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Recyclable, strong and highly malleable thermosets based on boroxine networks

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Supporting Information Placeholder

ABSTRACT: Traditional thermoset materials have favorable material properties but are unable to reprocess and difficult to recycle. Small molecule boroxines have been shown to undergo reversible exchange reaction. Herein we employ boroxine as dynamic crosslinks to construct a novel type of thermoset material that is strong, highly malleable, and recyclable. The synthesis and dynamic mechanical properties of boroxine networks are described. Upon heating in water the material can be recycled back to its monomer. With a multitude of tunable variables, we anticipate this system to be a platform for the development of a range of new dynamic materials.

The development of strong, reprocessable, and recyclable thermoset materials is a major challenge in polymer science. The chemically crosslinked structure of thermosets that gives rise to their favorable material properties simultaneously leads to difficulty in reprocessing or recycling the material. Several reports have described malleable thermosets by introducing dynamic covalent linkages into networks. Such malleable thermosets were called covalent adaptable networks (CANs) [1] or vitrimers.[2] In the seminal work by Montarnal *et al.*,[2] thermally triggered malleability was demonstrated in a network material using transesterification reactions under Lewis acid catalysis. These thermosets showed glasslike malleability yet retained their mechanical properties and solvent resistance like traditional thermosets. Since this work, several other malleable thermosets[3] have been reported by using trithiocarbonate exchange,[4] urethane exchange,[5] vinylogous urethane transamidation,[6] olefin metathesis,[7] imine exchange,[8] boronic ester exchange,[9] thiol-Michael reaction,[10] carbonate exchange,[11] and transalkylation[12] as the dynamic covalent chemistries.[13] Despite these important progresses, it remains a challenge to design mechanically strong and highly malleable thermosets that are not only reprocessable, but also easily recyclable to monomers.

Recently our laboratory has been interested in developing dynamic polymers using boron-oxygen (B-O) linkage because of B-O bond's unique combination of high thermodynamic stability and kinetic tunability. In a previous study,[9a] we demonstrated boronic ester as a viable dynamic covalent motif for malleable and healable polymers. In addition to boronic esters, boroxine is another interesting motif formed by simple dehydration of organic boronic acids.[14] Boroxine motif has been used for several materials applications, including flame retardants,[15] covalent organic framework (COF),[16] and polymers.[17] However, boroxine has not been reported for making malleable polymers. Meanwhile, a recent study reported recyclable, strong thermosets via paraformaldehyde condensation with diamines to form poly(hexahydro-triazine) network.[18] Given boroxine and hexahydrotriazine have analogous structures (both 6-membered ring, $(BO)_3$ versus $(CH_2N)_3$), we envision that boroxine chemistry can be used to design recyclable, strong and dynamic polymer networks. Herein, we report the first boroxine-based thermoset polymers that are strong, highly malleable, and completely reprocessable and recyclable (Figure 1).

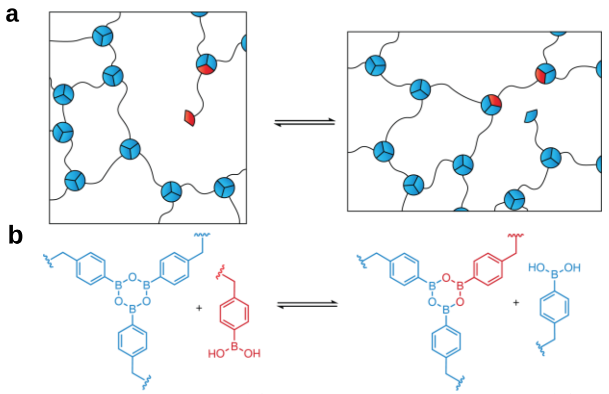


Figure 1. Design concept. (a) Malleable boroxine networks. (b) Putative boroxine exchange mechanism for network malleability.

To test the dynamic nature of boroxine linkage, we first conducted model studies of boroxine exchange kinetics. While boroxine exchange with boronic acids has been previously discussed,[19] no kinetic data was reported. For this purpose, we synthesized two model boroxines **1** and **2,** which upon dissolving in DMSO-d_6 underwent rapid exchange as evidenced by the appearance of three sets of benzylic protons next to methoxy group for **2** –**4.** Upon heating, the three peaks broadened and eventually coalesced into a singlet at 85 °C (Figure 2).

Using peak coalescence procedures, we obtained the activation energy of 81.6 kJ/mol for the model reaction. Because we added pyridine-based plasticizer in later

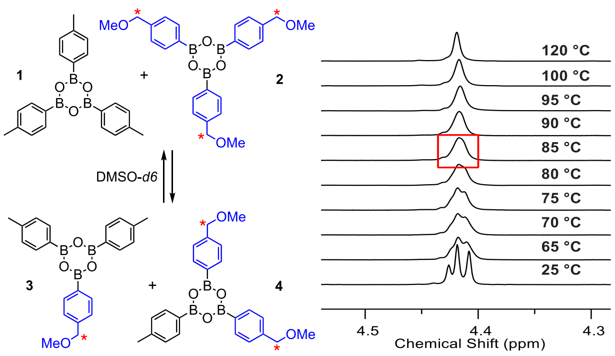
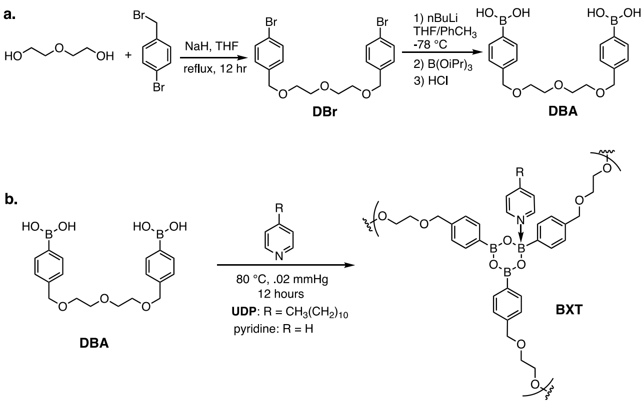


Figure 2. Variable temperature peak coalescence for boroxine dynamic exchange. Left: chemical structures of exchanging boroxines; Right: ^{1}H NMR peaks for the benzylic methylene's next to the oxygen (marked with an *) at different temperatures.

thermoset studies, we also investigated the exchange kinetics by adding one equivalent pyridine into the exchange solution. Using the same method, the activation energy was found to be 82.7 kJ/mol in presence of pyridine (see SI for more details). The addition of pyridine does not seem to impact the boroxine exchange kinetics. Putatively, boroxine exchange was facilitated by residual boronic acid resulting from hydrolysis with serendipitous water.

Encouraged by the small molecule exchange data, we set out to synthesize boroxine network. We first prepared a diboronic acid (**DBA**) monomer having a flexible linker. S$_N$2 substitution of 4-bromobenzyl bromide by fully deprotonated diethylene glycol gave **DBr** (Scheme 1a). Lithium halogen exchange, followed by treating with triisopropylborate led to a scalable synthesis of **DBA** monomer.[20]

Scheme 1. Synthesis of Diboronic acid DBA and Boroxine Network Material.



The boroxine network was formed by using a ligand facilitated boronic acid trimerization method previously reported[21] (Scheme 1b). **DBA** monomer was dissolved in pyridine and evaporated at room temperature for 12 hours followed by heating to 80 °C for 12 hours under high vacuum (Scheme 1b) to remove excess pyridine and promote full network formation. This method gave a robust material with reproducible mechanical properties. For mechanical tests, sample specimens were fabricated by melt pressing the material into testable dimensions.

The as prepared **DBA** boroxine thermoset (**BXT**) is strong but brittle. To make the thermoset more ductile and tougher, a plasticizer was added. In a previous study, Iovine and coworkers[14] added small molecule boroxine additives to a polystyrene/vinylpyridine copolymer with notable effects on the glass transition (T_g). Using similar boroxine/pyridine interactions, we added a long alkyl substituted pyridine, 4-undecylpyridine (**UDP**) (see synthesis in SI),[15] to boroxine thermosets as a plasticizer. The most preferred ratio of pyridine to boron in solid state structures is 1 to 3 or one pyridine per boroxine unit.[21] **UDP** was added to the pyridine solution of **DBA** before the slow evaporation with a feed ratio of 1:1 **UDP** to boroxine. We confirmed that the composition of our plasticized boroxine thermoset contained 1:1 **UDP** to boroxine (called **BXT/UDP**).

Consistent with thermoset structure, the network is insoluble in normal organic solvents. Due to the insolubility, we relied on several methods to confirm the structure of the thermoset. *First*, using toluene boronic acid as a model compound, we run condensation reaction under identical conditions as we used for polymerization. Based on ^{1}H NMR, boroxine with pyridine adduct was formed in high yield (see Scheme S4 and Figure S17 in the SI). Given the reaction conditions were identical, it is reasonable to assume that the dehydration of **DBA** during polymerization should afford similar structure in the network. *Second*, the dehydration during polymerization was supported by FTIR data. The **DBA** monomer displayed a strong band in > 3,000 cm^{-1} range corresponding to boronic acid OH stretching (see Figure S14 in the SI). This resonance almost disappeared in the final network, indicating the loss of OH during polymerization (see Figure S15 in the SI). *Finally*, despite the insolubility in normal solvents, the networks could be dissolved in methanol through methanolysis of the boroxine linkages. Taking advantage of this feature, we were able to confirm that a 1:1 **UDP**:boroxine composition was maintained in the boroxine thermoset using ^{1}H NMR spectroscopy (see Figure S16 in the SI).

To quantify the extent of boroxine formation in the thermoset, we employed a method[22] by titrating the amount of water generated from methanolysis. Methanolysis of pure boronic acids produces two molecules of water per boron, while reaction with pure boroxines produces only one. By measuring the amount of water generated from methanolysis of boroxine thermoset, we could estimate the extent of boroxine formation. Theoretical calculations show **BXT/UDP** would give 7.3 wt.% water if composed of 100% boroxine and 13.6 wt.% water if comprised completely of boronic acid (See SI for details). Methanolysis of our **BXT/UDP** network generated ~ 8.0 wt.% water, indicating that our network contains ≥ 89% boroxine, a value representing the lower bound of the boroxine content because any free water in the network or methanol should lead to overestimation of the boronic acid content.

The mechanical properties of the thermoset materials were first tested using uniaxial tensile method. Without the addition of **UDP** as plasticizer, the thermoset was stiff and relatively brittle (Figure 3a). At 10 mm/min strain rate, the Young's modulus was measured to be 768 MPa, tensile strength of 32.9 MPa, and strain at break of 5.58%. With the addition of **UDP** as plasticizer, the **BXT/UDP** was more ductile and tougher. While the material's Young's modulus decreased slightly (559 MPa), the extensibility (13.67%) and toughness (1.978 MJ/m^2) increased substantially when compared to the sample with no plasticizer. Full mechanical properties are displayed in Table 1.

Table 1. Boroxine network Mechanical Data with Varying UDP Levels (25 °C, 10 mm/min strain rate)

Sample	Young's Modulus (MPa)	Tensile Strength (MPa)	Strain at Break (%)	Toughness (MJ/m^2)
BXT	768	32.9	5.60	0.973
BXT/UDP	559	17.8	13.7	1.978

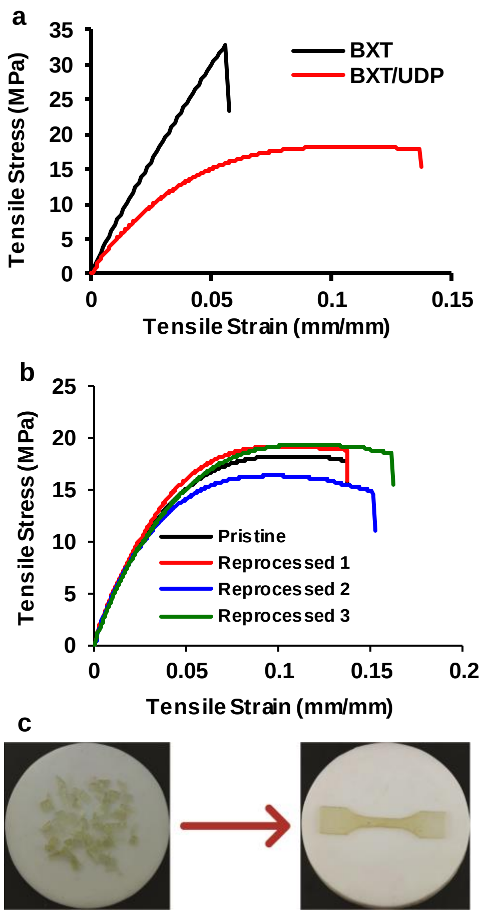


Figure 3. Tensile properties and reprocessability of boroxine networks. (a) Stress strain curves for **BXT** with or without **UDP**. (b) Reprocessability of the **BXT/UDP** thermoset. (c) Images of cut and reprocessed **BXT/UDP** samples.

The boroxine thermoset shows unusual mechanical behavior compared to traditional thermosets. Despite the highly cross-linked chemical structure and the mechanical strength, the material was found to be highly malleable. The malleability of the network material was investigated by both creep test (Figure S22 in SI) and stress relaxation experiments using compression mode dynamic mechanical analysis, from which the relaxation time was determined. Viscosity is related linearly to characteristic relaxation time (τ) or the amount of time it takes the material to relax to 1/e of the original stress. As expected, the material relaxed faster when the temperature was increased (Figure 4a). An Arrhenius plot was constructed using the relaxation time at different temperature[5] (Figure 4b).

The linear correlation of $\ln(\tau)$ with 1000/T indicates that the **BXT/UDP** sample exhibits Arrhenius flow characteristics. The activation energy of the relaxation process was calculated to be 79.5 kJ/mol, which is close to the activation energy measured for small molecule boroxine exchange reaction (82.7 kJ/mol). The excellent agreement supports that the malleability observed in bulk thermoset originates from boroxine exchange at molecular level. While the exact mechanism for boroxine exchange in bulk is not clear, putatively residual free boronic acids in the network facilitate exchange of boroxine linkages and afford the malleability in bulk.[19]

The linear Arrhenius plot shown in Figure 4b indicates that the material has vitrimer characteristics. The topological freezing temperature (T_v), defined as the temperature where the material no longer flows and has a viscosity greater than 10^{12} Pa*s, was obtained by calculating viscosity from characteristic relaxation time and extrapolating to the point where it equals 10^{12}Pa*s. Following published methods,[23] the T_v for our system was calculated to be −0.5 °C. This agrees with the observation that our boroxine thermoset is highly malleable at room temperature.

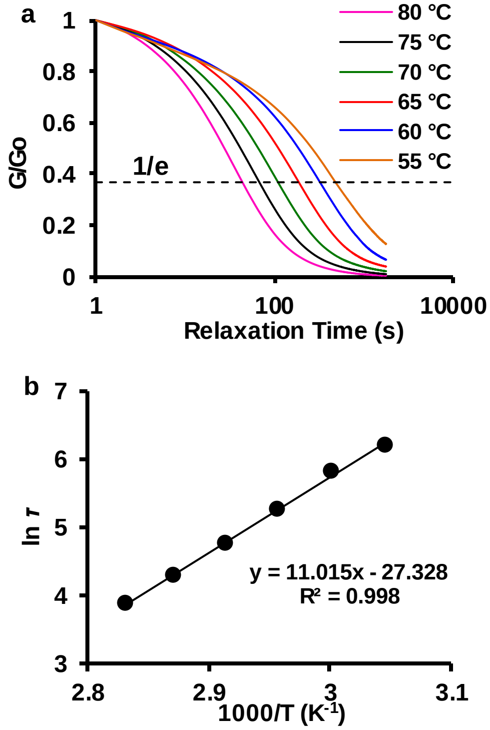


Figure 4. Malleability study of **BXT/UDP**. (a) Stress relaxation tests at various temperatures. (b) Fragility plot with linear fit. From this fit the activation energy is calculated to be 79.5 kcal/mol.

In addition to unusual mechanical properties (strong and highly malleable), another important attribute of this thermoset material is that it can not only be reprocessed repetitively, but also completely recycled to its monomer. For reprocessability test, a **BXT/UDP** sample was cut into many pieces which were then hot pressed in a Teflon mold at 110 °C to reform sample specimens (Figure 3c). The tensile stress-strain curves for the reprocessed samples are almost identical to this of the pristine sample (Figure 3b).

For monomer recyclability test, upon boiling in water the thermoset was found to disintegrate with time and eventually fully dissolve. After cooling the dissolved solution, a white precipitate was obtained. The solid was found to have a ^{1}H NMR spectrum identical to that of the starting **DBA** monomer (see Figure S18 in the SI). This experiment demonstrated the feedstock recyclability of boroxine thermosets. While being recyclable, it should be noted that the boroxine network is relatively stable under low humidity conditions. We confirmed this by exposing the **BXT/UDP** samples to various relative humidity levels in a humidity chamber. For example at 40% RH there was only 20% drop in the mechanical properties after several days (see SI for details, Table S1).

In conclusion, we have developed a strong, highly malleable, and fully reprocessable and recyclable new thermoset using the boroxine crosslinks. The network synthesis is simple (dehydration) and generally applicable to any boronic acid monomers. Consistent with thermoset structure, the network is insoluble in normal organic solvents. FTIR spectroscopy and methanolysis followed by water titration provided evidence of high level of boroxine formation (≥ 89%). The new thermoset exhibits unusual mechanical behavior. While showing high Young's modulus (559 MPa) and tensile strength (17.8 MPa), it is highly malleable and exhibits vitrimer properties. The bulk malleability of the boroxine thermoset was corroborated with the dynamic exchange of small molecule boroxines observed with variable temperature ^{1}H NMR experiments. Finally, the new thermoset was found to be not only reprocessable, but also fully recyclable back to the monomer. The strikingly high malleability of our boroxine thermoset is reminiscent of the high adaptability of a commodity material, silly putty. However, a major difference is that our thermoset is strong (Young's modulus > 0.5 GPa, and tensile strength > 17 MPa) while silly putty is soft and elastomeric. With a combination of unusual properties (strong, highly malleable, and recyclable) and a multitude of tunable variables (monomer structure, comonomer, plasticizer), we envision our boroxine thermoset to be a platform for the development of a range of new dynamic materials.

ASSOCIATED CONTENT

Supporting Information

All experimental details including synthesis and characterizations, model reaction, polymerization and sample preparation, and mechanical studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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