FOCUS REVIEW

Functional polymers from renewable plant oils

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Abstract

This focus review addresses recent progress on plant oil-based functional polymers and composites. Plant oils are one of the most ideal chemical feedstocks to replace fossil resources for a variety of industrial chemicals in the polymer industry. In this focus review, an environmentally benign coating system is demonstrated using plant oils as the starting substrate for the preparation of artificial urushi with high hardness and a high gloss surface. Epoxidized plant oils, mainly epoxidized soybean oil, are polymerized with designed inorganics, cellulose, and biodegradable aliphatic polyesters to afford functional biobased polymers and composites. Castor oil is used as the core of branched poly(lactic acid) to improve the physical properties of biobased plastics. These plant oil-based materials are significant for the molecular design of functional and high-performance biobased products for industrial applications to contribute to the reduction of greenhouse emissions.

Introduction

Today, fossil feedstock oils and gases are the most important raw materials for the chemical industry. Some parts of such raw materials are converted to polymers, mainly plastics and fibers, which are widely utilized in a variety of industries, including automobiles and medicines. The advantages of plastics are their high strength, light weight, durability and low cost. More than 200 million tons of plastics are produced every year worldwide. However, contemporary geopolitical and economic developments have led to disadvantages because of dependence on crude oils and their limited availability. The ultimate formation of greenhouse gas CO_2 from fossil feedstocks has had unpredictable and irreversible consequences on the global climate. Recently, there have been serious concerns regarding the nonbiodegradability of plastic waste for environmental problems.

Based on these backgrounds, the worldwide potential demand for replacing petroleum-derived raw materials with renewable plant-based materials in the production of polymeric materials is quite significant from the social and environmental viewpoints [1–5]. The use of bioresources as starting substrates for polymeric materials would help halt greenhouse warming and contribute to global sustainability without the depletion of scarce fossil resources.

The most extensively used renewable bioresources are natural oils, polysaccharides such as cellulose and starch, proteins and lignin. Among them, natural oils are expected to be an ideal alternative chemical feedstock, since oils derived from both plant and animal sources are found in abundance in the world. Triglyceride oils have been extensively used for coatings, inks, agrochemicals, etc. [6–11]. For such applications, innovative technologies to transform triglyceride oils into novel monomers and polymers have been developed. This focus review addresses recent progress on functional polymers from renewable plant oils.

Artificial urushi

For the last few decades, enzyme-catalyzed polymerization ("enzymatic polymerization") has been of increasing importance as a new trend in macromolecular science [12–19]. Enzyme catalysis has provided a new synthetic strategy for useful polymers, most of which are difficult to produce by the use of conventional chemical catalysts. In vitro enzymatic syntheses of polymers via nonbiosynthetic (nonmetabolic) pathways, therefore, are recognized as a new area of precision polymer syntheses. To date, several oxidoreductases, peroxidase, laccase, bilirubin oxidase, etc., have been reported to catalyze the oxidative polymerization

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of phenol derivatives. Among them, peroxidase is the most often used.

As "Japan" implies the meaning of "a lacquer or varnish giving a hard, glossy finish" and/or "objects decorated and lacquered in the Japanese style", urushi wares are regarded as one of the most typical symbols of Japanese art. Oriental lacquer (urushi) from Japan and China is a natural resinous sap of the *Rhus vernicifera* tree. Urushi coating is hard enough to give a brilliant polish and is highly durable (for more than a thousand years under appropriate conditions) and solvent resistant in comparison with synthetic coatings.

The most important components of urushi are known to be "urushiols", whose structure is a catechol derivative with unsaturated hydrocarbon chains consisting of a mixture of monoenes, dienes, and trienes at the 3 or 4-position of catechol. The crosslinking of urushiol is supposed to be accomplished mainly by the laccase-catalyzed oxidative coupling of the phenol moiety of the urushiol and the subsequent autoxidation of unsaturated alkyl chains in air. First, laccase catalyzes the oxidation of the catechol unit of the urushiol to give the semiquinone radical, which then reacts by a number of competing pathways, yielding a mixture of dimers and oligomers with complicated structures.

Urushi can be regarded as the only example of practical natural paints utilizing in vitro enzymatic catalysis for hardening. Film formation by urushiols proceeds under air at room temperature without organic solvents; hence, urushi seems very desirable as a coating material from an environmental standpoint. In addition to urushiol, similar natural phenolic lipids (plant oils in a broad sense), laccol from Taiwan and Vietnam and thitsiol from Thailand and Myanmar, are produced in Southeast Asian countries. They are inexpensive and often used for primer coating. The laccase-catalyzed crosslinking of urushiol, laccol, and thitsiol was examined in the presence of a protein hydrolysate [20]. Laccase efficiently catalyzed the crosslinking of urushiol and laccol to produce a film with a high-gloss surface and high hardness. However, modeling studies of urushi have been limited, mainly due to the difficulty of the chemical preparation of the urushiol.

A new concept of artificial urushi has been proposed, in which new crosslinked polymeric films were enzymatically synthesized from newly urushiol analogs, phenols bearing an unsaturated group in the side chain [21–24]. This new concept has expanded the scope of enzyme catalysis to the environmentally benign production of functional coating materials. The reason the synthesis of natural urushiols involves multistep, tedious procedures is that the reactive unsaturated group cannot be directly introduced onto the catechol moiety; protection and deprotection of the catechol moiety is required. To date, several attempts to synthesize urushiol model compounds have been made, mainly due to
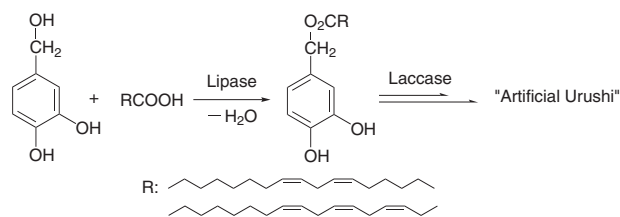
Fig. 1 Enzymatic syntheses of urushiol analogs and artificial urushi via the analogs

the difficulty of the chemical synthesis of urushiol. New urushiol analogs obtained by convenient synthetic processes were proposed for the preparation of "artificial urushi" by using unsaturated higher fatty acids from plant oils (Fig. 1). The urushiol analogs were synthesized using lipase as a catalyst in a single step. They were cured using *Pycnoporus coccineus* laccase as a catalyst in the presence of acetone powder (AP, an acetone-insoluble part of the urushi sap containing mainly polysaccharides and glycoproteins) under mild reaction conditions without the use of organic solvents, yielding a brilliant film ("artificial urushi") with a high-gloss surface. Starch-urea phosphate (SP), a synthetic material, was also usable as a substitute for AP for in vitro enzymatic curing of the urushiol analogs, although the film hardness was lower than that obtained in the presence of AP. The use of SP as the third component provided artificial urushi from exclusively synthetic compounds. The viscoelastic properties of the artificial urushi were similar to those of natural urushi.

Another type of "artificial urushi" was prepared by oxidative polymerization of the urushiol analog with an unsaturated group from plant oils using iron-*N,N'*-ethylenebis (salicylideneamine) (Fe-salen) as a catalyst, followed by curing of the resulting crosslinkable polyphenol [25, 26]. Fe-salen showed high catalytic activity for the oxidative polymerization of phenols. The polymerization of the urushiol analog catalyzed by the Fe-salen catalyst was performed using hydrogen peroxide as an oxidizing agent in tetrahydrofuran at room temperature under air, yielding an oily soluble polymeric precipitate. ^{1}H NMR analysis of the product showed that the unsaturated moiety was not reacted during the polymerization. Curing of the product polymer by thermal treatment afforded a film with high hardness.

Cardanol, a major component obtained by the thermal treatment of cashew nut shell liquid (CNSL), is a phenolic lipid with a meta substituent consisting of a C15 unsaturated hydrocarbon chain, usually containing 1–3 double bonds. Since CNSL is nearly one-third of the total nut weight, a large amount of CNSL is formed as a byproduct of mechanical processes for the edible use of the cashew kernel. Only a small part of the cardanol obtained in the production of cashew kernel is used in industrial fields, although it has various potential industrial uses, such as

resins, friction lining materials, and surface coatings. Therefore, new applications of cardanol are very attractive.

Cardanol was oxidatively polymerized by Fe-salen catalyst to give a new class of crosslinkable phenolic polymers with an unsaturated alkyl group in the side chain (Fig. 2) [27, 28]. The resulting polymer was cured by cobalt naphthenate catalyst or thermal treatment to give a crosslinked film with high hardness and a high-gloss surface. In curing by thermal treatment, the crosslinking behaviors and properties of the resulting film were similar to those of a commercially available CNSL-formaldehyde resin. This prepolymer is synthesized from renewable plant-based material without the use of toxic formaldehyde. In the curing stage, the crosslinked polymeric film is obtained in the absence of organic solvents at ambient temperature under air. Therefore, this method is expected to be an environmentally benign process of polymer coating, giving an example of green polymer chemistry. This prepolymer can be regarded as artificial urushi in a broad sense.

A crosslinkable polymer was also obtained from cardanol by enzymatic oxidative polymerization using peroxidase as a catalyst [29]. When horseradish peroxidase was used as a catalyst for cardanol polymerization, the reaction took place in the presence of a redox mediator (a phenothiazine derivative) to give the polymer. The resulting polymer was rapidly cured at room temperature to give a hardened dry coating with a dark brown color. Anacardic acid, separated from CNSL, was also oxidatively polymerized by peroxidase in the presence of phenothiazine-10-propionic acid to give a polymer with a molecular weight of several thousand kDa. The coating of the resulting polymer provided effective antibiofouling against both gram-positive and gram-negative bacteria.

A crosslinkable epoxide-containing polyester was synthesized from unsaturated fatty acids of plant oils using lipase as a catalyst via two routes [30]. *Candida antarctica* lipase efficiently catalyzed the epoxidation of unsaturated fatty acids and of polyesters containing an unsaturated group, as well as the polymerization of divinyl sebacate,
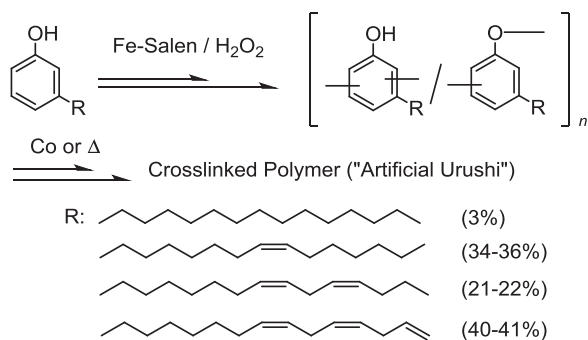
Fig. 2 Synthesis of polycardanol by oxidative polymerization and its curing to artificial urushi

glycerol, and fatty acid derivatives. The resulting polyesters were thermally cured to give transparent films with a high-gloss surface, which showed good biodegradability. Crosslinkable phenolic polymers and polyesters were also prepared by a similar synthetic route, and their curing behaviors were examined [31–33].

## Network polymers from epoxidized plant oils

Triglyceride oil-based polymeric materials often do not the show properties of rigidity and strength required for structural applications by themselves. In some cases, triglyceride is a minor component in polymeric materials, used solely as a modifier to improve their physical properties. Thus, more reactive triglycerides, such as epoxidized triglycerides, are useful as starting substrates for the preparation of plant oil-based polymers.

Biobased epoxy materials were synthesized from functionalized plant oils, such as epoxidized soybean oil (ESO) and epoxidized linseed oil (ELO), using methyltetrahydrophthalic anhydride (MHPA), an anhydride curing agent, in the presence of tetraethylammonium bromide as catalyst (Fig. 3) [34]. The curing reaction proceeded at 130 °C to produce transparent soft plant oil-based epoxy materials. The thermal and mechanical properties of the ESO/MHPA polymer depended on the feed molar ratio of oxirane/anhydride. The storage modulus in the rubbery region and the tensile strength of the ELO/MHPA polymer were greater than those of the ESO/MHPA polymer due to the high crosslinking density, and the glass transition temperatures of the ESO/MHPA and ELO/MHPA polymer were found to be 35 and 110 °C, respectively. The ELO/MHPA polymer showed excellent shape memory recovery behaviors, whereas the ESO/MHPA polymer could not be fixed in a temporary shape.

There has been enormous interest in organic–inorganic nanocomposites due to their unexpected hybrid properties derived from unique combinations of each component. Among them, nanocomposites of organic polymers and inorganic clay minerals with layered structures have been extensively studied because they often exhibit improved tensile strength and moduli, reduced gas permeability, decreased thermal expansion coefficients, and enhanced thermal stability when compared with pure polymers or conventional micro- and macrocomposites. Montmorillonite is of particular interest, since it has a high aspect ratio of silicate nanolayers and a high surface area, which are suitable for reinforcement purposes.

Green nanocomposites were prepared by the acid-catalyzed curing of epoxidized plant oils in the presence of organophilic clay (Fig. 4) [35–37]. A nanocomposite

Fig. 3 Synthesis of a transparent network polymer from ESO and MHPA
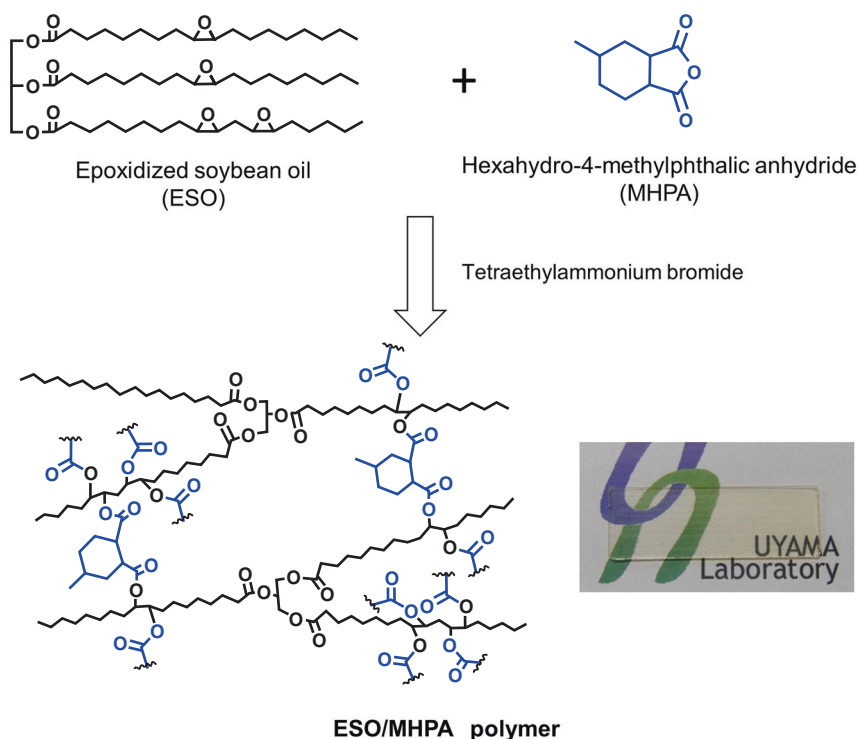
with a homogeneous structure of its organic and inorganic components was obtained, in which silicate layers of the clay were intercalated and randomly distributed in the polymer matrix. The reinforcement effect resulting from the addition of clay was confirmed by dynamic viscoelasticity analysis. The barrier property of the nanocomposite toward water vapor was superior to that of the corresponding oil polymer.

Various high-performance organic polymer-silica nanocomposites have been prepared via a sol–gel route. Functional silane coupling reagents, such as 3-glycidoxypropyltrimethoxysilane (GPTMS) and 3-aminopropyltrimethoxysilane, are often used as modifiers of organic polymer precursors. In an acid-catalyzed reaction of GPTMS, a polymerization of the oxirane moiety in GPTMS, which builds up an organic polymer network, is simultaneously achieved with the formation of inorganic, yielding transparent hybrid materials in which organic and inorganic units are linked together via covalent bonds.

Green nanocomposite coatings were prepared by the acid-catalyzed curing of epoxidized plant oils with GPTMS (Fig. 5) [38]. The nanocomposite showed excellent film properties; the hardness and mechanical strength were improved by incorporating the silica network into the organic polymer matrix, and good flexibility was observed. The dynamic viscoelasticity analysis clearly showed the reinforcement effect of the inorganic network. Furthermore, the nanocomposite exhibited good biodegradability, contributing to global sustainability. An oxetane-containing
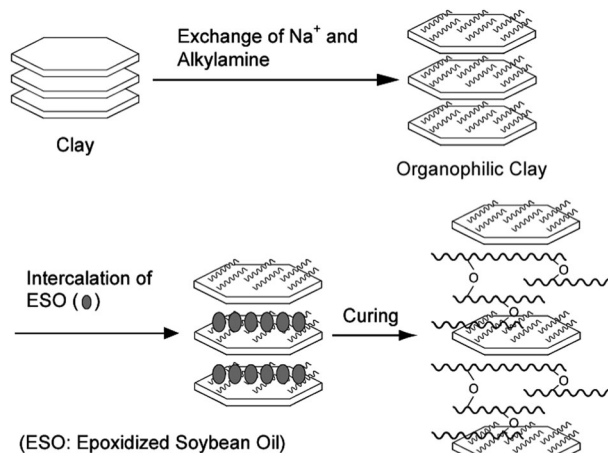


Fig. 4 Synthesis of a polyESO/clay nanocomposite

silane coupling agent and reactive polyhedral oligomeric silsesquioxane were used to produce polyESO-silica nanocomposites, in which the physical properties of polyESO were greatly improved [39, 40].

A biocomposite of an oil-based network polymer and cellulose nanofiber was prepared by the acid-catalyzed curing of ESO in the presence of a microfibrillated cellulose (MFC) sheet or fine cellulose fibers [41, 42]. A great improvement in the mechanical and thermal properties of the ESO polymer was achieved by using MFC as the filler. The Young's modulus and maximum tensile strength reached 2500 MPa and 59 MPa, respectively, which were

Fig. 5 Synthesis of a plant oil-based network polymer/silica nanocomposite from ESO and GMTMS
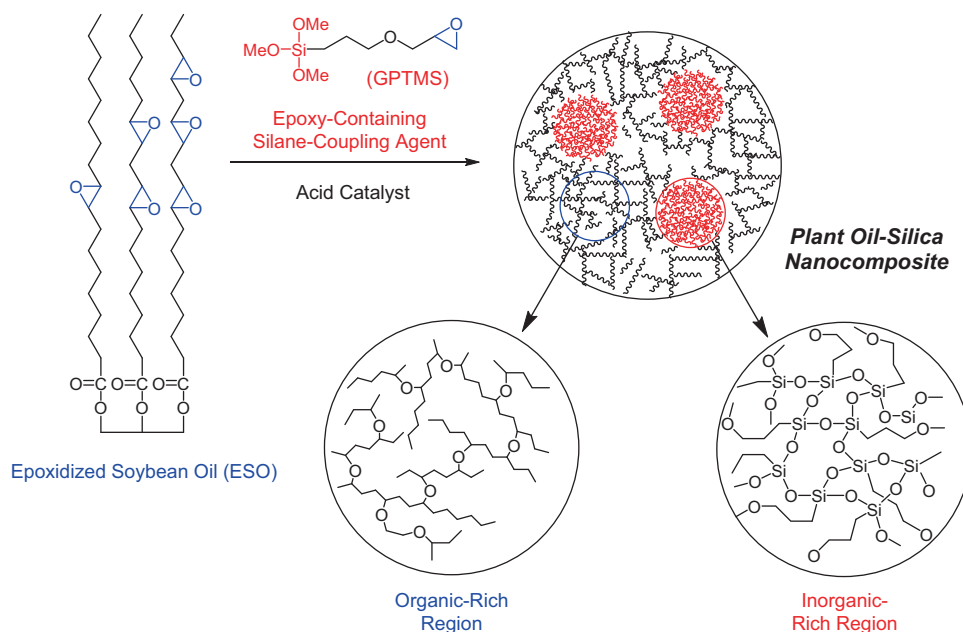
**Fig. 6** Synthesis of polyESO/PLLA and its shape memory function
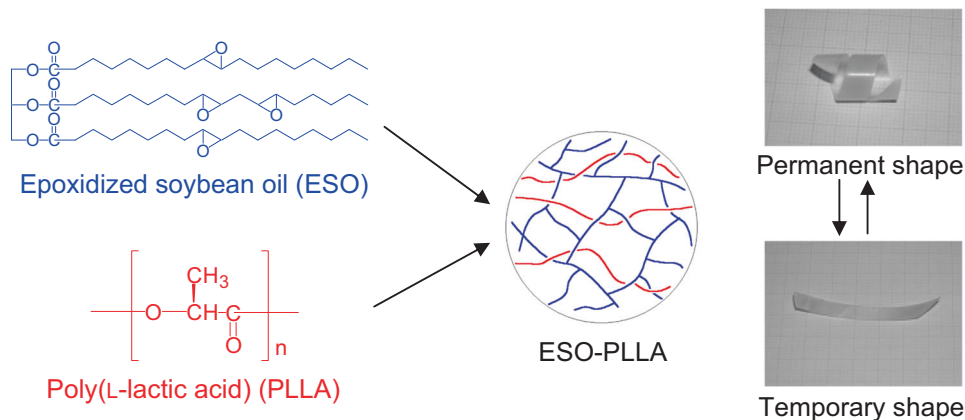
comparable to those of conventional plastics. When the MFC mat was used, the ESO polymer was effectively reinforced by the cellulose fibers; a relatively high content of cellulose in the oil polymer-based composite was achieved.

A regenerated cellulose gel from a Ca(SCN)$_2$ aqueous solution was impregnated with ESO by immersion, and the subsequent acid-catalyzed curing of ESO gave a composite material obtained wholly from renewable resources [43]. The composite showed relatively good transparency with improvements in mechanical properties due to the nanoscale network structure of the cellulose gel. The introduction of cellulose resulted in the low thermal expansion of the composite.

Poly(L-lactic acid) (PLLA) is one of the most famous biodegradable aliphatic polyesters and is produced from lactic acid derived from the fermentation of starch from corn, potato, and other sources. Due to its good mechanical

strength and excellent biocompatibility, PLLA exhibits great potential applications in many fields, such as packaging, automotive industries, and biomedical devices. A new class of fully biobased shape memory materials were obtained by the acid-catalyzed curing of ESO in the presence of PLLA [44]. The mechanical properties, such as the tensile modulus and stress, were improved by the incorporation of PLLA. The strain at break of polyESO/PLLA was larger than that of the ESO homopolymer and neat PLLA due to the plasticization effect of the plant oil. Furthermore, polyESO/PLLA exhibited excellent shape memory recovery properties, and the strain fixity depended on the feed ratio of ESO and PLLA (Fig. 6).

A plant oil-based shape memory material was also synthesized from a combination of ESO and PCL [45]. The acid-catalyzed crosslinking of ESO in the presence of PCL produced a flexible material with a semi-interpenetrating network structure. The PCL component in polyESO/PCL
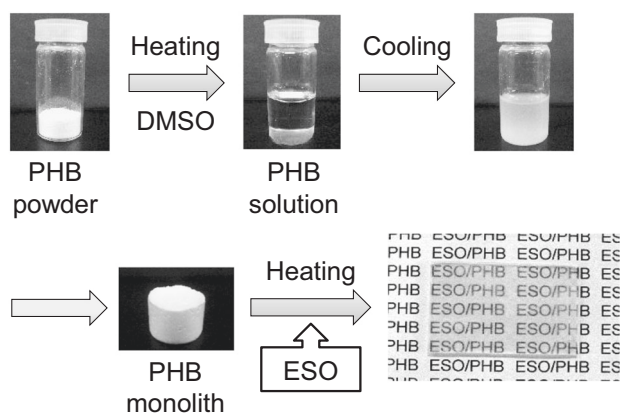
Fig. 7 Synthesis of a polyESO/PHB composite using PHB monolith

was partly miscible with the ESO polymer, and the crystallinity of the PCL component decreased. The mechanical properties of the maximum stress and strain at break were effectively improved by the incorporation of the PCL component. The PCL component in polyESO/PCL was gradually hydrolyzed by lipase from *Pseudomonas cepasia*. Furthermore, polyESO/PCL exhibited excellent shape memory recovery behaviors. The strain fixity depended on the feed ratio of ESO and PCL, and the deformation and recovery processes could be performed repeatedly.

A series of poly(3-hydroxyalkanoate)s, including a poly (3-hydroxybutyrate) (PHB) homopolymer and the related copolymers, are naturally occurring thermoplastics that behave as intercellular-carbon and energy-storage compounds in microorganisms such as bacteria. PHB is a highly crystalline and brittle polymer but possesses melting point and mechanical properties comparable to those of petroleum-based synthetic polymers. The brittleness of PHB is attributed to large spherulites and secondary crystallization.

A plant oil-based green composite using a porous PHB monolith was developed (Fig. 7) [46]. A monolith is a type of functional material with a three-dimensional continuous porous structure [47–50]. The PHB monolith was fabricated by thermally induced phase separation (TIPS) using DMSO as the solvent. The PHB monolith was immersed in ESO with thermally latent catalyst, and the subsequent curing of ESO gave the ESO/PHB composite. The resulting composites were relatively transparent due to the nanoscale fibrous structure of PHB. The DSC and DMA results of the composite showed two glass transitions and the melting behavior of PHB. The Young's modulus and the tensile strength of the ESO/PHB composite were greater than those of the ESO homopolymer. The incorporation of the PHB monolith also increased the strain at break, indicating that the resulting composite is effectively reinforced without sacrificing toughness.

A monolith of poly(glycidyl methacrylate-co-methyl methacrylate) (PGMA), an acrylic polymer bearing oxirane groups, was fabricated via TIPS using ethanol aqueous solution as a solvent. The PGMA monolith was immersed in ESO containing a thermally latent catalyst under vacuum conditions, and the subsequent crosslinking reaction produced polyESO/PGMA with relatively good transparency [51]. The DMA results of polyESO/PGMA showed two glass transitions due to the immiscibility of the polyESO and PGMA components. The Young's modulus and the tensile modulus of polyESO/PGMA were greater than those of the ESO homopolymer. Enhancement of the strain at break by the incorporation of the PGMA monolith was observed, leading to the effective reinforcement of the monolith. Furthermore, polyESO/PGMA exhibited excellent shape memory properties.

Branched poly (lactic acid) with castor oil as core

In contrast to common plant oils consisting of triglycerides, such as soybean and palm oils, castor oil is mainly composed of ricinoleic acid bearing a secondary hydroxy group and glycerol. Castor oil is produced primarily in India and classified as a nonedible oil due to its nauseant properties. Various industrial applications of castor oil and its derivatives have been developed. They are used as polyols for polyurethanes, which have wide acceptance in the automotive, building, and furniture industries.

Branched poly(lactic acid) (BP) was prepared by the ring-opening polymerization of lactide in the presence of castor oil (Fig. 8) [52]. The molecular weight of BP could be controlled by the feed ratio of lactide and castor oil. BP was applied as a polymeric plasticizer for PLLA. The blended film of PLLA and BP showed a good plasticization effect on PLLA. Only a small amount of BP was sufficient to plasticize PLLA. Although the strain at break of the blended film was not high, the tensile stress was scarcely changed by the addition of BP, indicating that the as-obtained plasticized PLLA film maintained its mechanical strength with improved brittleness. The glass transition temperature (T_g) and crystallization (T_c) of PLLA were slightly lowered by the addition of BP. As the content of BP increased, gradual decreases in both values were observed. Furthermore, the addition of BP to PLLA reduced the crystal size of PLLA. Some of these behaviors were specific to this polymeric plasticizer and not observed for the reported plasticizers with low molecular weight. In addition, polymeric plasticizers such as BP may be useful to prevent the migration or volatilization of plasticizers, leading to good stability over time.

Fig. 8 Synthesis of branched poly(lactic acid) with different terminal groups
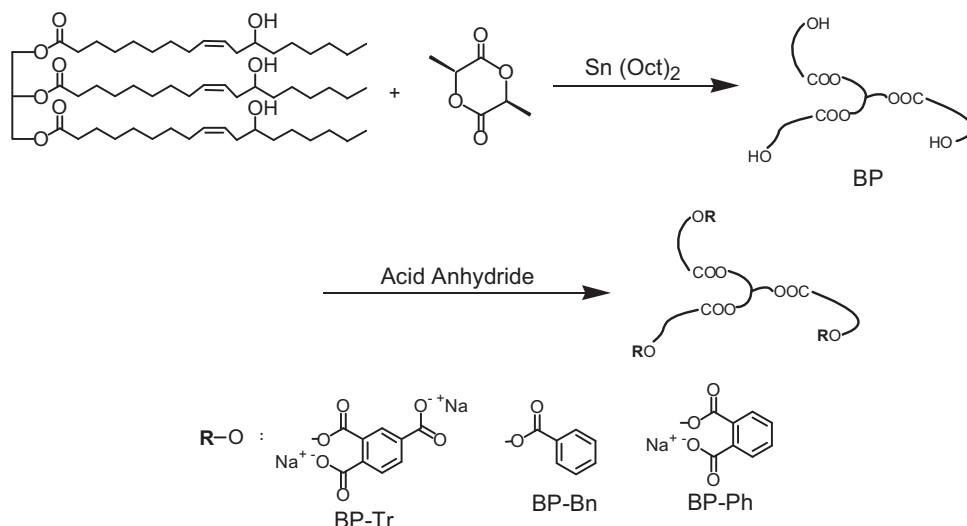
BP was also effective as the nucleating agent of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), a type of bacterial polyester [53]. The addition of BP enhanced the crystallization of PHBV to enable completion during the cooling process, whereas crystallization of the PHBV/linear poly(lactic acid) blend was not complete under the same conditions. During isothermal crystallization, the crystallization rates of the PHBV/BP blends were markedly higher than that of neat PHBV. BP acted as an effective heterogeneous nucleating agent by inducing phase separation, which markedly promoted crystallization and increased the crystallization rate. The spherulite size of PHBV was dramatically decreased by the incorporation of BP.

The terminal structure of BP was modified by different acid anhydrides. Among the prepared samples (Fig. 8), the trimellitoyl-terminated branched poly(lactic acid) (BP-Tr) showed excellent performance as a nucleating agent for PLLA [54]. Good transparency was found in the blended film of PLLA and BP-Tr. In isothermal crystallization, the crystallization rate of the blend was higher than that of neat PLLA, showing that BP-Tr effectively accelerated the crystallization of PLLA. The spherulite size of PLLA was decreased by the incorporation of BP-Tr. These results indicate that BP-Tr has high potential as a nucleating agent for PLLA. The strain at break of the PLLA/BP-Tr blend was greater than that of neat PLLA, suggesting that BP-Tr acts as a nucleating agent without an increase in brittleness. Furthermore, the addition of BP-Tr resulted in low thermal expansion of the blended film.

The plant cuticle covers nearly all aerial parts of terrestrial plants and forms the interface between plants and the environment, with thicknesses varying widely among different plant species and different organs of the same plant. It is mainly composed of epicuticular and intracuticular waxes, cutin, polysaccharides, glycerol, and small amounts of phenolics. Cutin is a matrix of polyhydroxylated C_{16} and/or C_{18} fatty acids crosslinked by ester bonds.

Ricinoleic acid is a major fatty acid moiety of castor oil. A biomimetic cuticle was fabricated from hyperbranched poly(ricinoleic acid) (HBPRA) and cellulose film through a UV-initiated thio-ene click reaction [55]. The biomimetic cuticle had high transmittance in the visible light region. SEM analysis showed that the biomimetic cuticle was composed of perfectly attached two layers. The properties of the two surfaces of the biomimetic cuticle displayed significant differences. The cellulose side was hydrophilic with a contact angle of ~44° and pencil hardness >6 H. In contrast, the HBPRA side was hydrophobic with a contact angle of ~91° and pencil hardness ≈ B. In contrast to the slippery cellulose side, the HBPRA side could attach to various substrates under gentle force. In addition, the tensile test showed good mechanical properties. The elongation at break and maximum stress of the biomimetic cuticle were 44% and 29 MPa, respectively.

Conclusion

In this focus review, recent progress on plant oil-based polymeric materials and their composites is described. Dependence on depleting petroleum resources is a serious concern in the plastic industry; thus, research on industrially applicable renewable alternatives for plastics is one of the most important and urgent issues. Furthermore, the use of biobased plastics can contribute greatly to the reduction of greenhouse emissions. There are many advantages of using plant oils because of their worldwide availability and low prices, which are highly attractive for industries.

This focus review demonstrates the great potential of plant oil-based polymers for industrial applications. An

artificial urushi system using plant oils as the starting substrate is significant because it is an environmentally benign process of polymer coating without the use of any organic solvents at ambient temperature under air, leading to a crosslinked polymer thin film with a high-gloss surface and good elastic properties. Epoxidized plant oils afford functional network polymers by combination with inorganics, cellulose fibers, or aliphatic polyesters. Reinforcement effects obtained by the addition of a suitable filler enhance the physical properties of the oil polymers are enhanced, which expands their industrial applications. Branched poly (lactic acid) with castor oil as the core is useful as an additive for improving the bioplastics PLLA and PHBV. This focus review is believed to contribute to further studies on high-performance functional polymers derived from plant oils.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Drumright RE, Gruber PR, Henton DE. Polylactic acid technology. Adv Mater. 2000;12:1841–6.
2. Steinbüchel A. Perspectives for biotechnological production and utilization of biopolymers: metabolic engineering of polyhydroxyalkanoate biosynthesis pathways as a successful example. Macromol Biosci. 2001;1:1–24.
3. Raquez J-M, Habibi Y, Murariu M, Dubois P. Polylactide (PLA)-based nanocomposites. Prog Polym Sci. 2013;38:1504–42.
4. Iwata T. Biodegradable and bio-based polymers: future prospects of eco-friendly plastics. Angew Chem Int Ed. 2015;54:3210–5.
5. Reddy MM, Vivekanandhan S, Misra M, Bhatia SK, Mohanty AK. Biobased plastics and bionanocomposites: current status and future opportunities. Prog Polym Sci. 2013;38:1653–89.
6. Xia Y, Larock RC. Vegetable oil-based polymeric materials: synthesis, properties, and applications. Green Chem. 2010;12:1893–909.
7. Kunduru KR, Basu A, Zada MH, Domb AJ. Castor oil-based biodegradable polyesters. Biomacromolecules. 2015;16:2572–87.
8. Llevot A. Sustainable synthetic approaches for the preparation of plant oil-based thermosets. J Am Oil Chem Soc. 2017;94:169–86.
9. Zhang C, Garrison TF, Madbouly SA, Kessler MR. Recent advances in vegetable oil-based polymers and their composites, composites. Prog Polym Sci. 2017;71:91–143.
10. Miao S, Wang P, Su Z, Zhang S. Vegetable-oil-based polymers as future polymeric biomaterials. Acta Biomater. 2014;10:1692–1704.
11. Mosiewicki MA, Aranguren MI. Recent developments in plant oil based functional materials. Polym Int. 2016;65:28–38.
12. Kobayashi S, Uyama H, Ohmae M. Enzymatic polymerization for precision polymer synthesis. Bull Chem Soc Jpn. 2001;74:613–35.
13. Kobayashi S, Uyama H, Kimura S. Enzymatic polymerization. Chem Rev. 2001;101:3793–813.
14. Uyama H, Kobayashi S. Enzyme-catalyzed polymerization to functional polymers. J Mol Catal B Enz. 2002;19-20:117–27.
15. Uyama H, Kobayashi S. Enzymatic synthesis of polyphenols. Curr Org Chem. 2003;7:1387–97.
16. Kim Y-J, Uyama H, Tsujimoto T. Enzymatic synthesis of phenolic polymers and their applications. Polym Sci Technol. 2009;20:465–71.
17. Kobayashi S, Makino A. Enzymatic polymer synthesis: an opportunity for green polymer chemistry. Chem Rev. 2009;109:5288–353.
18. Kadokawa J, Kobayashi S. Polymer synthesis by enzymatic catalysis. Curr Opin Chem Biol. 2010;14:145–53.
19. Shoda S, Uyama H, Kadokawa J, Kimura S, Kobayashi S. Enzymes as green catalysts for precision macromolecular synthesis. Chem Rev. 2016;116:2307–413.
20. Tsujimoto T, Ando N, Oyabu H, Uyama H, Kobayashi S. Laccase-catalyzed curing of natural phenolic lipids and product properties. J Macromol Sci, Part A: Pure Appl Chem. 2007;44:1055–60.
21. Kobayashi, S, Ikeda, R, Oyabu, H, Tanaka, H & Uyama, H. Artificial urushi: Design, synthesis, and enzymatic curing of new urushiol analogues. Chem. Lett. 2000: 1214–5.
22. Ikeda R, Tsujimoto T, Tanaka H, Uyama H, Kobayashi S. Man-made urushi. Preparation of crosslinked polymeric films from renewable resources via air-oxidation processes. Proc Jpn Acad. 2000;76B:155–60.
23. Ikeda R, Tanaka H, Uyama H, Kobayashi S. Preparation of artificial urushi via environmentally benign process. Bull Chem Soc Jpn. 2001;74:1067–73.
24. Kobayashi S, Uyama H, Ikeda R. Artificial urushi. Chem Eur J. 2001;7:4754–60.
25. Tsujimoto, T, Ikeda, R, Uyama, H & Kobayashi, S. Synthesis and curing of crosslinkable polyphenols from urushiol analogues. Chem. Lett. 2000: 1122–3.
26. Tsujimoto T, Ikeda R, Uyama H, Kobayashi S. Crosslinkable polyphenols from urushiol analogues. Macromol Chem Phys. 2001;202:3420–5.
27. Ikeda R, Tanaka H, Uyama H, Kobayashi S. A new crosslinkable polyphenol from renewable resource. Macromol Rapid Commun. 2000;21:496–9.
28. Ikeda R, Tanaka H, Uyama H, Kobayashi S. Synthesis and curing behaviors of a crosslinkable polymer from cashew nut shell liquid. Polymer. 2002;43:3475–81.
29. Ikeda R, Tanaka H, Uyama H, Kobayashi S. Enzymatic synthesis and curing of poly(cardanol). Polym J. 2000;32:589–93.
30. Uyama H, Kuwabara M, Tsujimoto T, Kobayashi S. Enzymatic synthesis and curing of biodegradable epoxide-containing polyesters from renewable resources. Biomacromolecules. 2003;4:211–5.
31. Tsujimoto T, Uyama H, Kobayashi S. Synthesis and curing behaviors of crosslinkable polynaphthols from renewable resources: preparation of artificial urushi. Macromolecules. 2004;37:1777–82.
32. Tsujimoto T, Uyama H, Kobayashi S. Enzymatic synthesis of crosslinkable polyesters from renewable resources. Biomacromol. 2001;2:29–31.
33. Tsujimoto T, Uyama H, Kobayashi S. Enzymatic synthesis and curing of biodegradable crosslinkable polyesters. Macromol Biosci. 2002;2:329–35.
34. Tsujimoto T, Takeshita K, Uyama H. Bio-based epoxy resins from epoxidized plant oils and their shape memory behaviors. J Am Oil Chem Soc. 2016;93:1663–9.
35. Uyama H, Kuwabara M, Tsujimoto T, Nakano M, Usuki A, Kobayashi S. Green nanocomposites from renewable resources: Plant oil-clay hybrid materials. Chem Mater. 2003;15:2492–4.
36. Uyama H, Kuwabara M, Tsujimoto T, Nakano M, Usuki A, Kobayashi S. Organic-inorganic hybrids from renewable plant oils and clay. Macromol Biosci. 2004;4:354–60.

37. Tsujimoto T, Kuwabara M, Uyama H, Kobayashi S, Nakano M, Usuki A. Preparation and properties of green nanocomposites from epoxidized triglycerides and a modified clay. J Adhes Soc Jpn. 2010;46:131–6.

38. Tsujimoto T, Uyama H, Kobayashi S. Green nanocomposites from renewable resources: biodegradable plant oil-silica hybrid coatings. Macromol Rapid Commun. 2003;24:711–4.

39. Tsujimoto T, Uyama H, Kobayashi S. Green nanocomposites from epoxidized plant oils and oxetane-containing silane coupling agent. J Netw Polym. 2004;25:124–30.

40. Tsujimoto T, Uyama H, Kobayashi S, Oikawa H, Yamahiro M. Green nanocomposites from renewable plant oils and polyhedral oligomeric silsesquioxanes. Metals. 2015;5:1136–47.

41. Imai N, Nakagaito AN, Yano H, Uyama H. Biocomposite from epoxidized soybean oil and microfibrilled cellulose. Wood Res J. 2013;4:41–45.

42. Tsujimoto T, Ohta E, Uyama H, Endo T. Biocomposites from epoxidized soybean oil and cellulose ultrafine fibers. J Netw Polym. 2011;32:78–82.

43. Tsujimoto T, Ohta E, Uyama H. Bio-based composites from epoxidized plant oil and cellulose gel. J Netw Polym. 2013;34:85–89.

44. Tsujimoto T, Uyama H. Full biobased polymeric material from plant oil and poly(lactic acid) with a shape memory property. ACS Sus Chem Eng. 2014;2:2057–62.

45. Tsujimoto T, Takayama T, Uyama H. Biodegradable shape memory polymeric material from epoxidized soybean oil and polycaprolactone. Polymers. 2015;7:2165–74.

46. Hosoda N, Tsujimoto T, Uyama H. Plant oil-based green composite using porous poly(3-hydroxybutyrate). Polym J. 2014;46:301–6.

47. Okada K, Nandi M, Maruyama J, Oka T, Tsujimoto T, Kondoh K, Uyama H. Fabrication of mesoporous polymer monolith: a template-free approach. Chem Common. 2011;47:7422–4724.

48. Sun X, Fujimoto T, Uyama H. Fabrication of a poly(vinyl alcohol) monolith via thermally impacted non-solvent-induced phase separation. Polym J. 2013;45:1101–6.

49. Yoneda S, Han W, Hasegawa U, Uyama H. Facile Fabrication of poly(methyl methacrylate) monolith via thermally induced phase separation by utilizing unique cosolvency. Polymer. 2014;55:3212–6.

50. Xin Y, Xiong Q, Bai Q, Miyamoto M, Li C, Shen Y, Uyama H. A hierarchically porous cellulose monolith: a template-free fabricated, morphology-tunable, and easily functionalizable platform. Carbohydr Polym. 2017;157:429–37.

51. Tsujimoto T, Ohta E, Uyama H. Plant oil-based shape memory polymer using acrylic monolith. EXPRESS Polym Lett. 2015;9:757–63.

52. Tsujimoto T, Haza Y, Yin Y, Uyama H. Synthesis of branched poly(lactic acid) bearing a castor oil core and its plasticization effect for poly(lactic acid). Polym J. 2011;43:425–30.

53. Hosoda N, Lee E-H, Tsujimoto T, Uyama H. Phase separation-induced crystallization of poly(3-hydroxybutyrate-co-hydroxyvalerate) by branched poly(lactic acid). Ind Eng Chem Res. 2013;52:1548–53.

54. Tsujimoto T, Nishio S, Uyama H. Bio-based branched polymer bearing castor oil core as a nucleating agent for poly(l-lactic acid). J Polym Environ. 2015;23:559–65.

55. Zhang B, Uyama H. Biomimic plant cuticle from hyperbranched poly(ricinoleic acid) and cellulose film. ACS Sus Chem Eng. 2016;4:363–9.

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