

## Ductile thermoset polymers by controlling network flexibility

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### Supporting information

Ionic liquids are important class of materials that are used in many applications as catalysts<sup>1-3</sup>, dispersion aids<sup>4-5</sup>, surface property modifiers<sup>6-7</sup>, gas separation enhancers<sup>8</sup>, and as solvents for intractable natural polymers<sup>9-11</sup>. Ionic liquid has also been used as a plasticizer for tough thermoplastics<sup>12-13</sup>, however an enhancement in thermo-mechanical properties as achieved in the present study has never been reported. Here ionic liquid is used as a small molecule modifier for epoxy resin that exhibits excellent miscibility over a wide range of compositions and enhances the toughness of the thermosets.

#### 1. Experimental section

##### Materials

The epoxy precursor diglycidyl ether of bisphenol A (DGEBA) with epoxide equivalent weight of 172–176 and curing agent 4,4'-methylenedianiline (MDA) were purchased from Aldrich Chemical Co. 1-butyl-3-methylimidazolium chloride (BMIM[Cl]) was obtained from Fluka. All the materials were used as received.

##### Preparation of epoxy-IL networks

The epoxy precursor DGEBA and a weighed amount of BMIM[Cl] ionic liquid were mixed together, stirred and heated at 80 °C until the mixtures became homogenous. Then, a stoichiometric amount of the curing agent MDA was added into the mixtures with vigorous stirring until homogeneous solutions were again obtained. The ternary mixture was immediately poured into preheated molds and cured at 120 °C for 10 h and post-cured at 180

°C for 2 h. Samples of varied compositions were prepared by varying the weight percent ratios of BMIM[Cl] from 10 to 60 wt% in 10 wt% intervals.

### **Fourier transform infrared (FTIR) spectroscopy**

Fourier transform infrared (FTIR) spectra of epoxy samples were measured by a Burker Vertex 70 FTIR Spectroscopy in the attenuated total reflectance (ATR) mode. The spectra were recorded by the average of 32 scans in the standard wavenumber range of 400–4000  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ . For monitoring the curing reaction, the premixed samples were heated at 120 °C and immediately placed over the ATR cell at every 5 min intervals and spectra were taken at each time.

### **Differential scanning calorimetry (DSC)**

DSC experiments were performed using 5–10 mg of the samples under an atmosphere of nitrogen gas with a TA-DSC model Q200 instrument. The samples were first heated to 100 °C and held at that temperature for 5 min to remove the thermal history. Then, the samples were cooled to -80 °C at the rate of 20 °C/min, held for 5 min, and again heated from -80 °C to 250 °C at 20 °C/min (second scan). The  $T_g$  values were taken as the midpoint of the transition in the second scan of the DSC thermograms.

### **Dynamic mechanical thermal analysis (DMTA)**

Dynamic mechanical tests were performed on a dynamic mechanical thermal analyzer (DMTA) (TA Q800, USA) in a single-cantilever mode under liquid nitrogen. The frequency was 1 for all samples and the heating rate was 3.0 °C/min. The specimen dimensions were 60 × 12 × 3  $\text{mm}^3$ . The storage modulus ( $G'$ ), loss modulus ( $G''$ ) and  $\tan \delta$  were measured from

30 °C to 250 °C. The  $T_g$  was taken at the maximum of the  $\tan \delta$  curve in the glass transition region.

### **Mechanical tests**

The tensile properties of the composites were measured on an Instron 30 kN SD tensile testing machine. The tests were conducted with dumbbell shaped specimens according to ASTM standard D638. At least five specimens were tested to obtain the average values of tensile properties for all the specimens.

For fracture toughness measurements, the single-edge-notch three point-bending (SENB) test was used according to ASTM standard D5045. The tests were performed on an Instron 30 kN instrument at a test speed of  $2 \text{ mm min}^{-1}$ . An initial crack was generated carefully by tapping the thumbnail shape crack front using a fresh razor blade prior to testing. K<sub>1C</sub> of the samples was determined by testing at least five specimens.

### **Scanning electron microscopy**

The morphology of the composite sheets was examined scanning electron microscopy (SEM) using a JEOL Neoscope at an activation voltage of 10 kV. The free surfaces were coated with thin layers of gold before the observation.

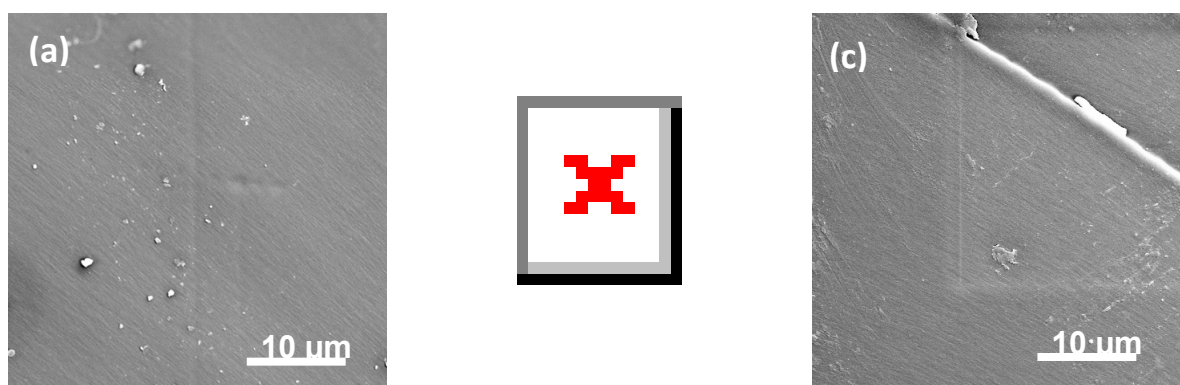
### **Swelling experiments**

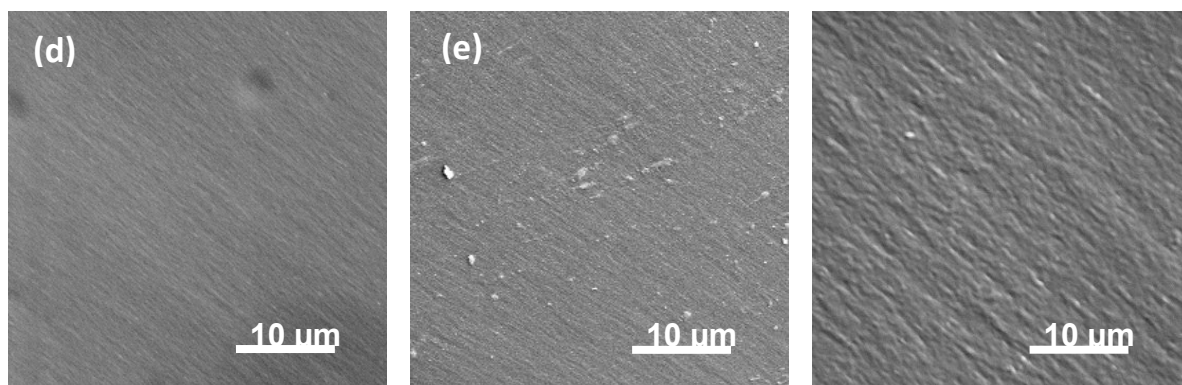
For swelling experiments, the samples with a dimension of 20mm x 10mm x 3mm were immersed and heated in trichlorobenzene at 100°C for 24 hours.

### **Density Functional Theory calculations**

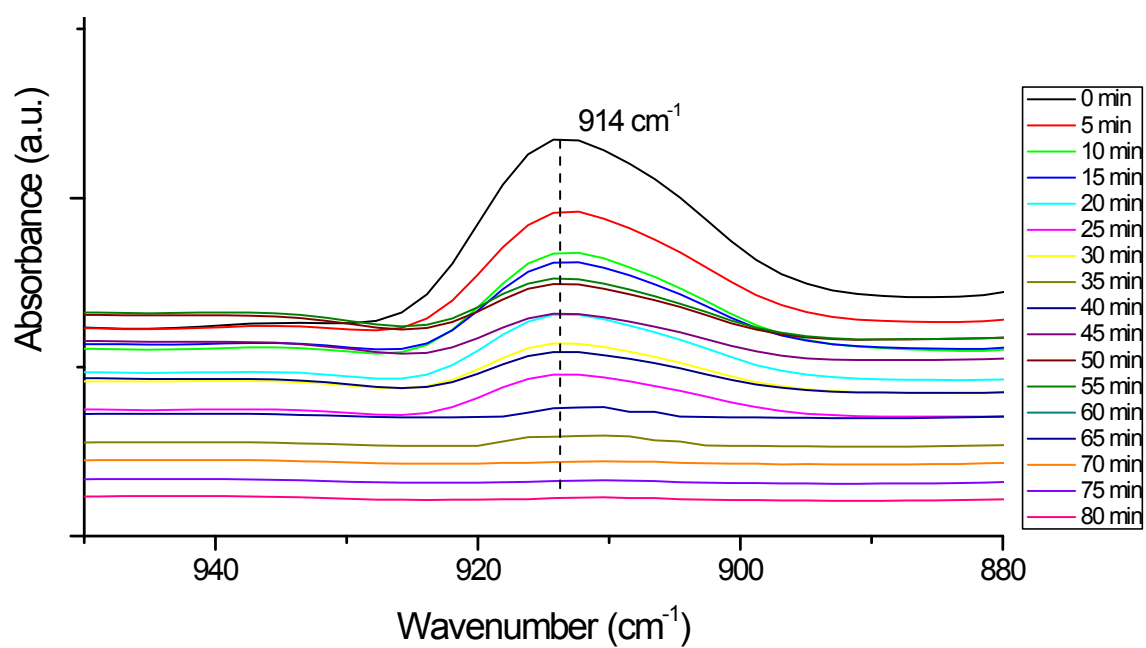
As an approximation to the experimental system, a complex between BMIM<sup>+</sup>[Cl<sup>-</sup>] unit and a fragment of a single polymer chain (see Fig 1C in the main text), containing four hydroxyl groups, was modelled using quantum chemical methods. Each of the four hydroxyl groups in the polymer fragment was located in a slightly different environment (self-associated and non-self associated), to ensure a range of hydroxyl vibrational frequencies could be captured. We considered both the polymer fragment alone, and, the polymer fragment complexed with the BMIM<sup>+</sup>[Cl<sup>-</sup>] unit. In both cases, we performed a geometry optimization at the PBE0/6-31G\* level of theory<sup>14</sup>. The Gaussian09<sup>15</sup> software package was used, with analytic second derivatives employed at each step of the geometry optimizations. Vibrational frequencies were calculated in both cases to ensure true minima were identified, and to predict the infrared spectrum in each case. Previous studies using this level of theory has been demonstrated to perform at the level of more sophisticated approaches, for more simple systems<sup>16</sup>. From these calculations we can predict the vibrational frequency of each hydroxyl in the polymer fragment, both with and without the presence of the BMIM<sup>+</sup>[Cl<sup>-</sup>] unit. We recognize that we have not exhaustively explored all possible arrangements of the polymer fragment and the BMIM<sup>+</sup>[Cl<sup>-</sup>] unit. However, we believe our findings generated here give an indication of the possible structure of the EDA-epoxy complex.

## 2. Results

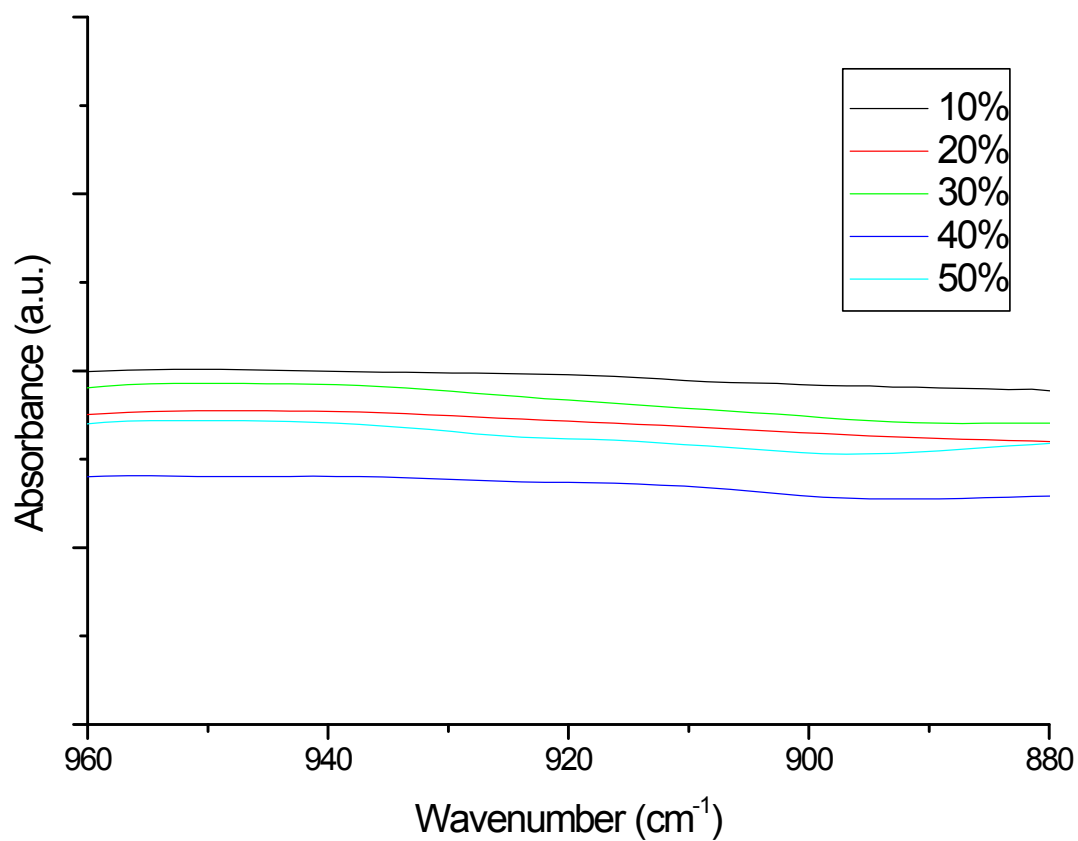




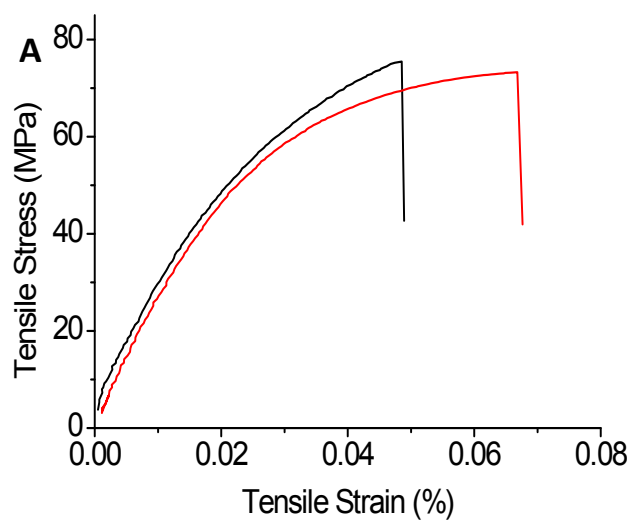
**Figure S1.** The SEM images of epoxy-IL networks containing (a) 10%IL, (b) 20%IL, (c) 30%IL, (d) 40%IL, (e) 50%IL and (f) 60%IL.

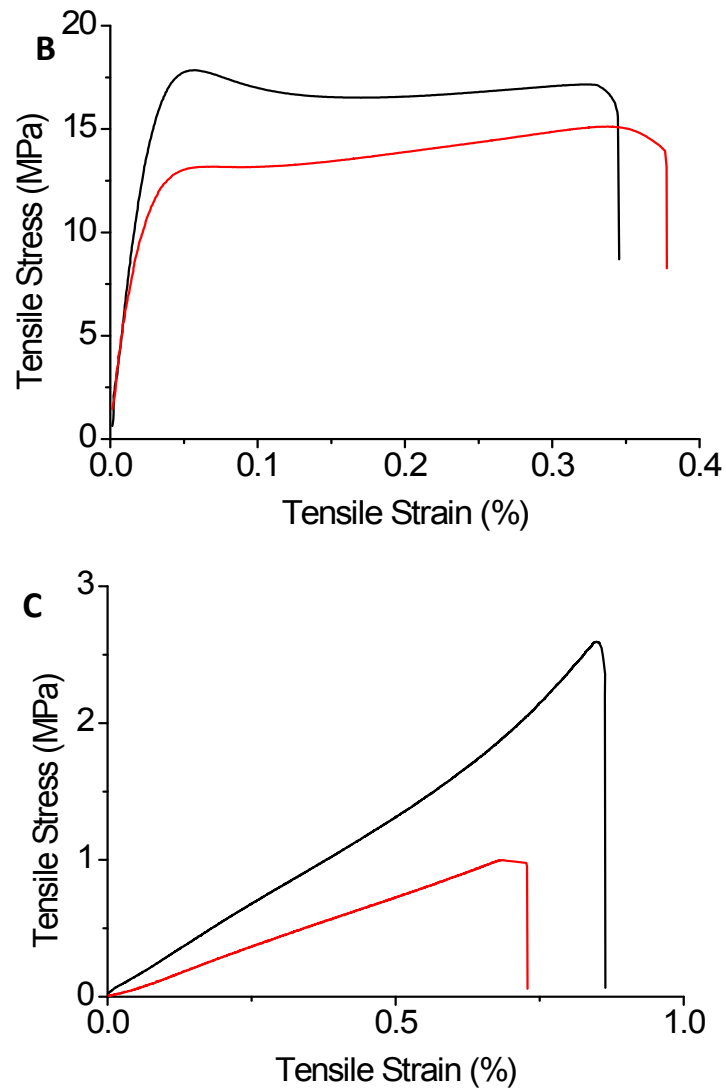


**Figure S2.** Infrared spectra showing the curing behavior of epoxy-IL networks. Spectra were taken every 5 mins.

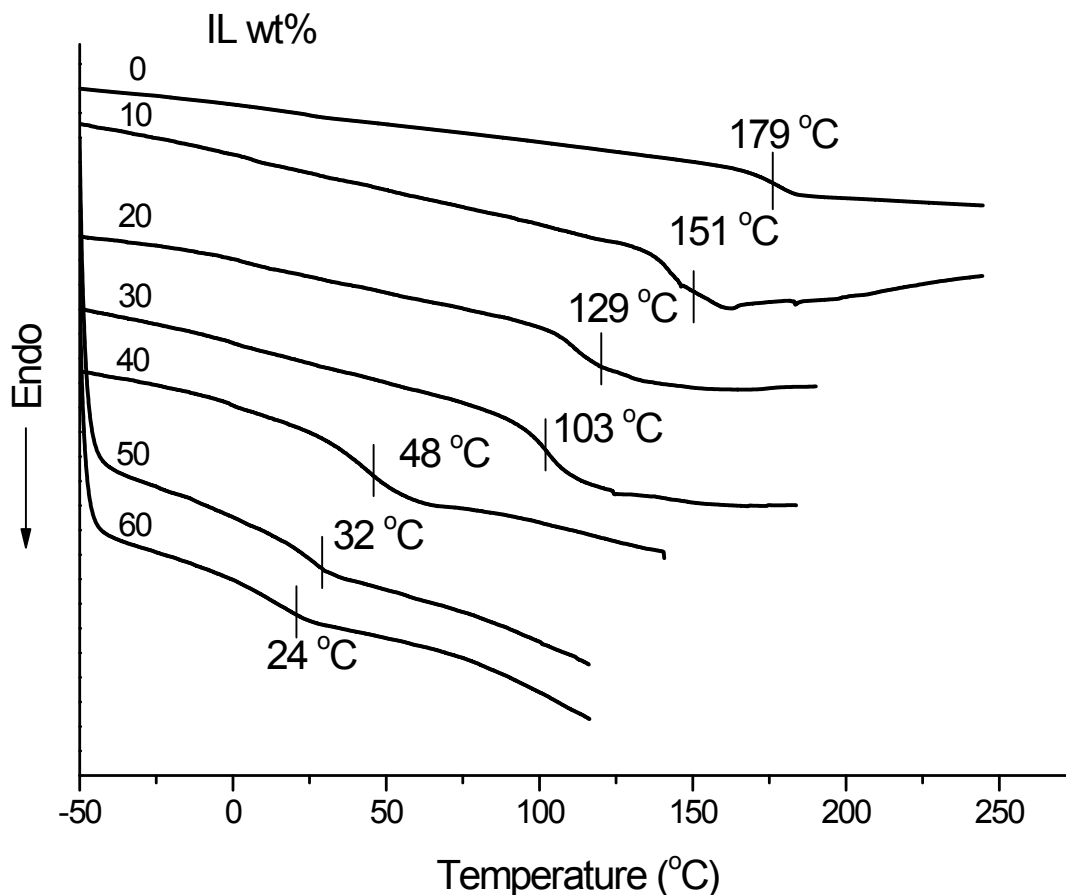


**Figure S3.** Infrared spectra of completely cured epoxy-IL networks.





**Figure S4.** (A) Tensile stress-strain curves of *hard thermosets* showing perfectly brittle fracture at 10 and 20% of IL, the ductile behavior of *plastic thermosets* at 30 and 40% of IL, and the S-shaped curves of *elastomeric thermosets* at 50 and 60% of IL (S-shape is not obvious in the case of 60% IL samples).



**Figure S5.** DSC curves of the second scan of epoxy-IL networks.

**Movie S1.** The hard epoxy thermoset is heated and twisted and cooled for a few seconds to achieve the fusilli shape. The material is heated again to regain its shape without any deformation. The heating causes the internal structure of the material to break the CT complexes and the network to flow. Upon cooling the complexation occurs again to form the hard thermoset material.

Link to video1: [http://youtu.be/ysX0Kr6a\\_7w](http://youtu.be/ysX0Kr6a_7w)

Link to video2: <http://youtu.be/eBcooeiWnTs>



**Movie S2.** The room temperature twisted plastic-like thermoset is flexible enough to bend or twist several times. They retain the physical shape after the stress is removed.

Link to video: [http://youtu.be/t\\_PQEhtyFN8](http://youtu.be/t_PQEhtyFN8)

**Movie S3.** The elastomeric thermoset is flexible so that it can be twisted or bend multiple times to any shape at room temperature. The material returns to original shape when the applied force is removed.

Link to video: <http://youtu.be/Hhkc3VSMfuM>

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