-Supporting Information-

Ultra-stretchable Ionic Nanocomposites: From Dynamic Bonding to Multi-Responsive Behavior

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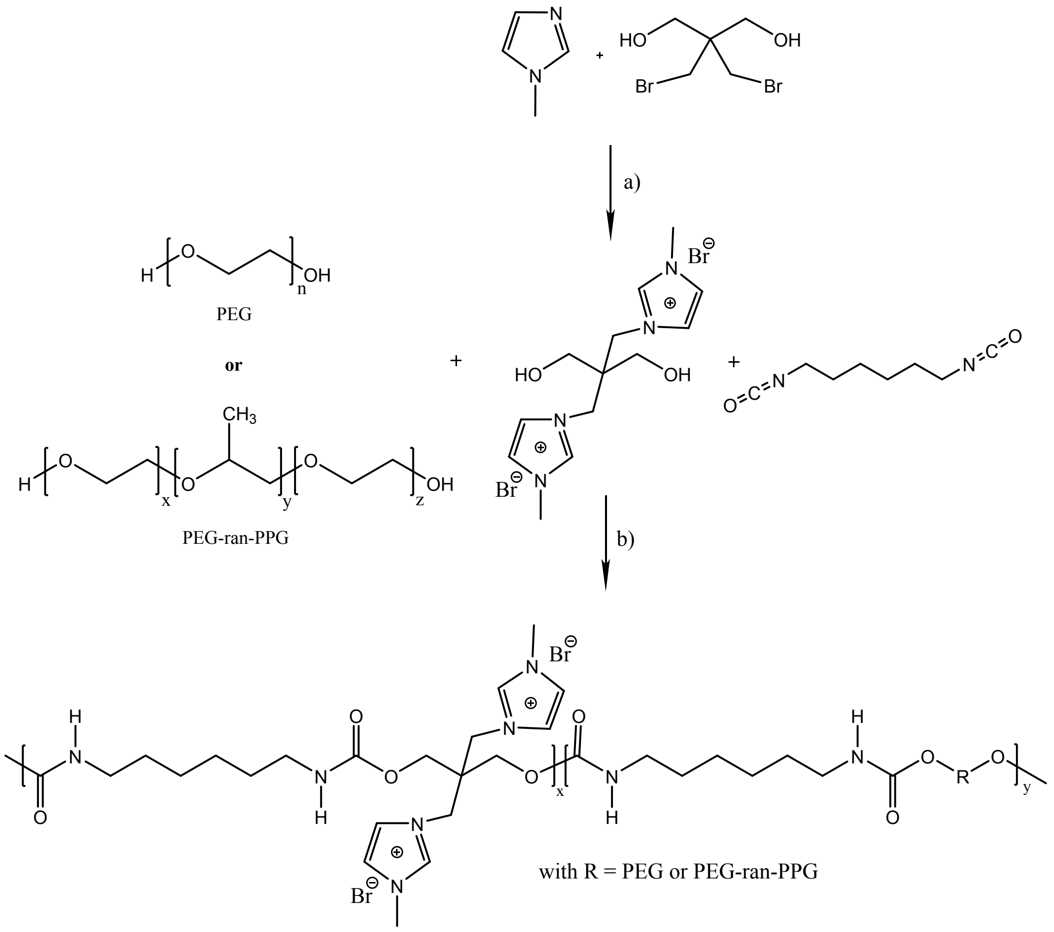

Fig. S1 a) Synthesis of imidazolium-based diol from methyl-imidazole and BBPDO; and b) Synthesis reactions for imidazolium-functionalized polyurethane synthesized from polyethylene glycol-based (PEG or PEG-*ran*-PPG) oligomer with the as-produced imidazolium and HMDI.

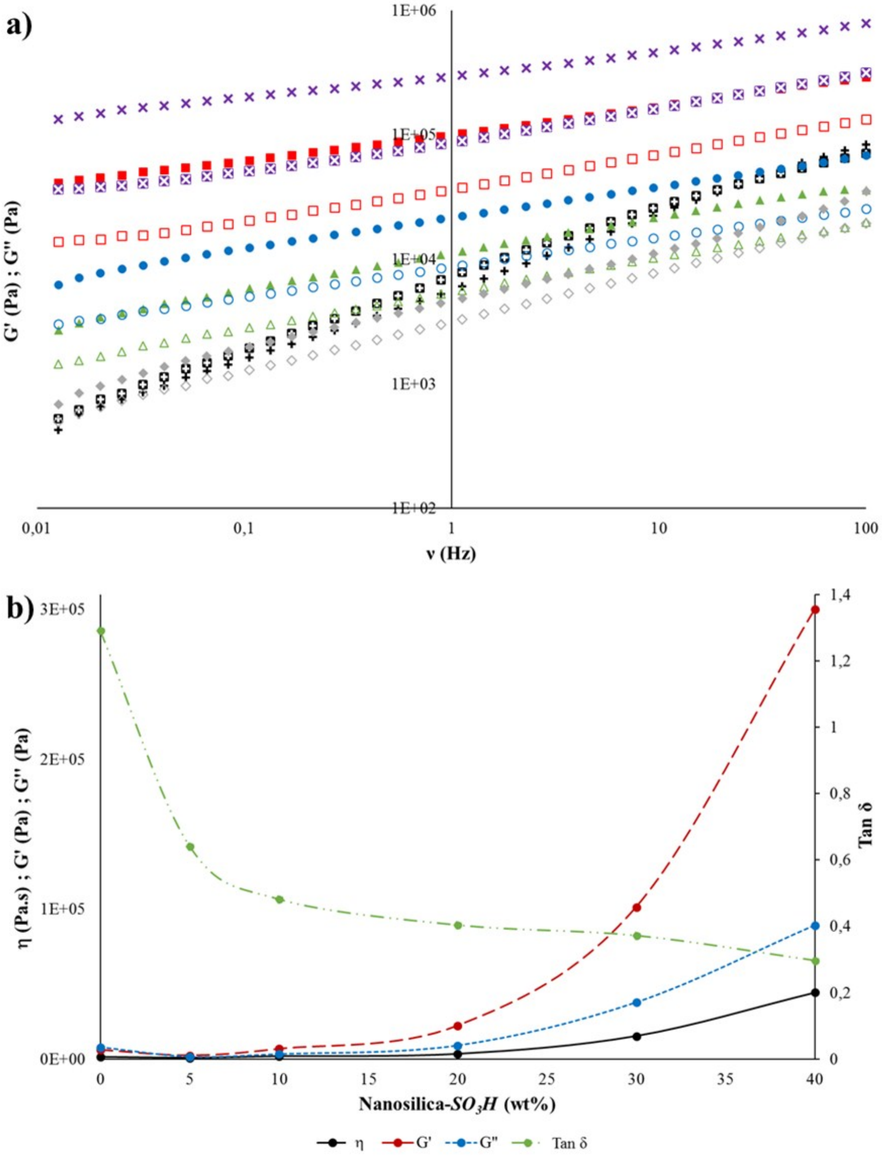

Fig. S2 (a) Storage G’ (full dots) and loss G” (open dots) modulus as a function of frequency ν, of neat polymer (black, plus signs) and nanocomposites containing 5 wt% (grey, diamonds), 10 wt% (green, triangles), 20 wt% (blue, circles), 30 wt% (red, squares) and 40 wt% (purple, crosses) of silica nanoparticles ; (b) Complex viscosity η (solid black line), storage modulus G’ (long dash red line), loss modulus G” (short dash blue line) and tangent delta Tanδ (broken dash green line) at frequency ν of 1 Hz (similar behavior at other frequencies) of nanocomposites as a function of nanosilica content.

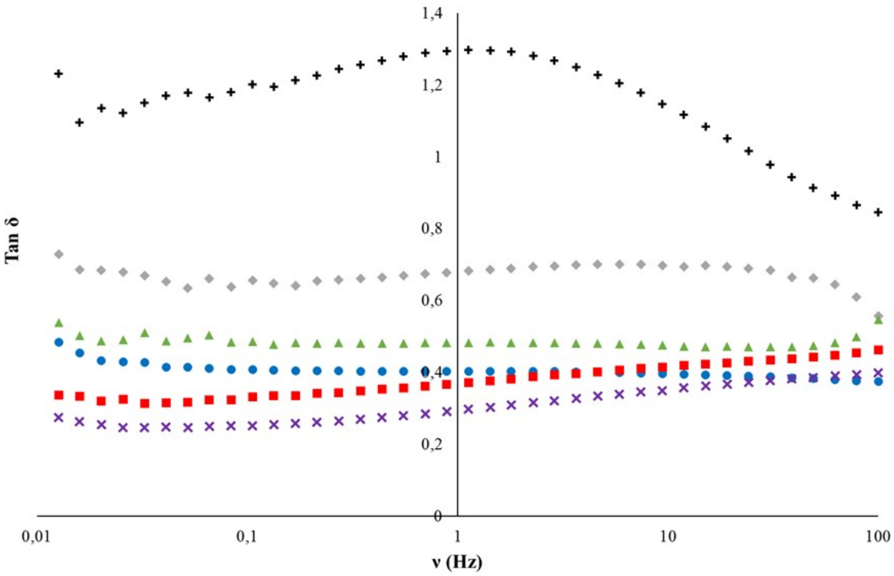

Fig. S3. Tangent delta Tan δ as a function of frequency ν, of neat polymer (black, plus signs) and nanocomposites containing 5 wt% (grey, diamonds), 10 wt% (green, triangles), 20 wt% (blue, circles), 30 wt% (red, squares) and 40 wt% (purple, crosses) of silica nanoparticles.

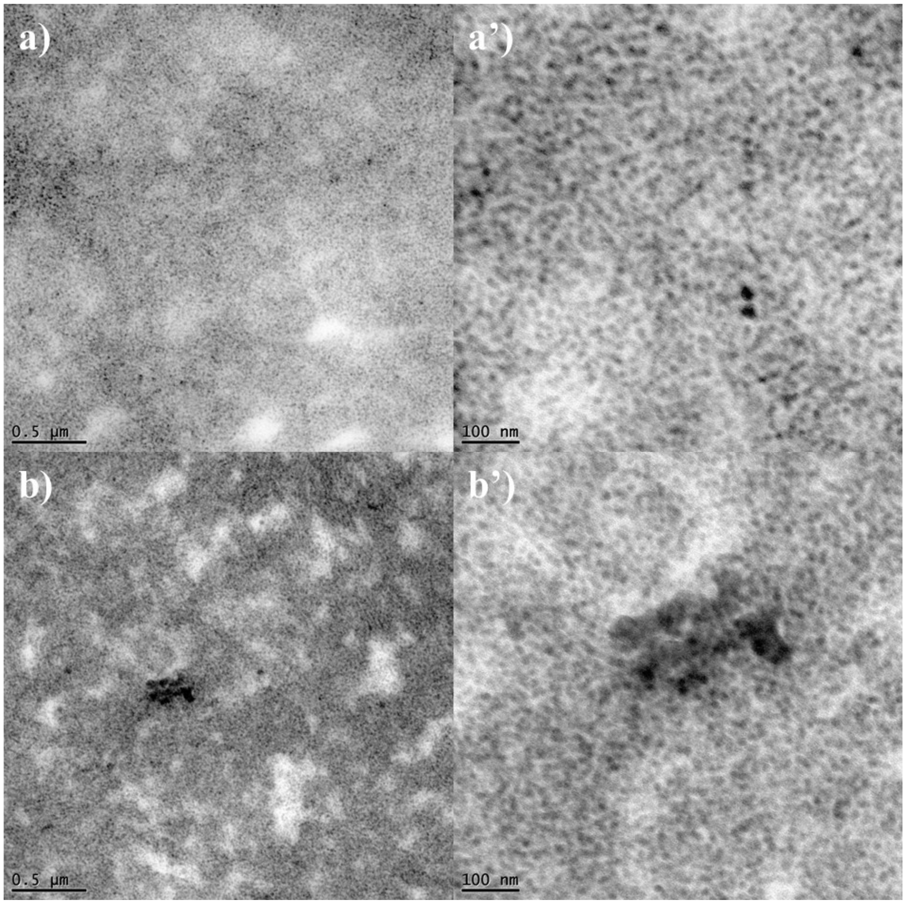

Fig. S4 TEM micrographs of nanocomposites containing 20 wt% (a and a') and 40 wt% (b and b') of silica nanoparticles.

Tab. S1 Tensile characteristics of neat polymer and nanocomposites with different silica nanoparticles loading.

SiO_2-SO_3H content (wt%)	**E (MPa)**	**ε_b (%)**	**TT ($MJ.m^{-3}$)**
0	12 ± 2	44 ± 15	0.3 ± 0.1
5	31 ± 5	129 ± 16	3 ± 0.5
10	30 ± 1	412 ± 28	10 ± 1
20	27 ± 2	463 ± 28	12 ± 1
30	29 ± 5	342 ± 18	8 ± 1
40	24 ± 2	158 ± 11	6 ± 1
20 (-SO_3Na)	25 ± 5	177 ± 19	3 ± 0.5

E: Young's modulus ; ε_b: strain at break ; TT: tensile toughness.

Tab. S2 Tensile characteristics of neat polymer and nanocomposites at different strain rates.

SiO_2-*SO_3H* content (wt%)	**Tensile speed ($mm.min^{-1}$)**	**E (MPa)**	**ε_b (%)**	**TT ($MJ.m^{-3}$)**
0	10	12 ± 2	44 ± 15	0.3 ± 0.1
0	100	20 ± 5	30 ± 5	0.3 ± 0.1
0	1000	19 ± 2	27 ± 3	0.3 ± 0.1
20	10	27 ± 2	463 ± 28	12 ± 1
20	100	25 ± 2	539 ± 21	17 ± 3
20	1000	24 ± 2	558 ± 11	19 ± 1

E: Young's modulus ; ε_b: strain at break ; TT: tensile toughness.

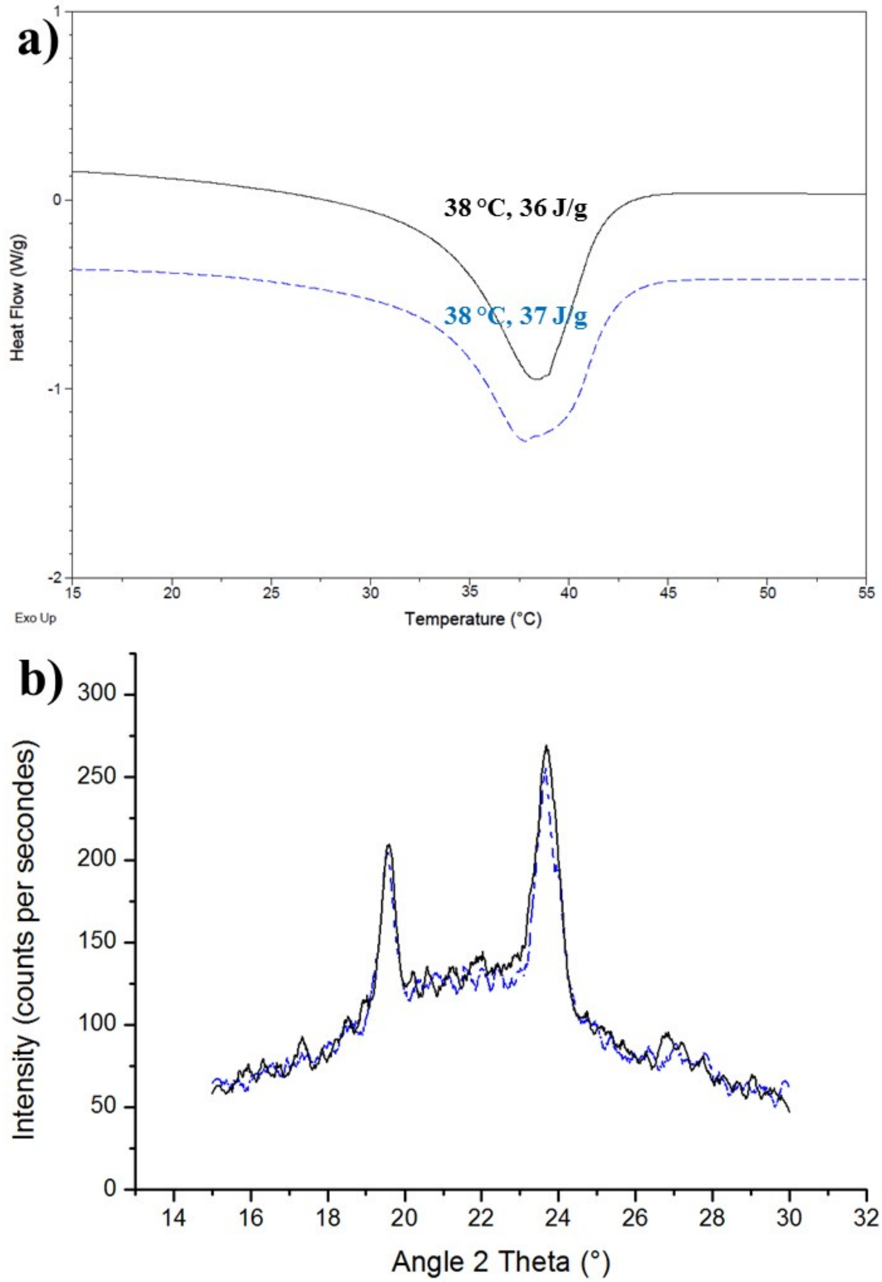

Fig. S5 (a) DSC and (b) XRD patterns of nanocomposites containing 20 wt% of silica nanoparticles stretched at 10 mm/min (solid black line) and 1000 mm.min^{-1} (dash blue line).

Supplementary information about the ionic nanocomposites preparation

1. Synthesis of imidazolium-based diol

1 eq. of BBPDO and 2 eq. of 1-methyl-imidazole were dissolved in dry THF into a glass flask and refluxed at 65 °C for 24h under stirring. After reaction, the imidazolium-based diol was recovered by solvent evaporation under vacuum (yield ≈ 83 %, ^{1}H NMR (DMSO, δ, ppm): 3.4 (4H, s, CH_2OH), 3.73 (6H, s, CH_3), 3.87 (4H, s, -N-CH_2-), 5.14 (2H, s, OH), 7.18 and 7.34 (2H and 2H, s, -N-CHCH-N-), 8.18 (2H, s, -N-CH-N-)).

2. Synthesis of imidazolium-functionalized polyurethanes (im-PEG or im-PEG-ran-PPG)

1 eq. of either semi-crystalline PEG or amorphous PEG-*ran*-PPG and 0.1 eq. of the imidazolium-based diol synthesized above were dissolved in dry DMF in a glass flask. Then, 1.2 eq. of HMDI and catalytic amounts of DBTDL were subsequently added to the solution under stirring. The polymerization was performed at 60 °C for 6h under a nitrogen atmosphere. Finally, the imidazolium-functionalized polyurethane was recovered by precipitation into a 10-fold excess of diethyl-ether, followed by filtration and drying under vacuum (*im*-PEG: yield ≈ 98 %, $M_n \approx$ 27.200 g/mol, Đ ≈ 1.5 ; *im*-PEG-*ran*-PPG: yield ≈ 98 %, $M_n \approx$ 23.000 g/mol, Đ ≈ 1.4 ; ^{1}H NMR (DMSO, δ, ppm): 8.2 (2H, s, -N-CH-N-) confirmed the incorporation of imidazolium moieties into the polyurethane molecules).

3. Sulfonate functionalization of nanosilica

Briefly, Ludox HS 30 colloidal silica (3 g) was diluted in a flask with deionized water (22 ml). In another flask, 3-(trihydroxysilyl)-1-propane sulfonic acid (4 g) was diluted with deionized water (20 ml). The colloidal silica suspension was slowly added to the SIT suspension, while stirring vigorously. To the mixture, a solution of sodium hydroxide (1 M) was added dropwise until a pH of about 5 was reached. The entire solution was then heated to 70 °C and stirred vigorously for

24h. After that, the suspension was cooled to room temperature and placed into dialysis tubing and dialyzed against deionized water for 3 days while changing the water twice a day. After dialysis, the functionalized silica solution was run through an ion exchange column to remove Na^+ ions and fully protonate the surface sulfonate groups. A suspension of sulfonated nanosilica at 5 wt% was prepared with deionized water for further use ($d \approx 17 \pm 5$ nm, $M_{SO3H} \approx 1$ mmol, $R_{organic} \approx 24$ %).

4. *Preparation of ionic nanocomposites*

Semi-crystalline *im*-PEG and amorphous *im*-PEG-*ran*-PPG at 50/50 wt% ratio were dissolved in deionized water to a concentration of 10 wt%. Then, the sulfonated silica suspension (5 wt%) was added to the polymer solution under stirring and stirred for an additional 3h. The resulting solution was sonicated and placed in a vaccum oven for drying until all the water was removed. Thin films of the resulting hybrids were prepared by compression-molding at 60 °C for 3 min. Differential Scanning Calorimetry (DSC) showed a glass transition at *ca.* $T_g = -55$ °C and a melting point at *ca.* T_m □ 40 °C for the neat polymer as well as all nanocomposites indepent of the amount of nanosilica added.