Heat- or Water-Driven Malleability in a Highly Recyclable Covalent Network Polymer

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Covalent network polymers, which offer robust mechanical properties, generally lack the ability to be recycled.[1] There has been a great deal of research effort to incorporate reversible crosslinks into network polymers in order to obtain mechanically tough materials with self-healing properties.[2–13] Many have employed non-covalent crosslinks to achieve this goal. Ionic and hydrogen bonds are readily reversible and have been known to achieve efficient self-healing performances.[14–17] However, these systems are generally vulnerable to heat as well as water and other polar solvents, and are not as resilient as covalent network polymers. Leibler and co-workers introduced the concept of incorporating a certain type of dynamic covalent interaction (i.e., reversible ester linkages) in a covalent network polymer, and demonstrated the malleability of epoxy-acid network polymers at elevated temperatures.[2] Recently, Guan and co-workers demonstrated that a crosslinked polybutadiene network becomes malleable when the olefin exchange reaction is enabled by introducing Grubbs' Ru complex.[3] These polymers can be reshaped, healed, and molded together because of efficient crosslink exchange reactions wherein new crosslinks are formed at the same time as the original crosslinks are cleaved. This enables the polymer to maintain a constant crosslink density throughout the process.[18] However, these polymers' reprocessing requires very high temperatures (ca. 180 °C) or relies on catalyst additives which add cost and complexity, and potentially limit the polymer lifetime due to catalyst quenching. Some catalyst-free malleable polymers have been developed,[4,12] but these exhibit highly active crosslink exchange at ambient temperatures which leads to undesirable polymer creep in any load-bearing application.

Imine chemistry, also known as Schiff base chemistry, is the most often employed reversible covalent interaction, and includes two distinct processes: imine condensation/hydrolysis, and imine exchange.[19] The wide variety of commercially available diamines and dialdehydes makes polyimines highly accessible functional polymers, with many well-demonstrated unique functionalities.[20–24] Polyimines, which are described as dynamers by Lehn,[25,26] are stimuli-responsive polymers, most notably exhibiting macroscopic responses to changes in pH.[27,28] Several imine-containing polymers have been demonstrated, including pH-responsive hydrogels[20] and a working organic light-emitting diode (OLED).[23] However, the potential of polyimines as malleable, mechanically resilient polymeric materials, as well as their processability, have remained largely unexplored. We envision that imine-linked polymers can take malleability in covalent network polymers to the next level of simplicity, affordability and practicality. Herein, we present the first catalyst-free malleable polyimine which fundamentally behaves like a classic thermoset at ambient conditions yet can be reprocessed by application of either heat or water. This means that green, room temperature processing conditions are accessible for this important class of functional polymers.

A crosslinked polyimine network was prepared from commercially available monomers: terephthaldehyde, diethylene triamine, and triethylene tetramine (**Figure 1**a). A polyimine film was obtained by simply mixing the three above components in a 3:0.9:1.4 stoichiometry in the absence of any catalyst in a mixture of organic solvents (1:1:8, v/v/v, CH_2Cl_2/EtOAc/EtOH), then allowing the volatiles to evaporate slowly. Alternatively, the polymer can be obtained as a powder by using ethyl acetate as the only solvent. The polymerization reaction was confirmed by infrared spectroscopy, which revealed that aldehyde end groups were consumed while imine linkages were formed (Figure S2, Supporting Information). The resulting translucent polymer is hard and glassy at room temperature (T_g is 56 °C) (Figure S1, Supporting Information) and has a modulus of near 1 GPa with stress at break of 40 MPa (Figure S3, Supporting Information).

The time and temperature dependent relaxation modulus of the polyimine film was tested to characterize the heat-induced malleability. Figure 1b depicts the results of a series of relaxation tests over a wide range of temperatures (50–127.5 °C) on a double logarithmic plot. Specifically, at 80 °C, the bond exchange reaction is initiated and the normalized relaxation modulus is decreased from 1 to 0.11 within 30 min, indicating an 89% release of the internal stress within the thermoset polymer. By shifting each relaxation curve horizontally with respect to a reference temperature at 80 °C, a master relaxation curve was constructed (Figure 1c), which indicates the stress relaxation of the polyimine follows the classic time-temperature superposition (TTSP) behavior. The plot of time-temperature shift factors as a function of temperature (Figure 1d) shows that the polyimine's stress-relaxation behavior exhibits Arrhenius-like temperature dependence. Using the extrapolation, we calculated that while it takes 30 min for the stress to be relaxed by ca. 90% at 80 °C, the same process would take ca. 480 days at room temperature. The polyimine is thus the first reported

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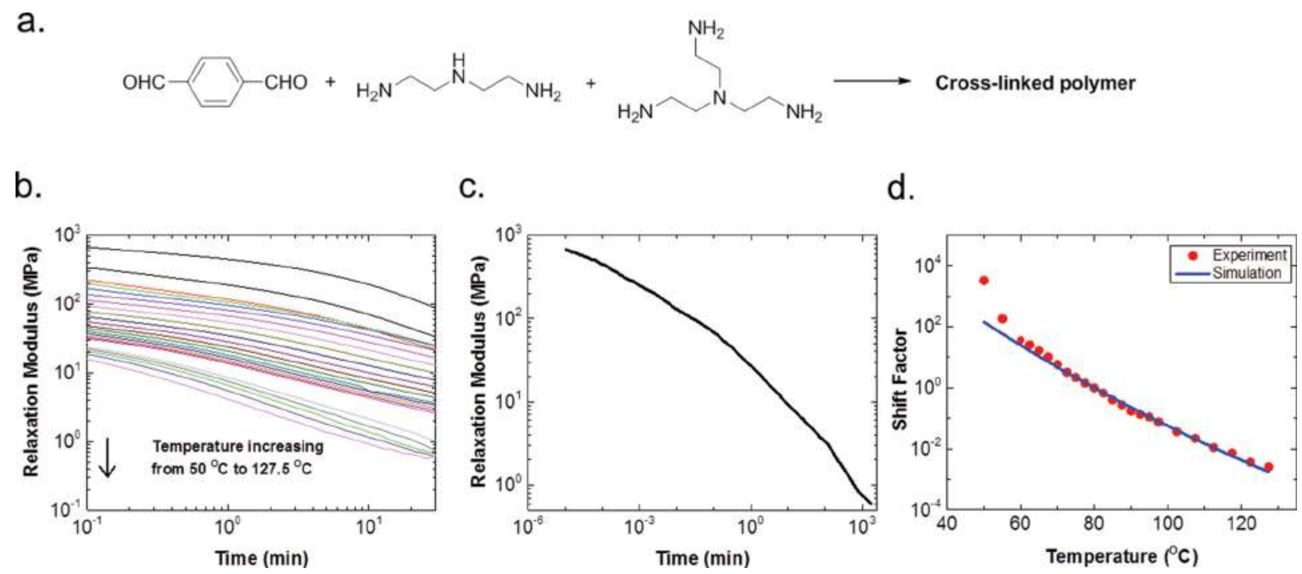

Figure 1. Polymer synthesis and stress-relaxation studies. a) Synthesis of crosslinked polyimine. b) Stress relaxation curves at various temperatures over a time period of 30 min. This data was used for the temperature-time superposition calculations. c) Temperature-time superposition master curve derived from data in Figure 1b. d) Shift factor vs. temperature plot for temperature–time superposition experiment. The blue line is derived from 80 °C reference temperature data from Figure 1c.

catalyst-free malleable polymer that mimics a classic thermoset at ambient temperatures and could be used for load bearing applications. The temperature (80 °C) required for fast bond exchange in the polyimine is easily obtainable, yet beyond the operating conditions encountered in most applications.

After the malleable behavior of the polyimine was confirmed, the recyclability of the material was explored. We investigated the durability of the imine-linked polymer toward complete reprocessing from powder to solid. It should be noted that this is a very demanding test as the transition from powder to coherent solid requires perfect healing across many thousands of interfaces between particles. Molding a batch of as-synthesized polymer powder under a pressure of 90 kPa for 45 min at 80 °C (**Figure 2**a) formed a solid polymer disc (Figure 2b). The disc was subsequently ground into a fine powder (Figure 2c) and the recycling process was repeated 3 times. Our study shows that the recycled materials exhibit no degradation in mechanical strength through 4 generations of recycling. A slight decrease in elastic modulus through the first few recycling generations was observed (Figure 2d), indicating that the polymer becomes more flexible as it is recycled. Notably, there is no loss in the tensile strength of the polymer, but rather a slight increase is observed from the 1st through the 4th generation (Figure 2d). Overall, this catalyst-free polyimine exhibits impressive recyclability, indicating that the imine bond is resilient against recycling fatigue.

Imine linkages are often considered susceptible to cleavage by hydrolysis. However, the extent of hydrolysis is a simple matter of chemical equilibrium.[29] It has previously been shown that certain crystalline organic molecular cages containing multiple imine bonds have greatly improved resistance to hydrolysis.[30] We examined the characteristic stress-strain behavior for polyimines at various levels of atmospheric humidity (Figure S6, Supporting Information). Like wood, the polyimine material becomes more pliable with increasing atmospheric humidity, but even at very high atmospheric humidity levels (90% RH), the polymer's mechanical properties are drastically different than when it is saturated with water. When the polymer disc is immersed in water, the hard glassy polymer becomes soft and flexible as it swells. The sample reaches saturation and the swelling remains constant after 12 h (Figure S5, Supporting Information). Importantly, the polymer retains its mechanical integrity even after 1 week under water at 96 °C. This combination of pliability and insolubility suggests that the malleability of the polyimine could also be activated by water. To characterize the malleability caused by water, a stress-relaxation experiment was performed under water at 25 °C on a polymer film sample that was initially saturated in water for 24 h. It reveals that the stress relaxation of the polyimine in water is comparable to the behavior observed at elevated temperatures. More importantly, the underwater condition allows more expedient stress relaxation than heating the polymer to 127.5 °C (**Figure 3**g). Such water-induced stress-relaxation behavior offers the remarkable opportunity of green and energy neutral reprocessing and reshaping of the polyimine thermoset. For instance, as-synthesized polyimine powder was reprocessed into a translucent polymer disc by simple molding in water for 24 h at room temperature under 90 kPa (Figure 3b & 3e). After drying under vacuum, the resulting polymer disc showed typical hard polymer behavior: high elastic modulus, and relatively small elongation at break. The water-healed polymer is more elastomeric compared to the heat-pressed powder (Figure 3f). In sharp contrast, when dry powder was reprocessed under the same conditions, a brittle disc of compacted powder was obtained (Figure 3d). There was thus no macro-scale evidence of bond exchange reactions in the absence of water at room

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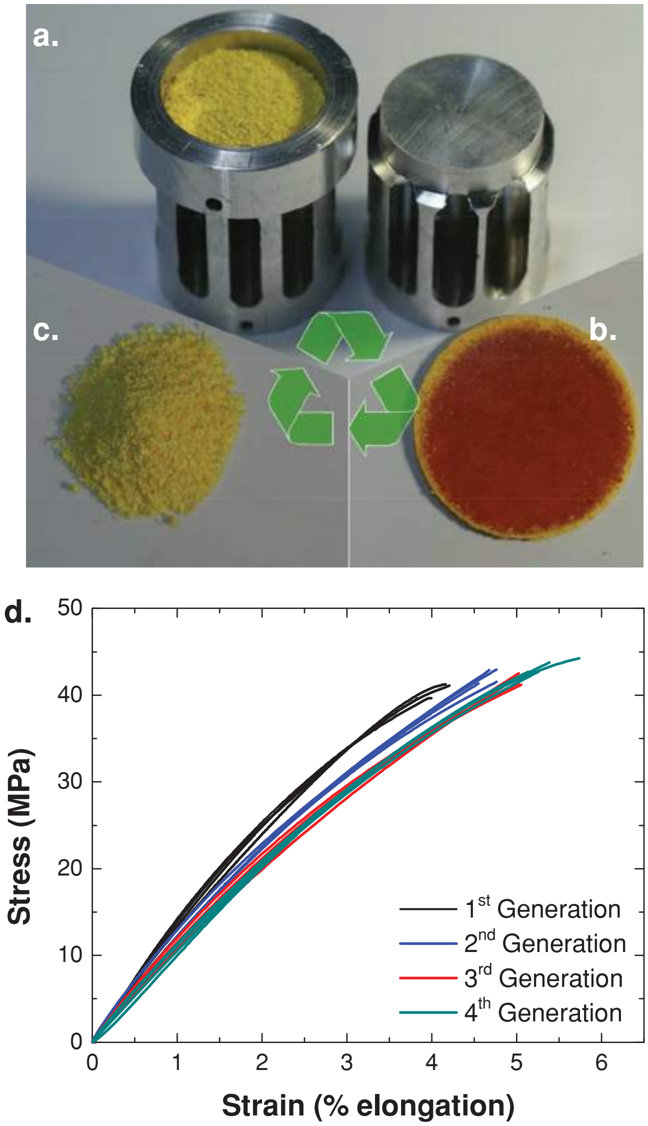

Figure 2. Recycling study. a) Aluminum mold used to heat press polyimine powder into solid disc. b) Solid polyimine disc formed from powder by pressing at 80 °C. This is the material used for stress–strain testing in Figure 2d. c) Polyimine powder obtained by grinding the solid disc in Figure 2b with sandpaper. d) Stress–strain curves for the solid shown in Figure 2b through four generations of recycling from powder to solid. For each generation, four separate stress-strain experiments are displayed. Black curves: 1st generation solid formed by heat-pressing the fresh as-synthesized polymer powder into a solid disc. Blue curves: 2nd generation solid formed by heat pressing the powder obtained by grinding the first generation solid. Red curves: 3rd generation solid formed by heat pressing the powder obtained by grinding the 2nd generation solid. Green curves: 4th generation solid formed by heat pressing the powder obtained by grinding the 3rd generation solid.

temperature. These results clearly show that water can turn on the malleability of the polymer.

The use of water to reshape a thermosetting polymer is environmentally friendly, economical, and also highly desirable for applications where it would be impossible to use heat. As a demonstration, a polyimine film was reshaped using water at room temperature. A 0.31 mm thick sample of dry polymer film was submerged in water for 3 h (**Figure 4**a,b). The wet, newly pliable film was stretched over a round mold (Figure 4c), and allowed to dry in a plastic zip bag containing drying

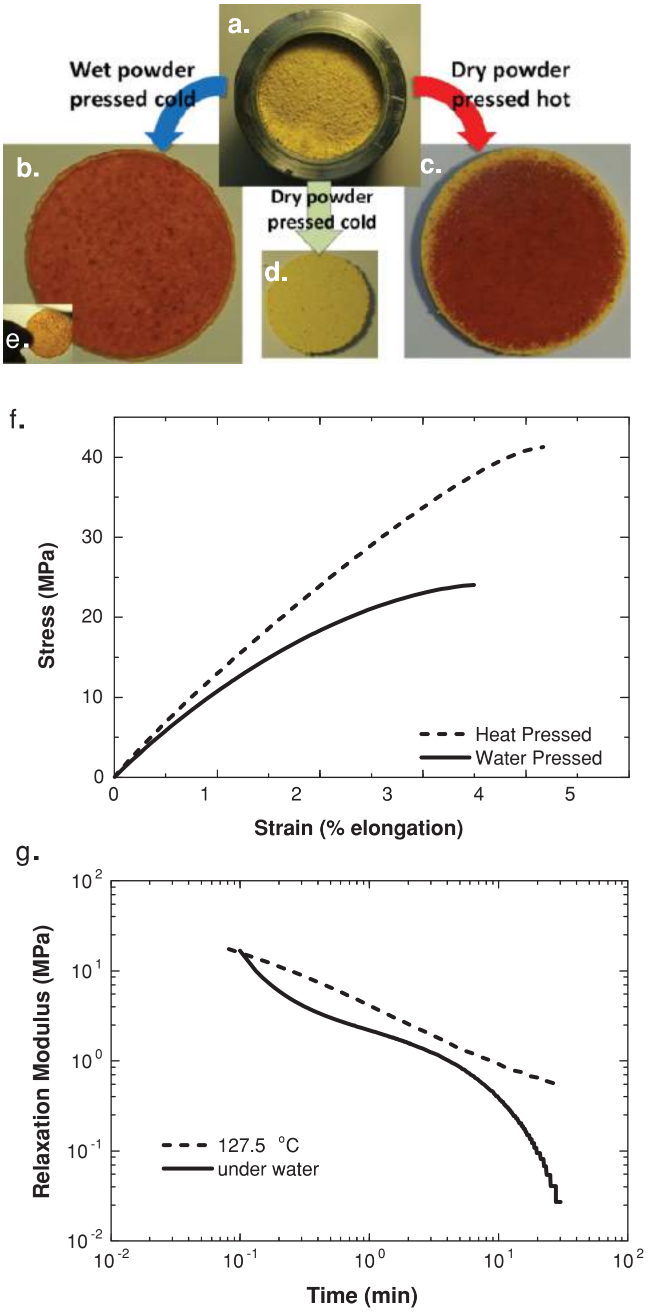

Figure 3. Processability summary. a) Polyimine powder in aluminum mold. b) Polyimine disc formed by pressing the wet powder under 90 kPa at room temperature for 24 h. c) Polyimine disc formed by heat pressing the dry powder under 90 kPa at 80 °C for 40 min. d) Brittle polyimine disc formed by pressing the dry polyimine powder under 90 kPa for 96 h at room temperature. e) The translucent nature of the solid disc in Figure 3b. f) Stress–strain experiments of recycled polymer discs under heat vs. water. The hard resilient polymer disc formed by pressing in water has lower tensile strength and elastic modulus compared to the disc formed by heat pressing of the polyimine powder. g) The stress-relaxation behavior of polyimine discs under water vs. heat. The presence of water enables more efficient relaxation than the highest temperature condition.

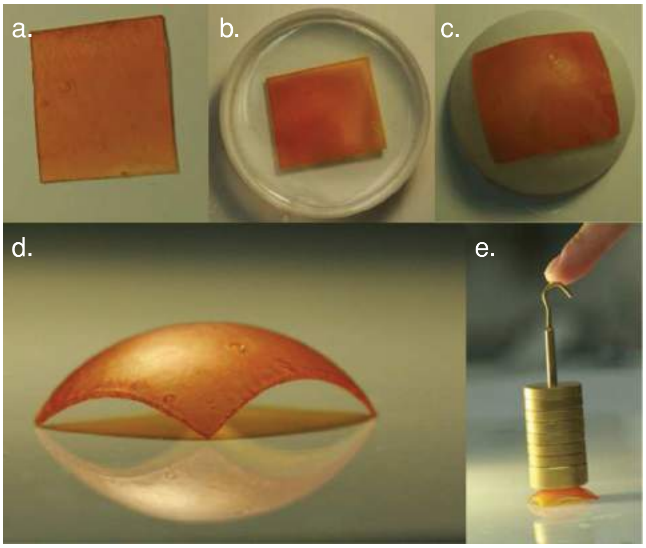

Figure 4. Water-induced malleability experiments. a) The solid polyimine film which is dry, hard, and glassy. b) The film sample after soaking in tap water for 3 h. c) The wet film sample is stretched over a round mold made from ping pong ball. d) The film sample from Figure 4c following 24 h in a plastic zip bag with a drying agent. The dried film sample is equally hard and glassy as it was in Figure 4a, but retains its rounded shape. e) The polymer's ability to retain its new shape is demonstrated by applying a pressure in excess of 190 g without substantial deformation of the solid.

agent for 24 h to obtain a dry polymer film which retained its new shape (Figure 4d). The dried material exhibits robust mechanical properties. The film could support loads in excess of 190 g without significant flexure (Figure 4e). When the object was flattened completely under multi-kg loads, it immediately sprang back to its rounded shape upon removal of the load. These results demonstrate that the polyimine material can be reshaped by simply soaking with water, transforming into a new shape, and drying to set the new shape of the mechanically resilient covalent network polymer.

To corroborate the theory that stress relaxation and malleability in the bulk polymer occurs as a result of imine exchange under heat, we studied imine exchange kinetics at various temperatures. Subsequent to the mixing of two parent imine molecules, dibenzylideneethane-1,2-diamine (**aa**), and bis(4-bromobenzylidene)ethane-1,2-diamine (**bb**), the formation of a new imine species (**ab**) was monitored by NMR spectroscopy at three different temperatures: 35 °C, 45 °C, and 60 °C (Figure S4, Supporting Information). We observed that the reaction reaches equilibrium most quickly at 60 °C while the reaction at 35 °C takes the longest to equilibrate. Though the bond exchange conditions in the bulk polymer would be different from those of small molecules in solution, the model study demonstrates the feasibility of utilizing imine exchange reactions as a temperature-dependent approach to achieve stress relaxation and malleability of the polymer.

Since the polymer material remains insoluble in water even at high temperatures (96 °C), it is likely that the equilibrium condition involves hydrolysis of only a small proportion of imine linkages. We examined the extent of imine hydrolysis in the equilibrium state by measuring the ratios of imine linkages to aldehyde end groups in the dry and water-saturated polymer using magic angle spinning ^{13}C NMR spectroscopy. The imine to aldehyde ratio in the wet polymer (ca. 40:1) was comparable to that of the dry polymer (ca. 60:1) within the error of the measurement (Figure S7, Supporting Information), indicating that relatively few imine linkages are hydrolyzed when the polymer is saturated in water. Since the degree of hydrolysis in the polymer is insignificant, hydrolysis alone is not likely the cause of the observed malleable behavior. It should also be noted that several other solvents (i.e., toluene, dioxane, and EtOH) tested are unable to reprocess or reshape the polyimine material. It is therefore plausible that water induces hydrolysis and facilitates the subsequent imine/amine exchange reactions, which are responsible for the polymer's capacity to transform from powder to coherent solid when immersed in water.

We have shown that an inexpensive, catalyst-free network polyimine material exhibits Arrhenius-like malleability in response to heat, leading to >100% recycling efficiency through multiple generations. This malleable covalently crosslinked network polymer can also be recycled and reshaped at ambient temperature using only water, potentially leading to energy-neutral green processing of the material. To the best of our knowledge, this is the first report of water driven malleability in a highly-recyclable covalent network polymer. Starting from either film or powder, simple molds can be used with either heat or water to form strong polymeric structures of any shape. This represents an ideal system for do-it-yourself prototyping of crosslinked polymeric solids, which will retain intrinsic value as the polymer can easily be recycled. Similar recyclability and solid state processing should be attainable for many functional polyimines, such as conductive polyimines. Furthermore, the use of water for stress-relaxation in polyimines could provide an additional (moisture) trigger for elastomer actuator applications.

Experimental Section

Polymer Preparation: The polyimine films were prepared by first dissolving 1 molar equivalent of terephthaldehyde (purchased from Sigma–Aldrich and subsequently purified by silica gel column chromatography using 1/4 CH_2Cl_2/hexanes) in a minimum amount of dichloromethane:ethyl acetate:ethanol (1:1:8 volume ratio). Then 0.3 molar equivalents of diethylene triamine (purchased from Sigma–Aldrich and used without further purification) and 0.4667 molar equivalents of triethylene tetramine (purchased from Alfa Aesar and used without further purification) were dissolved together in ethanol, and then added to a box-shaped tray made by folding silicone-coated paper. The terephthaldehyde solution was then added to the same tray. The solvent was allowed to evaporate in a fume hood under ambient conditions, leaving a defect-free polymer film. The film was then gradually cured in a drying oven: 30 min at 75 °C, then 30 min at 85 °C, and finally 30 min at 105 °C.

The polyimine powder was prepared by predissolving each of the monomers in the same stoichiometric ratios as above in ethyl acetate, and adding together to an open 200 mL beaker in an oil bath at 65 °C in a fume hood. When the ethyl acetate is evaporated, the polymer powder is collected from the dry beaker.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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