Production and closed-loop recycling of biomass-based malleable materials

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ABSTRACT The search of biomass-based substitutes for fossil-based plastics has become a pressing task due to the severe long-term threats of plastic wastes to the ecosystem. However, the development in this area is strongly impeded by the high cost of biomass separation and the poor processability of unseparated biomass. Herein, we demonstrate, for the first time, an efficient and scalable method to generate greener plastics by directly integrating unseparated biomass waste (i.e., wood powder) with crosslinked covalent adaptable networks. Through a simple compression molding process, the wood biomass and polymer particles can be fused together to form a continuous material, which is endowed with repairability, reprocessability, and closed-loop full recyclability. The method demonstrated in this work paves the way for large-scale industrial production of environmentally friendly biomass-based plastics.

Keywords: wood biomass, plastic, polyimine, recyclable, vitrimers

INTRODUCTION

Plastics are the most widely used man-made materials and have become the integral part of our modern life. They are lightweight, durable, low-cost and hardly replaceable by other synthetic materials [1]. Since their first common use around 1950, the world has produced over 8300 million tons of plastics [2,3], most of which are produced from petroleum-based chemicals and hard to degrade [4–6]. Only recently have people realized the long-term threats of plastic wastes, which enter ecosystem as millimeter- and micrometer-sized particles after natural fragmentation [7,8]. The use of polymeric biomass as a green replacement for traditional fossil-based materials has gained momentum in the past few years due to their

abundance, renewability, low cost and biodegradability [9–14]. However, natural lignocellulose biomass is a complex mixture of cellulose, hemicellulose, lignin, and others [15]. The separation of biomass components for biomaterials on an industrial scale imposes high demands on cost and energy consumption. Moreover, due to strong hydrogen-bond network of polysaccharides, biomass does not melt or soften, and thus cannot be processed. The poor processability together with low mechanical properties, and hydrophilicity of biomass make them hard to be used like conventional plastics. As a result, there has been little recent success in using unseparated biomass to produce value-added plastic materials [16,17].

We demonstrate how we can incorporate unseparated biomass waste into covalent adaptable networks (CANs) to prepare completely reprocessable, recyclable, and easily repairable plastic-like materials with high mechanical properties. Different from the traditional wood-plastic composite materials (WPC) wherein the interactions between biomass phase and insert polymer phase are extremely weak, biomass and polymer are highly crosslinked in our materials. The key strategy involves the replacement of traditional thermoplastics or thermosets with polyimine (PI) CANs that can form efficient dynamic noncovalent or covalent bonding interactions with biomass. The PI CANs with high-density imine and amine functional groups are used, which are capable of (i) forming dynamic hydrogen bonding interactions with polysaccharide rings, and (ii) undergoing dynamic exchange reactions without decreasing the overall network connectivity under external stimuli. When subjected to heat and pressure, such CAN particles can be fused together to form a continuous polymer matrix binding and

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encapsulating biomass particles. As a result, simple compression molding of a mixture of biomass and CAN powders is sufficient to bring them together to form a continuous material (Fig. 1), which are malleable like plastics but mechanically strong and chemically stable like thermosets. The bonding interactions between the CANs and biomass can be further strengthened by oxidizing the polysaccharide rings to provide surface aldehyde groups that form stronger dynamic covalent imine bond through efficient Schiff base reaction. The material containing 30 wt%–70 wt% of biomass can be easily remolded, laminated, reshaped, fully degraded, 100% recycled, and exhibit good mechanical properties, which may greatly extend the potential of biomass-based materials.

EXPERIMENTAL SECTION

Sample preparation

The PI CANs were synthesized by reacting three commercially available monomers: a dialdehyde (terephthalaldehyde), a diamine (diethylenetriamine (DETA) (**1**) or bis(3-aminopropyl)amine (**2**) or 3,3'-diamino-*N*-methyldipropylamine (**3**)), and a triamine (tris(2-aminoethyl)amine, TREN) at 1:0.3:0.47 stoichiometry in ethanol at room temperature in the absence of any catalyst. The oxidized wood powders were prepared by oxidizing original wood powders with NaIO_4 at 50°C for 16 h. The PI-wood (PW) films were prepared by heat-pressing PI/wood powder mixtures at 0.89 MPa for 20 min, followed by 1.24 MPa for 20 min, finally at 1.60 MPa for 10 min under 130°C. To demonstrate the thermo-processing property of PW films, the films were molded into 3D shapes by applying stress under heat-treatment. Multiple single-layer composites were laminated by heat-pressing. The damaged samples were repaired by filling the damaged area with PI/wood powder

mixture, followed by heat-pressing. The PW films were ground into powders, then were re-molded into a new batch of PW films. To recycle the PW films, the samples were degraded using pure DETA solution in EtOH. The resulting oligomer/precursor solution was supplemented with terephthalaldehyde and TREN and re-polymerized into a new batch of PI thermosets. The recycled PI CANs and wood powders were then heat-pressed together again to prepare recycled PW films.

Characterizations

The chemical structures of PI CANs and PW films were characterized by infrared (IR) spectrometer (Cary 630, Agilent, USA). The glass transition temperatures (T_g) of PI and PW materials (PWs) were measured by dynamic mechanical analyzer (DMA, TA Q800, New Castel, USA). The thermogravimetric (TG) curves of PWs were measured using a TGA5500 instrument (USA) under N_2 atmosphere. The surface and cross-section morphologies of PWs were characterized by scanning electron microscopy (SEM, jms-6480LV, Japan). The tensile strength, three-point flexural strength, and compression strength of the samples were tested on an Instron universal material testing machine (Instron 5800, USA). Three parallel specimens were tested for one sample.

RESULTS AND DISCUSSION

Preparation of PW films

Crosslinked PI CANs (**P1**, **P2**, and **P3**) with high density of secondary and tertiary amines and imines were prepared from commercially available, short aliphatic diamine, triamine and an aromatic dialdehyde: PIs terephthalaldehyde (TPA), linear diamines (diethylenetriamine for **P1**, bis(3-aminopropyl)amine for **P2**, or 3,3'-diamino-*N*-methyldipropylamine for **P3**), and TREN.

Figure 1 Schematic representation of the preparation of the PW films. The wood powders (Aspen, 80 mesh) composed of polysaccharides and PI powders containing imines and amines were mixed thoroughly using an agate mortar and compression molded to provide a continuous phase material.

Thin films of the biomass-polymer materials were fabricated by compression molding from a solid mixture of biomass and polymer powders. These CANs enable molecular level bindings with biomass through efficient hydrogen bond formation with polysaccharides. Considering that wood is the most abundant renewable non-food biomass resource in nature, we used wood powder (Aspen, 80 mesh) as an example of biomass waste. To strengthen the bonding interactions, oxidative cleavage of polysaccharide rings was also conducted which provides surface aldehyde groups that can undergo efficient Schiff base reaction with amines. Efficient bonding and fusion of polymer particles defines the properties of the resulting bulk materials. The PI CANs were chosen as the polymer component for the following reasons: (i) they can be easily prepared in <5 μm sized spherical particles using a bench-top grinder with sanding wheels. The shape and particle size of the polymer powders are critical to minimize the formation of voids during particle fusion process, which is one of the primary factors causing defects and crack initiation and weakening mechanical strength of the materials. Irregular particle shapes create complicated contact patterns between particles, leading to more voids. The spherical particles of varying sizes can effectively minimize the void formation. The heat created at the interface during the grinding process triggers the malleability of the PI CANs, enabling the formation of spherical particles. (ii) The crosslinked PIs have good mechanical properties (Young's modulus ~ 1 GPa) and thermal stabilities (<2% weight loss at 250°C) to provide robust materials for various applications [18–21]. (iii) The hydrogen bonding interactions between imines/amines with hydroxy groups of the polysaccharides and dynamic imine exchange reactions within the polymer network provide the essential conditions for the polymer particle fusion and their integration into the voids between wood particles. A continuous, coherent solid film thus can be obtained by simple compression molding under heat. (iv) Owing to the reversibility of imine bonds, the PIs exhibit heat-driven malleability and can be easily laminated and reprocessed multiple times into any desired shape even from fine powders. They are also easily repairable by patching a new piece of the film or applying powder form of the materials followed by heat-pressing [20,21]. (v) PI networks can be readily depolymerized to form short soluble oligomers when soaked in a monomer solution, due to the shift of the equilibrium of the dynamic exchange reactions according to Le Chatelier's principle [22,23]. All the chemical component and wood powders

can thus be recovered and re-entered into the production cycle of similar value materials, realizing closed-loop recycling of the materials.

Morphology and chemical structure of PW films

The compression molding of the powder mixture of the polymer and wood powders provided a coherent solid film as shown in Fig. 1. This material can be easily produced in large-scale with tailored mechanical properties by individually adjusting the properties and compositions of PI and wood powders. PWs with a range of tensile (modulus 1.0–1.6 GPa, strength 20–40 MPa, elongation at break 1.2%–3.9%) and flexural properties (modulus 3.5–4.8 GPa, strength 55–73 MPa, strain at break 1.3%–3.8%) were obtained by changing the wt% of wood powders (30 wt%–70 wt%) and PI compositions (Fig. S1). Homogeneous distribution of wood particles within the malleable PI networks was achieved, resulting in the inherent isotropy of materials properties. The spherical PI particles efficiently fuse and form a continuous polymer matrix encapsulating the irregular shaped wood particles under the pressure of <1.6 MPa and heat <130°C (Fig. 2a–d). No obvious voids and large gaps were observed at the PI-wood interface (Fig. 2e, f), indicating their excellent interfacial compatibility. The hydrogen bonding interactions between the amines/imines and the hydroxyl groups of the polysaccharide rings are clearly supported by the IR absorption spectra of the materials, where a red shift of the hydroxyl stretching band from 3310 to 3278 cm^{-1} is observed (Fig. S2). The ability of PI particles to undergo thermally activated stress-relaxation

Figure 2 SEM images of PW film. The SEM images of wood powders (a), PI (P1) particles prepared from TPA, DETA and TREN (b), PW1 film (c, d), and close-up images of PW1 interface (e, f). The particle fusion of spherical PI powders provides a continuous coating layer on irregular-shaped wood powders, which makes it difficult to view wood-PI interface in the cross-section image. To observe the wood-PI interface, wood powders were sprinkled on top of the PI film and heat-pressed. The cross-section was prepared by carefully cutting through the wood particle and the PI film attached together. (e, f) show that there are no obvious gaps between the PI layer and wood surface.

and large deformation enables interface healing between neighboring polymer particles to form strong and coherent polymer layers around the wood particles [18,19]. Such particle deformation and interface healing are enabled by heat-driven dynamic imine exchange reactions between polymer chains rather than weak non-covalent interactions [18–21].

Mechanical, waterproof, and thermal properties of PW films

The PW films behave like hard plastics, with tensile

modulus over 1.0 GPa. After introduction of the wood powder, the PWs become much stiffer than the pure polymers. In all three cases, the tensile moduli were increased (Fig. 3a, b). For example, the tensile modulus of **P3** was increased from 0.88 to 1.10 GPa with 30 wt% wood powder. The tensile strengths of the wood-filled PIs **PW1** and **PW2** are considerably higher than that of most common commercially available plastics, such as high-density PE (HDPE) [24], polypropylene (PP) [25], polyvinyl chloride (PVC) [26], polyester [27], and poly-

Figure 3 Mechanical and waterproof properties of the PW films. (a) Tensile stress-strain curves of PIs (**P1**, **P2**, **P3**) and the corresponding PW films (**PW1**, **PW2**, **PW3**) with 30 wt% wood powder. After introduction of the wood filler, the PIs become stiffer, showing slightly decreased tensile strength and reduced elongation at break. (b) Comparison of tensile moduli of PIs and PW films. The tensile moduli of PW films are comparable or even higher than those of PIs. (c) Comparison of tensile strengths of commercially available plastics and the PW films, showing PWs exhibit comparably high tensile strength. (d) The elastic ratios of various wood species and **PW1**. The elastic ratio of wood is less than 0.1 whereas it is unity in **PW1**, showing orthotropic nature of woods and the isotropic nature of PWs. E_T and E_L represent the elastic modulus of wood perpendicular to grain and parallel to grain, respectively. (e) PWs show excellent water-resistance performance comparable to polyethylene (PE). The water drops were completely absorbed by the wood surface after 30 s. (f) The compression curve of the dome-top arch with the thickness of 3 mm made from a laminated multilayer **PW1**. It shows that the material can support a load of ~30 kg.

urethane (PU) [28] (Fig. 3c). PWs also show higher tensile strength, flexural strength, and flexural modulus than conventional wood-plastics composites (Table S1). Unlike wood materials with drastically different independent mechanical properties in the three perpendicular axes, longitudinal, radial, and tangential [29], PWs have isotropic properties and their behaviors are easier to predict (Fig. 3d). Therefore, compared with orthotropic wood materials, PWs would be greatly advantageous in the fabrication of complex structures which are under biaxial or multi-axial stress conditions rather than uniaxial loading. Although woods can be wet quickly (absorbs water droplets within 30 s), PWs are water resistant like common plastics (Fig. 3e). In addition, the DMA results in Fig. S3 show **PW1** is malleable like pure PI (**P1**). The T_g of **PW1** is 130°C. The TG curves in Fig. S4 shows PWs own excellent thermostability when the temperature is lower than 250°C.

Multilayer welding of PW films

Multilayer sheets can be easily fabricated by simply welding multiple single-layer sheets together (120°C, 0.80 MPa for 1 min). The multilayer laminates show almost the same mechanical strength as the original single-layer sheet and homogeneous phase without any discernible interface, suggesting highly efficient interface

healing and high bonding strength between the adjacent sheets (Fig. S5a–e). A mechanically robust and highly rigid 3D dome-top arch was created by molding a ~3 mm thick sheet (10 cm×10 cm) laminated from six-layer **PW1** (Fig. 3f). The compression test reveals this 3D curvature can support a load of ~30 kg. Two of such 3D curvatures were strong enough to support an adult (~50 kg) (Fig. S5f). When we used oxidized wood powders (NaIO_4 , 16 h), the Young's moduli of **PW1** was increased almost two-fold from 1.05 to 1.92 GPa (Fig. S6), suggesting the strengthening of the interfacial interactions between wood powders and PIs through covalent bonding of the aldehyde groups and residual amines in the PIs.

Reshaping, repairing, and re-molding of PW films

The presence of imine bonds, which can undergo dynamic exchange reactions, renders the thermally activated malleability of the PW films [18–21]. The abilities of these PWs to reshape, repair, remold, and recycle are evident from the images in Fig. 4 and Fig. S7. A flat single-layer **PW1** film can be easily reshaped into many different shapes by applying deformation and heat (Fig. S7). In principle, it can be reshaped unlimited times into any desired shape by activating the materials' plasticity, which is enabled by scrambling dynamic covalent bonds between polymer chains. It should be noted that the mal-

Figure 4 Repairing, remolding, and recycling of PW films. (a) The materials can be repaired by filling the damaged area with the mixture of wood and PIs powders followed by heat-pressing. The sample can be completely ground into powders and remolded into a coherent solid. At the end-of-life, the materials can be degraded into the monomers and reused in the production of next generation of similar value materials. These repairing, remolding, and recycling processes can be repeated multiple times without significant loss of mechanical properties. (b) The repaired sample recovered >120% and 95% of tensile modulus and tensile strength. (c) Complete reprocessing from powders to a film results in average recovery of >86% tensile modulus and >89% tensile strength of the pristine sample. (d) The materials prepared from the recycled degradation solution retain >130% tensile modulus and >92% tensile strength. Three parallel specimens were tested for one sample.

leability is enabled by imine bond exchange reactions, and therefore the crosslinking density and material integrity remain unchanged during the reshaping process. The damaged sample can be easily repaired by a particle infusion method. Even large-area damage can be repaired by filling the area with a powder mixture of wood and PI and compression molding them to achieve the healing effect (Fig. 4a). The mechanical properties are mostly restored in the repaired samples, showing the recovery percentages of the 1st repaired **PW1** (121%, 97%, 97%, and 100%) and the 2nd repaired **PW1** (124%, 95%, 99%, and 100%) for tensile modulus, tensile strength, flexural modulus, and flexural strength, respectively (Fig. 4b and Fig. S8). PWs also offer more sustainable and greener end-of-life approach. They can be ground into powders and re-molded to form a new product of any desired shape with excellent recovery of mechanical properties (100%, 96%, 98%, and 92% recovery of tensile modulus, flexural modulus, tensile strength, and flexural strength, respectively) (Fig. 4a, c and Fig. S9). Such grinding and remolding cycle can be repeated multiple times. After two times of complete reprocessing from powders to a coherent solid, the material still retains 86% tensile modulus, 86% flexural modulus, 89% tensile strength, and 82% flexural strength of the pristine sample. The excellent reparability and re-processability suggest damaged wood-PI materials can be 100% reused *via* simple repairing and processing.

Closed-loop recycling of PW films

The closed-loop recycling of traditional thermoset and thermoplastics represents a grand challenge due to their non-degradable nature [30–32]. By contrast, PIs connected through dynamic covalent bonds can be depolymerized by upsetting the stoichiometric balance between aldehyde and amine groups in PI networks *via* introducing excess primary amines [18–21]. **PW1** films can be completely degraded into soluble species and wood powders by soaking (room temperature, 15 h) in a dilute solution of DETA in ethanol (0.3 mmol L^{-1}) (Fig. 4a). The recycled solution can be 100% reused by adding the complementary amount of TPA and TREN and re-polymerizing the mixture into a new generation of PIs. It shows recycled PIs have the same chemical structure and similar T_g to that of original PI (Fig. S10). The solubilization of PI matrix will release wood powders, which can directly re-enter into next production cycle after simple drying. The first-generation recycled **PW1** (1st recycled **PW1**) prepared from the recycled PIs and wood powders through compression molding shows the recovery of

134% tensile modulus, 81% flexural modulus, 92% tensile strength, and 93% flexural strength of the original sample (Fig. 4d and Fig. S11). The first generation of recycled sample is degraded again and reused to prepare second-generation recycled sample (2nd recycled **PW1**), which exhibits even better recovery of mechanical properties (140%, 87%, 92%, and 98% recovery of tensile modulus, flexural modulus, tensile strength, and flexural strength, respectively).

CONCLUSIONS

We have demonstrated an efficient way to process biomass into greener plastics with excellent reparability, reprocessability, and closed-loop full recyclability. The materials can contain up to 70% wood biomass and exhibit good mechanical properties comparable to or better than commonly used plastics. The key strategy is to incorporate imines and amines in the polymer network, thus (i) facilitating their binding with wood particle through hydrogen bonding interactions between amines/imines and the polysaccharide hydroxyl groups and also Schiff base chemistry between surface aldehyde groups and amines; (ii) realizing the malleability and full recyclability of the materials by taking advantage of the dynamic nature of the imine bonds; (iii) enabling easy and convenient large-scale production of materials through particle fusion process. The properties of the materials can be conveniently engineered by individually controlling the properties and compositions of the PIs and wood powders. For instance, the material prepared from the oxidized wood powders shows substantially high mechanical properties compared with the one from untreated wood powders. The use of biomass waste and excellent reparability, reprocessability and end-of-life recycling potential would effectively reduce the overall production cost, providing much greener plastics that can replace many existing non-degradable thermoplastics and thermosets. The easy processing and reuse of biomass presented herein potentially have broader implications for environmentally friendly and sustainable plastics.

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- 1 Sardon H, Dove AP. Plastics recycling with a difference. *Science*, 2018, 360: 380–381
- 2 Geyer R, Jambeck JR, Law KL. Production, use, and fate of all plastics ever made. *Sci Adv*, 2017, 3: e1700782
- 3 Tang X, Chen EYX. Toward infinitely recyclable plastics derived from renewable cyclic esters. *Chem*, 2019, 5: 284–312
- 4 Rahimi AR, García JM. Chemical recycling of waste plastics for new materials production. *Nat Rev Chem*, 2017, 1: 1

- 5 Garcia JM, Robertson ML. The future of plastics recycling. *Science*, 2017, 358: 870–872
- 6 Jambeck JR, Geyer R, Wilcox C, *et al.* Plastic waste inputs from land into the ocean. *Science*, 2015, 347: 768–771
- 7 Yoshida S, Hiraga K, Takehana T, *et al.* A bacterium that degrades and assimilates poly(ethylene terephthalate). *Science*, 2016, 351: 1196–1199
- 8 Bergmann M, Mützel S, Pimpke S, *et al.* White and wonderful? Microplastics prevail in snow from the Alps to the Arctic. *Sci Adv*, 2019, 5: eaax1157
- 9 Delidovich I, Hausoul PJC, Deng L, *et al.* Alternative monomers based on lignocellulose and their use for polymer production. *Chem Rev*, 2016, 116: 1540–1599
- 10 Yu X, Jia J, Xu S, *et al.* Unraveling substituent effects on the glass transition temperatures of biorenewable polyesters. *Nat Commun*, 2018, 9: 2880
- 11 Lligadas G, Ronda JC, Galà M, *et al.* Renewable polymeric materials from vegetable oils: a perspective. *Mater Today*, 2013, 16: 337–343
- 12 Zhu Y, Romain C, Williams CK. Sustainable polymers from renewable resources. *Nature*, 2016, 540: 354–362
- 13 Mohanty AK, Vivekanandhan S, Pin JM, *et al.* Composites from renewable and sustainable resources: challenges and innovations. *Science*, 2018, 362: 536–542
- 14 Si WJ, An XP, Zeng JB, *et al.* Fully bio-based, highly toughened and heat-resistant poly(*L*-lactide) ternary blends *via* dynamic vulcanization with poly(*D*-lactide) and unsaturated bioelastomer. *Sci China Mater*, 2017, 60: 1008–1022
- 15 Zhu H, Luo W, Ciesielski PN, *et al.* Wood-derived materials for green electronics, biological devices, and energy applications. *Chem Rev*, 2016, 116: 9305–9374
- 16 Song J, Chen C, Zhu S, *et al.* Processing bulk natural wood into a high-performance structural material. *Nature*, 2018, 554: 224–228
- 17 Fu Q, Ansari F, Zhou Q, *et al.* Wood nanotechnology for strong, mesoporous, and hydrophobic biocomposites for selective separation of oil/water mixtures. *ACS Nano*, 2018, 12: 2222–2230
- 18 Taynton P, Yu K, Shoemaker RK, *et al.* Heat- or water-driven malleability in a highly recyclable covalent network polymer. *Adv Mater*, 2014, 26: 3938–3942
- 19 Whiteley JM, Taynton P, Zhang W, *et al.* Ultra-thin solid-state Li-ion electrolyte membrane facilitated by a self-healing polymer matrix. *Adv Mater*, 2015, 27: 6922–6927
- 20 Zou Z, Zhu C, Li Y, *et al.* Rehealable, fully recyclable, and malleable electronic skin enabled by dynamic covalent thermoset nanocomposite. *Sci Adv*, 2018, 4: eaaq0508
- 21 Taynton P, Ni H, Zhu C, *et al.* Repairable woven carbon fiber composites with full recyclability enabled by malleable polyimine networks. *Adv Mater*, 2016, 28: 2904–2909
- 22 Jin Y, Lei Z, Taynton P, *et al.* Malleable and recyclable thermosets: the next generation of plastics. *Matter*, 2019, 1: 1456–1493
- 23 Belowich ME, Stoddart JF. Dynamic imine chemistry. *Chem Soc Rev*, 2012, 41: 2003–2024
- 24 Röttger M, Domenech T, van der Weegen R, *et al.* High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis. *Science*, 2017, 356: 62–65
- 25 Papageorgiou DG, Kinloch IA, Young RJ. Hybrid multifunctional graphene/glass-fibre polypropylene composites. *Compos Sci Tech*, 2016, 137: 44–51
- 26 Wang H, Xie G, Ying Z, *et al.* Enhanced mechanical properties of multi-layer graphene filled poly(vinyl chloride) composite films. *J Mater Sci Tech*, 2015, 31: 340–344
- 27 Bora C, Bharali P, Baglari S, *et al.* Strong and conductive reduced graphene oxide/polyester resin composite films with improved mechanical strength, thermal stability and its antibacterial activity. *Compos Sci Tech*, 2013, 87: 1–7
- 28 Phua SL, Yang L, Toh CL, *et al.* Reinforcement of polyether polyurethane with dopamine-modified clay: the role of interfacial hydrogen bonding. *ACS Appl Mater Interfaces*, 2012, 4: 4571–4578
- 29 Green DW, Winandy JE, Kretschmann DE. Mechanical properties of wood. In: Ross RJ (Ed.) *Wood Handbook: Wood as an Engineering Material*. Madison: Department of Agriculture, USDA Forest Service, Forest Product Laboratory, 1999: 1–45
- 30 Liu Y, Mecking S. A synthetic polyester from plant oil feedstock by functionalizing polymerization. *Angew Chem Int Ed*, 2019, 58: 3346–3350
- 31 Christensen PR, Scheuermann AM, Loeffler KE, *et al.* Closed-loop recycling of plastics enabled by dynamic covalent diketoenamine bonds. *Nat Chem*, 2019, 11: 442–448
- 32 Ogden WA, Guan Z. Recyclable, strong, and highly malleable thermosets based on boroxine networks. *J Am Chem Soc*, 2018, 140: 6217–6220

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

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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生物质基可锻造材料的制备和闭环循环利用

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摘要 塑料废弃物的大量积累已经对生态系统造成了严重的威胁. 因此, 寻找和开发可以替代石油基塑料的生物质基材料成为亟待解决的问题. 然而, 分离生物质中各组分的成本较高, 且生物质材料不具备传统塑料的加工特性, 从而制约了生物质基塑料材料的开发. 本文报道了一种通过直接复合未分离的生物质和动态共价聚合物高效制备生物质基塑料的方法. 通过简单的热压复合生物质/动态共价聚合物混合物即可获得连续相的塑料状材料. 该材料不仅具有优异的可修复、再加工和热塑形特性, 而且可以完全降解和回收利用. 该研究为大规模工业化生产环境友好型生物质基塑料开辟了新道路.