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Investigation of the drying process of linseed oil using FTIR and ToF-SIMS

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Abstract. The drying process of linseed oil, oxidized at 80 °C, has been investigated with rheology measurements, Fourier transformation infrared spectroscopy (FTIR), and time of flight secondary ion mass spectrometry (ToF-SIMS). The drying process can be divided into three main steps: initiation, propagation and termination. ToF-SIMS spectra show that the oxidation is initiated at the linolenic (three double bonds) and linoleic fatty acids (two double bonds). ToF-SIMS spectra reveal peaks that can be assigned to ketones, alcohols and hydroperoxides. In this article it is shown that FTIR in combination with ToF-SIMS are well suited tools for investigations of various fatty acid components and reaction products of linseed oil.

1. Introduction

Increased environmental awareness is a driving force for developing new environmental friendly coatings, lacquer, varnish, lubrication systems and a development in this direction is to use coatings based on vegetable oils for galvanized steel and stainless steel.

Historically, drying oils have been key components of oil paint and many varnishes [1]. The most commonly used drying oils are linseed oil, tung oil, and walnut oil. Common for these paints and varnishes are long drying times. It is of interest to develop new coating systems based on raw material produced from a renewable feedstock, e.g. vegetable oil derivatives and methyl esters of vegetable oil [2]. Advancement in modern crops techniques has introduced new ways to alter the concentration of different fatty acids in the vegetable oil so they will mainly contain the fatty acid structures desired for a specific application [3]. One possible application for tailored oils with a high concentration of poly unsaturated fatty acids in the oil could be permanent coatings for metals. In the development of new coatings it is necessary to improve the knowledge about the complex reaction mechanisms involved in the drying process and to develop new methods for this research. Static time of flight secondary mass spectrometry (ToF-SIMS) is a method that can be used for investigating polymers and biologic materials [4].

The drying process of linseed oil occurs through an oxidative reaction. It is generally accepted that the oxidation process of poly unsaturated can be described within the framework of the free radical propagation theory and this explain the formation of an initiation step prior to the propagation step [5]. The oxidation of the linoleic and linolenic acid is initiated by free radical abstraction of a hydrogen atom from the relatively weak C-H bond of the bis-allylic methylene, schematically illustrated in

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Figure 1 [6-8]. The delocalized radical can react with an oxygen molecule under the formation of a peroxy radical. In the next step the peroxy radical can extract a hydrogen atom from an adjacent fatty acid in the same oil molecule or from an adjacent oil molecule which leads to a propagation of the radical reaction and the formation of hydroperoxide. Beside oxidation the radical reaction can lead to a polymerisation reaction by the formation of C-C, C-O-C, C-O-O-C bonds between the fatty acid chains. For the diene structure shown in figure 1 the initial process in forming hydroperoxide is coupled to an isomerisation leading preferentially to conjugation of the double bonds.

In this work we have investigated the oxidative process of linseed oil with rheology measurements, Fourier transformation infrared spectroscopy (FTIR), and ToF-SIMS. The main research question addressed is which information about the drying process that can be extracted using the ToF-SIMS analysis technique. Data presented here are selected to give information about the initial step, propagation step and the termination step.

2. Experimental

The vegetable oil was a special linseed oil high in linoleic acid content, supplied by Svenska Lantmännen AB, and was used in the as-received condition. Table 1 shows the name, formula, characteristic ions and weight distribution of the different fatty acids in the linseed oil. The linseed oil molecule is a glycerol ester and the distribution of the three fatty acids is random within the oil molecule. The characteristic ions are obtained by breaking the ester bond to the glycerol molecule. The samples were investigated in both positive ion and negative in mode. In this article we present the result obtained in the negative ion mode.

Table 1. The formula, characteristic ions in SIMS and concentration of fatty acids.

Name	Formula	Characteristic ions - SIMS	Weight-%
Palmitic acid	C ₁₅ H ₃₁ COOH	C ₁₅ H ₃₁ COO ⁻	6.1
Stearic acid	C ₁₇ H ₃₅ COOH	C ₁₇ H ₃₅ COO ⁻	3.9
Oleic acid	C ₁₇ H ₃₃ COOH	C ₁₇ H ₃₃ COO ⁻	16.1
Linoleic acid	C ₁₇ H ₃₁ COOH	C ₁₇ H ₃₁ COO ⁻	70.6
Linolenic acid	C ₁₇ H ₂₉ COOH	C ₁₇ H ₂₉ COO ⁻	2.1
Others	-	-	1.2

The samples were prepared in two steps. In the first, a batch of linseed oil was heated up to 80 °C under continuous stirring by a magnetic stirrer. Oil samples taken from the batch at different times were investigated with viscosity measurements FTIR, ToF-SIMS. In the second step the thin film sample was prepared by coating pre-oxidized oil (40 h) on a Si wafer substrate. The thin film sample was then heated in an oven for 24 h at 80 °C.

Rheology measurements were carried out with a Physica MCR-301 rheometer. FTIR measurements were performed with a Perkin Elmer Spectra One attenuated total reflectance FTIR spectrometer using an energy resolution of 4 cm⁻¹. ToF-SIMS analyses were performed with a PHI TRIFT II instrument using a 15 keV pulsed liquid metal Ga ion source isotopically enriched in ⁶⁹Ga, at a base pressure < 2*10⁻⁸ Pa. Negative ion spectra were obtained using a 600 pA DC primary ion beam pulsed with a frequency of 8 kHz (m/z = 0.5-2000 amu), a pulse width of 12 ns (~1 ns bunched) and rastered over a surface area of 100×100 μm². The total integrated primary ion dose was below 10¹² ions/cm² ensuring static analyzing conditions. The mass resolution at mass 25 (C₂H) was around m/Δm = 4500. All spectra were calibrated using the exact masses of peaks of known composition. Peak identification was done on the basis of the exact mass of the secondary ions.

Results and discussion

Figure 2 shows the change in viscosity as a function of heating time. During the first 32 h the viscosity increases slowly, almost linearly, with time. At 32 h there is a sudden change in the inclination of the curve hereafter the viscosity increases faster as a function of time. The first part up to 32 h is the

initiation step and after this the propagation step follows [5]. The change in slope of the viscosity as a function of time indicates that the polymerisation reaction has resulted in the formation of larger oligomers involving several oil molecules.

Figure 3 shows the structures around 2900 cm^{-1} in the FTIR spectra from the pure oil (Pure), oil oxidized for 40 h (oil ox 40 h) and the sample prepared from the thin film (Thin film ox 24 h). The spectral feature at 2927 cm^{-1} and 2855 cm^{-1} representing the C-H stretching (asymmetric and symmetric, respectively) of CH_2 and the shoulder on the 2927 cm^{-1} peak at 2956 cm^{-1} representing the asymmetric C-H stretching of CH_3 . All samples show this characteristic structure even if the spectrum from the thin film showed a much lower total intensity and has to be multiplied by a factor of 25 in order to compare the spectra. The structure at 3010 represent the C-H stretching of aliphatic $-\text{CH}=\text{CH}-$ related to un-conjugated *cis*-double bonds. The trend is that it decreases as a function of time and has completely vanished in the spectra from the thin film. The prevalent interpretation for this development is that the decline in intensity is due to *cis-trans* isomerisation that is a result of the oxidation and polymerisation [7,9].

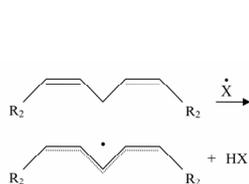


Figure 1. Initial radical formation

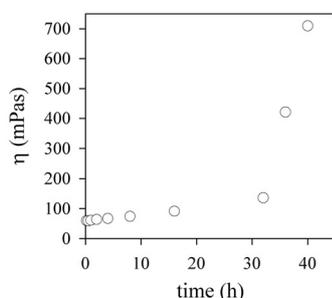


Figure 2. Change in viscosity as a function of heating time.

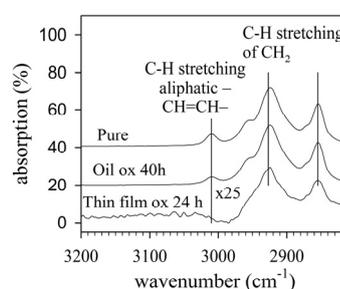


Figure 3. FTIR in the region $3200\text{-}2910\text{ cm}^{-1}$

Figures 4 shows ToF-SIMS spectra recorded in negative ion mode. The different peaks are assigned to their corresponding ion fragment. The mass spectra of the pure oil display peaks at masses 255, 277, 279, 281 and 283 amu characteristic for the fatty acids: palmitic, stearic, oleic, linoleic, and linolenic acid, respectively. The peaks are labelled in figure 4 by the characteristic fragments. All spectra are normalized in such a way that the intensity of the fragments from the palmitic acid has the same intensity in the all spectra. The intensity of the different peaks in the spectrum from the pure oil corresponds well to the nominal values given in table 1.

After 40 h of oxidation the intensity of the peaks corresponding to the linoleic (two double bonds), and linolenic acid (three double bonds) decreases markedly. For the linoleic acid the decrease is about a factor of 2. The intensity in the peaks corresponding to oleic acid (single double bond) and the stearic acid (saturated) is almost the same as in the spectra from the pure oil. In the spectra from the thin film the spectral intensity from the unsaturated fatty oils is missing. This shows that the surface of the thin film sample has been thoroughly cured and all unsaturated fatty acids have reacted. This condition represents the termination step where even the oleic acid has reacted. The only un-reacted fatty acids that are left are the saturated palmitic and stearic acids.

In addition to the peaks corresponding to the fatty acids, peaks are detectable at 293 amu ($277 + 16$), 295 amu ($279 + 16$), 297 amu, and 311 amu ($279+32$). Since oxygen has a mass of 16 amu this indicates that these later peaks correspond to oxidized fatty acids. The pure oil does display these structures, indicating that the fatty acid was partly oxidized in the as received condition. The intensity of these structures increases in the spectra from the oil oxidized for 40 h. In the spectra from the thin film the spectral shape changes and it is only the peaks at 297 and 311 amu that shows an appreciable intensity. Based on their mass and chemical formula it is proposed that the fragments of the $\text{C}_{17}\text{H}_{29}\text{OCOO}^-$ (293 amu), $\text{C}_{17}\text{H}_{31}\text{OCOO}^-$ (295 amu), and $\text{C}_{17}\text{H}_{33}\text{OCOO}^-$ (297 amu) correspond to oxidized fatty acids where the oxygen bond is in the form of ketones and/or alcohols. It is likely that

the structure at 297 amu corresponds to a linoleic (279 amu) acid that has abstracted one O and two H forming both a ketone and alcohol. This interpretation is rather uncertain and there exist other possibilities. Following this line of interpretation it is proposed that the $C_{17}H_{31}O_2COO^-$ (311 amu) fragment is related to hydroperoxides of the linoleic acid.

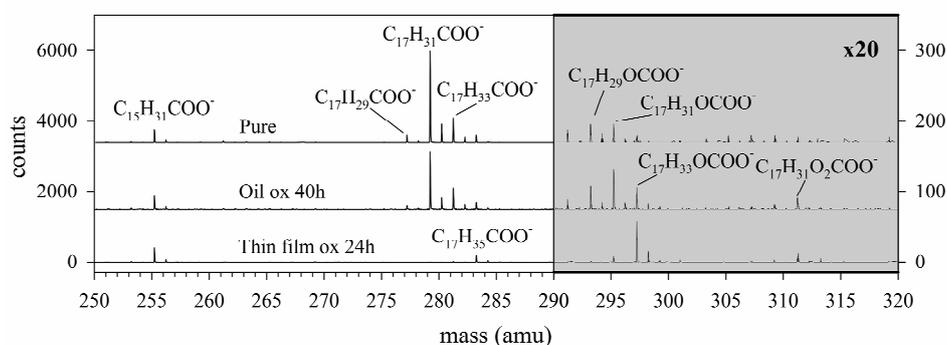


Figure 4. SIMS spectra recorded in negative mode. The y-scale in spectra between mass 290 and 300 is multiplied by a factor of 10.

The pure oil was slightly oxidized as is evident by the presence of oxidized fragments in ToF-SIMS spectra (Pure in figure 4). The rheology measurements is in accordance with earlier published studies [5] and FTIR spectra from the pure oil showed similar structure as reported in the literature for pure linseed oil [7,9]. This combined show that it can be assumed that the pre-oxidation have little effects on the results presented here.

Summary

In summary, the oxidation process of linseed oil was studied with rheology measurements, FTIR and ToF-SIMS measurements. It was possible to follow the reaction by combing the information obtained from the three techniques. The rheology measurements give a clear indication on the transition from the initiation step to the propagation step. FTIR gives information on a molecular level on chemical state of the reaction. With ToF-SIMS it is possible to follow the reaction of the different fatty acids during the course of the oxidation.

Acknowledgment

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