Chapter 3
Oleaginous Biomass for Biofuels, Biomaterials, and Chemicals

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Abstract Concerns about negative environmental impacts and questions of future availability surrounding the long-term use of fossil sources as a basis for production of fuels, and a plethora of derivatives, are matters of increasing importance. Consequently, plant biomass sources capable of efficiently replacing fossil fuel resources are gaining relevance as biofuels and in the oleochemical industry. The array of chemical compositions of vegetable oils and fats, the possibility of producing biomass in a sustainable way, and the development of routes for their transformation are the main drivers of this growing demand. This chapter covers topics of global production and consumption of the principal vegetable oil commodities, the comparative chemical composition of oils and fats, the potential use of the biological storage structures of oils and fats, the main processes of transforming oils into biofuels, and the production of bio-based polymers. Also, mechanisms of the functionalization of vegetable oils are stressed.

Keywords Oleochemistry • Fatty acids • Biodiesel • Polymers • Vegetable oils

3.1 Introduction

Lipids are important sources of food and renewable energy (Christie 2017; Cyberlipid Center 2017). Lipids encompass oils, fats, greases, steroids, cholesterols, lipid-soluble vitamins, and phospholipids and are the basis for a range of products, from personal care to the hardware industry. Conceptually, lipids are compounds that are insoluble in water but soluble in organic solvents such as ether, benzene, and alcohols. Oils and fats are the main commodities within lipids and are

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S. Vaz Jr. (ed.), *Biomass and Green Chemistry*,
https://doi.org/10.1007/978-3-319-66736-2_3

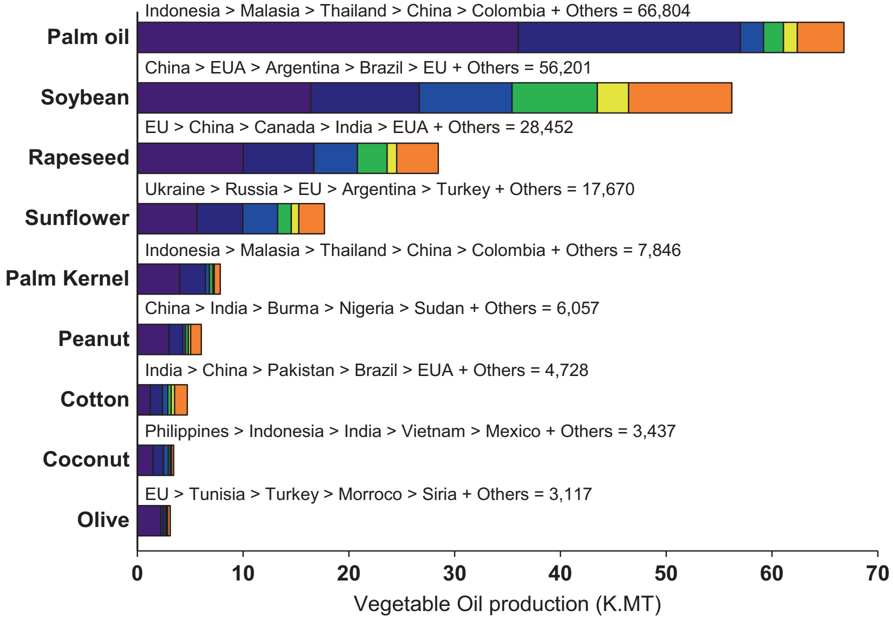


Fig. 3.1 Overview of the world's principal vegetable oil sources and production in 2017 (From USDA (2017))

the basis for the oleochemical industry. Their main market and their applications are in the food industry, but since 2001 a significant part of their increasing use is for biofuels production, especially biodiesel (Knothe 2010; Gunstone 2013).

The world production of fats and vegetable oils has increased steadily in the past 25 years, reaching 206 million tons in 2016 (USDA 2017). Although many promising oleaginous plant species are available in the wild, around 94% of the world's production comes from the seven best known sources (Fig. 3.1). Since 2004, palm oil (*Elaeis guineensis*) has become the main commodity produced and consumed, surpassing soybean (*Glycine max*), the long-standing leader. Considering its pulp and kernel oil, palm oil accounts for 38% of world production, followed by soybeans with 29% (Fig. 3.1).

The hydric and temperature needs of palm oil for productive growth and yield require its cultivation to be concentrated between parallels 10° north or south of the equator, whereas soybeans can be grown in a wider dispersion area. The main reasons for palm oil predominance as an industry base product are its desirable physicochemical characteristics and oil productivity. Averaging 3500 kg oil/ha (10,000 m^2), it can produce more than 6000 kg/ha, about tenfold the productivity of soybean, which supported the oleochemical industry for several decades and is still of great use. The soybean was domesticated in China more than 3000 years ago, and for centuries its oil provided light to cities and meal for animal feed. In the first quarter of the twentieth century, the soybean arrived in Europe and then the United States (USA), being then used mainly for industrial purposes to produce inks, varnishes, coatings, soap stocks, lubricants, and textiles. After soybean crushers were established in the USA, solvent extraction processes were developed and its oils replaced cotton and linseed oils, and, later, tallow. The need to feed the troops and the limitations on oil imports during the Second World War led to further development of soybean agricultural production systems and technological processes (Johnson and Myers 1995; Shurtleff and Aoyagi 2015). Nowadays soybean oil is mostly consumed as an edible oil. With the surge in biodiesel production it is filling a dual purpose, with strong environmental appeal: oil (food, fuel, oleochemical) and the world's leading source of high-quality vegetable protein.

The oleochemical industry also absorbs around 12×10^6 ton from several other oil sources, usually of local importance, which depends on their availability and the potential application of their added value. A good example is castor oil (*Ricinus communis*), which is used to produce specialized lubricants and coatings (McKeon 2016; Patel et al. 2016), and animal fats, used in biodiesel production (Bousba et al. 2013; Van Gerpen 2014). The usage of a given oil source is basically defined by the characteristics and proportions of its fatty acids profile. These fatty acids are the drivers of the technological routes that can be used and the final products to be obtained. As details on lipid structure and labeling are abundant in the literature (Lehninger et al. 2000; Scrimgeour 2005), this chapter focuses on the utilization of oils and fats in renewable chemistry.

3.1.1 Oils and Fats

The major components of oils and fats are glycerol-esterified fatty acids, which, as triols, can form mono-, di-, or triglycerides. In general, triglycerides (TAGs) predominate in the composition of oils and fats (Fig. 3.2).

Fatty acids are unbranched carbon chains, varying from 4 to 22 carbons, with a terminal carboxyl group. They are called saturated when all carbons are linked by single bonds and unsaturated when one or more carbons are linked with double bonds. With a single double bond, they are monounsaturated, and polyunsaturated when they contain two or more double bonds (Fig. 3.3).

The amphiphilic nature of fatty acid molecules causes oil to be stored intracellularly inside the organelles of oleaginous plants, called body oils (BOs) (Fig. 3.4), rather than storage as a dispersed continuous layer (Purkrtova et al. 2008). The BO structural model shows the TAG matrix encompassed within a phospholipid monolayer (Lin and Tzen 2004; Tzen et al. 1993), protected by a layer of structural proteins, predominantly oleosines (Huang 1992; Furse et al. 2013). The polar side is exposed to the cytosol, and the acyl group turns inside and interacts with TAGs (Beisson et al. 1996).

Figure 3.5 shows an example of body oil (BO) structures in the pulp and nut of the fruit of the macauba palm (*Acrocomia aculeata*), both of which contain high levels of oil (Lescano et al. 2015). The spherical fruit contains lipid bodies embedded in the cytoplasm. The oil bodies (OB) are scattered in the pulp, which is rich in

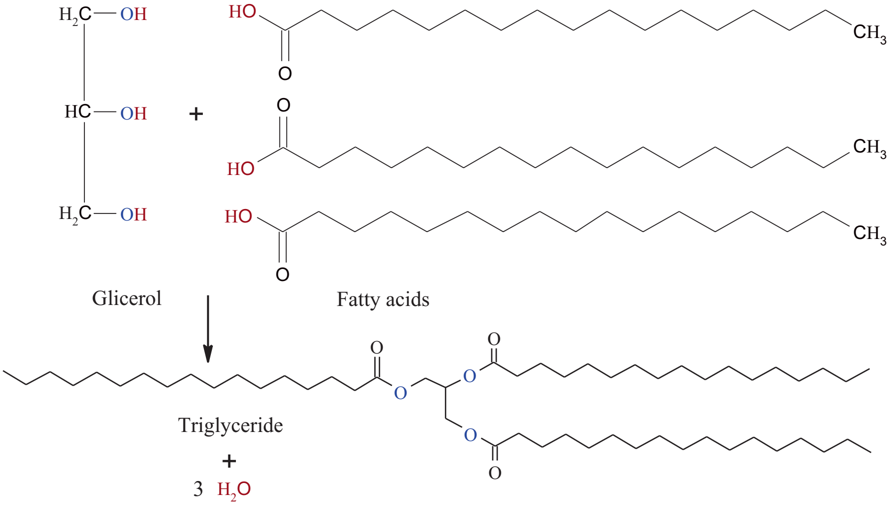


Fig. 3.2 Triglyceride formation

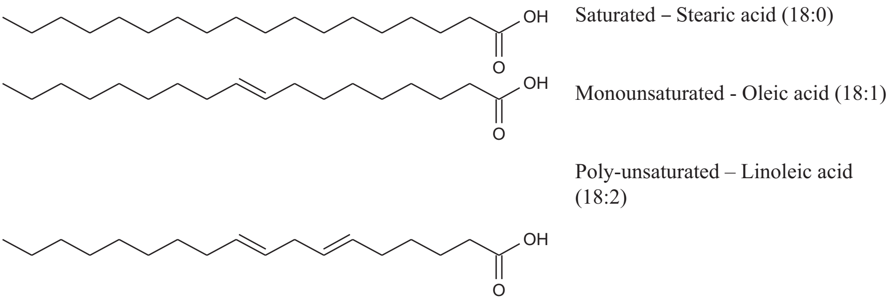


Fig. 3.3 Fatty acid structures

fibers (Fig. 3.5a). Nuts, in addition to their richness in oil, also have a significant amount of protein that is also stored as individualized structures (protein bodies, PB) (Fig. 3.5b).

The emulsifying character of BO allows the development of nano-emulsions capable of carrying hydrophobic molecules as functional components, antioxidant metabolites, vitamins, and drugs, among others (Zhao et al. 2016). Thus, they can be added to the formulation of foodstuffs (Nikiforidis et al. 2014), pharmaceuticals (Hou et al. 2003), and cosmetics (Marcoux et al. 2004) or utilized as biotechnological tools (Peng et al. 2004; Leng et al. 2016; Montesinos et al. 2016).

In fact, the development of oleaginous biomass-based products goes beyond the regular usage of extracted plant oils and fats. The industry of renewable derivatives is a fertile ground for the use of the original matrix of the vegetal tissue, or the products obtained by their modification.

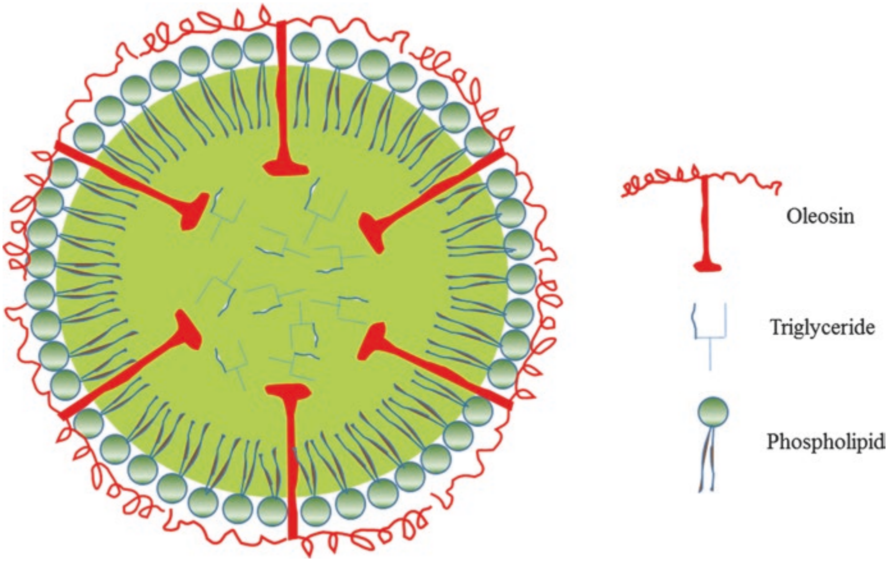


Fig. 3.4 Body oil structural model

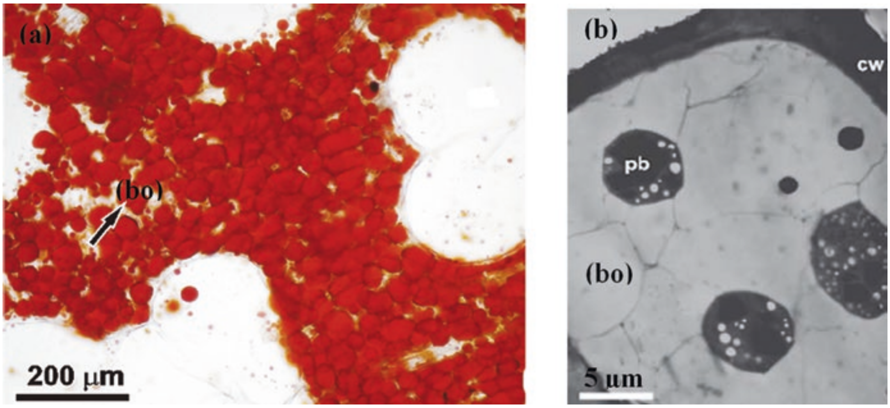


Fig. 3.5 Body oil (*bo*) and body protein (*pb*) in macauba (*Acrocomia aculeata*) pulp (**a**) and kernel (**b**). **a** Light microscopy of pulp body oil colored in *red* with Sudan III (Reis et al. 2012) (Reproduced with permission. Copyright © Rodriguesia). **b** Transmission electron microscopy of kernel (Moura et al. 2010) (Reproduced with permission. Copyright © Scientia Agricola)

3.1.2 Fatty Acids Composition

There is a broad variety of fatty acids composition in nature, varying as functions of oleaginous plant species, the storage organ, and intraspecies variability. Fatty acid composition also is influenced by environmental determinants of plant growth, such as soil characteristics and climate, as well as general post-harvest conditions. Table 3.1 was constructed to show a general view of fatty acids profiles of sources

Table 3.1 Fatty acid composition of different oleaginous biomasses

Sources	Caproic (C:6	Capryli c(C8:0)	Capric (C10:0	Lauric (C12:0)	Miristic (14:0)	Palmitic (C16:0)	Palmitoleic (C16:1)	Estearic (C18:0)	Oleic (C18:1)	Linoleic (C18:2)	Linolenic (C18:3 (9Z,12Z,15Z)	α-Eleostearic (18:3 9Z, 11E,13E)	β-Eleostearic (18:3 9E, 11E,13E)	Punic (18:3 9Z, 11E,13Z)	Arachidic (C20:0)	Gadoleic (20:1)	Behenic (C22:0)	Erucic (22:1)	Nervonic (24:0)	Ricinoleic (18:1 OH)	Iodine value (g of I/100 g of oil)
Indaiá (*Attalea dubia*)[1]	3.5	10.9	8.5	55.8	11.6	3.8		5.8													7,1
Coconut (*Cocus nucifera*)[2]	ND-0.7	4.6-10.0	5.0-8.0	45.1-53.2	16.8-21.0	7.5-10.2		2.0-4.0	5.0-10.0	1.0-2.5	ND-0.2				ND-0.2						6.3-10.6
Babassu (*Attalea speciosa*)[2]		2.6-7.3	1.2-7.6	40.0-55.0	5.2-11.0			1.8-7.4	9.0-20.0	1.4-6.6											10 - 18
Palm Kernel Oil[2]	ND-0.8	2.4-6.2	2.6-5.0	45.0-55.0	14.0-18.0	6.5-10.0		1.0-3.0	12.0-19.0	1.0-3.5											14.1-21.0
Bacuri (*Scheelea phalerata*)[3]		5.8	6.0	35.1	11.5			4.3	22.6	5.2											25,4
Tallow[4]					2.6	25.9	1.2	24.8	39.3	1.7	0.3				0.2						33.3
Macauba (*Acrocomia aculeata*) /kernel [5,6,7]		5.2	4.4	40.5	9.5	8.3	0,1	3,2	25.2	3.4	0,04				0,2						36
Palm Oil (*Elaeis guineenses*)[2]				ND-0.5	0.5-2.0	39.3-47.5	ND-0.6	3.5-6.0	36.0-44.0	9.0-12.0	ND-0.5				ND-1.0	ND-1,0					50.0-55.0
Macauba (*A aculeata*)/pulp [5, 7,8, 9,10, 11]				0.8	0.6	14.8-24.4	1.32-4.6	2.1-4.2	47.05-72.6	1-13	1-4				0.2						66-74
Olive (*Olea europaea*)[12]						7.5-20.0	0.3-3-5	0.5-5.0	55.0-83.0	3.5-21.0											75-94
Jatropha curcas[13]				0.1	0.01	12.2	0.8	0.1	39.0	36.8	0.7				0.3						101
Crambe abyssinica[14,15]							1.7	0.5	18.4	10.8	2.3				0.9		1.6	59.1			88,7
Peanut (*Arachis* hypogaea)[2]				0.1		8.0-14.0		1.0-4.5	35.0-69.0	12.0-43.0	ND-0.3				1.0-2.0	0.7-1.7	1.5-4.5		0.5-2.5		86-107
Rapeseed (*Brassica napus*)[2]						1.5-6.0	ND-3.0	0.5-3.1	8.0-60.0	11.0-23.0	5.0-13.0				ND-3.0	3.0-15.0					94-120
Sunflower(Helianthus annuus)[2]						5.0-7.6		2.7-6.5	14.0-39.4	48.3-74					0.1-0.5		0.3-1.5				94-122
Cotton (*Gossypium spp*)[2]				ND-0.2	0.6-1.0	21.4-26.4	ND-1.2	2.1-3.3	14.7-21.7	46.7-58.2	ND-0.4				0.2-0.5						100-123
Soya bean (*Glycine* max)[2]						8.0-13.5		2.0-5.4	17-30	48.0-59.0	4.5-11.0				0.1-0.6						124-139
Castor (*Ricinus* communis)[16,17]						1.25		1.31	3.81	5.27	0.81					0.38				87,1	125-145
Tung (*Vernicia fordii*)[18,19]						2.3	2.2		6.4	7.23	0.28	75.3	6.3								161,3
Flaxseed (*Linum usitatissimum*) [20,21]						4.4-7.2		3.4-4.2	18.2-19.0	16.0	54.0- 57.1				0.20						170-196
Pomegranate (*Punica granatum)*[22]						2.2-4.2		1.7-2.8	7.6-9.1	7.5-8.8				71-77	0.6-0.8						214-227

[a] Ferreira et al. (2012)

[b] Codex Alimentarius (1999)

[c] Miyahira (2011)
[d] Yılmaz et al. (2010)
[e] Lescano et al. (2015)
[f] Silva et al. (2016)
[g] Oliveira et al. (2017)
[h] Nunes et al. (2015)
[i] da Conceição et al. (2015)
[j] Del Río et al. (2016)
[k] Ciconini (2012)
[l] Codex Alimentarius (1981)
[m] Souza et al. (2016)
[n] Silveira et al. (2016)
[o] Lalas et al. (2012)
[p] Ogunniyi (2006)
[q] Canoira et al. (2010)
[r] Chen et al. (2010)
[s] Zhang et al. (2014)
[t] Anwar et al. (2013)
[u] Khattab and Zeitoun (2013)
[v] Juhaimi et al. (2017)

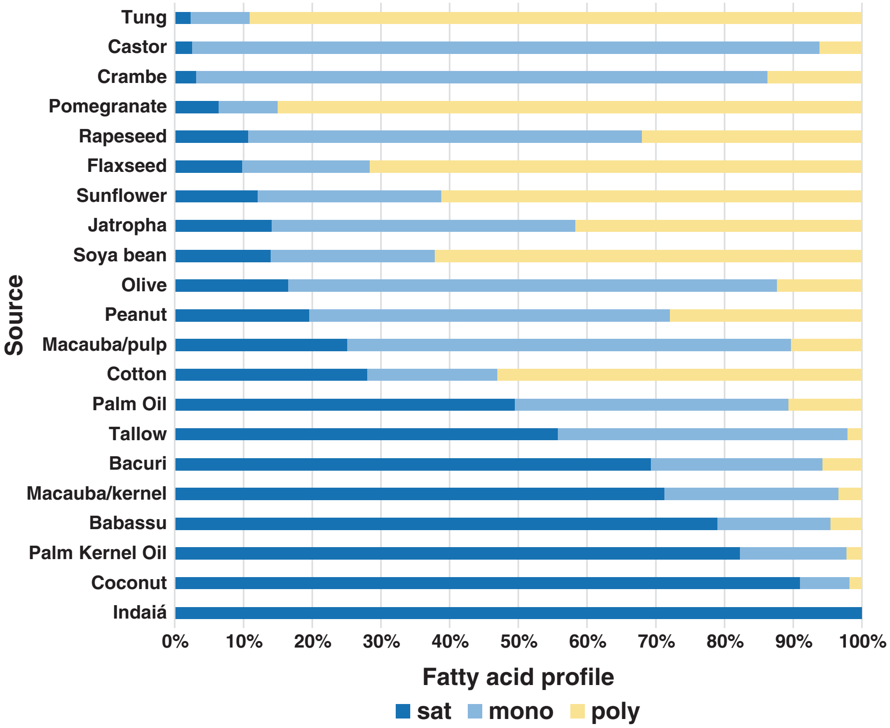


Fig. 3.6 Composition of saturated, monounsaturated, and polyunsaturated fatty acids in fats and oils

that predominantly produce saturated fatty acids up to those with highly unsaturated profiles. The iodine value (IV) is also presented. IV is a reference index for the identity of the producing source, and expresses the total unsaturation of a given oil or fat. IV is largely utilized by the industry as a referential to estimate the melting point and the oxidative stability, being also a quality control measurement of hydrogenation. More accurate methodologies have been developed to relate fatty acid composition to the physicochemical properties of the oils (Knothe 2002), but IV is still commonly used in processes with oleaginous plants and as determinant parameter in oils and fats trading. The mean values of fatty acids shown in Table 3.1 and Fig. 3.6 were assembled to illustrate the composition of the oils in saturated, mono-, and polyunsaturated fatty acids. The information contained in both table and figure contributes to the selection of an oil, or even to establishing mixtures of oils for specific applications.

Palm nuts are the primary sources of saturated fatty acids (Table 3.1 and Fig. 3.6). The indaia palm (*Attalea dubia*) has the lowest IV, with 100% saturated fatty acids, followed by coconut (*Cocos nucifera*), with IV up to 10.6. On the other hand, tallow is the most representative saturated animal fat in use, mainly for biodiesel production (Esteves et al. 2017). On the other extreme are oils from flaxseed (*Linum usita-*

tissimum, IV from 170 to 196) and pomegranate (*Punica granatum*, IV 212 to 212). Oils from crambe (*Crambe abyssinica*), tung (*Vernicia fordii*), and castor show less than 3% saturation. Tung, pomegranate, and flaxseed are rich polyunsaturated sources by the presence of three unsaturations. On the other hand, olive oil and macauba pulp oil show a high proportion of monounsaturation, being rich in oleic acid. Castor oil monounsaturation is the result of the high proportion of ricinoleic fatty acid, which is differentiated from others because it is a hydroxy acid. Erucic acid is responsible for the high proportion of monounsaturations in *Crambe*.

3.2 Vegetable Oils as Biofuels

Research in the usage of vegetable oils as fuel usually aims to replace the fossil fuels gasoline, kerosene, and diesel, derived from petrol. Gasoline is mainly a mixture of chained hydrocarbons, varying from 4 to 12 carbons, obtained by distillation of petrol in a temperature range of 30 °–220 °C; kerosene is a mixture of chained hydrocarbons, varying from 8 to 18 carbons, obtained by distillation within a 150 °–300 °C temperature range; and diesel is a combination of several classes of aliphatic, naphthenic, and aromatic hydrocarbons, and a lower concentration of some composts containing sulfur, nitrogen, and oxygen in a chain of 8–40 carbons (Haddad et al. 2012).

It is possible to regulate and optimize engines to work in accordance with the characteristics of a given fuel, bearing in mind that combustion is influenced by fuel density, viscosity, volatility, and oxidative stability. Apparently, at the beginning of the twentieth century, Rudolph Diesel, inventor of the Diesel cycle engine, successfully tested vegetable oils (Knothe 2001). However, their direct use in current engines may cause carbon deposition, injector blocking, and incomplete combustion because of their high viscosities, low volatilities, and polyunsaturated character, among others (Soares et al. 2008). On the other hand, small modifications in the injection system, or preheating of the fuel line or the fuel itself, can be an alternative solution to run stationary engines and gas turbine engines fully on vegetable oils alone, with some “green” advantages such as their low embodied fossil energy and renewable performance (Soo-Young 2017).

In this sequence, we present the main processes related to the usage of vegetable oils as fuels.

3.2.1 Vegetable Oil Micro-Emulsions

Micro-emulsions are small liquid drops of 100–1000 Å formed when two immiscible liquids and a surfactant are mixed, resulting in a system macroscopically homogeneous and thermodynamically stable (Attaphong and Sabatini 2012). Oil is used as a nonpolar phase, with the polar phase being an alcohol, plus a surfactant of

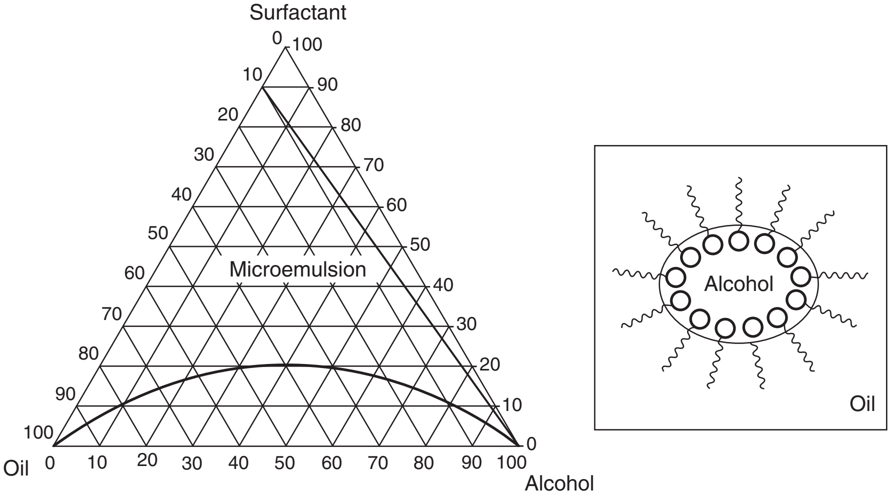


Fig. 3.7 Microemulsion of alcohol in oil

intermediary polarity (Fig. 3.7). The composition of these components can be rearranged in a phase diagram, forming an area of micro-emulsion that can reduce as much as ten times the viscosity of a vegetable oil, although it may give incomplete burning.

3.2.2 *Vegetable Oil Cracking*

Free fatty acids can be obtained from triglycerides of a vegetable oil after thermal decomposition in the temperature range 300 °–500 °C, releasing, after deoxygenation, chained hydrocarbons such as those present in gasoline, up to diesel (Speight 2008).

Cracking may be thermic or thermocatalytic. In the latter, a catalyst is added to redirect the catalytic route and generate a given product, with the advantage of processing at a lower temperature (Zhao et al. 2017). An example is the use of mesoporous matrixes of silica to generate hydrocarbons in the diesel range (Soltani et al. 2017). Several zeolites have also shown activity in cracking reactions, being useful as support to some metals (Emori et al. 2017). A scheme for a vegetable oil cracking is shown in Fig. 3.8.

3.2.3 *Transesterification/Esterification*

A transesterification reaction happens between an oil or a fat and an alcohol, usually of short length, in the presence of a catalyst and heating with the release of a mono-alkyl ester (Fig. 3.9). If the reaction is between a free triglyceride and an alcohol, it is then called esterification, in which case it is necessary to use an acid catalyst to avoid neutralization reactions.

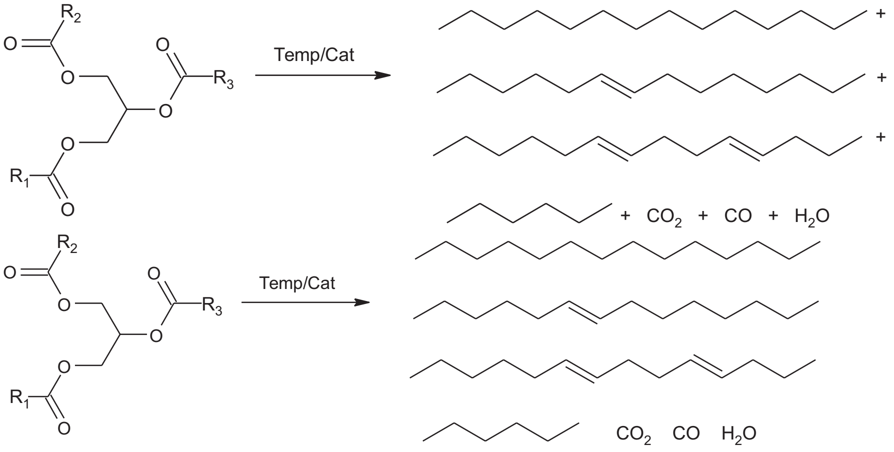
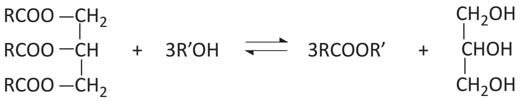


Fig. 3.8 Thermocatalytic cracking of a vegetable oil

Fig. 3.9 Transesterification reaction scheme



$$\begin{matrix} RCOO-CH_2 \\ | \\ RCOO-CH \\ | \\ RCOO-CH_2 \end{matrix} + 3R'OH \rightleftharpoons 3RCOOR' + \begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix}$$

Table 3.2 Characteristics of diesel derived from petrol and of biodiesel

Property	Diesel oil	Biodiesel
Specific mass (kg l^{-1})	0.883	0.880
Calorific value (MJ^{-}/l^{-1})	38.3	33.3
Viscosity (mm^2/s at 40 °C)	3.86	4.70

The resulting monoalkyl ester shows characteristics similar to those of diesel derived from petrol (Table 3.2), being then denominated as biodiesel (Knothe 2016). Biodiesel may be used as a fuel of its own or in blends with diesel oil. Both their specific mass and viscosity are close, but calorific value of biodiesel is lesser, because it contains more oxygenated molecules.

In the transesterification/esterification reactions, both homogeneous and heterogeneous (acids and bases) catalysts may be used, either chemical or enzymatic (Akoh et al. 2007). Nowadays, industrial processes of transesterification mostly use homogeneous base catalysts, whereas esterification processes are mostly based on homogeneous acid catalysts.

An alternative process is hydroesterification, by which a triglyceride is hydrolyzed to glycerol and acid, and then the acid is converted to ester by esterification. Such a process is preferred when the fatty raw material shows high acidity, and the excess free fatty acids may be an inconvenient path to transesterification (Pourzolfaghar et al. 2016).

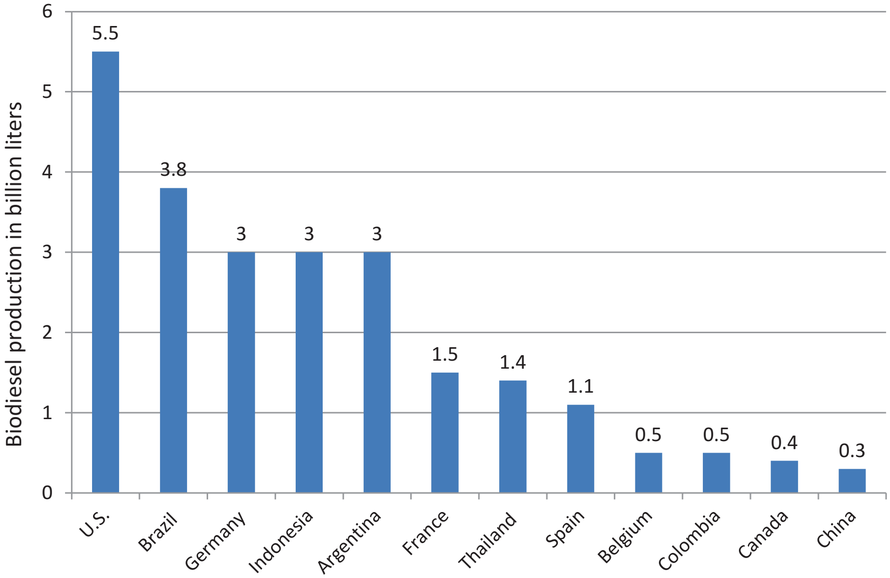


Fig. 3.10 Global biodiesel production by country in 2016

3.2.4 Biodiesel Production

In the past decade, biodiesel production has gained worldwide projection. Nowadays, 64 countries around the world have either targets or mandates to use biofuels, a broad term that includes biodiesel or bioethanol (Biofuelsdigest 2016). Also, the biodiesel production technologies acquired a maturity stage during this time.

The biodiesel industry is based on a few raw material sources, resulting from adjusting well-established crop production systems around the world. Thus, soybean, canola oil, palm oil, cotton seed, and sunflower seed are the main sources in use. In each case, attention is necessary for their saturated and polyunsaturated fatty acids contents, because they may affect the cold flow and stability of the resulting biodiesel. Independently of the oleaginous source used, the use of biodiesel as an alternative fuel has resulted in important environmental, social, and economic gains. The USA (5.5 billion l) and Brazil (3.8 billion l) are the world's largest producers so far, but Argentina, Germany, and Indonesia are also important (Fig. 3.10) (The Statistics Portal, 2017).

3.2.4.1 Biodiesel Quality

Despite its physicochemical similarity to diesel oil, biodiesel has some particularities that need to be looked after when blending it (Rodrigues et al. 2017). It is less stable than diesel, because of the unsaturated chains, caused by oxygen; absorbs

Table 3.3 Biodiesel standards in Europe, USA, and Brazil

Biodiesel standards		Europe	USA	Brazil
Specification		EN 14214:2012	ASTM D 6751-15	Res. 45/2014
Density 15 °C	g $(\text{cm}^3)^{-1}$	0.86–0.90		0.85–0.9 (20 °C)
Viscosity 40 °C	mm^2/s	3.5–5.0	1.9–6.0	3.0–6.0
Distillation	% / °C		90%, 360 °C	
Flashpoint (Fp)	°C	101 min	93 min	100 min
CFPP	°C	[a]Country specific		[a]Per region
Cloud point	°C		[a]report	
Sulfur	mg kg^{-1}	10 max	15 max	10 max
Carbon residue	%mass		0.05 max	
Sulfated ash	%mass	0.02 max	0.02 max	0.02 max
Water	mg kg^{-1}	500 max		200 max
Total contamination	mg kg^{-1}	24 max		
Cu corrosion max	3 h/50 °C	1	3	1
Oxidation stability	hrs;110 °C	8 h min	3 h min	8 h min
Cetane number		51 min	47 min	[a]Report
Acid value	mg KOH g^{-1}	0.5 max	0.5 max	0.5 max
Methanol	%mass	0.20 max	0.2 max or Fp $<$ 130 °C	0.20 max
Ester content	%mass	96.5 min		96.5 min
Monoglyceride	%mass	0.7 max	0.4 max	0.7 max
Diglyceride	%mass	0.2 max		0.2 max
Triglyceride	%mass	0.2 max		0.2 max
Free glycerol	%mass	0.02 max	0.02 max	0.02 max
Total glycerol	%mass	0.25 max	0.24 max	0.25 max
Iodine value		120 max	[a]Report	
Linolenic acid ME	%mass	12 max		
Phosphorus	mg kg^{-1}	4 max	10 max	10 max
Na, K	mg kg^{-1}	5 max	5 max	5 max
Ca, Mg	mg kg^{-1}	5 max	5 max	5 max

[a] *CFPP*, cold filter plugging point

water in an easier pattern; and may be obtained from several oleaginous sources, with different chemical and fatty acids profiles. Because of these characteristics, most countries have devised strict policies for quality control of biodiesel use and its blend with diesel (seen in Table 3.3).

Most countries have applied their own legislation regarding biodiesel quality, but for some parameters there is not a given mandatory specific range. In this case, results are monitored and checked for more detailed evaluation if values are far outliers.

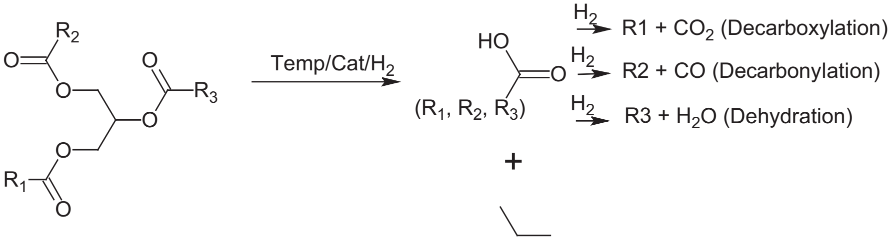


Fig. 3.11 Hydrogenation of a triglyceride

3.2.4.2 Biodiesel Glycerin

Glycerin is an important subproduct of biodiesel production. There is a large market for glycerin, which finds use in the food industry as well as cosmetics and pharmaceuticals. One kilogram (kg) of raw glycerin is generated for every 10 kg of biodiesel produced. As it still contains some residual fatty acids, methanol, and ashes, the raw glycerin must be purified for further use, which, depending on the desired purity, and hence the required purification process, may result in elevated costs. Considering such costs and the large volume produced, several studies are being conducted to find other added-value bioproducts from raw glycerin. Most promising is the use of microorganisms that produce metabolites such as succinic, citric, propionic, lactic, and glyceric acids (Vivek et al. 2017).

3.2.5 Hydrotreating

Hydrotreating is the elimination of heteroatoms from organic compounds by reactions with oxygen, under controlled temperature and pressure, and in the presence of a catalyst such as nickel and molybdenum in a high specific area material. When applied to vegetable oils, a hydroprocessed vegetable oil (HVO) results (Vrtiska and Simacek 2016). To convert vegetable oils to hydrocarbons with the physicochemical characteristics of a diesel oil, which would be then called green diesel, the reaction procedure is of hydrodeoxygenation (HDO) (Pattanaik and Misra 2017; Sugami et al. 2017) (Fig. 3.11).

Last, but not the least, there are other relevant issues to be taken into consideration besides the physicochemical characteristics of the biodiesel when planning to substitute a petrol-derived fuel, as pointed out by Refaat (2009). Perhaps the most important characteristic is the scale of the necessary substitution, as it is a function of raw material availability and affordability: this may be the driving force behind investors' evaluations on the technological route and the raw material.

3.3 Bio-Based Polymers

3.3.1 Functionalization of Vegetable Oils to Produce Bio-Based Polymers

The use of vegetable oils to produce biomaterials such as bio-based polymers has gained great attention for its versatility and abundant availability as well as eco-friendly global initiatives (Lligadas et al. 2013; Fernandes et al. 2017; Mucci et al. 2017). Plant oils-based polymers have shown a powerful capacity of application in varied technological fields to produce coatings, resins, paint, inks, and lubricants (Mucci et al. 2017).

Vegetable oils had been employed in paints and coatings since a long time ago once the unsaturated bonds are able to polymerize when exposed to the air (Van De Mark and Sandefur 2005). Also, biorenewable polymers have been developed by using unmodified vegetable oils once the carbon–carbon double bonds are capable to react by thermal or cationic polymerization as described by Larock's research group (Li and Larock 2003, 2005).

However, depending on the final application or the polymerization route, it is more practical to functionalize its chemical structure. Recently, new strategies to achieve vegetable oil-based polymers also involve functionalized vegetable oils. Use of modified vegetable oils in free radical polymerization, step-growth polymerization, acyclic diene metathesis polymerization (ADMET), and ring-opening metathesis polymerization (ROMP) has been reported in the scientific literature, as well as the available commercial materials based on these biosources (e.g., Vikoflex 7190, Ebecryl 860, Drapex 6.8).

The functionalization of vegetable oils has a fundamental role in polymer chemistry because it is possible to modify some final properties of polymeric matrices, for example, to impart stiffness, or improve the characteristics of commercial polymers to increase the potential application as resin or coating (Wool and Sun 2005).

Basically, the major component of vegetable oils corresponds to triglycerides, whose structure is shown in Fig. 3.12.

The potential sites to functionalize the triglycerides are (i) double bonds, (ii) allylic carbons, (iii) ester group, and (iv) carbons alpha to the ester group (Bonnaillie and Wool 2007). According to the open literature, the most important pathways to modify the vegetable oils for production of bio-based polymers can be organized in these three methods (Khot et al. 2001):

i. Functionalization of double bonds of triglycerides by epoxidation or maleinization followed by attaching of vinyl functionalities to the triglyceride chains
ii. Conversion of triglycerides to monoglycerides through glycerolysis or amidation reaction (ester/glycerol linkage)
iii. Synthesis of monoglycerides or diglycerides through glycerolysis or amidation reaction and functionalization of unsaturations by hydroxylation/acrylation (combination of methods i and ii).

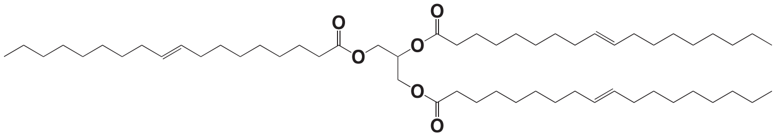


Fig. 3.12 Generic structure of triglycerides

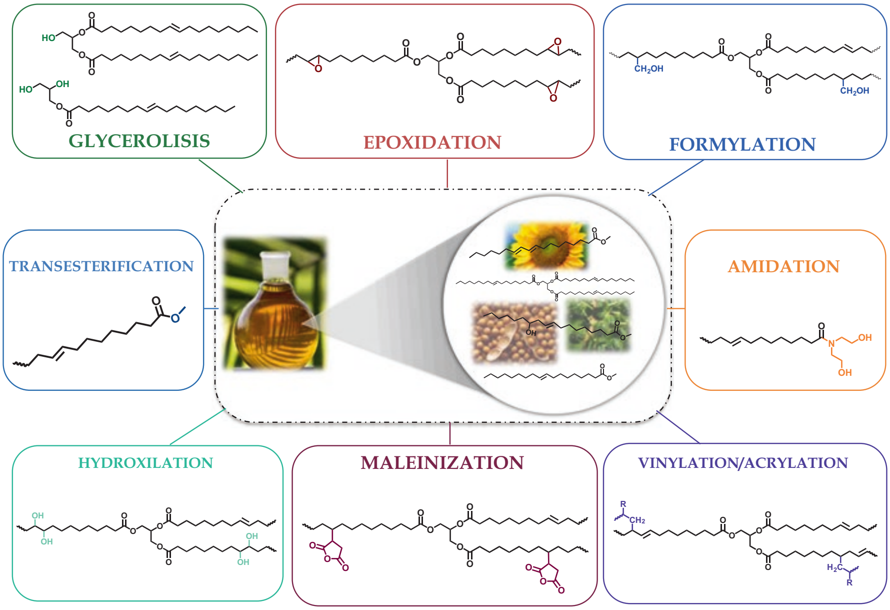


Fig. 3.13 Illustrative scheme with some possibilities of modifying the structure of vegetable oils

Figure 3.13 reviews schematically some important routes of vegetable oil functionalization.

Depending on the modification strategy, the modified monomers are able to polymerize through free radical polymerization or step-growth polymerization. It is noteworthy that natural epoxy or hydroxyl functional triglycerides such as castor oil, *Sterculia striata* (chicha oil), and *Exocarpos cupressiformis* are also easily modified by these cited pathways (Mangas et al. 2012).

Functionalized monomers from vegetable oils as soybean, sunflower, and castor oil are extensively employed to produce bio-based monomers through free radical polymerization (Bonnaillie and Wool 2007; Scala and Wool 2002; Campanella et al. 2010; Jensen et al. 2014; Medeiros et al. 2015). In this scenario, the work developed by Wool (Bonnaillie and Wool 2007), La Scala (Scala and Wool 2002), Campanella (Campanella et al. 2010), Jensen (Jensen et al. 2014), and Medeiros et al. (2015) are examples of functionalization of triglycerides/monoglycerides with in situ generated organic peracid followed by a ring-opening reaction with acrylic acid (Fig. 3.14).

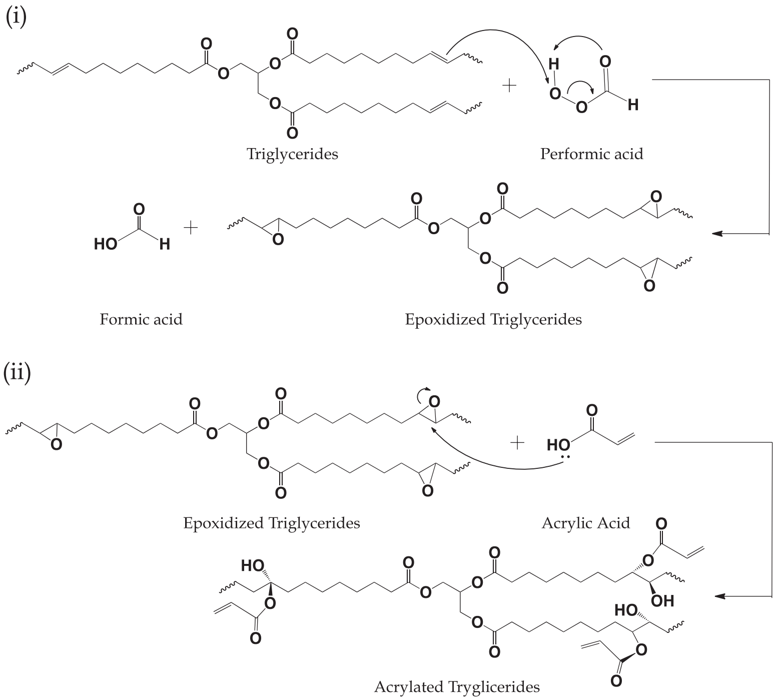


Fig. 3.14 Epoxidation reaction of triglycerides from vegetable oil (i) and ring-opening reaction with acrylic acid (ii) (Medeiros et al. 2015) (Adapted and reproduced with permission. Copyright © 2015 Elsevier Ltd.)

Can et al. (2001, 2002) have reported studies on the functionalization of vegetable oil to produce bio-based thermosettings. In accordance with these studies, maleate half-ester monoglycerides from soybean oil are obtained by two steps. First, the glycerolysis process is carried out to obtain monoglycerides (SOMGs), followed by reaction with maleic anhydride (Fig. 3.15).

In the same way, triglycerides can be functionalized by dicarboxylic acids such as maleic acid and cyclohexane dicarboxylic anhydride to generate oligomers (Fig. 3.16) (Khot et al. 2001). The introduction of cyclic rings into the structure provokes the increase of the entanglement density as well as the stiffness of the polymeric material. According to the authors, the oligomers can be blended with styrene and cured in the same manner as an unmodified AESO resin (Khot et al. 2001).

The use of unsaturated vegetable oils in the polymer field intended to produce bio-based polymeric materials has several advantages, as, for instance, low cost associated with the production process, a large range of structural changes of the vegetable oil and/or polymers, and reduction of the environmental impact by using renewable resources.

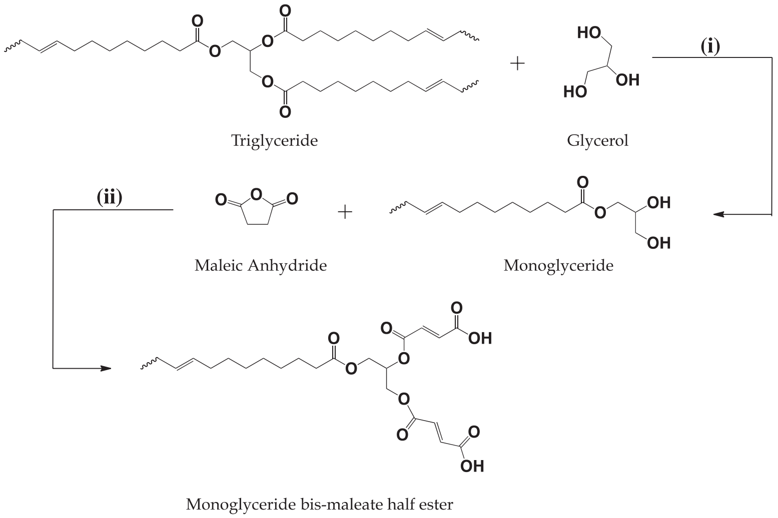


Fig. 3.15 Synthesis of (i) SOMGs and (ii) modified maleinated SOMGs (Can et al. 2002) (Adapted and reproduced with permission. Copyright © 2002 Wiley Periodicals)

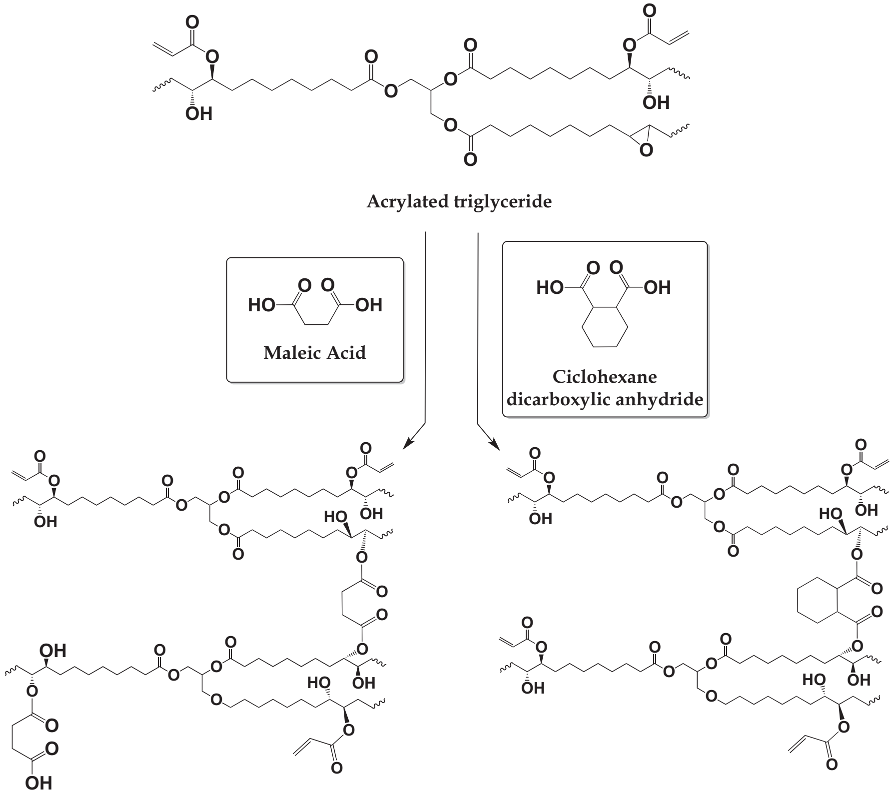


Fig. 3.16 Oligomers from AESO obtained with maleic acid and cyclohexane dicarboxylic anhydride (Khot et al. 2001) (Adapted and reproduced with permission. Copyright © 2001 Wiley Periodicals, Inc.)

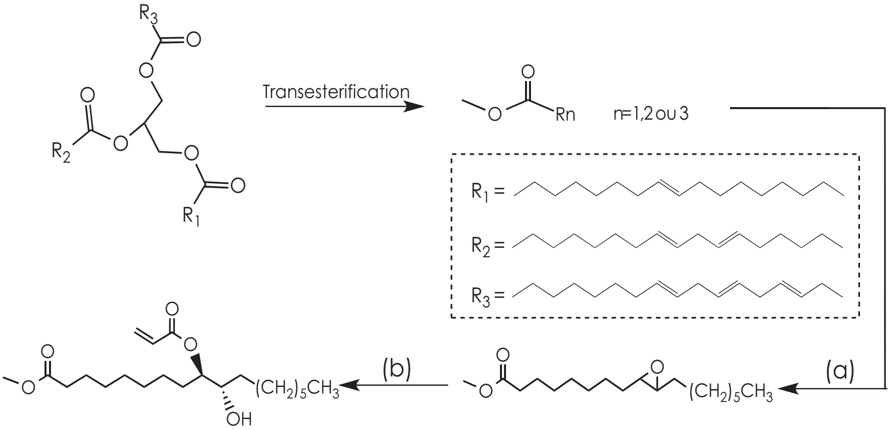


Fig. 3.17 Epoxidation of fatty acid methyl ester (FAME) (a) and ring-opening reaction of epoxidized fatty acid methyl ester (EFAME) (b) (Medeiros et al. 2017) (Reproduced with permission. Copyright © 2017 Wiley Periodicals, Inc.)

In this field, the combination of modified vegetable oils with traditional vinylic monomers is very attractive as new polymeric materials can be successfully synthesized with tailor-made final properties by using the classical industrial polymerization processes, such as, for instance, mass, solution, suspension, emulsion, or mini-emulsion.

Medeiros et al. (2017) have described the synthesis of a bio-based monomer, acrylated fatty acid methyl ester (AFAME), from soybean oil by the epoxidation reaction followed by ring-opening using acrylic acid (see Fig. 3.17). It was demonstrated that the synthesis of poly(styrene-*co*-AFAME) is easily accomplished by free radical copolymerization of styrene and AFAME in a mini-emulsion polymerization process.

Research has shown that increase of AFAME content in the polymeric structure led to a significant decrease in the glass transition temperature of the poly(styrene-co-*AFAME*). As stated by the authors, as the glass transition temperature decreased with increase of AFAME content, the synthesized polymers exhibited improved softness and malleability features (Fig. 3.18).

Ferreira et al. (2015) have evaluated the copolymerization reaction between epoxy-acrylated fatty acids from soybean oil and methyl methacrylate. Figure 3.19 illustrates the experimental steps used for the synthesis of bio-based polymers. It was demonstrated that copolymerization reactions exhibiting high reaction rates can be performed with excellent colloidal stability. In addition, the polymer particles obtained showed a very narrow particle-size distribution, and both average molar mass and glass transition temperature were very dependent on the epoxy-acrylated fatty acid mixture composition in the reaction medium.

In addition, the synthesis of bio-based polymers derived from plant oils has been extensively studied for pressure-sensitive adhesive (PSA) purposes. Numerous

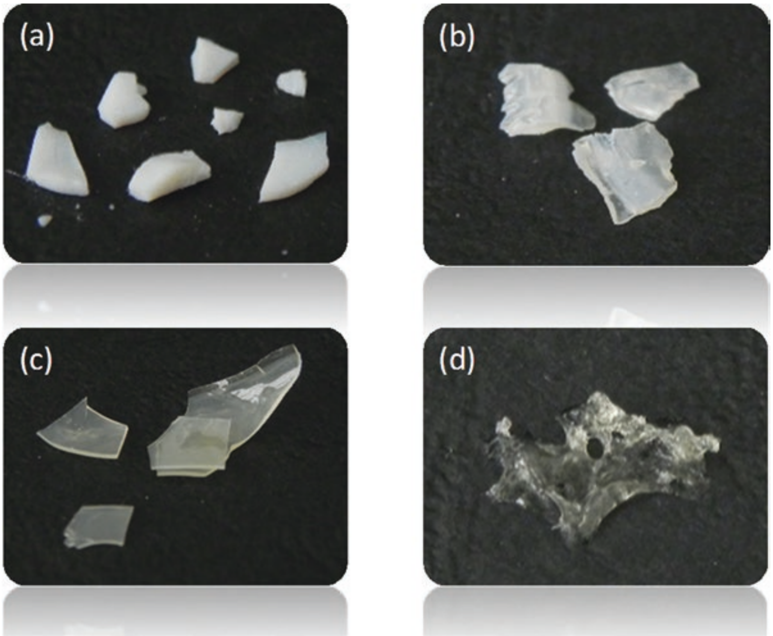


Fig. 3.18 Images of poly(styrene-*co*-AFAME): 100/0 (**a**), 95/5 (**b**), 75/25 e (**c**), 50/50 (**d**) (Medeiros et al. 2017) (Reproduced with permission. Copyright © 2017 Wiley Periodicals, Inc.)

studies have described the synthesis of PSAs from biorenewable feedstock with compatible or improved properties compared to commercial PSAs (Meier et al. 2007; Sharmin et al. 2015; Li and Sun 2015; Maassen et al. 2016; Peykova et al. 2012).

Meier and co-authors have demonstrated the excellent adhesion properties of synthesized bio-based polymers from plant oils. Bio-based polymers were obtained by polymerization of monomers derived from acrylated methyl oleate (AMO). The researchers proposed the modification of bio-based monomer precursors via a one-step, two-step, or three-step route (Fig. 3.20) (Maaßen et al. 2015).

As illustrated in Fig. 3.21, the synthesized AMO homopolymer p(AMO) presented cohesive forces (*left* in the figure) in relation to cure time. The authors affirmed that p(AMO) exhibited pronounced maximum peel strength and tack in about 5 h of curing time because of spanning network formation.

In addition, it was also shown in the study by Meier et al. (Maassen et al. 2016) that better performance, such as adhesive force and peel strength (Fig. 3.22a), and in presence of water (Fig. 3.21b), occurred on low-energy substrates of plant oils-based PSAs as compared with commercial PSAs.

As displayed in Fig. 3.22, it is reasonable to affirm that the homopolymer based on plant oil feedstock (pAMO and pAMO/MMA) achieved better results when compared to commercial PSAs, such as Acronal V212. The graphs indicate that pAMO and pAMO/MMA showed higher adhesive capacity and retained peel strength in water immersion.

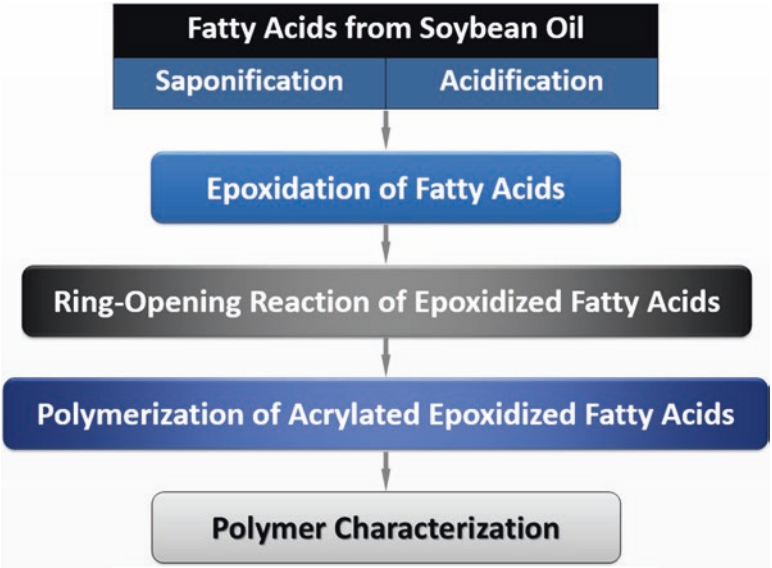


Fig. 3.19 Main experimental steps employed for the synthesis of soybean-based polymeric compounds (Ferreira et al. 2015) (Reproduced with permission. Copyright 2014 © Elsevier)

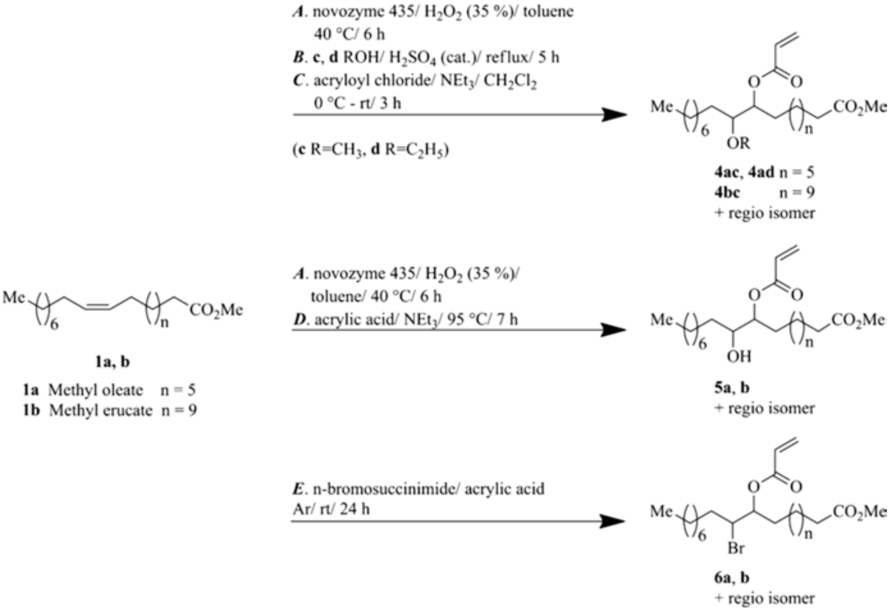


Fig. 3.20 Schematic route related to the synthesis pathways to oleate and erucate derivatives: 4AC (AMO), 4AD, 4BC, 5AB, and 6AB (Maaßen et al. 2015) (Reproduced with permission. Copyright © 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)

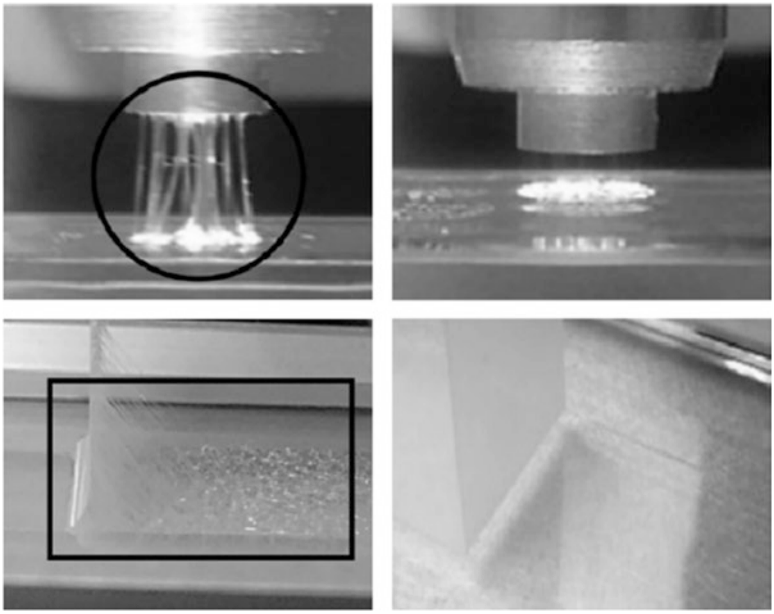


Fig. 3.21 Photographs of cohesive (*left*) and adhesive (*right*) failure in tack and peel measurements of cured p(AMO) (Maassen et al. 2016) (Reproduced with permission. Copyright © 2015 Elsevier Ltd.)

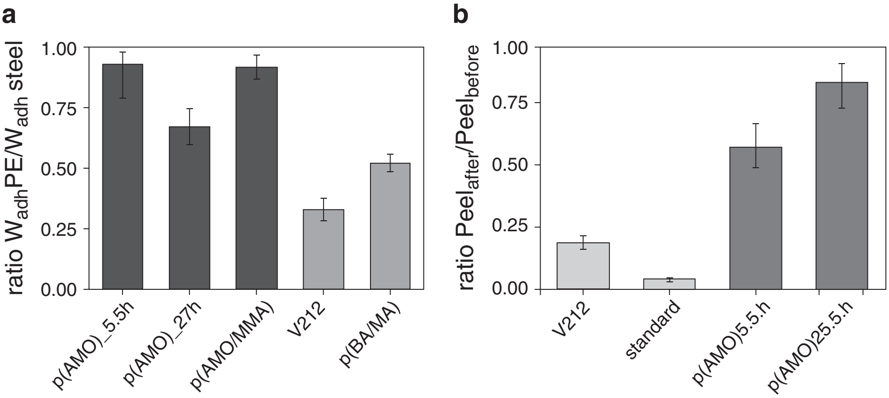


Fig. 3.22 (**a**) Ratio of W_{adh} (adhesion force) measured on polyethylene (PE) and on steel of a cured homopolymer p(AMO) at 5.5 h and of p(AMO) at 27 h compared to acrylate copolymer dispersion Acronal V212 and model solution-based copolymer p(BA/MA). (**b**) Remaining peel strength after 24 h water immersion of acrylate copolymer Acronal V212, a standard office tape (tesa SE product), and cured p(AMO) after 5.5 h and 25.5 h of curing time, respectively (Maassen et al. 2016) (Reproduced with permission. Copyright © 2015 Elsevier Ltd.)

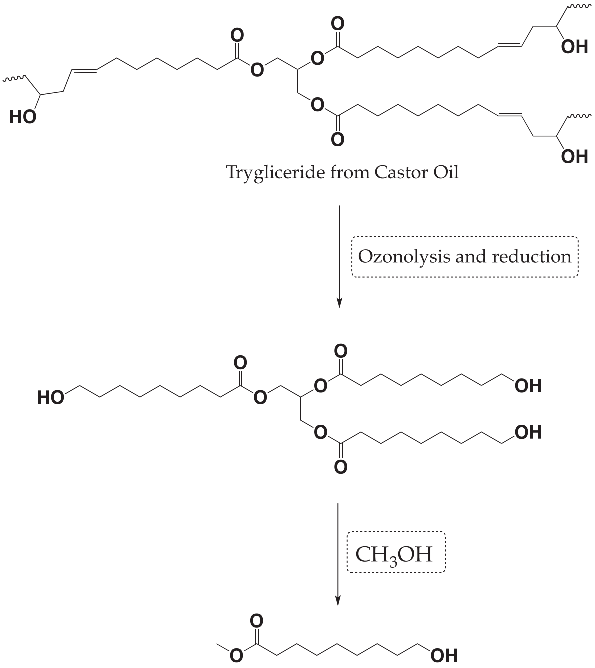


Fig. 3.23 Synthesis of high molecular weight linear polyester (HNME) from castor oil (Petrovic et al. 2010) (Adapted and reproduced with permission. Copyright © 2010, American Chemical Society)

Modified bio-based monomers have been also used to synthesize polymers from a condensation process (Das et al. 2013; Ng et al. 2017; Fan et al. 1999; Deng et al. 1999; Koch 1977; Nayak 2000). Polyurethanes, polyesters, and polyamides obtained from modified bio-based monomers, mainly those derived from castor, soybean, and rapeseed oil, have exhibited suitable properties compared to the commercial products, as, for instance, nylon 22, which has been developed by Noordover and co-authors (Noordover 2011). According to the authors, they have developed a bio-based polyamide from castor oil, one of the most important bio-based polymers, which is used in the manufacture of automotive and engineering components.

Bio-based polyesters from castor oil that have the potential to replace industrial polyester resins have been reported. Slivniak and co-authors (Slivniak et al. 2005, 2006; Slivniak and Domb 2005) demonstrated the synthesis of copolyester produced by different ratios of ricinoleic acid (RA) and lactic acid (LA). The authors achieved liquid polyester at room temperature by random polymerization, using 15% or more than 50% RA, with potential application as a sealant or an injectable drug carrier.

Petrovic et al. (2010) have demonstrated the synthesis of thermoplastic with high molecular weight linear polyester (HNME) by ozonolysis followed by methanolysis of castor oil according to the route depicted in Fig. 3.23. The authors affirmed that the bio-based polyester obtained by self-transesterification of HNME leads to formation of high molecular weight polymeric chains with a structure similar to polycaprolactone (PCL). The presence of long hydrocarbon chains between ester groups allowed it to display better thermal stability (~250 °C), higher melting point (70 °C), higher glass transition temperature (−31 °C), and lower solubility in chlorinated solvents than PCL.

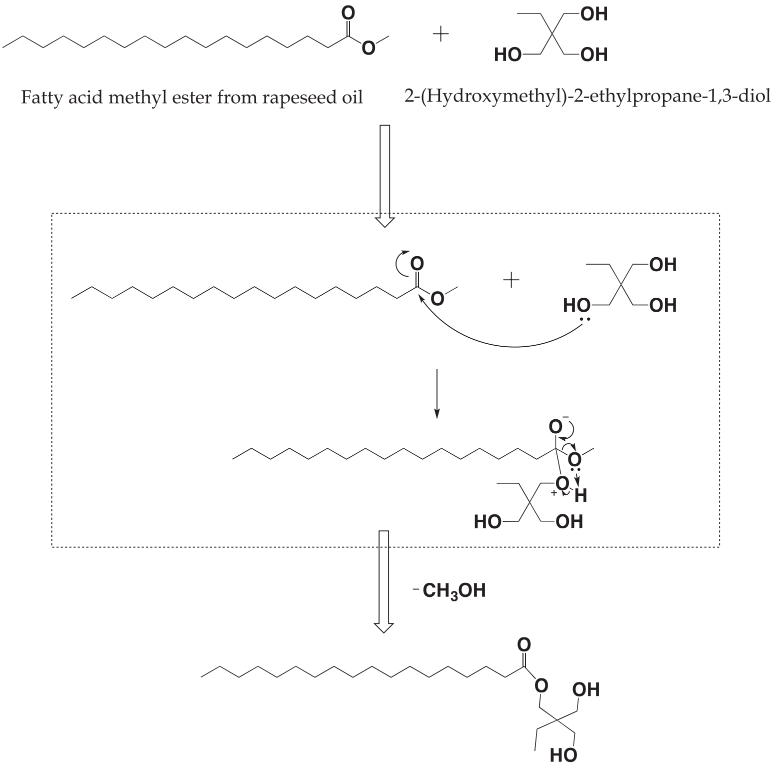


Fig. 3.24 Equimolar use of fatty acid methyl esters and 2-(Hydroxymethyl)-2-ethylpropane-1,3-diol (TMP) leads statistically to a fictive diol (Philipp and Eschig 2012) (Adapted and reproduced with permission. Copyright © 2011 Elsevier B.V.)

Waterborne polyurethanes based on soybean, castor, and rapeseed oil have been also synthesized for use as coating materials (Akram et al. 2017; Das et al. 2013; Ng et al. 2017; Philipp and Eschig 2012; Xia and Larock 2011). Philipp and co-authors (Philipp and Eschig 2012) have evaluated the use of fatty acid methyl esters as alternatives to technical fatty acids and vegetable oils in the synthesis of polyester polyurethane coatings (see Fig. 3.24) and converted to polyurethane dispersions. According to the authors, the use of fatty acid methyl esters leads to a significant reduction of the reaction time during polycondensation. However, as stated by Philipp and collaborators, the use of fatty acids is more favored in coating applications when compared to fatty acid methyl esters because of the unsaturation(s) of some fatty acids (for example, when esters are derived from oleic, linoleic, linolenic, ricinoleic, and other unsaturated compounds).

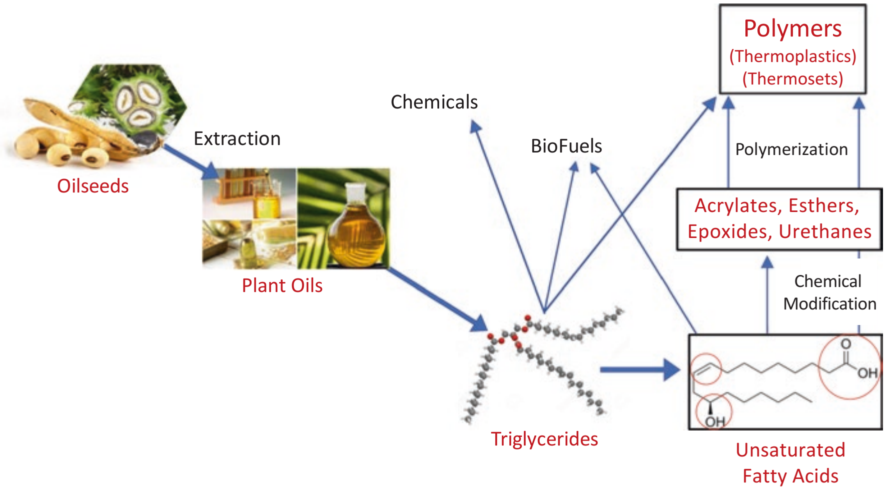


Fig. 3.25 Flowchart for the production, procurement, modification, and use of materials from renewable sources to produce polymers

3.3.2 *Vegetable Oil-Based Polymers*

Currently, several lines of research are being focused on the potential of vegetable oils and their derivatives in the polymer materials industry. These studies have been aimed mainly at obtaining thermoplastic or thermosetting polymers with different or superior properties in relation to commercial products, as well as the reduction or elimination of the use of petroleum raw material and the possibility of obtaining biodegradable materials that lead to a better response to current principles of sustainability.

In this sense, this section discusses the main polymerization reactions and modifications of synthetic routes of the various plant oils, derivatives, and constituents that are being studied and have potential use in the chemical and polymer industries (Fig. 3.25).

The industrial production of thermosetting polymers achieved approximately 35 million tons in 2015 (MordorIntelligence 2017), which corresponds to 13% of the world production of plastic materials in the same year (about 269 million tons: related to thermoplastics, thermosets, adhesives, coatings, sealants, fibers, and biopolymers, among others), according to *PlasticsEurope* (the Association of Plastics Manufacturers in Europe) (PlasticsEurope 2016). The value of 13% of the total of a market is impressive and justifies that financial investments be made to incorporate and produce biopolymers from renewable matrices.

Thermosetting polymeric materials generally have good chemical resistance, high stiffness, and excellent thermomechanical properties, and they decompose at high temperatures. These properties are closely related to the cross-linking ability of the multifunctional monomers to form cross-linked materials during the polymerization reaction. The main types of thermoset polymer materials are epoxy resins, polyurethane networks, polybenzoxazines, and unsaturated polyesters. Production is mainly focused on the market for adhesives, coatings, molding parts, automotive parts, flooring, electrical insulation, mortars, and other items (Llevot 2017).

Thermoplastic materials have in common the fact that they are formed by an arrangement of linear chains that present as their main characteristic the possibility of being moldable several times when submitted to temperature action. These materials are generally obtained through a chain-growth polymerization mechanism, and the use of monomers from renewable sources has contributed to the development of bio-based and biodegradable thermoplastic elastomers (Maisonneuve et al. 2013).

3.3.3 Analytical Techniques

Regardless of the classification of the polymer material, the final, physical, and chemical properties of polymers define the commercial and industrial applications, as well as the route of manufacture. Properties such as average molar mass, glass transition temperature, thermal stability, tensile and impact strength, stiffness, cohesion, and adhesion are extremely important and require different analytical techniques for characterization.

To produce biomaterials that may replace some commercial polymers obtained from nonrenewable feedstocks, rheological studies essential to characterize the mechanical properties have been carried out by several authors (Li et al. 2017; Hu et al. 2015; Garrison et al. 2014; Lu and Larock 2008; Tüzün et al. 2016). Lu and Larock (2008) and Garrison and collaborators (Garrison et al. 2014) have studied the effect of the fraction of unsaturated compounds (carbon–carbon double bonds), degree of hydroxylation, and ring-opening method on the mechanical properties of polymer films obtained from polyurethane dispersions that were synthesized from polyols derived from vegetable oils (peanuts, soybeans, etc.). Tüzün and coworkers (Tüzün et al. 2016) have obtained films of thermoset polymers based on benzoxazine with different degrees of hardness and flexibility through thermal curing of bis-benzoxazine monomers via the fatty acid metathesis reaction.

Dynamic mechanical analyses that evaluate such factors as tension, hardness, tensile strength, impact and compression, adhesion, cohesion, and tack (Fig. 3.26) are of extreme importance to the characterization of physical properties. For example, the experimental results obtained by Lu and Larock (2008) showed that the mechanical properties (stress–strain) of oil-based polymeric materials can be modulated, varying from elastomers to rigid plastics (Fig. 3.26a), and that the increase of the residual double content raises the glass transition temperature values, toughness, rupture resistance, modulus, and reductions in breakdown stress values. However, enhancement in the degree of hydroxylation and rigid sequencing lead to a rise in the degree of cross-linking and an effective improvement of the hydrogen bonds between the chains.

Stress–strain measurements performed by Tüzün et al. (2016) indicate that materials exhibiting different mechanical properties can be tailor made (Fig. 3.26b) from the ideal choice of a monomer precursor (benzoxazine) containing stiffened ester groups in its main chain.

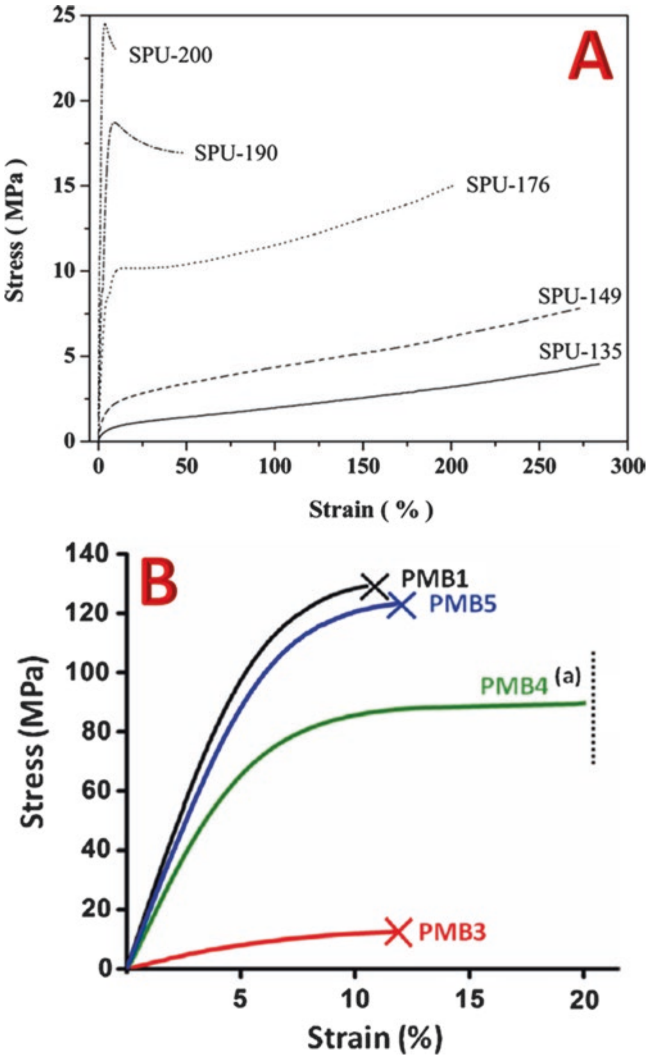


Fig. 3.26 (**A**) Soybean-oil-based waterborne polyurethane (SPU) films from methoxylated soybean oil polyols(MSOLs) with different OH numbers; (**B**) Dynamic mechanical thermal analysis (DMTA) measurements of bis-NPhenybenzoxazine derivatives (MB1, MB4, and MB5) and N-Propyl benzoxazine derivative (MB3) samples [N. B. In Figure (**B**) the letter (a) corresponds to the curve ends at the DMTA measurement limit (no sample break)]

Nuclear magnetic resonance (NMR) appears to be one of the main analytical techniques for monitoring reactions of modification of the reagents/monomers (Bunker and Wool 2002; Sehlinger et al. 2015; Medeiros et al. 2015), being fundamental for the characterization of bio-based materials obtained through the polymerization processes (Medeiros et al. 2015; Lluch et al. 2015; Gratia et al. 2015). NMR allows the analysis of several properties of a polymer (global conversion, microstructure, composition, sequences, etc.) and can also be used in the monitor-

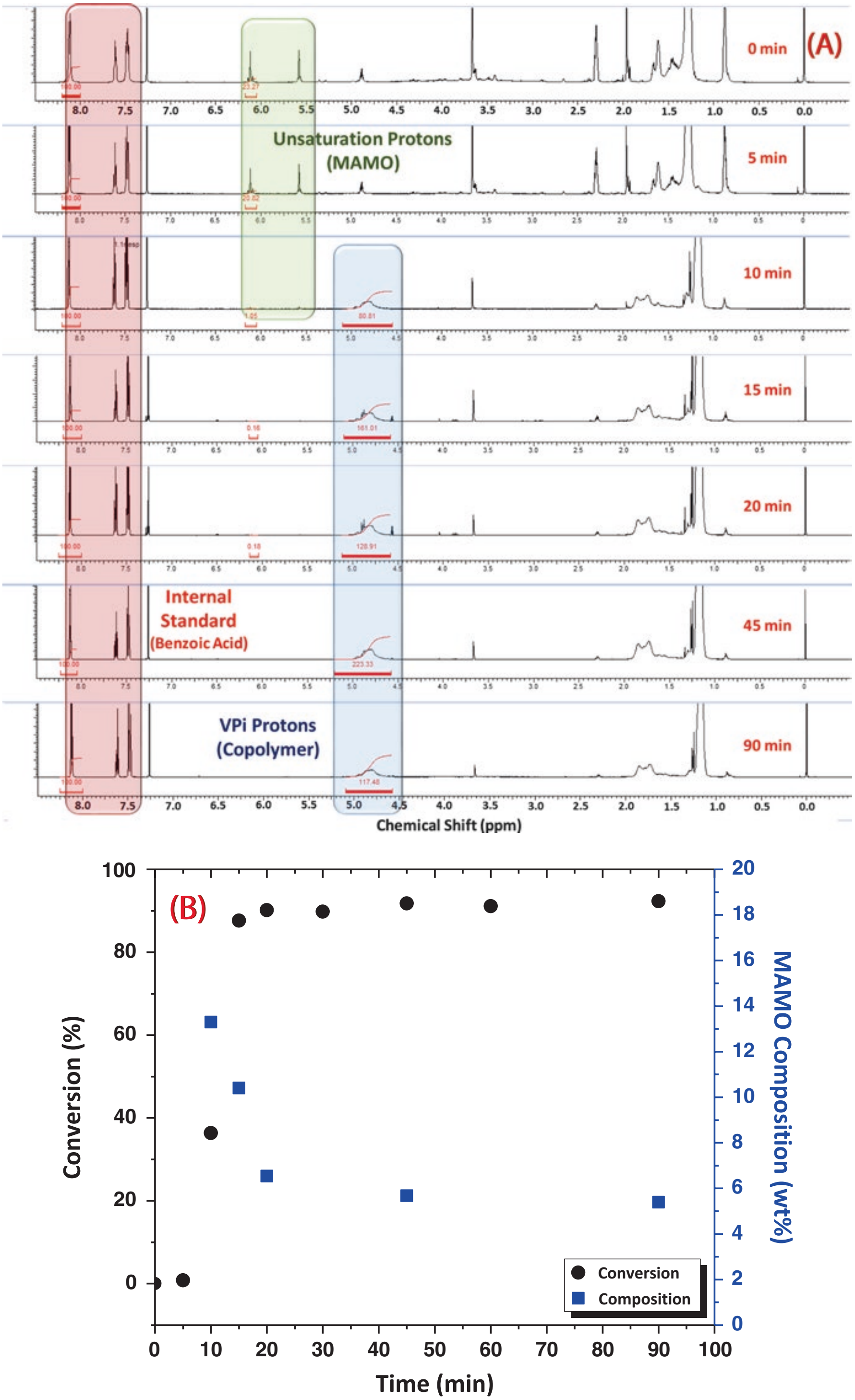


Fig. 3.27 (**a**) Off-line monitoring of the polymerization reaction via quantitative nuclear magnetic resonance (NMR) and the composition profile of methacrylated methyl oleate (MAMO) (**b**) with polymerization reaction (Jensen et al. 2016) (Reproduced with permission. Copyright © 2016 Wiley Periodicals, Inc.)

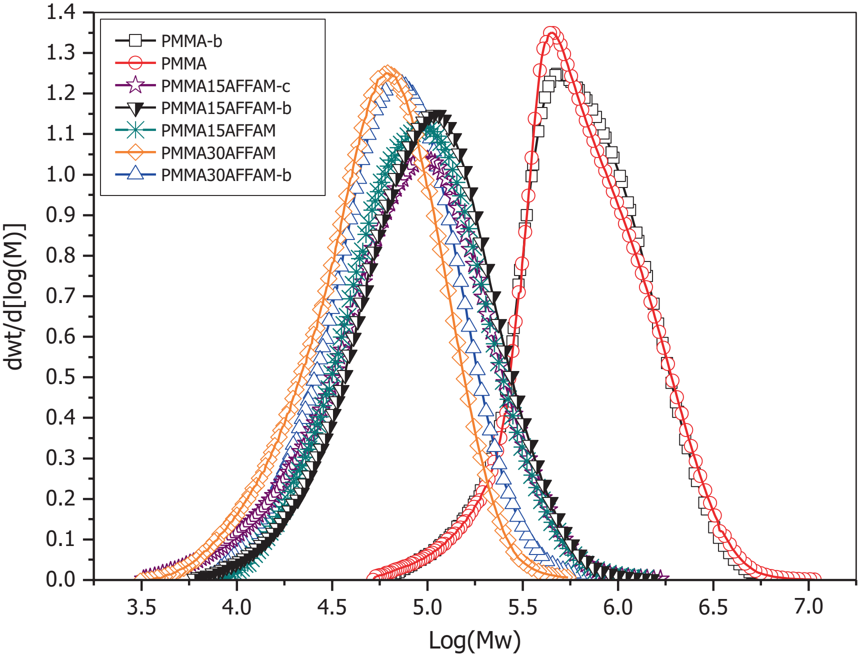


Fig. 3.28 Molar mass distributions of copolymers characterized by gel permeation chromatography (GPC) (Ferreira et al. 2015) (Reproduced with permission. Copyright 2014 © Elsevier)

ing and characterization of the molar fraction and reactivity of the monomers in copolymerization reactions. Figure 3.27 portrays experimental results obtained by Jensen et al. (2016) during classic emulsion copolymerization of a modified fatty acid (methacrylated methyl oleate, MAMO) with a vinyl monomer, vinyl pivalate (VPi), where the copolymer composition was monitored off line via quantitative NMR. Based on the NMR measurements, it was verified that MAMO was effectively incorporated into the polymer chains and that this vegetable oil-based monomer presents significant reactivity compared to VPi, which means that oleic acid-derived monomers can be successfully used in dispersed medium polymerizations, such as suspension, emulsion, or mini-emulsion.

The final properties of a polymer are directly influenced by both the average molar masses and molar mass dispersity. In spite of the existence of different forms of characterization [for instance, dynamic light scattering and NMR (Türünç et al. 2011)], gel permeation chromatography (GPC) (Türünç and Meier 2010; Kolb et al. 2014) is currently the most widely used characterization technique despite the need for particular solvent solubility and/or external calibration standards, depending on the type of detector. The molar mass of a polymer can be controlled by several methods and can also vary with the polymerization process being employed. Thus, Ferreira et al. (2015) evaluated the emulsion copolymerization of an acrylated monomers mixture (AFFAM) from soybean oil (see Fig. 3.18). The molar mass distributions obtained via GPC (Fig. 3.28) indicate that a reduction of the mass-average molar mass occurs as a result of the increase in the AFFAM fraction in the copolymer chains.

Thermal analyses such as thermogravimetry (TG) and differential scanning calorimetry (DSC) are important for the characterization of some properties of the polymeric materials, such as glass transition temperature of amorphous or semi-crystalline polymers and melting and crystallization temperatures. In this scenario, glass transition temperature appears as one of the most important features of copolymeric materials, because these materials may have distinct characteristics that depend on the organization of the polymer chains. Thus, studies of substances from renewable sources as monomers in polymerization reactions use DSC to evaluate different thermal events, as well as to establish a relationship between the renewable monomer content and the physical and chemical properties of the bio-based material.

Miao et al. (2013) have synthesized polymers based on soybean oil that present structural memory properties and which may have their shape altered at temperatures that vary according to the glass transition temperature (Tg) of the materials. Caillol et al. (2012) and Miao et al. (2010) have observed an increase in the Tg of thermosetting materials because there is an increase in the fraction of hydroxyl groups in the chains of polymerizable vegetable oils, whereas several studies (Liu et al. 2015; Ferreira et al. 2015; Jensen et al. 2014, 2016) have shown that reduction in the Tg of the polymer may reflect a primary effect of the increase in the fraction of modified vegetable oils incorporated into the polymer chains (Fig. 3.29) (Jensen et al. 2016).

Péres and collaborators (2014) have developed a superparamagnetic biopolyester based on ricinoleic acid and magnetite nanoparticles. It was observed that the polymerization of ricinoleic acid with surface-modified iron oxide magnetic nanoparticles presented a high reaction rate, indicating a catalytic effect attributed to the presence of the magnetite nanoparticles. As additional information, the magnetic nano-composites exhibited good magnetic response and superparamagnetic behavior.

More recently, Péres and coworkers (2017) have evaluated the synthesis of a new bio-based magnetic poly(urethane ester) from ricinoleic acid, 1,6-diisocyanatehexane, and glycerol (Fig. 3.30). According to the authors, the observed increase in the polymer chains enhances the thermal stability of the final material. It was also observed that the glass transition temperature of the superparamagnetic bio-based poly(urethane ester) was significantly increased in comparison to that observed in poly(urethane ester).

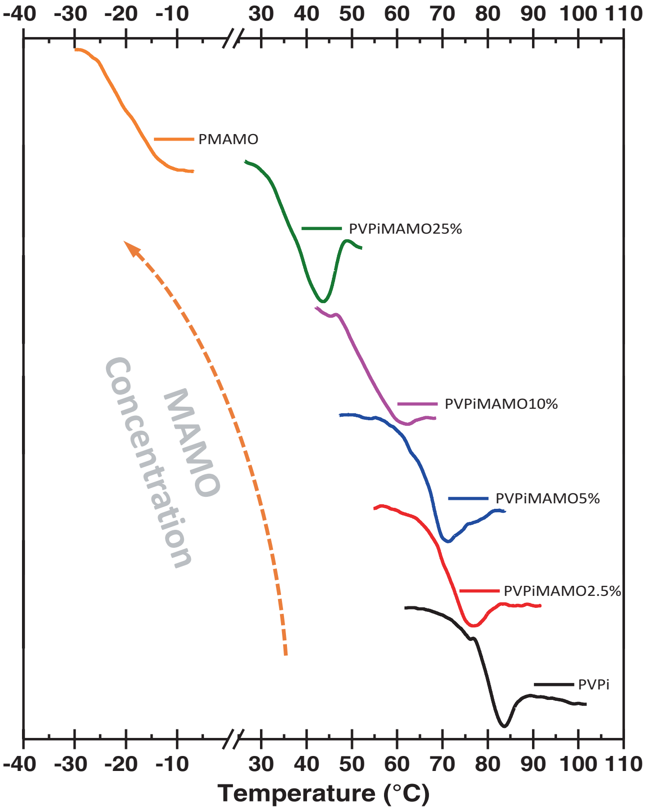


Fig. 3.29 Glass transition temperatures (Tg) and the effect of increasing the MAMO fraction on the copolymer chains obtained with vinyl pivalate (VPi) (Jensen et al. 2016) (Reproduced with permission. Copyright © 2016 Wiley Periodicals, Inc.)

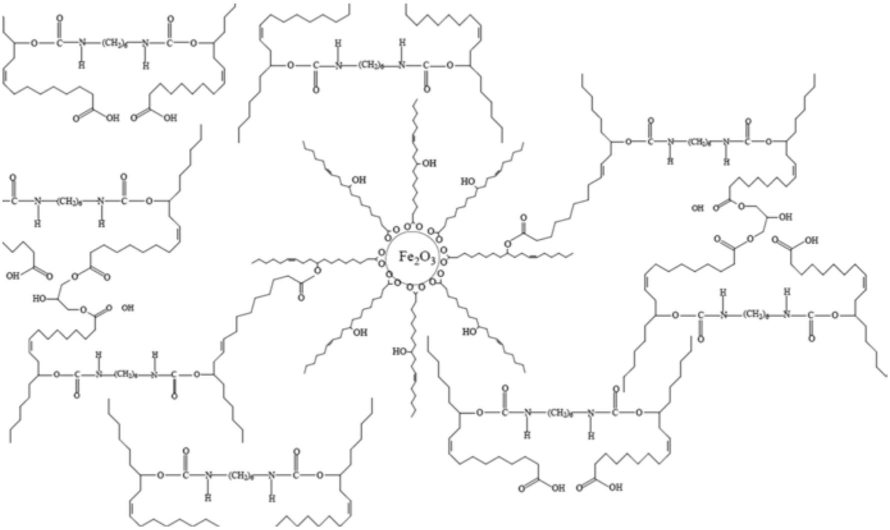


Fig. 3.30 Representation of the magnetic poly(urethane ester) based on ricinoleic acid, 1,6-diisocyanatehexane, and glycerol (Péres et al. 2017) (Reproduced with permission. Copyright © 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)

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