Supplementary Information

Suspension electrospinning of SBR latex combined with photo-induced crosslinking: control of nanofiber composition, morphology and properties

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SBR/PEO electrospinning

Initially, in order to assess the feasibility of the latex electrospinning process to produce rubber fibrous membranes, formulations without neither photoinitiator nor crosslinker was investigated. The electrospinning of SBR/PEO suspensions (without any irradiation) resulted in successful fabrication of uniform and continuous fibers. SBR/30PEO mat showed an average fiber diameter of ≈820 nm and a diameter distribution in the range 670–1000 nm (Figure S2a). It is important to notice that the SBR/PEO fibers did not display any trace of latex particles in their structure, being quite smooth, thus suggesting that the rubber particles were completely embedded in the template polymer or they had coalesced during the electrospinning process.

FTIR spectroscopy was performed on the SBR/30PEO fibrous mats to study their chemical composition: Figure S2b shows the spectrum of SBR/30PEO electrospun fibers, compared with those of a SBR and a PEO cast flat film. The characteristic absorption peaks of SBR are: CH groups in the aromatic ring (styrene) at 699cm^{-1}, out-of-plane vibrations of the CH groups near the double bond of the butadiene vinyl group at 910 cm^{-1}, out-of-plane (wagging) vibrations of the CH groups near the double bond in *trans*-butadiene units at 962 cm^{-1}, stretching vibrations in *cis*-butadiene units ν(C-C) at 1029 cm^{-1}, vinyl-butadiene δ(CH) in CH_2=CH- at 1451 cm^{-1}, stretching vibrations of the C atoms in the aromatic ring at 1601 cm^{-1}. The characteristic absorption peaks of PEO are: -CH_2-CO rocking/stretching group at 843 cm^{-1} and C-O-C group at 1104 cm^{-1}. In the FTIR spectrum of the electrospun SBR/PEO fibers, the peaks around 699 cm^{-1} and 1601 cm^{-1}, due to the aromatic rings of SBR, and the peaks around 843 cm^{-1} and 1104 cm^{-1}, associated to the ether groups in PEO, were detected, thus confirming the presence of both SBR and PEO constitutes in the fibrous membranes. Therefore, the green electrospinning process allowed the successful formation of nanofibrous membranes composed of both SBR and PEO starting from a rubber latex.

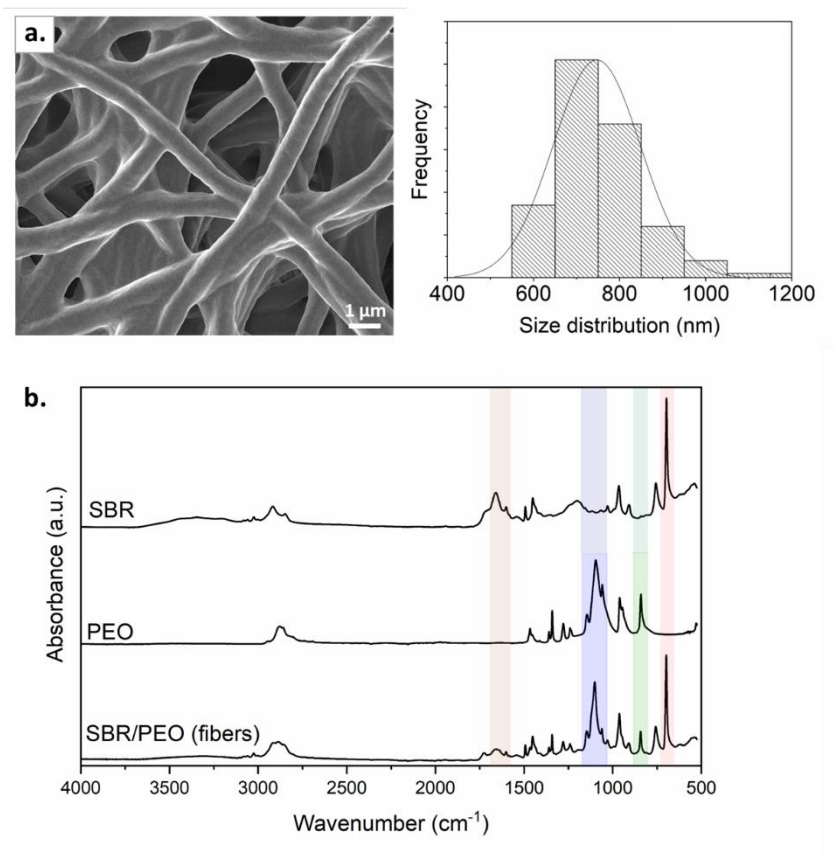

Fig. S1. SBR/30PEO electrospun membranes. FE-SEM image and fiber diameter distribution analysis (a), and ATR FTIR spectra of SBR/PEO electrospun fibers, SBR cast film, and PEO cast film (b).

Photo-crosslinking process

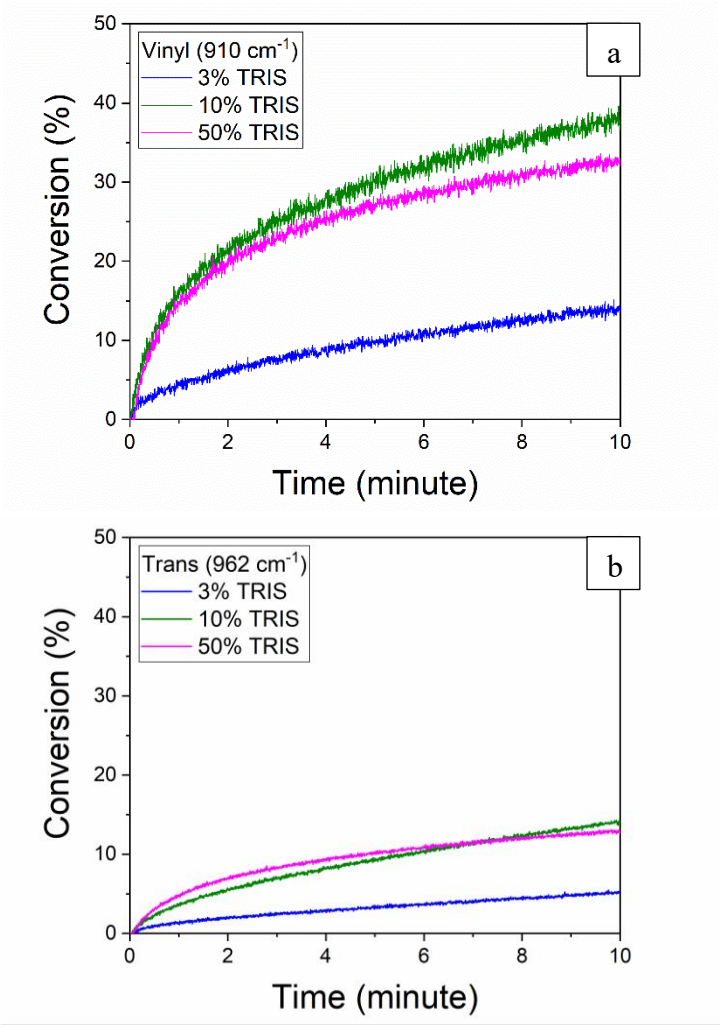

Fig. S2. C=C conversion as a function of UV irradiation time by real-time FTIR spectroscopy for SBR/30PEO/3TRIS, SBR/30PEO/10TRIS and SBR/30PEO/50TRIS electrospun mats: vinyl conversion, evaluated by analyzing the decrease of the peak centered at 910 cm^{-1} (a), and conversion of the backbone 2-butene C=C bonds, evaluated by following the decrease of the peak centered at 962 cm^{-1} (b).

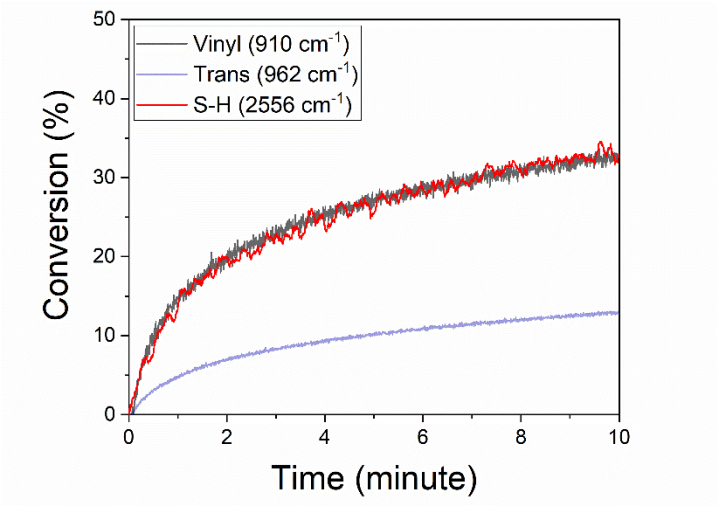

Fig. S3. Vinyl C=C, 2-butene C=C, and thiol SH conversion as a function of UV irradiation by real-time FTIR spectroscopy for SBR/30PEO/50TRIS electrospun mat.

Morphology of electrospun photo-cured membranes

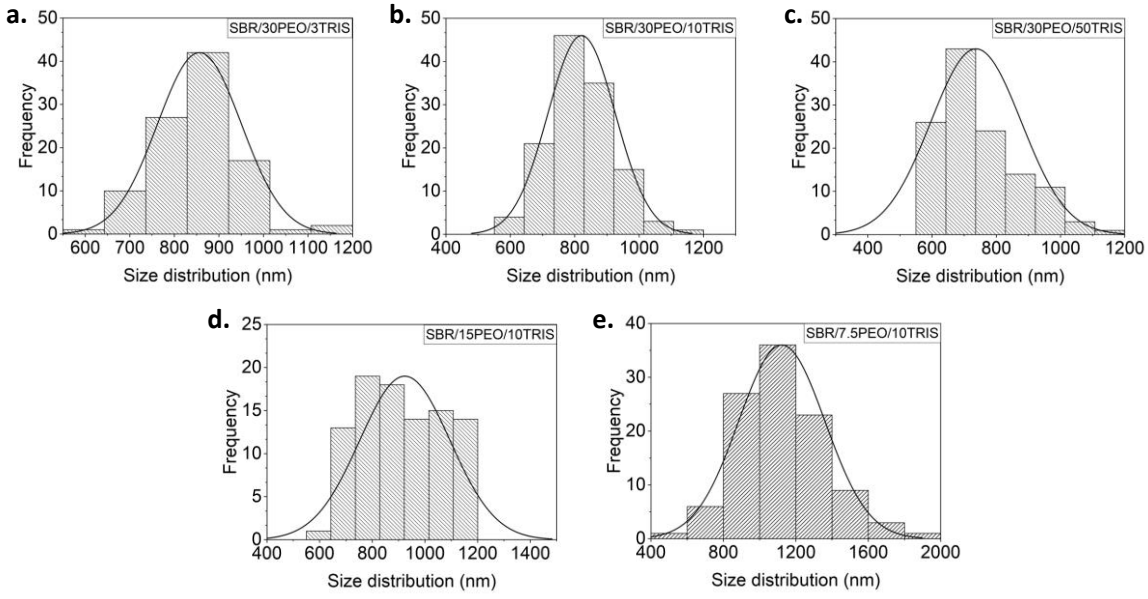

Fig. S4. Fiber diameter distribution of the photo-crosslinked electrospun membranes fabricated from SBR/PEO/TRIS aqueous suspensions: SBR/30PEO/3TRIS (a), SBR/30PEO/10TRIS (b), SBR/30PEO/50TRIS (c), SBR/15PEO/10TRIS (d), and SBR/7.5PEO/10TRIS (e).

Characterization of the photo-crosslinked SBR electrospun membranes after PEO removal

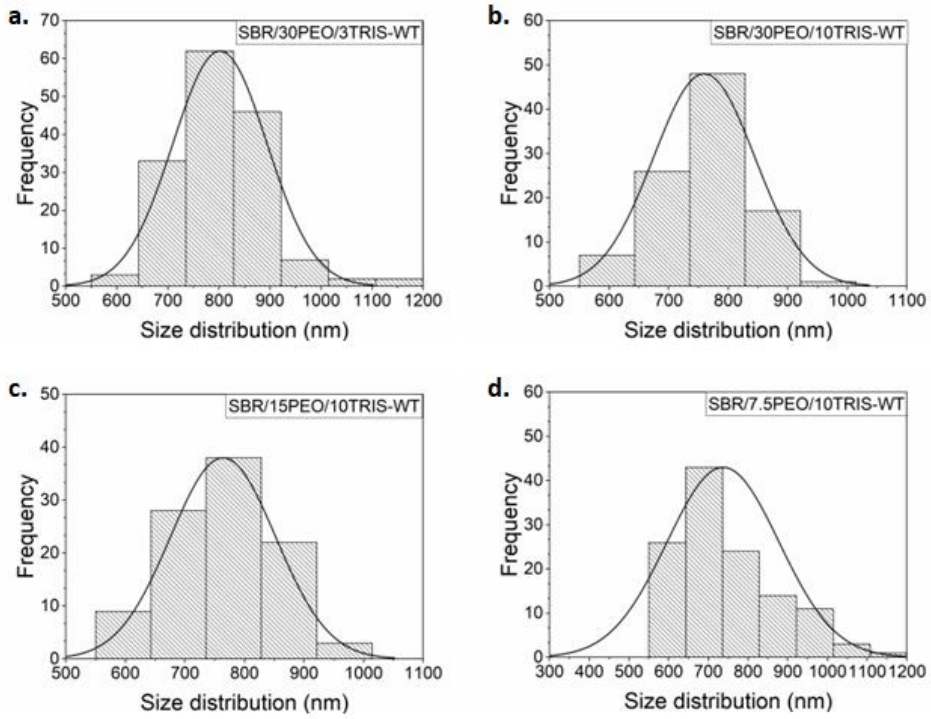

Fig. S5. Fiber diameter distribution of the photo-crosslinked electrospun membranes after water treatment (WT) for PEO removal: SBR/30PEO/3TRIS-WT (a), SBR/30PEO/10TRIS-WT (b), SBR/15PEO/10TRIS-WT (c), and SBR/7.5PEO/10TRIS-WT (d).

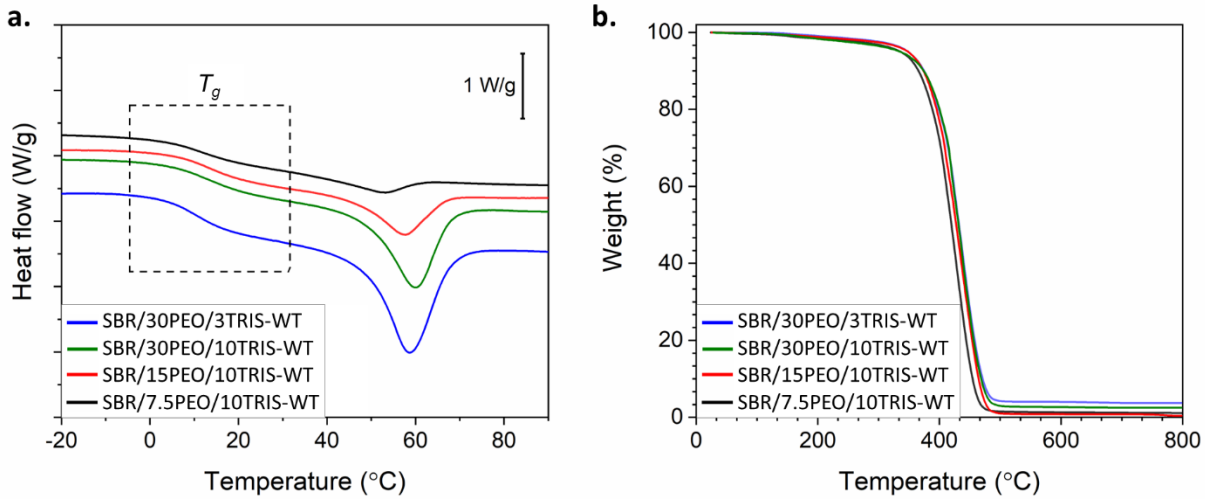

Fig. S6. Thermal analyses of the photo-crosslinked SBR electrospun membranes after water treatment (WT) for PEO removal: DSC scans of the second heating cycle (a) and TGA thermograms (b).

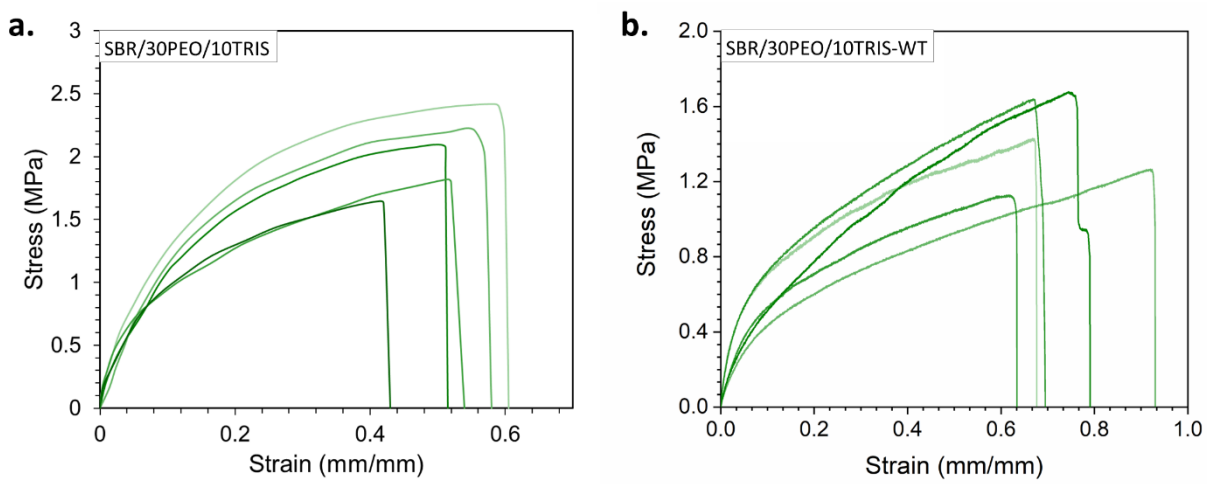

Fig. S7. Tensile stress-strain curves of SBR/30PEO/10TRIS photo-crosslinked electrospun membranes prior (a) and after (b) water treatment (WT) for PEO removal: DMTA results (a), and an example.