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Ductile thermoset polymers by controlling network flexibility

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We report the design and synthesis of a polymer structure from cross-linkable epoxy/ionic liquid system which behaves like a hard and brittle epoxy thermoset, perfectly ductile thermoplastic and an elastomer, all depending on controllable network compositions.

Conceptually, thermosets are materials that can be irreversibly polymerized and molded into solid structures with desired shapes[1]. Epoxy resins are the most important class of thermoset materials, being used in a large variety of structural and functional applications. Thermosets, when compared to thermoplastics, have high dimensional stability, high mechanical, thermal, and environmental resistance; and are therefore unique in many challenging applications, such as in the automotive and aircraft industries[1]. Thermoset precursors are low viscosity liquids prior to cross-linking and their high fluidity facilitates the incorporation of fillers and fibers for the preparation of composites[2].

On the other hand, among the limitations encountered by thermosets and their fiber reinforced composites, these materials must be molded while manufacturing because once the cross-linking reaction is completed, these materials are neither transformable nor fashionable by solvent or heat. The relatively slow curing and molding process has impeded the adoption of these materials in automotive applications in particularly which requires processes that can form or stamp parts in seconds. Moreover, epoxy thermosets are highly brittle leading to the fracture of the epoxy based structural components and in most cases the whole panel has to be remolded and replaced. In current context of reducing energy consumption and waste, it is highly desirable to prolong the life time of components and find alternatives where one can make components without molding. Making thermosets flexible and formable is an exciting alternative that can find applications to a whole variety of transformation methods that exists for glass and metals. A number of systematic approaches have been reported on achieving networks with bonds that can disrupt and reform[3,4], based on exchange reactions by addition-fragmentation in the presence of radicals[5,6], bond breaking and reforming based on chemical equilibrium. However, these networks have limited reversibility or the chemical equilibrium can be displaced towards depolymerisation leading to unfavorable network structure and performance[7]. A recent report[8]

has shown the synthesis of reversible networks based on reversible exchange reactions by transesterification producing malleable thermoset materials, however with different synthetic routes using carboxylic acids and zinc catalysts. This method was further extended to other olefin containing polymers[9].

Here we show that making highly cross-linked networks flexible could provide a way to combine processability, formability and high performance[10-12]. In this work, we report a new thermoset composition that can be ductile and deformable after cross-linking and behave like a thermoplastic and even an elastomer at room temperature. These materials can be heated to a temperature such that they become soft, flexible and formable without suffering from degradation or structural loss typical of thermoset polymers and as such they have the potential to be rapidly stamped or formed rather than molded or cured. This new property of the thermoset material allows us to prepare structures or shapes that have been otherwise impossible by molding. Here, the flexibility is induced into the brittle epoxy network by incorporating molten salts known as ionic liquids (ILs). Structurally, ILs are molecular ions containing a bulky organic cation and a small anion[13]. Moreover, ILs are non-volatile, non-flammable, recyclable and possess excellent thermal and electrochemical stability[14,15]. Here, ILs works as an easily miscible molecular liquid to form complexes and become part of the cross-linked network giving materials unique thermo-mechanical properties[16,17]. In a previous study Matsumoto etal used a hydrophobic IL and examined the ionic conductivity and morphology of the blend materials[18].

To establish this concept, we used charge transfer complexation reaction to confine the bulky ionic liquids within the cross-linked networks. We synthesized classic epoxy networks of diglycidyl ether of bisphenol A (DGEBA) cured by a stoichiometric mixture of diamine curing agent, 4,4'-methylenedianiline (MDA). The charge transfer complexation was performed using the room temperature ionic liquid, 1-butyl-3-methylimidazolium chloride (BMIM[Cl]) and both cations and anions are involved in the complexation reaction. The oxygen and hydrogen atom of the epoxy hydroxyl groups form electron donor-electron acceptor (EDA) complexes with the charged species of the IL (**Figure** 1A). The EDA complexation of ILs has been reported with intractable natural polymers during their dissolution process[19,20]. The two centers of the species must be

positioned close enough to allow the charge transfer and complexation. The complexation leads to the uniform confinement of ILs molecules within the epoxy chains and thus all components become part of the cross-linked network.
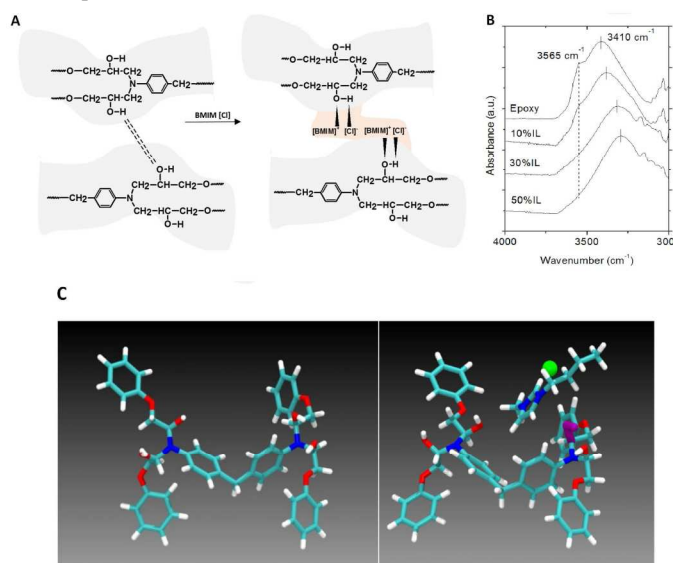

Figure 1. The formation of EDA complexes between epoxy and BMIM[Cl]. (A) The self-associated hydrogen bonding interaction in epoxy networks is changed to stronger EDA complex interaction in epoxy-IL network. (B) The hydroxyl stretching region in the infrared spectra of epoxy-IL cross-linked networks. (C) DFT-optimized structures of the epoxy chain fragment (left) and EDA-complex (right). Cl$^-$ is indicated in green. In the EDA-complex, the hydroxyl closest to the BMIM$^+$ ring is highlighted in purple.

The EDA complex formation results in the stretching of hydroxyl groups of epoxy network which was monitored by infrared spectroscopy (**Figure 1B**). Epoxy is a self-associating polymer due to the presence of its hydroxyl groups. Pure cured epoxy shows two distinct bands in the hydroxyl region. A broad band centered at 3410 cm^{-1} and a shoulder band at 3565 cm^{-1}, which can be attributed to the stretching vibrations of self-associated hydroxyl groups and non-associated free hydroxyl groups, respectively[21]. However, upon charge transfer complexation in the presence of ionic liquids, the peak corresponding to the free hydroxyl groups disappears and associated hydroxyl stretching band at 3410 cm^{-1} is shifted to lower frequencies indicating hydroxyl groups of epoxy are stretched due to complexation. This redshift also confirms that the bonding in EDA complexes is stronger than the self-associated hydrogen bonding in cured epoxy network, providing materials with modified and more flexible network structure.

Our density functional theory (DFT) calculations support this explanation. In these calculations we considered both a fragment of the epoxy chain (presenting four slightly different hydroxyl environments) in isolation, and, this same fragment of the epoxy chain in a complex with the BMIM$^+$[Cl$^-$] unit. In each case we optimized the geometry, and have calculated the vibrational frequency for each hydroxyl in both the uncomplexed and complexed cases. The predicted structures are given in **Figure 1C**, showing that the BMIM$^+$ unit is close to most of the hydroxyls in our epoxy chain fragment. In the complexed case, three of the four hydroxyls showed some reduction of the vibrational frequency compared with the uncomplexed case. Notably, we found that the hydroxyl located closest to the ring of the BMIM$^+$ unit in the complex exhibited the greatest reduction of vibrational frequency

(26 cm^{-1}). The hydroxyl most distant from the BMIM$^+$ unit showed negligible frequency change (+2 cm^{-1}).

Cross-linked epoxy-IL networks were prepared by varying the amount of IL from 10% up to 60% of epoxy resin by weight and a stoichiometric amount of MDA was added in all the mixtures to complete the curing reaction. The ternary mixture was premixed at 80 ºC and immediately poured into preheated molds and cured at 120 ºC for 10 h and post-cured at 180 ºC for 2 h. The mixtures were all transparent at 80 ºC before curing, hence indicating the macroscopic homogeneity of the mixtures in the molten state. The cured thermoset materials were also transparent at all compositions as shown in **Figure 2F**, and no evidence of phase separation was observed. The thermosets were examined under SEM (**Figure S1**) and the images show that the materials at all compositions were completely homogeneous proving that IL was totally miscible with the epoxy thermoset and no phase separation occurred during the curing process. The curing reaction was monitored using infrared spectroscopy and the disappearance of the peak at 914 cm^{-1} corresponding to the asymmetric stretching of epoxide groups indicate that the reaction is complete within 60 minutes (**Figure S2**). Moreover, the final thermoset polymer at each composition was also checked to ensure the complete conversion of epoxy groups (**Figure S3**). The cross-linked epoxy network behavior was confirmed by swelling experiments. The samples were heated with trichlorobenzene at elevated temperatures for 10 hours and it was confirmed that the samples were insoluble.

At room temperature, the materials show three distinct physical and mechanical behaviors with increasing concentration of IL in the composition; as a classic hard and brittle epoxy thermoset, perfectly ductile thermoplastic and like an elastomer. These behaviors are well understood from the tensile mechanical properties of the material shown in **Figure 2**. The materials behave like hard and brittle epoxy thermoset up to 20% of IL. This thermoset material showed analogous or better tensile stress and Young's modulus compared to the neat epoxy thermoset. As an example, hard thermoset with 10% IL exhibited a modulus of 2217 MPa and stress at break of nearly 75 MPa at room temperature. The percentage strain of this material was 11% which is comparable to neat epoxy thermoset. Surprisingly, the fracture toughness (K_{1C}) of the epoxy was increased by 101% by adding 20% of IL. It is believed that the transient crosslinking of the epoxy due to the formation of charge transfer complex between the ionic liquid and epoxy is responsible for the simultaneous improvement in both modulus and fracture toughness. The materials behave like a ductile plastic with 30% and 40% IL. The ductile behavior of this material is apparent in the stress-strain curves shown in **Figure 2A**. As an example, the plastic thermoset polymer with 30% IL has a modulus of 615 MPa and elongation and stress at failure of about 0.334 and 17.96 MPa, respectively. The strain to failure of this material is 66%. The fracture toughness was still 30% higher than the neat epoxy thermoset. The materials behave like elastomers at 50% and 60% of IL content. The elastomeric thermoset with 50% IL showed typical S-shaped curve (**Figure S4**) with a strain and stress at failure of 0.82 and 2.55 MPa, respectively with a modulus of 3.04 MPa. The percentage elongation of this material is 280%.

The hard thermosets are flexible upon heating and can be bent or twisted in to any desirable shape without breaking them. A complex fusilli shape was created for all three different materials by hand twisting and the change in shape is shown in Figure 2. The plastic and elastomeric thermoset materials are flexible at room temperature by applying a small local force. The plastic thermosets retain their shape upon bending or twisting, however the elastomeric thermosets return to the original shape when the force is removed.
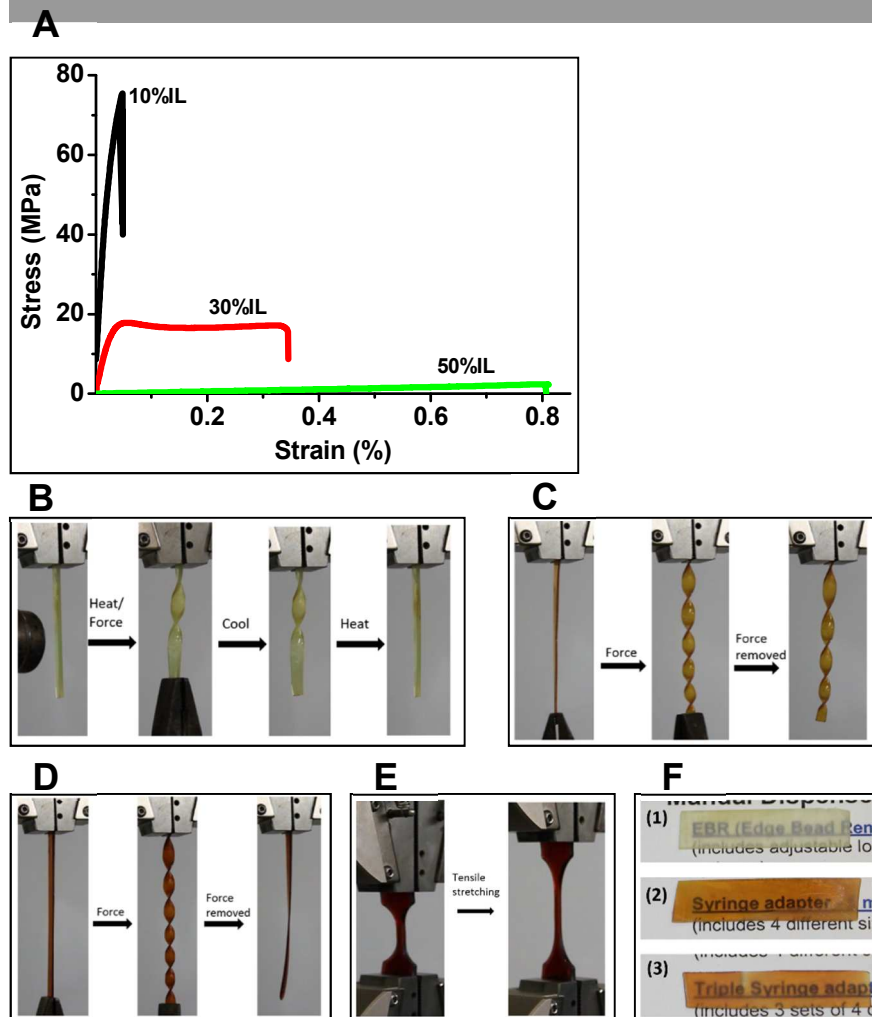
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Figure 2. The tensile mechanical properties of the multifunctional ductile thermosets at various IL concentrations and their physical appearance and behavior at room temperature. (A) Tensile stress-strain curves of *hard thermosets* (black curve) showing perfectly brittle fracture at 10% IL, *plastic thermosets* showing ductile behavior of at 30% of IL (red curve) and S-shaped curves of *elastomeric thermosets* at 50% IL (green curve). (B) The *hard thermosets* can be reversibly bent or twisted by applying local heat and force and the polymer retains the new shape and original material properties after the cooling. The material returns to its original shape when heated again. (C) At room temperature, the *plastic thermosets* can be bent and twisted by applying a relatively small force and the polymer retains the new shape even after the force is removed. (D) The *elastomeric thermosets* can be bent and twisted by applying small force and it returns to original shape after the force is removed. (E) The *elastomeric thermosets* before and after 280% elongation. (F) The transparency of thermoset materials; (1) *hard thermosets* at 10% IL, (2) *plastic thermoset* at 30% IL and (3) *elastomeric thermosets* at 50% IL.

The DMA thermomechanical properties of thermosets materials are presented in **Figure 3**. The storage modulus (G') of the hard thermosets is remarkably higher than that of the neat epoxy at room temperature. The hard thermoset at 20% of IL showed about 60% improvement in G' of glassy epoxy at 30 °C which is considered to be significant. The G' value of plastic thermoset at 30% of IL was marginally higher (12%) than that of neat epoxy despite being a soft material. These materials at any specified composition shows a single glass transition temperature (T_g) representing single phase system with no phase separation (**Figure S5**). The T_g of the materials

decreases with increasing ionic liquid content. The addition of 60% of IL brought the T_g of elastomeric thermoset down to ~27 °C. This provides the material with elasticity and flexibility at room temperature. The thermosets show composition dependant sub-T_g relaxation behaviors in Fig 3 (A) and (B). It is assumed that the these relaxations were observed due to the segmental mobility arised by the intermolecular mixing of epoxy and ionic liquid which in turn is responsible for the ductile behavior of the thermoset material.

Rheological experiments provide a classic way to reveal the viscosity and flow behavior of polymeric materials at high temperature. The heating-cooling rheology profiles (**Figure 3B**) of

these three types of thermosets show distinct viscosity characteristics. The cross-linked materials were heated to 150 °C and then cooled down to room temperature to observe the viscosity variations. There is no apparent change in the complex viscosity (η^*) of the hard thermosets at 10% of IL indicating a highly cross-linked network structure. However, for the plastic thermoset and elastomeric thermoset, a decrease in η^*value was observed near the T_g. The drop in η^* for elastomeric thermoset at 50% IL is significant and the value nearly approaches zero and then stabilizes indicating the polymer chains within the sample are flexible and relax their stresses at higher temperatures.
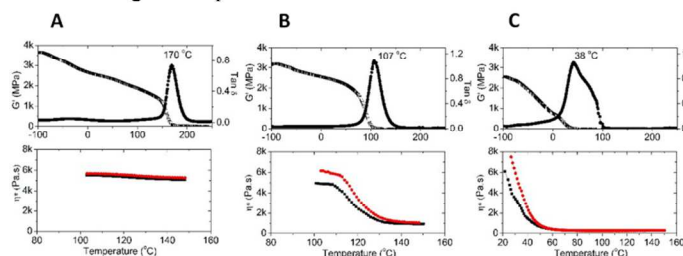

Figure 3. (*top*) Variation of storage modulus and *tan* δ with temperature and (*bottom*) the effect of complex viscosity with heating (black curve) and cooling (red curve) for (A) *hard thermosets* at 10% IL, (B) *plastic thermoset* at 30%IL and (C) *elastomeric thermoset* at 50% IL. In Fig 3B, the black curve indicates the heating and red curve is the cooling profile.

The thermal flexibility and improved mechanical properties of hard thermosets and plastic/elastomeric behaviors of soft thermosets can be explained by the charge transfer complexation and confinement of IL molecules within the highly cross-linked epoxy thermoset. As previously explained the strong complex formed between bulky IL ions and the epoxy hydroxyl groups acts like a coupling between the brittle chains network resulting in high modulus and toughness. At elevated temperatures, these complex bonds break and the presence of detached bulky ions leads to flexible networks and reduced glass transition region. Upon cooling, these ions again rearrange for network complexation preserving the network integrity, thus making the process reversible (**Figure 4**).

Acknowledgement

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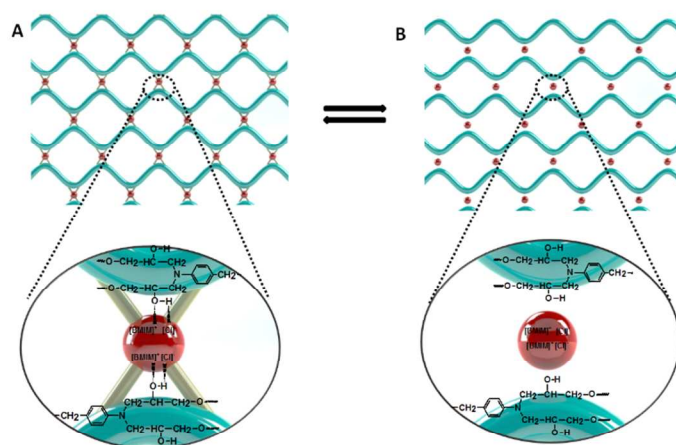9. Lu, Y.-X., Tournilhac, F., Leibler, L. & Guan, Z. *J. Am. Chem. Soc.* **2012**, *134*, 8424–8427.

Figure 4. The reversible complex formation in epoxy-IL networks during heating. *(The regularity in the epoxy chains and IL molecules are for illustrative purpose only).*

In summary, we have designed and prepared a multifunctional epoxy composition, which can be easily processed from readily available ingredients. The thermally flexible, formable and insoluble epoxy cross-linked materials can be easily be scaled up for their use as thermoplastics, elastomers and composites. The ability to tune network flexibility can lead to the development of a variety of thermoset polymers with a range of thermo-mechanical properties and will be of enormous interest to the automotive industry where there is a drive to produce composite components in less than a minute.

Notes and references
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Additional information
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