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Sustainable Bioplastic Made from Biomass DNA and Ionomers

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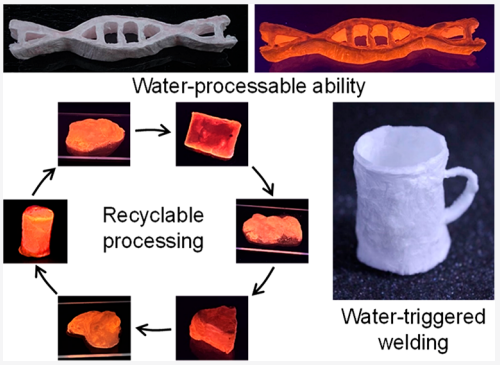
ABSTRACT: Plastics play important roles in modern life and currently the development of plastic recycling is highly demanding and challenging. To relieve this dilemma, one option is to develop new sustainable bioplastics that are compatible with the environment over the whole material life cycle. We report a sustainable bioplastic made from natural DNA and biomass-derived ionomers, termed as DNA plastics. The sustainability involves all aspects of the production, use, and end-of-life options of DNA plastics: (1) the raw materials are derived from biorenewable resources; (2) the water-processable strategy is environmentally friendly, not involving high-energy consumption, the use of organic solvents, and the production of byproducts; (3) recyclable and nondestructive use is achieved to significantly prolong the service lifetime of the plastics; and (4) the disposal of waste plastics follows two green routes including the recycling of waste plastics and enzyme-triggered controllable degradation under mild conditions. Besides, DNA plastics can be "aqua-welded" to form arbitrary designed products such as a plastic cup. This work provides a solution to transform biobased hydrogel to bioplastic and demonstrates the closed-loop recycling of DNA plastics, which will advance the development of sustainable materials.



INTRODUCTION

Polymers commonly called plastics are key components of almost all modern technologies. Environmental concerns caused by the production, use, and end-of-life options of plastics are becoming more and more severe due to global plastic pollution.[1,2] Raw materials of plastics are mainly distilled from nonrenewable petrochemicals, and the distillation process requires a lot of energy with mass production of greenhouse gases and toxic byproducts.[3] Every year around 51−88 million tons of waste plastics accumulate in the environment globally, and the accumulation quantity is increasing at an alarming rate year by year.[4,5] Current disposal methods including landfilling (79%) and incineration (12%) lead to serious pollution of the agricultural environment and produce toxic substances that deplete the ozone layer.[2,6] When plastics are landfilled, the degradation of plastics generally requires more than 450 years. Moreover, microplastics produced from the incomplete degradation of plastics have contaminated all compartments of ecosystems across different trophic levels.[7] For example, microplastics have been found in many organisms, such as bivalves, fish, and mammals, which will be ultimately harmful to human health.[8,9]

One option to relieve the dilemma is to develop sustainable materials that are compatible with the environment over the whole material life cycle.[10,11] Previous studies have focused on the recycling of petrochemical-based plastics and improving the added value of waste plastics, which have strong practical significance.[12−16] For the long run, developing sustainable biobased plastics will be a satisfactory choice to reduce the dependency on nonrenewable petrochemicals and follow the principles of green chemistry and engineering in service of a sustainable society. Despite the fact that a variety of bioderived raw materials, such as cellulose,[17,18] starch,[19] plant oil,[20] chitosan,[21] and protein,[22] have been developed into bioplastics, the production, use, and end-of-life options of these bioplastics fail to follow the principles of green chemistry and engineering. For example, the processing generally requires high temperature, hot pressing, and the use of organic solvents.[1,23] Although these bioplastics are generally degraded under natural conditions, the recycling and reuse of bioplastics in a green and low energy-consumption mode remain a challenge, resulting in the severe waste of biological resources after the end-of-life usage of bioplastics.[1,24] Recycling plastics for reuse could save more energy as compared to processing raw materials: 1 ton of recycled plastics saved up to ∼130 million kJ of energy.[25] Current recycling methods generally require high temperature, strong acid/alkali conditions, and the use of catalysts generating reactive species, which might bring inevitable risks on the decrease of mechanical properties and recyclability of plastics.[15,25−27] Moreover, current bioplastics

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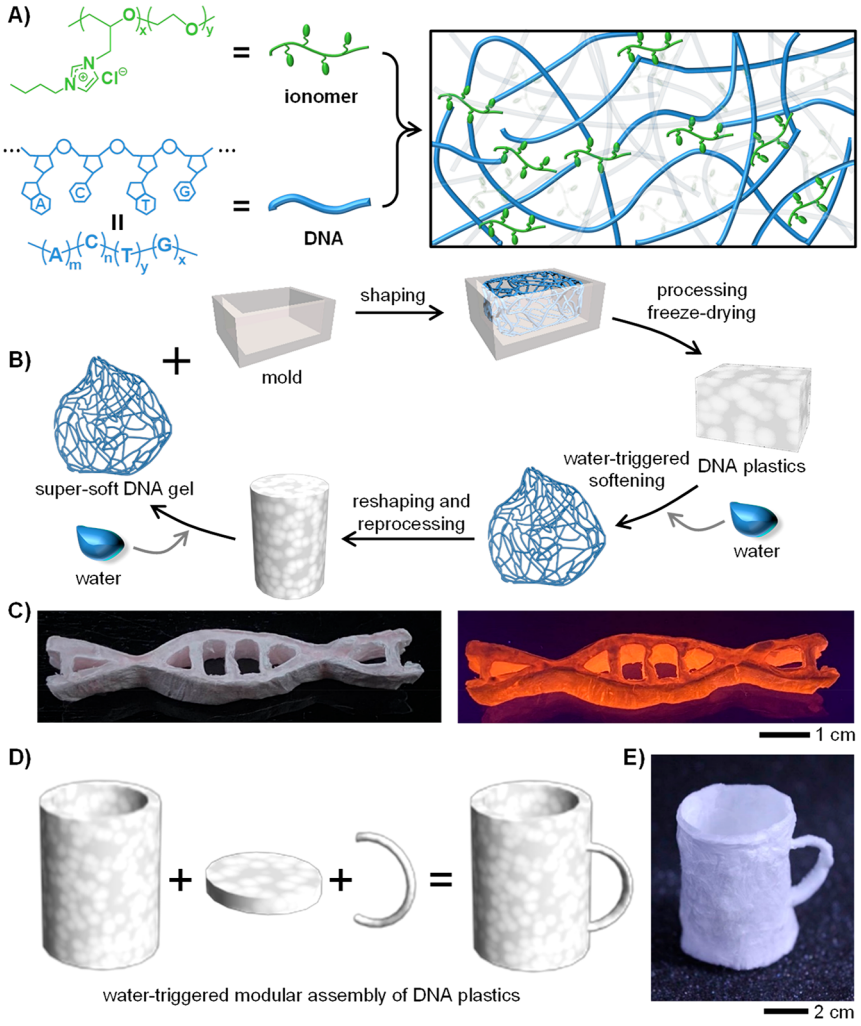

Figure 1. Design and preparation of sustainable DNA plastics. (A) Scheme of the formation of DNA/ionomer hydrogel networks. (B) Scheme of the recyclable use of DNA plastics. (C) Digital photos of DNA plastics with the shape of double helix structure of DNA. The wavelength of UV light was 312 nm. (D) Scheme of the modular assembly process to form a plastic cup. (E) Digital photo of a plastic cup. Without special explanation, DNA plastics were stained green and red by SYBR Green I and GelRed, respectively.

are mainly derived from crops, resulting in competion with agricultural resources such as farmland and water.[28]

In recent decades, DNA has been utilized as functional macromolecules for the construction of a variety of polymeric materials including DNA hydrogels, dendrimer-like DNA, and DNA nanoparticles that are structurally programmable and biodegradable.[29−32] Moreover, DNA is an inexhaustible biopolymer, which can be extracted from any organisms including plants, animals, and microorganisms. The total amount of DNA is approximately 50 billion metric tons on Earth.[33] We expect that if DNA is developed into bioplastics, the increasing demand of plastics that has reached 348 million metric tons/year will be effectively relieved in theory.[34] Herein, we create sustainable DNA plastics that are compatible with the environment: (1) all raw materials are derived from biorenewable resources; (2) processing approaches are environmentally friendly, not involving high-energy consumption; (3) recyclable and nondestructive use is achieved to significantly prolong the service lifetime of plastics; (4) the disposal of waste plastics follows two green routes including the recycling of waste plastics and enzyme-triggered controllable degradation under mild conditions. To the best of our knowledge, our reported DNA plastics are the most environmentally sustainable materials of any other known plastics.

RESULTS

Design and Preparation of Sustainable DNA Plastics.

Generally, polymers were hot-pressed into plastics, which required high temperature to melt and process polymers. This was a high-energy consumption process, involving the rupture of polymer chains and the decrease of plastic quality.[26,27] We herein propose a quite different freeze-drying process to transform physically cross-linked DNA hydrogels into sustainable DNA plastics, which is a relatively low-energy-consumption process. To prepare physically cross-linked DNA gels, elastomeric ionomers served as macromolecular cross-linkers (2.2×10^5 Da) which mediated the assembly of salmon sperm DNA (1.2×10^7 Da) to form DNA networks (Figure 1A). Cationic groups of ionomers interacted with phosphate groups of DNA driven by electrostatic attraction, meanwhile hydrocarbon chains of ionomers interacted with DNA bases through hydrophobic interactions.[35]

As one component of DNA plastics, elastomeric ionomers were synthesized through the introduction of ionic groups to elastomers, which have attracted recent attention for various

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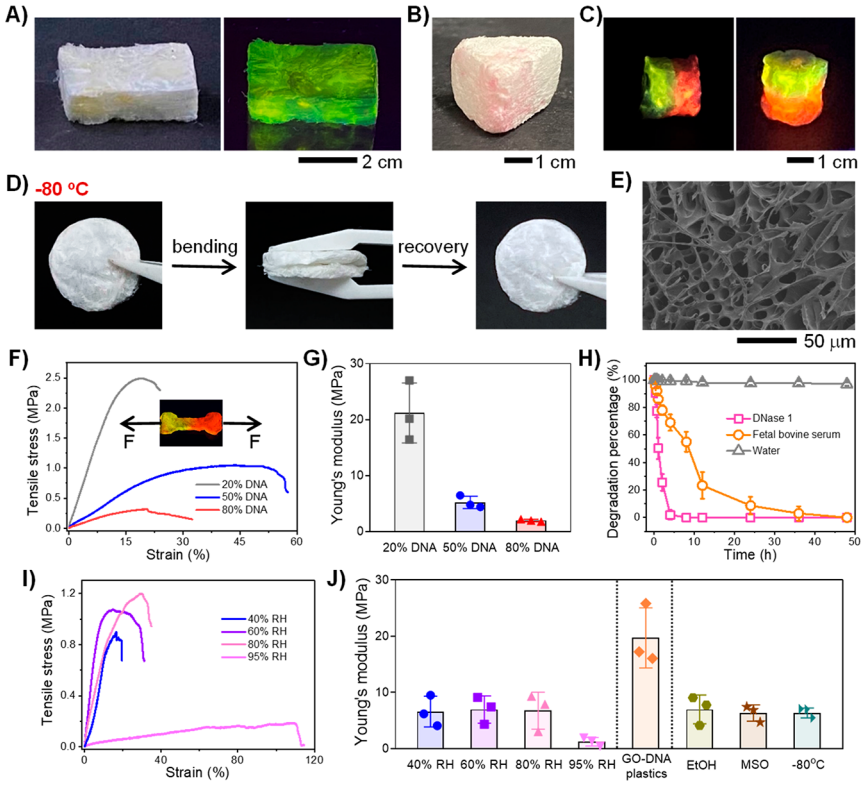

Figure 2. Characterization and performance of sustainable DNA plastics. (A–C) Digital photos of DNA plastics with different shapes: (A) cuboid; (B) triangular prism; and (C) cylinder. The wavelength of UV light was 312 nm. (D) Digital photos of the bending and recovery process of plastics at −80 °C. (E) Scanning electron microscope (SEM) image of plastics. (F) Tensile stress–strain curves of plastics with different DNA contents. (G) The Young's modulus of plastics. Results are presented as means ± standard deviation (SD) (n = 3). (H) Degradation curves of plastics in different conditions including DNase I, fetal bovine serum (FBS), and water. Results are presented as means ± standard deviation (SD) (n = 3). (I) Tensile stress–strain curves of plastics incubated at different relative humidity (RH) levels for 3 days. (J) The Young's modulus of plastics incubated at different conditions for 3 days. Results are presented as means ± standard deviation (SD) (n = 3).

applications such as biomedicine and energy science.[36,37] In this design, poly(epichlorohydrin-*co*-ethylene oxide) (ECO)-based ionomers were synthesized by the one-pot quaternization reaction between ECO and 1-butylimidazole, in which 1-butylimidazole acted as both reactants and green solvents (Figure S1A of the Supporting Information, SI). During the whole preparation process of DNA plastics, ethyl ether was the only organic solvent used as a precipitant for the purification of ECO-based ionomers. Both ^{13}C NMR and ^{1}H NMR results demonstrated the synthesis of ECO-based ionomers with the grafting rate of 46.8% (Figure S1B,C). Our choice of ECO-based ionomers was mainly based on two considerations: (1) ECO was a renewable and biomass-derived elastomer, which has been brought into the market; (2) the chloromethyl group of ECO provided a highly reactive site to synthesize water-soluble ionomers.[38]

Freeze-drying was utilized to process DNA plastics (Figure 1B). First, supersoft DNA gels were prepared and conformed to the shape of a mold. Freeze-drying was then applied to transform DNA gels to shaped plastics through removing remaining water under vacuum conditions. As a demonstration, a DNA plastic with the shape of the double helix structure of DNA was prepared (Figure 1C). Under ultraviolet light, DNA plastic that was stained by a DNA-specific dye (GelRed) showed bright red fluorescence, demonstrating that the entire plastic was composed of DNA. In practical use, the deformation, damage, and aging of plastics were inevitable, severely shortening the service lifetime of plastics.[2,15] Recyclable and nondestructive use of plastics was thus urgently required; and remarkably, our DNA plastics could achieve this goal! We used water, the greenest solvent, to soften DNA plastics to form shapeless gels. Afterward, DNA gels were reprocessed to plastics with arbitrary shape through freeze-drying, such as reprocessing DNA plastics to cuboidal to cylindrical shapes (Figure 1B). Previous studies have demonstrated that freeze-drying could preserve molecular structures of polymers without the rupture of polymer chains.[39]

To process DNA plastics with three-dimensional (3D) architectures, a water-triggered modular assembly strategy was proposed (Figure 1D). As a demonstration, a DNA plastic cup was successfully prepared (Figure 1E). First, three structural parts of a plastic cup, including the handle, base, and body were separately processed through freeze-drying. Afterward, a little water was coated at the joints of these parts to soften plastics, making the DNA networks at the joints show a liquid-like nature to promote the assembly process. After allowing the plastic cup to air-dry for 2 min, a self-standing and stable DNA plastic cup was prepared.

Characterization and Performance of Sustainable DNA Plastics. DNA plastics could be processed into arbitrary shapes such as cuboid, triangular prism, and cylinder (Figure 2A–C). Cuboid-shaped plastic was stained by SYBR Green I and showed bright green fluorescence under ultraviolet light (Figure 2A). Further, a bicompartmental cylinder made from DNA plastics was processed, in which one-half was loaded with

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SYBR Green I, and another half was loaded with GelRed. Under ultraviolet light, two compartments of the cylinder were spatially segregated, showing two different fluorescent colors (Figure 2C). Such multicompartmental materials loaded with different compositions were of importance in many fields, such as sensing, drug delivery, and tissue engineering.[40] We next investigated the effects of types of functional groups of ionomers on the formation of DNA plastics (Figure S2). Increasing the charge density of ionomers was favorable to the formation of DNA plastics, however increasing the hydrogen-bond density of ionomers would result in self-gelation of ionomers, blocking subsequent cross-linking reactions with DNA to form plastics.

DNA plastics showed good folding recoverability even at low temperature (−80 °C), which has great potential for applications in electronic skins and soft robots under extreme cold weather conditions.[41] This property was totally different from petrochemical plastics that showed limited folding capacity. In other words, DNA plastics behaved like polymeric rubbers in terms of folding recoverability. A cylinder-shaped plastic could be bent to a large degree (180°) without tearing at −80 °C and 25 °C, and then perfectly recovered its original shape (Figures 2D and S3A). To further demonstrate the folding recoverability, the plastic was bent to 180° and then immersed into liquid nitrogen (−196 °C) to fix the folded shape for 10 min. When plastic was taken out from liquid nitrogen, shape recovery of the folded plastic was achieved (Figure S3B). To characterize the micromorphology of plastics, scanning electron microscopy (SEM) was conducted and the results confirmed the formation of 3D porous structures (Figures 2E and S4A). It was inferred that 3D porous structures were responsible for the good folding recoverability.[41] Mechanical performance of plastics could be rationally regulated by altering DNA contents (Figure 2F). When DNA contents decreased from 80%, 50% to 20%, Young's modulus increased from 2.0 MPa, 5.2 to 21.2 MPa, respectively (Figure 2G). Although Young's modulus increased 10 times by decreasing DNA contents from 80% to 20%, the toughness of DNA plastics was compromised (Figure 2F). DNA content was thus fixed as 50% to prepare plastics with balanced mechanical strength and toughness. To investigate the fracture mechanism, SEM was conducted, and the results indicated that crack propagation of 3D porous structures was responsible for the fracture of plastics (Figure S4B). To prove the applicability of DNA plastics, surface hardness, impact, and flexural performance were measured. Surface hardness was 42.16 ± 3.26 KPa, impact strength was 7.27 ± 1.49 KJ/m^2, and flexural strength was 2.73 ± 0.13 MPa.

Controllable degradation was critical for the end-of-life options of plastics.[1] Unlike other bioplastics that required multiple bioenzymes to achieve complete degradation in a relatively long time (from months to years),[17−19,28] DNA plastics could be specifically and rapidly degraded in a controllable fashion when exposed to DNA digesting enzymes. To investigate the degradation kinetics, plastics were coincubated with DNase I (DNA digesting enzyme, 5U/μL), fetal bovine serum (FBS) containing DNA digesting enzymes and water at 37 °C for 48 h (Figure 2H). In DNase I solution, the degradation time was approximately 4 h, while the degradation time increased to 36 h in FBS. As a control, DNA plastics incubated in water did not degrade in 48 h. To verify the dimensional stability, a cylinder-shaped DNA plastic was incubated at room temperature for 2 months. The results indicated that the plastic maintained its original shape without degradation in 2 months (Figure S5A,B). Considering the excellent stability of DNA in a dry state,[42] we believe that DNA plastics could maintain the dimensional stability over a longer time period. To verify the effects of UV radiation on the stability and recyclability of DNA plastics, a triangular prism-shaped DNA plastic stained by GelRed was subjected to UV radiation for 40 min in a closed chamber. The radiation intensity was 1.5 W/cm^2, which was strong enough to destroy DNA structures in solutions.[42] Moreover, the radiation intensity was 10 000 times higher than that from sunlight.[43] Within 40 min, shape deformation and rigidity change were not observed, demonstrating the good durability of DNA plastics under UV radiation (Figure S5C). The enhanced resistance to UV radiation was probably derived from two aspects: (1) ionomers provided protection for biomass DNA; (2) DNA in a dry state decreased the production and transfer of UV-mediated free radicals.[42] Further, a triangular prism-shaped DNA plastic subjected UV radiation could be recycled to prepare a new DNA product, demonstrating the good recyclability of DNA plastics (Figure S5D). To verify the biocompatibility of DNA plastics, a cytotoxicity test was conducted. The results confirmed the high biocompatibility of DNA plastics (Figure S6A). Moreover, DNA plastics could be used as a cell culture matrix for cell growth (Figure S6B).

We noticed that water was able to soften DNA plastics. To confirm whether DNA plastics were stable under moist conditions, plastics were incubated at different relative humidity (RH) levels (40%, 60%, 80% and 95%) for 3 days and then tensile tests were conducted (Figure 2I). The plastics showed very similar Young's modulus when RH levels increased from 40% to 60% to 80% (Figure 2J). Generally, the RH level was approximately 80% in a rainy day, which demonstrated the stability of plastics even in a rainy day. When the RH level reached 95%, the Young's modulus decreased from 6.6 MPa (40% RH) to 1.3 MPa, indicating the softening of plastics under 95% RH level. Under this condition, the elongation at break of plastics increased from 21.2% (40% RH) to 110.2% (95% RH), due to the toughness enhancement of softened plastics. Unlike petrochemical plastics that were unstable and even dissolved in organic solvents,[44] DNA plastics were stable in polar solvents such as ethanol (EtOH) and nonpolar solvents such as petroleum ether (MSO). When plastics were immersed in EtOH and MSO for 3 days, the Young's modulus almost did not change, suggesting that organic solvents had negligible effects on the mechanical performance (Figure 2J). Similarly, the low temperature environment (−80 °C) did not affect the mechanical performance of plastics (Figure 2J). Besides, to enhance the mechanical strength, graphene oxide (GO, 0.01%) was doped into DNA plastics, and the results demonstrated that Young's modulus of GO-doped plastics increased by 3 times reaching to 19.7 MPa compared with pristine DNA plastics (Figures 2J and S7). It was inferred that GO was able to block crack propagation of 3D porous structures, thus enhancing the mechanical performance of plastics.[45]

Recyclable Processing and Reuse of DNA Plastics. Recyclable use of plastics was a fascinating feature to significantly extend the service lifetime and effectively relieve white pollution.[15,25,46] Considering that water was able to soften DNA plastics, we proposed a mild recyclable strategy to use water instead of high temperature to achieve the mobility of polymeric DNA chains, which enabled the processability of

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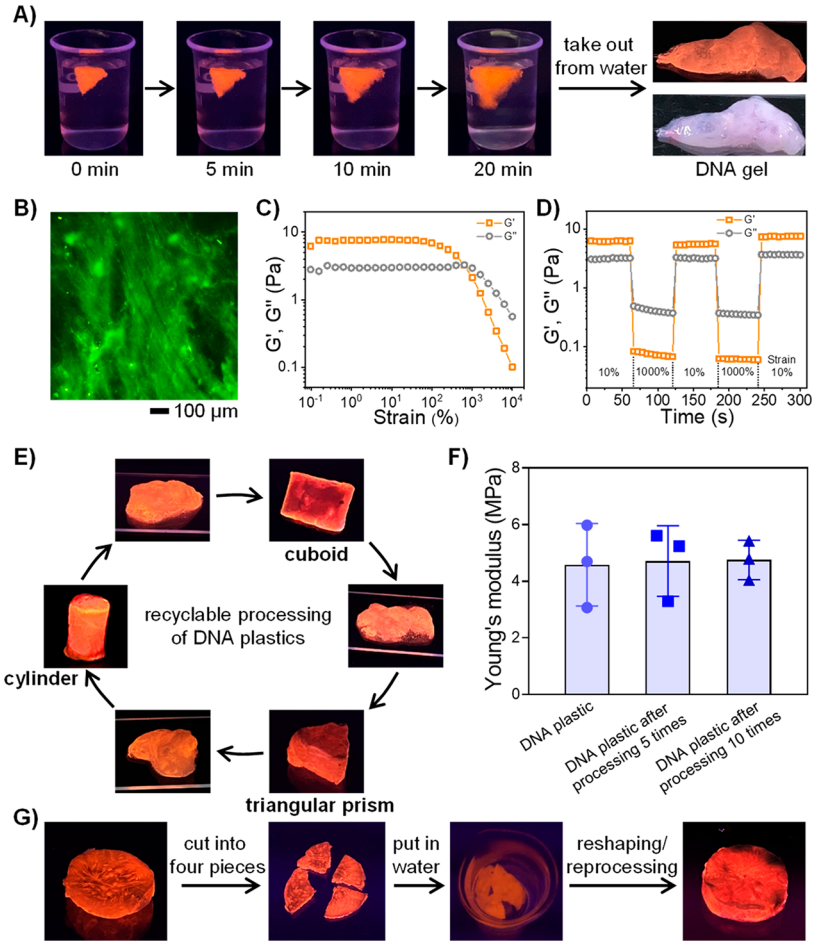

Figure 3. Recyclable processing and reuse of DNA plastics. The wavelength of UV light was 312 nm. (A) Digital photos of the softening process of plastics in water. (B) Fluorescence image of DNA gels stained by SYBR Green I. (C) Storage modulus (G') and loss modulus (G'') of DNA gels as a function of strain. (D) Recovery properties of DNA gels by successively applying alternating low (10%) and high (1000%) strain conditions. (E) Digital photos of the recyclable processing of plastics from cuboid, triangular prism to cylinder. (F) Young's modulus of plastics after reprocessing 5 and 10 times. Results are presented as means ± standard deviation (SD) (n = 3). (G) Digital photos of processing 4 pieces of broken plastics into a cylinder-shaped plastic.

plastics for different shapes. To investigate the softening process of plastics, a triangular prism-shaped plastic was immersed into water. The results indicated that the swelling of plastics occurred and gradually transformed to shapeless gels in 20 min (Figure 3A). The gels could be stained green by SYBR Green I (Figure S8A). Under fluorescence microscopy, gels showed oriented microstructures induced by the cover glass during the sample preparation, demonstrating the easy processing characteristics of gels (Figures 3B and S8B). It was inferred that the supersoft property of gels was responsible for the easy processing characteristics. To verify the supersoft property, rheological tests were conducted. Under the strain sweep mode, the storage modulus (G') value was higher than the loss modulus (G'') value when the strain was less than 660%, which demonstrated the gel property (Figure 3C). When the strain was larger than 660%, the G'' value was higher than the G' value, indicating the liquid property. Notably, the G' value of DNA gels was only 6 Pa, demonstrating the supersoft mechanical strength. In our previous work, we have demonstrated that supersoft mechanical strength was a unique characteristic of DNA gels, which was difficult to be achieve with other polymeric hydrogels.[29,30] Generally, polymeric hydrogels showed relatively high mechanical strength, and the G' value was higher than 1000 Pa with a fixed shape.[29,47] Owing to the supersoft property, the gels formed by the softening of DNA plastics could be easily conformed to the shape of a new mold, which endowed DNA plastics with the ability of repeated processing. Besides, DNA gels showed recovery ability to keep their original gel states. To verify this point, two consecutive cycles at low (10%) and high (1000%) strain conditions were applied to DNA gels alternately. Although DNA gels maintained a liquid state ($G' < G''$) at 1000% strain for 60 s, the gels could rapidly recover the initial modulus at 10% strain (Figure 3D). Physically cross-linked DNA hybrid networks were responsible for the cyclic gel–liquid transition.[29,30]

To confirm the recyclable processing capability of plastics, one piece of DNA plastic was successively processed into different shapes from cuboid, triangular prism to cylinder (Figure 3E). We first prepared a cuboid-shaped plastic. After the water-triggered softening process, supersoft DNA gels were obtained and then processed into a triangular prism-shaped plastic through freeze-drying. Using this softening/reprocessing strategy, triangular prism-shaped plastic was continuously processed into different shapes from triangular prism, cylinder to the original cuboid. To verify whether the reprocessing process affected the mechanical performance of plastics, tensile tests were conducted. DNA plastics with reprocessing 5 and 10

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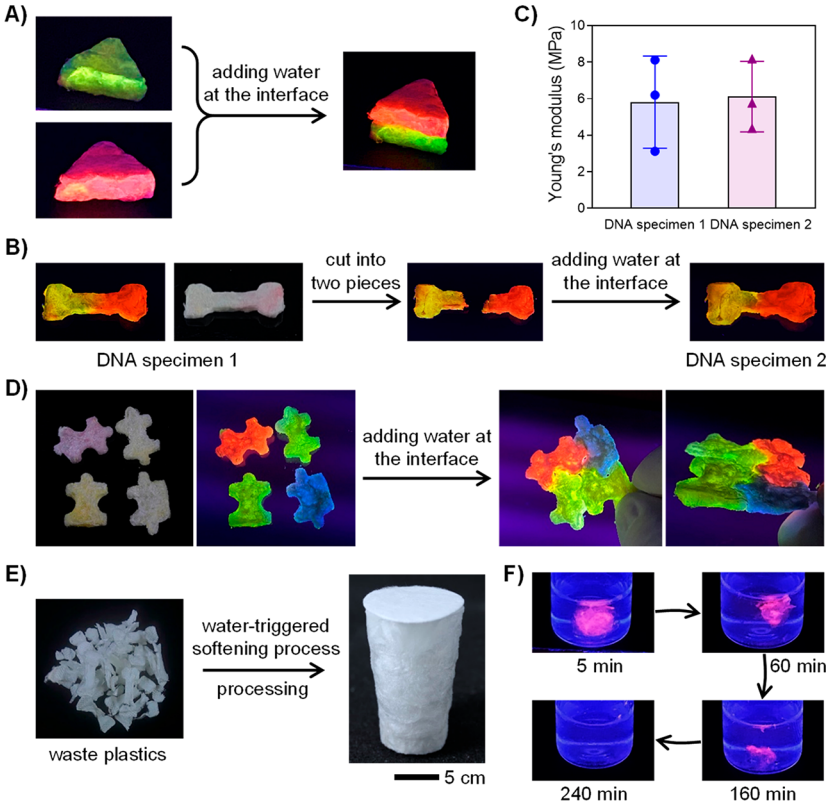

Figure 4. Healing and welding of sustainable DNA plastics to form 3D architectures using water. The wavelength of UV light was 312 nm. (A) Digital photos of the healing process of two pieces of triangular prism-shaped plastics that were stained green and red, respectively. (B) Digital photos of the healing process of a fractured dumbbell-shaped specimen. (C) Young's modulus of original and healed plastic specimens. Results are presented as means ± standard deviation (SD) (n = 3). (D) Digital photos of the healing process of four pieces of plastic puzzles. The puzzles were stained red, green, blue, and green by GelRed, SYBR Green I, carbon dots, and fluorescein, respectively. (E) Preparation of a plastic cup with a cover using waste DNA plastics. (F) Digital photos of the degradation of plastics in DNase I solution (5 U/μL).

times showed a similar Young's modulus compared to original plastics (Figure 3F). The results indicated that this softening/reprocessing strategy was nondestructive to achieve recyclable use of plastics. In practical use, the damage of plastics is inevitable, however, our DNA plastics could well address this issue. As a demonstration, we cut a cylinder-shaped plastic into four pieces (Figure 3G). Afterward, the four pieces were put into water to form supersoft DNA gels. Due to the strong physical interactions and mobility of DNA networks, different pieces of gels healed and formed an integrated gel network, which was further processed into a new cylinder-shaped plastic through freeze-drying.

Healing and Welding of Sustainable DNA Plastics to Form 3D Architectures Using Water. To prepare DNA plastics with complicated 3D structures, water-triggered modular assembly strategy was proposed. DNA plastics could be healed and welded to form 3D architectures using water. As a demonstration, we prepared two triangular prism-shaped plastics that were stained green and red, respectively (Figure 4A). A little water was added on the top surface of green plastic and then red plastic was lightly put on the green one to achieve healing at the interface. After air-drying for 2 min, a bicompartmental and triangular prism-shaped plastic was prepared. Using this strategy, multicompartmental plastics containing different compositions could be prepared for various applications. It was inferred that softened plastics exhibited liquid-like nature to promote the diffusion and mobility of dynamic DNA networks, thus promoting the healing process.[48,49] Further, we processed a DNA plastic specimen in the form of dumbbell shape to visually demonstrate the healing property (Figure 4B). One half of the specimen was stained green and another half was stained red. The specimen was then cut into two pieces. A little water was added at the fracture site to achieve the healing between the red specimen and green specimen. To verify whether the healing process affected the mechanical performance of plastics, the Young's modulus of the original and healed specimens was measured. Healed plastics showed similar Young's modulus compared with original plastics (Figure 4C). The results suggested that water-triggered healing process did not affect the mechanical performance of plastics. In addition, we prepared four pieces of plastic puzzles that were stained red, green, blue, and green, respectively (Figure 4D). Using a water-triggered assembly strategy, these plastic puzzles were stably spliced into an integrated plastic sheet.

End-of-life options of plastics were critically vital to relieve the surplus crisis of plastics and reduce the environmental burden.[50,51] Using this softening/reprocessing strategy, recycling and reuse of waste plastics were achieved. As a demonstration, we used waste plastics as raw materials to prepare a plastic cup with a cover (Figure 4E). If waste plastics were not recycled, then enzyme-triggered degradation of waste plastics under mild conditions was another environmentally friendly choice. Being treated with DNase I (5 U/μL), DNA plastics could be completely degraded in 4 h (Figures 4F and S9). In practical applications, FBS might be a convenient

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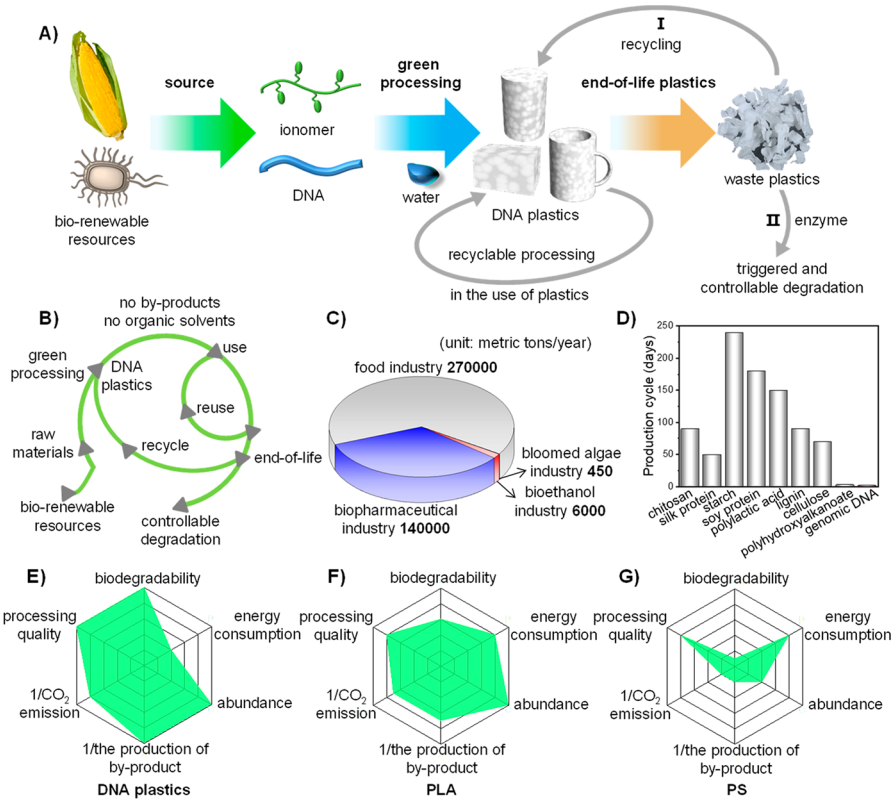

Figure 5. Future perspectives and challenges of sustainable DNA plastics. (A) Scheme of the production, use, and end-of-life options of plastics. (B) Scheme of the dual closed-loop recycling of plastics. (C) Global analysis of the productive potentials of DNA. (D) Analysis of the production cycle of DNA plastics and other biobased plastics. (E–G) Radar plots of DNA plastics (E), polylactic acid (PLA)[18,59] (F), and polystyrene (PS)[4,60] (G).

choice to completely digest DNA plastics in 36 h. Although the tendency of DNA plastics to rehydrate upon immersion in water hindered the direct comparison to petrochemical plastics in some applications,[52] DNA plastics were endowed with some unique material characteristics, such as coating ability and mild surface modification capability.[53] Considering the good compatibility of DNA with other materials, a variety of materials such as graphene oxide, iron oxide, polydopamine, clay, and poly(3,4-ethylenedioxythiophene)-poly-(styrenesulfonate) (PEDOT:PSS) could be coated onto DNA-based materials.[54] Moreover, DNA-based materials could serve as a wire sheath for coating copper wires. Owing to the presence of multiple functional groups of DNA, such as phosphate groups, nitrogenous bases, and hydrophobic groups, mild surface modifications could be achieved for DNA plastics.[55] In this work, we further demonstrated the water-processable ability and water-triggered welding ability of DNA plastics. These fascinating characteristics would enable the use of DNA plastics in some applications where water resistance was not a main consideration.[53]

DISCUSSION

In this work, we report a freeze-drying method to transform DNA gels into sustainable DNA plastics, which will be a general strategy to advance the development of sustainable bioplastics. The sustainability involves all aspects of the production, use, and end-of-life options of DNA plastics (Figure 5A). Raw materials are fully derived from biorenewable resources. Using a green processing method (freeze-drying), plastics are prepared without the use of organic solvents and the production of chemical byproducts. Freeze-drying is a relatively low-energy-consumption process compared with the conventional melt processing method. The total energy consumption per functional unit of polystyrene (PS) and polylactic acid (PLA) was 563.6 and 587.5 MJ, respectively.[56] In contrast, the total energy consumption per functional unit of DNA plastics (processing time was 5 h) was 26.9 MJ,[57] which was only 4.8% of PS and 4.6% of PLA, respectively. Further, the preparation process did not involve the production of chemical byproducts instead of CO_2. The total CO_2 emission was calculated by coal and electrical consumption multiplied by corresponding emission factors, respectively.[58] The total CO_2 emission per functional unit of PS and PLA was 28 and 13.9 kg, respectively.[56] Remarkably, the total CO_2 emission per functional unit of DNA plastics would be only 3% of PS and 35% of PLA, respectively.[58] Regarding the use and end-of-life options of plastics, a dual closed-loop recycling route is demonstrated (Figure 5B). Recyclable and nondestructive use of plastics is achieved through repeated processing, which enables the infinite service-lifetime in theory. Besides, two green routes can be chosen to dispose waste plastics. One is to reprocess waste plastics into new plastic products, another one is to achieve the triggered and controllable degradation of waste plastics upon DNA digesting enzymes under mild conditions. Although some great efforts have been devoted to disposing waste plastics,[9,12−14,27,49,61−65] our reported disposal routes of DNA plastics are still competitive and show potential for long-term use. Current plastic recycling strategies mainly depend on the design of chemically dynamic molecular networks,[12,63] and the recycling is achieved through the

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depolymerization of polymeric plastics to regenerate monomers in specific conditions such as low pH and high temperature.[27,65,66] In contrast, our reported physical recycling route does not involve the rupture of polymer chains, which requires extra energy. Other disposal strategies including the transformation of waste plastics into high-value chemical products,[13,61,62] and the search for novel plastic-degrading enzymes,[14,64] cannot achieve the closed-loop recycling of plastics, which might cause extra energy consumption and the waste of raw materials. In practical use, in principle, DNA plastics could be processed into any products such as biological patches, electronic devices, and packaging. In these applications, water resistance is not a main consideration. As an application example, a water-soluble film is widely used for packaging in our daily life.

The potential of DNA that is rapidly and massively produced by the market is of great importance for future applications of DNA plastics. Although mass production of DNA still remains a challenge, we have found several potential ways to achieve the production of DNA at the metric ton scale (Figure 5C). In the food industry, the production of fruit generated 266 million metric tons of pomace waste annually, which could be utilized for extracting 270 000 t of DNA.[67] In the biopharmaceutical industry, the generation of microbial residues during antibiotic production was 14 million metric tons annually, providing 140 000 t of DNA every year.[68] In the bioethanol industry, the data showed that the commercial market could provide 2 million metric tons of dry yeast annually to extract 6000 t of DNA.[54] In the bloomed algae industry, the commercial production of dry algae was 15 000 t annually, enabling the extraction of 450 t of DNA every year.[69] To achieve the rapid production of DNA in industrial settings, DNA extraction from algae and bacteria is much more established and easy. Moreover, the production cycle of DNA is approximately 3 days. Similarly, the production of polyhydroxyalkanoate (PHA) that is a commercial biopolymer derived from bacteria needs several days, demonstrating the great potential of industrialized production from microorganisms. In contrast, the production of other biopolymers that are derived from animals and plants generally requires more time, from 50 days to 240 days, due to the fact that mass DNA extraction should wait for the animals and plantsto reach maturity (Figure 5D).[70,71]

In addition, the advantages and defects of DNA plastics are systematically illustrated. DNA, the raw material of DNA plastics, is considered as an inexhaustible and green biopolymer derived from any organism. Where there is life, there is DNA. In contrast, raw materials of polylactic acid (PLA, bioplastics) are mainly derived from crops (starch), resulting in competion with agricultural resources. The raw materials of polystyrene (PS, petrochemical-based plastics) are benzene and ethylbenzene, which are flammable, toxic, and carcinogenic. Freeze-drying is a relatively low-energy-consumption and nondestructive strategy to prepare DNA plastics, not involving the rupture of polymer chains. The use of DNA plastics is recyclable without the compromise of plastic performance. The water-processable strategy avoids the use of complex and expensive machines and harsh processing conditions. Disposal of waste plastics follows two green routes including the recycling of waste plastics and enzyme-triggered degradation under mild conditions. In practical use, DNA can be rapidly extracted from algae and bacteria within 3 days using industrial settings. Moreover, DNA shows great potential for mass production (hundreds of thousands metric tons/year) by the market. Owing to the high biocompatibility, DNA plastics can be processed into biological patch for biomedical applications. Multicompartmental DNA plastics loaded with different bioactive compositions show great potential for biosensing, drug delivery, and tissue engineering. Owing to the good folding recoverability at low temperature (−80 °C), DNA plastics show potential for applications in electronic skins and soft robots under extreme cold weather conditions. Encouraged by the wide application of water-soluble polymeric films, DNA plastics will be used for packaging in our daily life. Despite these advances, there remains some challenges for DNA plastics in real-world settings: for example, (1) compromised water tolerant stability of DNA plastics limits the use in some application scenarios; (2) the balance between mechanical strength and sustainability should be considered; and (3) long-time stability of DNA plastics under UV radiation should be improved.

We next evaluate the overall sustainability of DNA plastics using a radar plot compared to petrochemical-based plastics (PS) and bioplastics (PLA) (Discussion S1). Comparative analysis of processing equipment for DNA plastics and PLA/PS is summarized (Discussion S2). A lyophilizer that was easily available in industrial settings and laboratories was used to prepare the DNA plastics, avoiding the use of complex and expensive machines and harsh processing conditions. As displayed in Figure 5E−G, DNA plastics show obvious superiority in terms of biodegradability, abundance, the production of byproducts, CO_2 emission, energy consumption, and processing quality. These data further highlight the sustainability of DNA plastics, and we believe that our DNA plastic represents a potential sustainable material, which paves a new avenue to develop more sustainable biobased materials. Although there are still some challenges remaining for DNA plastics in some applications, such as the compromised water tolerant stability and mechanical strength, current studies have provided many available methods to address these issues.[72−75] Inspired by the practical use of paper such as a paper cup, surface coating technologies could be adopted to improve the water tolerant stability of DNA plastics.[72,75] Encouraged by our work, we expect that more biobased materials with excellent sustainability and performance will be created and result in a positive impact in the future sustainable society.

MATERIALS AND METHODS

Materials. Poly(epichlorohydrin-*co*-ethylene oxide) (ECO, Epichlomer C 49 mol % epichlorohydrin unit) was purchased from Osaka Soda Co., Ltd., Japan. ECO was dried in vacuo prior to use. 1-Butylimidazole (98%) was utilized as received from J&K Scientific Ltd., China. Salmon sperm DNA (DNA, ∼20 000 base pairs) (from Sigma-Aldrich) was utilized for preparing the DNA plastics. GelRed nucleic acid dyestuff, SYBR Green I nucleic acid dyestuff, fluorescein, and DNase I (7.5 U/μL) were obtained from TIANGEN BIOTECH. Petroleum ether (MSO), ethanol (EtOH), and *N*,*N*-dimethylformamide were purchased from Aladdin Chemical Technology Co., Ltd. Graphene oxide (GO) was gifted from Prof. Quanhong Yang at Tianjin University. Poly(dimethylsiloxane) (PDMS) (Dow Corning, U.S.A.) and PDMS cross-linker (Sylgard 184, Dow Corning, U.S.A.) were used to prepare PDMS-based molds with different shapes.

Synthesis of ECO-Based Ionomers. ECO-based ionomers were synthesized through the quaternization reaction of ECO with 1-butylimidazole. Specifically, a three-neck round flask (1000 mL) was first charged with ECO (0.05 mol chloromethyl functionality, 30.0 g, 18.45 wt % Cl). 1-Butylimidazole (118.5 g, the molar ratio of Cl/imidazole monomer was 1/6) was then slowly added into the flask

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under nitrogen. The mixture was homogenized through the mechanical stirring and subjected to refluxing at 115 °C for 20 h using an oil bath. Afterward, the mixture was cooled to 25 °C, precipitated from ethyl ether, and washed multiple times with ethyl ether. To purify the ECO-based ionomers, the mixture was redissolved in ethanol and then precipitated from ethyl ether. Finally, the mixture was dried in a vacuum oven at 40 °C for 48 h to remove the remaining solvents and yield yellowish-brown viscous ionomers (45.77 g, 92%). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 9.93 (d, J = 140.8 Hz, 1H), 8.00 (s, 2H), 4.62−4.22 (m, 4H), 1.79 (s, 2H), 1.24 (s, 2H), 0.88 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6, δ, ppm): 137.70, 137.46, 123.85, 122.59, 76.53, 70.58, 70.20, 69.13, 50.16, 48.88, 31.96, 19.23, 13.78.

Synthesis of ECO−OH-Based Ionomers. To synthesize the OH group modified ECO-based ionomers (ECO−OH-based ionomers), an optimized quaternization reaction was utilized. First, ECO was dissolved in *N*,*N*-dimethylformamide (1:10 mass ratio) in a three-necked flask at 130 °C. Mechanical stirring was applied to dissolve ECO for approximately 1 h. 2-(1H-imidazol-1-yl) ethanol was then added to the flask with a 1.5-fold molar ratio of Cl, and a quaternization reaction was carried out under a N_2 atmosphere at 130 °C for 24 h. Finally, the resulting product was precipitated from acetone. Prior to use, the product was dried at 40 °C for 24 h to remove the solvents.

Fabrication of PDMS-Based Molds. The molds with different shapes were prepared through the polymerization reaction of PDMS oligomers in a suitable 3D-printed models. Specifically, PDMS oligomers and the cross-linkers were thoroughly mixed in a ratio of 10:1 (w/w) and the generated bubbles were removed using a vacuum desiccator. The mixture was then poured over the 3D-printed model and cured at 70 °C for 4 h. The PDMS mold was peeled off from the 3D-printed model.

Preparation of DNA Plastics. To prepare DNA plastics, physically cross-linked DNA gels needed to be synthesized first. Salmon sperm DNA was dissolved in water and the concentration was fixed as 2 w/v%. ECO-based ionomers were dissolved in water with the concentration of 10 w/v%. To synthesize DNA gels, ECO-based ionomers were mixed with DNA solution to form soft DNA gels in a few seconds. In this process, DNA gels with different DNA contents could be prepared by changing the volume ratio of DNA and ionomers. Afterward, DNA gels were added in the molds with different shapes to endow DNA gels with a temporary shape. DNA gels were then freeze-dried for 5 h to transform DNA gels to shaped DNA plastics through removing the remaining water from DNA gels. Finally, DNA plastics were taken out from the molds. To prepare fluorescence dye loaded DNA plastics, the fluorescence dye was first thoroughly mixed with DNA and then DNA gels and plastics were prepared.

Characterization of DNA Plastics. Scanning electron microscopy (SEM, Hitachi S-4800, Japan) was conducted to characterize the morphology of the DNA plastics. Fluorescence microscopy (Nikon, Type 108, Japan) was conducted to characterize the micromorphology of the DNA gels. Nuclear magnetic resonance spectroscopy (NMR, 400 MHz Bruker AVANCE II spectrometer) was used to confirm the chemical structures of the synthesized functionalized elastomeric ionomers. Tensile tests were performed on a universal testing machine (Instron 3360) equipped with a 1 kN electronic load cell and mechanical grips. The DNA specimens were prepared in a dumbbell-shaped mold with the dimensions of 5 mm in width, ∼1 mm in thickness, and ∼10 mm in length. The tests were conducted at 25 °C and −80 °C with the crosshead speed of 2 mm/min. Surface hardness was measured through a nanoindenter (Piuma) with a 0.47 N/m probe, and the value was calculated by the software (Dataviewer, Piuma). Impact strength was measured using a pendulum impact tester (XCJD, Chengde Jinhe Instrument Manufacturing Co., Ltd.) Flexural strength was measured using an electronic universal testing machine (Shenzhen Suns Technology Stock Co., Ltd.). Flexural strength was calculated using the following formula:

$$\text{flexural strength (MPa)} = 3FL/2bh^2$$

where F is the applied force (N); L the length of span, 64 mm; b the specimen width (mm); and h the specimen thickness (mm).

Rheology Tests of DNA Gels. The rheological properties were carried out on a HR-2 rheometer (TA Instruments) equipped with a temperature controller. The test was performed in an 8 mm parallel-plate geometry using 100 μL DNA gels. Strain scanning was conducted from 0.1% to 10 000% with a fixed frequency (1 Hz) at 25 °C. The recovery properties of the DNA gels were investigated by successively applying the alternating low (10%) and high (1000%) strain conditions.

Triggered Degradation of DNA Plastics. DNA plastics were incubated in different solutions to investigate the degradation behaviors. In this experiment, DNase I (5 U/μL), bovine serum albumin (BSA), and water were used. The degradation of DNA plastics was characterized through measuring the volume of the remaining DNA gels. To visually observe the degradation of DNA plastics, GelRed-stained DNA plastics were prepared.

In Vitro Cell Culture. H9C2 myocardial cells were utilized as target cells to investigate the biocompatibility of DNA plastics. Before the cell seeding, DNA plastics were purified in PBS, followed by sterilized by 75% ethanol for 24 h. DNA plastics were placed in a 96-well plate with Dulbecco modified Eagle medium (DMEM) and swelled to an equilibrium state at 37 °C. Cells were then seeded on plastics for the incubation of 3 h, allowing for cell attachment. Afterward, cells grown on plastics were stained with calcein AM and observed by fluorescence microscope. The viability of H9C2 cells grown on plastics was analyzed using a thiazolyl blue tetrazolium bromide (MTT) assay. MTT solution was added into 96-well plates containing plastics and cells, and then the plates were incubated at 37 °C for 4 h for the measurement of cytotoxicity (490 nm).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c08888.

Analysis of the sustainability of DNA plastics, comparative analysis of processing equipment, ^{1}H NMR and ^{13}C NMR results of ECO-based ionomers, bending and recovery process of DNA plastics, SEM images of DNA plastics, weight changes of DNA plastics incubated for different times, DNA plastics doped with different contents of graphene oxide, fluorescence images of DNA gels, and the degradation of DNA plastics when exposed to DNase I solution (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS USED

ECO, poly(epichlorohydrin-*co*-ethylene oxide); SEM, scanning electron microscope; FBS, fetal bovine serum; RH, relative humidity; MSO, petroleum ether; GO, graphene oxide; PHA, polyhydroxyalkanoate; PLA, polylactic acid; PS, polystyrene

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