Supporting information

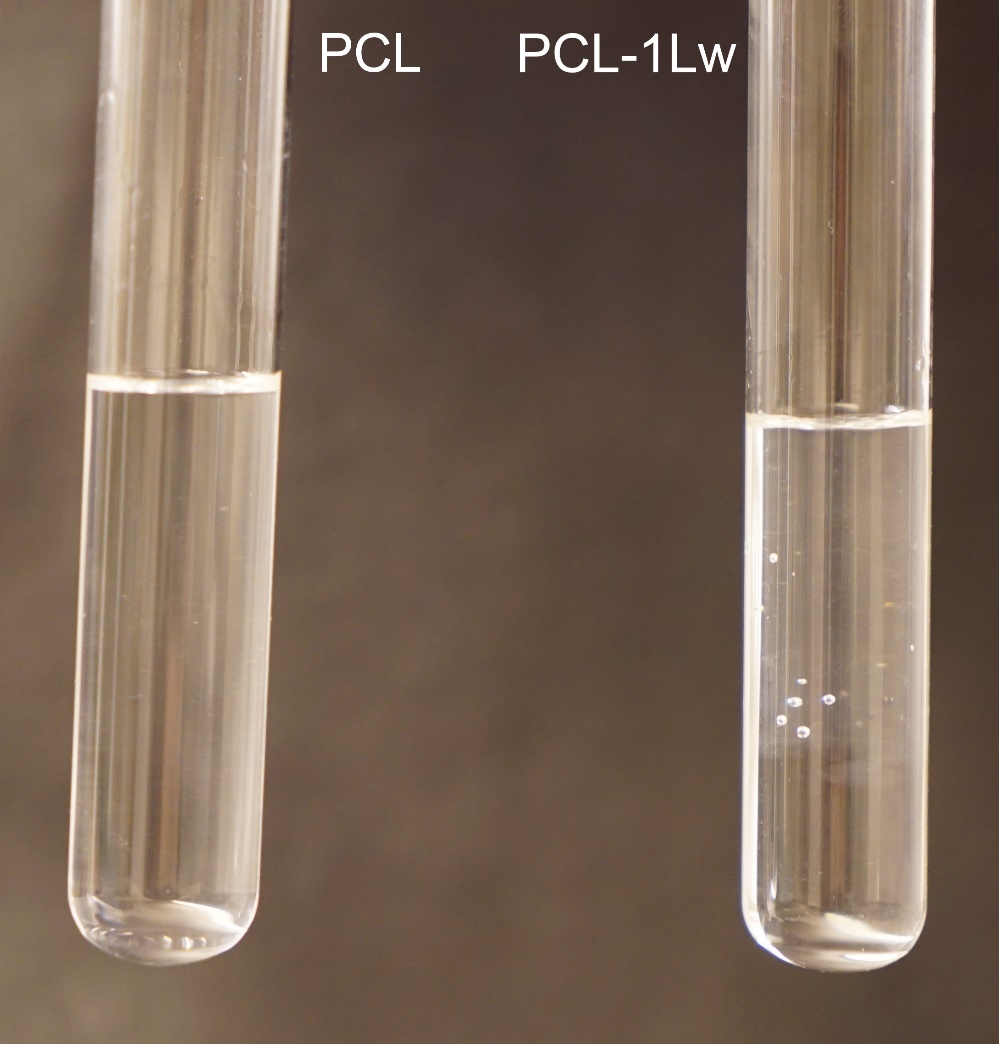
Substantial effect of water on radical melt crosslinking and rheological properties of poly(ε-caprolactone)

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**Figure S1.** Photo of test tubes containing neat poly(ε-caprolactone) (PCL) and PCL reacted with 1 wt% peroxide in the presence of water (PCL-1Lw), after 24 h in solution with dichloromethane.

**Table S1.** Thermal properties of neat and reacted PCL detected by Thermogravimetrical analysis (TGA) and Differential Scanning Calorimetry (DSC). TGA: Onset temperatures of degradation (*T*5% ) evaluated at 5 % weight loss; degradation temperature (*T*d) evaluated as the peak temperature of DTG; char residue at 550 °C. DSC: Glass (*T*g) and melting (*T*m) temperatures detected from the second heating scan; melting enthalpy (ΔHM) and crystallinity (χDSC) detected from the melting peak in the second heating scan (from 15 to 65 °C); crystallization temperature (*T*c) detected from the cooling scans.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Material | ***T*5% [°C]** | ***T*d [°C]** | **Char [%]** | ***T*g [°C]** | ***T*m [°C]** | **ΔHM [J·g-1]** | **χDSC [%]** | ***T*c [°C]** |
| PCL | 363 | 400 | 1 | -62 | 57 | 63.73 | 47.0 | 35 |
| PCL-0.1L | 290 | 398 | 1 | -63 | 57 | 62.51 | 46.1 | 30 |
| PCL-0.25L | 304 | 398 | 3 | -65 | 57 | 60.36 | 44.5 | 31 |
| PCL-0.5L | 331 | 398 | 2 | -62 | 57 | 62.9 | 46.4 | 37 |
| PCL-0.5Lw | 325 | 398 | 2 | -61 | 57 | 59.23 | 43.7 | 36 |
| PCL-1L | 345 | 398 | 0 | -62 | 57 | 63.26 | 46.6 | 35-40 |
| PCL-1Lw | 347 | 399 | 2 | -58 | 59 | 61.34 | 45.2 | 41 |

Chart

Description automatically generated

**Figure S2.** Curves from thermogravimetrical analysis (TGA) of neat and reacted PCL with different wt% of peroxide during dry (PCL-xL) or water-assisted (PCL-xLw) melt processing.



**Figure S3.** Derivative thermogravimetric (DTG) curves of neat and reacted PCL.



**Figure S4.** Thermograms from second heating scan of Differential Scanning Calorimetry (DSC) of neat and reacted PCL.

Chart, diagram, schematic

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**Figure S5.** X-Ray diffractograms of PCL and PCL reacted with 1 wt% peroxide during dry (PCL-1L) or water-assisted (PCL-1Lw) melt processing.

Chart, histogram

Description automatically generated

**Figure S6.** Stress-strain curves from tensile tests at room temperature neat and reacted PCL*.*

**Table S2.** Mechanical properties assessed from tensile tests at room temperature. Each value represents the average of 5 measurements with the standard deviation. \*Data extracted at the upper limit of the instrument.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Material** | **Young’s modulus [MPa]** | **Yield stress [MPa]** | **Ultimate tensile strength [MPa]** | **Elongation at break [%]** |
| PCL | 284 ± 5 | 19.2 ± 0.5 | 38.7 ± 0.6 \* | 1200 \* |
| PCL-0.1L | 262 ± 3 | 18.7 ± 0.4 | 39 ± 0.5\* | 1200\* |
| PCL-0.25L | 262 ± 2 | 18.5 ± 0.1 | 39.1 ± 0.9\* | 1200\* |
| PCL-0.5L | 248 ± 6 | 18.4 ± 0.1 | 38.8 ± 2.4 \* | 1175 ± 44 \* |
| PCL-0.5Lw | 218 ± 8 | 16 ± 0.4 | 39.8 ± 0.1 \* | 1200 \* |
| PCL-1L | 242 ± 13 | 17.3 ± 1 | 33.6 ± 1.3 | 941 ± 57 |
| PCL-1Lw | 225 ± 14 | 17.1 ± 0.5 | 44 ± 1.2 | 1035 ± 48 |