Supporting Information for

Controlling coefficients of thermal expansion in thermoplastic materials: Effects of zinc cyanide and ionic liquid

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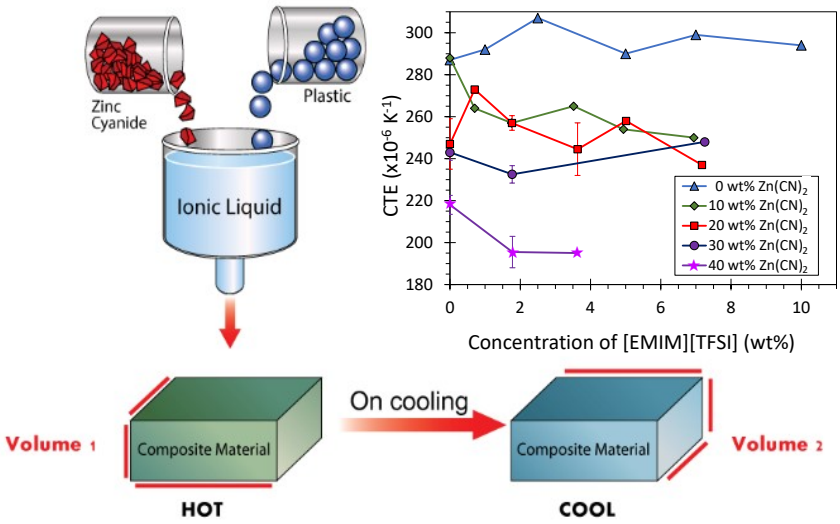

Contents

1. Experimental procedures

Experimental materials

Low-density polyethylene (LDPE) (906 kgm^{-3}; M_w = 35000 gmol^{-1}; M_n = 7700; Product number 427799) and $Zn(CN)_2$ powder (98% purity; Product number 256498) were supplied by Sigma-Aldrich. 1-ethyl 3-methylimidazolium bis(trifluoromethyl sulfonyl)imide ([EMIM][TFSI]) was prepared and characterized according to Bara *et al.*[41]

Preparation of $Zn(CN)_2$-filled LDPE composites

The composite samples are denoted by their mass proportion of $Zn(CN)_2$ and IL. For example, C-10-2.5 refers to LDPE composite that contains 10 wt. % $Zn(CN)_2$ and 2.5 wt. % ionic liquid. The composition of the samples was based on additions of 0, 10, 20, 30, and 40 wt. % $Zn(CN)_2$, to which 0, 2.5, 5, or 10 wt. % [EMIM][TFSI] was added.

Samples were prepared by adding a total of 3 g of material to a 30 mL glass vial. For example, 2.4 g of LDPE, 0.3 g of $Zn(CN)_2$ and 0.196 mL [EMIM][TFSI] was used for C-10-10. The vial heated to 150 °C on a

hot plate until the LDPE was molten, followed by manual stirring for 5 minutes to ensure uniform dispersion of $Zn(CN)_2$. The molten mixture was poured into a PTFE mould to cast a rectangular specimen (h x w x t; 10 x 10 x 5 mm (Coefficient of thermal expansion (CTE) measurements) or 120 x 10 x 5 mm (tensile measurements)). The mould was then placed under vacuum at 170 °C for 2 h to allow bubbles to escape. Upon removal from the vacuum oven, the moulds were left to cool at ambient temperature to solidify prior to removal from the mould.

Powdered X-ray diffraction (PXRD)

PXRD data was collected using a Philips PW1729 Cu-based X-ray diffractometer (λ= 1.5418, voltage: 40 kV, current: 30 mA). Data was recorded in the 2θ range from 5 to 50° where data was collected every 5 s at intervals of 0.01°.

Scanning electron microscopy

Scanning electron microscopy (SEM) was completed on a JEOL JSM-7000F microscope operated at 15 keV. Samples were prepared by freezing in liquid nitrogen followed by fracturing with a hammer to establish clean fractures and expose the interior. Each sample was coated with gold/palladium for 180 seconds using DC sputter coater at 30 mA. Magnifications of 50, 250, 1000, and 10000x were used to capture secondary electron images.

Thermomechanical analysis

The coefficient of linear thermal expansion (CTE) was measured using thermomechanical analysis (TMA) (Netzsch TMA 402 F1 Hyperion®, NETZSCH-Gerätebau GmbH, Germany). Cuboidal specimens (h x w x t; ~10 x 10 x 5 mm) were cooled to -40 °C and held for 15 min, heated to 80 °C at 2 $K \cdot min^{-1}$ and held for 2 min, cooled to -30 °C at 5 $K \cdot min^{-1}$, cooled to -40 °C at 2 $K \cdot min^{-1}$ and held for 5 min, and finally re-heated to 80 °C at 2 $K \cdot min^{-1}$. Standard linear thermal expansion measurements were performed using fused silica fixtures under a nitrogen atmosphere. The CTE values reported are average values for the range -40 °C to 80 °C.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed using a NETZSCH STA 449 F3 Jupiter®. The temperature was ramped from 25 to 800°C at a heating rate of 10 $K \cdot min^{-1}$ under a nitrogen atmosphere.

Tensile testing

The mechanical properties of the composites were determined using tensile testing on a universal testing machine (UTM, Model 5965, Instron, USA) with a 5 kN loadcell. Prior to testing, replicate specimens (n = 2-6) were cut into flat rectangular coupons (l x w x t = 70 mm x 10 mm x 5 mm). Uniaxial tensile stress-strain tests were performed at 20 °C to determine the Young's modulus (E), ultimate tensile strength and elongation at break (or strain to failure) of each composite at a constant crosshead displacement rate of 50 mm/min. The displacement and strain of each sample was determined by the linear variable differential transformer (LVDT) for the crosshead of the UTM. A curve-fitting model was used on the stress versus strain data to determine the Young's modulus (ESI Section 4). The toughness was calculated from the area under the force-displacement curve up until failure. All samples exhibited non-linear stress-strain behaviour from the onset of testing.

2. Thermogravimetric analysis (TGA)

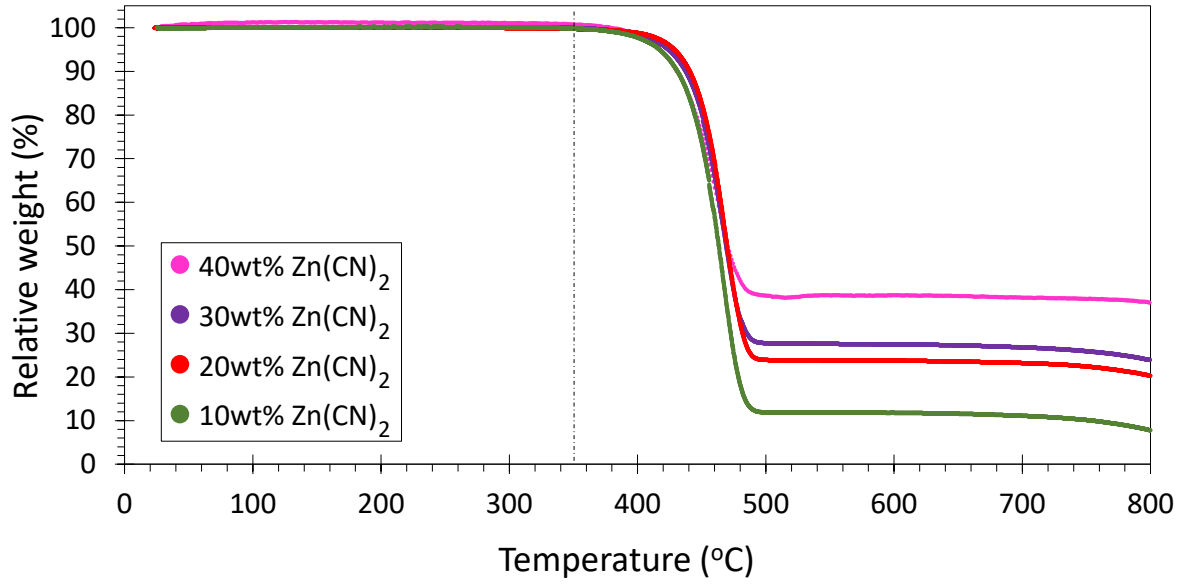

Figure S1. TGA data for the polyethylene composite material containing 10, 20, 30, and 40 wt% zinc cyanide and 7 wt% [EMIM][TFSI] (C-10/20/30/40-7). The TGA data indicates that no water is present in the sample and that both the polyethylene and [EMIM][TFSI] burn off around 350 °C, as expected. The residual weights at ca. 500 °C correlate with the amount of $Zn(CN)_2$ in the composite.

3. PXRD

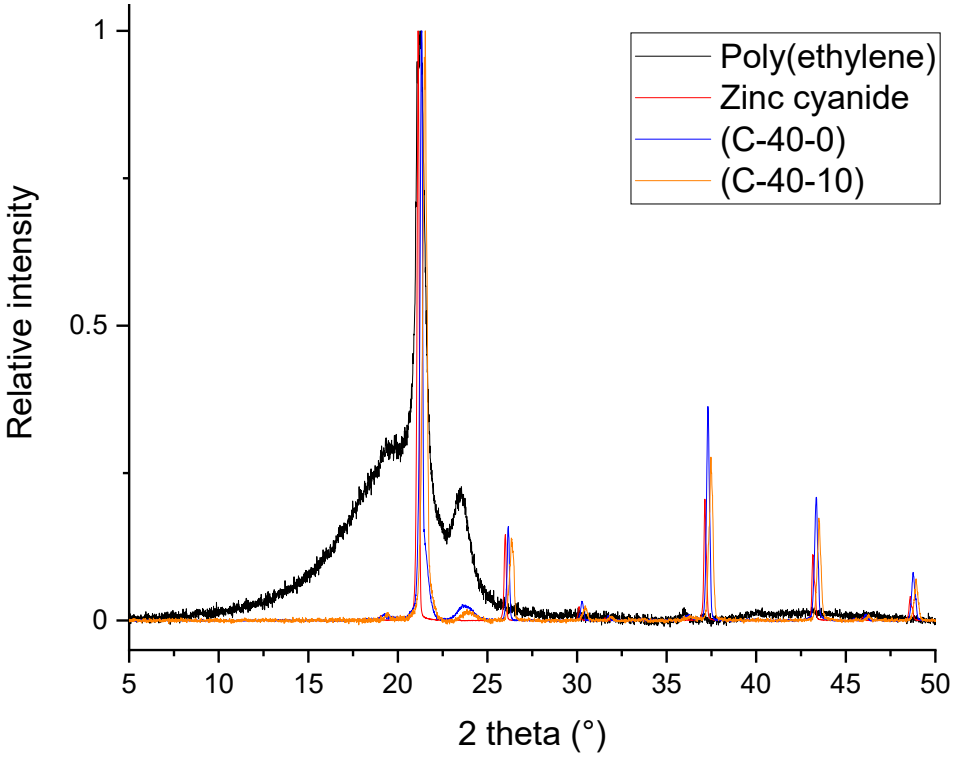

Figure S2. PXRD showing that zinc cyanide retains its crystalline structure within the composite.

4. Correlation of volume fraction model to observed CTE values

The experimental CTE measurements of the composite samples were compared to the CTE predicted from applying the rule of mixtures (ROM) using the equation below and coefficients from Table S1.

$$\alpha_c = \alpha_m v_m + \alpha_f v_f + \alpha_l v_l$$

where, α_c is the thermal expansion coefficient of the composite, α_m is the thermal expansion coefficient of the matrix material (polyethylene), v_m is the volume fraction of the matrix material (polyethylene) present in the composite, α_f is the thermal expansion coefficient of the filler ($Zn(CN)_2$), v_f is the volume fraction of the filler ($Zn(CN)_2$) present in the composite, α_l is the thermal expansion coefficient of the liquid component ([EMIM][TFSI]), v_l is the volume fraction of the liquid component ([EMIM][TFSI]) present in the composite.

Table S1. Coefficients of thermal expansion for the materials used in the preparation of composites.

Material	Coefficient of thermal expansion (x 10^{-6} K^{-1})
Polyethylene	291
Zinc cyanide	-16
[EMIM][TFSI]	649

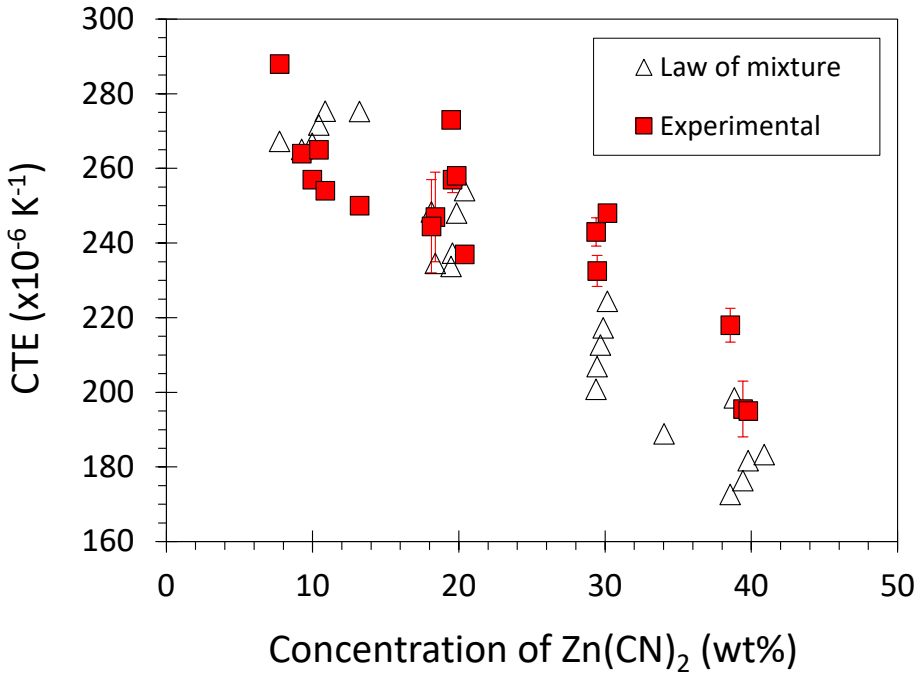

Figure S3. CTE of zinc cyanide-filled polyethylene composites as a function of the zinc cyanide content, showing a comparison of the rule of mixtures and experimentally-derived values. Error bars represent the standard error of the mean of measurements on replicate samples.

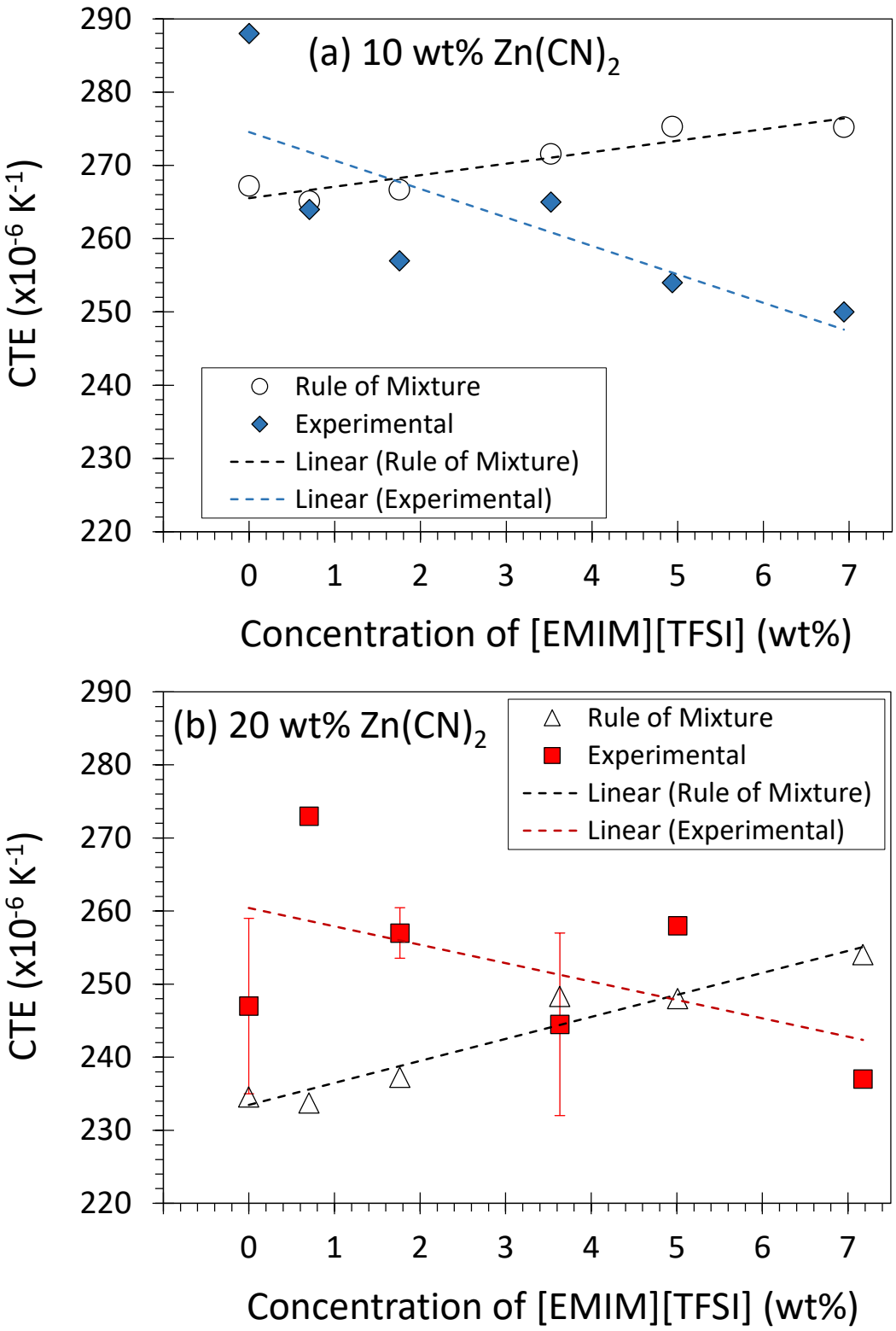

Figure S4. CTE values of LDPE / $Zn(CN)_2$ / [EMIM][TFSI] composites with change in ionic liquid loading. Open symbols were calculated using the law of mixtures. Solid symbols are data. (a) 10 wt. % $Zn(CN)_2$ and (b) 20 wt. % $Zn(CN)_2$. Trend lines are provided to guide the eye. Error bars represent the standard deviation of measurements on replicate samples.

5. Tensile tests

All the samples showed yielding once elongation started, and there was no linear regime. Thus, Young's modulus could not obtained directly from the slope of stress versus strain curve. The data were fitted to the following function for the first 200 points:

$$\sigma = \frac{\sigma max \gamma}{A + \gamma}$$

where σ is tensile stress, σ_{max} and A are fitting parameters, and γ is strain in %. Even if it is not perfect fit especially at stress between 4 and 6 MPa, it can still give a good value for Young's modulus as long as it fits well around the origin.

After obtaining the two parameters by fitting the data (Figure S4), the first derivative was taken to give Young's modulus at the origin:

$$Y = \sigma'(\gamma = 0) = \frac{\sigma max}{A}\Big|_{\gamma = 0}$$

where Y is Young's modulus.

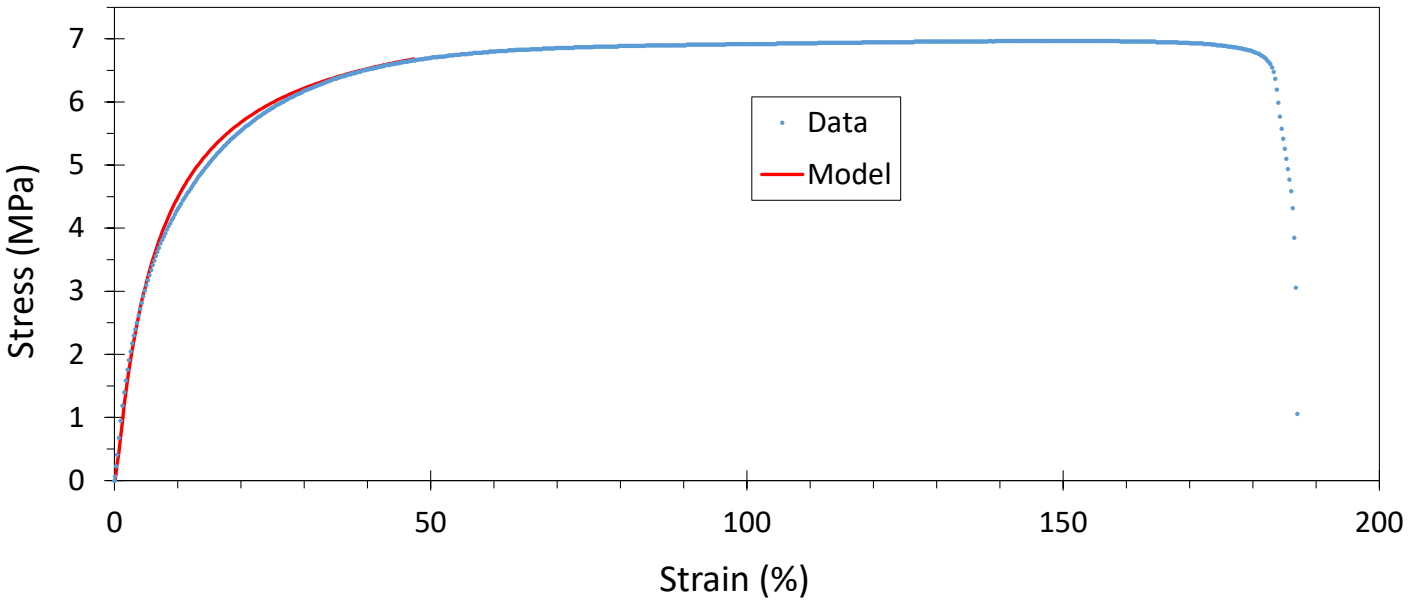

Figure S5. Stress versus strain for pure LDPE elongated at 50 mm/min. Red line is the fitting model.

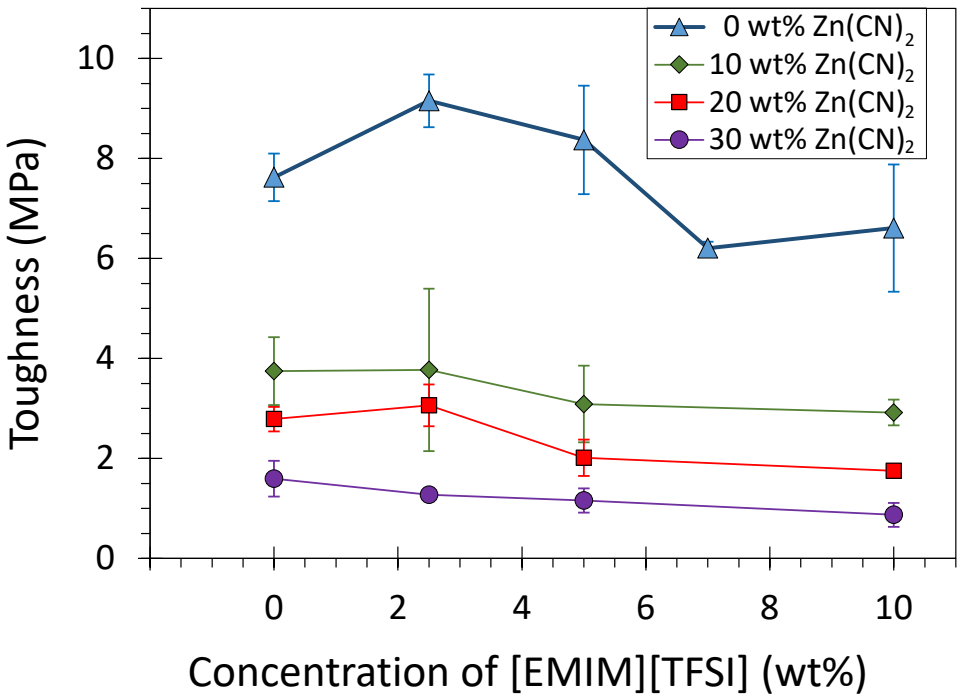

Figure S6. Toughness for zinc cyanide-filled polyethylene composites as a function of [EMIM][TFSI] content. Toughness is almost invariant with the concentration of [EMIM][TFSI]. Note that composites with no $Zn(CN)_2$ phase separated and produced inconsistent results. Trend lines are to guide the eye. Error bars represent the standard error of the mean of measurements on replicate samples.

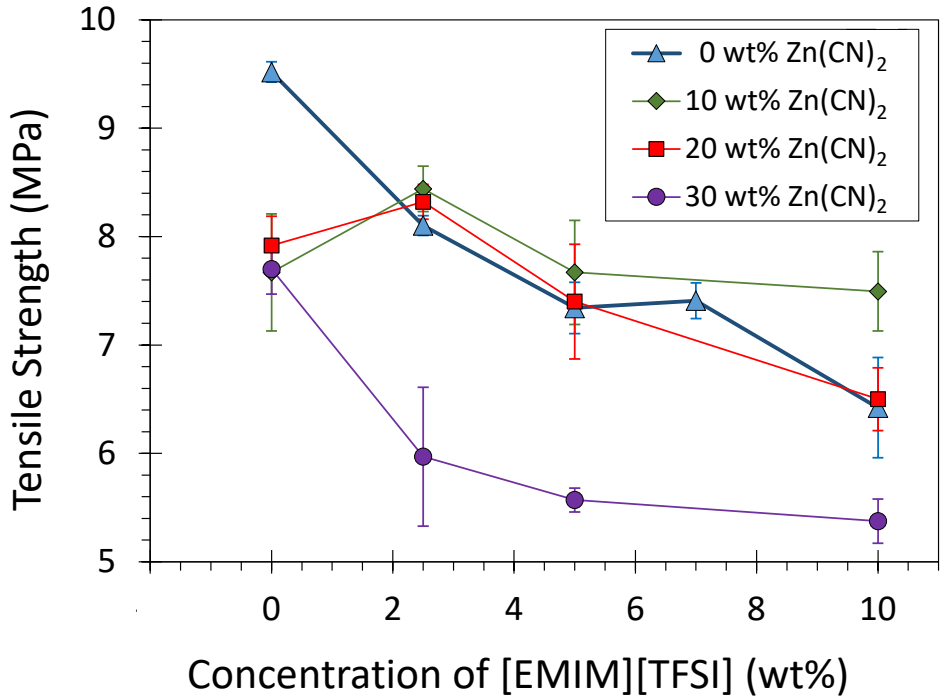

Figure S7. Tensile strength of zinc cyanide-filled polyethylene composites as a function of [EMIM][TFSI] content. Trend lines are to guide the eye. Error bars represent the standard error of the mean of measurements on replicate samples.

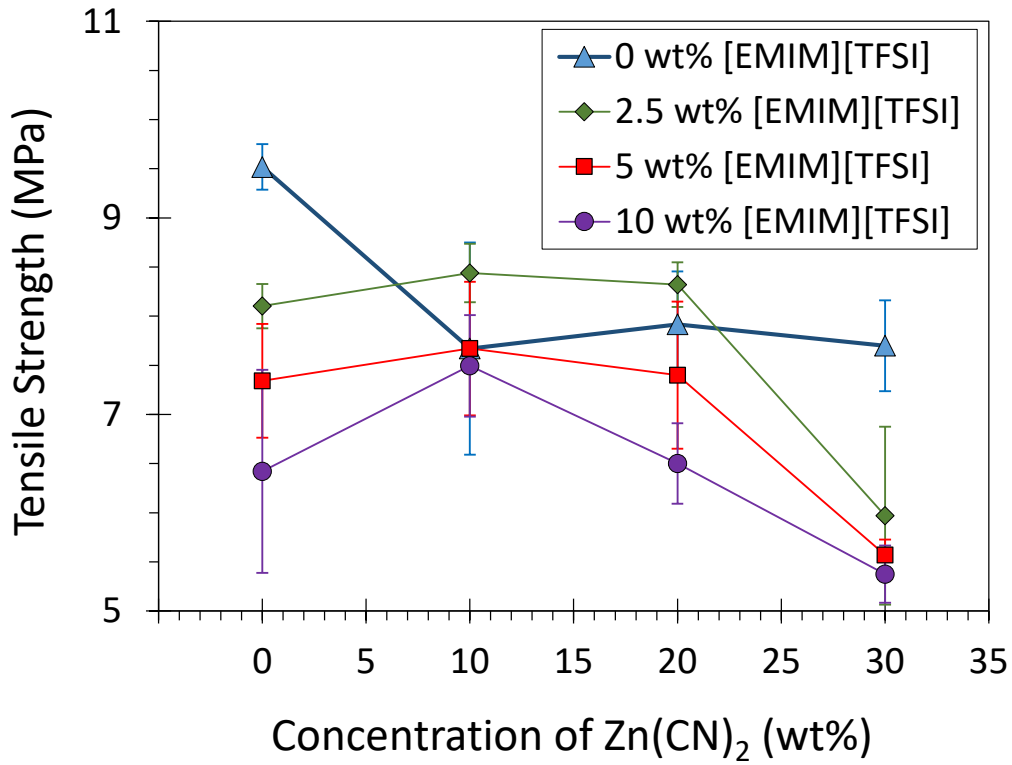

Figure S8. Tensile strength for LDPE/$Zn(CN)_2$/[EMIM][TFSI] composites. Tensile strength is weak function of $Zn(CN)_2$. Lines are provided to guide the eye. Error bars represent the standard deviation of measurements on replicate samples.

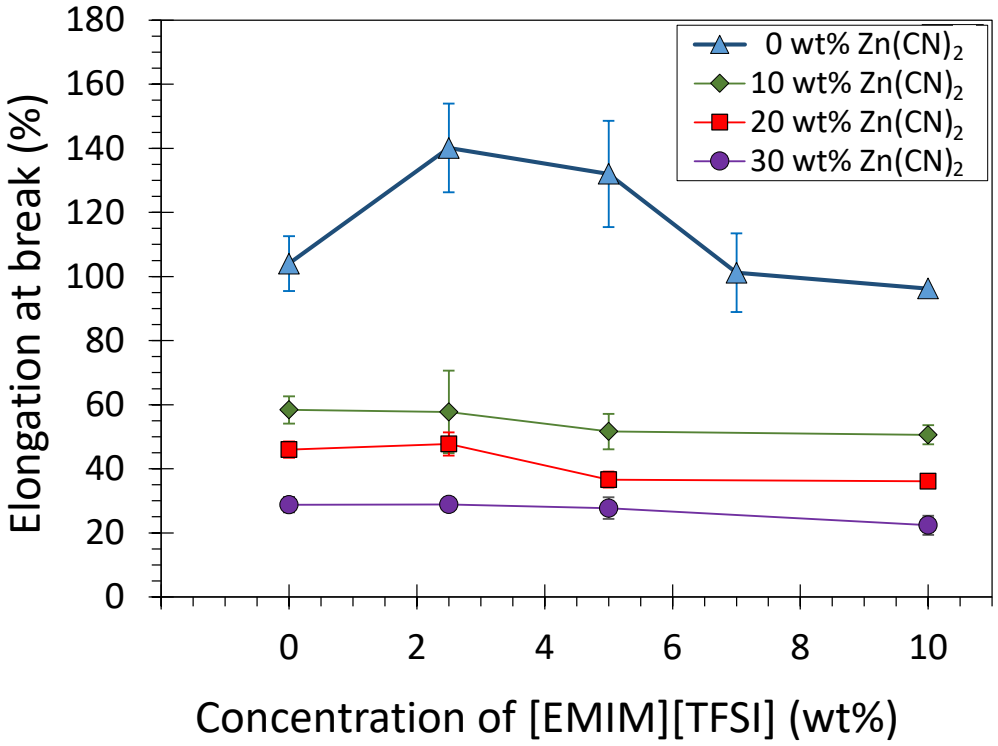

Figure S9. Elongation at break of zinc cyanide-filled polyethylene composites as a function of [EMIM][TFSI] content. Trend lines are to guide the eye. Error bars represent the standard error of the mean of measurements on replicate samples.

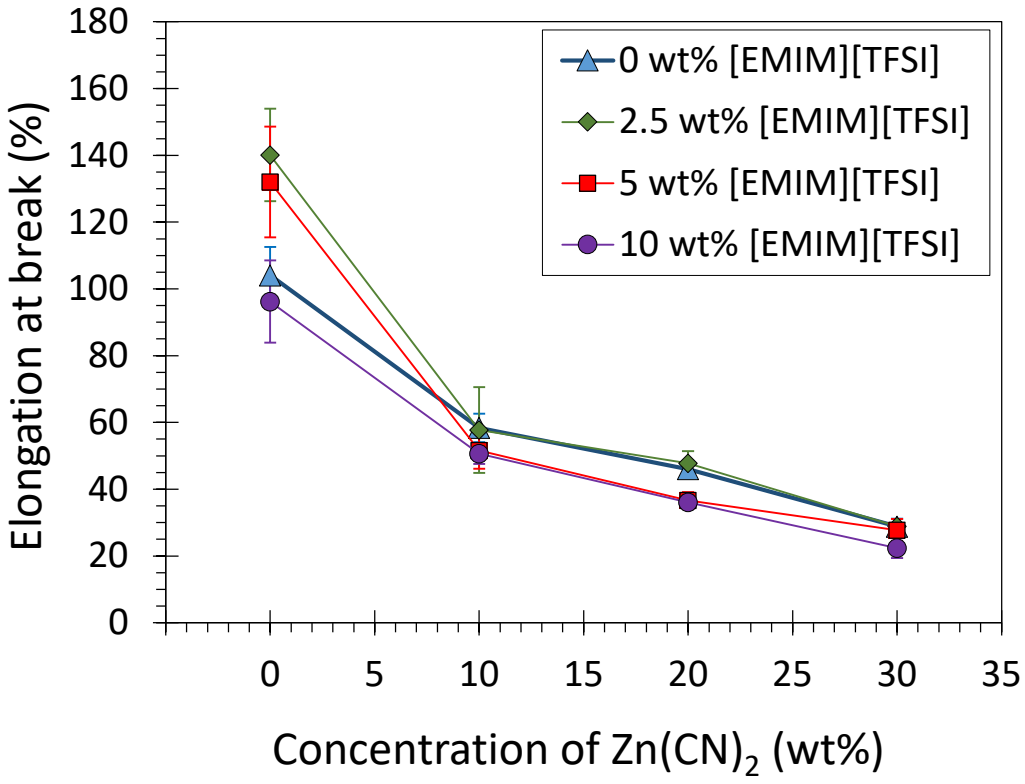

Figure S10. Elongation at break for polyethylene/zinc cyanide/[EMIM][TFSI] composites. Elongation at break decreases with the concentration of zinc cyanide. Trend lines are to guide the eye. Error bars represent the standard error of the mean of measurements on replicate samples.

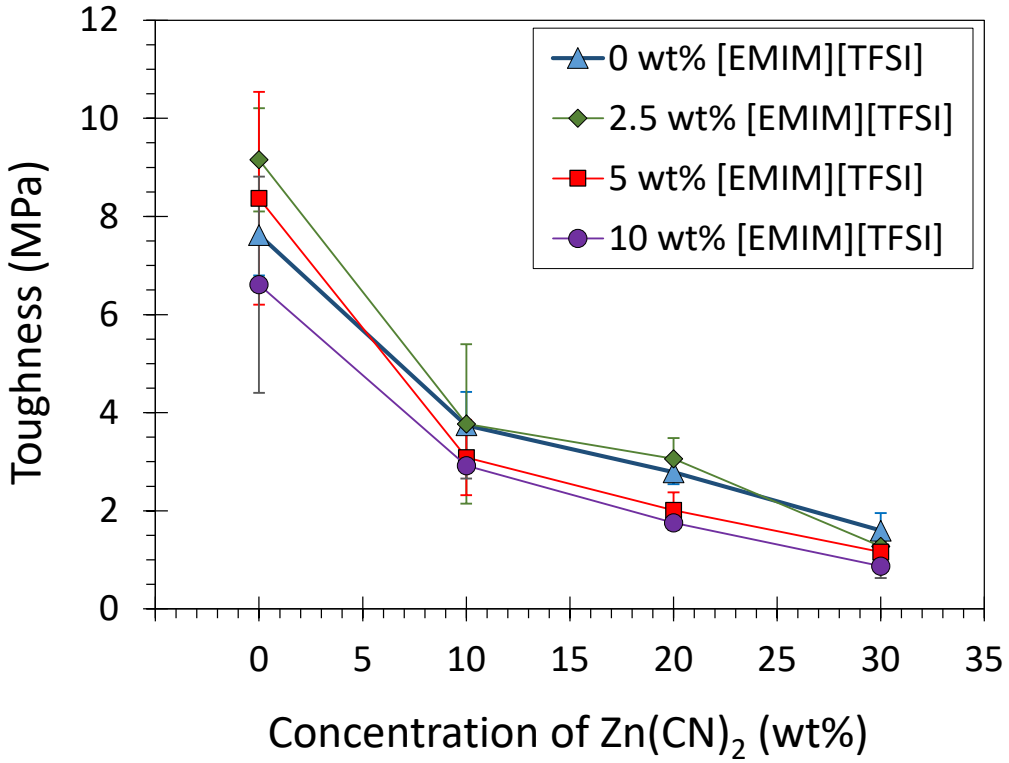

Figure S11. Toughness for LDPE/$Zn(CN)_2$/[EMIM][TFSI] composites. Toughness decreases with the concentration of $Zn(CN)_2$ while that is a weak function of [EMIM][TFSI]. Lines are provided to guide the eye. Error bars represent the standard deviation of measurements on replicate samples.