

Supporting Information for Healing by Joule effect of electrically-conductive poly(ester-urethane)/carbon nanotubes nanocomposites

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The electronic supporting information contains details of all different structures optimized in this work (Fig. S1-S4), compositions investigated, electrical and molecular properties (Tables S6 and S8) as well as thermogravimetric results (Fig. S5), extrusion force (Fig. S7) and dispersion of MWCNTs in the composites (Fig. S9).

S.1. Synthesis of the 1-(3-hydroxypropyl)-1H-pyrrole-2,5-dione (MAL(OH)) (adapted from the literature)¹

Exo-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride (Furan-A) (50 g) and ethanol (75 ml) were added to a two-neck round bottom flask with a stir bar. A solution of 3-amino-propane-1-ol (23.7 ml) and ethanol (20 ml) was added dropwise to the solution of Furan-A (1.03 molar excess of 3-amino-propane-1-ol to Furan-A). The resulting mixture was refluxed at 85°C for 6 h, during which the solution turned to orange. After the reaction, the solution was cooled overnight in a freezer and the obtained crystallized product was removed off via suction filtration. Before being dried under vacuum overnight at 50°C the crystal was washed with cold ethanol till the product became completely white (yield 32.08%, mp 120°C). MAL(OH) synthesis was confirmed by ¹H NMR spectroscopy (Fig. S1).

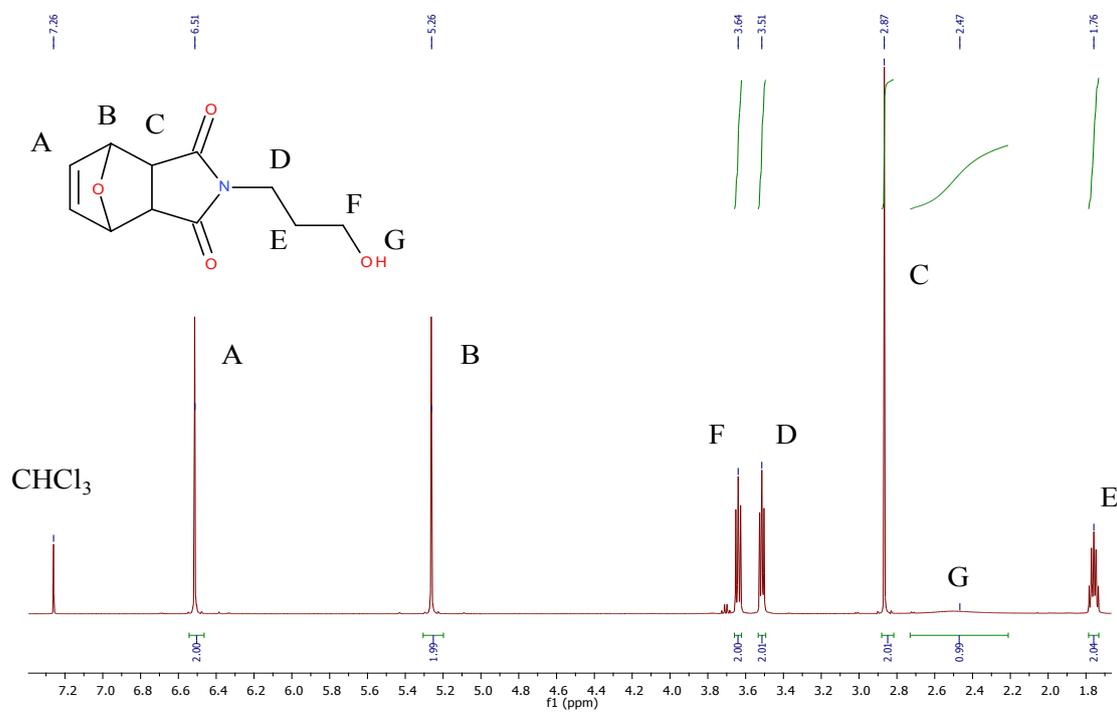
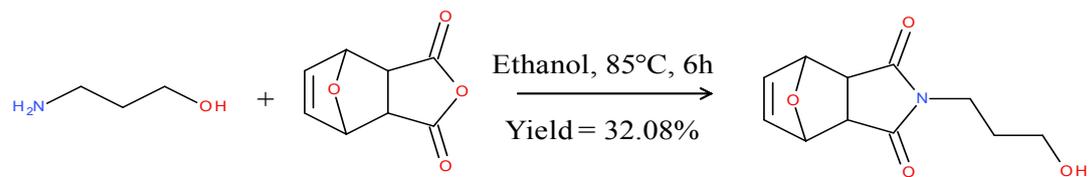


Fig. S1. $^1\text{H NMR}$ spectrum of MAL(OH) (500MHz, CDCl_3)

S.2. Synthesis of PCL end-functionalized with furfuryl moieties, PCL(FUR)₂ and PCL(FUR)₄

Procedure for the end-functionalized of PCL(OH)₂ and PCL(OH)₄ (4000 and 8000g/mol respectively) is described in the Experimental section. The complete end-functionalization with furfuryl moieties was attested by the disappearance of the α -hydroxymethylene functions (3.65 ppm) in the ¹H NMR spectrum of PCL(FUR)₄ presented hereafter (**Fig. S2**).

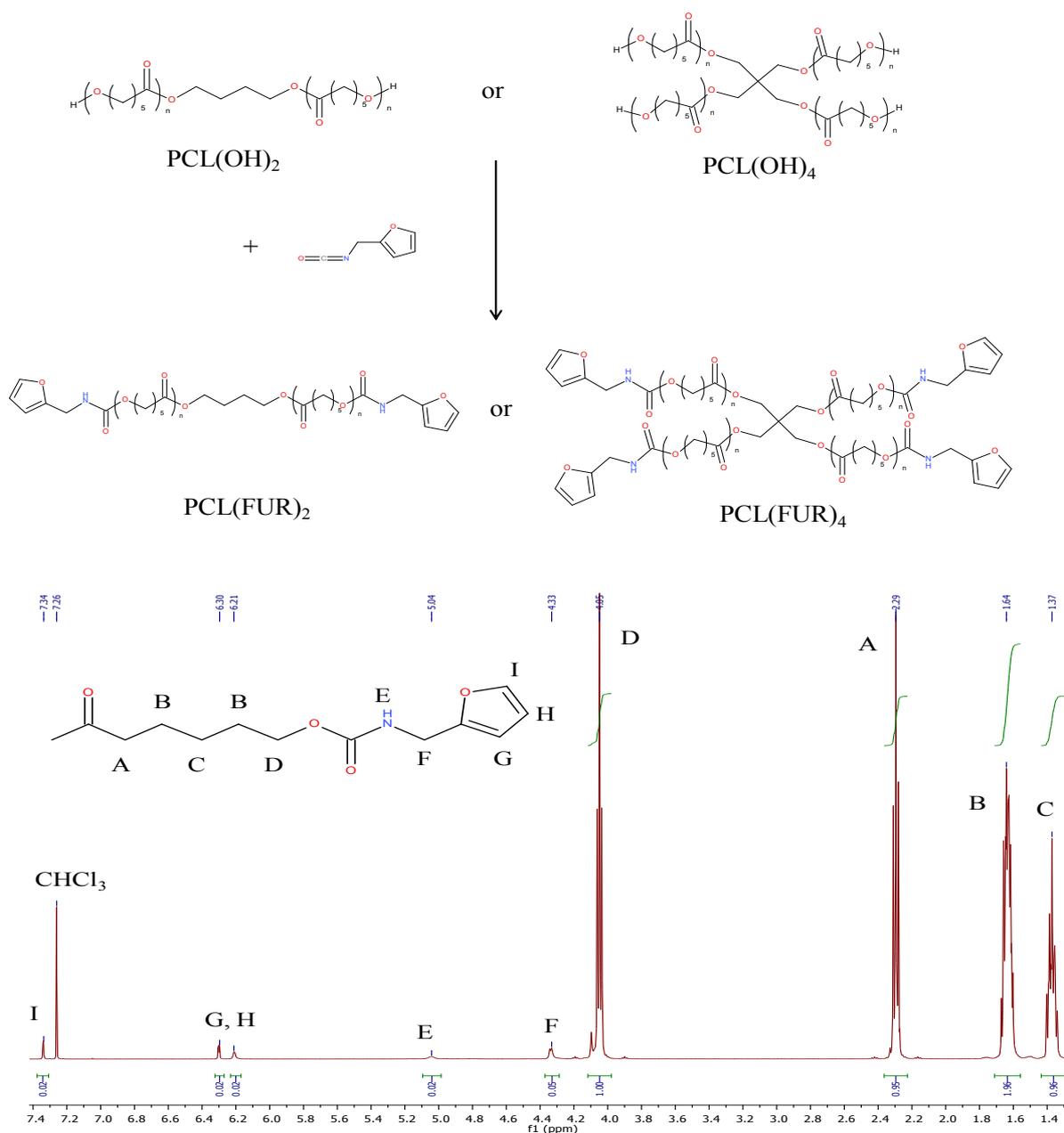
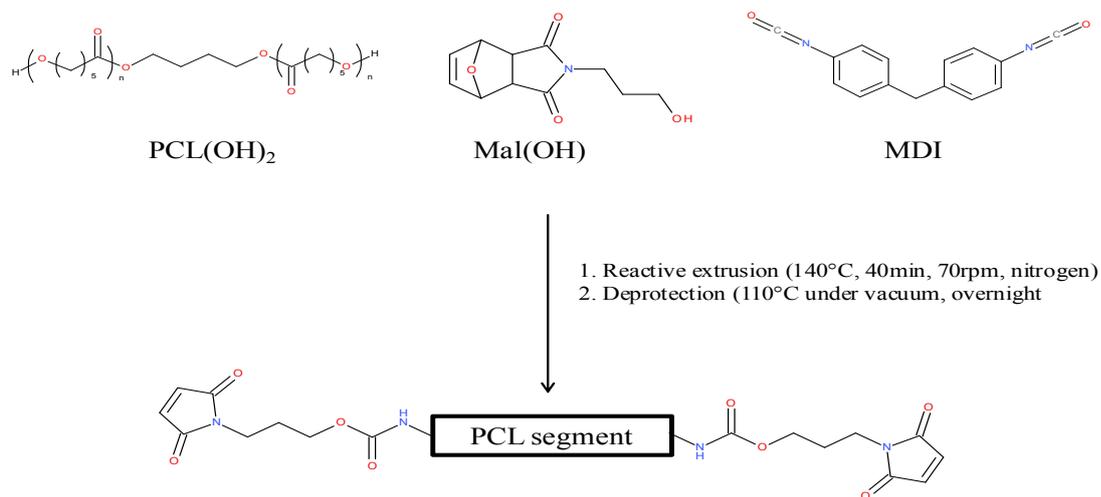


Fig. S2. ¹H NMR spectrum of PCL(FUR)₄ (500MHz, CDCl₃)

S.3. Synthesis of PCL end-functionalized with maleimide moieties, PCL(MAL)₂

Procedure for the synthesis of PCL(MAL)₂ is described in the Experimental section. The structure was attested by ¹H-NMR performed in CDCl₃ (M_n = 9000 g/mol, PDI = 1.7, SEC in THF) (**Fig. S3**).



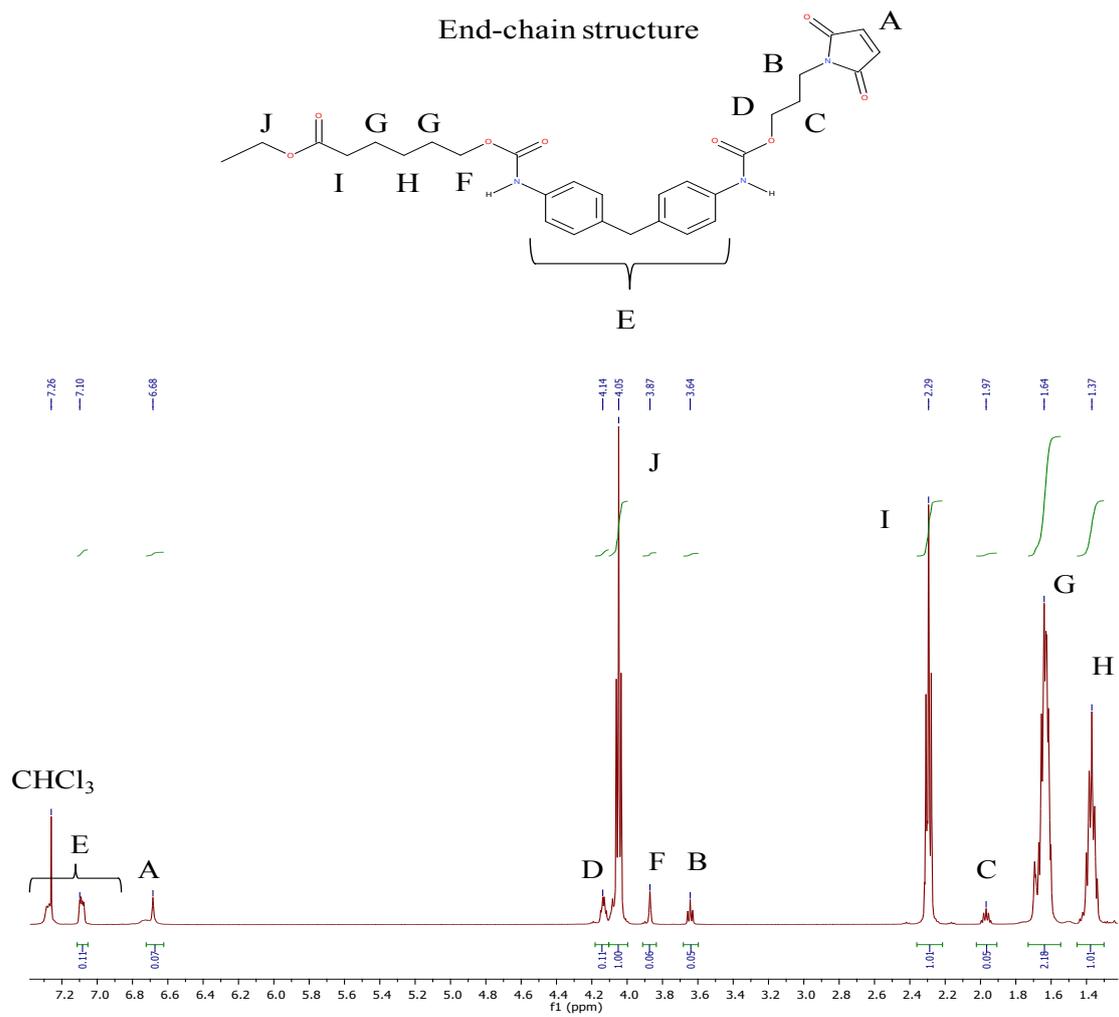


Fig. S3. 1H NMR spectrum of $PCL(MAL)_2$ (500MHz, $CDCl_3$)

S.4. Picture of the reactive extrusion set-up and FTIR spectrum of the composite obtained by reactive extrusion of $\text{PCL}(\text{FUR})_2$ and N,N' -(1,3-phenylene)dimalaideimide (at 0.25% wt. MWCNTs)

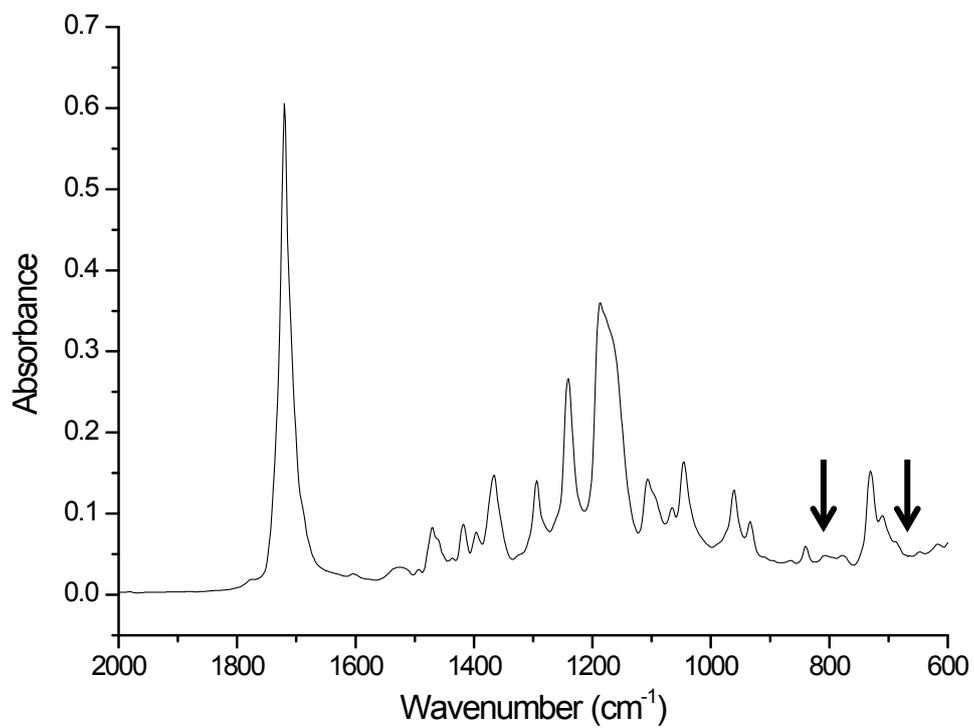


Fig. S4. (Top) 15cm³ vertical mini-extruder DSM and (Bottom) FTIR spectrum of the composite obtained by reactive extrusion of $\text{PCL}(\text{FUR})_2$, N,N' -(1,3-phenylene)dimalaideimide and 0.25% wt. of MWCNTs

S.5. Thermal stability of the 2%wt containing MWCNTs linear thermo-mendable nanocomposite

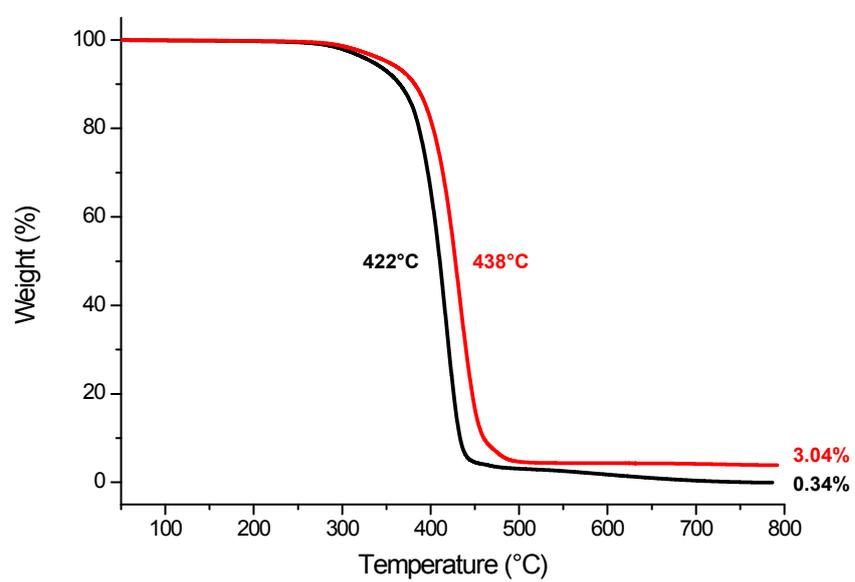


Fig. S5. TGA thermograph of the linear thermo-mendable PCL without (black) and with (red) 2% wt MWCNTs

S.6. Composition of the synthesized networks containing 2% wt. MWCNTs

Table S6. Composition of the synthesized networks containing 2% wt. MWCNTs

Weight ratio in PCL(FUR) ₄ / PCL(FUR) ₂	Molar ratio in PCL(FUR) _x /PCL(MAL) ₂ ^{a)}
[%]	
0/100 (fully linear)	50/50
25/75	50/50
50/50	50/50
75/25	50/50
100 (fully cross-linked)	50/50

^{a)} Where X = 2 or 4

S.7. Extrusion force evolution for different PCL(FUR)₂/PCL(FUR)₄ ratios containing 2% wt. of MWCNTs

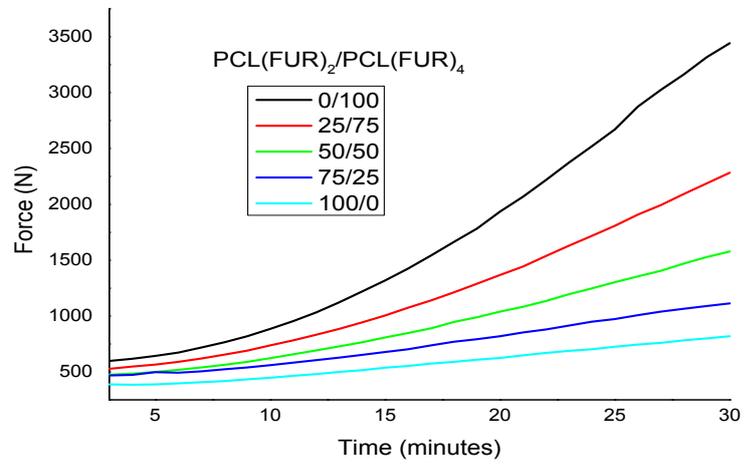


Fig. S7. Extrusion force evolution for different PCL(FUR)₂/PCL(FUR)₄ ratios containing 2% wt. of MWCNTs

S.8. Electrical and molecular parameters of the linear and fully cross-linked composites containing 2% wt. of MWCNTs

Table S8. Electrical and molecular parameters of the linear and fully cross-linked composites containing 2% wt. of MWCNTs

Weight content in PCL(FUR) ₄ [%]	DA Conversion [%] ^{a)}	Cross-linking density [10 ⁻⁵ mol.g ⁻¹] ^{b)}	Volume conductivity [10 ⁻² S.cm ⁻¹] ^{d)}
0 (linear)	>99	/ ^{c)}	1.4
100 (cross-linked)	>99	7.1	0.8

^{a)} According to FTIR analyses

^{b)} Attested by swelling test in chloroform during 24h

^{c)} Soluble in chloroform

^{d)} Determined by four-probe electrical measurement

S.9. Dispersion of carbon nanotube (2% wt.) in poly(ester-urethane) networks

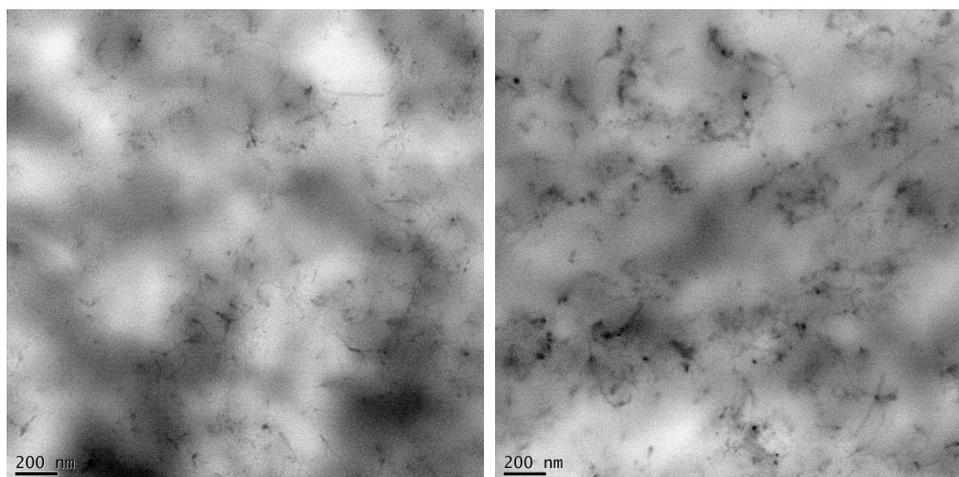


Fig. S9. TEM images of the linear (100% PCL(FUR)₂, left) and fully cross-linked networks (100% PCL(FUR)₄, right) containing 2% wt. of MWCNTs

REFERENCES

1. W. M. Gramlich, M. L. Robertson and M. A. Hillmyer, *Macromolecules*, 2010, **43**, 2313-2321.