Electronic Supplementary Information

LED-cured self-replenishing hydrophobic coatings based on Interpenetrating Polymer Networks (IPNs)

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Thermomechanical Properties:

Fox equation (Equation S1) was applied to determine the acrylate/epoxide ratios for the co-continuous phases. The storage and loss modulus for each composition have been given at room temperature (25°C), showing a mechanical improvement by the increase of epoxide ratio. All corresponding data are given in Table S1.

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} \quad \text{..... (S1)}$$

Table S1: Acrylate/epoxide ratios of co-continuous phases according to Fox equation, and storage and loss modulus data obtained by DMA measurements.

Sample	T_g (°C)	Ratios calculated by using Fox equation (%)		Storage Modulus (E') at 25°C (Mpa)	Loss Modulus (E'') at 25°C (MPa)
		Acrylate	Epoxide		
40A60E	18 (shoulder) 79	64 32	36 68	984	206
50A50E	24 68	60 37	40 63	255	70
60A40E	7 57 (shoulder)	71 42	29 58	96	27
70A30E	-10 41 (shoulder)	83 51	17 49	21	4
40A60E 1F	24 (shoulder) 75	60 34	40 66	837	196
50A50E 1F	30 57	57 42	43 58	274	89
60A40E 1F	0 61 (shoulder)	76 40	24 60	146	37
70A30E 1F	-11 50 (shoulder)	84 46	16 54	16	3

Maldi-Tof experiments

In an overview of all the Maldi-ToF spectra of extractables (Figure S1A), the presence of PCL-block from the dangling chains can be confirmed by the periodically repeating peaks with a difference of one caprolactone unit (m/z = 114.1) between the adjacent peaks. At a zoomed-in scale, all these repeating peaks are located at the same m/z values with the –OH terminated dangling chains, which is a low amount of impurity, in the initial material. However, at the same m/z values with the majority –MA terminated dangling chains, there were no detective signals in the spectra of extractables. This is a clear indication that all the –MA terminated dangling chains have been bonded to the networks. The non-bonded dangling chains could originate from the low amount of –OH terminated dangling chains. Besides, the repeating peaks generally appeared at lower m/z values when compared with the initial dangling chains. This also indicates another possible source for the PCL signals, the bond cleavage during sonication or the degradation by hydrolysis at the ester bond in the PCL blocks, which could generate a –OH terminal group. In summary, the presence of dangling chains in the extractables is attributed to a low amount of –OH terminated dangling chains in the initial materials or the hydrolysis at ester bonds.

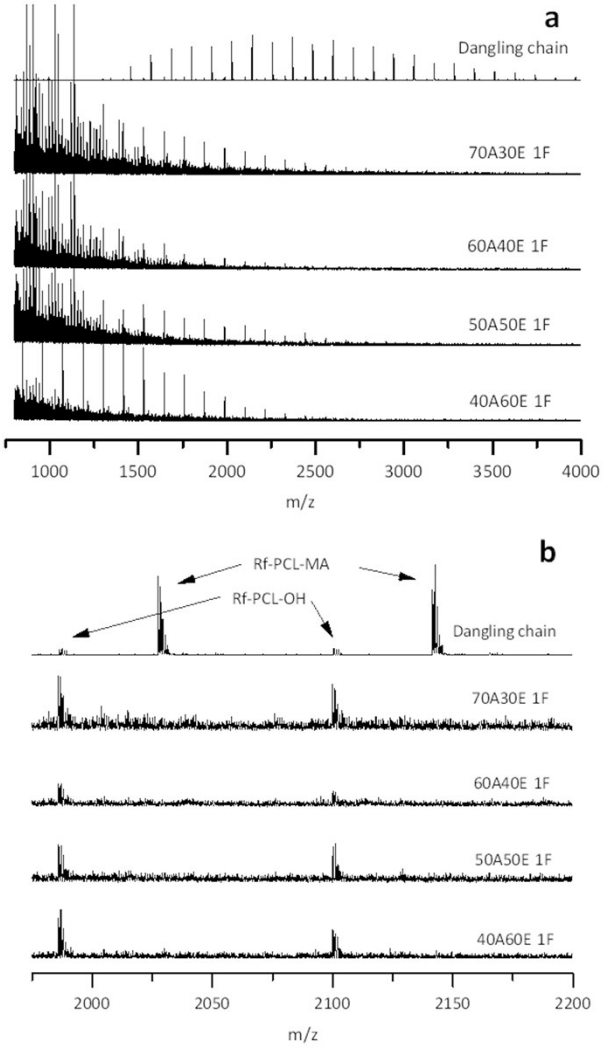

Figure S1. A) The repeating peaks of PCL blocks can be recognized in the Maldi-ToF spectra of extractables for all the LED-cured films. The spectrum of the initial dangling chain is added for a comparison purpose. B) when zooming in A), the repeating peaks in the extractables indicate all the extracted dangling chains are –OH terminated, instead of –MA terminated.

Additional AFM images

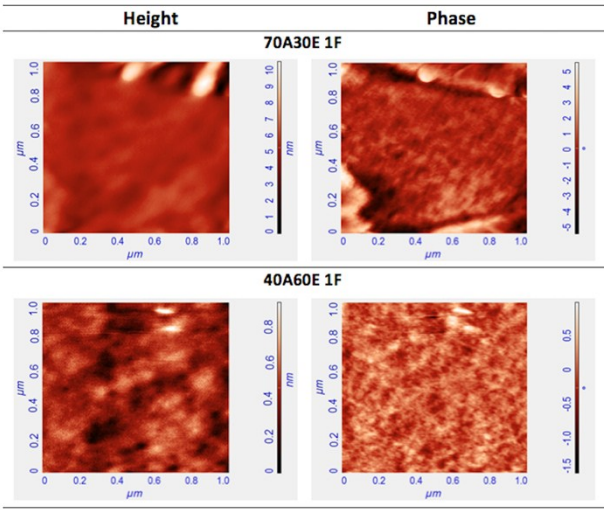

Figure S2. AFM height and phase images (1×1 µm^2) of crystals-free areas for 70A30E 1 F and 40A60E 1 F coatings.

Crystallinity investigations

Differential scanning calorimetry (DSC Q200, TA instruments) was used to investigate the crystallinity of LED-cured films under nitrogen atmosphere (50 mL/min), using samples of about 6 mg in aluminum hermetic pans, heated at 10 °C.min^{-1}. Wide Angle X-Ray Diffraction (WAXD, Rigaku, with Cu-Kα radiation (λ=0.154nm)) was performed on the films within the scanning range 2θ from 10° to 30°.

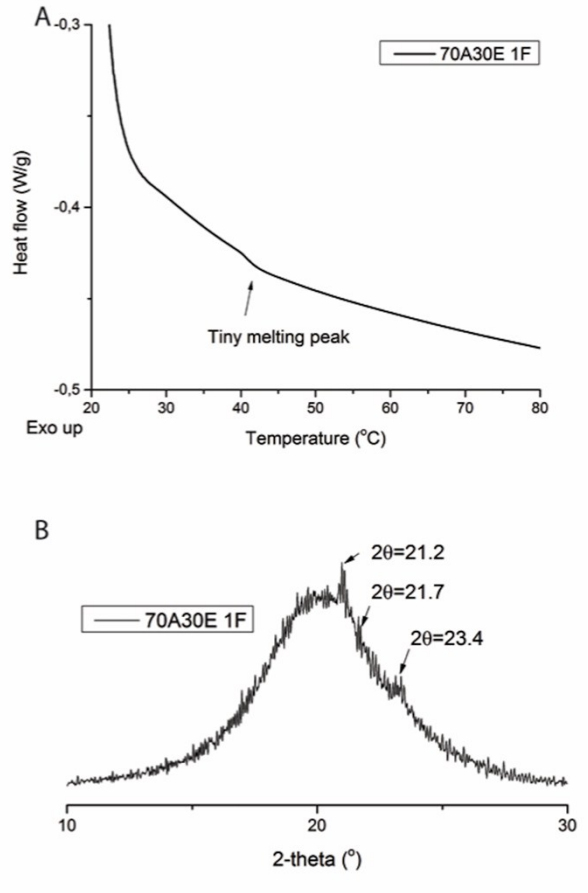

Figure S3: A) DSC thermogram (1st heating run) and B) X-Ray Diffraction (XRD) pattern of 70A30E 1F LED-cured film.

DSC experiments performed on 70A30E 1F LED-cured film showed a tiny melting transition at around 43 °C (Figure S3A). XRD results indicated several diffraction peaks at 2θ=21.2°, 21.7° and 23.4° (Figure S3B). These values are close to the melting temperature and XRD pattern of PCL crystals already reported in the literature for similar experimental conditions.

Additional AFM images

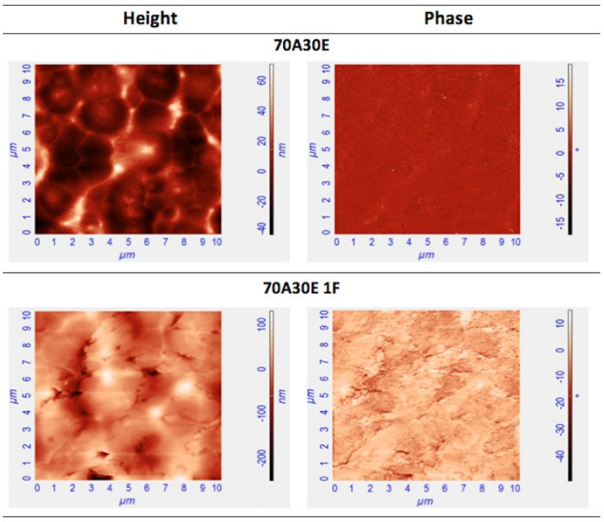

Figure S4. AFM height and phase images (10×10 µm^2) of surface in contact with substrate for 70A30E and 70A30E 1 F coatings.