Electronic Supplementary Material (ESI) for RSC Advances.

Thermally flexible epoxy/cellulose blends mediated by an ionic liquid

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1. Experimental

1.1. Materials and preparation of samples

The epoxy precursor diglycidyl ether of bisphenol A (DGEBA) with epoxide equivalent weight of 172–176 and the curing agent 4,4’- methylenedianiline (MDA) were purchased from Aldrich Chemical Co. Microgranular cellulose was also purchased from Sigma Aldrich and was characterized in our previous studies[1-3]. 1-butyl-3-methylimidazolium chloride (BMIM[Cl]) was obtained from Fluka. The cellulose samples were dried at 80 ºC under vacuum for about 5 hours to remove moisture. All other materials were used as received.

Cellulose with varying concentration was first dissolved in BMIM[Cl] before mixing with epoxy resin. The amount of epoxy was fixed initially and the cellulose content was calculated with respect to epoxy concentration to obtain 5 to 40 wt% cellulose against 100% epoxy. The BMIM[Cl] concentration was also fixed at 40% of epoxy content. A pre-weighed amount of cellulose was mixed with calculated amount of BMIM[Cl], heated and stirred at 100 °C to obtain a mixture. The cellulose was completely miscible in BMIMCL at lower cellulose concentrations (up to 10wt%), however the mixture above this concentration was found to be only partially miscible (swollen) due to insufficient IL content. The epoxy precursor and the above made cellulose/IL solution were accurately mixed together, stirred and heated at 100 °C until the mixtures became visually 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 poured into preheated molds and cured at 150 °C for 12 h and post-cured at 180 °C for 2 h. Samples of varied compositions were prepared by varying the weight percent ratios of cellulose and IL in DGEBA.

2. Characterization

2.1. FTIR-ATR spectroscopy

The FTIR-ATR spectra of all the samples were measured on a Bruker Vertex-70 FTIR spectrometer. The samples were cut into uniform thickness and dried under vacuum in an oven at 100 °C before measurements. The spectra were recorded at the average of 32 scans in the standard wavenumber range of 400-4000 cm^{-1} at a resolution of 4 cm^{-1}.

2.2. Differential scanning calorimetry (DSC)

DSC experiments were carried out using a TA-DSC model Q200 instrument. The measurement was performed using 5-10 mg of the sample under an atmosphere of nitrogen gas. The samples were first heated to 100 °C and held at that temperature for 5 minutes to remove the thermal history. Then the samples were cooled to 0 °C at a rate of 20 °C/min, held for 5 minutes, and subsequently heated from 0 to 200 °C at 20 °C/min (second scan). Glass transition temperature (T_g) values were taken as the midpoint of transition in the second scan of DSC thermograms.

2.3. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical tests were performed on a dynamic mechanical thermal analyzer (DMTA) (TA Q800, USA) in tensile mode at a heating rate of 3 °C/min. The specimen dimensions were 50 mm x 12 mm x 3 mm^3. The storage modulus (G'), loss modulus (G'') and tan δ were measured from 100 °C to 250 °C. The T_g was taken at the maximum of the tan δ curve in the glass transition region.

2.4. Thermogravimetric analysis (TGA)

Thermogravimetric analyses (TGA) were performed on Netzsch STA 409 thermogravimetric analyzer over a temperature range of 25-600 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

2.5. Scanning electron microscopy (SEM)

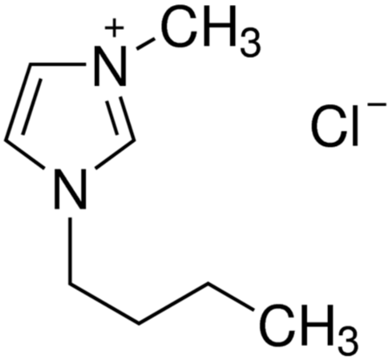
The morphology of the blend materials was examined with a JEOL Neoscope scanning electron microscope (SEM) at an activation voltage of 10 kV. The cryo-fractured surfaces were coated with thin layers of gold before the observation.

2.6. Thermal flexibility

To check the thermal flexibility, all the samples were heated at 80 °C for 5 min and twisted or bent physically by holding on either side of the sample strip. Each sample was reversibly bent or twisted at least five times and no deformation or change in shape or size was observed. The same experiment was repeated after 4 weeks to check the repeatability of the flexible behavior.

2.6. Mechanical test

The tensile behavior of the materials was analyzed using Instron 30 kN SD tensile testing machine. The specimens were thin rectangular strips (20×6×0.2 mm). The load-displacement curves of the samples were obtained at room temperature at a strain rate of 1 mm/min at 75% relative humidity and 20 ºC temperature.



Scheme S1. The chemical structure of BMIM[Cl]

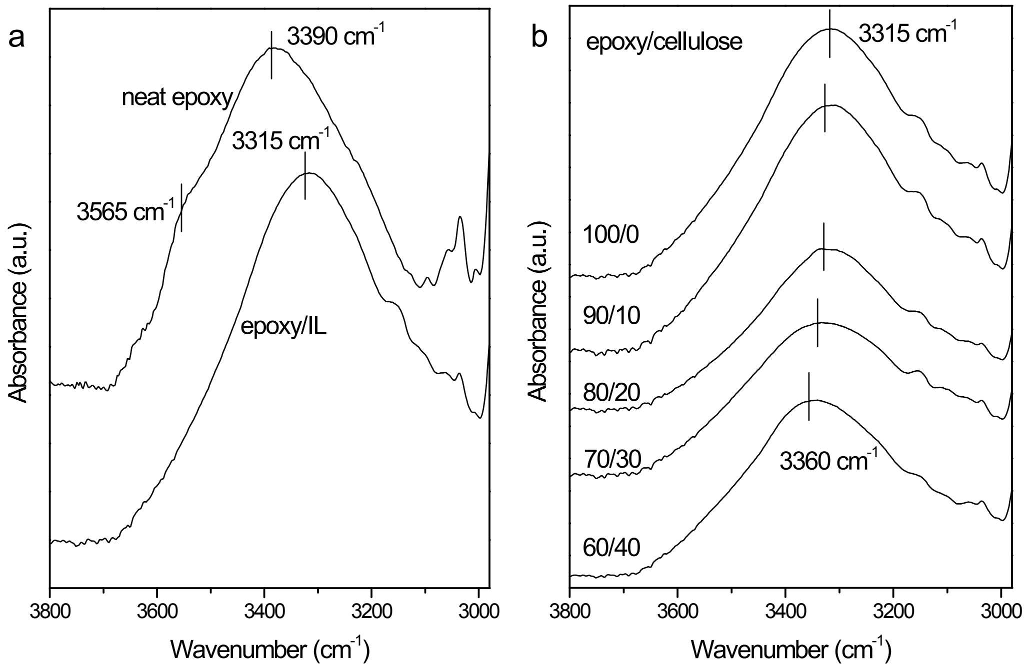


Figure S1. The hydroxyl stretching region in the FTIR spectra of (a) epoxy/IL complexes and (b) epoxy/cellulose blends containing IL.

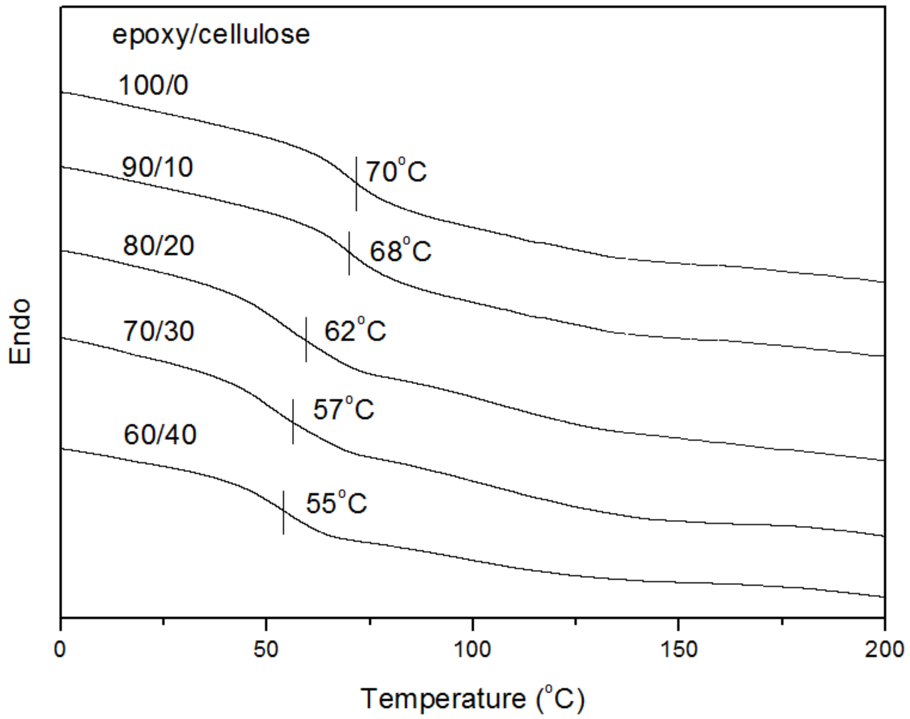


Figure S2. The DSC thermogram during the second heating of ER/cellulose blends.

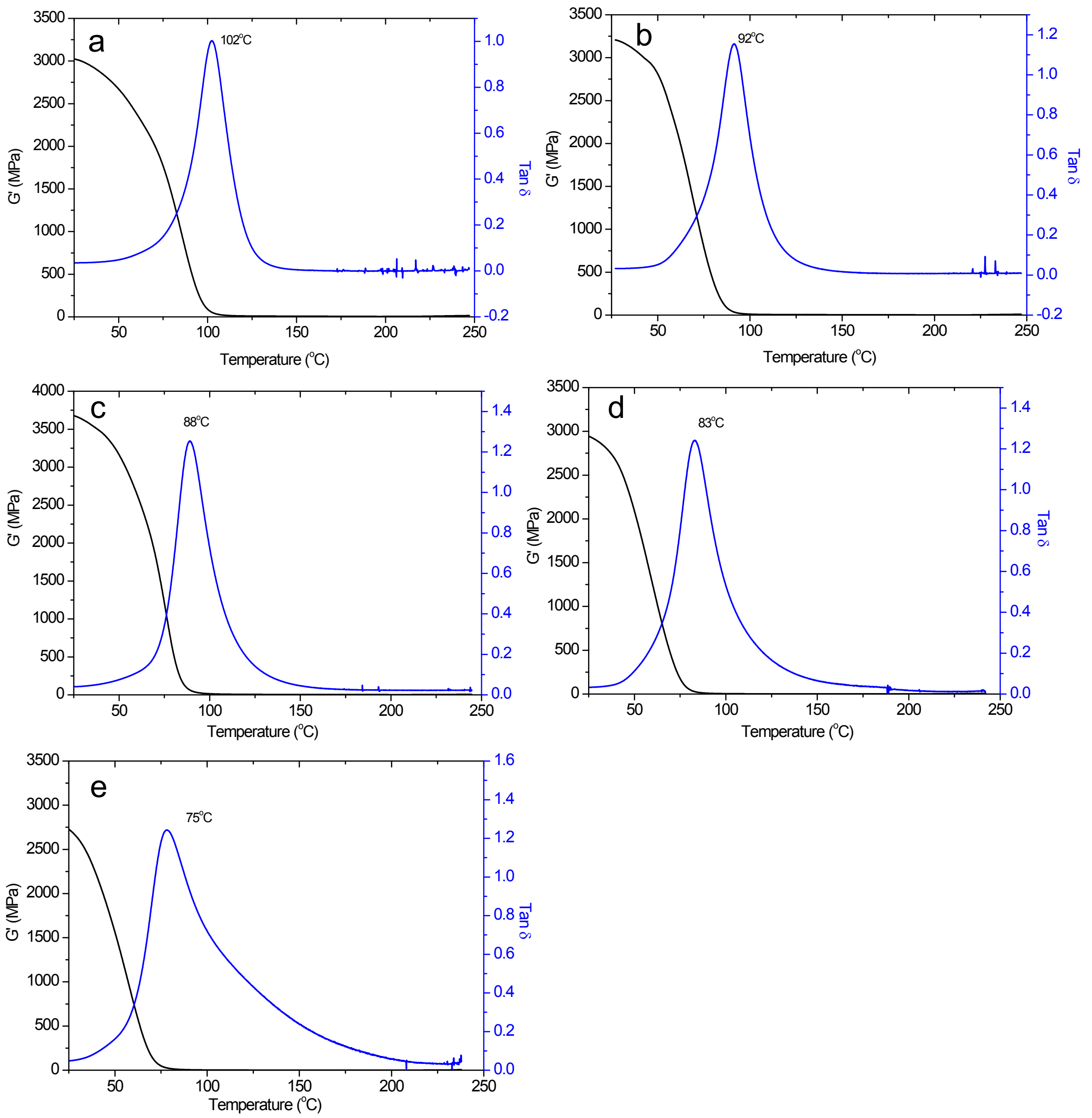


Figure S3. Variation of storage modulus and *tan δ* with temperature of ER/cellulose blends containing, (a) 0, (b) 10, (c) 20, (d) 30 and (e) 40 wt% of cellulose. All blends contain 40% IL.

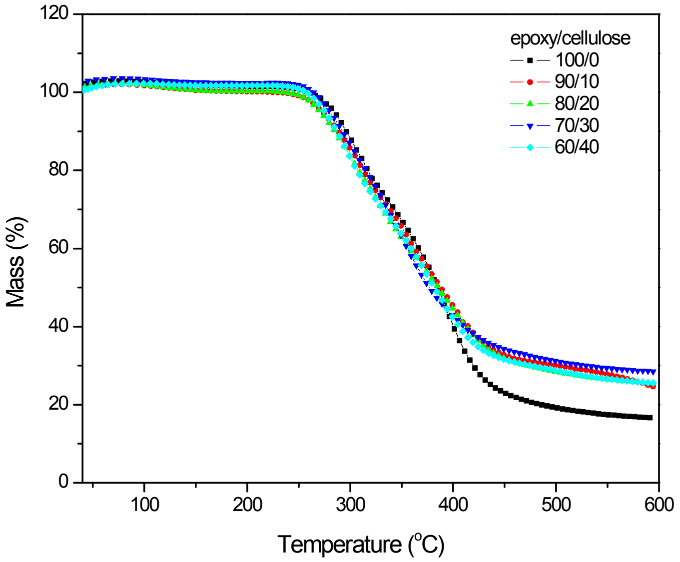


Figure S4. TGA curves of ER/cellulose blends containing 40% IL.

References

1. Hameed, N.; Xiong, R.; Salim, N. V.; Guo Q. *Cellulose*, **2013**, *20*, 2517.
2. Hameed, N.; Guo, Q. *Carbohyd. Polym.* **2009**, *78*, 999.
3. Hameed, N.; Guo, Q. *Cellulose* **2010**, *17*, 803.