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Metal-Catalyzed Transesterification for Healing and Assembling of Thermosets

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Supporting Information

ABSTRACT: Catalytic control of bond exchange reactions enables healing of cross-linked polymer materials under a wide range of conditions. The healing capability at high temperatures is demonstrated for epoxy−acid and epoxy−anhydride thermoset networks in the presence of transesterification catalysts. At lower temperatures, the exchange reactions are very sluggish, and the materials have properties of classical epoxy thermosets. Studies of model molecules confirmed that the healing kinetics is controlled by the transesterification reaction rate. The possibility of varying the catalyst concentration brings control and flexibility of welding and assembling of epoxy thermosets that do not exist for thermoplastics.

The ability to be welded by simple heating is an important feature of metals and silica glasses. Indeed, welding allows manufacturing of complex objects. For thermoplastic polymers, welding induced by the diffusion of polymer chains through the interface via a reptation process have been observed above[1] and slightly below[2] the glass transition temperature. However, the temperature must be carefully controlled to avoid material flow because the viscosity drops abruptly in a very narrow temperature range near the glass transition.[3] Chemically cross-linked polymers, also called thermosets, have outstanding thermal and mechanical properties and are irreplaceable in demanding applications, such as in structural parts needed by the aircraft and automotive industries. However, thermosets are not easily welded, as any kind of reprocessing is impossible once the curing reaction is complete. Various methods of assembly by adhesion have been envisaged, such as rough surface interlocking[4] and interdiffusion of network defects[5] or added linear thermoplastic chains[6] at the interface. For more robust welding, it is possible in some cases to stop the curing reaction before it goes to completion. Welding can then be induced by restarting the reaction once the desired parts are in contact.[7]

Recently, elegant dynamic covalent chemistries[8] have been introduced in thermosetting polymers to yield self-mending or stress-relaxation properties,[9] as predicted from theoretical works.[10] Wudl and co-workers have developed a thermosetting material based on the thermoreversible Diels−Alder reaction.[11] When heated, the sample can be mended, and the initial properties are recovered after cooling. However, depolymerization causes an abrupt viscosity drop during heating.[12] Therefore, if molds are not used, the assembly temperature range must be well-controlled as in the case of thermoplastics. Other reversible reactions such as amino/carbonyl reactions[13] or siloxane equilibration[14] have also been studied. Another method consists of using radicals to initiate exchange reactions[15] and plasticity in thermosets.[16] Materials cross-linked with such radical-exchangeable reactions exhibit good mending properties either thermally,[17] photochemically,[18] or even trigger-free.[19] Unfortunately, these methods require purpose-made monomers, which limits immediate widespread utilization.

Here we show that classical and largely available epoxy thermosets can be welded efficiently by inducing and controlling transesterification reactions. Such epoxy resins are currently widely employed in applications such as coatings, electronics, adhesives, and light-emitting diodes or as structural matrices in composites.[20] To allow for transesterification, the hardeners must be chosen from among carboxylic acids and acid anhydrides. Both react with epoxy rings to yield ester links.[20,21]

We recently demonstrated that with proper catalysis, the topologies of epoxy−acid and epoxy−anhydride networks can be rearranged by transesterification exchange reactions without modification of the numbers of links and average functionality.[22] At high temperatures, the networks can flow by topology rearrangements and behave like viscoelastic liquids. When the temperature is decreased, the transesterification exchanges slow down, and the topology of the network freezes. Below the topology freezing transition, the materials have properties of permanently cross-linked thermosets. The reversible transition from the viscoelastic liquid state to the elastic solid has the attributes of a glass transition. The viscosity gradually decreases when the temperature is increased, following an Arrhenius law as for the glass transition in silica and a few other inorganic compounds, the so-called strong glass formers.[23] We call this new class of organic materials exhibiting the network topology freezing glass transition “vitrimers”. Like classical thermosets, vitrimers are insoluble irrespective of temperature. The purpose of this paper is to prove that autogenous welding of two pieces of vitrimer can be done over a very broad range of temperatures. The principle of welding by exchange reactions is presented in Figure 1a.

The epoxy−acid networks used in this study were synthesized from the diglycidyl ether of bisphenol A (DGEBA) and a mixture of dicarboxylic and tricarboxylic

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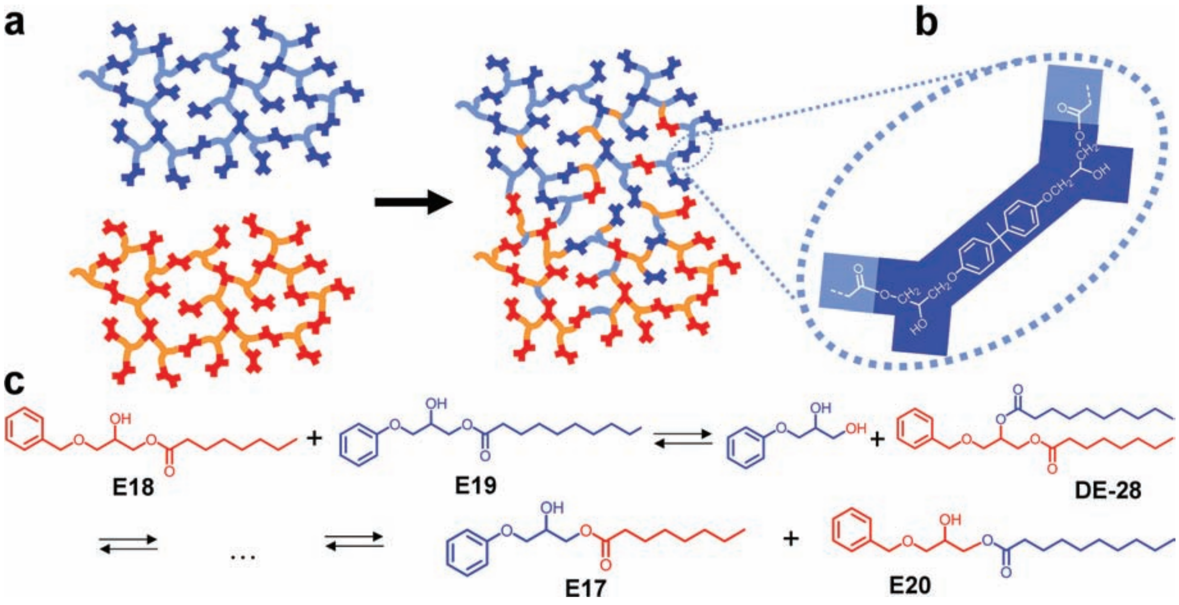

Figure 1. (a) Scheme illustrating the welding of two pieces of epoxy resin by transesterification exchange reactions. (b) Structure of the epoxy−acid network used in the study. The epoxy resin DGEBA is linked through β-hydroxy esters to dicarboxylic and tricarboxylic acids. (c) Model molecules E18 and E19 investigated to mimic β-hydroxy ester links. Numerous transesterification products appear when the mixture is heated, such as diester DE28 and β-hydroxy esters E17 and E20.

fatty acids (Figure 1b). The reaction of epoxy rings with carboxylic acids is rather complex, because several backside reactions can affect the network structure and properties. Three main reactions have been reported: (a) the addition of carboxylic acid groups on epoxy rings, yielding β-hydroxy esters; (b) the addition of hydroxyl groups on epoxy rings, yielding ethers; and (c) Fischer esterification of the hydroxyl groups by carboxylic acids [see the Supporting Information (SI)].[24] Several catalysts, such as 2-methylimidazole (2-MI), have been used over the years to promote reaction (a) over (b) and (c).[25] Under these conditions, the gelation may be predicted from the stoichiometry and average functionality using Monte Carlo simulations.[26] Also, for a stoichiometry of one acid to one epoxy ring, all of the ester and hydroxyl groups are obtained in equal amounts and are more prone to transesterification reactions.[27]

To quantify the kinetics of transesterification and control the dynamics of exchanges by metal catalysis, model compounds were studied. We synthesized two different β-hydroxy esters, E18 and E19 (where Ex is the β-hydroxy ester with x carbon atoms; Figure 1c), that mimic the ester links formed between a carboxylic acid and an epoxy unit. The exchange reaction was studied by GC−MS. Indeed, by design the exchange products are distinguished by the number of carbon atoms, and thus, they could be well-separated on a GC chromatogram and easily identified by mass spectrometry. After the mixture of model compounds E18 and E19 was heated, transesterification products appeared. Thus, at slightly shorter and longer retention times than the initial esters (Figure 2a), we observed the formation of the monoesters E17 and E20, respectively. At long retention times, the diester products corresponding to all six transesterification combinations among E17, E18, E19, and E20 were also present (an example is DE28 in Figure 1b; see the SI). As the four monoesters have very similar structures, a quantitative kinetics study could be performed by following the area ratio $r = (\text{E17} + \text{E20})/(\text{E18} + \text{E19})$ as a function of time.

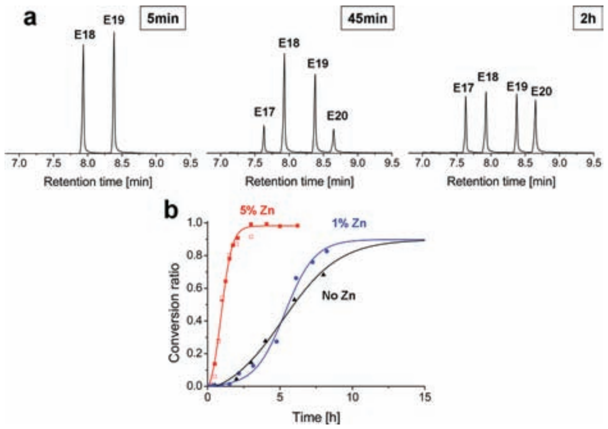

Figure 2. (a) Normalized GC chromatograms of an E18 + E19 mixture with 6 mol % 2-MI + 5 mol % $Zn(acac)_2$ at 150 °C after 5 min, 45 min, and 2 h. A quantitative kinetics study was performed by following the appearance of E17 and E20 with time. (b) Transesterification kinetics results for the model molecules. With no metal catalyst added or the addition of only 1 mol % $Zn(OAc)_2$, equilibrium was attained after 15 h. With 5 mol % $Zn(OAc)_2$ (□) or $Zn(acac)_2$ (■), this time was reduced to 2 h.

Without the addition of any metal catalyst, the transesterification reaction took ~15 h at 150 °C (Figure 2b). The method allowed us to screen different catalysts selected from the literature.[28] By adding metal salts such as zinc acetate or zinc acetylacetonate at 5 mol %, we were able to reduce the exchange time to only 2 h. Interestingly, zinc acetate is also an efficient esterification catalyst[25] and can thus be used alone in epoxy−acid networks. The metal concentration plays an important role, as shown in Figure 2b.

Epoxy−acid networks were synthesized in the presence of zinc acetate. The synthesis produced a soft epoxy network exhibiting a T_g of ~15 °C, a storage modulus of 4 MPa, and good elastomeric properties at room temperature.

To investigate the welding properties of these networks, we used the lap-shear test (Figure 3a). This test is intrinsically difficult to pass for material assemblies, since a fracture is easily initiated at the interface.[29] In our experiments, two rectangular samples of material (25 mm × 5 mm × 1.4 mm) were superimposed on a 15 mm length and held together under pressure for welding times ranging from 15 min to 15 h at a controlled temperature (room temperature or 100, 125, or 150 °C). A good contact was ensured by applying a 25% compression during the treatment. The welding efficiency was then evaluated by carrying out tensile tests at room temperature with a cross-head speed of 10 mm/min on the assembly and comparing the forces at break.

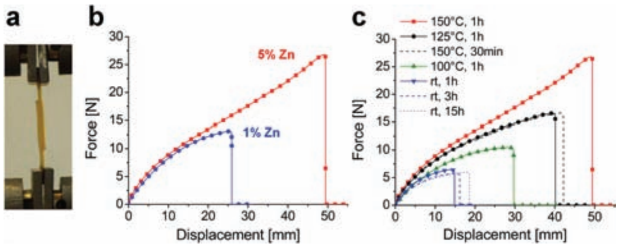

Figure 3. (a) Photograph of a sample during the lap-shear test. (b) Stress−strain curves of samples loaded with different catalyst concentrations and welded for 1 h at 150 °C. (c) Stress−strain curves of samples loaded with 5 mol % $Zn(OAc)_2$ and welded under different conditions.

With 1 mol % $Zn(OAc)_2$, after 1 h at 150 °C, the assembly broke quickly, with a force at break of ~15 N. Welded under the same conditions, a sample catalyzed at 5 mol % broke at 27 N (Figure 3b). For comparison, a simple rectangular ribbon with the same total length (35 mm × 5 mm × 1.4 mm) broke at 35 N. Welding for a longer time led to full recovery of the mechanical properties: after several hours at 150 °C, the rupture became cohesive and occurred in the bulk material far from the welded interface. For an easier comparison with results from model molecules, we limit the discussion here to temperatures up to 150 °C. Faster weldings were achieved at higher temperatures, however.

Figure 3c shows stress−strain curves of assemblies of material catalyzed at 5 mol % that were welded for various times at different temperatures. Just above the glass transition (room temperature), only adhesion due to interdiffusion of polymer chains (network defects) across the interface contributed to the separation force, which was ~6 N after welding for 1 h. Longer times (3 or 15 h) did not improve the adhesion very much. In contrast, at 150 °C, longer welding times resulted in better assembly properties (see the SI). It is noteworthy that the same welding properties could be obtained at two different temperatures by adjusting the treatment time: identical behavior was indeed observed with welding for 1 h at 125 °C or 30 min at 150 °C. This confirms that in contrast to thermoplastics, efficient welding can be achieved over a broad span of temperature. Thus, it should be possible to adjust more easily the welding temperature and welding time for any object dimensions. Indeed, by applying a contact pressure that is small compared to the elastic modulus of the sample, the interfaces can be healed without modification of the dimensions of the welded parts (see the SI). Because chemical moieties are only exchanged and not consumed during the welding process, several cycles can be done consecutively on the same samples (see the SI).

To extend this welding process to technologically relevant hard epoxy resins, networks were synthesized from DGEBA and glutaric anhydride. When stoichiometric amounts of epoxy rings and acid anhydrides were used, the addition−esterification reaction yielded only diesters and no hydroxyl groups. However, studies with model molecules showed that the presence of hydroxyl groups is crucial for transesterification reactions (Figure 4a). Under the same conditions of catalysis and temperature, full transesterification exchange between two hydroxy esters occurred within 2 h, only 50% exchange was obtained between *β*-hydroxy ester E18 and diester DE29 after 30 h, and no exchange at all could be observed between the two diesters DE26 and DE29 even after 24 h. Hydroxyl groups are thus needed in the exchange process, and their concentration controls the welding kinetics.

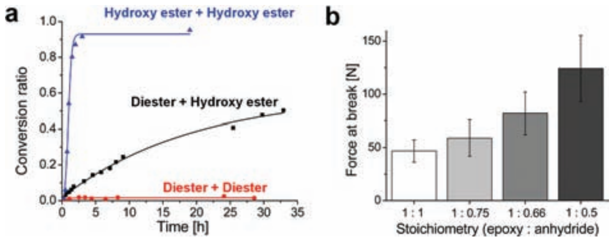

Figure 4. (a) Model molecule studies confirm the importance of hydroxyl groups in the exchange reactions. (b) The stoichiometry between epoxy rings and anhydride groups plays an important role in the welding properties, as it influences the concentration of hydroxyl groups in the network. The cross-sectional area was 1.4 mm × 5 mm. Each value is an average of five independent tests.

Experimentally, hydroxyl groups are observed in epoxy−anhydride networks when an excess of epoxy is introduced.[30] The epoxy−anhydride reaction has been extensively studied in the literature,[21] and the commonly accepted mechanism suggests that the reaction is an alternate ring-opening polymerization of anhydrides and epoxides.[31] In a first step, an anhydride is opened by a hydroxyl group or a catalyst, yielding a monoester and a carboxylic acid. In a second step, this acid opens an epoxy ring to form a diester and regenerate a hydroxyl group (see the SI). With an excess of epoxy, homopolymerization initiated by hydroxyl groups also occurs at the end of the process.[32] Since both reactions regenerate hydroxyl groups, all of the hydroxyl groups present in the cured material should have been present from the beginning. In the present case, hydroxyl groups could be the result of epoxy-opening reactions by water molecules, which are naturally present in the metal catalyst. When the relative ratio between the anhydride and epoxy was varied from 1:1 to 0.5:1, IR studies showed that the quantity of hydroxyl groups in the networks increased (see the SI).

Swelling experiments confirmed that the materials are well above the gel point and are insoluble. Dynamic mechanical experiments and differential scanning calorimetry showed that these networks have a storage modulus ranging from 60 to 100 MPa, and a T_g above 60−70 °C. The materials are therefore hard resins, comparable to those used in composites. The addition of a transesterification catalyst in such formulations enables efficient welding, as confirmed by lap-shear tests at room temperature at 0.1 mm/min. Figure 4b shows that the welding is stronger at lower anhydride/epoxy ratios.

These experiments demonstrate that metal-catalyzed transesterification permits the controlled establishment of chemical links at the interface between two epoxy networks. The key parameters controlling the kinetics and final strength of the welding are the concentration and the nature of the transesterification catalyst and the concentration of hydroxyl groups present in the networks. As for silica glass, the welding process is robust and can be achieved in different time−temperature windows without any changes in the material dimensions. Catalysis brings additional control and flexibility of process that do not exist for thermoplastics. The concept, already illustrated here for both soft and hard epoxy networks, can be readily extended to other polyester networks[33] and other systems that exhibit exchange reactions.

■ ASSOCIATED CONTENT

Supporting Information

Curing main reactions; synthesis of networks; synthesis and NMR and GC studies of model molecules; lap-shear tests; and FTIR spectra of hard networks. 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 interest.

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