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Polymers from renewable materials

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ABSTRACT

With the World facing depletion of its oil reserves, attention is being focused on how the plastics industry will address shortages and price increases in its crucial raw materials. One renewable resource is that of vegetable oils and fats and about a dozen crop plants make up the main vegetable oil-seed market. The main constituents of these oils are saturated and unsaturated fatty acids that are unique to the plant in which they have been developed. Moreover, technological processes can produce more well-defined and pure oils, and the fatty acid contents in the vegetable oils can be altered with modern crop development techniques. This account describes recent advances in utilizing such vegetable oils in sourcing new polymeric materials. It also gives the context for the development of polymers based on renewable materials in general.

Keywords: *plastics, renewable, saturated, unsaturated fatty acids, vegetable oil*

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Introduction

This article focuses on the potential of vegetable-based oils and fats to supply the raw materials for the production of polymeric products (plastics, fibres, lubricants, etc.) on which much of everyday life depends. This issue will become increasingly significant as we approach the 'oil peak', i.e. that point at which more than half of the World's easily-accessed oil will have been utilized [1]. The article begins with a survey of the nature and sources of vegetable oils. It then moves on to chemical conversion and manufacturing processes, initially referring to the earlier work on polymeric materials based on polylactides and other polyhydroxyalkanaoates, with subsequent developments, and then considering recent studies on materials based on vegetable oils.

Vegetable oils and fats: context

Naturally occurring oils and fats could become one of the major players in the chemical and engineering industry in the near future. This might result in a new order by placing the agricultural industry as the largest wealth-generating sector although farmers may not yet realize that they are potential oil barons. The oil they control is not below the ground, however, but rather above, contained in the seeds of plants. These plants are renewable in that they are produced by sunlight. Such natural products, in particular sugar, starch, cellulose or proteins and natural fats and oils could provide the starting materials to make not only currently available polymeric materials but also to make new products plastics with novel properties. An early industrial-level process to achieve a non-petroleum-based product was that introduced by ICI in the form of 'Biopol', which is discussed below.

Currently, petroleum-based fossil fuels are used to provide the raw materials to make a wide variety of industrial chemicals and nearly all types of plastics. However, nowadays plant-derived materials could potentially provide an alternative, renewable, biodegradable source of high value speciality products such as fibres, adhesives, paints, cosmetics, lubricants, components of detergents and plastics. The sustainability of this industrial sector is dependent in the long term on a fundamental shift in the way in which resources are used, by moving from a non-renewable to a renewable basis, from high levels of waste to high levels of reuse and recycling, and from products based on lowest first cost to those based on life cycle costs and full cost accounting, especially as applied to waste and emissions from the industrial processes that support construction activity [2].

Over the next several decades, plant oils will become just as essential to everyday life as fossil fuels are today. This is why scientists are interested in making plastics from plant-based materials because they can produce an amazing array of compounds that could be used as the starting monomers to produce plastics. (The monomer is the individual molecule that, on polymerisation, forms the polymer chain). Moreover, plant oils and fats have the same basic chemical structure as petroleum: both are made up of long chains of carbon atoms, i.e. are hydrocarbons.

Oils and fats (animal or vegetable in origin) have long been identified as possible substitutes for petrochemical derivatives in the production of polymers for many applications [3-7]. Large proportions of the vegetable oils such as coconut, palm and palm kernel oil come from countries with tropical climates. Soybean, rapeseed and sunflower oils come from moderate climates. Animal fat is obtained from the meat industry with beef tallow being the most abundant fat.

Oils and fats make up the greatest proportion of the current consumption of renewable raw materials in the chemical industries as they offer a large number of possible applications [5,6]. Of the approximately 101 million tonnes of fats and oils which were produced worldwide in 1998, by far the largest share was used in human foodstuffs and the amount produced has increased continuously by approximately 3% per year. It is predicted that this trend will continue in the medium and long terms [5,8,9]. Figure 1 shows the amount involved in world production and uses of oils and fats in millions of tonnes.

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Oil and fats are triglycerides which are esters of glycerol and saturated and unsaturated fatty acids; an example is given in Fig. 6.

Plant-derived triglycerides offer two reactive sites, the double bond in the unsaturated fatty acid chain, and the ester group. 90% of the derivatization reactions are carried out at the carboxylic group. Only 10% of oleochemical reactions involve the alkyl chain or the double bond. For most other uses, oils and fats must be split into the so-called oleochemical base materials: fatty acids, glycerol, and, as hydrogenation products of the fatty acid methyl esters, fatty alcohols [8]. Oleochemicals are chemicals derived from biological oils or fats. Palm, soybean, rapeseed, and sunflower oil, as well as animal fats such as tallow, contain mainly long-chain fatty acids (e.g., C-18, saturated and unsaturated) and are used as raw materials for polymer applications and lubricants [10,11].

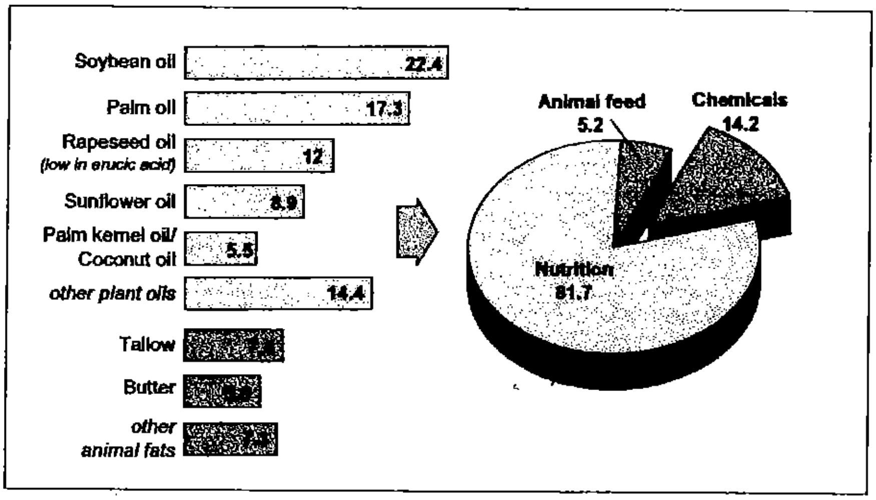

Figure1: World production and uses of oils and fats (1998, in million tonnes) [acc. to Oil World, Hamburg][16].

Most plastic products are currently made from petroleum-based synthetic polymers that do not degrade in a landfill or in a compost-like environment. Based on results from cycle analyses and ecological and toxicological studies for selected cases, one can assume that products based on renewable resources are usually much more ecologically compatible when compared with petrochemical-based substances — an important criterion in the development of a new product, which is just as significant as price performance [12,13]. Therefore, because the disposal of the petroleum-based products poses a serious long-term environmental problem, an environmentally-conscious alternative is to design or synthesize polymers that are biodegradable.

Chemistry and engineering teams are now working to transform renewable raw materials into new chemicals, polymers, formulated products and composite materials, known as "bio-materials". When discussing bio-materials, it may seem elementary, but it is important to note that plants do not cause any negative effects to the ecosystem, they can grow in different climatic zones, they recycle the carbon dioxide for the atmosphere of our Earth, and many work to improve soil fertility. Therefore, in summary, it is necessary to shift our usage from petroleum-based product to renewable and recyclable materials since renewable resources generally do not contain environmentally damaging substances and reduce our landfill requirements. The significance of this developing field is illustrated by the increased level of publication on related topics in such journals as 'Biomacromolecules' published by the American Chemical Society.

Vegetable oils; Sources and Importance

Vegetable oils are renewable resources and for industrial purposes, originate from five principal crops: soybean, oil palm, rapeseed, sunflower, and coconut [14]. Figure 2 shows the countries which are most significant as exporters of vegetable oils and fats. The world supply of vegetable oils from the ten major sources in 2004-2005 was about 110 million tons [15]. According

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to Oil World [16], ten oilseeds can be divided into three groups based on their levels of production, refer to Figure 3.

Soybean represents over 30% of the ten principal seeds, followed by four seeds (rapeseed/canola, cottonseed, sunflower and groundnut, each in the range of 7-13% of the total) making up a further 40% of the world consumption of oilseeds. Another five seeds (palm kernel, coprah, sesame, linseed and castor), each in the range 0.5-2%, make up the balance of the total production of oil seeds.

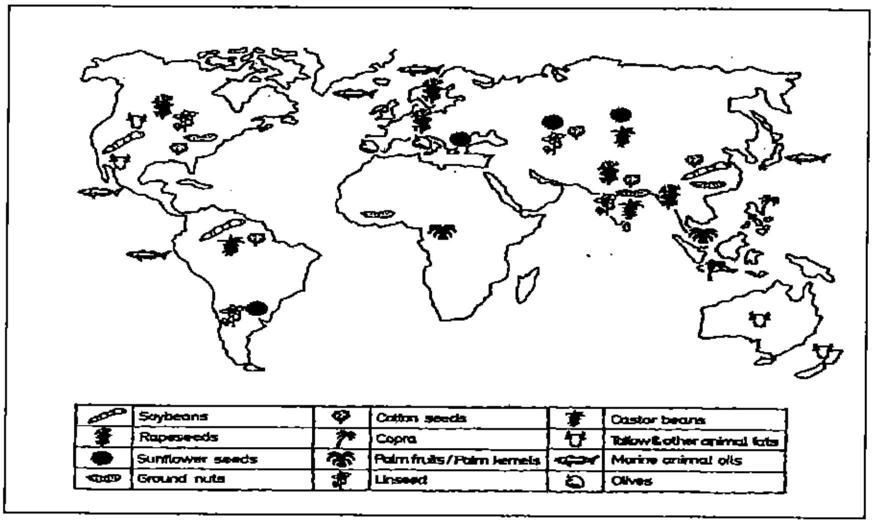

Figure 2: Chief exports of renewable raw materials [8]

Thus, information on nearly the totality of oil sources are distributed among 5 groups [15] as shown below:

1. ***Main world sources of oils***
   Palm oil, rape oil, soya oil, sunflower oil
2. ***Seven other important oils***
   Arachis (groundnut), cotton, coprah, palmkernel, maize (corn), olive, sesame
3. ***Minor vegetal oils***

Almond seed, camelina, carthame, grape seed, hazel-nut, linseed, poppy seed, walnut

4. ***Oils used in dietetics, cosmetics and lipochemistry***
Avocado pear, blackcurrant, borage, cacao, castor bean, evening primrose, kukui oil, wheat germ

5. ***Vegetal butters and margarine***

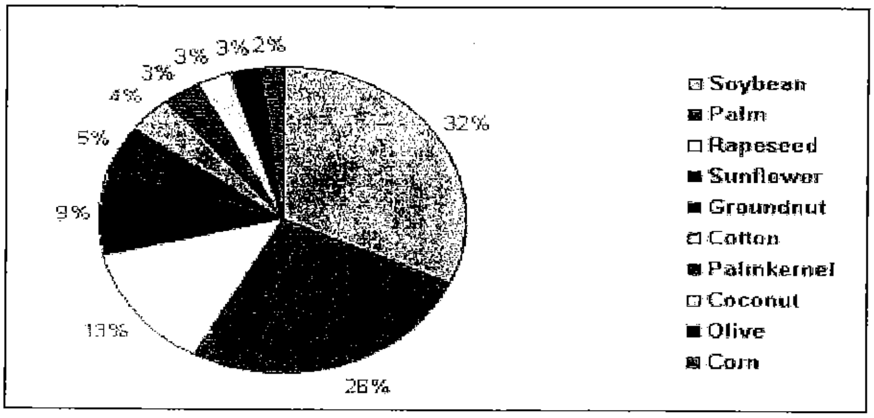

Figure 3: World supply of vegetable oils from the ten major sources in 2004-2005 [15]

Besides acting as a food source, these oils also have wide industrial application, for example, soyabean oil is attracting more attention for industrial application because it is readily available for large scale production. More than 600 million pounds of the soybean oil produced annually in the United States are used for nonedible applications, including the production of industrial materials. More than half of this use of soybean oils falls in the category of fatty acids, soaps and feed. The remainder of the nonedible soybean market is used for the manufacture of inks, paints, varnishes, resins, plastics and biodiesel.

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Composition and biogenesis of vegetable oils

Since about 1990, genetically modified oils have been developed using either mutation/selection breeding or the tools of biotechnology, and represent some of the most significant new products developed for the oils and fats industry. The main constituent of these oils is saturated and unsaturated fatty acids that are unique to the plant in which they have been developed as shows in Figure 5.

Modern technology can produce more well-defined and pure oils, and fatty acid contents in the vegetable oil can be altered with modern crop development techniques. The new crops that are of interest include those that contain a higher percentage of a desirable fatty acid or a lower percentage of undesirable fatty acids, and those that contain a unique fatty acid [18]. The availability of fatty acids that are functionalized (e.g. epoxidated) in the fatty acyl chain would facilitate speciality products such as epoxy resins, polyurethanes or polyesters. Figure 4 shows an example of an oilseed crop that contains a naturally occurring functionalized epoxidated fatty acid, namely vernolic acid in *Euphorbia lagascae.*

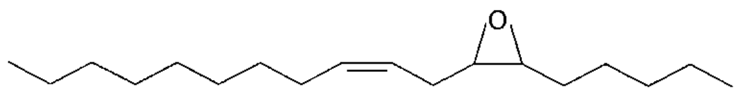

Figure 4: Fatty acid (vernolic acid) in *Euphorbia lagascae*

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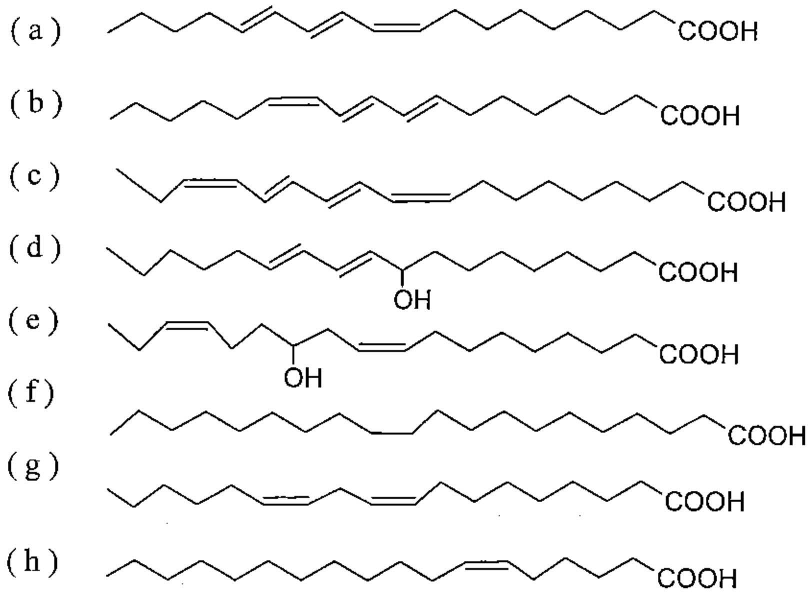

Figure 5: Unusual fatty acids in the seed oil of one-year old plants [17]. (a) α-elaeostearic acid from *Centranthus macrosiphon Boiss;* (b) calendulic acid from *Calendula officinalis L.;* (c) α-parinaric acid from *Impatients balsamina L.;* (d) dimorphecolic acid from *Dimorphotheca pluvialis;* (e) densipolic acid from *Lesquerella lescurii* (Gray) Wats.; (f) lesquerolic acid from *Lesquerella gracilis* (Hook.) Wats.; (g) crepenic acid from *Crepis alpina* L.; (h) petroselinic acid from *Coriandrum sativum* L.

An example of a vegetable crop that contains a long-chain fatty acid, which makes the material more flexible, is epoxidized soybean oil (ESO). ESO possesses functional epoxy groups within the triglyceride molecule which can react with suitable reagents. Each triglyceride contains three fatty acid chains linked by a single glycerol molecule, as shown in Figure 6.

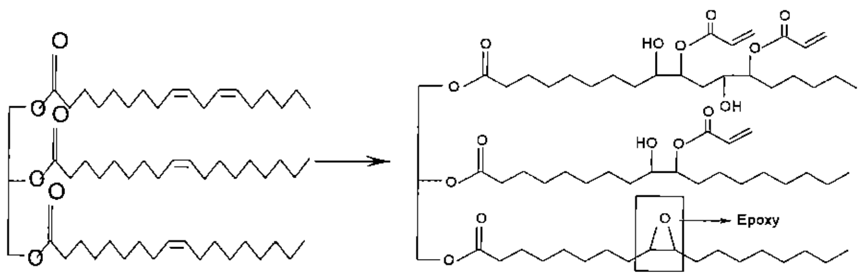

Figure 6: A triglyceride contains three fatty acid chains linked by a glycerol molecule; a naturally occurring triglyceride can be functionalised by appropriate treatment.

The fatty acid chains have 0–3 double bonds and vary in length from 16–22 carbon atoms [19]. The ESO contains a long-chain fatty acid, which makes the material more flexible. They can be cross-linked to form elastomeric networks and are attractive raw material resources for polymer synthesis [20] Low-cost soy-based resins would offer a significant cost reduction through the partial replacement of epoxy resin for composite applications. Furthermore, vegetable oils are biodegradable and, therefore, environmentally friendly.

Palm Oil Controversy

Palm oil overtook soybean oil as the most widely produced edible oil at the end of 2006 due to the rapid rate of palm planting in Indonesia and Malaysia At the same time, Indonesia took the first position as producer from Malaysia. The 2006 breakdown of production is given in Figure 7 [21].

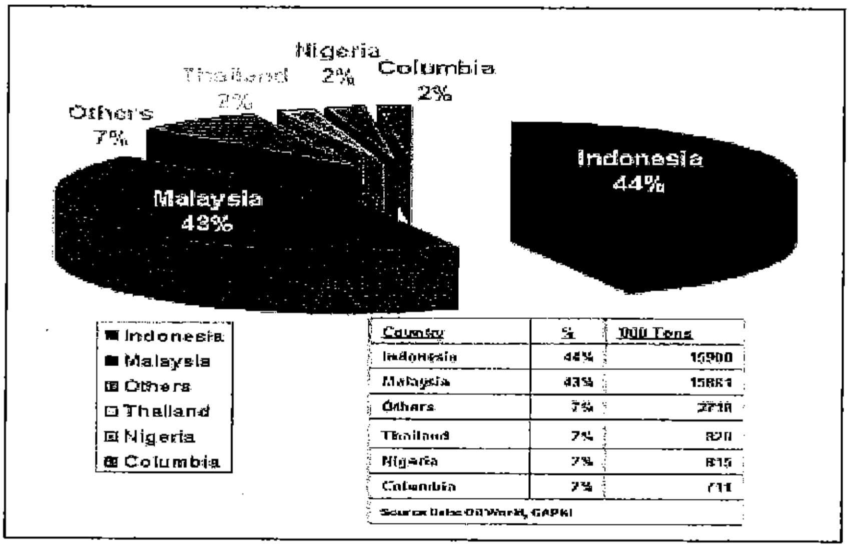

Figure 7: 2006 World Palm Oil Production [21]

The reasons for the demand for palm oil are legion: not only does it play a major role in the foodstuffs industry but it is a raw materials for soaps, detergents and bioplastics and, notably because the fluctuations in the world price of oil, fuel for modified car engines [22]. The dietary consequences of consuming products derived from palm oil are discussed in detail on the website for the American Palm Oil Council [22].

The increased area of land devoted to planting of palm trees has prompted a vigorous debate on the associated environment issues, in particular the deforestation of tropical rain forests to make way for new plantations. Attention has focused on such developments in Borneo (loss of habitat) [23], Indonesia (generation of gigatons of carbon dioxide, CO_2 and Malaysia.

Utilization of the entire waste biomass of oil palm as feedstock for power generation within the plantation; and as feedstock in the production of renewable energy, cellulosic ethanol, biogas, bio-hydrogen and bio-plastic, has increased the feasibility of the plantation industry. Most importantly, it has greatly reduced the carbon dioxide emissions into the environment [24]. The Malaysian palm oil industry practices an advanced form of sustainable agriculture to ensure environmental conservation and has been instrumentally in the forefront in bringing the roundtable discussions on sustainable palm oil (RSPO) to a successful conclusion [25].

New biodegradable polymeric products for manufacturing

Biodegradable polymers are classed as biosynthetic, semi-biosynthetic or chemosynthetic depending on their manner of preparation, while the term 'biodegradable' has been defined as the gradual breakdown of material mediated by specific biological activity. Plastics made from renewable resources such as corn, starch or lipid are attractive because naturally derived polymers are usually biodegradable and find use in composites reinforced with natural fibres referred as biocomposites.

At present, important biosynthetic examples of biopolymers that have received much attention from an overall market perspective are the polylactides (PLAs), the general class of polyhydroxyalkanoates (PHA's), starch and starch blends and cellulose derivatives.

- **Polylactic acid (PLA)**

Polylactic acid (the simplest widely-used polhydroxyalkanoate) is a versatile polymer made from renewable agricultural raw materials such as woody biomass. Starch from such a starting material is converted to dextrose which is fermented to lactic acid. In the industrial manufacture of PLA, the

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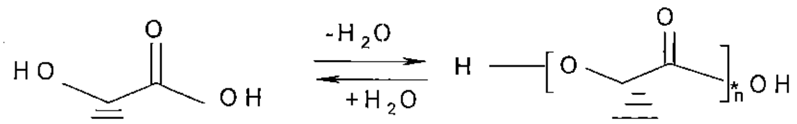
fermentation of corn sugar by biotechnological processes has the advantage of providing the required high-purity lactic acid. The lactic acid is then processed via a cyclic dilactone, where the lactide monomer is subjected to ring opening polymerisation through condensation process to give the desired polylactic acid or polylactide (Fig.8).

The main synthetic route starting from lactic acid is the direct polycondensation reaction or ring-opening polymerization of a lactide monomer in the present of a Lewis acid catalyst. Cargill Dow LLC, the largest current producer of PLA, has developed and patented a low-cost continuous process for producing a lactic acid-based polymer [26].



L-lactic acid poly L-lactide

Figure 8: Polymerization of lactic acid to polylactide

Although, PLA is commercially interesting because of its good strength properties, film transparency, biodegradability, biocompatibility and availability from renewable resources [27], polylactide polymers are brittle and stiff materials, and it is therefore necessary to use plasticizers to improve the elongation and impact properties [28] or by forming copolymers with more flexible biodegradable polymer such as polycaprolactone. However, in general, these properties of PLA are highly dependent on molecular weight

Referring to Table 1, the PLA that is currently produced commercially has the added benefit of generating lower greenhouse gas emissions than the conventional petroleum-based plastics. PLA generates only 0.27 pounds of carbon dioxide per pound of plastic produced, according to results published last year in *Industrial Biotechnology* [24].

Table 1 Summary of commercially available polylactic acids (PLAs)

Manufacturer	Product Name
Shimadzu Corporation	Lacty
Mitsubishi Plastic	Ecoloju
Birmingham Polymers, Inc	Lactel, Absorbable
Boehringer Ingelheim	Resomer®
Cargill-Dow LLC	NatureWorks™
Galactic SA	Galactic
PURAC	Purasorb
Ecodear	Toray [29]

- **Poly(hydroxyalkanoates) (PHAs)**

A related class of biodegradable aliphatic polyesters which has been developed commercially is the poly(hydroxyalkanoates) (PHAs). These have been reviewed in great detail by Philip et al. [30] and only brief coverage is merited here. Examples include polyhydroxybutyrate and poly(B-hydroxyvalerate) [31]. PHAs are naturally produced by a microbial process on a sugar-based medium acting as a carbon- and energy-storage material in bacteria. PHAs from waste material left over from the production of ethanol from the stalks and leaves of corn plants and currently produced commercially from industrial are shown in Table 2.

Table 2 Summary of commercially available poly(hydroxyalkanoates) (PHA)

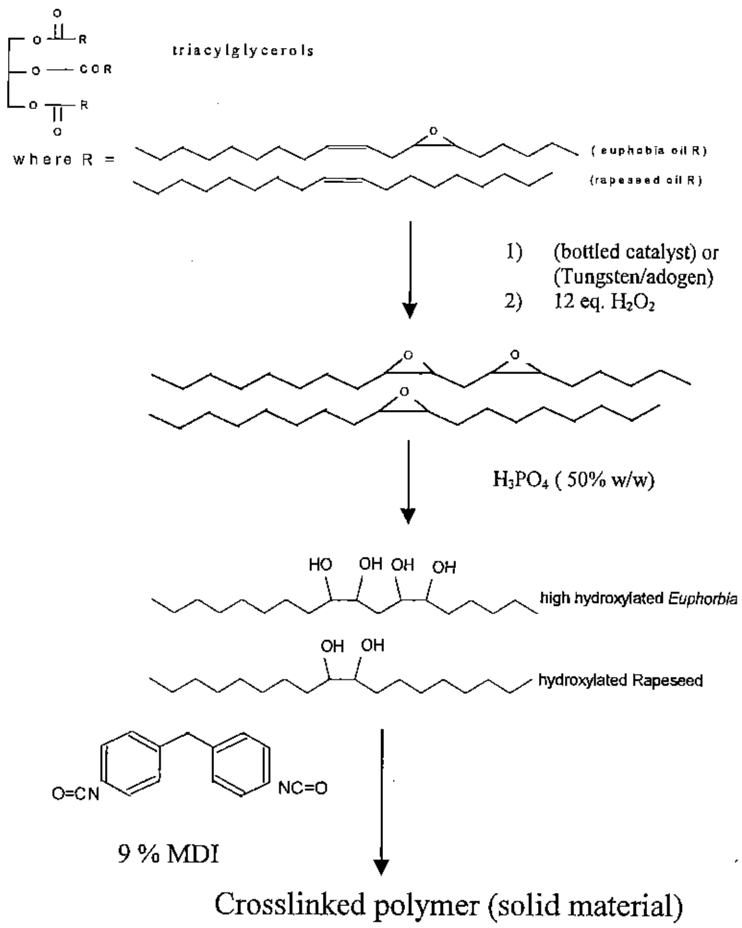
Manufacturer	Product Name
Procter & Gamble	Nodax™
Metabolix, Inc.	PHA, Biopol
Biomer	
Biomatera Inc.	
BASF	Ecoflex [32]
Tepha	TephaFLEX ® [33]

- **Renewable polyurethane (PU) polymers from rapeseed, palm and sunflower oils (RSPU, PPU and SFPU respectively)**

Renewable RS-PUs can be prepared by reacting the hydroxylated rapeseed monomer with of 4,4′-methylene-bis-(phenylisocyanate) (MDI) [34-36]. The preparation of the hydroxylated monomer was divided into two stages, beginning with the preparation of the catalyst (hydrogen peroxide / tungsten powder / phosphoric acid) to generate the epoxides from the unsaturated fatty compounds, while the second stage comprised the acid-catalysed ring-opening of the epoxides to form polyols.

The level of cross-linking influences the mechanical properties of the resulting polymer. The use of high-functional reactants, for example, polyol and diisocyanate, leads to a cross-linked network. Moreover, with an excess of diisocyanate (NCO/OH > 1), allophanate or biuret bonds form from excess diisocyanate-urethane that may cause chain branching and chemical crosslinking. Such a highly crosslinked polymer is useful for applications such as insulation materials e.g. for surface coatings in the corrosion protection of optical cables or as automotive internal components when a highly stiff structural composite can be obtained.

This procedure is based on that of Venturello et al. [34] and a schematic of the overall process is given in Scheme 1.



Scheme 1. Preparation of hydroxylated vegetable-oil based monomers: condensation method

PU's also one of the most important groups of polymers because of their versatility and they can be manufactured in a wide range of grades, densities and stiffness.

Applications of biopolymers and biocomposites

Enforcement both by government institutions and private sectors have banned the used of non-degradable materials and thus created the new policy of "going green", forcing suppliers to stock up a wide range of environmentally responsible consumer products from packaging materials and paper products to refrigerators, and from carpets to chairs.

Supermarket chains in Europe are now becoming more interested in certain foodstuffs biopackaging film based on PLA because of its transparency and barrier properties. Research on modifications of PLA to allow its use in a wider range of food packaging has been pursued through activities such as the European Union 5th Framework BIOPACK research project [27,37].

The relatively high cost of PLA arises from many factors, especially the need for very pure lactic acid as a starting material. Accordingly the price of PLA has tended to favour high-value applications such as in medical applications, and biocompatible PLA composites can now replace steel nails, plates and other objects as surgical implants. The bioresorbability of a PLA composite can be controlled by matching the reactions with the rate at which a fractured bone repairs. Furthermore, secondary operations to replace the implant are generally unnecessary when bioresorbable PLA-based materials are used [38]. Tepha Medical Devices Inc. has recently announced FDA clearance of its TephaFLEX product as an absorbable suture material [33].

Biocomposites made up from biopolymers are now commonly extended to composites in which inorganic fillers (e.g. nanoclays, silica) but biocomposites reinforced with natural fibres should be fully biodegradable. In addition to this characteristic, biocomposites containing natural fibres generally exhibit enhanced mechanical properties and cost advantages. This is because the partial replacement of the biopolymer matrix with less costly material, means that these are less expensive than the starting polymer in overall material costs.

In recent years, the use of polymers made from renewable materials has been developed in diverse areas especially automotive or building components. In 2003, Ford Motor Co. showcased a biomaterials theme on the Model U concept vehicle. The Model U demonstrated "green" materials and manufacturing with a variety of technologies: polymer foams derived from soybeans for the seat cushions, a soy-based resin tailgate, corn-based tyres, a corn-based compostable roof, and biolubricants [36,39].

Conclusion

Materials can be classified as natural or synthetic, recycled or virgin, renewable or non-renewable, degradable, non-degradable or biodegradable. There are no clear-cut answers on which is least environmentally damaging. However, new technologies and incorporation of appropriate advanced technology into product and processes should be safer, more effective, less costly and furthermore can make a significant contribution to improving their environment performance.

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