SUSTAINABILITY CRITERIA
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Physico-chemical durability criteria of oils and linked bio-based polymers

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Abstract – The oxidative stability or durability is an important indicator of performance that depends on the composition of the sample. The fatty oil or polymer degradation processes have generally been established as being free radical mechanism yielding primary oxidation products. We propose to explain in detail all the analytical methods and tools used for the determination of the initial physico-chemical properties of oils and the properties in ageing conditions. Chemical titrations for acid or peroxide value, Rancimat method or thermogravimetric measurements are discussed. Accelerated ageing tools for thermal or photochemical exposures are also shown. After the assessment of oil durability, the development of new bio-based polymer with vegetable oil is tackled because of its industrial interest. It is essential to understand the long term behavior of oils and biopolymers and to assess exactly the durability which is useful to produce life cycle analysis of materials. At last we underline the advantages of a new Fourier transform infrared (FTIR) instrumentation with in-situ irradiation and gas cell to give a screening of the durability of various oils or polymers. Main durability criteria of oils and biopolymers are linked to the production of volatile organic compounds and the resistance to the oxidation process.

Keywords: Fatty acid / thermal degradation / photochemical degradation / durability criteria / bio-based polymers

Résumé – Critères de durabilité physico-chimique des huiles et polymères bio-sourcés associés. La stabilité ou la durabilité oxydative est un indicateur important de performance qui dépend de la composition de l’échantillon. Les processus de dégradation d’une huile ou d’un polymère ont généralement été établis comme étant un mécanisme radicalaire conduisant à des produits d’oxydation primaires. Nous proposons de détailler tous les méthodes et outils d’analyses pour la détermination des propriétés physico-chimiques initiales d’huiles ainsi que les propriétés en conditions de vieillissement. Les dosages chimiques pour un indice d’acide ou un indice peroxyde, la méthode Rancimat ou les mesures thermogravimétriques sont discutés. Des outils de vieillissement accéléré pour exposition thermique ou photochimique sont aussi présentés. Après l’estimation de la durabilité d’une huile, le développement de nouveaux polymères bio-sourcés à partir d’huile est abordé en raison de son intérêt pour les industriels. Il est essentiel de comprendre le comportement à long terme des huiles et des biopolymères et d’estimer avec précision la durabilité, paramètre qui est utilisé pour produire l’analyse du cycle de vie de matériaux. Finalement nous soulignons les avantages d’un nouvel instrument de spectroscopie infra-rouge à transformée de Fourier (FTIR) avec une irradiation in-situ et une cellule gaz, qui donne un screening de la durabilité de différentes huiles ou polymères. Les principaux critères de durabilité des huiles et biopolymères sont associés à la production de composés organiques volatils et à la résistance par rapport au processus d’oxydation.

Mots clés : Acide gras / dégradation thermique / dégradation photochimique / critère de durabilité / polymères bio-sourcés

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1 Introduction

Initial physical and chemical properties of oils have been often assessed to explain their main differences. The properties of oil evolve systematically with time during storage or use conditions. Vegetable oils are often chemically unstable due to the sensitivity to oxidation of unsaturated fatty acids. The evaluation of oxidative stability can be determined by standard analytical test methods (acid value, iodine value, saponification value and peroxide value). The effect of ageing or storage on oil quality is a subject of industrial interest. Durability or stability studies are linked to oil ageing, and are essential for good use and extensive applications.

Sustainable crops and productions are linked to a protection with all the existing tools, mechanical, biological and chemical (Bernard, 2007). Production increase of major vegetable oils will face many challenges relating to environmental issues, competition between food and non-food uses (Lecomte et al., 2012). Today almost one quarter of the global vegetable oil production is dedicated to non-food applications. Palm, soya and rapeseed oils represent three quarters of the global oil production. These oils are considered as a major source of renewable materials because of their low cost, abundance and high level of chemical reactions (Chollet et al., 2012). The development of new bio-based materials is a major challenge and vegetable oils can be a source of raw materials for bio-based polymers. French chemical industry uses 9% of vegetable-based raw materials and announces 15% in 2017. The focus on valorizing biomass will contribute to this position. Change in thinking and environmental concerns in the design process of new materials is now a necessity. This approach is supported by standardized tools, such as life cycle analysis (LCA), which quantifies the environmental impacts of industrial products. It is interesting to reduce energy consumption and to use renewable resource which can store carbon dioxide due to photosynthesis.

After the presentation of how to assess the physico-chemical properties of oil and to study the oil durability, we will discuss about the bio-based polymer durability then explain main durability criteria or requirements in LCA of materials. We will consider the oil durability with physico-chemical approach.

2 Assessment of the physico-chemical properties of oils

Oil stability depends on storage conditions. In normal storage conditions (without light, at controlled temperature) the evolution of physico-chemical properties will be acceptable. Evaluation methods to determine oil oxidation level are colorimetric measurements, such as iodine value for unsaturation rate, acid value for free fatty acids rate, iodometry for peroxide rate, anisidine value for aldehyde rate and saponification index. AFNOR standards are linked to the measurements of acid index (NF EN ISO 660), iodine index (NF EN ISO 3961) and peroxide value (NF EN ISO 3060). Developments in Fourier Transform infrared spectroscopy instrumentation (FTIR) allowed to determine oil adulteration and to monitor the oxidation process (Vlachos et al., 2006). The loss of edible oil quality is associated to both sensorial (rancidity) and nutritional value (loss of different fatty acids and vitamins A, E). Only a slight degree of degradation can result in the loss of organoleptic properties (taste and flavour). In the case of edible oils the assessment of rancidity is a major method with experts on sensorial analysis (Cuvelier and Maillard, 2012). Nethertheless, this method is time consuming.

The chemical composition with the fatty acid profile is determined by gas chromatography (GC) after transesterification of triglycerides. Identification and quantification of volatile organic compounds from oxidation of oil are assessed by Solid Phase Microextraction (SPME) combined with GC-mass spectrometry (GC-MS) (Juita et al., 2012). Traditionally in edible oil industry, a classical method used for determining oxidative stability of oils is the active oxygen method (AOM) or Swift method. The purified air is bubbled through a sample held in a heated oil bath at 98 °C and peroxide values are determined at several time intervals (Rudnik et al., 2001). The Rancimat method is linked to a conductance measurement with time. This method is operated at 110 °C and allows the detection of carboxylic acid (termination products). The induction time (IT) is finally given. The Rancimat test is easy to carry out but is time consuming (around 10 h). Thermal analysis can be also carried out to monitor the thermo-oxidation of oil as a function of time. Recently thermoanalytical methods are more commonly used for characterization of oils. Melting point, crystallization and oxidation process can be studied. Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) are useful to assess the oxidative stability of oils and can be suitable for the evaluation of the efficiency of anti-oxidants (Santos et al., 2014; Rudnik et al., 2001). Near Infrared Emission photometer (NIRES) allows the determination of the induction time of edible oils by monitoring the emissivity of hydroperoxide band (2900 nm, 3450 cm⁻¹). The measurement is associated to luminance induced by heating the sample, from which emittance and emissivity are calculated (Senna Vieira and Pasquini, 2013). The authors underlined fast analysis and operational simplicity. Electrospray resonance (ESR) has been recently used for the oxidative stability determination of oils. The measurements took only a few minutes but are linked to a high cost equipment (Thomsen et al., 2000). Size exclusion chromatography (SEC) of soluble species can be carried out with the assessment of the distribution of average molecular mass (Lazzari and Chiantore, 1999).

The diversity of tools, limits, sensitivity and specificity does not allow to obtain an easy comparison of results (Cuvelier and Maillard, 2012). What we really measure corresponds to the oxidation resistance or the induction period.

3 Ageing of oils and biopolymers

For a screening of various oils it is essential to use accelerated ageing tests. The evolution of oils is based on oxidative mechanism with radical reactions. The choice of accelerated ageing test is turned towards observed degradation reactions. We have to pay attention to use accelerated tool, representative of natural ageing (or storage conditions). Thermal ageing can be accelerated with temperature from 80 to 120 °C.
Above 130 °C degradation reactions are too specific and unpresentable of natural ageing. Photo-chemical ageing can be accelerated with irradiation tool with wavelengths above 300 nm (see Fig. 1). SEPAP 12-24 from ATLAS can be used for this kind of ageing. The source is linked to 4 medium pressure mercury vapour lamps (Mazda MA 400W). Samples are rotated in a carousel at a constant distance (20 cm) from the lamps. The temperature is controlled by the microprocessor which regulates the air input and the heaters. The air flow produced by two fans guarantees a homogenous temperature distribution on the sample surface. The Pt (Platinum) temperature sensor measures the temperature on the surface of the sample. The values are within a range of +45 °C to +80 °C, with a ±2 °C accuracy. The rate of acceleration for ageing in SEPAP 12/24 is 8 times under these conditions for polypropylene compared to natural ageing in Clermont-Ferrand. Oils can be irradiated in small glass tubes at the chosen temperature.

4 Oxidation mechanism and detection

The oxidative mechanism is based on radical and complex reactions (Fig. 2) because of the presence of long aliphatic or unsaturated carbon chains. The relative instability of polyolefins to ageing is mainly due to the possibility of abstracting hydrogen atoms from the polymer chain in presence of specific impurities. The resulting macroalkyl radicals react quickly with oxygen leading to the formation of peroxy radicals, which finally convert, into hydroperoxides by a second hydrogen abstraction. Because of their instabilities, these thermal and photochemical hydroperoxides do not accumulate in the matrix but are decomposed into more stable products, such as ketones (also unstable in the case of photo-oxidation), carboxylic acids and alcohols (Lacoste et al., 1991).

The oil degradation can be delayed by protecting it from light, heat, oxygen and metals (Cuvelier and Maillard, 2012). Another way is to increase the retention of endogenous antioxidants naturally contained in oil seeds.

The chemical composition of oils includes triglycerides and free fatty acids (saturated, mono-or poly-unsaturated). Fatty acids can react by isomerisation reaction (cis to trans) observed with IR spectroscopy (Nakavoua et al., 2011, 2013). The acid index is a marker of lipid degradation, as free fatty acids content in oils increase with time. It has been shown on cucurbita pepo seed oil that the highest temperature of storage (30 °C) favoured the release of free acids from triglycerides. Acid, iodine and peroxide values increase with time while saponification values remain almost unchanged for jojoba oil (Kaul et al., 2009). The evolution of acid, iodine and peroxide values is linked to chain scission and peroxidation reactions. The saponification index is also linked to average molar mass and chain length.

TG analysis of palm oil exhibited two mass losses (Santos et al., 2014). The largest mass loss (88%) occurred in the range 325–486 °C is linked to the decomposition of triglycerides. The lowest mass loss (190–310 °C) is explained by the evolution of impurities (free acids and lower mass triglycerides). The mass residue was 11.4%. Accelerated ageing at various temperatures (from 130 °C to 200 °C) were carried out with DSC on Toogga oil (Gardette and Baba, 2013). Kinetic parameters (such as activation energy and kinetic rate constant) were then determined. The thermal degradation of Toogga oil followed first order kinetics. The calculated parameters allowed to assess the induction time of the oil, assuming it is possible to extrapolate the Arrhenius law at room temperature. With thermo-analytical methods on linseed oil it was found that a high content of unsaturated fatty acids leads to reduced oxidation stability (Rudnik et al., 2001). The increase of viscosity is linked to polymerization reaction and cross-linking (Nakavoua et al., 2013). The modification of composition was also observed with IR spectroscopy on linseed oil (Lazzari and Chiantore, 1999; Mallegol et al., 2000). The concentration of end products with hydroxyl bonds increased with time while the concentration of unsaturated products decreased. Yellowing of linseed oil increased during thermal ageing but decreased with irradiation. The decrease was explained by oil contaminants responsible for the yellowing, they were then photo-oxidized. Volatile organic compounds identified in the vapour space of linseed oil include aldehydes, ketones, alcohols, carboxylic acids and furans (Juita et al., 2012). These compounds arise in oxidation of linolenic and linoleic chains that form glycerides present in the linseed oil. The abstraction of the double allylic hydrogen present in the linolenic or linoleic chains results in the formation of pentadienyl radical, then peroxyl radicals.

Linseed oil has better performance compared with other common oils for its faster drying, due to higher concentration of linolenic acid (Lazzari and Chiantore, 1999). The initial step

Fig. 1. Photo-ageing device.

Fig. 2. Peroxides formation during degradation.
of drying consists of the autoxidation phenomenon of the unsaturated fatty acids 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. SEC results attested from a continuous distribution of higher molecular weight fractions and also from small amounts of low molecular weight molecules.

If natural anti-oxidants present in plants are not completely removed after oil extraction the oil durability can be improved.

5 Studies in the work group “Polymer Life Cycle” (Cycle de Vie des Polymères - CVP)

In the aim of biomass valorization vegetable oils are used for the development of new bio-based polymers with high performance results in terms of properties and durability. Several oils were studied at initial state and after various thermal and photo-chemical ageings. Storage conditions and ageing tests were carried out on cucurbitea pepo seed oil (Nakavoua et al., 2011–2013). Classical chemical methods such as acid index, peroxide index and saponification index were used. GC, DSC, IR and UV spectroscopies were performed to determine the oil durability or stability.

A comparison with rapeseed oil and linseed oil was then proposed to understand relations between chemical composition and oxidation level. Analysis of density and viscosity (Brookfield) were done. IR Spectroscopy with Attenuated Total Reflection (ATR- diamond crystal) tool was used to assess the chemical evolution during ageing. Figure 3a gives the IR band position (cm$^{-1}$) of initial raw rapeseed oil. Figure 3b shows the comparison of rapeseed and linseed oils spectra.

The IR vibrational assignments of rapeseed oil for the band positions are given in Table 1.

The comparison of spectra of rapeseed oil and linseed oil shows a main difference for the rate of double bonds (with bands at 3007, 1660 and 980 cm$^{-1}$). The rate of double bonds is higher for linseed oil (due to a high composition of linolenic acid).

Figures 4a and 4b show the IR spectra after the thermal ageing at 100 °C of rapeseed and linseed oils. This kind of analysis allowed to assess the induction period corresponding to a relative stable period of oil. The evolution of viscosity and density was therefore very weak during this period. The times of ageing are 0 (top spectrum), 192, 216 and 576 h (low spectrum). The induction period is 180 h for rapeseed oil and linseed oil. After the induction period, the detection of hydroxyl groups is linked with two bands at 3670 and 3500 cm$^{-1}$. As usual a radical mechanism is linked to the detection of oxidation products. The detection of shoulders at 1710 cm$^{-1}$ is linked to acid group. The decrease of double bonds band intensity is mainly observed on linseed oil spectra and is linked to cross-linking reactions. The vibration linked to trans unsaturation at 970 cm$^{-1}$ is increased after thermal ageing. These results are consistent with the increase of the rate of free acids and the cis/trans isomerisation reaction.

Figures 5a and 5b are given for the photo-chemical ageing of oils in SEPAP 12-24. The photodegradation is proposed for 200 h. The development is weak for the two oils. In both case the induction period is 160 h. We observed a small decrease of the 3007 cm$^{-1}$ band and an increase of a band at 970 cm$^{-1}$. It means that isomerisation appears also after this kind of ageing. Photochemical and thermal ageings are quite similar for rapeseed and linseed oils.

With UV measurements main developments are linked with the thermal oxidation of linseed oil which gave a high level of yellowing.

The assessment of thermal decomposition is correlated to chain scission reactions. As shown on Figure 6, the decomposition temperature is below linseed oil temperature. The thermal stability of rapeseed oil is a little weaker.
As previously stated, we can assess oxidation products directly with IR spectroscopy-ATR. These measurements are linked to a long period because of the induction period. A FTIR method with simultaneous UV and thermal exposure and analysis of the gases evolved from polymers was developed in our laboratory (Madeleine-Perdrillat et al., 2014). The description of the specific cell and the sample compartment are given in the paper. The sample compartment was equipped with an oven-regulated gas cell with temperatures from room temperature to 220 °C. A Hamamatsu light generator equipped with a Lightning cure LC6 source (Xe/Hg, medium pressure) was affixed to the IR device. The light intensity and the irradiation duration are setting for each experiment. The samples introduced to the gas cell are liquids or solids. Liquids are introduced in a rectangular crucible adapted for the gas cell. The spectrometer’s soft series option permits time-selective monitoring. We can choose various acquisition intervals during the global experimental times. The tool enabled to distinguish the oxidation level in the first hours of ageing of each polymer. Most of measurements of carbon dioxide, carbon monoxide and degradation products generated during the exposure were carried out in 90 or 320 min. This development in FTIR spectroscopy instrumentation will prove useful in the field of oils for bio-based polymers. The gas cell is suitable for analyzing low or high temperature evolved gases from various oils or polymers. In addition, the gas cell can be connected to a TG analyser system.

For example we study the durability of polyester obtained with vegetable oils as one monomer. Figure 7 shows the graphic representation of the experimental results obtained with the FTIR method with simultaneous UV exposure. Figure 7a is a 2D representation. Figure 7b is a 3D representation of the same experiment. In the first stage of oxidation, only water (fine rotational structure at approximately 1600 and 3700 cm⁻¹) and small organic compounds with ether bond were detected. After 30 min, carbon dioxide (peaks at 661 and 2350 cm⁻¹) and other oxygenated species were increasingly emitted. Over time, the gas phase reached a steady level of carbonyl products and carbon dioxide. The evolution of gas resulted from scissions of branched parts of polymers at the beginning of ageing. The emission of volatiles products is closely correlated with the increasing concentration.
of oxidation products observed on solid state. With the new instrumentation we are able to easily and quickly assess the polymers’ durability. Analysis occurred over 90 or 180 min for most samples and enabled sample discrimination.

Another experiment with the FTIR instrumentation was carried out on polyurethane based on oleic acid. This bio-based polyurethane was a hybrid material obtained with the anchoring of an organo-modified hydroxide double lamellar filler (Ramone et al., 2014). This new bio-based polymer exhibited a good durability. With our flexible FTIR tool, we are able to study the durability of different vegetable oils and linked biopolymers. We underlined the simplicity and flexibility of the tool. As conclusion, the photo-IR tool is useful and promising for the quick analysis of oils and linked bio-based polymers durability.

For LCA, an environmental analysis is carried out to quantify the environmental impact and to check the green claim of the production of bio-based polymers. For example, analysis will highlight the abiotic depletion, the acidification, the eutrophication, the global warming and the photochemical oxidation (Bourmaud et al., 2011). The integration of economical allocation will be also in discussion. Thus, the environmental interest of bio-based polymers can be underlined. Several bio-based materials exhibit good initial mechanical properties and develop a good durability. In LCA, an important step is the assessment of the durability of polymers. Main durability criteria or requirements are linked to the resistance of oxidation process and the production of volatiles evolved from degradation. From our point of view it is essential to assess the production of volatile organic compounds with the flexible FTIR tool or with SPME-GC-MS. The FTIR equipment with gas cell allows to determine the quick screening of various samples. SPME-GC-MS serves to identify and quantify volatile organic compounds formed in degradative reactions. The stability period linked to a resistance to oxidation process can be assessed by classical methods (chemical titration, conductance measurement or direct FTIR spectroscopy).

References


