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Polymer Degradation and Stability 65 (1999) 303–313

Polymer Degradation and Stability

Drying and oxidative degradation of linseed oil

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Received 1 September 1998; received in revised form 16 February 1999; accepted 20 February 1999

Abstract

The drying and oxidative degradation of linseed oil have been investigated through exposition of samples in form of thin films to indoor laboratory conditions, or treated at a constant temperature of 80°C, or with irradiation at wavelengths >295 mm. Structure and property changes resulted almost independent of the different treatments and were followed by Fourier transform infrared analysis (FTIR), thermogravimetry (TG), differential scanning calorimetry (DSC), insoluble determination and size exclusion chromatography (SEC). The initial phase of drying consists of the autoxidation phenomenon of the unsaturated fatty acid components with the development of extensive cross-linking, together with formation of conjugated unsaturations. The following stage of slow consumption of labile cross-links gives rise to a highly stable network, which contains small amounts of low molecular weight molecules, either formed by fragmentation or still present as unreacted triglycerides. The oxidative degradation of linseed oil consists of the continuation of the hardening process, and only for long periods of artificial ageing, corresponding to years of natural ageing, the oxidation also takes place on the alkylic segments, leading to partial fragmentation of the structure. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Linseed oil; Triglycerides; Drying; Hardening; Oxidative degradation

1. Introduction

Drying oils are natural fatty oils, largely composed of mixtures of triglycerides. These are esters formed between one molecule of glycerol and three molecules of various linear fatty acids. The most common fatty acids encountered in the composition of drying oils are saturated acids with 12, 14, 16 or 18 carbon atoms (lauric, myristic, palmitic and stearic acids, respectively) and C_{18} polyunsaturated acids with 1, 2 or 3 double bonds (oleic, linoleic and linolenic acids, respectively) [1]. The drying power of such oils is directly related to the chemical reactivity conferred on the triglyceride molecules by the double bonds of the unsaturated acids, which allows them to react with the oxygen of air and with one another to form a polymeric network.

Since the fifteenth century drying oils, and in particular linseed oil, were extensively used as a medium for paintings [2], owing to their capacity, after being spread out in a thin layer, to form a continuous film with good optical and mechanical properties within a reasonable time [3]. The better performances of linseed oil compared with other common oils are mainly related with its faster drying, due to higher concentration of linolenic acid (Table 1) [4].

The hardening of linseed oil has been the subject of several studies but it is still far from being completely understood. It is generally considered to be due to a process of autoxidation followed by a polymerisation [5–8]. After an induction period attributed to the presence of natural antioxidants [9], the oil absorbs large amounts of oxygen giving rise to the formation of peroxidic compounds. The oxidation has been related with the presence of double bonds, and the first phase was thought to consist on the formation of either hydroperoxides [6] or cyclic peroxides [7]. The polymerization process essentially consists of the intermolecular coupling of radicals originated by decomposition of the relatively unstable peroxide groups, with formation of cross-linked structures. Although a film of linseed oil becomes *touch-dry* in a few days, the drying reactions continue for many years and, as cross-linking proceeds, a progressive hardening occurs. On the other hand, this hardening is moderated by the presence of unchanged glycerides which act as plasticizers. The rate at which the oil dries can be modified by using additives or

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PII: S0141-3910(99)00020-8

Table 1
Fatty acid compositions of some drying oils (wt%) [4]

Oil	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Linseed	6–7	3–6	14–24	14–19	48–60
Walnut	3–7	0.5–3	9–30	57–76	2–16
Poppyseed	10	2	11	72	5
Tung[a]	3	2	11	15	3

[a] The main component is elaecostearic acid (59%).

through some special pre-treatments that permit to obtain the so-called *boiled*, *blown* and *stand-oils* [10].

This paper is devoted to a detailed investigation of the hardening process and of the subsequent oxidative degradation of linseed oil, exposed to both natural and accelerated weathering conditions. To this end, linseed oil in form of thin films appropriately supported has been treated in the following ways:

- constant temperature of 80°C;
- indoor laboratory conditions;
- accelerated photo-ageing.

Structure and property changes during the different treatments were followed by Fourier transform infrared analysis (FTIR), thermogravimetric analysis (TG), differential scanning calorimetry (DSC), insoluble determination and size exclusion chromatography (SEC).

2. Experimental

The investigation was performed on a commercial linseed oil, Raw Purified 027 (Talens, The Netherlands). The oil was uniformly spread on selected supports in order to obtain film thickness of 80 ± 10 μm, and then exposed to different conditions. The thermal treatment was carried out in a forced-air circulation oven at a constant temperature of 80 °C, whereas the natural ageing was performed in the laboratory, by leaving the sample in a normally illuminated area, at room temperature simply sheltered from dust. The photo-ageing was performed in a high-speed exposure unit Suntest CPS (Heraus, Germany), equipped with a Xenon-lamp; a special UV glass filter was used for limitation of radiation at wave lengths greater than 295 nm, corresponding to outdoor solar exposure.

The effects of ageing were measured directly on films supported on KBr discs with a Perkin–Elmer (USA) 1710 FTIR instrument run under SpectraCalc (Galactic Inc., USA) control and data acquisition. The determination of gel content was performed by treating the oven-aged films with 10 cm^3 of chloroform for 1 h. The suspensions were filtered through a 0.2 μm membrane filter and the washed gel was vacuum-dried at room temperature to constant weight. The soluble fractions were recovered by vacuum-drying and analysed by SEC, with a Waters (USA) M-45 pump, a Rheodyne (USA) 7010 injection valve, PL Gel type columns (Polymer Laboratories, UK), 5 μm particle diameter, and a differential refractometer ERC 7510 (Erma, Japan). SEC data were acquired and treated with Chromstar (Bruker, Germany) dedicated software. Infrared characterisation of soluble fractions was performed on films cast from chloroform solutions on KBr discs.

Thermal characterisation was carried out either under nitrogen or air flow (60 cm^3/min) with a DuPont (USA) system consisting of a Model 951 Thermobalance, a DSC Cell Unit and a 2100 Control Unit.

3. Results and discussion

3.1. Isothermal treatment at 80°C

3.1.1. FTIR spectroscopy and SEC

The band assignment for the vibrational IR spectrum of raw linseed oil is summarised in Table 2 [11]. Spectral changes related with the structural modifications taking place during drying are visible in Fig. 1, where initial spectrum is compared with those of samples treated at 80°C for 5 and 6 h, respectively, conditions in which the passage from viscous liquid to touch dry film took place. Several spectral changes can be seen and particularly:

- almost complete disappearance of peaks at 3011 and 1654 cm^{-1} and decrease of the absorption at 723 cm^{-1}, attributed to isolated double bonds;
- appearance of a broad band centred at ca. 3430 cm^{-1}, due to hydroxyl groups, and of a weak absorption at 1633 cm^{-1} related with the formation of conjugated double bond;
- broadening of carbonyl absorption;
- complex changes in the region of skeletal vibrations.

Table 2
IR vibrational assignments of raw linseed oil

Band position (cm^{-1})	Intensity[a]	Assignment[b]
3011	m	ν(C–H)=CH
~2960	sh	ν_a(C–H)CH_3
2926	s	ν_a(C–H)CH_2
2855	s	ν_s(C–H)CH_2
1747	s	ν(C=O)
1658	w	ν(C=C)
1464	s	$\delta(CH_2)$
1418	w	wag(CH_2)–CH_2–CO–O–
1378	m	wag(CH_2)
1240	m	ν_a(C–C–O)
1164	s	ν(C–O)
1100	m	ν_a(O–CH_2–C)
723	s	γ–$(CH_2)_n$– + wag(C–H)=CH

[a] s: strong; m: medium; w: weak; sh: shoulder.

[b] ν: stretching; δ: bending; wag: wagging; γ: rocking; $_a$: asymmetric; $_s$: symmetric.

By observing that treating dry films at 155°C under inert atmosphere the –OH absorption decreased, it is possible to deduce that hydroperoxide groups were formed in the oil. Treatments up to 400 h did not induce further changes apart from a progressive enlargement of the carbonyl absorptions. As the spectral intensities of main peaks remained constant, it may be assumed that degradative reactions involving extensive weight losses are not occurring. The trends of hydroxyl groups and unconjugated double bonds on the samples subjected to the above treatments were also measured. Absorbance readings were expressed as indexes and the peak at 1462 cm^{-1}, corresponding to the CH_2 bending, was used as a reference (Fig. 2). After an induction time of around 4 h, a fast increase of hydroxyl groups to a constant value, and the disappearance of isolated double bonds visible, pointing out that under these accelerated conditions most of the transformations involved in the drying process occurred in the short range between 4 and 8 h.

Structural changes in presence of oxygen often occur with the development of cross-linking, and the formation of insoluble material as a function of time is reported in Fig. 3. There is a fast accumulation of insoluble polymer during the first 16 h of treatment, followed by a slower growth which apparently continues up to complete cross-linking. The soluble part extracted from the films

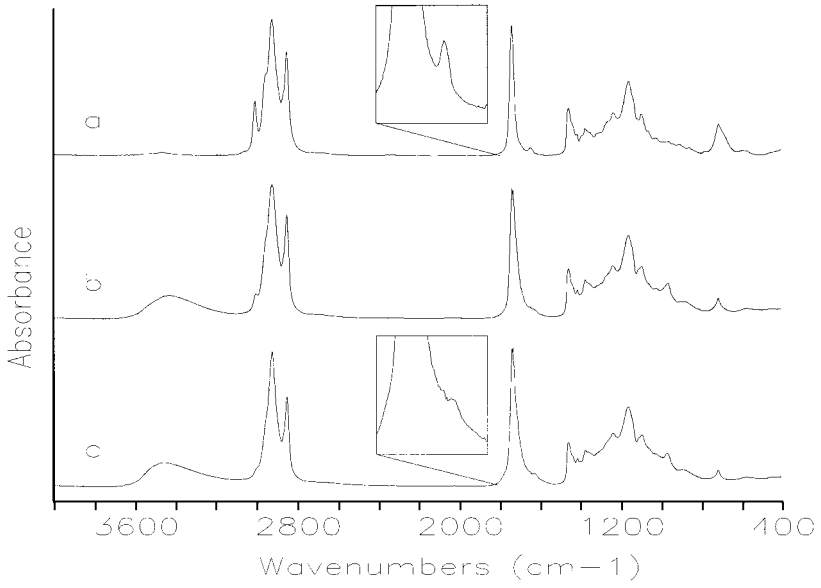


Fig. 1. FTIR spectra of linseed oil: (a) original, (b) treated at 80°C for 5 h and (c) for 6 h.

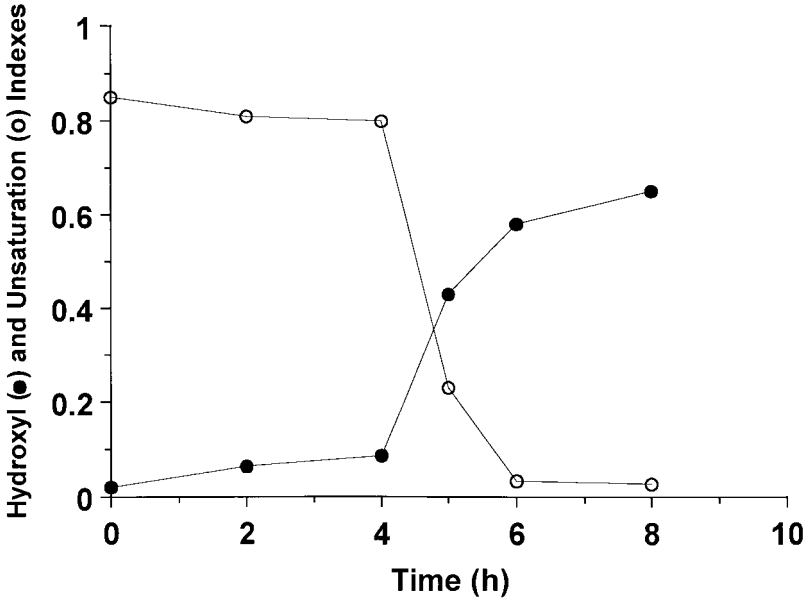


Fig. 2. Change of hydroxyl (●) and unsaturation concentrations (○) in linseed oil treated at 80°C.

was examined by SEC and IR spectroscopy. An example of the results is reported in Fig. 4, where the chromatogram of the fractions soluble after 16 h is compared with that of the raw oil. In the raw oil, together with the triglyceric component, other substances are visible as two minor peaks at both sides of the main component. The peak with lower molecular weight, centred at ca. 36.5 min, has been attributed to impurities present in the oil, whereas the peak eluting at ca. 32.5 min may be tentatively attributed to dimeric fractions already formed by autoxidation phenomena. The chromatogram of aged samples shows a broader and more complex molecular weight distribution: in addition to the peak of the original component and to the second well resolved peak of dimers, a continuous distribution of higher molecular weight fractions is present, together with a partial enrichment of the low molecular weight fractions. The same peaks are present in the chromatogram of any sample treated at different times. This pattern can be explained through a drying mechanism which includes a main process of polymerization that easily brings the formation of insoluble fractions, and a secondary process of fragmentation of the triglyceride molecules. An indication of the type of reactions which lead to bond breaking has been obtained by IR analysis of the soluble fractions. In Fig. 5, the IR spectrum of the fractions extracted from a sample treated 150 h is compared with that of the same sample before the

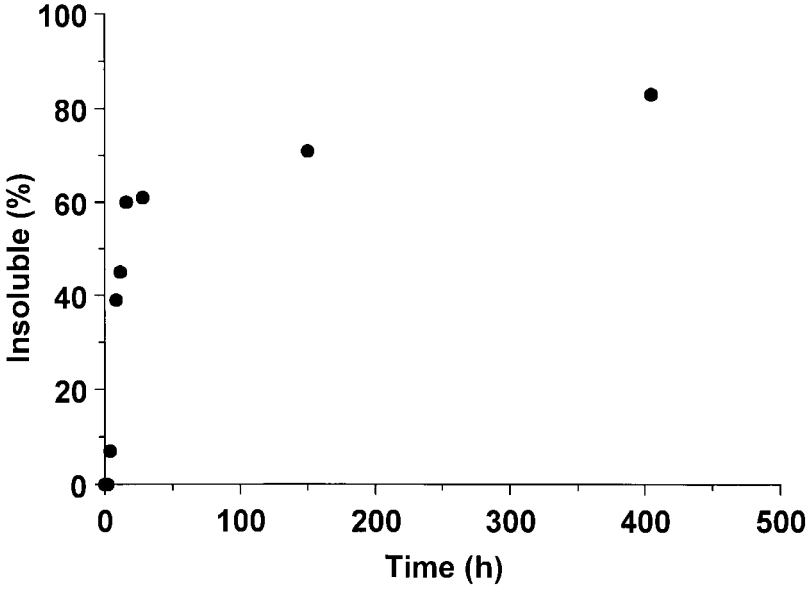


Fig. 3. Change of cross-linked fractions during oxidation at 80°C.

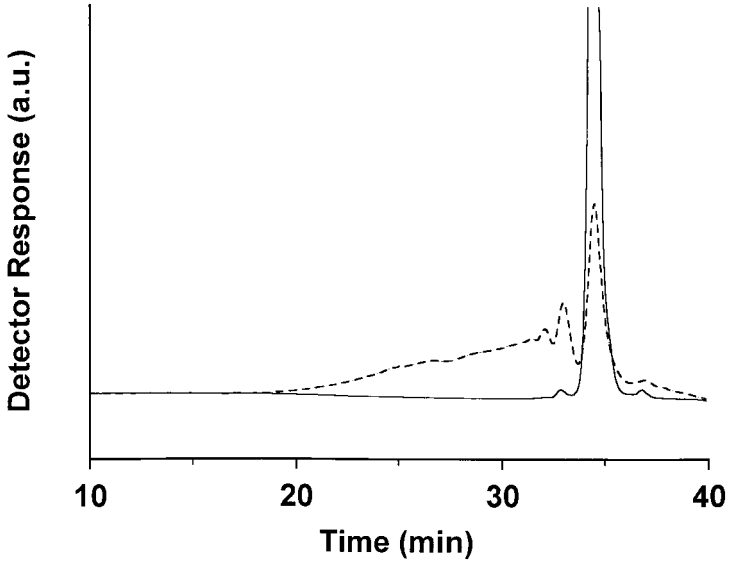


Fig. 4. SEC curves of raw linseed oil (—) and of its soluble fraction extracted after 16 h of treatment at 80°C (- - - -).

extraction. The same peaks are visible in both spectra, but in the soluble part the absorptions attributed to ester groups, for example at 1746, 1241, 1167 and 1099 cm^{-1}, respectively, show a relatively lower intensity in comparison with those of methylene peaks. Such apparent enrichment in methylene groups suggests a process of fragmentation in which aliphatic chains are preferentially released from the insoluble network.

The gradual conversion of the oil through a soft gel to a rubbery solid takes place with a progressive yellowing of the films. Several structures have been suggested as possible sources of this yellow colour, including diketones and metal salts of their enol form [12], or quinoid structures [13]. However, taking into account the interpretation of the IR spectra of treated samples (Fig. 1), it may be also suggested that the chromophoric groups are the conjugated double bonds appearing for treatments longer than 4 h.

3.1.2. Oxygen absorption

The initial phase of oxygen absorption has been monitored by following weight changes of a sample treated under air flow in thermobalance, at a constant temperature of 80°C (Fig. 6). As in the case of hydroxyl and unsaturation indexes, an induction time of about 4 h is shown, followed by a weight increase up to a

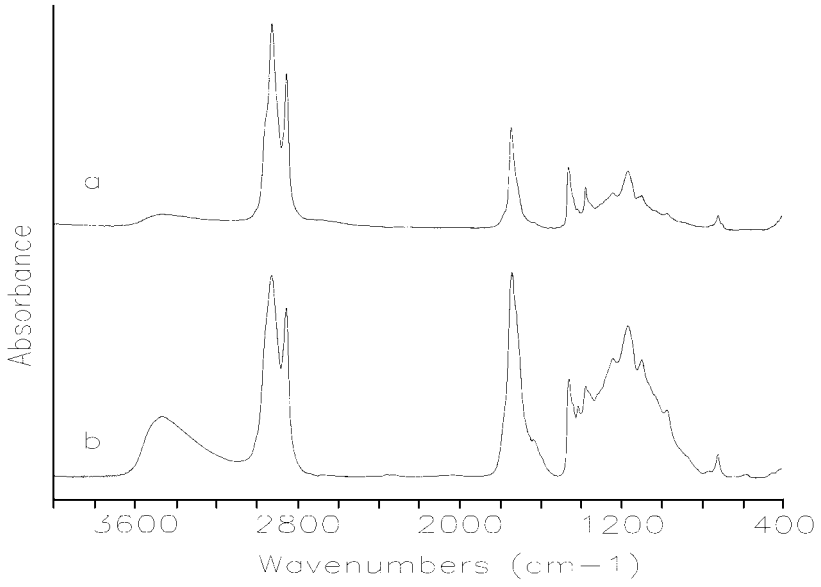


Fig. 5. (a) FTIR spectra of the soluble fraction extracted after 150 h at 80°C and (b) of the same sample before the extraction.

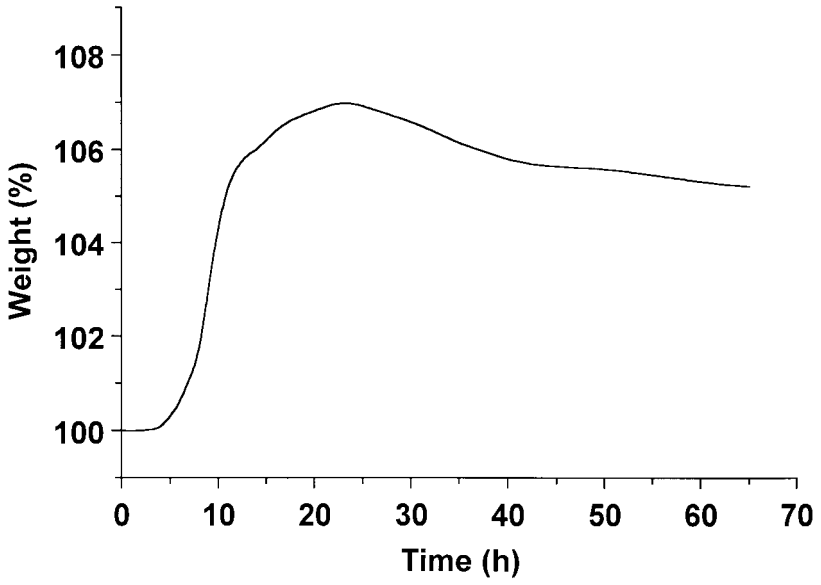


Fig. 6. Weight changes of linseed oil treated under air flow at a constant temperature of 80°C.

maximum of 7% after 20 h of treatment. The phase of weight increase may be related with the initial fast accumulation of insoluble fractions (Fig. 3), both underling the main stage of hardening. As far as the treatment proceeds, the development of cross-links occurs with a slower rate, and the weight decrease after 20 h indicates that secondary scission reactions, bringing to the formation of small amounts of volatiles, become predominant on oxygen absorption.

3.1.3. Thermal analysis

Thermal stability of samples treated at 80°C for different times have been investigated by DSC and TGA, both under nitrogen and air flow. The measurements in inert atmosphere are not reported here because under such conditions the differences of behaviour among the samples resulted not indicative.

In Fig. 7 is reported the DSC trace of raw linseed oil obtained under air flow at a heating rate of 10°C/min, together with those of samples aged for 8 and 405 h, considered as representative of different stages of hardening. On the basis of these measurements and taking also into account the weight loss curves of the same samples reported in Fig. 8, it is possible to schematise the thermo-oxidative behaviour of linseed oil. The degradation of raw oil may be depicted as follows [Figs. 7(a) and 8(a)]:

- between 150 and 250°C: exothermic process related to the oxidation of unsaturated fatty acids [14];
- between 250 and 400°C: first stage of oxidative decomposition;
- above 400°C: main processes of decomposition (combustion) which give rise to a complete volatilisation.

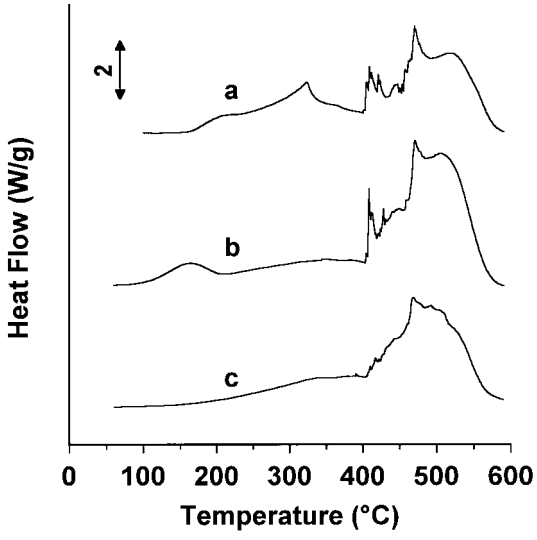


Fig. 7. DSC curves under air flow at a heating rate of 10°C/min of linseed oil: (a) original, (b) treated at 80°C for 8 h and (c) for 405 h.

By comparing Figs. 7b and 8b, which are examples of the behaviour at the end of the early stage of hardening (between 6 and 100 h), with the measurements concerning raw oil, a few differences are visible. In particular, an exothermic process which involves a partial weight loss, appears in the range between 100 and 200°C. This may be explained by considering the formation of the peroxides and the conjugated double bonds during the first phases of treatment, as observed by FTIR. At temperatures higher than 100°C the peroxy groups easily decompose with formation of radicals, whose reaction with double bonds gives rise to an exothermic process of cross-linking. At the same time thermogravimetry shows a partial weight loss, probably due to a secondary process of fragmentation.

Samples subjected to treatments longer than 100 h [Figs. 7(c) and 8(c)] only show processes of oxidative decomposition starting at temperatures higher than 200°C.

3.1.4. Cross-linking mechanism

The drying process of linseed oil begins after a few hours of induction time, through the typical mechanism of hydrocarbon oxidation [15,16] and is promoted by

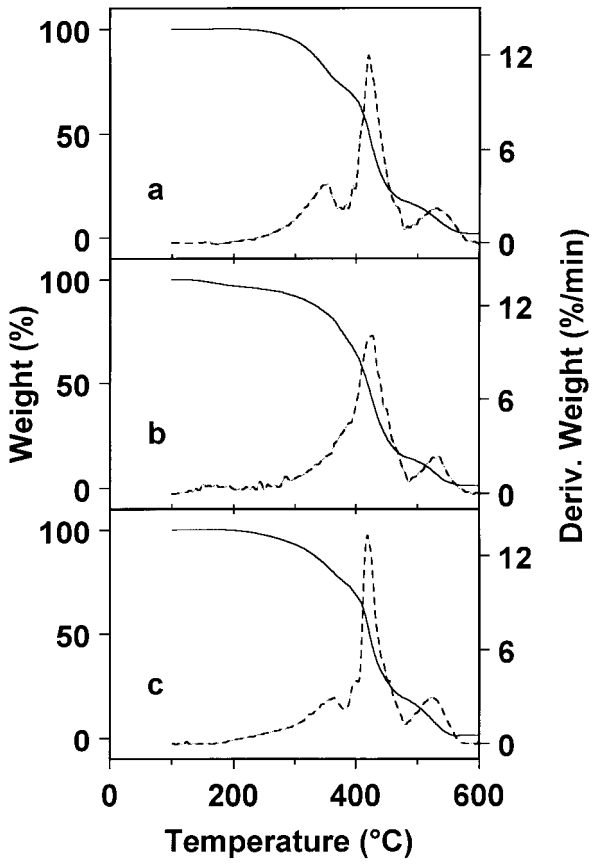


Fig. 8. Thermogravimetric curves (——) and corresponding derivative curves (- - -) under air flow at a heating rate of 10°C/min of linseed oil: (a) original, (b) treated at 80°C for 8 h and (c) for 405 h.

the reactive hydrogen atoms on the allylic positions of the molecules. Hydroperoxide formation is easier on linoleic and linolenic components where one and two methylene groups, respectively, are situated between two unconjugated double bonds. As an example, in Scheme 1 is reported the mechanism of hydroperoxidation for a linoleic chain.

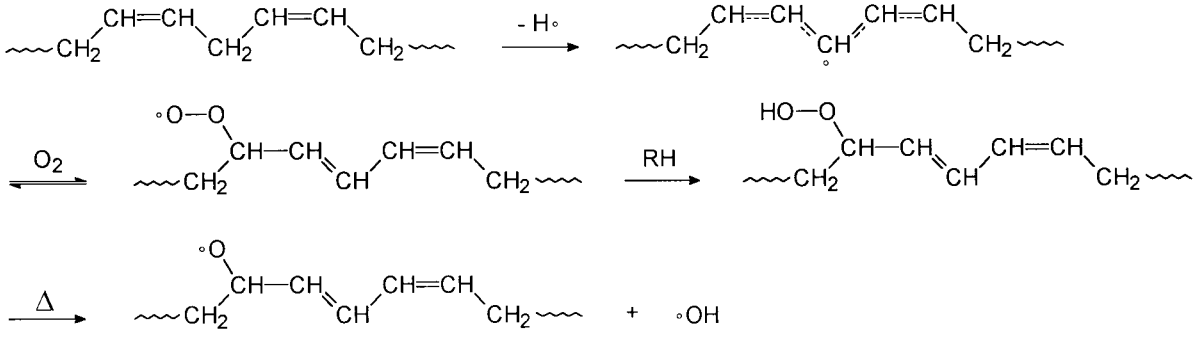
The pentadienyl radical with W configuration [17] can react with oxygen at one of the two ends to produce a mixture of hydroperoxides, with *trans*, *cis* conjugated configuration. Moreover, the reversibility of oxygen addition leads to an isomerised W radical, which may be converted to *trans*, *trans* products [18–20]. It has been reported in a study on the autoxidation of fatty acids that on linoleic acid only external hydroperoxides are formed, whereas on linolenic acid, where two pentadienyl radicals are produced, the formation of hydroperoxides occurs on both internal and external positions [21]. Alkoxy radicals arising from decomposition of hydroperoxides may give the reactions of Scheme 2, leading to the formation of either oxygenated structures, such as alcohols and different carbonyl groups, or products of cross-linking.

The development of three-dimensional cross-linked structures, which soon becomes insoluble, may also occur by bimolecular combination of any radicals formed in the system or by their direct addition to double bonds. In case of a cage combination of peroxy radicals, rearrangement by Russel mechanism is likely to take place [22], followed by disproportionation (Scheme 3).

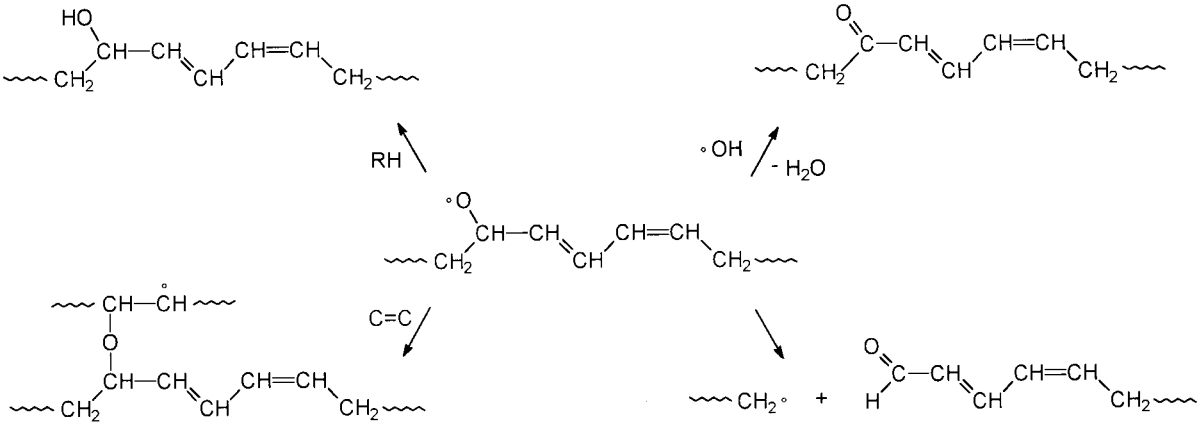
Recently, ^{13}C NMR [23] and mass spectrometry [24] have been applied on model compounds of alkyd resins in order to establish the type of cross-links formed during the oxidation under indoor laboratory conditions. Ether and peroxy linkages were found to be present in roughly the same amount, whereas C–C cross-links were formed to a minor extent, at least in conditions of good oxygen diffusion. In this work, the presence of labile cross-links, probably peroxides, has been indirectly confirmed by DSC measurements on the oil treated at 80°C for times between 6 and 100 h [see Fig 7(b) and related discussion].

3.2. Natural conditions

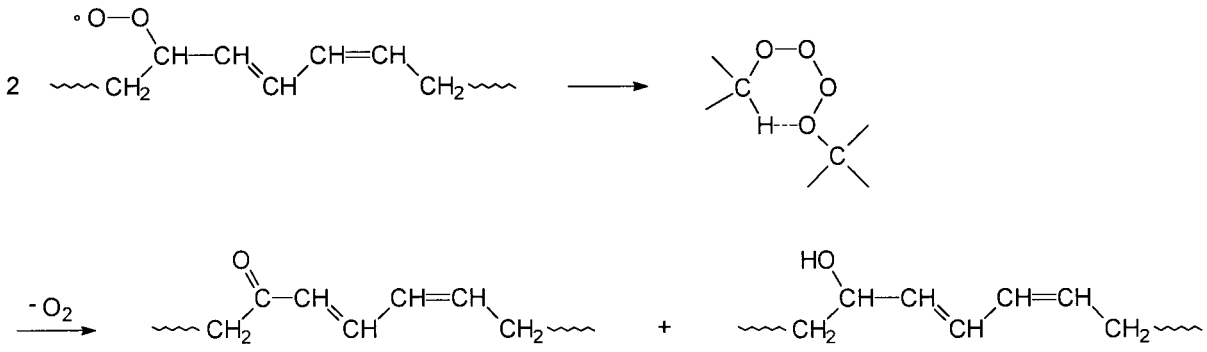
A sample of oil in form of film has been exposed in the laboratory at room temperature, which means in the usual conditions of ageing of a pictorial film, but without any pre-treatment for increasing the rate of cross-linking nor the effects due to the presence of pigments [25,26]. The drying was followed by FTIR and



Scheme 1.



Scheme 2.



Scheme 3.

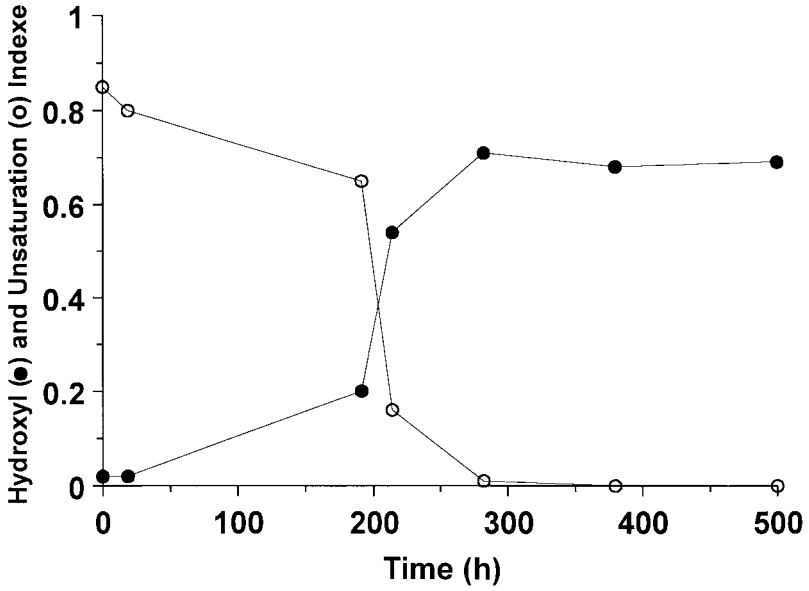


Fig. 9. Change of hydroxyl (●) and unsaturation concentrations (○) in linseed oil exposed to indoor laboratory conditions.

the same spectral changes already seen above on samples treated at 80°C have been found. By comparing the trends of hydroxyl groups and unsaturations (Fig. 9) with those obtained under accelerated conditions (Fig. 2), one can see the similitude between the kinetics of the two processes, where the same stationary concentration is reached for hydroxyls while unconjugated unsaturations completely disappear.

It may be therefore supposed that the treatment of linseed oil in presence of oxygen at temperatures moderately higher than room temperature, simply produces an acceleration of the natural processes of drying and degradation, and that the type and extension of involved reactions is not appreciably modified. On this basis, it was also possible to quantify the accelerating factor for the thermal treatment at 80°C by considering the time at which the hydroxyl index reaches half of the plateau value: the simulated ageing gives an acceleration of approximately 40 times.[1] Our accelerated treatment extended to 420 h therefore corresponds to about 2 years of natural ageing.

3.3. Accelerated photo-ageing

In order to obtain more detailed informations on the behaviour of linseed oil for ageing longer than the 2 years simulated by isothermal treatment at 80°C, other conditions have been tested to give the highest possible accelerating factor, and, at the same time, to produce degradation mechanism as much as possible similar to that in which the material would degrade in natural conditions. A further increase of temperature was rejected, to avoid possible phenomena of thermal degradation, and consequently a system for accelerated photo-ageing with Xenon lamp reproducing solar radiation was chosen. The FTIR spectra of linseed oil exposed for growing times in the photo-ageing apparatus showed, at least

[1] The accelerating factor permits the comparison between a simulated ageing and natural ageing conditions. However, it is always necessary to take into account that the correlation is approximate, since under natural exposure the ageing is influenced by a series of factors which are of difficult reproducibility in accelerated tests.

for the early stages, the same structural variations already detected during both thermal treatment and natural drying. By comparing the hydroxyl and unsaturation indexes relative to the first 20 h of photo-ageing (Fig. 10) with those reported for the previous ageing conditions (Figs. 2 and 9), is evident that the process takes place at a higher rate. The factor calculated for this accelerated photo-ageing condition is around 260 (see footnote 1).

Extension of the treatment up to ca. 2000 h has also permitted to obtain further details on the degradative mechanism. In Fig. 11 the FTIR spectra of oil exposed for 487 and 1987 h are compared with that obtained after the first phase of hardening. Large spectra differences can be seen, in particular.

- decreasing of absorption due to methylene vibrations (2928, 2856 and 727 cm^{-1});
- increased intensity and further broadening of the OH band, together with the appearance of a shoulder at ca. 2600 cm^{-1} due to hydroxyls bonded with carboxylic groups [27];
- broadening of carbonyl absorption with comparison of new components;

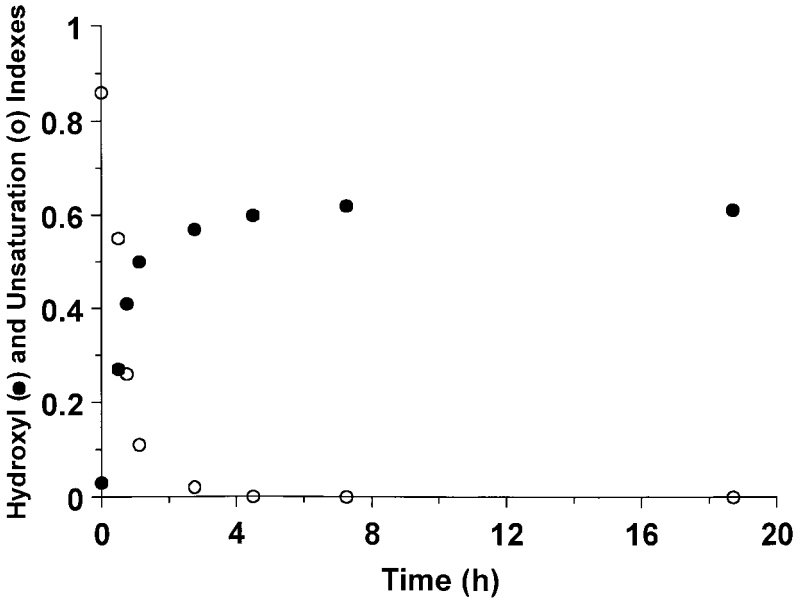


Fig. 10. Change of hydroxyl (●) and unsaturation concentrations (○) in photo–aged linseed oil.

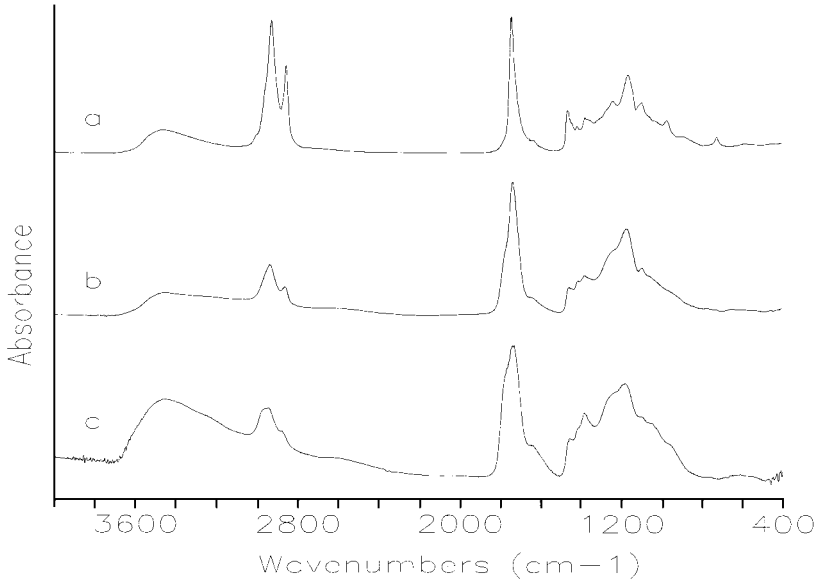
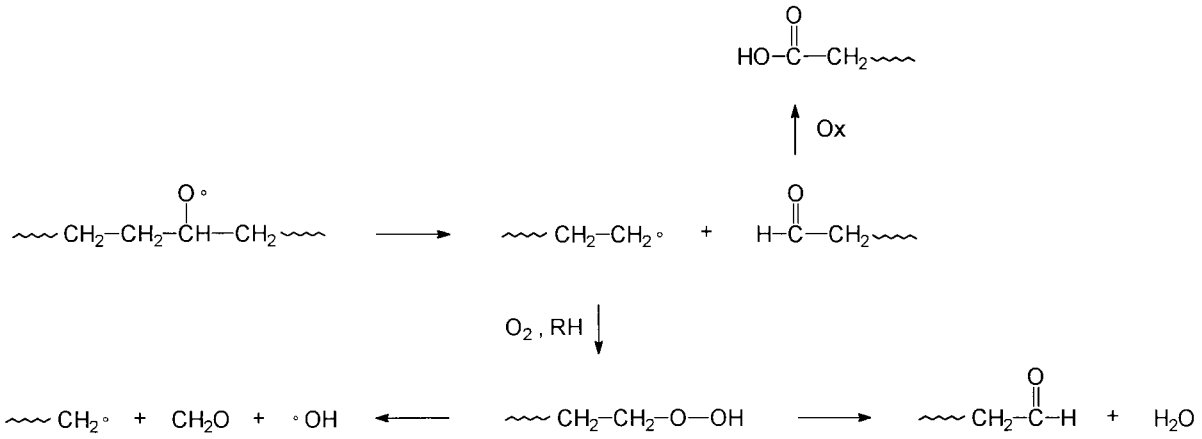


Fig. 11. FTIR spectra of linseed oil photo-aged for (a) 7 h, (b) 487 h and (c) 1987 h.



Scheme 4.

- extensive loss of structural resolution in the region between 1400 and 800 cm^{-1}.

Moreover, it is important to observe that the concentration of conjugated double bonds remains nearly constant during the whole treatment.

All these results lead to the conclusion that the extension of the photo-ageing gives rise to a further oxidation which occurs through partial decomposition of the tridimensional network formed by hardening, with evolution of alkylic fragments.

3.4. Degradation mechanism

The photo-oxidative degradation of linseed oil may simply be considered as the continuation of the hardening process. The initial phase of oxidation occurs with the formation of hydroperoxides in preferential positions and, by their decomposition, of alkoxy radicals which can undergo cross-linking reactions (Schemes 1–3). After hardening, the dried oil shows a noteworthy stability, and degradation occurs only at long ageing times, through slow and progressive oxidation on the alkylic chains.

For the alkoxy radicals formed by the classical mechanism of autoxidation on a generic position along the chain, several reaction paths are possible: cross-linking by coupling reactions, extraction of a hydrogen atom or decomposition by β scission. However, the stiffening of the chains, due to the progressive formation of cross-links, is likely to hinder further coupling reactions, making more and more competitive other degradative pathways and in particular the decomposition by β scission (Scheme 4).

The alkoxy radicals can undergo C–C scission on either side of the carbon bearing oxygen, with formation of an aldehyde and an alkyl radical. The radical can then react with oxygen, and eventually produce an aldehyde, which can be further oxidised to carboxylic acids. Independently on the nature of the terminal groups, if the scission occurs on the glyceryl ester side of the radical, the fragment remains in the network. On the other hand, if the scission occurs on the side of the hydrocarbon end of the fatty acid then the fragments are compounds with low molecular weight, which remain liquid inside the network [10,25] or even volatilise.

4. Conclusions

Investigation of the ageing of linseed oil has permitted to clarify its mechanism of drying and degradation. The structural changes that occur during different ageing treatments resulted almost independent from the system used for carrying out the treatment itself. It has been therefore possible to perform simulations up to a maximum corresponding to ca. 60 years of natural ageing (1987 h of photo-ageing by an accelerating factor equal to 260).

The early stages of oxidation of triglycerides, corresponding to the drying phase, consist of the autoxidation phenomenon of the unsaturated fatty acid components that occurs with formation of conjugated unsaturations and with the development of extensive cross-linking. On a following stage, the slow consumption of the labile cross-links gives rise to a highly stable network, which still contains unreacted triglycerides and low molecular weight molecules formed by fragmentation. Only at ageing times corresponding to years of natural ageing a progressive oxidation also takes place of the alkylic segments, leading to partial fragmentation of the structure together with the formation of larger amounts of oxygenated groups.

Acknowledgements

This work has been realised with financial support from Consiglio Nazionale delle Ricerche, Comitato Nazionale "Scienza e Tecnologia per i Beni Culturali", Italy.

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