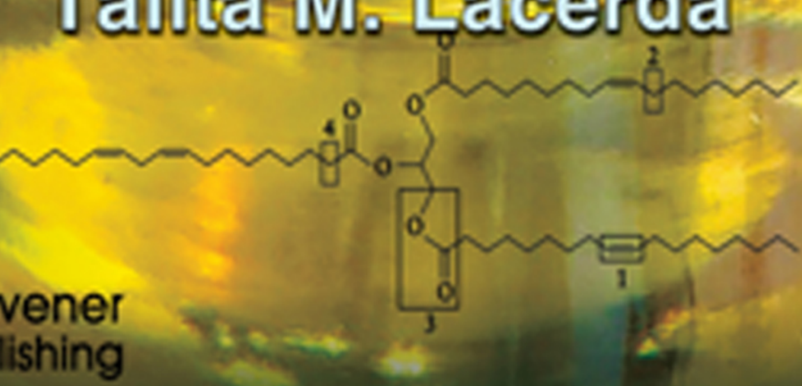
Polymers *from* Plant Oils

2ND EDITION

Alessandro Gandini
Talita M. Lacerda



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Preface to First Edition

Vegetable (or plant) oils, shown here as plant triglycerides, constitute one of the most abundant variety of renewable resources on our planet. They have been exploited by humans for millennia for three major purposes: *food and feed*, *energy sources* and precursors to useful *products and materials*. Ancient utilisations and applications (empirical by definition) contributed to ensure: daily sustenance for people and animals; comfort through heating and illumination; development of protective, writing and artistic coatings in the form of film-forming materials that 'dried in air'. They were then adopted as pristine natural compounds, though in some instances other components were mixed with them, as in the case of inks and lacquers. Simple chemical transformations carried out empirically were also developed, as in the manufacture of soaps simulating the process applied to animal fats.

Unraveling of their chemical structure, and hence understanding of their reactivity, favoured more rational processing and widened the range of applications throughout the twentieth century. Another more important 'revolution' has begun at the start of the third millennium with expansion of the research/development of biofuels and macromolecular materials.

This book is devoted *exclusively* to the latter realm, with particular emphasis on recent trends, progress, achievements and perspectives, with broad treatment of the subject, including inks, paints and coatings, in addition to the more conventional bulk thermoplastic and thermosetting polymers.

In the field of film-forming materials, use of alkyd resins incorporating plant oils or their derivatives has been a standard practice for a century, but no major qualitative advance was introduced until recently. The same applies for bulk polymers based on vegetable oils, of which linoleum (first commercialised in the middle of the nineteenth century) was for a long time the only important representative of these materials. Nylon 11 (commercialised under the name of Rilsan based on castor oil as a precursor) has been an important addition to this small family from the 1950s onwards. In other words, vegetable oils represented a very modest presence as basic constituents of macromolecular materials up to about a decade ago, but the situation has evolved radically since then.

The purpose of this book is to highlight this impressive and promising ongoing trend, which is also occurring in all other areas of the novel burgeoning domain of polymers from renewable resources.

We wish to thank most heartedly Joan Gandini for her constant help in improving the language and style of the manuscript. The authors kindly acknowledge FAPESP for T.M.L.'s post-doctoral fellowship (2012/00124-9) and CNPq for A.G.'s visiting professorship (Science Without Borders programme, PVE 401656/2013-6).

February 2015

Preface to the Second Edition

The publishers of the first edition of this book (2015), Smithers Rapra, relinquished their copyright to the authors who prepared the present second edition for publication under the auspices of Scrivener Publishing. There are no *qualitative* changes in the contents of this edition with respect to the first, which we still considered quite appropriate, whereas our attention focused on bringing up to date a number of issues related to recent relevant facts and important contributions. We feel that the topic of the book has maintained a high level of interest, as judged by the continuing flow of publications and new materials being developed by both academic and industrial research activities throughout the world. We trust therefore that the message contained in the original preface remains fully justified.

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Alessandro Gandini and Talita M. Lacerda
August 2018

1 Introduction

1.1 Setting the Stage

World production of major oilseeds has increased from 331 million tonnes to 573 million tonnes in the last decade, whereas the harvested area has increased from 186 million acres to 278 million acres in the same period. According to the United States Department of Agriculture (USDA), soybean oilseeds represent over half of the total production of oilseeds and are mainly grown in Brazil, USA and Argentina; followed by rapeseed (grown in European Union (EU)-27, Canada and China), cottonseed (China and India) and sunflower oilseeds (Ukraine, EU-27 and Russia). **Figure 1.1** shows the total production of major oilseeds around the world in 2017/2018.

2017/2018 Total Oilseed Production (Mt)

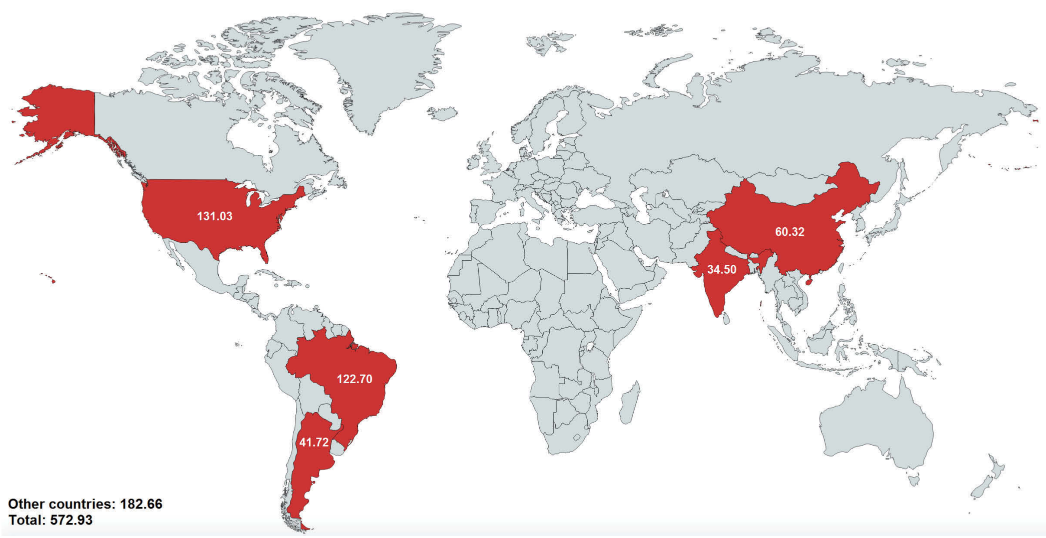

Figure 1.1 Total production of oilseeds 2017/2018 (Mt).
Adapted from United States Department of Agriculture
http://www.fas.usda.gov/psdonline
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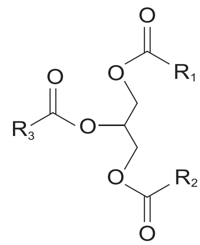
The figures shown above translate from 96 million tons (Mt) in 2002/2003 to 199 Mt in 2017/2018 of actual oils, with an average growth rate of ~7 Mt a year, (**Table 1.1**) [1]. This increasing demand is associated with the needs to feed an increasing population and, more recently, to the demand for biodiesels as partial replacements for fossil fuels. Minor vegetable oils such as castor oil and linseed oil are almost solely used for industrial applications because they are not appropriate for consumption by humans or animals.

Table 1.1 Major vegetable oils: world supply and distribution (Commodity view) – (million metric tonnes) [1]

Oils	2002/2003	2017/2018			
	Production	Production	Imports	Exports	Consumption
Coconut	3.16	3.54	1.50	1.69	3.25
Cottonseed	3.51	5.09	0.05	0.09	5.02
Olive	2.51	3.27	0.88	1.00	2.86
Palm	27.71	69.72	47.23	50.15	65.17
Palm kernel	3.36	8.15	2.75	3.19	7.55
Peanut	4.62	6.00	0.24	0.28	5.98
Rapeseed	12.21	28.75	4.34	4.61	29.07
Soybean	30.57	55.81	10.23	10.71	55.43
Sunflower seed	8.12	18.35	8.10	9.54	17.09
Total	**95.77**	**198.68**	**75.31**	**81.25**	**191.42**

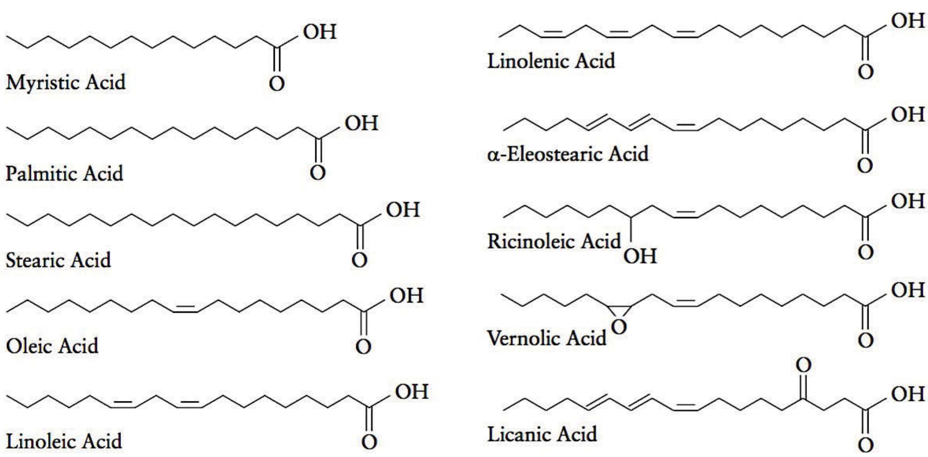
Palm oil and soybean oil are the most important (as well as the most widely exported) oils, followed by rapeseed and sunflower counterparts (**Table 1.1**).

The common structure of vegetable oils discussed here is that of aliphatic triglycerides (**Scheme 1.1**), in which the 'fatty acid chains' R_1, R_2 and R_3 are most often identical, but can also vary, within a given molecule. The length of the fatty-acid chain is 14–22 carbon atoms, but most members bear 16 or 18 units. The other important feature of these linear aliphatic motifs is the possible presence of C=C unsaturations, which range from 0 to 3. More than 1,000 fatty acids have been identified, but only »20 are present in appreciable quantities in vegetable oils [2, 3].



Scheme 1.1 Generic structure of a natural triglyceride component of vegetable oils in which R_1, R_2 and R_3 are fatty-acid chains

Vegetable oils comprise a mixture of triglycerides (albeit with one or two specific structures which usually predominate). These compositions vary according to plant species, crop type, season, and growing conditions [4]. **Table 1.2** enumerates the most common fatty acids in the triglycerides of plant oils and **Scheme 1.2** shows their structures.



Scheme 1.2 Structures of the most common fatty acids

Table 1.2 Most common fatty acids in vegetable triglycerides [5, 6]

Trivial name	Systematic name	Structure (C:DB)*	Formula
Lauric acid	Dodecanoic acid	12:0	$C_{12}H_{24}O_2$
Myristic acid	Tetradecanoic acid	14:0	$C_{14}H_{28}O_2$
Palmitic acid	Hexadecanoic acid	16:0	$C_{16}H_{32}O_2$
Stearic acid	Octadecanoic acid	18:0	$C_{18}H_{36}O_2$
Arachidic acid	Eicosanoic acid	20:0	$C_{20}H_{40}O_2$
Behenic acid	Docosanoic acid	22:0	$C_{22}H_{44}O_2$
Lignoceric acid	Tetracosanoic acid	24:0	$C_{24}H_{48}O_2$
Palmitoleic acid	*Cis*-9-hexadecenoic acid	16:1	$C_{16}H_{30}O_2$
Oleic acid	*Cis*-9-octadecenoic acid	18:1	$C_{18}H_{34}O_2$
Linoleic acid	*Cis,cis*-9,12-octadecadienoic acid	18:2	$C_{18}H_{32}O_2$
Linolenic acid	*Cis,cis,cis*-9,12,15-octadecatrienoic acid	18:3	$C_{18}H_{30}O_2$
a-Eleostearic acid	*Cis,trans,trans* -9, 11,13-octadecatrienoic acid	18:3	$C_{18}H_{30}O_2$
Erucic acid	*Cis*-13-docosenoic acid	22:1	$C_{22}H_{42}O_2$
Ricinoleic acid	12-Hydroxy-*cis*-9-octadecenoic acid	18:1	$C_{18}H_{34}O_3$
Vernolic acid	12,13-Epoxy-*cis*-9-octadecenoic acid	18:1	$C_{18}H_{32}O_3$
Licanic acid	4-Oxo-*cis,trans,trans*-,11, 13-octadecatrienoic acid	18:3	$C_{18}H_{28}O_3$

*C indicates the number of carbon atoms and DB the number of double bonds in the fatty-acid chain

Some fatty acids (e.g., lauric, myristic, palmitic, stearic) are saturated, whereas others are monounsaturated (e.g., oleic, erucic) or polyunsaturated (e.g., linoleic, linolenic). In most vegetable oils, the double bonds of the fatty-acid chains are in the *cis* configuration (e.g., oleic, linoleic), although *trans* counterparts may also be present (e.g., a-eleostearic, licanic). The double bonds are more often non-conjugated (e.g., in linoleic and linolenic motifs) but conjugated sequences are also encountered (e.g., in eleostearic and licanic structures). Some oils contain fatty acid esters with other moieties along their chains, such as ricinoleic, vernolic and licanic structures with hydroxyl, epoxy and carbonyl groups, respectively.

Isolation of vegetable oils from their seeds is carried out mechanically or by solvent extraction [7]. The mechanical process consists of submitting the beans, cells and oil bodies to shearing to liberate oil. Heat is generated during this procedure, which can induce a negative effect on the proteins therein. Advantages of the mechanical-isolation process reside in its low cost, low investment and safety in terms of environmental concerns because it does not involve solvents or hazardous substances. It is, nevertheless, marred by poor yields of oil extraction because the amount of oil left in the ensuing residues can be £7%.

The principle of this type of solvent extraction is based on diffusion of solvent through seeds and subsequent solubilisation of oil. The most common solvents used in this process are alkanes with low boiling points such as hexane. The key parameter of this process is the rate of diffusion of the solvent into the oil body. This process is more efficient than its mechanical counterpart but involves use of volatile organic solvents (though their recuperation is highly optimised).

After isolation, vegetable oils are refined to obtain high-quality products free from impurities such as phosphatides, free fatty acids, gummy substances, coloured bodies, tocopherols, sterols, hydrocarbons, ketones, and aldehydes [2].

Composition of vegetable oils is highly variable as a function of the associated species, which determines their possible applications as renewable feedstock. **Table 1.3** provides the typical composition of some vegetable oils in terms of their fatty-acid residues. In the case of the more exotic castor, oiticica and tung oils, the main fatty-acid residues are ricinoleic (87.5%), licanic (74%) and a-eleostearic acids (84%), respectively. These contents can, however, be modified by breeding or genetic modification of crops [8, 9]. For instance, erucic acid (43%) is the main fatty acid in standard rapeseed oil, but several of the rapeseed varieties in cultivation are based on zero content of erucic acid [10], given its toxicity in humans if ingested at high doses.

Physical and chemical properties of vegetable oils are dependent upon their fatty-acid composition. The numbers of double bonds (as well as their positions within the aliphatic chain) strongly affect oil properties. The actual number of carbon atoms comprising the aliphatic chains has a very minor role because most of these triglycerides have 18 of them and a few have 16. **Table 1.4** summarises some relevant properties of common vegetable oils and fatty acids. The average degree of unsaturation is measured by the iodine value (i.e., the amount of iodine (mg) that reacts with the double bonds of 100 g of a given oil).