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Renewable polymeric materials from vegetable oils: a perspective

Gerard Lligadas, Juan C. Ronda, Marina Galià and Virginia Cádiz*

Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, C/ Marcel lí Domingo s/n, 43007 Tarragona, Spain

The utilization of vegetable oils is currently in the spotlight of the chemical industry, as they are one of the most important renewable platform chemicals due to their universal availability, inherent biodegradability, low price, and superb environmental credentials (i.e., low ecotoxicity and low toxicity toward humans). These natural properties are now being taken advantage of in research and development, with vegetable oil derived polymers/composites being used in numerous applications including paints and coatings, adhesives, and biomedicine.

Introduction

In recent years there has been an increasing demand for the application of natural products to address problems in the environment, in waste disposal, and in the depletion of non-renewable resources. Renewable resources can provide an interesting sustainable platform to substitute partially, and to some extent totally, petroleum-based polymers through the design of biobased polymers that can compete or even surpass the existing petroleum-based materials on a cost-performance basis with a positive environmental impact [1–3].

Clearly, the current move of the chemical industry to substitute a growing part of fossil feedstocks with renewable carbon is not driven only by a fear of dwindling fossil resources or global warming; there are other driving forces at play. In some cases the knowledge and technology to process one type of biomass is already present, demanding only small capital investments, such that the low-value nature of a certain biomass feedstock may be exploited. The products may also be substances with no petrochemical equivalent, such as lactic acid or furfural, which can already compete on completely commercial terms. A second factor is the general demand for renewable or green products from consumers, exemplified by the PlantBottle from the Coca-cola Company. Such initiatives provide a sustainable image to all agents involved in the value chain: something everybody can benefit from. Finally, on the political side, subsidies and funding are provided to reduce the dependence of fossil resources and to decrease the environmental impact.

The interest in converting biomass into chemicals has increased sharply over the last ten years within industrial companies. The price of fuels from biomass is still governed by the cost of processing, making it difficult for these to become competitive with fossil counterparts. Moreover, oil prices have not risen as quickly as predicted several years ago. Fuels are a very high-volume, narrow-margin business and volume targets are hard to meet without making enormous investments in new biorefineries. With this being the case, companies have changed direction, finding valuable markets outside of fuels and are opting for higher-margin products such as speciality chemicals [4].

The utilization of renewable raw materials meets the 7th principle of *12 Principles of Green Chemistry* that contributes to sustainability in chemistry [5]. The design framework of these principles has been a template for many advances in the field; however, they were not meant to be twelve independent goals but rather an integrated cohesive system of design. Only through the application of all the principles can one hope to achieve a truly sustainable process.

Although the recent development of renewable polymers has shown great progress, the small share (<5%) of renewable polymers in the commercial market is largely due to their high cost and inferior performance compared with synthetic polymers produced from petroleum chemicals. A synthetic challenge for the biorenewable industry is to make materials with properties that match those of chemicals currently in use. There is a need to think about the low cost, high volume, high-mass materials as commodity polymers and how to prepare these kinds of polymers from renewable resources.

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*Corresponding author: Cádiz, V. (virginia.cadiz@urv.cat)

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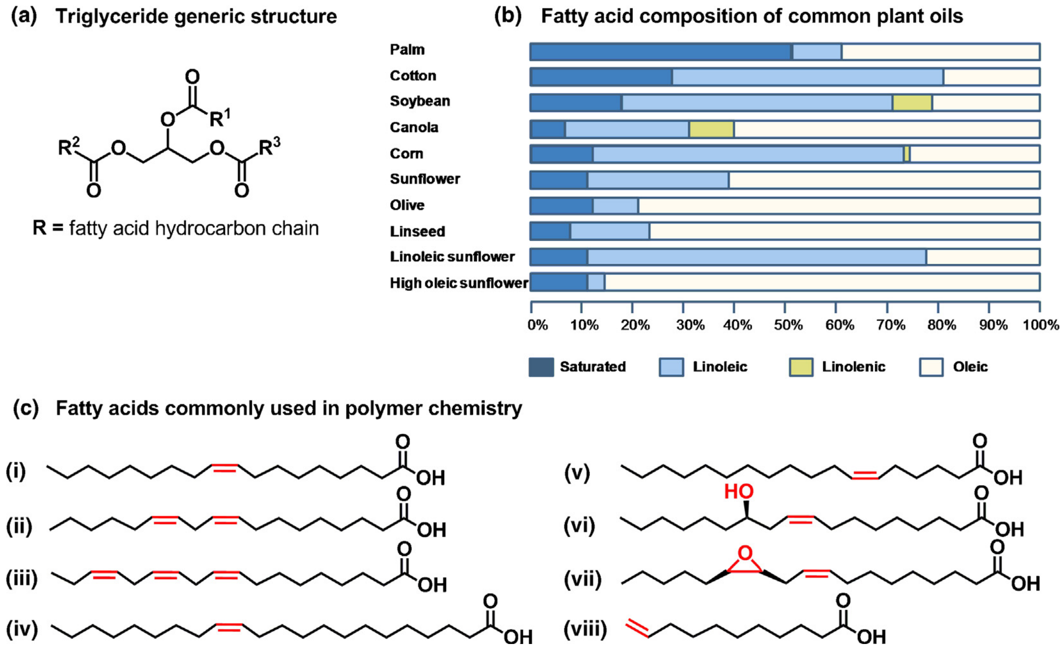

FIGURE 1

(a) General triglyceride structure. (b) Fatty acid percentage composition of common plant oils. (c) Fatty acids commonly used in polymer chemistry: (i) oleic acid, (ii) linoleic acid, (iii) linolenic acid, (iv) erucic acid, (v) petroselinic acid, (vi) ricinoleic acid, (vii) vernolic acid, (viii) 10-undecenoic acid.

Vegetable or plant oils represent a renewable resource that can be used as reliable starting material to access new products with a wide array of structural and functional variations. The abundant availability and the relatively low cost make plant oils an industrially attractive raw material for the plastics industry. Naturally occurring plant oils and fatty acids derived thereof, are considered to be the most important renewable feedstock processed in the chemical industry and in the preparation of biobased functional polymers and polymeric materials [6–9].

The annual global production of the major vegetable oils (from palm trees, soybeans, rapeseeds, cotton, sunflower, palm kernel, olives, and coconuts) amounted to 84.6 million tons (Mt) in 1999/2000 and increased to 137.3 Mt in 2009/2010 (an increase of 62%). The production of fatty acids is the highest volume oleochemical process and accounts for about 52% of industrially used oils and fats. The world supply of fatty acids has almost doubled from 2001 to 2008 [10].

The main constituents of plant oils are triglycerides which are the product of esterification of glycerol with three fatty acids. Fatty acids account for 95% of the total weight of triglycerides and their content is characteristic for each plant oil. The chemical structures of some frequently studied fatty acids are summarized in Fig. 1.

These triglycerides contain several reactive sites, such as double bonds and ester groups, opening up various possibilities to tailor new structures.

Most of the scientific literature available today has been centered on modifying vegetable oils to prepare well-defined linear structures, 3D networks and also matrices for biocomposites and hybrid materials. Fig. 2 summarizes suitable approaches to obtain thermoplastic and thermosetting materials from triglycerides and triglyceride-derived building blocks.

In this review our motivation is to provide a perspective on how vegetable oil-based materials are used in a great number of applications; not only restricted to the industrial arena (paints, coatings and adhesives) but also to biomedical field.

Structural applications: composites and hybrid materials

Vegetable oils have been extensively used for the production of polymer composites incorporating organic or inorganic particles or fibers, both synthetic and natural, and sized from the macro- to the micro- to the nano-scale [11–13]. In recent decades there has been a clear trend to increase the percentage of ''green''-based raw materials in the formulations of commodities as well as specialty polymers/composites for high value-added applications. In this way, a literature search for vegetable oil composite materials shows that the number of articles has grown exponentially since the end

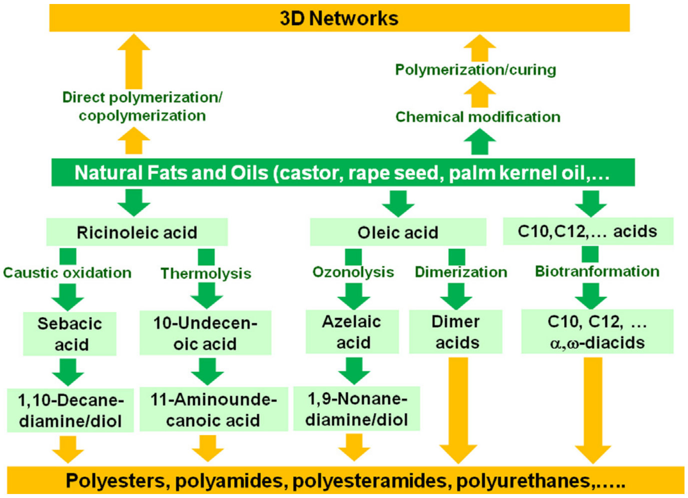

FIGURE 2

Main approaches to obtain thermoplastic and thermosetting materials from triglycerides and triglyceride-derived building blocks.

of the nineties to the present where hundreds of articles are published every year. This increasing interest is not only academic but also industrial due to the emergence in the support of producing renewable-based materials that offer sustainability, reduced energy consumption, low cost and comparable performance to composites from non-biorenewable resources [14]. Commonly, thermosets and thermoplastics derived from plant oils exhibit long-chain polymer characteristics i.e. high elongation at break and relatively low stiffness [11]. For this reason, with the exception of highly functionalized triglyceride derivatives, it is not common to have pure bioresins as part of a composite, but to blend a synthetic and a renewable resin together.

Mixtures of vegetable oils (soybean oil, corn oil, linseed oil, isomerized/conjugated oils, etc.) with styrene and divinilbenzene have been radically or cationically polymerized in the presence of various fillers and fibers such as organic clays, glass, hemp, flax, jute or kenaf fibers, wood flour, sugarcane bagasse, spent germ, corn stover, wheat straw and regenerated cellulose [11,15]. Greener polymerization methodologies such as olefin metathesis polymerization have also been applied to biocomposite production [16]. The resulting biocomposites show significant improvements in the mechanical properties and thermal stabilities.

One of the key features in composite preparation consists of getting enough compatibility between the hydrophilic surface of the filler/fiber and the hydrophobic nature of plant-based resin. In this way the surface treatment and functionalization of the reinforcing materials [17] and the use of more reactive and polar functionalized triglyceride derivatives are two of the common approaches used in addressing these shortcomings.

Amine cured combinations of epoxidized soybean oil and conventional epoxy resins, acrylated soybean oil alone or copolymerized with styrene and divinylbenzene, and more significantly polyurethane resins, prepared from polyols derived mainly from castor oil, have been extensively used to prepare composite materials with excellent mechanical properties and other useful target properties such as high impact resistance, good barrier properties or low dielectric constant with low expansion coefficients [18,19]. In the case of the polyurethane based composites the reaction between the isocyanates and the hydroxyl groups in the glass-OH or fiber-OH groups is believed to be the responsible for the high modulus and tensile strengths of the resulting composites [20,21].

Moreover, the increasing interest in nanostructured materials resulted in a number of plant oil-derived nanocomposites mostly based in the incorporation of nanoclays [12,22] but also using other nanoparticles and nanofibers. In general, when adequate dispersion of the nanofiller is achieved, mechanical properties like Young's modulus, tensile strength and elongation at break are largely improved at comparatively low nanofiller loadings. Moreover, thermal behavior as well as vapor barrier properties was improved in a similar way as observed for conventional petroleum based nanocomposites. The production of nanocomposites from plant-derived organic/siloxane hybrid materials has also been considered by several authors as a way to control the molecular structure of the material. The hydrosilylation of 10-undecenoic acid derivatives [23], the thiol-ene addition of thiol functionalized polyhedral oligomeric silsesquioxane (POSS) to acrylated castor oil [24] or the incorporation of epoxy functionalized POSS units to an epoxidized linseed oil [25] are examples of this strategy.

Thermoplastic composites and nanocomposites with glass or carbon fibers and with a variety of nanofillers (gold, nanotubes, ceramics, silica, etc.) have also been described as useful materials for injection molding and laminate technologies [12,19,22]. In this case the thermoplastic polymers, typically, polyesters, polyamides, polyesteramides and polyurethanes are prepared from linear difunctional monomers produced by chemical transformation of vegetable oils [26,27]. The most significant example is Nylon 11, a polyamide prepared from the 10-undecenoic acid obtained by pyrolysis of castor oil which is used in the production of automotive and engineering components [28]. It is worth noting that this polyimide has also been used to prepare fibers for textile applications.

Referring to the applications of these plant oil based composites most of them are tailored for structural applications in which low cost and sustainability issues are determinant over the material performance. A successful example is the development, by Ashland researchers, of a polyester resin based, in part, on soybean oil and corn ethanol. This resin was first used to manufacture sheet molding compound composite panels that were used in John Deere tractors and harvesters.

Functional materials for special applications have also received much attention and thus several plant oil based-composite coatings, adhesives, foams and shape memory materials have been developed [12].

Finally, it must be pointed out that even some of the reported literature focuses in the potential biodegradability of these composites, despite their plant origin they are not biodegradable and show many of the environmental concerns of plastics derived from petroleum.

Paints, coatings and adhesives

Vegetable oils have been used as binders or additives in paints and coatings for many centuries, dating back to the days of cave paintings. The primary use of vegetable oil in coatings is as drying oil. Drying oils are highly unsaturated oils that will oligomerize or polymerize when exposed to the oxygen in air, usually in the presence of a catalyst. The result is an increase in the molecular weight as a consequence of crosslinking. This led to the development of renewable resources based coating formulations with improved performance [29].

Vegetable oil derivatives as value added polymers/monomers have found enhanced applications as environment friendly hyperbranched or waterborne coating materials that offer improved performance and reduction or elimination in the use of volatile organic solvents. Oil coatings are used to finish wood carving, to stain and finish wood decks, to coat cedar shingles, and in other applications for which penetration is desired and a slow cure rate is not a significant problem.

Water-soluble resins, emulsions, dispersions, latex, and water-reducible resins are all considered waterborne coatings. The development of waterborne materials from vegetable oils is the most challenging task due to the hydrophobic nature of oil chains. The development of an oil-modified latex technology tries to reduce the need for a coalescent aid by incorporation of the oil into the latex resin. After application, the oil portion of the resin, which lowers the glass transition temperature to allow coalescence into a film, crosslinks to produce a hard, durable finish [30]. Acrylated oils are an excellent comonomer to use in the synthesis of the latex. In this way, soybean oil-based waterborne urethane-acrylic hybrid latexes were synthesized by emulsion polymerization [31]. Grafting polymerization of the acrylate monomers onto the soybean-oil-based polyurethane (PU) network occurs, leading to a significant increase in the thermal and mechanical properties of the resulting hybrid latexes. Other examples of soybean-oil-based waterborne PUs with high performance, have been described from soybean-oil-based polyols prepared by the ring-opening of epoxidized soybean oil (ESO) with methanol [32]. Also, a waterborne PU wood coating based on rapeseed fatty acid methyl esters [33] and a castor-oil-based waterborne PU dispersions cured with an aziridine-based crosslinker, have recently been reported [34]. Also, the preparation of a coating from a waterborne epoxidized linseed oil was recently reported [35] as shown in Fig. 3. Linseed oil is epoxidized and reacted with diethanolamine to produce a waterborne oil with hydroxyl groups which were further reacted with phthalic anhydride leading to a resin with free carboxylic acids. The final coating is prepared by curing a mixture of this resin with a phenol-formaldehyde resin.

One of the fastest-growing areas of coatings is that of radiation cures. This area is divided into three types: radical UV cure systems, ionic cure systems and e-beam. Of the three, the radical cure systems are the most popular owing in part to their cost, cure speed, high efficiency, and contribution toward a safe and healthy working environment, combined with an acceptable performance of their coatings [36]. Acrylic oligomers and monomers are important components of free-radical type UV-cure coating systems that primarily dictate performance properties and their end-use applications. Bio-based UV-cure oligomers have successfully been synthesized from epoxidized soybean oil derivatives using 2-hydroxylethyl acrylate, in the presence of a strong acid catalyst. The process yields low viscosity products with a very high degree of acrylation, under mild reaction conditions [37]. UV systems are employed for decorating and protecting diverse substrates, for example, computer chips, paper, optical fibers, composites, and automobile parts. However, UV-curable coatings have limitations such as high material and equipment cost, curing limits with pigmented systems, poor three-dimensional curing, and sensitivity to oxygen and moisture.

UV-curable chemistries based upon thiol-ene functionality offer many advantages such as lack of oxygen inhibition, extremely uniform networks, delayed gel points and improved polymerization control, reduced polymerization shrinkage, and reduced stress [38]. Vegetable oil acrylates from castor oil were blended with a trifunctional thiol and crosslinked via UV irradiation [39]. Thiol-ene curable coatings incorporating vegetable oil macromonomers as prepolymers are useful for applications that require good flexibility throughout the lifetime of the coating, such as coil coatings, optical fiber coatings, and paper coatings.

The use of natural plant oils in the production of adhesives has been the focus of much research. Adhesives have been synthesized from soybean-oil-based polymers from different chemical pathways, exhibited thermophysical and mechanical properties that are competitive with those of petrochemical based adhesives [40–42]. Among the different classes of adhesives, pressure-sensitive adhesives are one of the most widespread types and represent a potential application that would benefit from the use of renewable materials. Self-adhesive tapes, labels, stamps and sticky notes are ubiquitous in everyday life and can be found everywhere (electronic industry, automotive parts, etc.). They adhere by simply applying pressure to a huge variety of materials and often the bond is reversible. The main advantage of pressure sensitive adhesives compared with other type of adhesives is the convenience of use. There are no storage issues, no mixing or activation necessary and no waiting is involved. Pressure-sensitive adhesives are

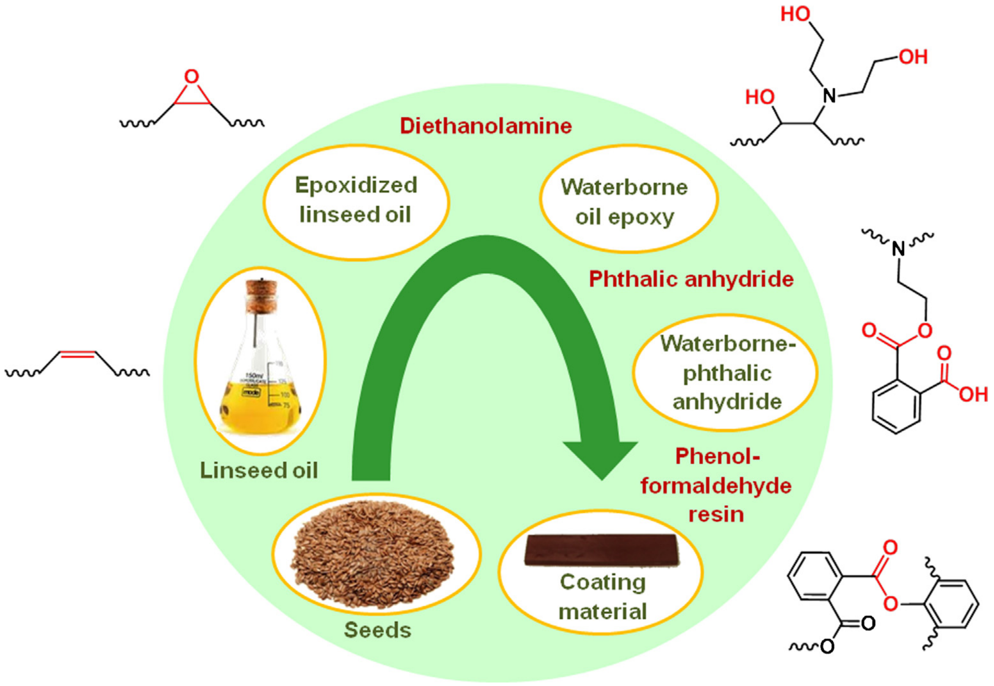

FIGURE 3

Preparation of waterbone coating material from linseed oil.

viscoelastic materials combining a liquid-like dissipative character necessary to form molecular contact under a light pressure and solid-like character to resist macroscopic stress during debonding phase, properties that can be achieved with slightly crosslinked low Tg polymer networks. Tuning network adhesive performance can also be done via the incorporation of functional groups. Fatty acid derivatives are an attractive resource for the development of biobased adhesives because of their intrinsically low glass transition temperature. Acrylated methyl oleate has been used in aqueous emulsion polymerization and the resulting polymer has shown physical properties comparable to petroleum based polymers and display typical pressure-sensitive properties. While both kinds of polymers have comparable tack, shear strength and elasticity, the peel of the oleate based polymers was lower [43]. Self-adhesive coatings with tunable viscoelastic properties containing carboxylic acid groups as adhesion promoters have been described. These adhesive gels were formulated from hydroxy-functional polyesters, synthesized via bulk polycondensation of dimer fatty acids and dimer fatty diols, in combination with maleinized triglycerides [44].

Thermal stability and optical transparency are important factors for flexible electronics and heat-related applications of pressure sensitive adhesives. Soybean oil-based pressure-sensitive adhesives are particularly good candidates for application in advanced flexible electronic devices such as displays, semiconductors and solar cells because of their thermal properties and for transparent tapes for labeling and packaging for the high transparency. Pressure-sensitive adhesives from epoxidized soybean oil/dihydroxyl soybean oil systems, by balancing the resin ratio of tacky groups and the degree of crosslinking, have been developed [45]. The peel strength of these tapes on glass substrate with 30 s drying was comparable to commercial pressure sensitive tapes as Scotch Magic Tape and much stronger than Postit Notes (Fig. 4). Reusability on glass substrate has comparable peel strength to Postit Notes during 10 repetitions.

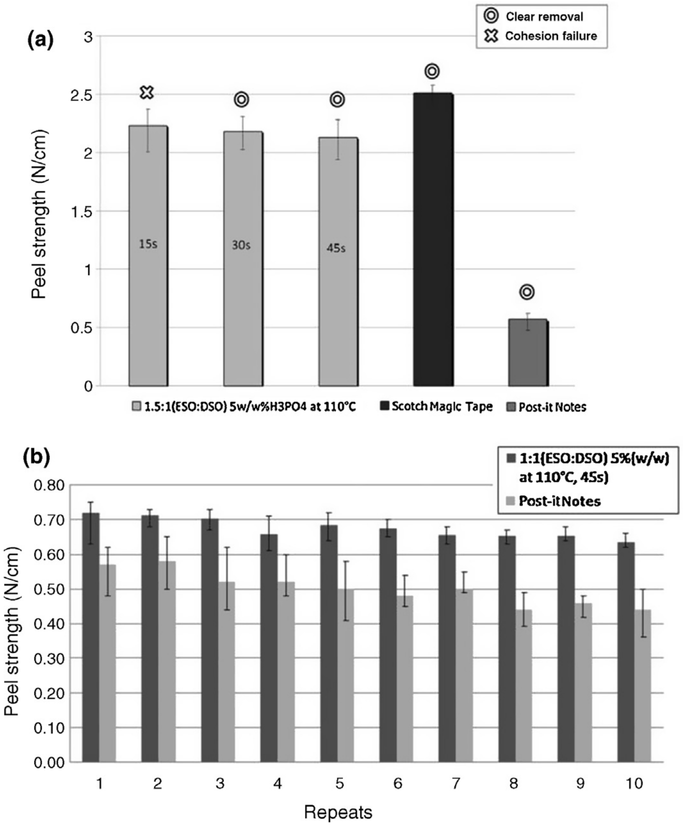

FIGURE 4

(a) Epoxidized soybean oil pressure sensitive adhesives on aluminum foil carrier in terms of drying time vs Scotch magic tape and Postit Notes. (b) Peel strength of epoxidized soybean oil pressure sensitive adhesive vs Postit Notes regarding reusability.

Biomedical applications

Applications of vegetable oil-based polymeric materials are not restricted to the industrial arena and can also be extended to a variety of biomedical applications as surgical sealants and glues, pharmacological patches, wound healing devices, and drug carriers to scaffolds for tissue engineering. This is mainly because vegetable oil is a biobased raw material that can be metabolized in the human body, and therefore materials derived from them are potentially biocompatible. Moreover the incorporation of vegetable oil moiety can enhance the biodegradation of the material. In fact, they have been attractive for several biomedical applications requiring materials that range from soft to hard. For example, poly(glycerol sebacate) has been used in several soft tissue engineering applications such as retinal [46], nerve [47], vascular [48] and myocardial repair [49], as well as adhesive sealant [50]. Importantly, the two monomers, glycerol and sebacic acid are both endogenous compounds found in human metabolism. In this line, poly(propylene sebacate)-based polyesters were found to be promising shape memory polymers with tunable switching temperature. In vitro fibroblast response and degradation demonstrated that these polymers are potentially biocompatible and biodegradable, rendering them as good candidates for biomedical devices such as different stents [51]. On the other hand, poly(ester-anhydride)s, derived from sebacic acid and ricinoleic acid have also been used as drug carriers, particularly as liquid polymers that can be injected into a patient. Thus, formulations loaded with cis-platinum and paclitaxel, showed promising results for localized antitumor agent delivery [52–55]. The same polymers were used for controlled release of protein and peptide drugs [56], delivery of local anesthetics [57] and delivery of gentamicin sulphate for the treatment of osteomeylitis [58]. Fig. 5a shows the rate of gentamicin release from some of these pasty poly(ester-anhydride)s into buffer phosphate. It can be seen that formulations with 20% gentamicin have slower release profiles than that of formulations with 10% gentamicin, probably due to salt formation between gentamicin and the fatty degradation products of the polymer. As described in Fig. 5b, poly(ester-anhydride) ($M_n = 4500$) loaded with 20% gentamicin was chosen for osteomyelitis treatment in a rat model showing promising results.

Alternatively, harder materials such as polymeric soybean oil-*g*-polystyrene membranes [59] and polyurethane networks based on soybean [60] and sunflower oils [61] were investigated as scaffolds for tissue engineering showing promising cell adherence and proliferation. Moreover, cell adhesion properties of fatty acid-derived linear and crosslinked polyurethanes have also been improved by blending or surface modification with different bioactive molecules including gelatine [62], chondroitin sulphate [63] and collagen [64]. Unfortunately, for most of the above

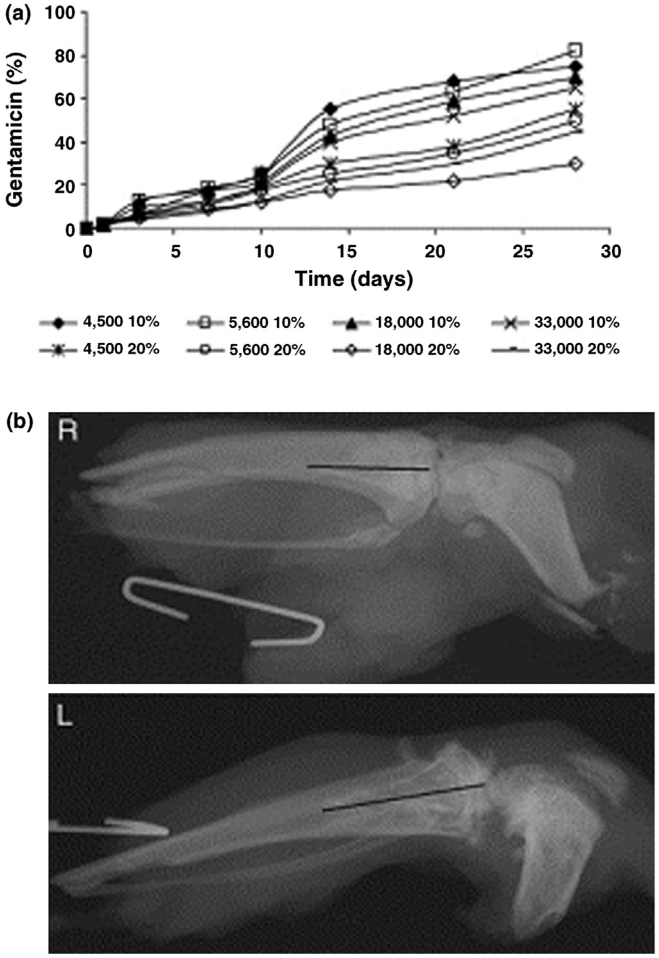

FIGURE 5

(a) Release of gentamicin sulfate from poly(eter-anhydrides) (sebacic acid:ricinoleic acid 3:7, w/w) with different number molecular weight (M_n) and amount of drug. The gentamicin sulfate release was performed in 0.1 M buffer phosphate pH 7.4 at 37 °C with constant shaking at 100 RPM. (b) Treatment of osteomyelitis in a rat model by P(SA-RA). Osteomyelitis was induced by injection of *S. aureus*. The rats were treated 2 weeks later by soft polymer P(SA-RA) with gentamycin. The rats were analyzed by radiology after an additional 3 weeks. A representative radiograph shows lysis of the medullary area with blearing of the cortex in the left tibia, suggesting osteomyelitis (L) and no radiogloic signs in the right one (R). The line indicates the affected area.

elastomer materials, the degradability was bad because of the presence of non-degradable urethane crosslinked bonds. Interestingly, the preparation of a series of biodegradable and biocompatible elastomers based on phosphoester crosslinked vegetable oils was reported [65]. Implantation test for the elastomer polymers in animal skin showed that this kind of elastomers can be absorbed completely within three months, accompanying the restoration of the implantation sites to their normal architecture. Taking advantage of the same chemistry (epoxy/P-OH), the same authors developed a covalently dexamethasone-conjugated drug release system based on crosslinked vegetable oil without any toxic catalyst and initiator. The good cytocompatibility and osteogenic differentiation effect for human bone mesenchymal stem cells in vitro endows this crosslinked vegetable oil system with great potential applications in bone tissue engineering besides acting as an excellent carrier for dexamethasone linear release [66].

Conclusion and prospects

The production of commodity plastics meets the demands of green chemistry for lean and clean production by using solvent-free processes with efficient use of resources, no byproduct formation, waste management, and even exploitation of renewable resources.

At the beginning of the 21st Century and unlike any other class of materials, sustainable plastics with an attractive balance of low cost and high performance are essential for meeting the demands of the growing global population with respect to health, shelter, clothing, communication, mobility, food and energy. Plastics play a key role in sustainable development. Development of new industrial products or commercial processes is the objective of continued research in both public and private interests.

In principle, the production of renewable oils and monomers has been demonstrated to be technologically feasible and capable of substituting petrochemical feedstocks. Almost from the beginning of the revival that started at the end of the last century, renewable oils were also proposed as composite matrices, and this trend is continuously growing with promising results. Some of the vegetable oil based biopolymers and precursors are currently commercially viable and there are companies that offer derived bio-based polymers (epoxy, alkydic and polyurethanes precursors being the most frequently found) for specific applications. In some cases, natural oil thermosetting materials provide new opportunities in some specific realms, like biomedical applications, which have not been considered for petroleum based materials.

In the near and far future, renewable feedstocks will also represent the only alternative to finite, irreplaceable fossil feedstock reserves. It is interesting to remark that although the initial use of plant oil based polymers was presented as a partial replacement of synthetic polymers to introduce ‘‘green’’ materials in the formulation, and little more than that, the current trend is to increase the percentage of biobased materials maintaining good overall performance and/or developing tailored special properties.

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