 % oleic acid varies in ϵ_r with respect to temperature by 3.3; 4 % oleic varies by 18 and 6 % oleic varies by 29.6 % and the saturated to unsaturated ratio increases from 2.8 to 3.4. Even though the percentage of rise in dielectric constant increases with increase in oleic acid, addition of 2 % has not created drastic changes in the characteristic behavior of model oil. Hence this combination can be used for frying with good oxidative stability. Rancidity in oil can also be retarded with the addition of antioxidants. Citric acid and TBHQ are also added to study the polarizing behavior in the oil. A 5.8 % increase in dielectric constant is observed with citric acid and 17.5 % change has been illustrated from TBHQ. Controlled electrostatic charges are observed in pure rice bran oil and also rice bran oil added with 2 % of oleic acid.

Figure 1b shows the variation of dielectric constant with temperature for pure sesame oil and modeled oil. Dielectric constant of sesame oil decreases with increase in the range of temperature from 25 to 70 °C as the polarization effect surged by 9.7 %. Increase in 7 % of dielectric constant is observed with the addition of 2 % of oleic acid, 15 % rise for 4 % of oleic acid and 19.8 % upsurge with the addition of 6 % oleic acid in sesame oil. The saturated to unsaturated fatty acid ratio increases from 5 to 5.6. The increase in dielectric constant of sesame oil added with citric acid is 12.8 % and for TBHQ it is greater than 60 %. The above percentage of variation shows that it is better to use sesame oil added with 2 % of oleic, than pure oil added with citric acid for its good oxidative stability. Sesame oil contains several natural antioxidants of the lignin structure, such as sesamol, so it is not necessary to stabilize it.

Table 1 Constant and regression coefficient for Arrhenius equation relating dielectric constant and temperature

Oil	A	Activation energy (Ea) kJ/kg	R^2 value	Standard error
Rice bran oil	1.355	25.18	0.914	0.279
Rice bran +2%oleic	1.154	29.27	0.950	0.189
Rice bran +4%oleic	1.498	63.74	0.915	0.358
Rice bran +6%oleic	1.103	73.02	0.919	0.757
Rice bran +Citric	1.499	23.05	0.929	0.313
Rice bran +TBHQ	1.481	109.50	0.746	0.468
Sesame oil	1.624	26.55	0.983	0.675
Sesame +2%oleic	1.060	31.90	0.925	0.251
Sesame +4%oleic	1.998	62.24	0.915	0.541
Sesame +6%oleic	1.707	38.77	0.850	0.616
Sesame +Citric	1.579	25.75	0.985	0.088
Sesame +TBHQ	1.876	135.27	0.787	1.567
Sunflower oil	1.338	28.12	0.962	0.005
Sunflower +2%oleic	0.986	45.93	0.959	0.526
Sunflower +4%oleic	1.659	64.68	0.951	0.129
Sunflower +6%oleic	1.391	105.34	0.914	0.033
Sunflower +Citric	1.484	39.86	0.945	0.045
Sunflower +TBHQ	1.388	237.78	0.869	0.182

Table 2 Constant and regression coefficient for $1/\eta = A\varepsilon_r + B$ equation relating dielectric constant and temperature

Oil	A	B	R^2 value	Standard error
Rice bran	-4.520	1.637	0.958	0.361
Rice bran+ 2%oleic+citric	-1.585	1.645	0.992	0.154
Rice bran +2%oleic+TBHQ	-8.378	2.062	0.832	0.113
Sesame	-2.093	1.982	0.944	0.407
Sesame+ 2%oleic+citric	-3.875	1.803	0.985	0.139
Sesame+ 2%oleic+TBHQ	-25.14	3.552	0.811	1.330
Sunflower	-3.235	3.055	0.967	0.184
Sunflower+ 2%oleic+citric	-2.686	1.755	0.993	0.229
Sunflower+ 2%oleic+ TBHQ	-7.096	1.903	0.898	0.091

Addition of more natural or synthetic antioxidants leads to the formation of gum and long chain fatty acids which might produce toxicities or mutagenicities, and thus endanger the health of people (Williams et al. 1999; Tjaša et al. 2013).

Sunflower oil already has 69 % of oleic acid and unsaturated to saturated ratio increases from 7 to 7.8; hence the addition of more oleic acid also has impact on mobilization of electrostatic charges. Figure 1c illustrates least percentage of increase with the addition of citric acid and 4 % oleic acid. Polarization effect increases with increase in polar compounds observed with the addition of TBHQ and pure sunflower oil (Pokorny et al. 2001). Addition of antioxidant shows significant improvement in its oxidative stability. The study is highly used in designing model vegetable oil. Even a small change in dielectric constant greater than 0.01 indicates chemical changes in oil quality that needs to be evaluated by conventional oil analysis methods.

Effect of temperature on electrical property is studied using Arrhenius equation. The following Arrhenius equation can be used to determine the activation energy of the mobility of electrostatic charges in oil with temperature.

$$\varepsilon' = Ae^{E_a/RT} \quad (1)$$

E_a is the activation energy (kJ/kg), R is universal gas constant (8.314 kJ/kg mol K) and A is a constant. A plot of natural logarithm of dielectric constant and reciprocal of temperature exhibits linear graph for the oil, from which the value of E_a was evaluated. Table 1 lists out the values of constant A and B , correlation coefficient and standard error estimate (SEE) with least square approximation analyzed by SPSS (version 12). The correlation coefficient R^2 varies between 0.746 and 0.985. The least correlation coefficient is observed when oil is added with TBHQ; highest is observed in oil added with citric acid and pure oil. Activation energy for the polar charges ranges from 23.05 to 237.78 kJ/mol. Activation energy (E_a) was defined as minimum energy required for overcoming the energy barrier for electrostatic charges to flow. The E_a value increases with the addition of high % of oleic and TBHQ (solid content dissolved in oil).

A novel empirical equation relating dielectric constant and inverse value of viscosity was framed and analyzed for all the samples to study the determination coefficient between the parameters.

$$1/\eta = A\varepsilon_r + B \quad (2)$$

Table 2 lists out the values of constant A and B , correlation coefficient and standard error estimate (SEE) with least square approximation analyzed by SPSS (version 12). The

Table 3 Constant and regression coefficient for empirical equation relating viscosity and temperature for pure rice bran oil and its modeled oil

Oil	Model	A	B	C	R^2 value	Standard error
Rice bran(RB)	$\ln \eta = A + B * T$	5.12	0.033	—	0.956	0.086
	$\ln \eta = A + B * \ln T$	8.58	-0.301	—	0.977	0.266
	$\ln \eta = A + B * T * C * T^2$	5.18	-0.04	-0.002	0.984	0.198
	$\log \log (\eta + 0.8) = A + B * T$	0.749	-0.336	—	0.994	0.035
	$\ln \ln \ln (\eta) = A + B * \ln T$	0.998	0.765	—	0.998	0.036
RB +2%oleic+citric	$\ln \eta = A + B * T$	5.867	0.046	—	0.977	0.085
	$\ln \eta = A + B * \ln T$	10.68	-1.81	—	0.986	0.263
	$\ln \eta = A + B * T + C * T^2$	5.418	-0.03	-0.0001	0.998	0.235
	$\log \log (\eta + 0.8) = A + B * T$	0.942	-0.48	—	0.999	0.033
	$\ln \ln \ln (\eta) = A + B * \ln T$	0.945	-0.44	—	0.999	0.034
RB +2%oleic+TBHQ	$\ln \eta = A + B * T$	5.735	-0.05	—	0.972	0.098
	$\ln \eta = A + B * \ln T$	10.38	-1.80	—	0.956	0.317
	$\ln \eta = A + B * T + C * T^2$	6.749	-0.05	-0.0007	0.985	0.283
	$\log \log (\eta + 0.8) = A + B * T$	0.933	-0.45	—	0.980	0.049
	$\ln \ln \ln (\eta) = A + B * \ln T$	1.122	-0.567	—	0.976	0.066

Table 4 Constant and regression coefficient for empirical equation relating viscosity and temperature for pure sesame and its model oil

Oil	Model	A	B	C	R ² value	Standard Error
Sesame oil (SO)	$\ln \eta = A + B * T$	5.569	-0.052	–	0.964	0.118
	$\ln \eta = A + B * \ln T$	10.99	-2.038	–	0.982	0.372
	$\ln \eta = A + B * T + C * T^2$	5.379	-0.052	-0.001	0.989	0.235
	$\log \log (\eta + 0.8) = A + B * T$	1.075	-0.559	–	0.996	0.049
	$\ln \ln \ln (\eta) = A + B * \ln T$	1.098	-0.576	–	0.995	0.052
SO +2%oleic+ citric	$\ln \eta = A + B * T$	5.399	-0.041	–	0.967	0.09
	$\ln \eta = A + B * \ln T$	9.655	-1.06	–	0.984	0.273
	$\ln \eta = A + B * T + C * T^2$	5.235	-0.040	-0.0001	0.976	0.253
	$\log \log (\eta + 0.8) = A + B * T$	0.977	-0.479	–	0.981	0.05
	$\ln \ln \ln (\eta) = A + B * \ln T$	0.873	-0.412	–	0.987	0.035
SO +2%oleic+ TBHQ	$\ln \eta = A + B * T$	4.944	-0.033	–	0.957	0.028
	$\ln \eta = A + B * \ln T$	7.995	-1.187	–	0.929	0.135
	$\ln \eta = A + B * T + C * T^2$	5.198	-0.047	-0.0002	0.965	0.089
	$\log \log (\eta + 0.8) = A + B * T$	0.6962	-0.311	–	0.984	0.025
	$\ln \ln \ln (\eta) = A + B * \ln T$	0.829	-0.393	–	0.972	0.025

correlation coefficient R^2 varies from 0.811 to 0.993. A least correlation coefficient is observed when oil is added with TBHQ; highest is observed in oil added with citric acid and pure oil. The analysis can help a researcher to design a real time instrument that relates the dielectric constant in estimating the quality of oil.

Dielectric constant factor is examined at frequency ranges from 1 to 10^7 Hz as shown in Fig. 2. The measure of dielectric constant from the capacitance and equivalent resistance are measured using the following equation.

$$\varepsilon' = C_p / K_c \quad (3)$$

Where the dielectric constant is represented as ε' , and the capacitance is represented as C_p , cell constant is represented as K_c . The capacitance and cell constant were examined from measurements with Aldrich 227048 at each concentration. The resistance data can also be represented as the specific electrical conductivity, σ

$$\sigma = \varepsilon_0 / R_p K_c \quad (4)$$

Where the resistance of the sample is denoted as R_p , and ω is the angular frequency ($\omega = 2\pi f$), f is the frequency, ε_0 is the permittivity of a vacuum ($8.854 \times 10^{-12} \text{ Fm}^{-1}$). The ratio of the

Table 5 Constant and regression coefficient for empirical equation relating viscosity and temperature for pure sunflower and its model oil

Oil	Model	A	B	C	R ² value	Standard error
Sunflower oil (SO)	$\ln \eta = A + B * T$	5.087	-0.037	–	0.986	0.061
	$\ln \eta = A + B * \ln T$	8.875	-1.44	–	0.956	0.416
	$\ln \eta = A + B * T + C * T^2$	3.274	-0.05	-0.0011	0.995	0.062
	$\log \log (\eta + 0.8) = A + B * T$	0.819	-0.39	–	0.995	0.07
	$\ln \ln \ln (\eta) = A + B * \ln T$	5.087	-0.044	–	0.996	0.061
SO+2%oleic+citric	$\ln \eta = A + B * T$	5.255	-0.037	–	0.997	0.024
	$\ln \eta = A + B * \ln T$	9.157	-1.474	–	0.994	0.161
	$\ln \eta = A + B * T + C * T^2$	4.288	-0.0075	-0.0005	0.998	0.117
	$\log \log (\eta + 0.8) = A + B * T$	0.828	-0.384	–	0.989	0.03
	$\ln \ln \ln (\eta) = A + B * \ln T$	0.827	-0.385	–	0.991	0.029
SO+2%oleic+TBHQ	$\ln \eta = A + B * T$	4.964	-0.035	–	0.927	0.036
	$\ln \eta = A + B * \ln T$	8.232	-1.27	–	0.926	0.147
	$\ln \eta = A + B * T + C * T^2$	5.3	-0.654	-0.0002	0.985	0.108
	$\log \log (\eta + 0.8) = A + B * T$	0.732	-0.339	–	0.988	0.027
	$\ln \ln \ln (\eta) = A + B * \ln T$	0.93	-0.455	–	0.987	0.078

Fig. 1 Dependence of dielectric constant of Rice Bran (a), Sesame (b), Sunflower (c) and its modified oils with respect to temperature

dielectric constant and the loss from the capacitance and the resistance is termed as Quality factor Q .

$$Q = \tan \delta = \epsilon'' / \epsilon' = R_p / C_p \quad (5)$$

The measured values of dielectric constant, loss tangent, conductivity and resistivity are shown in Fig. 2. Concentration of polar compounds increases with the degradation of oil; hence dielectric constant can be regarded as the measure of degradation since dielectric constant is directly proportional to the polar compounds present in it. The polarization effect is due to the orientation of dipole with applied electric field (Hamparsun Hampikyan et al. 2011; Kumar et al. 2013). The variation is more at low frequency due to large relaxation time. It is evident from the figure that citric effectively decreases the dielectric constant than TBHQ. Figure 2a

illustrates the variation of dielectric constant, loss tangent, conductivity and resistivity of pure rice bran oil, rice bran added with citric and TBHQ. It is observed that the dielectric constant of rice bran oil added with antioxidants decreases from 3.6 to 2.7 with increase in frequency. It varies for small frequency value and remains constant for long frequency range. Figure 2b shows that pure sesame oil has less dielectric constant, and addition of bioactive compounds has less effect in reduction of antioxidants but maintains the stability for long frequency range (Kochhar 2000).

The dielectric loss tangent decreases with increase in frequency of applied alternating electric field. The loss tangent is found to be satisfactory at room temperature. It is observed that in Fig. 2a the tangent loss value of rice bran doped with citric is very low and varies up to 15 Hz whereas in rice bran oil doped with TBHQ it remains low only after 30 Hz. Figure 2b illustrates that sesame added with citric has low loss tangent and has variation less than 10 Hz; but sesame oil added with TBHQ has variation of about 50 Hz. This study emphasizes that oil added with citric has less polar compound effects and acts as best insulator. The dielectric constant and loss tangent will not be greatly affected because of the neutral fat which is in the form of saturated, free fatty acids and triglycerides. Dielectric constant and loss tangent are affected by the polar fat and free radicals that try to arrange themselves to the applied electric field. The majority of polar fat is unsaturated phospholipids. The polar fat is a fat in which two fatty acids and one base is attached to the glycerol molecule.

The higher the molecular weight of this oil the more is the specific resistance and lower is the loss tangent ($\tan \Delta$). The resistivity of the samples is found to decrease satisfactorily with the addition of antioxidants, which plays an important role in decreasing the specific resistance at low frequency. Figure 2a shows that the resistivity of rice bran oil, modeled oil added with bioactive compound, which decreases exponentially to a lowest value up to 8000 Hz, maintains the same till 10^{-7} MHz frequency. Figure 2b illustrates that the three samples of sesame oil show lowest saturation resistivity from 6000 Hz. It can be seen that sesame oil shows lesser loss tangent and higher resistivity as it has 9 % higher molecular weight compared to rice bran oil. Oil with higher molecular weight has shown lesser loss tangent and higher resistivity.

Dielectric constant was observed to decrease with increase in frequency as polarization takes place at low frequency. Loss tangent, conductivity and resistivity are interdependent parameters. Hence as the conductivity increases, resistivity decreases and loss tangent value decreases to a low value and remains to be a constant at high frequency (Risman and Bengtsson 1971).

The density of the oil influences the dependence of the dielectric constant on temperature - the less dense the oil is, the fewer is the number of oil molecules per unit volume. A smaller number of molecules per unit volume mean that there

Fig. 2 **a** Dielectric constant, conductivity, resistivity and loss factor versus frequency of rice bran oil. **b** Dielectric constant, conductivity, resistivity and loss factor versus frequency of sesame oil

is less interaction with the electric fields and therefore a decrease in the dielectric constant. As the temperature increases, the density decreases and hence the dielectric constant of the oil decreases which is shown in Fig. 3a. The density of pure oil decreases with increase in temperature due to the presence of double bond and decreases in number of molecules per unit volume due to thermal activity. The percentage variation of density in the case of rice bran oil is 1.754 %, in sesame oil 1.954 % and in sunflower oil it is about 0.88 %. To increase

the oxidative stability in oil, oleic acid and bioactive compounds are added (Rubalya et al. 2013). As shown in Fig. 3b densities of oil with 2 % of oleic acid added with citric acid remain to be stable during the temperature range of 50 to 60 °C. The main functional properties of antioxidant in oil are free electron scavenging, metal chelating and synergism. (Wanasundara and Shahidi 2005). From the literature survey, it was observed that antioxidants can be used in edible oil for slowing down the ionization reaction which leads to the

Fig. 3 Dependence of density of **a.** pure oil **b.** Oil with 2%Oleic+Citric Acid **c.** Oil with 2%Oleic+TBHQ with Temperature

breakdown of oil. The addition of antioxidants to oil may control the formation of trans-fats; retard the formation of triglycerides during the processing and heating of edible oil. Figure 3c shows the dependence of density on temperature for the three oils added with 2 % of oleic and TBHQ. Rice bran and sesame model oil start their stability from 40 °C whereas modeled sunflower oil exhibits its stability above 50 °C. From the stability, it is inferred that production of free radicals (peroxidants) is being protected by antioxidants, which helps to keep a balance up to a point. If the balance is tainted, “oxidative stress” occurs in oil that leads to deterioration, and consumption of that oil affects the normal cell functions and even causes cell death.

As the temperature increases, viscosity of the oil decreases which is shown in Fig. 4. Change in viscosity could be used as an index for the quality analysis of food product like milk, oil, beverage, etc. (Hosahalli et al. 2015). Viscosity increases with chain lengths of triglyceride fatty acids and decreases with unsaturation; in other words, it increases with hydrogenation. Presence of unsaturated fatty acids decreases the viscosity and power loss that take place in the measurement of dielectric constant. Decrease in viscosity of oil may be due to increase in mobility of polar molecules as the temperature increases.

Stabilizing agent like oleic acid with different proportion and antioxidants such as citric (Natural) and TBHQ (Synthetic) are added to determine the eminence of the oil. Figure 4a illustrates the exponential viscosity of pure rice

bran, sesame and sunflower oil with the temperature up to 70 °C. Viscous nature of oil depends on the percentage of saturated fatty acids in oil. Viscosity of oil decreases with increase in temperature as the intermolecular force exhibited between the atoms decreases with thermal acceleration. Figure 4b exemplifies the dependence of viscosity of oil with 2 % oleic acid and Citric acid. The percentage of variation of viscosity with temperature of modified oil, which is less from 40 °C, shows the potency of antioxidant added to the oil. Figure 4c epitomizes that addition of TBHQ produces more % of variation and does not maintain a constant change in the viscosity of oil. Synthetic antioxidants are widely used as food additives to prevent rancidification, owing to their high performance, low cost and wide availability. But this antioxidant used as preservative in the food industry may be responsible for liver damage and *carcinogenesis*; for this reason, interest in the use of natural antioxidants has increased (Kim et al. 2010).

Viscosity varies nonlinearly with temperature; hence four mathematical models, Andrade, Walther and Wright ASTM were used to study and analyze the flow properties of the pure oil and its modeled oil with temperature as given in Tables 3, 4 and 5.

1. Andrade equation

$$(1^{st} \text{ order}) \quad \ln \eta = A + B \cdot T \quad (6)$$

Fig. 4 Dependence of viscosity of a. pure oil b. Oil with 2%Oleic+Citric Acid c. Oil with 2%+TBHQ with Temperature

$$\ln \eta = A + B \cdot \ln T \quad (7)$$

$$(1^{st} \text{ order}) \quad \ln \eta = A + B \cdot T + C \cdot T^2 \quad (8)$$

Natural logarithm of kinematic viscosity $\ln \eta$, constants A and B are the computed by nonlinear curve fitting procedure and T is the temperature in °C. The regression analysis for the oil samples using the above equations are computed and exemplified in Table 3. Equation (6) exhibit determination coefficient ranges from 0.956 to 0.997 and the eccentricity of 6 to 8 % was observed between calculated and measured viscosity. Dependence of viscosity with independent factor temperature that varies in exponential and logarithmic form for the oil samples are analyzed. Equation (7) illustrates the calculated determination coefficient ranges from 0.984 to 0.995 and the variation ranges from 2 to 5 % of viscosity between calculated and experimental value. The variation of viscosity with temperature is correlated using Eq. (8) and the correlation coefficient for oil samples exhibit the value from 0.956 to 0.998. The deviance of 1.5 to 8 % was observed between calculated and experimental viscosity.

2. Walter equation

$$\log \log (\eta + 0.8) = A + B \cdot T \quad (9)$$

It is an ASTM (American Society for Testing Materials) charted equation relating viscosity with temperature. Regression analysis was done using graph pad software and the coefficient varied from 0.945 to 0.999. The experimental value varies by ± 2 %.

3. Wright equation (ASTM 341–93)

$$\ln \ln f n (\eta) = A + B \cdot \ln T \quad (10)$$

Wright modified Walter equation pointedly and linearized the discrepancy of viscosity with temperature by including the function of viscosity with quadratic equation. The correlation coefficient varies from 0.946 to 0.999. The accuracy (≤ 1.5 %) is observed to be more in this model compared to all the above modeling equations (Rubalya et al. 2015). Constants A, B and C are obtained from the correlation constants may depend on the saturated and unsaturated fatty acids present in the oil (Kim et al. 2010).

Conclusion

Electro-rheological characteristics of vegetable oil and modified vegetable oil are studied in the stability and quality investigation.

Even though many physical, chemical and analytical evaluations are done in food quality analysis, the non-invasive electric property of oil can be used as a sharp sensing parameter. To increase the shelf life and stability of the oil, it is modified with the addition of unsaturated fatty acid (oleic) and antioxidants. Oil like sunflower oil shows positive response with the addition of oleic acid and antioxidant like citric acid. It is also observed that the addition of more percentage of oleic acid may also increase the content of saturated fatty acids on degradation. A novel relation was demarcated between viscosity and dielectric constant for six samples except the oil added with TBHQ and was observed to be highly correlated ($R^2 > 0.96$). The electric properties of oil are stable above 5000 to 10^7 Hz. The increase in temperature decreases the molecular interaction between the fatty acids in oil and makes the viscosity decrease with increase in temperature. Andrade, Walther, Wright models are studied for the accuracy of data and were found that Walter and Wright are the best models. The outcome of the study could be used in pipelining design for oil transfer. The present study also emphasizes that the usage of synthetic antioxidant like TBHQ can be totally avoided as it neither provides stability nor reduces the adverse effect. The study can be used to device an instrument related with dielectric constant or conductivity in the quality analysis of oil in food industry.

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