Vapor phase infiltration of ZnO into thin films of cis-polyisoprene rubber: Supporting Info

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Figure S2: Atomic force microscopy topography images of 5 h pre-heated films (a) before and (b) after infiltration and 24 h pre-heated films (c) before and (d) after infiltration.



Figure S3: Thickness of the resulting ZnO layer after calcination of infiltrated polyisoprene films at 650 °C as a function of DEZ hold time. (a) Films pre-heated for 5 h, and (b) films pre-heated for 24 h prior to infiltration.

Diffusion kinetics

$$=\frac{\frac{M_t}{M_{\infty}}}{=}$$

Normalized slope: $k = \frac{1}{t}$

Diffusivity: $D = \left(\frac{kL}{2}\right)^2 \pi$

<u>0 h annealed</u>

Assumption: L= 80 nm

Infiltration temperature / °C	k	D / 10 ⁻¹⁴ cm ² /s	
60 °C	Not yet saturated		
80 °C	0.01	0.5	
100 °C	0.025	3	

<u>5 h annealed</u>

Assumption: L=70 nm

Two diffusion regimes

Infiltration temperature / °C	k ₁	D ₁ / 10 ⁻¹⁴ cm ² /s	k ₂	D ₂ / 10 ⁻¹⁴ cm ² /s
60 °C	0.06	14	0.012	0.55
80 °C	0.07	19	0.018	1.25
100 °C	0.12	55	0.011	0.5

24 annealed

Assumption: L=50 nm

Infiltration temperature / °C	k	D / 10 ⁻¹⁴ cm ² /s
All temperatures	0.025	1.1



Figure S4: Thickness of the resulting ZnO layer after calcination of infiltrated polyisoprene films at 650 °C as a function of purge after DEZ exposure. Films were pre-heated for 5 h prior to infiltration.

High-resolution XPS spectra of oxygen and carbon

Figure S5 shows high resolution XPS scans of O1s and C1s for uninfiltrated and infiltrated films pre-heated for 5 h. Upon infiltration, the oxygen peak (Figure S5 (a)) shifts to lower binding energy, which indicates an increased contribution from metal oxides (i.e. Zn-OH, cf. ref. 35 in manuscript). The carbon peak (Figure S5 (b)) slightly shifts to lower energy and contributions from C-O and C=O at the high binding energy side of the carbon peak appear to be decreased, which supports the conclusions drawn from FTIR (Figure 6) that these groups get consumed in the infiltration.



Figure S5: XPS high resolution spectra of (a) O1s, and (b) C1s of films pre-heated for 5 h before and after infiltration. Uninfiltrated films were sputtered for 10 s (500 eV ion energy) and infiltrated films were sputtered for 60 s (3000 eV ion energy). Spectra are shifted vertically for clarity.



Figure S6: ATR-FTIR spectra of polyisoprene films after infiltration, for polyisoprene films pre-heated at 80 °C in air for different durations (indicated the curves) prior to infiltration. Colored regions refer to O-H stretching (~3400 cm⁻¹), =C-H stretching (~3036 cm⁻¹), CH₃ and CH₂ stretching (2800-2900 cm⁻¹), C=O stretching (+ and * referring to carboxylic acids (~1766 cm⁻¹) and ketones (~1714 cm⁻¹), respectively), C-O-Zn-R (~1550-1650 cm⁻¹), and CH₂ and CH₃ deformation (1370 – 1450 cm⁻¹). Spectra are scaled to their respective maximum value, offset, and cut to the regions where the main absorptions occur (strong absorption of glass substrate below 1300 cm⁻¹). Dotted lines at the axis break serve as a guide for the eye.