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Kinetics of Autoxidative Polymerization of Sunflowerseed Oil

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The rates of polymerization of unhydrogenated and hydrogenated sunflowerseed oils were measured under atmospheric conditions in the various containers (glass, PET and metal). Polymerization rates showed a strong dependence on the degree of unsaturation and the light transmittance of the containers. The average molecular weights of polymerized oils were determined by viscosity measurements. The relationship between viscosity and average molecular weight was determined. It is seen that unhydrogenated sunflowerseed oil has a higher polymerization rate than hydrogenated oil samples in a glass container and they has higher viscosity values.

Key Words: Autoxidation, molecular weight, polymerization, reaction rate constant, unsaturation, viscosity.

Introduction

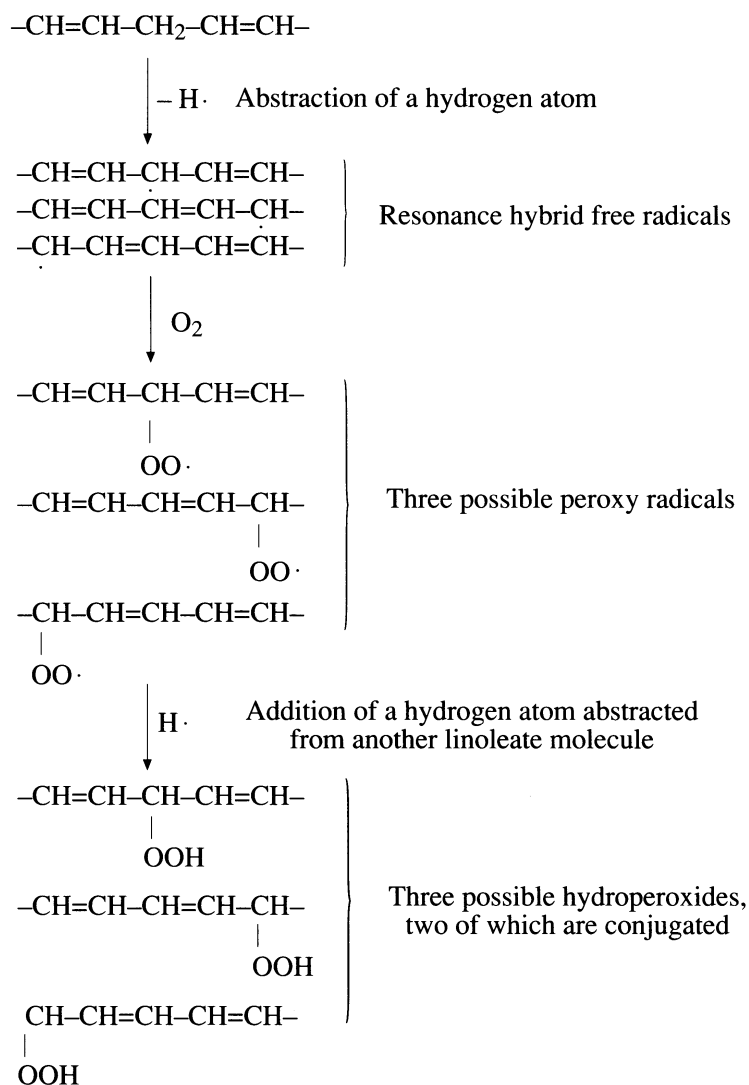
Traditionally, vegetable oils have been used not only for edible purposes, but for such nonfood applications as drying oils in paint, soaps, cosmetics, pharmaceuticals, synthetic rubber, and emulsifiers. The mechanisms for gum formation by oxidative polymerization in drying oils have been summarized in several reviews¹⁻³.

Rheineck and Austin⁴ summarized the major changes that occur during oxidative polymerization as follows:

1. A period of induction at the beginning of the reaction during which no visible change in physical or chemical properties in the oil is noticed. Natural antioxidant compounds are consumed during this period.
2. The reaction becomes perceptible and oxygen uptake is considerable. Discrete interaction of oxygen and olefins taken place followed by the formation of hydroperoxides.
3. Conjugation of double bonds occurs accompanied by isomerization of *cis* to *trans* unsaturation.
4. The hydroperoxides start to decompose to form a high free radical concentration. The reaction becomes autocatalytic.

5. Polymerization and scission reactions begin and yield high-molecular-weight cross-linked products and low-molecular-weight carbonyl and hydroxy compounds. Carbon dioxide and water are also formed and are present in the volatile products of film formation.

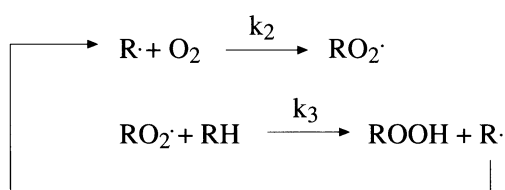
When oils containing linoleate or more highly unsaturated acids (such as sunflowerseed oil) are oxidized, conjugated diene concentration increases at about the same rate as oxygen uptake and peroxide formation. Today it is generally believed that the oxidation of linoleate⁵ proceeds as follows:



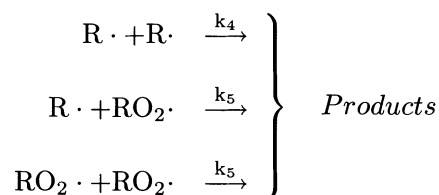
According to Uri⁶ the kinetics of the autoxidation of linoleate has three stages:

Initiation: production of R and RO₂ radicals at the rate r₁

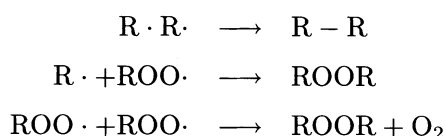
Propagation:



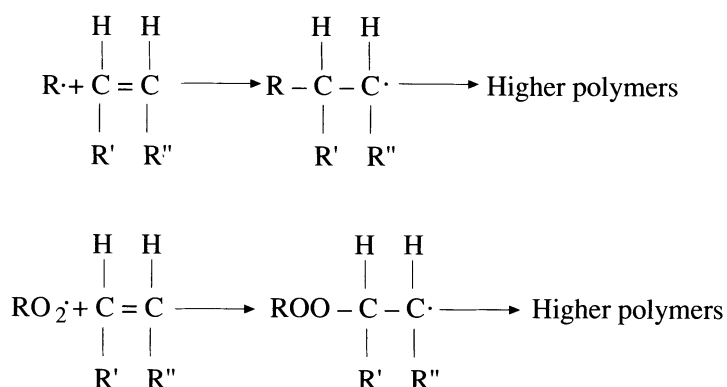
Termination:



It is the termination step that is of primary importance in the film-forming process. Polymers are formed by combination of free radicals.



In addition to these dimers formed by combination of radicals, higher molecular weight polymers are formed through vinyl polymerization:



The thermal polymerization of nonconjugated linoleic acid carried out by Wheeler and White⁷ and Sen Gupta and Scharmann^{8,9} yielded a complex of mono-, bi-, tricyclic ring structures present. McMahon and Crowell¹⁰ dealt with the characterization of products from clay-catalyzed polymerization of tall oil fatty acids. Morita et al.¹¹ studied on the metal-requiring and non-metal-requiring catalysts in the autoxidation of methyl linoleate.

Morrison and Robertson¹² evaluated the oxidative stability and polymer formation of hydrogenated sunflowerseed oil on heating. Frankel¹³ dealt with lipid oxidation. Brimberg¹⁴ studied the kinetics of the autoxidation of fats.

The aim of this study was to determine rates and rate constants of autoxidative polymerization of unhydrogenated and hydrogenated sunflowerseed oils in various containers.

Experimental

Materials

Unhydrogenated and hydrogenated sunflowerseed oils were supplied by the Thrace Union (Trakya Birlik) Co., Edirne, Turkey. Equal sized glass, PET (polyethylene terephthalate) and metallic containers (covered by tin) of 3 internal diameter were used as reaction vessels.

Instruments and Methods

Fatty acid composition was determined by a 2 m, 1/4" × 2 mm glass column packed with 5 % PEGA on chromosorb W 60-80 mesh at 175 °C in a Shimadzu GC 6 AM Model gas chromatograph (Shimadzu, Kyoto, Japan) (Table 1)¹⁵.

Table 1. Composition of Sunflowerseed Oils (weight %) by means of Gas Chromatography.

Fatty acid	Unhydrogenated	Hydrogenated
Myristic, C _{14:0}	0.1	0.1
Palmitic, C _{16:0}	7.7	8.5
Stearic, C _{18:0}	3.6	5.1
Oleic, C _{18:1}	24.7	76.6
Linoleic, C _{18:2}	63.9	9.7

The oil samples of 150 ml were placed into each other containers, and were exposed directly to sunlight in the presence of air oxygen under atmospheric conditions. The overall reaction time was 30 days, and the viscosity values were determined simultaneously within 2 day intervals at 25 °C.

The viscosity was measured with a Falling-ball viscometer¹⁶, Haake Type B 3, connected to a thermostat at 25 °C. The average molecular weights of the oil samples were determined by the viscosity method¹⁶ and the Mark-Houwink equation¹⁷

$$[\eta] = K\bar{M}^a \quad (1)$$

where $[\eta]$ is the intrinsic viscosity \bar{M} is the average molecular weight, K and a are constants depending on the solvent and the temperature. The values of K and a are 0.94×10^{-4} and 0.76 for benzene, respectively¹⁶. The constants K and a depend upon the type of polymer, the solvent, and the temperature of the viscosity determinations. The intrinsic viscosity may be calculated as follows:

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} \quad (2)$$

where c is the number of grams of the oil in 100 ml of benzene. A plot of η_{sp}/c versus c gives a straight line, and the extrapolated values is the intrinsic viscosity. The specific viscosity is

$$\eta_{sp} = \eta_r - 1 = \frac{t}{t_0} - 1 \quad (3)$$

where η_r is the relative viscosity, or viscosity ratio, which is η/η_0 ; and η_0 , and t and t_0 are the viscosities and the flow-times of solution and solvent, respectively.

Results and Discussion

The fatty acid composition of oil samples are presented in Table 1. The unhydrogenated sunflowerseed oil has a high linoleic acid content, while the hydrogenated oil has a high oleic acid content.

The viscosity values of oil samples were used as a measure of the degree of polymerization. The viscosity measurements for autoxidative polymerization at 25 °C are shown in Figures 1 and 2. Viscosity data for applied to an exponential mode¹⁸,

$$\eta = a e^{bt} \quad (4)$$

where η represents the viscosity value, t is time, and a and b are constants determined by the data (Table 2).

Table 2. Viscosity constants for autoxidative polymerization in the presence of air oxygen under atmospheric conditions in the different containers at 25 °C.

Constants	Container type		
	Glass	PET	Metal
For unhydrogenated oil:			
a ($\text{g cm}^{-1} \text{s}^{-1}$)	319.6	310.9	289.0
$b \times 10^{-3}$ (day^{-1})	8.5	7.9	5.8
For hydrogenated oil:			
a ($\text{g cm}^{-1} \text{s}^{-1}$)	445.4	444.5	443.5
$b \times 10^{-3}$ (day^{-1})	3.2	2.9	2.2

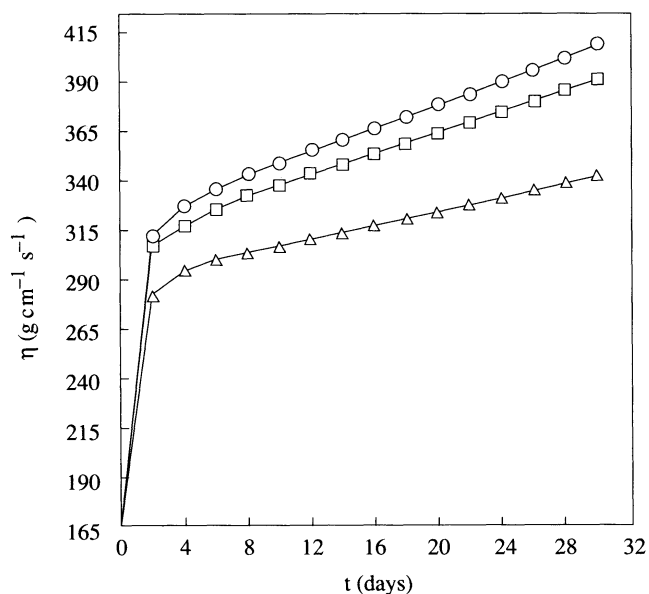


Figure 1. Viscosities of autoxidized unhydrogenated sunflowerseed oil in the presence of air oxygen under atmospheric conditions at 25 °C vs. time: \circ , in the glass container, \square , in the PET container, and Δ , in the metallic container.

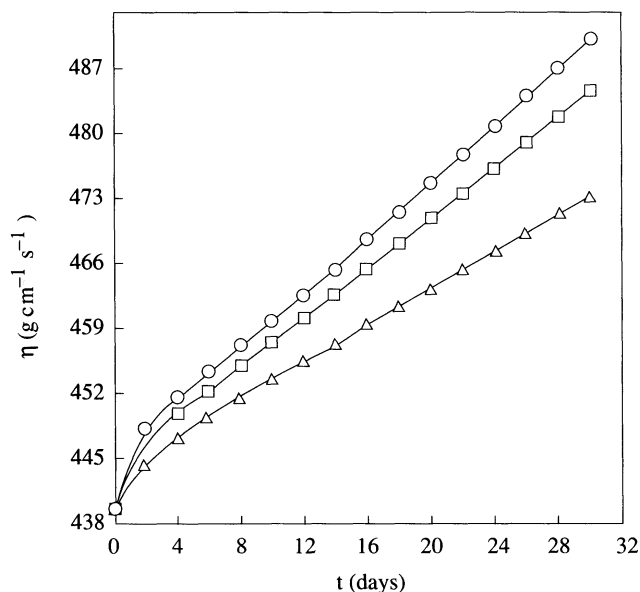


Figure 2. Viscosities of autoxidized hydrogenated sunflowerseed oil in the presence of air oxygen under atmospheric conditions 25 °C vs. time: \circ , in the glass container, \square , in the PET container, and Δ , in the metallic container.

Rates of autoxidative polymerization were measured a strong for unhydrogenated and hydrogenated sunflowerseed oil. Since the free-radical formation starts after the fourth day and there is apparently an increase in the viscosity value, we considered all values after that day. High linoleic acid unhydrogenated sunflowerseed oil showed a viscosity increase ca. 5/2 that of oleic hydrogenated for autoxidative polymerization, as can be seen in Figures 1 and 2.

Rates of autoxidative polymerization showed a strong dependence on the degree of unsaturation and container type. Unhydrogenated sunflowerseed oil has a higher viscosity than hydrogenated oil because unhydrogenated oil has more unsaturation (Table 1). Since the glass container has higher light transmittance than the PET and metallic containers, the oil samples kept in this container have higher viscosity values.

Average molecular weights of the oil samples for autoxidative polymerization are shown in Figures 3 and 4. Unhydrogenated oil showed an average molecular weight increase ca. 11/2 that of hydrogenated oil.

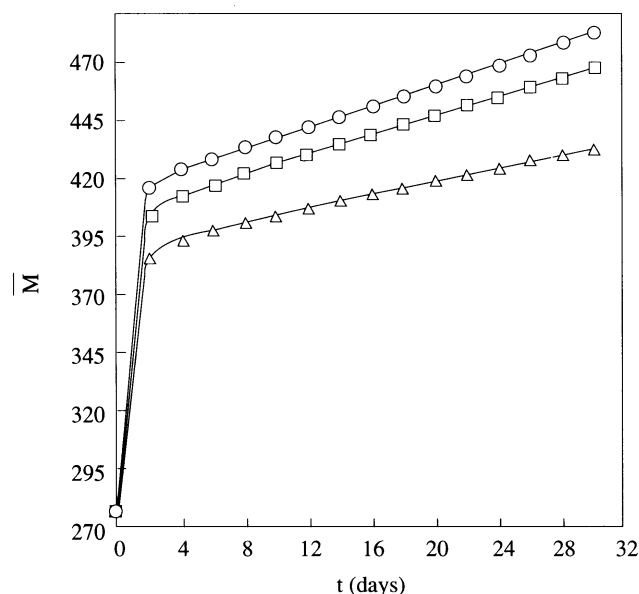


Figure 3. Average molecular weights of autoxidized unhydrogenated sunflowerseed oil in the presence of air oxygen under atmospheric conditions at 25 °C vs. time: ○, in the glass container, □, in the PET container, and Δ, in the metallic container.

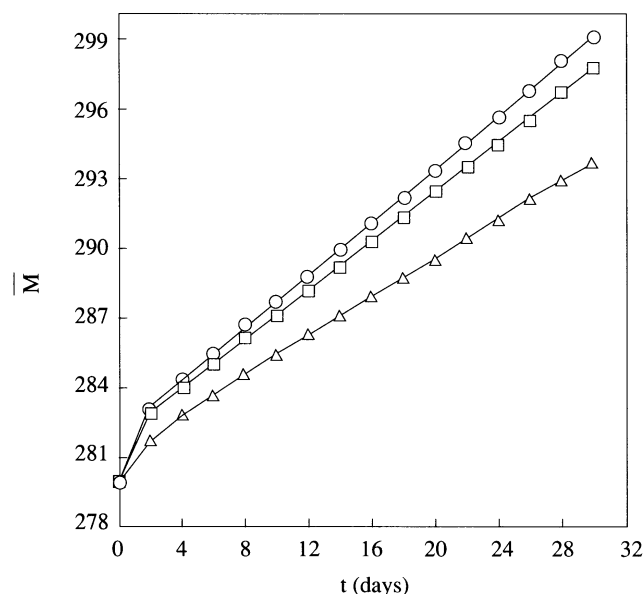


Figure 4. Average molecular weights of autoxidized hydrogenated sunflowerseed oil in the presence of air oxygen under atmospheric conditions at 25 °C vs. time: ○, in the glass container, □, in the PET container, and Δ, in the metallic container.

Since the autoxidative polymerization reaction has first-order kinetics¹⁹, the rate constants for this reaction were obtained by means of a plot of the logarithm of the average molecular weight values versus time (Figures 5 and 6). These values are given in Table 3. It seems that the reaction rate constants of autoxidative polymerization for unhydrogenated sunflowerseed oil are higher than those of hydrogenated oil and the values of the reaction rate constants for the samples in the glass container are higher than those in the pet and metallic containers.

Table 3. Reaction rate constants for autoxidative polymerization in the presence of air oxygen under atmospheric conditions in the different containers at 25 °C.

Container type	$k_{unh.} \times 10^{-3} \text{ (day}^{-1}\text{)}$	$k_{hyd.} \times 10^{-3} \text{ (day}^{-1}\text{)}$
Glass	4.8798	1.9695
PET	4.7064	1.8412
Metal	3.5938	1.4635

Viscosities for autoxidative polymerization versus average molecular weights are shown in Figures 7 and 8. Viscosity data are applied according to the relationship to unhydrogenated sunflowerseed oil in the glass container

$$\eta_g = 9.26 \times 10^{-3} \bar{M}^{1.73} \text{ g cm}^{-1} \text{ s}^{-1} \quad (5)$$

where \bar{M} is the average molecular weight. In the PET container

$$\eta_p = 13.16 \times 10^{-3} \bar{M}^{1.68} \text{ (g cm}^{-1} \text{ s}^{-1}\text{)} \quad (6)$$

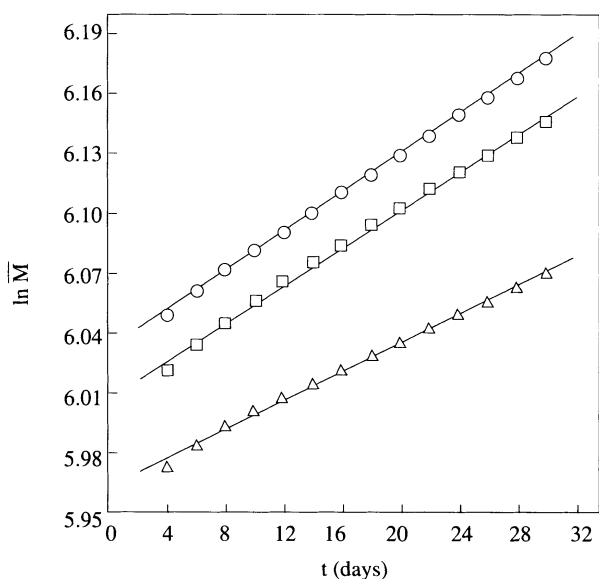


Figure 5. The plot of $\ln M_w$ vs. time for autoxidized unhydrogenated sunflowerseed oil in the presence of air oxygen under atmospheric conditions at 25°C: \circ , in the glass container, \square , in the PET container, and Δ , in the metallic container.

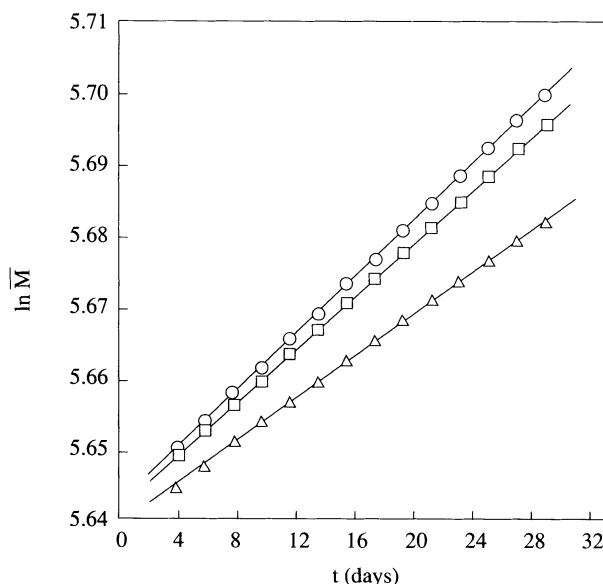


Figure 6. The plot of $\ln M_w$ vs. time for autoxidized hydrogenated sunflowerseed oil in the presence of air oxygen under atmospheric conditions at 25°C: \circ , in the glass container, \square , in the PET container, and Δ , in the metallic container.

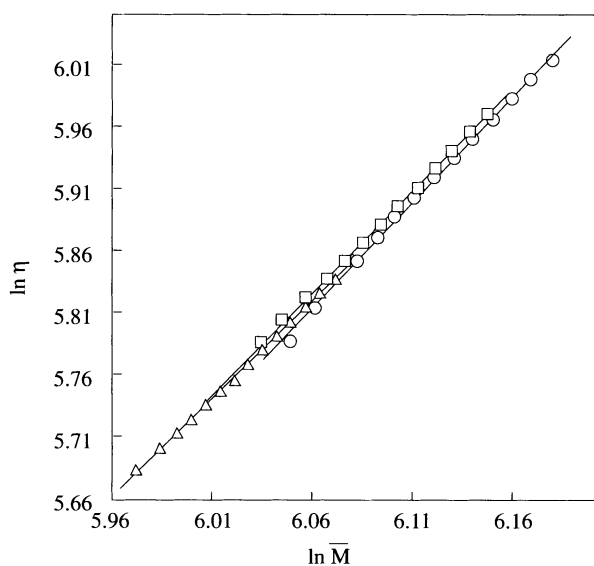


Figure 7. Longarithmic plot of viscosity vs. average molecular weight of polymerized unhydrogenated sunflowerseed oil by autoxidation in the presence of air oxygen under atmospheric conditions 25°C: \circ , in the glass container, \square , in the PET container, and Δ , in the metallic container.

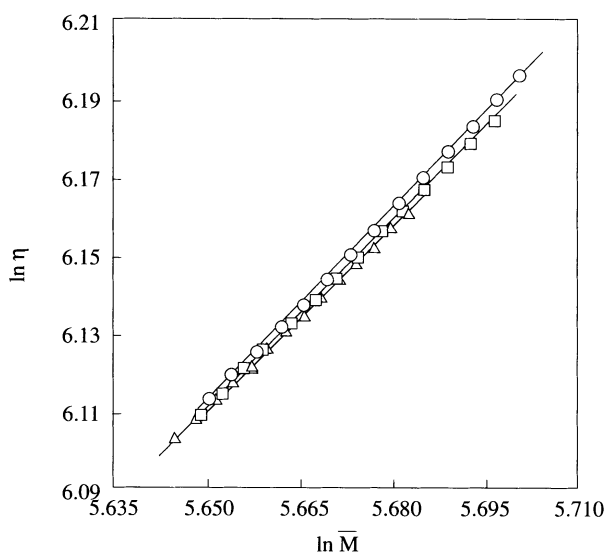


Figure 8. Longarithmic plot of viscosity vs. average molecular weight of polymerized hydrogenated sunflowerseed oil by autoxidation in the presence of air oxygen under atmospheric conditions 25°C: \circ , in the glass container, \square , in the PET container, and Δ , in the metallic container.

and in the metallic container

$$\eta_m = 18.83 \times 10^{-3} \bar{M}^{1.62} \text{ (g cm}^{-1} \text{ s}^{-1}\text{)} \quad (7)$$

For hydrogenated sunflowerseed oil in the glass container

$$\eta_g = 46.17 \times 10^{-3} \bar{M}^{1.63} \text{ (g cm}^{-1}\text{s}^{-1}\text{)} \quad (8)$$

in the PET container

$$\eta_p = 64.90 \times 10^{-3} \bar{M}^{1.57} \text{ (g cm}^{-1}\text{s}^{-1}\text{)} \quad (9)$$

and in the metallic container

$$\eta_m = 90.07 \times 10^{-3} \bar{M}^{1.51} \text{ (g cm}^{-1}\text{s}^{-1}\text{)} \quad (10)$$

These relationships are of the same form as the relationships describing polymer melt viscosities¹⁸. The high degree of linoleic unhydrogenated sunflower unsaturation produces viscosities by an exponent factor of an average of 1.68, and for hydrogenated sunflower by an average of 1.57. However, this exponential factor decreases by the decreasing unsaturation of oils and the light transmittance of the containers; therefore, the degree of polymerization also decreases.

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