Electronic supplementary information for

Physically cross-linked polyethylene via reactive extrusion

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Figure S1. $^1$H NMR spectra overlay of EVA, EVOH and polymer 3 (EVOH-UPy) recorded at 120 °C in deuterated TCE.

Figure S2. $^1$H NMR spectra overlay of PE-MAH, PE-MAH-EA and polymer 4 (PE-MAH-EA-UPy) recorded at 120 °C in deuterated TCE.
Table S1. Functional group content, melting temperatures ($T_m$), $\beta$ transition temperatures ($T_\beta$) degrees of crystallinity ($X_{cr}$) as well as molecular weights ($M_n$, $M_w$) and molecular weight distributions ($D_M$) of the starting polyolefins.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Functional group content [mol%]$^a$</th>
<th>$T_m^b$ [$^\circ$C]</th>
<th>$T_\beta^c$ [$^\circ$C]</th>
<th>$X_{cr}^d$ [%]</th>
<th>$M_n^e$ [g/mol]</th>
<th>$M_w^e$ [g/mol]</th>
<th>$D_M^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA</td>
<td>3.0</td>
<td>99.1</td>
<td>-9.5$^f$</td>
<td>11.7</td>
<td>13 500</td>
<td>69 100</td>
<td>5.1</td>
</tr>
<tr>
<td>PE-MAH</td>
<td>0.4</td>
<td>99.2</td>
<td>-16.4</td>
<td>9.3</td>
<td>2 500</td>
<td>5 900</td>
<td>2.4</td>
</tr>
</tbody>
</table>

$^a$Functional group content was calculated from $^1$H-NMR (400 MHz, 120 $^\circ$C, TCE $d_2$); PE-MAH with higher functional group content is not commercially available. $^b$Melting temperatures ($T_m$) were determined by DSC from the second heating scan. $^c$$\beta$ transition temperatures ($T_\beta$) were determined by DMTA from the maximum of tan $\delta$. $^d$Degrees of crystallinity ($X_{cr}$) were calculated dividing the melting enthalpy of 100% crystalline PE (286.2 J/g, B. Wunderlich, C. M. Cornier, Heat of fusion of polyethylene. Journal of Polymer Science Part A-2: Polymer Physics 1967, 5 (5), 987-988.) by melting enthalpy of a polymer determined by DSC from the second heating scan. $^e$Molecular weight and polydispersity were determined by SEC in oDCB at 150 $^\circ$C with respect to polyethylene standards. $^f$two $\beta$ transition temperatures were observed.

**Calculation of UPy units per chain**

Number of UPy/chain was calculated based on the amount of -OH grafted and $M_n$ of starting material according to the Equaton S1. Functional group content, hydrogen bonding motif content and $M_n$ of the functionalized PE can be found in the Table 1 and Table 2. Repeating unit other then ethylene is treated as a “comonomer” for this calculation even though the polymer might not have been obtained by copolymerization of this fragment with ethylene.

$$\text{UPy / chain} = \frac{M_n \left\{ \frac{\text{hydrogen bonding motif [mol%]}}{\text{functional group [mol%]} \cdot \frac{M_{\text{comonomer [mol/mol]}}}{M_{\text{ethylen [mol/mol]}}}} \right\} + \left(100 - \text{functional group [mol%]}\right) M_{\text{ethylene [mol/mol]}}} {M_n}$$

(1)
Figure S3. DSC first (black) and second (red) heating curve of UPy.

Figure S4. $^1$H NMR spectra overlay of polymer 1 (PE-HEMA1-UPy, black) and PE-HEMA1 extruded with UPy at 200 °C (red), recorded at 120 °C in deuterated TCE.
Figure S5. Representative melt viscosity changes recorded during the reactive extrusion of polymer 2 (PE-HEMA2-IPR-UPy)

Figure S6. IR spectra overlay of UPy (red line) and functional polyolefins grafted with UPy or IPR-UPy (black lines).
Figure S7. DSC second heating curves of PE-HEMA1 and polymer 1 (PE-HEMA2-UPy).

Figure S8. DSC second heating curves of PE-HEMA2, and polymer 2 (PE-HEMA2-IPR-UPy).
Figure S9. DSC second heating curves of EVA, EVOH and polymer 3 (EVOH-UPy).

Figure S10. DSC second heating curves of PE-MAH, PE-MAH-EA and polymer 4 (PE-MAH-EA-UPy).
Figure S11. DSC heating curves of polymer 3 (EVOH-UPy), maximal temperature was increased by 10 °C each time starting from 120 °C.

Figure S12. DSC heating curves of polymer 4 (PE-MAH-EA-UPy) maximal temperature was increased by 10 °C each time starting from 120 °C.
Figure S13. DSC heating curves of PE-HEMA1, maximal temperature was increased by 10 °C each time starting from 120 °C.

Figure S14. Rheology temperature sweep curves of PE-HEMA2 and polymer 2 (PE-HEMA1-UPy).
Figure S15. Rheology temperature sweep curves of EVOH and polymer 3 (EVOH-UPy).

Figure S16. Rheology temperature sweep curves of PE-MAH-EA and polymer 4 (PE-MAH-EA-UPy).
Figure S17. TGA curves of PE-HEMA1 and polymer 1 (PE-HEMA-UPy).

Figure S18. Rheology frequency sweep curves of EVOH and polymer 3 (EVOH-UPy).
Figure S19. Rheology frequency sweep curves of PE-MAH-EA and polymer 4 (PE-MAH-EA-UPy).

Figure S20. DMTA curves of EVOH and polymer 3 (EVOH-UPy).
Figure S21. DMTA curves of PE-MAH-EA and polymer 4 (PE-MAH-EA-UPy)
Figure S22. Representative stress-strain curves and Young’s modulus, toughness, ultimate strength and strain at break of EVOH and polymer 3 (EVOH-UPy).
Figure S23. Representative stress-strain curves and Young’s modulus, toughness, ultimate strength and strain at break of PE-MAH-EA and polymer 4 (PE-MAH-EA-UPy)