Review

Creating Shape Memory Polymers from Biobased Resources

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ABSTRACT: Developing polymer materials from biomass is a promising pathway to address serious environmental and resource issues. To date, a series of biobased general polymer materials have been successfully industrialized. However, exploring highly valuable functional polymers and intelligent polymer materials from biomass, such as shape memory polymers (SMPs) and self-healing materials, is still a great challenge. The present review intends to bridge a sustainable pathway for the creation of SMPs from biobased resources. Thus, we first recall some backgrounds of the design principle of SMPs and highlight the biobased monomers or building blocks for SMPs, and then we focus on the main varieties of biobased SMPs to clarify their fabricating approaches, functionalizing strategies, new manufacturing methods and the application potential.

Keywords: Shape memory polymer; Biobased; Vitrimers; Polyesters; 4D printing

1. Introduction

Polymer materials have been widely used in daily life, industry, agriculture, military, biomaterials, and other fields due to their advantages of low density, high specific strength, easy processing, corrosion resistance, and so on. However, most commercialized polymer materials come from fossil resources and petrochemicals, and a large number of undegradable products have been abandoned after a short period of service. It will cause serious resource and environmental problems if they have not been disposed of properly. In this context, developing biobased polymer materials become an emerging and sustainable pathway because it can reduce the consumption of fossil resources and decrease atmospheric CO_2 emissions [1].

Generally, there are two main routes to obtaining biobased polymers. One is utilizing natural polymers or their modified products directly, such as abundant cellulose, starch, lignin, and their derivatives, and several products have been industrialized. Another route is polymerizing biobased monomers or precursors, including aliphatic diols, dicarboxylic acids, hydroxy acids, diamines, and aromatic molecules that are produced via biotechnology from diverse biomass including agricultural crops, wood and forestry residues or (micro)algae [2–4]. The typical industrialized biobased polymers via this approach include polylactic acid (PLA), poly (butylene adipate-co-terephthalate) (PBAT), polybutylene succinate (PBS), and green polyolefins [5,6].

To date, researchers have not been satisfied with developing general polymer materials from biomass materials but turned their attention to highly valuable functional polymers and intelligent polymer materials, such as vitrimers [1,7–12], self-healing materials [13–21], and shape memory polymers (SMPs) [22–31]. Amongst, SMPs have the unique capacity to recover their original shapes from a temporarily deformed shape in response to external stimulus, which makes them attract tremendous attention from both academia and industry. To date, the molecular mechanisms of shape memory effects (SMEs) [32–36] have been profoundly disclosed, and various stimulus-response shape-shifting modes have been well-established, allowing SMPs widely applied in actuators, sensors, smart textiles [36,37], biomaterials [38,39] and space deploying devices [40]. Scientists can easily create SMPs more sustainably by using various biobased monomers or precursors after a full understanding of the molecular mechanism of SMEs. As we know, a lot of polymers with proper thermal transitions (e.g., crystalline-melting transition or glass transition), such as aliphatic polyesters, polyurethanes, and epoxy, can be utilized as building blocks for SMPs. Delightfully, the biomass synthetic pathway of this kind of polymers has been well-established, bringing great challenges as well as opportunities for the development of SMPs. Although many excellent reviews that focused on SMPs and biobased polymer material have been published by various groups active in these two areas respectively, it remains very necessary to unveil the latest notable progress aroused from the organic

combination of these two areas. The main purpose of the current review is to clarify the bridge between the SMP building blocks and the biomass resources and highlight the creating approaches, functionalizing strategies, and the application of this new class of SMPs from biobased chemicals.

2. Principle of Design SMPs

Designing SMPs from biomass resources can be regarded as a sustainable and promising direction, but the rational and wisely fabricating strategy is also very crucial. For this purpose, a deep understanding of the mechanism of SMEs is imperative. As we know, the phenomenon of shape memory was first observed in the metal alloy in 1951, and the first SMP product, heat-shrinkable cross-linked polyethylene (PE), was commercialized in the 1960s [41]. After decades of intensive investigation, the basic molecular working mechanisms of shape memory effects have been deeply revealed, and SMPs with diverse structures have been developed under this guidance.

2.1. Molecular Structure and Mechanism for SMPs

Essentially, as schematically illustrated in Figure 1a, SMPs can be divided into two functional units, netpoints and molecular switches. The netpoints are responsible for defining and memorizing the permanent shape of a SMP, and molecular switches answer for shape fixing and recovering. Generally, netpoints can be formed by physical or chemical cross-linking; the former involves physical interactions, stable chain entanglements, crystalline and glassy polymer segments [42], while the latter includes covalent chemical bonds, interpenetrating networks, or recently highly concerned dynamic networks [43–45].

The molecular switch is the key point to determining what kind of stimuli a SMP responds to. The most popular category involves polymer segments with thermal phase transition, such as glass transition for amorphous polymers [46–48], crystallization-melting transition for semicrystalline polymers [49] and liquid crystal-isotropic phase transition for liquid crystal polymers [50], etc. Naturally, the obtained SMPs are thermal-responsive. With the development of polymer science, some dynamic chemical and physical structures gradually act as molecular switches [51], such as hydrogen bonding interactions [52], reversible coordination interactions [53] and host-guest recognition interactions [54]. Taking advantage of these molecular switches, SMEs could be triggered by light, water, pH stimulus, and so on. Due to the nonthermal nature of the stimulus, this kind of SMPs is also called athermal SMPs. Besides classifying the SMPs by different stimuli, they also can be classified by shape-shifting modes as one-way SMPs (1W-SMPs) and two-way SMPs (2W-SMPs), the shape change of 1W-SMPs is irreversible and can only follow the path from temporary shape to permanent shape, meanwhile, 2W-SMPs can reversibly transform between two shapes. According to the number of shapes that can be displayed during the shape memory cycle, SMPs also include dual-, triple- and multi-SMPs.

2.2. Thermal-responsive SMPs

Thermal-responsive dual SMPs are conventional, and widely investigated in recent decades, many polymers exhibit a thermally induced SMEs based on phase transition. The phase transition can be vitrification/glass transition, crystallization/melting transition and liquid crystal phase-isotropic transition with a transition temperature (T_{trans}) of glass transition temperature (T_g), melting temperature (T_m) and liquid-crystalline clearing temperature (T_{cl}), respectively. Commonly, a full SMEs cycle of a 1W-SMP includes programming and recovery steps (Figure 1b). Taking a semicrystalline chemically-crosslinked network as an example, the detailed procedure can be described as follows: when SMPs are heated above the melting transition temperature (T_{trans}), the polymer segments exhibit rubbery elasticity and gain better mobility; the SMPs could be deformed under the action of external forces, after cooling to a fixing temperature ($T < T_{trans}$, T should be below the crystallization temperature T_c) under the external force, the polymer chains are frozen and the SMPs are in temporary shape after unloading the external force. When the SMPs are reheated above T_{trans} without external stress, the chain motility is reactivated and the SMPs regain their permanent shape owing to the action of entropic elasticity [36].

After a full understanding of the working mechanism of thermal-induced SMEs, one can easily design a SMP from numerous polymer candidates. Due to most polymers equipping either a T_g or a T_m, the T_g-based and T_m-based SMPs become the most common types. To meet the requirements in different application fields, the comprehensive performance of the materials such as mechanical properties also needs to be considered beside the SMEs with an adaptable T_{trans}. For T_m-based SMPs, the semi-crystalline polymer segments, such as polyolefins and their derivatives PE [41], ethylene-vinyl acetate copolymer (EVA) [55–57], aliphatic polyester poly(ε-caprolactone) (PCL) [58], poly(p-dioxanone) [59], or aliphatic polyethers poly(ethylene glycol) (PEG) [42,60], poly(tetramethylene glycol) (PTMEG) [61], can be employed as molecular switches. Moreover, it may realize triple- or multi-SMEs by introducing two or more segments with independent T_m into one SMPs [62–64].

For T_g-based SMPs, beyond traditional dual-shape systems, several new strategies have been developed for more functionalities. For example, Poulin and coworkers reported a shape and temperature memory composite nanotube fiber based on polyvinyl alcohol (PVA) with broad glass transition that induced by a large fraction of carbon nanotubes [62]. Xie first realized dual-, triple-, and at least quadruple-SMEs in the perfluorosulphonic acid ionomer (PFSA), which has only one broad glass transition [65]. Inspired by this strategy, different polymer systems with a broad glass transition were developed to achieve multi-SMEs, including poly(methyl methacrylate)/PEG semi-interpenetrating polymer networks containing broadened glass transition [66], linear gradient poly(styrene-methyl acrylate) copolymers with controllable broadening glass transition [67]. Liquid crystalline

elastomers (LCEs) are typical T_{cl}-based systems, and various mesogens, including commercially available liquid crystal monomers RM82, RM257, NBch15, etc., have been employed to develop the LCEs.
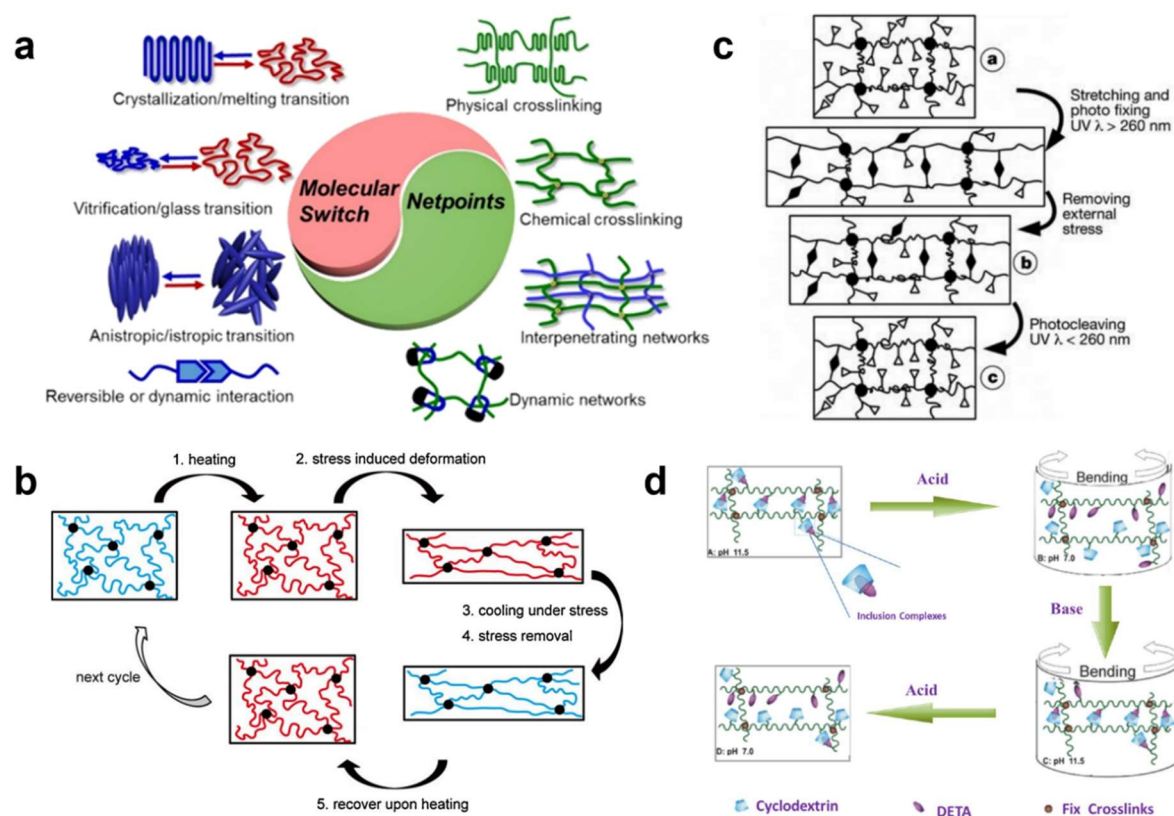

Figure 1. (**a**) The schematic molecular mechanism of the SMPs in a full review [68] (Copyright 2019 Elsevier B.V.), (**b**) thermal-induced SMEs [36] (Copyright 2015 Elsevier Ltd), (**c**) photo-induced SMEs [69] (Copyright 2005 Nature Publishing Group), and (**d**) chemical-induced SMEs [51] (Copyright 2017 American Chemical Society).

Except for the most common heat stimuli, indirect heating methods were also developed for the convenience of remote control during shape recovery. By incorporating functional fillers into the SMP matrix, different forms of energy such as electricity, magnetism and light can be converted into thermal energy and induce heat within materials to trigger the shape recovery process. Electrical-responsive SMPs could be obtained by adding conductive fillers such as carbon nanotubes, carbon black, carbon fibers and metal powders into SMPs [70,71]. When the conductive percolation network is constructed in a thermal-responsive SMP matrix, the shape recovery can be triggered by Joules heating. Similarly in magnetic-responsive SMPs, the composites containing Fe_3O_4 magnetic nanoparticles have been reported [72–74]. Via photo-thermal effect, light-responsive SMPs also can be achieved by irradiating light of certain wavelengths onto SMP composites containing carbon powders or metal nanofillers via photo-thermal effect [75–77].

2.3. Athermal SMPs Based on Reversible Switches

Besides the above-mentioned different kinds of thermal-responsive SMPs concerning about phase-transition, various athermal SMPs were also devised so that SMEs can be triggered under nonthermal conditions, expanding the scope of the shape programming approaches. The key factor in designing nonthermal SMPs is incorporating reversible switches into polymer chains, and thus, some light-responsive or chemical-responsive groups have attracted the great attention of the researchers.

As an external stimulus, light has the unique feature that it can be localized in time and space, which brings great advantage to precise control of a SMP in remote mode. The athermal light-responsive SMP was first developed by Lendlein and coworkers via incorporating cinnamic acid groups into a polymer matrix (Figure 1c), the light-induced SMEs can be triggered by photo-reversible [2+2] cycloaddition reaction under UV light with different wavelengths [69]. Similar chemical groups, including anthracenes and coumarin, also can occur reversible photo-cycloaddition reactions, which makes more possibility for SMPs design. Our group [60,61,63,78] developed a series of SMPs by introducing anthracene groups into PLA-PEG copolymers, realizing light-induced SMEs, triple-SMEs, 2W-SMEs, and photo-patterning. In addition to the photo-cycloaddition reaction, azo-benzene molecules with photo-isomerization properties were also employed as molecular switches [79,80].

Apart from UV light stimuli, chemical stimuli can also trigger the shape recovery process under athermal conditions. Taking advantage of supramolecular interactions as molecular switches to construct novel SMPs, various athermal chemical-responsive SMPs have been designed, which greatly broadened the triggering methods and application of SMPs [51,81–85] (Figure 1d). Supramolecular

chemistry including hydrogen bonding, host−guest interactions, metal coordination, ionic interactions, and hydrophobic interactions have been employed for the construction of SMPs. Since their structures can be reversibly modulated by chemical environment, they are ideal molecular switches working under nonthermal conditions [83,84,86]. For example, in early 2005, Huang et al. [85] discovered the unique water-induced shape memory effects in a shape memory polyurethane (SMPU) based on the gradient variation of glass transition temperature caused by the weakening of hydrogen bonding after immersing in room temperature water. Zhang et al. [87] prepared pH-sensitive SMPs by cross-linking β-cyclodextrin modified alginate and diethylenetriamine-modified alginate, which was triggered by the formation and dissociation of β-cyclodextrin and diethylenetriamine inclusion complexes.

3. Biobased Monomers and Their Polymers

Biobased monomers have a wide range of resources, which can convert by cellulose, lignin, fatty acids, vegetable oil, terpenoids, starch, sugars, proteins and other biosources. According to the chemical composition and structure of biobased monomers, they can be roughly divided into two categories: aliphatic monomers and aromatic monomers. Aliphatic monomers include various dicarboxylic acids, diols, polyols, amide and their ramification, for example, succinic acid, fumaric acid, itaconic acid, citric acid, hydroxyalkanoic acid, lactic acid, levulinic acid, adipic acid, 1,3-propanediol, 1,4-butanediol, 1,4:3,6-dianhydrohexitols, ethylene glycol, 1,8-octanediol, glycerol, D-sorbitol, 1,4-butanediamine, 1,5-pentanediamine, 1,6-hexanediamine, 1,8-octanediamine, 1,10-decanediamine, bioethylene, biopropylene and so on. Aromatic monomers include lactones, furan, vanillin and their ramification, for example, 3-hydroxybutyrolactone, propiolactone, angelilactone, γ-valerolactone, ε-caprolactone, 5-(hydroxymethyl)furfural, 2,5-furandicarboxylic acid, vanillic acid, divanillyl diol, terephthalic acid, vanillin and so on.

Succinic acid (SA) is widely present in nature, it has been listed as one of the 12 high-potential bio-based platform chemicals by the US Department of Energy (DOE) and become a potential substitute for current petrochemical production [88,89]. As a commodity chemical and precursor in the chemical industry, it is widely used in food, medicine, green solvents, biodegradable polymers and plasticizers [90–93]. Moreover, SA can also be chemically converted into a variety of important industrial chemicals such as 1,4-butanediol, butadiene, tetrahydrofuran and other monomers of biodegradable polymers. Itaconic acid (IA), another important high-potential bio-based platform chemical by US DOE [89], is also an important organic acid with a covalent double bond that is widely applied in plastics, medicine, textile, and paint as an alternative to the precursor of polymers and chemical intermediates based on petrochemical production [94–96]. Hydroxyalkanoic acid (HA) and its derivatives, as a special category in aliphatic acid, have been used to create a series of aliphatic polyesters [97–100], such as poly(3-hydroxybutyric acid), poly(3-hydroxypropionate), poly(4-hydroxybutyrate), poly(3-hydroxy-5-phenylvaleric acid) [101–103]. Lactic acid (2-hydroxypropionic acid, LA) is an important organic acid with both D-LA and L-LA enantiomeric forms existing as a result of the chiral carbon in molecular structure. Due to the wide range of applications, the demand for LA has increased significantly. Food waste, agricultural waste and lignocellulose have been explored to gain more economical and renewable fermentation substrates [104,105]. As a fundamental monomer of various polymers, LA has been widely applied in textiles and cosmetics [106–108].

Aliphatic diols are fundamental chemicals with two hydroxyl groups in the molecular structure that have a range of applications in basal chemicals, fuels, medicine, and polymer synthesis [109–112]. In particular, those platform green chemicals that can be biotechnologically produced by direct microbial bioconversion of biomass, including 1,2-propanediol (1,2-PDO), 1,3-propanediol (1,3-PDO), 1,4-butanediol (1,4-BDO) and 2,3-butanediol (2,3-BDO). Amongst, 1,3-PDO is a vital monomer of polytrimethylene terephthalate (PTT) with terephthalic acid (TPA) being the other. 1,4-BDO can convert to produce various products including the important biodegradable product polybutylene succinate and polyesters [113,114].

The platform chemicals furfural (FF) and 5-hydroxymethylfurfural (HMF) initiate the origin point for the synthesis of furan-based monomers as a result of their production from C5 and C6 saccharide-based renewable biomass resources [115–118] (abundant biomass carbon source such as rice husks, sugarcane bagasse, wheat bran, corncobs, oat and sawdust [119]). Furfuryl alcohol not only is the most important monomer in furan-based polymer synthesis but also set up the chemical platform of furfural-based subproduct development. Similarly, HMF as a vital chemical is mainly produced from fructose in biomass conversion, which is listed in the "Top 10 +4" as additions for an updated evaluation of DEO top 12 list of biobased chemicals [89]. Many intermediate chemicals and monomers can be converted by catalysis and oxidation of HMF, including 2,5-Furandicarboxylic acid, 5-Hydroxymethylfuroic acid, 2,5-Bishydroxymethylfuran, 2,5-Dimethylfuran, levulinic acid, adipic acid, 1,6-Hexanediol, caprolactone and caprolactam [120,121]. 2,5-Furandicarboxylic acid (FDCA) is a most attractive furan-based diacid as a platform chemical [90,122,123], which is normally synthesized through the oxidation of HMF [124].
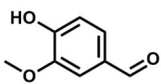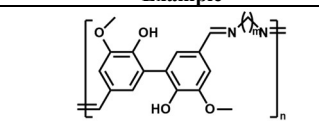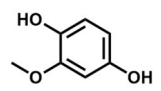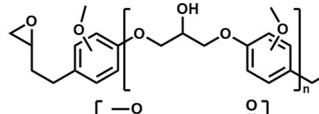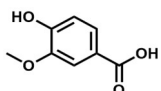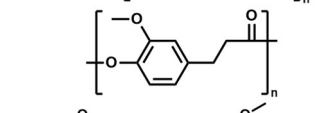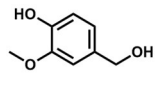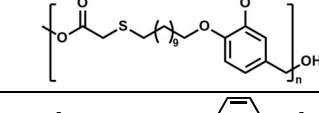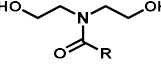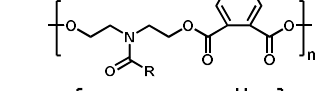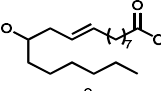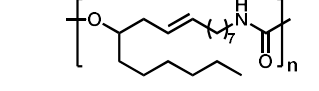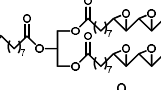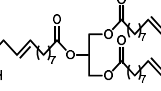
As one of the most abundant biomass resources, lignin is the main feedstock of renewable aromatic compounds [125–128]. Vanillin (4-hydroxy-3-methoxybenzaldehyde), as a representative oxidative product of lignin, is another important renewable aromatic compound containing functional groups such as aldehyde, phenol, and ether. Although vanillin cannot be directly applied to synthesize polyesters because there is no bifunctional esterification group in its molecule structure, the phenolic hydroxyl and aldehyde groups of vanillin can be easily modified into diols, diacids/diesters, or hydroxy acids/hydroxyesters [129]. Due to its great mouldability of the active functional group, vanillin has become an important intermediate monomer of various polymers, such as acrylic polymers, polyesters, epoxy polymers, polyacetals, phenolic resins, polyaldimines, polyalkenes and polybenzoxazines, as well as other polymers from the reductive coupling of aldehyde [130–134].

Vegetable oils are another important family of biomass resources, mainly composed of triglycerides with fatty acid chains [135–138]. Due to the C-C double bonds of unsaturated fatty acids, vegetable oils and their derivative are widely applied in the preparation of biobased promising polymers such as polyurethane, polyamide, vitrimer, epoxy, polyester, polyether and polyolefins [139–143]. Castor oil, soybean oil, linseed oil, oleic acids, etc. are important vegetable oil-based monomers to produce polymers using various methods including condensation, free radical copolymerization, cationic and olefin metathesis [142,144–146]. Moreover, researchers convert vegetable oils onto polyols, polyacids and epoxy monomers to develop novel polymers with different structures and properties through functional strategies [147–149]. These biobased monomers have also been summarized in Table 1.

Table 1. Various biobased monomers for biobased polymers reported in references.

Biobased Monomer	Chemical Structure	Source	Biobased Polymers	Example	Ref.
Succinic acid			PBS PES		[93]
Itaconic acid		Starch Sucrose Wood	Polyesters		[96]
3-Hydroxypropionic acid					[97]
2-Hydroxypropionic acid		Starch Cellulose Glucose Fatty acid	Polyesters		[98]
3-Hydroxybutyric acid					[99]
3-Hydroxypentanoic acid					[100]
Lactide		Cellulose Lignin	PLA		[108]
1,2-propanediol					[109]
1,3-propanediol		Glucose Sucrose Glycerol	polyesters, polyether, polyurethane, polyamide		[110]
1,4-butanediol					[111]
2,3-butanediol					[112]
THF					[116]
Furfural					[117]
5-hydroxymethylfurfural		Cellulose Hemicellulose Lignin Sugars	Polyesters, Epoxy polymers, Polyacetals, Phenolic resins, Polyanhydrides		[118]
2,5-Furandimethanol					[122]
5-Hydroxymethylfuroic acid					[90]
2,5-Furandicarboxylic acid					[123]

Table 1. *Continued.*

Biobased Monomer	Chemical Structure	Source	Biobased Polymers	Example	Ref.
Vanillin		Lignin	Acrylic polymers, Polyesters, Epoxy polymers, Polyacetals, Phenolic resins, Polyaldimines, Polyalkenes, Polybenzoxazines		[131]
2-Methoxyhydroquinone					[132]
4-Hydroxy-3-Methoxybenzoic acid					[133]
4-Hydroxy-3-Methoxybenzyl Alcohol					[134]
Linseed oil fatty acid		Vegetable oils	Polyurethane, Polyamide, Vitrimer, Epoxy, Polyester, Polyether, Polyolefins		[150]
Oleic acids					[151]
Epoxidized linseed oil				Crosslinked networks	[152]
Castor oil				Crosslinked networks	[153]

4. Creating SMPs from Biobased Resources

4.1. Biobased Shape Memory Polyesters and Polyurethanes

As the most common types in thermally-induced SMPs, shape memory polyesters and polyurethanes are easily tailored and fabricated from numerous kinds of diacid, diol, and diisocyanate. Bio-based platform chemicals already contain abundant dicarboxylic acids, diols, polyols, and so on, which provide a great convenience for developing biobased shape memory polyester and polyurethanes.

It is well known that PLA is one of the commercialized biobased and biodegradable aliphatic polyesters, and it is also a good candidate for designing SMPs intended for general use or biomaterials [143,154–157]. In 2005, Lendlein et al. [154] developed a completely amorphous and biodegradable shape memory copolyester-urethane network by employing an oligo [(rac-lactide)-co-glycolide] as switching segments (Figure 2a), which could show a more homogenous degradation than the semicrystalline polymers. Chen et al. [155] reported a full biobased shape memory PLA/natural rubber composite with a co-continuous structure via a dynamical vulcanizing strategy. Biodegradable PBS is another biobased aliphatic polyester that has been utilized to design SMPs and also has been intensively investigated. In our previous work [42], we designed a series of shape memory copolymers combined with a PBS hard segment and PEG soft segment that could be triggered by body temperature, which showed great potential in the application of biomaterials.

Besides the industrialized biobased aliphatic polyesters, the researchers begin to focus on the other available biobased monomers. Guo and Zhang [158,159] reported a new kind of biobased poly(propylene sebacate) from 1,3-propanediol, sebacic acid, and itaconic acid as the main raw materials, whose transition temperature and shape recovery speed could be tuned by changing the composition of the products (Figure 2b). The authors furtherly introduced the Boehmite (BM) nanoplatelets into biobased poly(propylene sebacate) (PPSe) to form the shape memory composites with significantly improved mechanical properties (Figure 2c). Recently, furan-based monomers have attracted the interest of researchers for the potential application in biobased SMPs. Zhou et al. [30] prepared a series of shape memory copolymers poly(ethylene 2,5-furandicarboxylate)-poly(ethylene glycol) (PEFEGs) from biobased ethylene glycol (EG), 2,5-furandicarboxylic acid (FDCA), and PEG (Figure 2d). Besides a good SMEs, the presence of the rigid ring structure also enable the material to the excellent thermal stability.
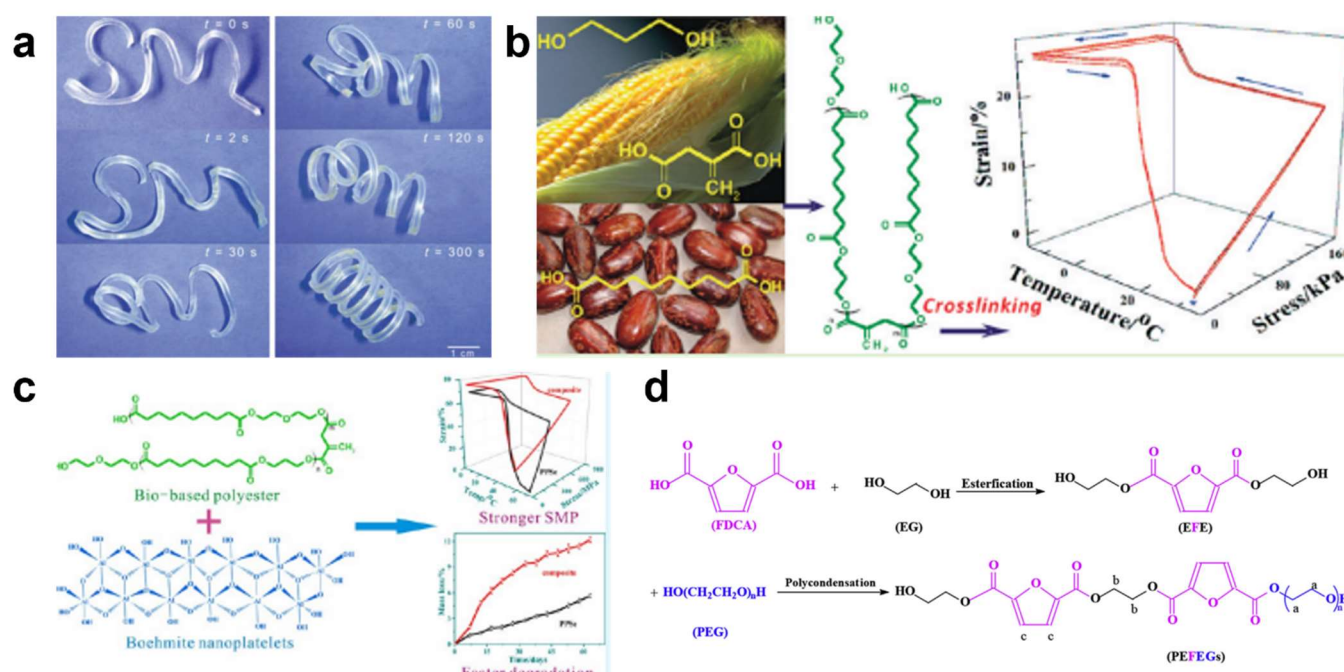
Figure 2. Biobased shape memory polyesters and polyurethanes. (**a**) Biobased SMP based on PLLA [154] (Copyright 2005, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim). (**b**) Biobased SMP based on poly(propylene sebacate) [158] (Copyright 2011 American Chemical Society) and (**c**) its Boehmite-contained nanocomposites [159] (Copyright 2012 American Chemical Society). (**d**) Biobased SMP based on poly(ethylene 2,5-furandicarboxylate) [30] (Copyright 2018 Elsevier Ltd).

4.2. Biobased Shape Memory Epoxy

Epoxy is a typical thermosetting resin owning excellent dimensional stability, chemical resistance, and superior mechanical properties, these features enable the shape memory epoxy to be applied in more harsh environments. Developing biobased shape memory epoxy from renewable resources has been considered a promising way [136]. The general fabricating strategy is to epoxidize the biomass chemicals with proper functional groups at first, and then cure the epoxy precursors to obtain the shape memory epoxy resins. Epoxidized soybean oil (ESO) is an important raw material to develop biobased epoxy [160,161]. Tsujimoto et al. [27] reported a biobased shape memory polyESO/PLLA by incorporating PLLA into acid-catalyzed cured ESO, which exhibited not only desirable mechanical performance but also excellent SMEs (Figure 3a). Yuan et al. [24] prepared shape memory networks from gallic acid and epoxidized olive oiled via a thiol-epoxy curing approach. Isosorbide is also a good candidate for biobased epoxy. It has been modified to biobased epoxy and diamine monomer by Zhu et al. [162] (Figure 3b), and the cured resin possessed a good shape memory effect as well as satisfied thermal stability owing to the presence of stiff ring structures. Eugenol is another important bioresource that has been explored to design biobased shape memory epoxy. For example, Zhang et al. [163] developed a multifunctional biobased epoxy by employing a eugenol-derived epoxy with succinic anhydride to realize shape memory, repairing and recyclability (Figure 3c). Miao et al. [164] fabricated dynamic cross-linked shape memory epoxy resin by decorating eugenol to trifunctional epoxy monomer and then curing with the disulfide bond-contained harder to pursue the reconfigurable feature. Tannic acid is also an attractive biomass derivative with a unique topological structure and abundant reactive groups, and not surprisingly, it has been utilized to develop shape memory epoxy thermosets, which can also exhibit high mechanical strength, damping, and recyclability (Figure 3d) [165].
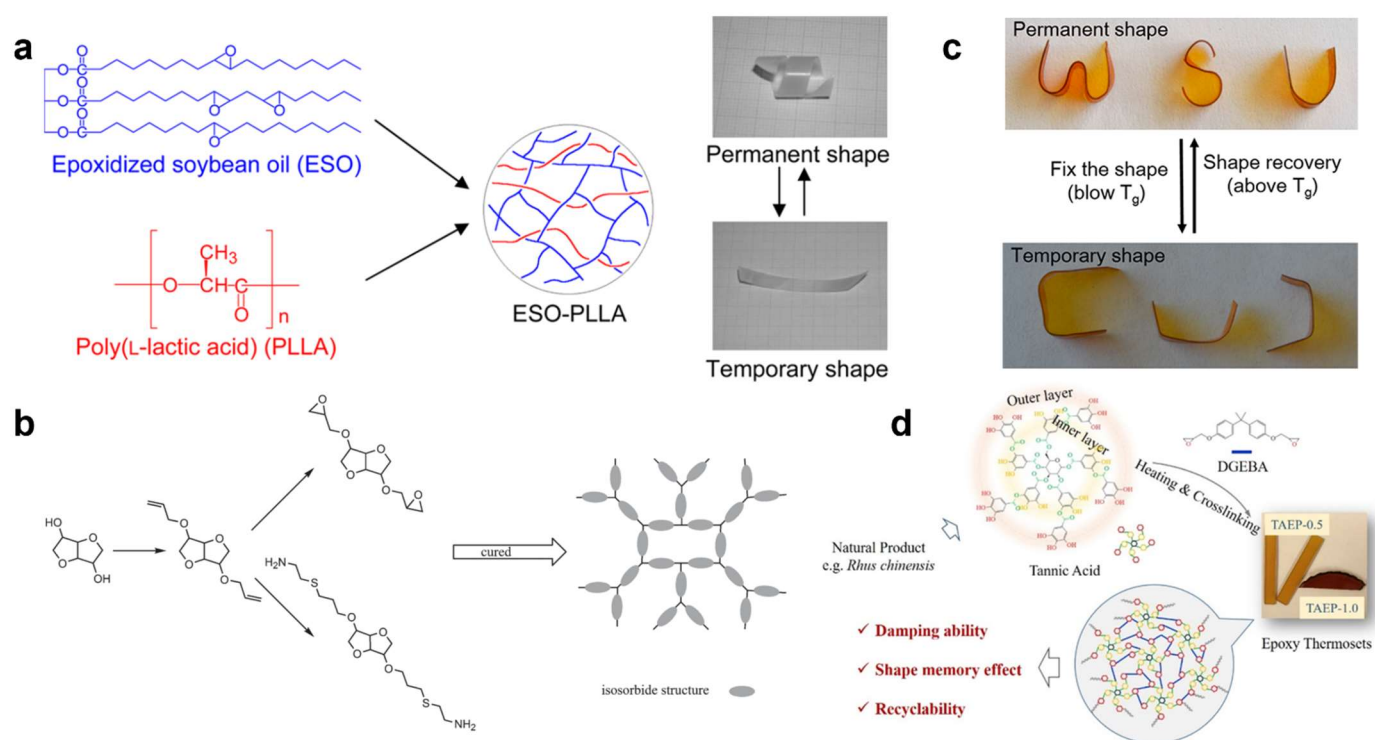
Figure 3. Biobased shape memory epoxy. (**a**) Shape memory epoxy based on polyESO/PLLA [27] (Copyright 2014 American Chemical Society). (**b**) Shape memory epoxy derived from isosorbide [162] (Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim). (**c**) Shape memory epoxy derived from eugenol [163] (Copyright 2017 American Chemical Society). (**d**) Shape memory epoxy derived from tannic acid [165] (Copyright 2019 American Chemical Society).

4.3. Biobased SMPs with Self-healing Capacity

Recently, with the increasing demand of sustainable polymer materials, self-healing materials have become the fast-growing category in smart materials. It also brings great opportunity and challenge for researchers to design biobased materials by combining shape memory and self-healing performances via a rational fabricating strategy from biobased resources. From the view of the working mechanism, the self-healing of polymers can be classified into two families: extrinsic and intrinsic. Amongst, intrinsic self-healing has been considered the most promising strategy. To design intrinsic self-healing polymers, two factors need to be concerned, one is the mobility of the chain that may promote its diffusion in the damaged area, and the other is the presence of the reversible bond in the matrix and its ability for reformation at suitable conditions. To date, various reversible bonds have been utilized to construct self-healing materials, including supramolecular interactions such as hydrogen bonds, π-π stacking, ionic interactions and metal-ligand interactions, as well as dynamic covalent bonds such as Diels-Alder reactions, acylhydrazone bonds, ester bonds, disulfide bonds, alkoxyamine bonds [21,166,167].

Supramolecular interactions commonly have low bonding energy but excellent reversibility in mild conditions, which may endow the materials with outstanding healing efficiencies. Introducing hydrogen bonding is a facile approach to designing a self-healing system, and certainly, it also works in a biobased SMP [19,167,168]. Hu et al. [169] introduced a hydrogen-bonding hindered phenol (AO-80) into a biobased PLA thermoplastic polyurethane (PLA-TPU), which was beneficial for the improvement of energy dissipation and self-healing performance. The results showed that a comprehensive self-healing efficiency of samples reached 81.98% in 5 min at 90 °C determined from both yield strength and elongation at break (Figure 4a). Besides, the hydrogen bonding interaction caused the increase of the T_g enabling this shape-memory composite to respond to the human body temperature. Frankly, it is still a great challenge for scientists to balance self-healing efficiency and mechanical properties, and recently several synergistic strategies have been developed to serve this dilemma. For example, Zhang et al. [170] reported an ionomeric elastomer composite with excellent recyclability, self-healing, and shape-memory properties based on lignin ramification. Importantly, this lignin/elastomer composite showed excellent mechanical properties as a result of the synergistic effect of the lignin domains and sacrificial coordination bonds (Figure 4b). In addition, remote control and targeted activation are fascinating characteristics for self-healing SMPs, and they can be facilitately realized by incorporating photothermal conversion fillers into the matrix. NIR light and heat-triggered SMEs and controllable self-healing performance were demonstrated by Wang et al. [171] in a CNTs-graft-poly(tetrahydrofurfury methacryla-co-lauryl acrylate-co-1-vinylimidazole) copolymer via the association and dissociation process of the supramolecular connections between VI and Zn^{2+} under the photothermal conversion of CNTs (Figure 4c), which exhibited self-healing capacities both under heating and NIR light-actuating, and the healing efficiencies of tensile strength reached 93.2% at 60 °C for 4 h and 83.6% within 60 s, respectively.
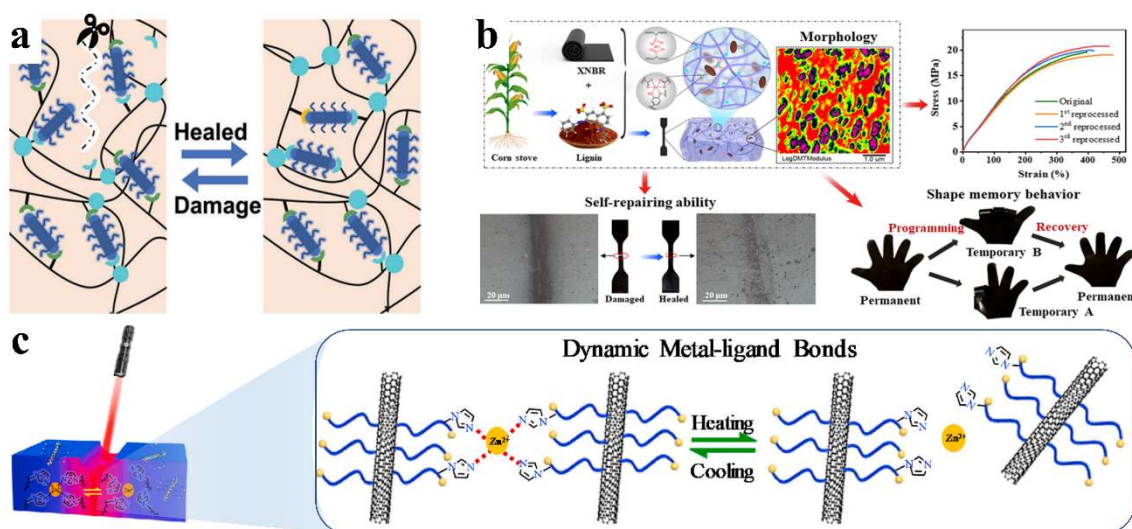
Figure 4. Biobased SMPs with self-healing capacity based on dynamic noncovalent bonds. (**a**) Schematic illustration of the self-healing mechanism based on hydrogen bonds [169] (Copyright 2022 Wiley-VCH Gmbh). (**b**) Ionomeric elastomer composites based on lignin ramification [170] (Copyright 2022 American Chemical Society). (**c**) Illustration of the association and disassociation process of Zn^{2+}/VI metal-ligand bonds in response to NIR light stimulus [171] (Copyright 2021 Elsevier Ltd).

Recently, various dynamic covalent bonds have been explored to create versatile vitrimers [172] or covalent adaptable networks (CANs) [173] that may possess self-healing, reprocessiable and recyclable features. Concerning biobased SMPs, it is crucial to well-adapt the dynamic bond with functional groups in biobased monomers as well as the resultant products. The exchangeable ester bond is one of the most favorable dynamic bonds used in vitrimers or CANs, including biobased shape memory systems. Feng et al. [174] prepared a series of biobased vitrimers with self-healable, recyclable and multiple responsive properties, via transesterification reaction between epoxy natural rubber (ENR) and dodecanedioic acids with the presence of aniline trimer (ACAT) (Figure 5a), and the authors verified that ACAT played a role of catalyst for transesterification reactions to ensure the reconfiguration of network topology and also accelerate the self-healing process, resulting a self-healing efficiency of 80% in the hot stage at 200 °C for 30 min according to the recovery ratio of tensile energy. In another example, a fully biobased vitrimer deriving from epoxidized soybean oil (ESO) and fumaropimaric acid (FPA) was produced by reacting the rich epoxy groups of ESO with the anhydride and carboxyl groups [175], the resultant transesterification-based ESO-FPA vitrimer equipped excellent self-healing and shape-memory properties (Figure 5b). Recently, a dynamic boronic ester bond was chosen to construct multifunctional networks from sustainable Eucommia ulmoides gum [176]. The obtained network is crystalline and owns a wide range of melting temperature that allows it to exhibit two-way shape-memory behavior whether under constant stress or stress-free conditions. Meanwhile, the dynamic characteristic of the boronic ester bond endows it with an excellent self-healing efficiency of tensile strength near 100% at 80 °C for 12 h, and the incorporating multiwalled carbon nanotubes enable the formed composite to respond to NIR light (Figure 5c). Li et al. [177] prepared TA-based polyurethane networks (TA-PU) with dynamic phenol-carbamate via reacting biobased monomer tannic acid (TA) with isocyanate groups. The target TA-PU not only displayed powerful shape-memory performance but also showed a good balance between robust mechanical properties and high self-healing efficiency (the tensile strength recovered 91.2% after healing at 120 °C for 2 h) (Figure 5d).

Although self-healing polymers can repair mechanical damage autonomously, difficulties remain in achieving efficient and repeatable recovery of multiple forms and structures of damage. There is an auxiliary strategy to promote healing that takes advantage of the shape memory effect to make the damaged interface contact with each other (Figure 6) [178,179]. Taking advantage of the change in chain segment conformation and viscoelastic characteristics of the glass transition process in SMPs may potentially allow materials to be equipped a sufficient molecular mobility for gradual self-closure and self-healing of damages under the appropriate stimulation. This shape memory-assisted self-healing strategy was also demonstrated in biobased systems. Lu et al. [180] prepared a biobased sustainable shape-memory and self-healing elastomer with the semi-interpenetrating network by green bulk radical polymerization of furfural, ethyl cellulose and fatty-acid-derived monomers. The prepared elastomers exhibited excellent multiple shape memory effects owing to a broad glass transition of semi-interpenetrating polymer networks. More importantly, the SMEs promoted the diffusion and rearrangement of molecular chains at the crack interfaces and led to a significant enhancement of healing efficiency, e.g., 81.2% of healing efficiency of the elongation at break at 80 °C for 5 min. Fu et al. [178] reported a biobased polymer with shape-memory effect and self-healing performance based on poly(propylene carbonate) and microfibrillated cellulose, the authors also verified that the composites with good shape memory ability also showed excellent scratch resistance and scratch self-healing behavior (the elongation recovered almost completely in oven at 60 °C).
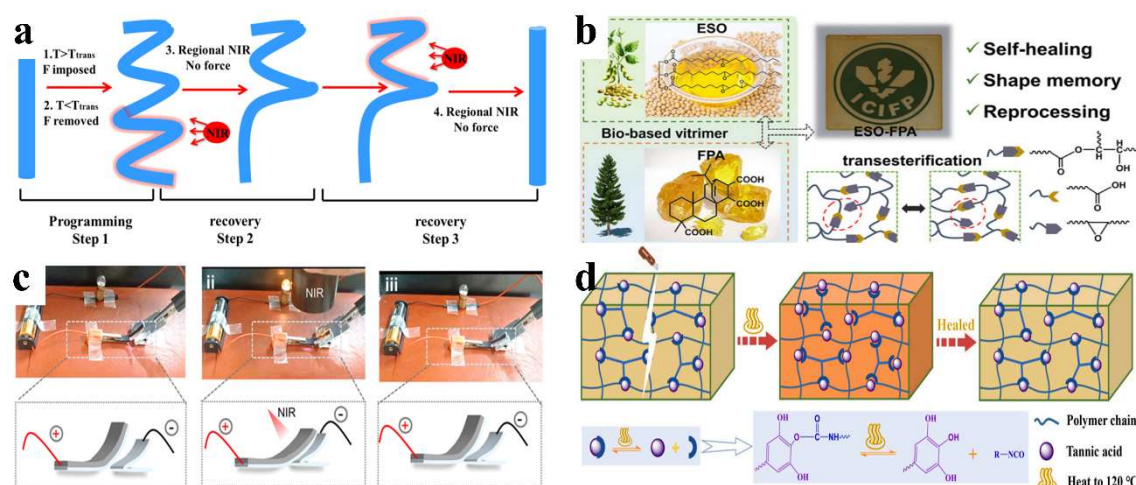
Figure 5. Biobased SMPs with the self-healing capacity based on dynamic covalent bond. (**a**) Mechanism of NIR-induced multistage shape recovery performance based on transesterification reactions [174] (Copyright 2018 American Chemical Society). (**b**) The ESO-FPA biobased vitrimer equipped with excellent self-healing and shape-memory properties [175] (Copyright 2019 Elsevier Ltd). (**c**) Schematic illustration for the preparation of the NIR light-driven switch [176] (Copyright 2023 American Chemical Society). (**d**) Schematic mechanism of the thermally induced self-healing behavior based on dynamic phenol-carbamate [177] (Copyright 2021 Elsevier Ltd).
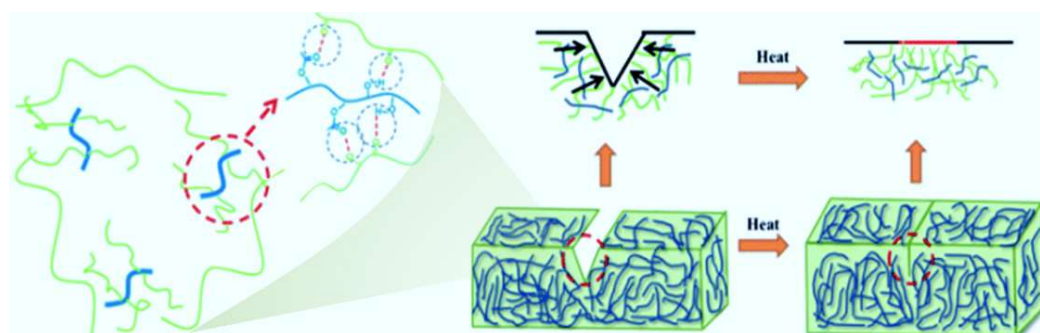

Figure 6. Schematic illustration of the shape-memory-assisted self-healing concept [178] (Copyright 2014 Royal Society of Chemistry).

5. 4D Printing Biobased SMPs

　　3D printing technology, as known as additive manufacturing, is committed to fabricating complex three-dimensional structures based on computer-aided design technology that is beyond the capacity of traditional manufacturing methods. In 2013, a new term "4D printing" was first proposed by Skylar Tibbit at a TED talk [181]. Compared with 3D printing, 4D printing increases the dimension of time which can be achieved by shape and property changes of 3D objects depending on time. Although 4D printing is developed from 3D printing, the most significant characteristic that distinguishes it from 3D printing endows a dynamic intelligent response deformation for static 3D objects. At present, 4D printing is a highly functional and refined technology, in which different printing devices and approaches adapt to the optimal structure of differentiated material properties [182]. These manufacturing methods include fused deposition modeling (FDM), direct ink-writing (DIW), stereolithography (SLA), digital light processing (DLP), and selective laser sintering (SLS) [183]. With the development of 4D printing technology, SMPs have once again ushered in optimized technological innovations and a wide range of applications. Printed SMP objects have a wide range of potential applications in biomedical devices [184–187], flexible electronic devices [188], smart actuators [189], smart wearable devices [190], and aerospace [191].

　　Biobased shape memory objects based on 4D printing in many vital fields also have significant advantages. With the demand increase for 3D printed downstream products in different industry fields, functionalized materials have been introduced into 3D printing processes. FDM is a convenient technology to print thermoplastics, and biobased SMPs are no exception. PLA is a typical thermoplastic that can be printed by FDM. Hua et al. [192] fabricated photo-responsive actuators based on PLA and multi-walled carbon nanotubes via FDM printing (Figure 7a). FDM was also employed to print the PLA/PCL-based bio-polyurethanes [193], and a moderate cross-linking was established by using chitooligosaccharide (COS) to promote the microphase-separated structure, which resulted in a desirable printability and presumptive shape memory behavior (Figure 7b). However, FDM still has inevitable disadvantages, since the interlayer force of printed materials only depends on a physical interaction that brings the apparent anisotropy of mechanical properties. In our previous work [194], we put forward a UV-assisted FDM strategy to print fully biobased shape memory copolyesters derived from biobased monomers dimethyl itaconate, dimethyl sebacate, and 1,4-butanediol, the in-situ photo-crosslinking during the FDM printing greatly enhanced the interlayer adhesion, and thus, the printed object displayed a good mechanical performance with low anisotropy effect, as well as a desirable SMEs as an overheat protection carrier (Figure 7c).
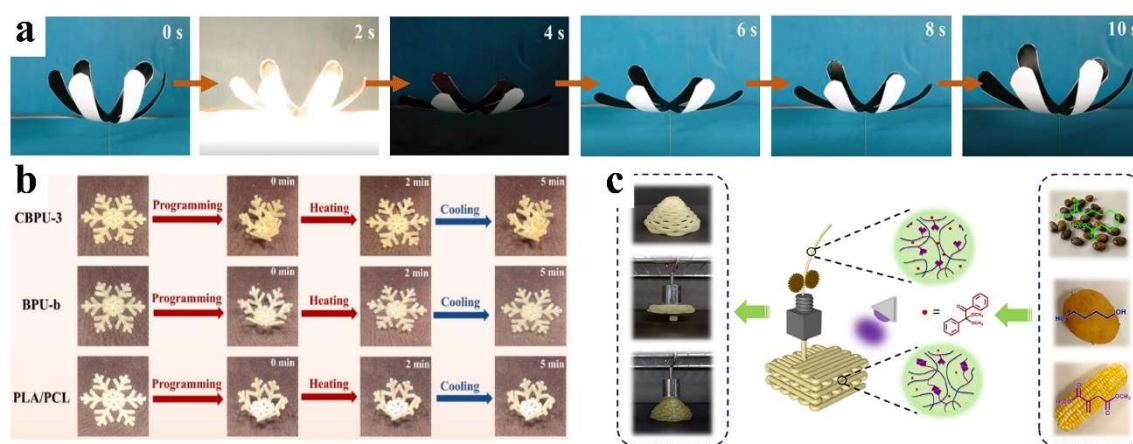
Figure 7. Application of 4D printing biobased SMPs. (**a**) Shape recovery process of the actuator under near-infrared irradiation and recovery to the original shape [192] (Copyright 2018 Royal Society of Chemistry). (**b**) Thermal stimulus-response process of 4D printed snowflake models [193] (Copyright 2022 Elsevier Ltd). (**c**) 4D printed objects of fully biobased shape memory copolyesters [194] (Copyright 2022 American Chemical Society).

4D printing exhibits great advantages in the manufacture of biomaterials or biomedical devices, especially in the personalized customization and precise control of implantation structures. Furthermore, invasive surgery generally desires to avoid an open surgical wound, while the stimulus-response deformation of SMPs is considered to be the most promising approach [195]. In general, biomedical devices require excellent biocompatibility, biodegradability, suitable mechanical property, low biotoxicity, and even no toxicity. PLA and its ramifications are the most widely used 4D printing substrates [196]. Leng et al. [197] designed a series of biobased and remotely controllable shape memory occlusion devices by FDM printing technology (Figure 8a), which achieved a self-expanded performance after minimally invasive implantation under a certain strength magnetic field. A similar material was applied in bone repair to match the complex bone defect shape (Figure 8b) [73] and bioinspired tracheal scaffold combined with 4D printing (Figure 8c) [198]. FDM also can be used to print the sacrificing materials for porous scaffolds. Zhang et al. [199] fabricated a cytocompatibility porous scaffold based on biobased castor oil/PCL copolyester by removing a FDM printed PLA sacrificing materials from the cured matrix to simulate the nonuniform distribution of porosity found within natural tissues, and the resultant scaffold displayed enhanced attachment, proliferation, and differentiation. The authors also developed a smart biomedical scaffold from photocurable biobased soybean oil epoxidized acrylate using an SLA printing strategy. The obtained scaffold showed good biocompatibility and SMEs that can be triggered by body temperature (Figure 8d) [200]. Moreover, the remote responsive SMPs have significant advantages in precise control compared with body temperature stimulation. Graphene oxide functionalized polybutylene succinate/PLA biobased materials (GO-PBS/PLA) showed attractive photothermal performance under near-infrared irradiation, and the printed porous scaffold confirmed the feasibility of precise and remotely controllable structure transformation (Figure 8e) [201].
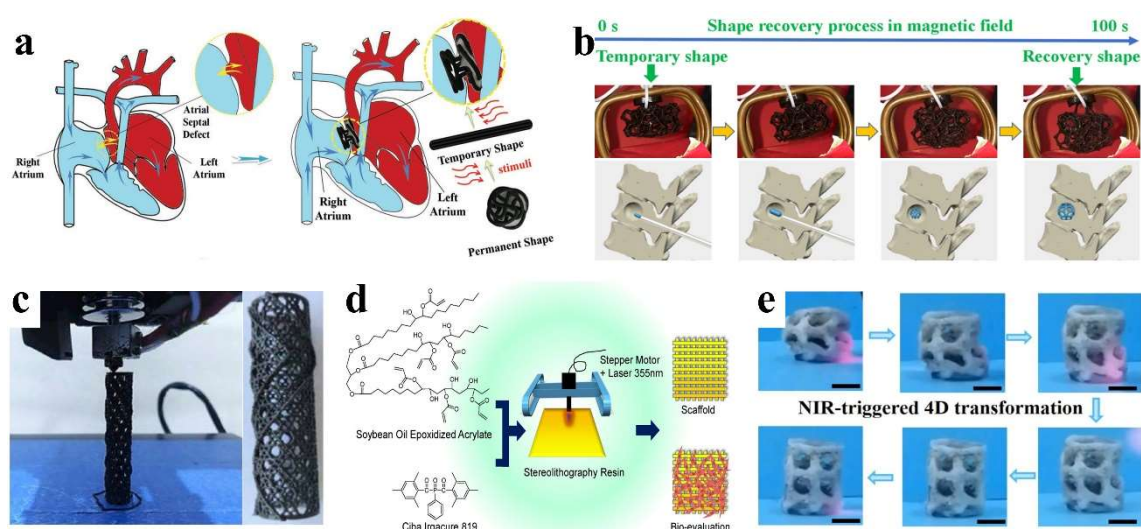
Figure 8. Biomedical application of 4D printing biobased SMPs: (**a**) 4D printed biodegradable and remotely controllable shape memory occlusion devices [197] (Copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim). (**b**) 4D printed structures in the shape of spinal bone defect [73] (Copyright 2019 Elsevier Ltd). (**c**) 4D printing of bioinspired tracheal scaffold [198] (Copyright 2019 Elsevier Ltd). (**d**) Schematic of soybean oil epoxidized acrylate fabrication process from raw material through resin fabrication and application [200] (Copyright 2016 Springer Nature). (**e**) the precise and remotely controllable transformation process of GO-PBS/PLA porous scaffold [201] (Copyright 2021 Elsevier Ltd).

6. Summary and Outlook

The extensive research on SMPs greatly enriches their molecular mechanisms, stimulus types, and actuating mode, and has resulted numerous fascinating systems, which exhibit tremendous potential in actuators, sensors, smart textiles, biomaterials and space deploying devices. While the main trend at present is focused on the structure, performance and application of SMPs, we should not ignore the increasing demand for more sustainable materials, since the environment and resources are globally crucial issues. Creating SMPs from sustainable and renewable resources become an important development concept, which draws the great interest of researchers. The recent fast development of the industrialization for biobased monomers, provides various building blocks for biobased SMPs. For instance, versatile biobased polyesters, polyurethanes, epoxies, and vitrimers have been developed, which show promising application prospects in general materials as well as the biomaterials field. Nevertheless, the present biobased SMPs are far away from the practical demands, and several challenges still need to be addressed in the future, including exploring adaptive biobased monomers, more economical synthesis routes, rational tailoring of the architecture of SMPs, and establishing more facile manufacturing strategies.

Author Contributions

References collection, K. Luo, Z. Y. Xu and R. Zhan; Writing – Original Draft Preparation, K. Luo, Z. Y. Xu and R. Zhan; Writing – Review & Editing, K.K. Yang; Funding Acquisition, K.K. Yang.

Ethics Statement

Not applicable.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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