

Supporting Information

3D Printed Remendable Polylactic Acid Blends with Uniform Mechanical Strength Enabled by a Dynamic Diels-Alder Reaction

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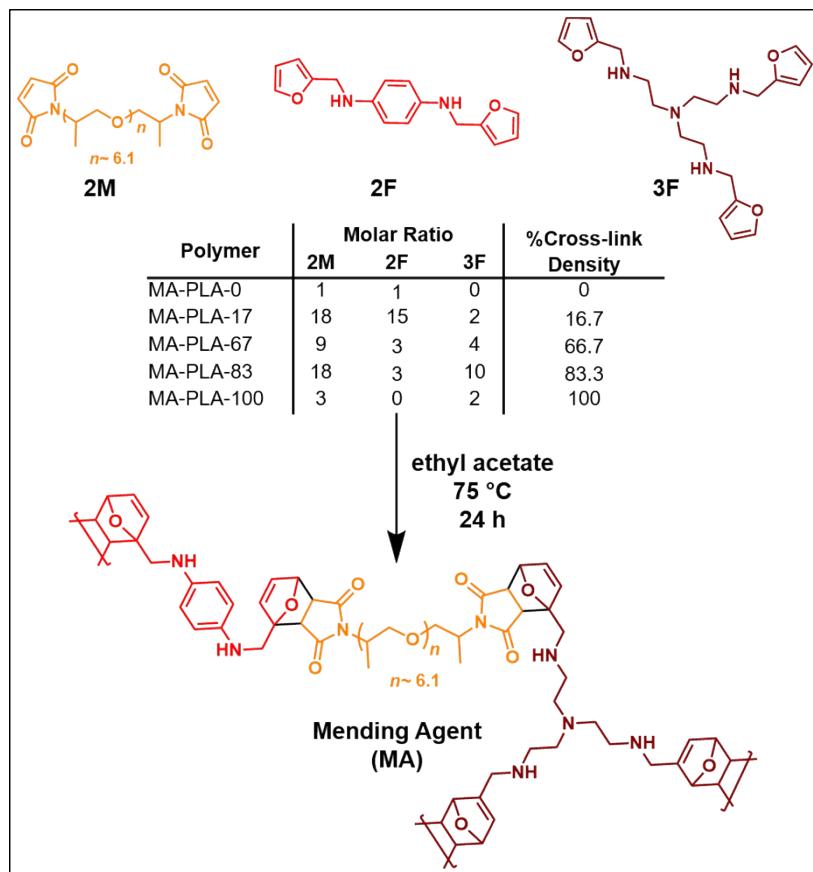
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Synthetic Procedures



Synthesis of Mending Agent Polymers. In order to synthesize the MA-PLA blends with 0, 16.7, 66.7, 83.3, and 100% cross-link density, the monomers 2M, 2F, and 3F were reacted together according to the molar ratios given in shown table. Ethyl acetate (5 mL) was used as the solvent and the mixtures were heated at 75 °C for 24 h. Then the solvent was removed at 60 °C in a vacuum oven (< 1 mmHg) for 24 h. The crosslink density is calculated based on the contribution of the furan groups from monomer 3F to form the fmDA adducts (cross-links), to the total available furan groups in each MA-PLA blend.

Preparation of MA/PLA blends. Each of these synthesized MA polymers were then mixed with PLA in 1,4-dioxane at 80 °C to obtain a series of 25 wt% MA/PLA blends with 0, 16.7, 66.7, 83.3, and 100% cross-link density. The solvent was removed under vacuum at 60 °C for 24 h.

Processing Methodology of Polymer Blends

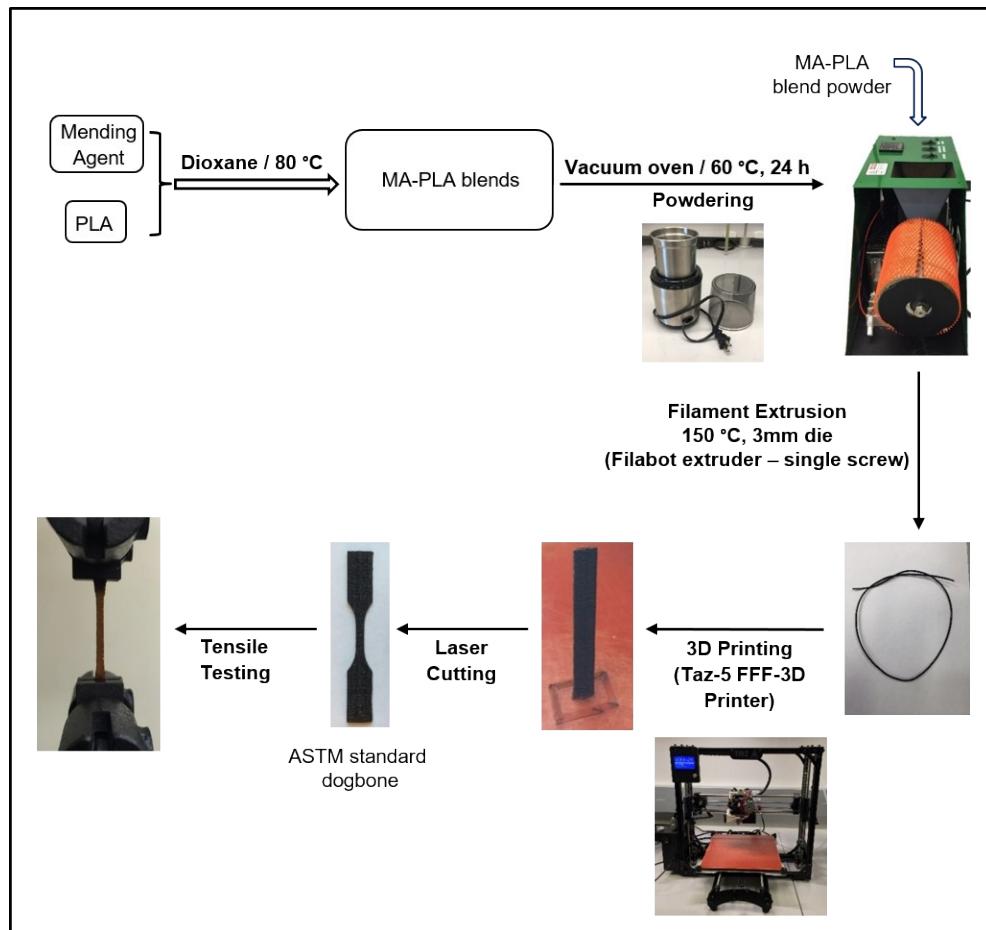
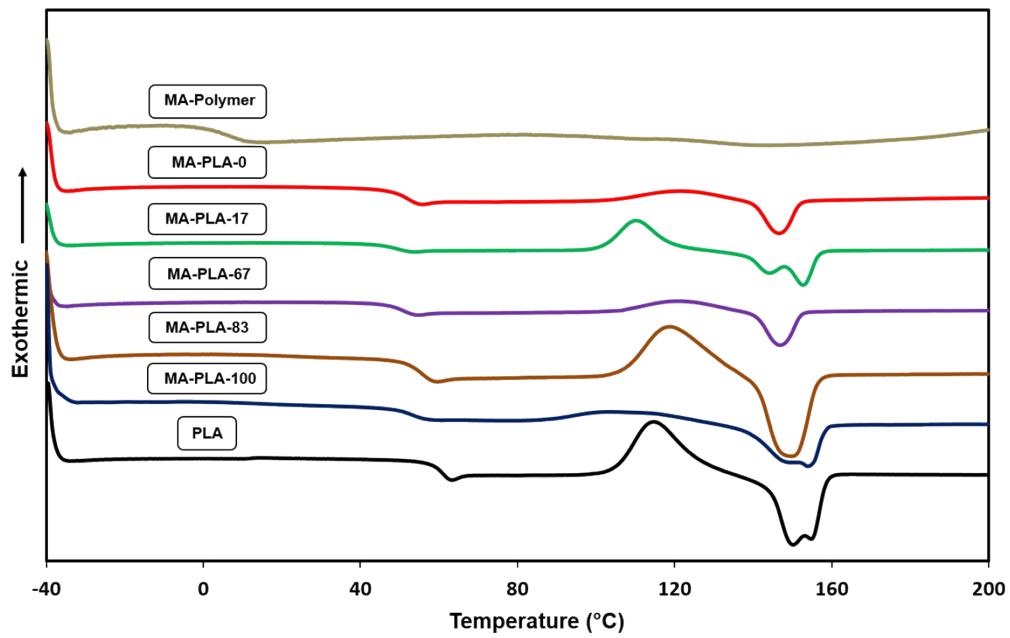


Fig. S1 Filament fabrication, 3D printing, and tensile testing of the MA-PLA blends.

Thermal Analysis of Polymer Blends



| Material | T _g (°C) |
|------------|---------------------|
| MA-Polymer | 6.98 |
| MA-PLA-0 | 50.29 |
| MA-PLA-17 | 50.45 |
| MA-PLA-67 | 51.46 |
| MA-PLA-83 | 54.27 |
| MA-PLA-100 | 55.57 |
| PLA | 61.91 |

Fig. S2 Differential scanning calorimetry analysis of MA-Polymer (16.7% cross-link density), MA-PLA blends, and PLA followed by their T_g values tabulated.

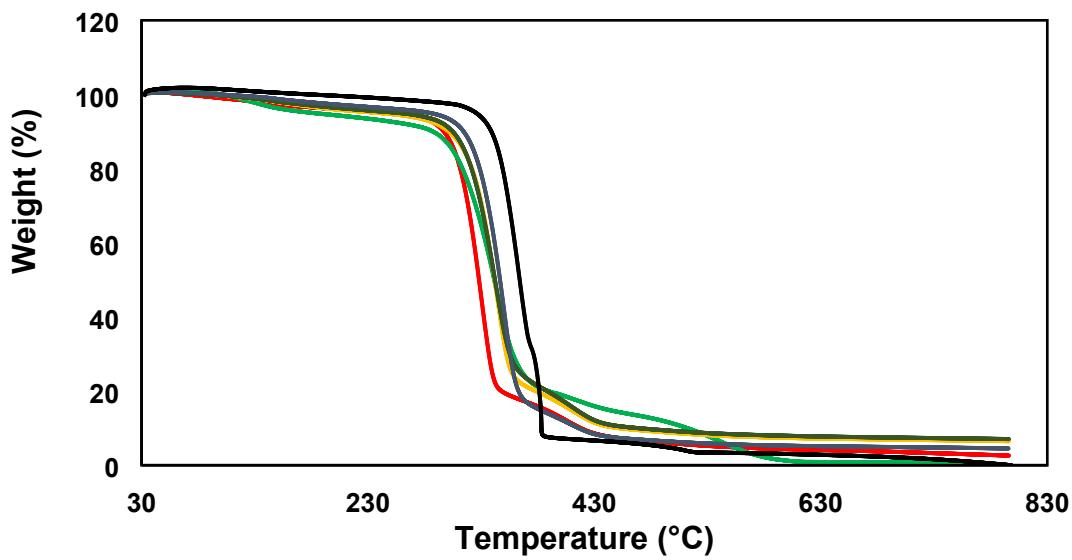


Fig. S3 Thermogravimetric Analysis of PLA and MA-PLA blends. PLA (black), MA-PLA-100 (blue), MA-PLA-83 (brown), MA-PLA-67 (purple), MA-PLA-17 (green), and MA-PLA-0 (red).

Mechanical Testing of Polymer Blends

Table S1-Ultimate strength (MPa) values for PLA and MA-PLA blends along each print direction.

| Print Direction | MA-PLA blends | | | | | |
|-----------------|---------------|----------------|-----------------|-----------------|-----------------|------------------|
| | PLA (MPa) | MA-PLA-0 (MPa) | MA-PLA-17 (MPa) | MA-PLA-67 (MPa) | MA-PLA-83 (MPa) | MA-PLA-100 (MPa) |
| X | 41.41 ± 1.18 | 36.36 ± 3.10 | 39.73 ± 1.13 | 35.07 ± 0.52 | 36.01 ± 0.17 | 47.61 ± 1.62 |
| Y | 29.94 ± 3.35 | 28.83 ± 0.07 | 33.74 ± 0.79 | 34.15 ± 1.92 | 32.72 ± 1.57 | 48.04 ± 4.82 |
| Z | 11.44 ± 1.26 | 17.59 ± 1.68 | 23.89 ± 1.07 | 23.46 ± 1.44 | 27.77 ± 1.26 | 44.62 ± 1.24 |

Table S2-Toughness (MJ/m³) values for PLA and MA-PLA blends along each print direction.

| Print Direction | MA-PLA blends | | | | | |
|-----------------|--------------------------|-------------------------------|--------------------------------|--------------------------------|--------------------------------|---------------------------------|
| | PLA (MJ/m ³) | MA-PLA-0 (MJ/m ³) | MA-PLA-17 (MJ/m ³) | MA-PLA-67 (MJ/m ³) | MA-PLA-83 (MJ/m ³) | MA-PLA-100 (MJ/m ³) |
| X | 0.43 ± 0.02 | 0.39 ± 0.04 | 0.44 ± 0.04 | 0.43 ± 0.06 | 0.40 ± 0.07 | 0.60 ± 0.03 |
| Y | 0.27 ± 0.02 | 0.29 ± 0.02 | 0.35 ± 0.03 | 0.40 ± 0.03 | 0.39 ± 0.03 | 0.69 ± 0.06 |
| Z | 0.04 ± 0.02 | 0.13 ± 0.02 | 0.19 ± 0.03 | 0.21 ± 0.02 | 0.25 ± 0.02 | 0.50 ± 0.03 |

Table S3-Comparison of the %increase of ultimate strength along Z print axis for each of the MA-PLA blend vs. PLA.

| Material | %Increase of Ultimate Strength along Z axis vs. PLA |
|------------|---|
| MA-PLA-0 | 53.76 |
| MA-PLA-17 | 108.83 |
| MA-PLA-67 | 105.07 |
| MA-PLA-83 | 142.74 |
| MA-PLA-100 | 290.03 |

Table S4-Comparison of the %increase of Toughness along Z print axis for each of the MA-PLA blend vs. PLA.

| Material | %Increase of Toughness along Z axis vs. PLA |
|------------|---|
| MA-PLA-0 | 225 |
| MA-PLA-17 | 375 |
| MA-PLA-67 | 425 |
| MA-PLA-83 | 525 |
| MA-PLA-100 | 1150 |

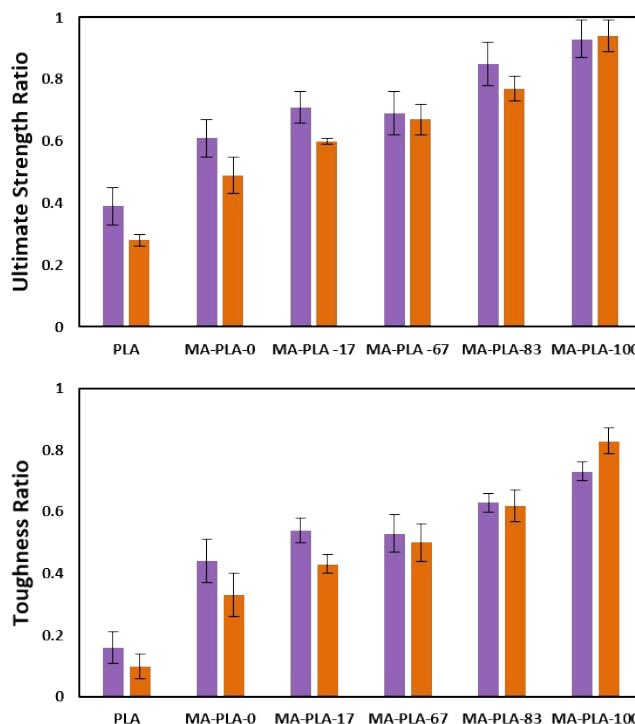


Fig. S4 Ultimate Strength and toughness ratios of print patterns Z to Y (purple) and Z to X (orange) for PLA and MA-PLA blends with varying crosslink density.

Table S5-Comparison of ultimate strength ratios along Z print direction to Y and Z print direction to X for PLA and MA-PLA blends.

| Material | Ultimate Strength ratio of Z to Y | Ultimate Strength ratio of Z to X |
|------------|-----------------------------------|-----------------------------------|
| PLA | 0.39 ± 0.06 | 0.28 ± 0.02 |
| MA-PLA-0 | 0.61 ± 0.06 | 0.48 ± 0.06 |
| MA-PLA-17 | 0.71 ± 0.05 | 0.60 ± 0.01 |
| MA-PLA-67 | 0.69 ± 0.07 | 0.67 ± 0.05 |
| MA-PLA-83 | 0.85 ± 0.07 | 0.77 ± 0.04 |
| MA-PLA-100 | 0.93 ± 0.06 | 0.94 ± 0.05 |

Table S6-Comparison of Toughness ratios along Z print direction to Y and Z print direction to X for PLA and MA-PLA blends.

| Material | Toughness ratio of Z to Y | Toughness ratio of Z to X |
|------------|---------------------------|---------------------------|
| PLA | 0.16 ± 0.05 | 0.09 ± 0.04 |
| MA-PLA-0 | 0.44 ± 0.07 | 0.33 ± 0.07 |
| MA-PLA-17 | 0.54 ± 0.04 | 0.43 ± 0.03 |
| MA-PLA-67 | 0.53 ± 0.06 | 0.49 ± 0.06 |
| MA-PLA-83 | 0.63 ± 0.03 | 0.63 ± 0.05 |
| MA-PLA-100 | 0.73 ± 0.03 | 0.83 ± 0.04 |

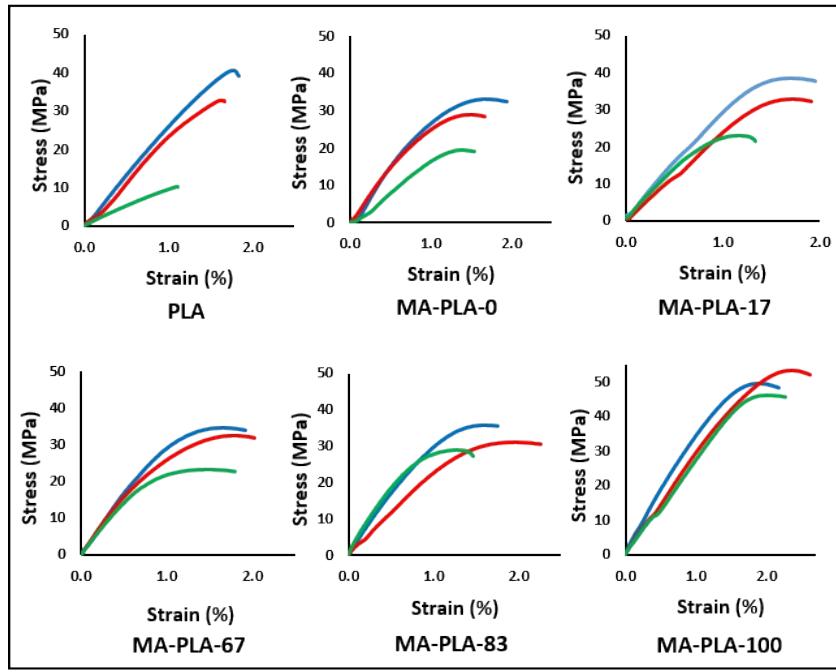


Fig. S5 Stress vs. strain curves of PLA and MA-PLA blends as dogbones for each print pattern X (blue), Y (red), and Z (green).

Thermal Stability Tests

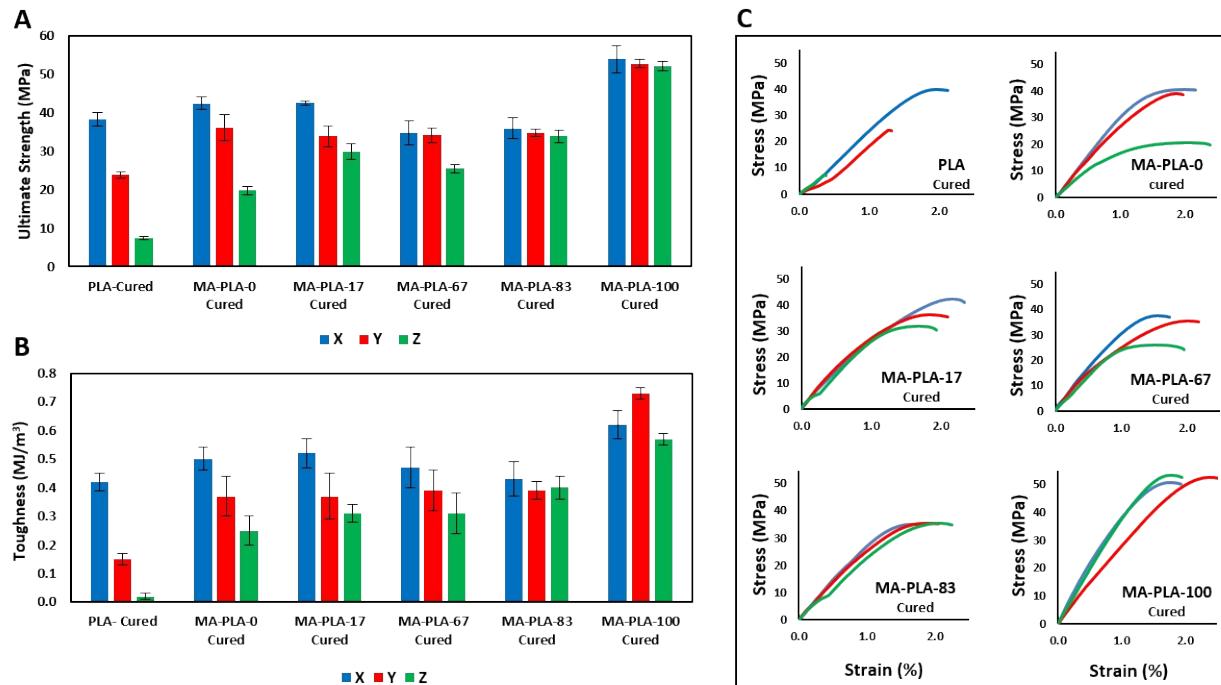


Fig. S6 Ultimate strength (A) and toughness (B) values for PLA and MA-PLA blends heated under 65 °C/15 min conditions. Related stress vs. strain curves (C).

Table S7-Ultimate Strength (MPa) values for PLA and MA-PLA blends along each print direction after heating under 65 °C/15 min conditions.

| Print Direction | MA-PLA blends | | | | | |
|-----------------|---------------|----------------|-----------------|-----------------|-----------------|------------------|
| | PLA (MPa) | MA-PLA-0 (MPa) | MA-PLA-17 (MPa) | MA-PLA-67 (MPa) | MA-PLA-83 (MPa) | MA-PLA-100 (MPa) |
| X | 38.24 ± 1.80 | 42.41 ± 1.59 | 42.55 ± 1.13 | 34.84 ± 3.13 | 35.98 ± 2.70 | 53.86 ± 3.51 |
| Y | 23.81 ± 0.79 | 36.01 ± 3.37 | 33.90 ± 0.79 | 34.10 ± 1.87 | 34.77 ± 0.92 | 52.72 ± 1.10 |
| Z | 7.42 ± 0.45 | 19.76 ± 1.12 | 29.89 ± 1.07 | 25.44 ± 1.07 | 33.86 ± 1.56 | 52.07 ± 1.29 |

Table S8-Toughness values (MJ/m³) for PLA and MA-PLA blends along each print direction after heating under 65 °C/15 min conditions.

| Print Direction | MA-PLA blends | | | | | |
|-----------------|--------------------------|-------------------------------|--------------------------------|--------------------------------|--------------------------------|---------------------------------|
| | PLA (MJ/m ³) | MA-PLA-0 (MJ/m ³) | MA-PLA-17 (MJ/m ³) | MA-PLA-67 (MJ/m ³) | MA-PLA-83 (MJ/m ³) | MA-PLA-100 (MJ/m ³) |
| X | 0.42 ± 0.03 | 0.50 ± 0.04 | 0.52 ± 0.05 | 0.47 ± 0.07 | 0.43 ± 0.06 | 0.62 ± 0.05 |
| Y | 0.15 ± 0.02 | 0.37 ± 0.07 | 0.37 ± 0.08 | 0.39 ± 0.07 | 0.39 ± 0.03 | 0.73 ± 0.02 |
| Z | 0.02 ± 0.01 | 0.25 ± 0.05 | 0.31 ± 0.03 | 0.31 ± 0.07 | 0.40 ± 0.04 | 0.57 ± 0.02 |

References

1. Y. Zhong, X. Wang, Z. Zheng and P. Du, *J. Appl. Polym. Sci.*, 2015, **132**, 41944.
2. A. Gandini, D. Coelho, M. Gomes, B. Reis and A. Silvestre, *J. Mater. Chem.*, 2009, **19**, 8656-8664.