Supplementary Information for

Comprehensive investigation of a water-repelling polymer coating for cellulose-based samples by a direct comparison of un- and modified fibres

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S1 – SEM images of cellulose samples with higher magnification



**Figure S1** SEM images of LP (a), EP (b), PCLP (c), and PCEP (d) at 1500x magnification

On the SEM images a higher entanglement is observed for LP (Figure S1 (a)) than for EP (Figure S1 (b)). After the coating the surface is smoother and the entanglements could not be distinguished anymore.

S2 – Fluorescence Microscopy images of unmodified cellulose samples

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**Figure S2** Fluorescence Microscopy images of the unmodified paper samples LP (a) and EP (b). The scale bar represents 300 µm

Fluorescence Microscopy images show a homogeneously distributed, slight fluorescence caused by the background light in the laboratory.

S3 – Raman Spectroscopy

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**Figure S3** Raman spectrum of P(S-co-MABP-co-PyMA) with the labeled polymer bands. The spectrum was taken with 10 accumulation and 10s integration time each

The Raman spectrum of the terpolymer P(s-co-MABP-co-PyMA) showed a superposition of the Raman spectra of the single components PS, BP, and Pyrene. The green labeled peaks in the Raman spectrum are listed in Table S1.

**Table S1** Characteristic vibrational motions of cellulose (Osterberg, Schmidt, and Jaaskelainen 2006), PS (Brun et al. 2013; Hong et al. 1991), BP (Babkov et al. 2006), and Pyrene (Xie et al. 2010)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Label (Fig. 5 and Fig. S3) | Raman shift (cm-1) | Bond | Movement | Material |
| P1 | 137-225 | Carbonyl group | Deformation and Torsion | Benzophenone (BP) |
| C1 | 379-516 | CC, COC OCC, OCO | Skeletal bend | Cellulose |
| P2 | 405 |  | Skeletal stretching | Pyrene, BP |
| P3 | 619 | Phenyl ring | Deformation | BP |
| P4 | 1000 | CH, CC | Rocking, Stretching | PS, BP |
| C2 | 1095, 1118 | CC, CO | Stretching | Cellulose |
| C3 | 1290 | HCC, HCO | Bending | Cellulose |
| P5 | 1151-1392 | CH, CCC, CH | Stretching, Bending | Pyrene, BP, PS |
| C4 | 1334, 1376, 1476 | HCC, HCO, HOC, HCH | Bending | Cellulose |
| P6 | 1598 | CC, Ring | Stretching | Pyrene, PS, BP |
| C5 | 2800-3000 | CH, CH2 | Stretching | Cellulose |
| P7 | 2800-3000 | CH, CH2 | Stretching | PS, BP |
| P8 | 3058 | CH | Stretching | PS, BP |
| C6 | 3200-3500 | OH | Stretching | Cellulose |

Hydration experiments with *in situ* Raman spectroscopy using point scans are shown in Figure S2 (a) and (b) for linters and eucalyptus, respectively. The results of the humidity experiments with an extended adjustment time of 180 min are given in Figure S2 (c) and (d). For the adjustment times of 60 min point Raman measurements were used, while for the extended humidity adjustment times (180 min) mapscans were used.

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**Figure S4** Results from hydration experiments with in situ Raman spectroscopy for different humidity adjustment times: 60 min (a and b) and 180min (c and d) and different materials: LP and PCLP (a and c), EP and PCEP (b and d). The unmodified paper samples are represented in red (left bar), the polymer coated ones in blue (right bar). The integrated intensity is the summed intensity in the OH stretching spectral region (3200-3500 cm-1)

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