SUPPLEMENTARY INFORMATION

Novel Tough and Transparent Ultra-Extensible Nanocomposite Elastomers Based on poly(2-methoxyethylacrylate) and Their Switching between Plasto-Elasticity and Viscoelasticity

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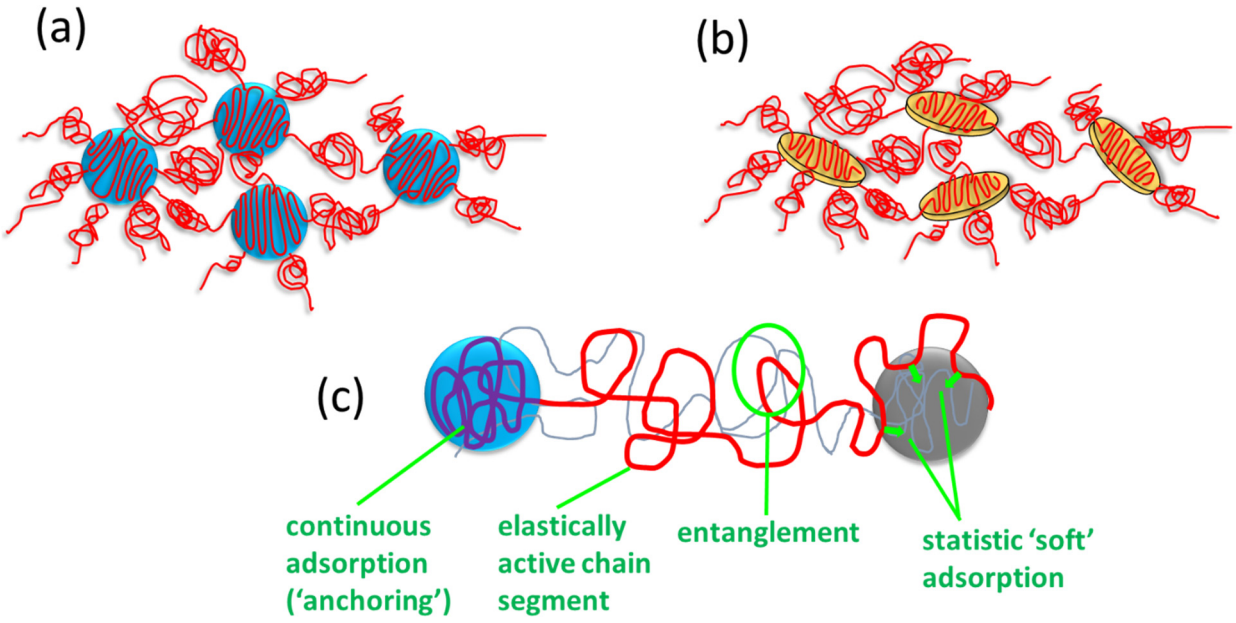
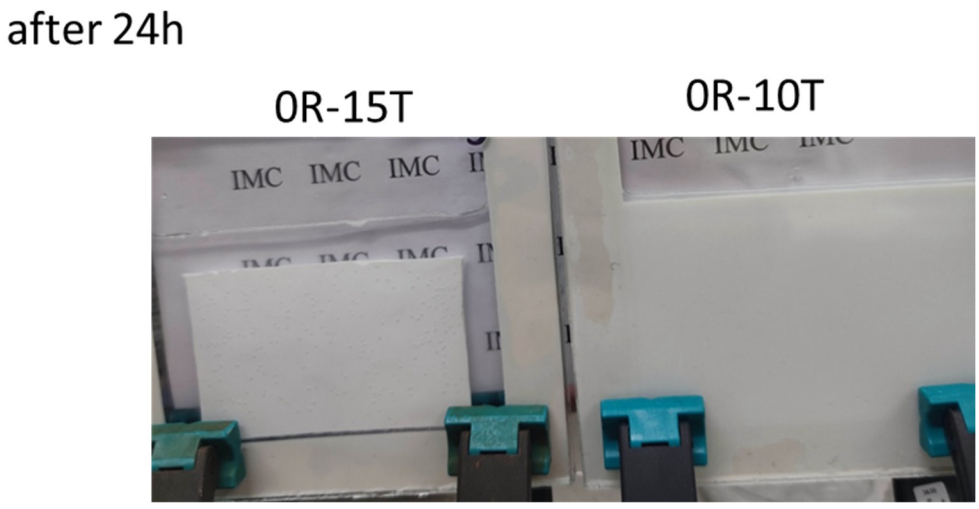
1. Synthesis



SI-Figure S1. *Idealized self-assembly of the nanocomposite elastomeric networks polyMEA/nano-SiO2 (a) and polyMEA/clay (b), based entirely on physical crosslinking.*



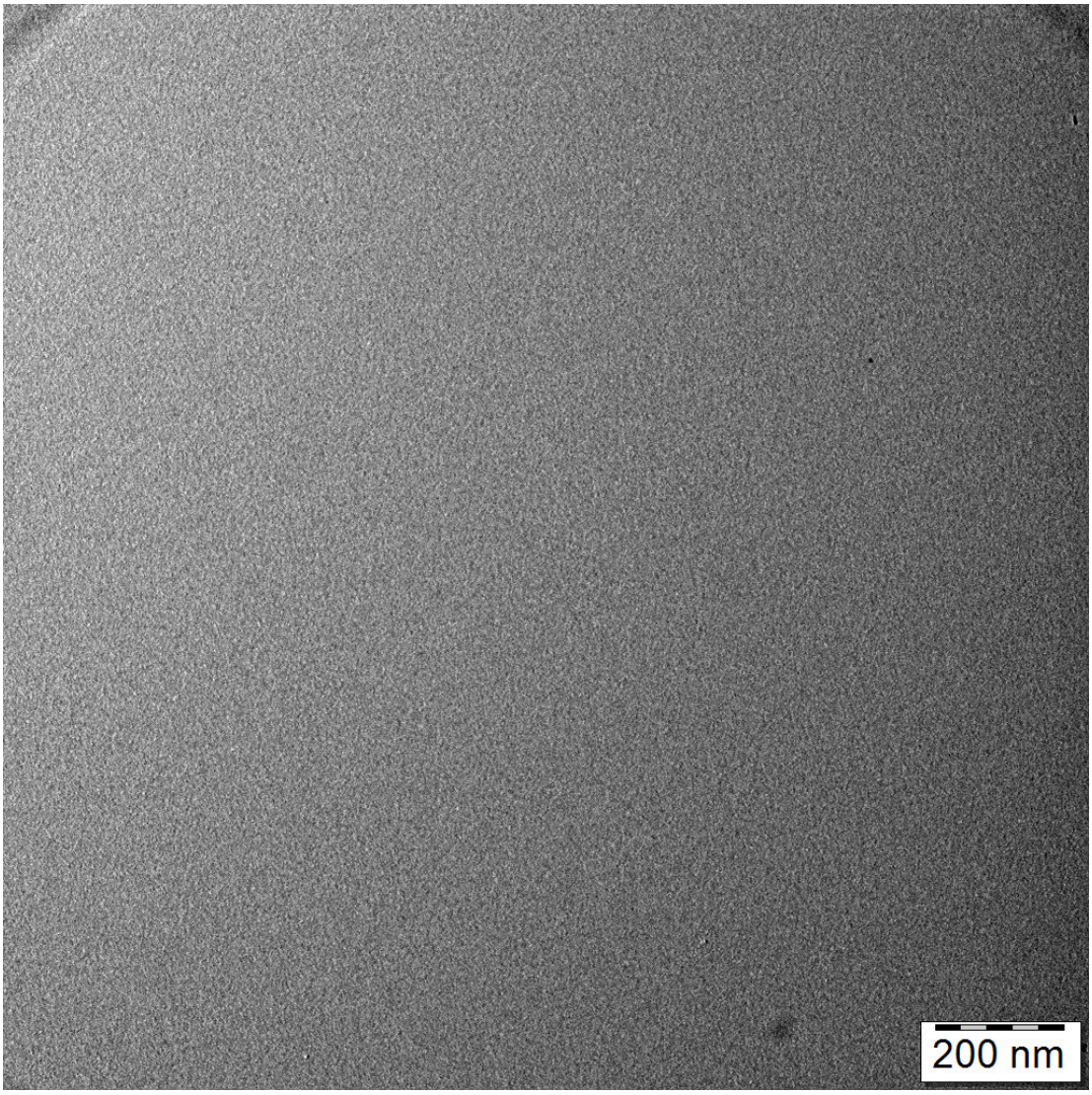
SI- Figure S2. *Comparison of appearance of shrinking synthesis mixture with 15 or more wt.% of in-situ nano-silica (example: 0R-15T, left) with a non-shrinking one (example: 0R-10T, right); appearance after 24 h since the start of the synthesis.*

Morphology: TEM ('as prepared' state): High-resolution images

SI-Figure S2 – multi-page:

neat polyMEA

(a)

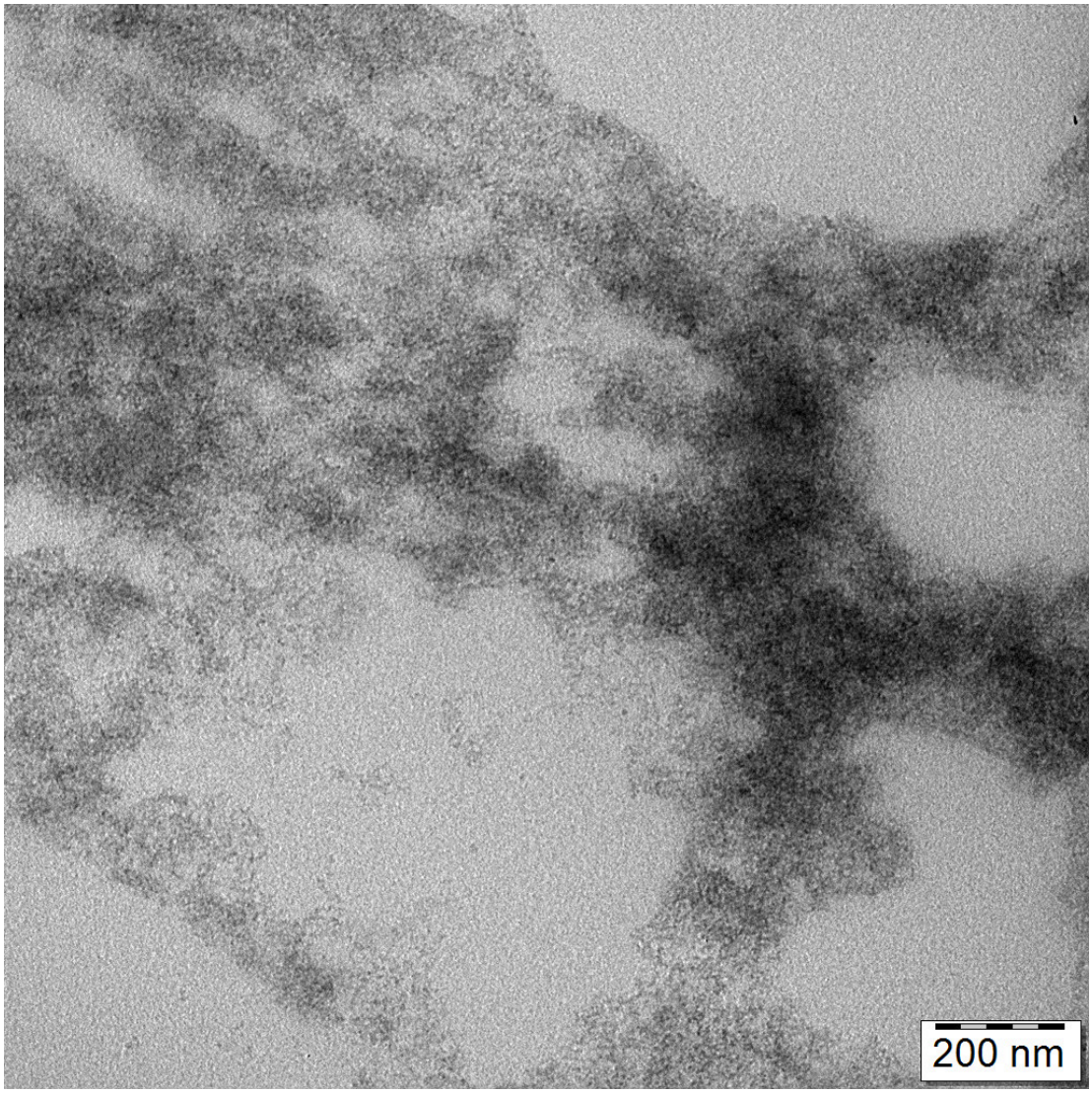


SI-Figure S2 – multi-page: *(a) High-resolution version of the TEM image of neat polyMEA.*

SI-Figure S2 – multi-page (continued):

0R-5T

(b)

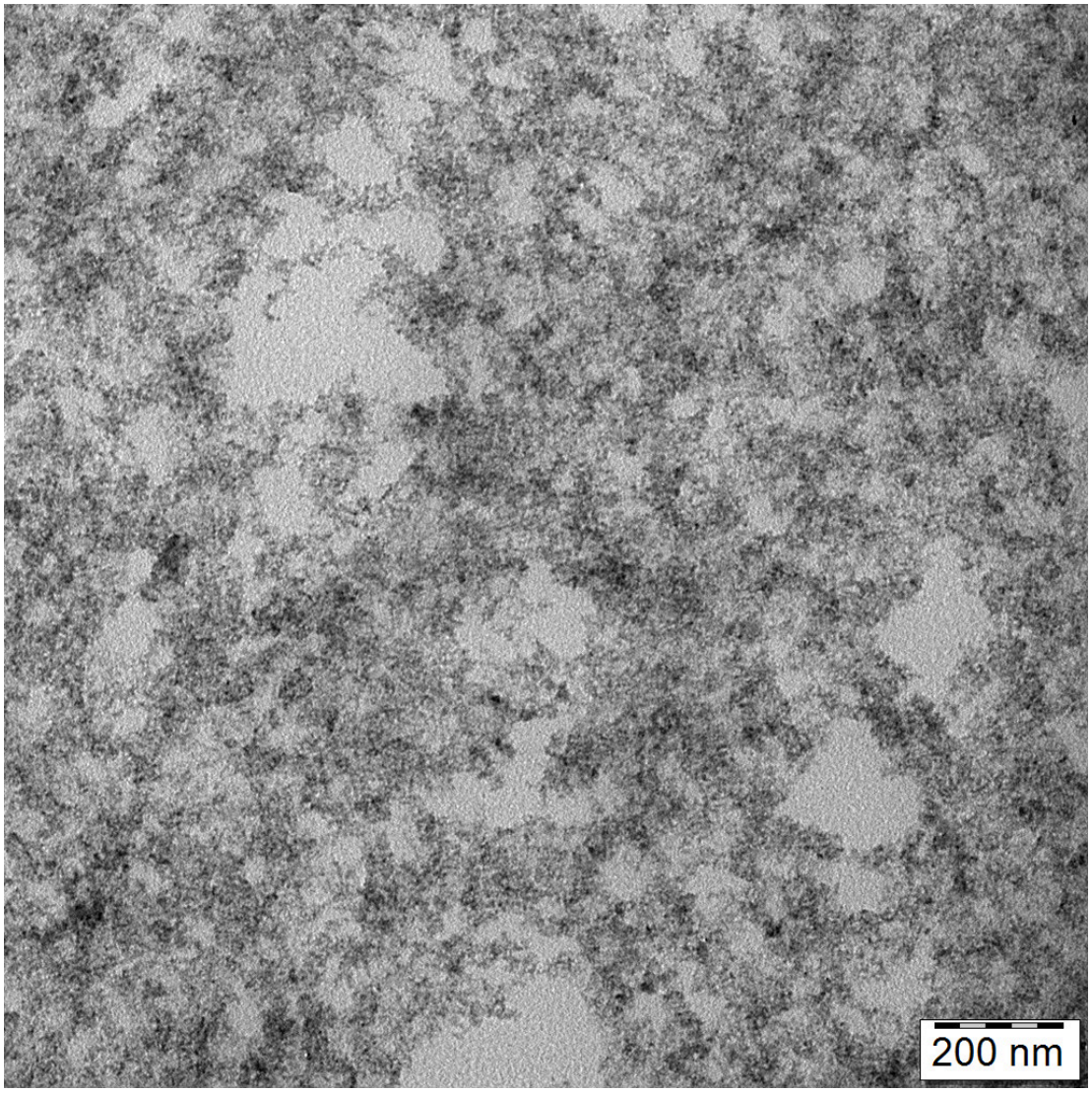


SI-Figure S2 – multi-page (continued): *(b) High-resolution version of the TEM image of 0R-5T.*

SI-Figure S2 – multi-page (continued):

0R-15T

(c)

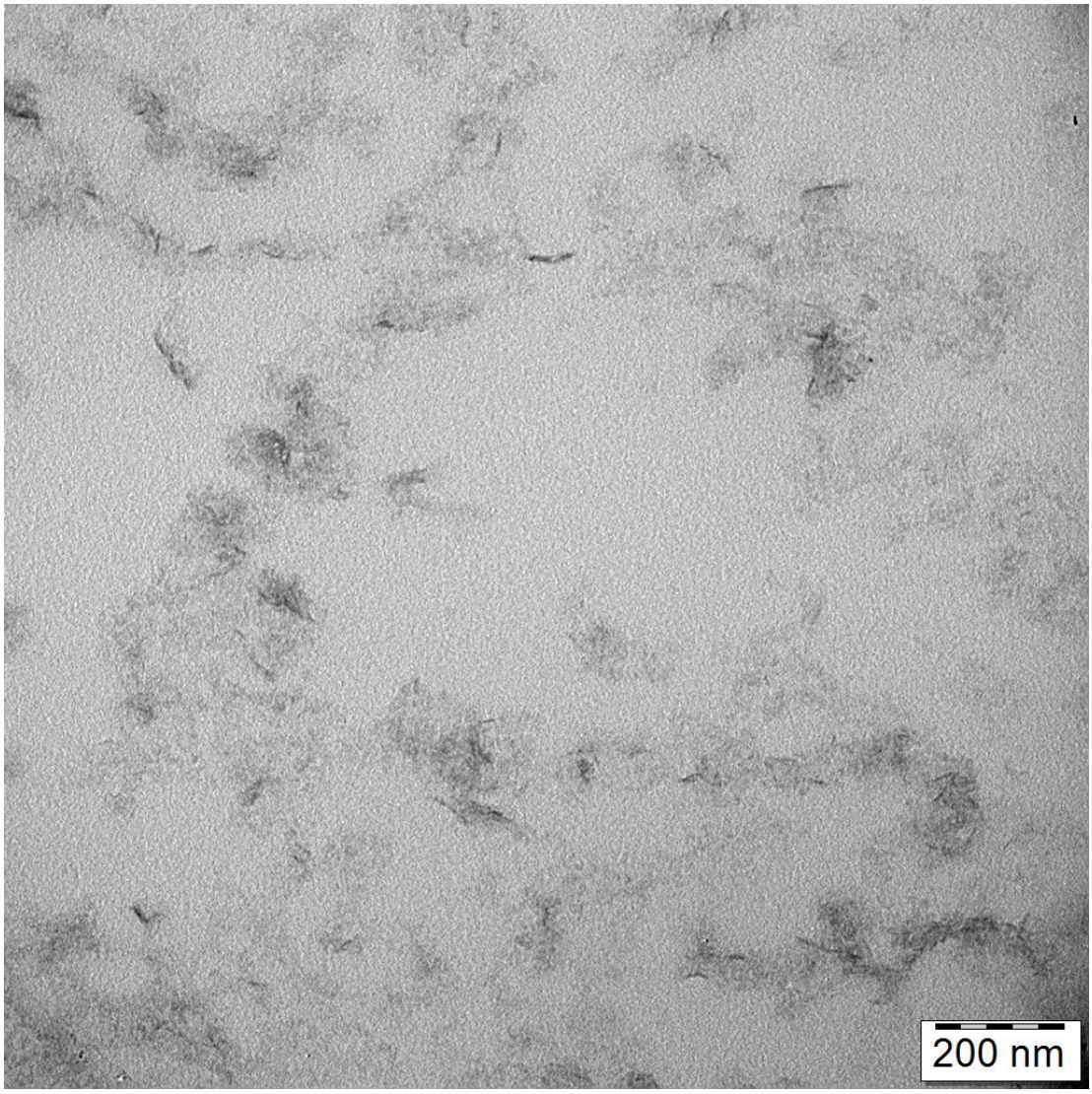


SI-Figure S2 – multi-page (continued): *(c) High-resolution version of the TEM image of 0R-15T.*

SI-Figure S2 – multi-page (continued):

4R-0T

(d)

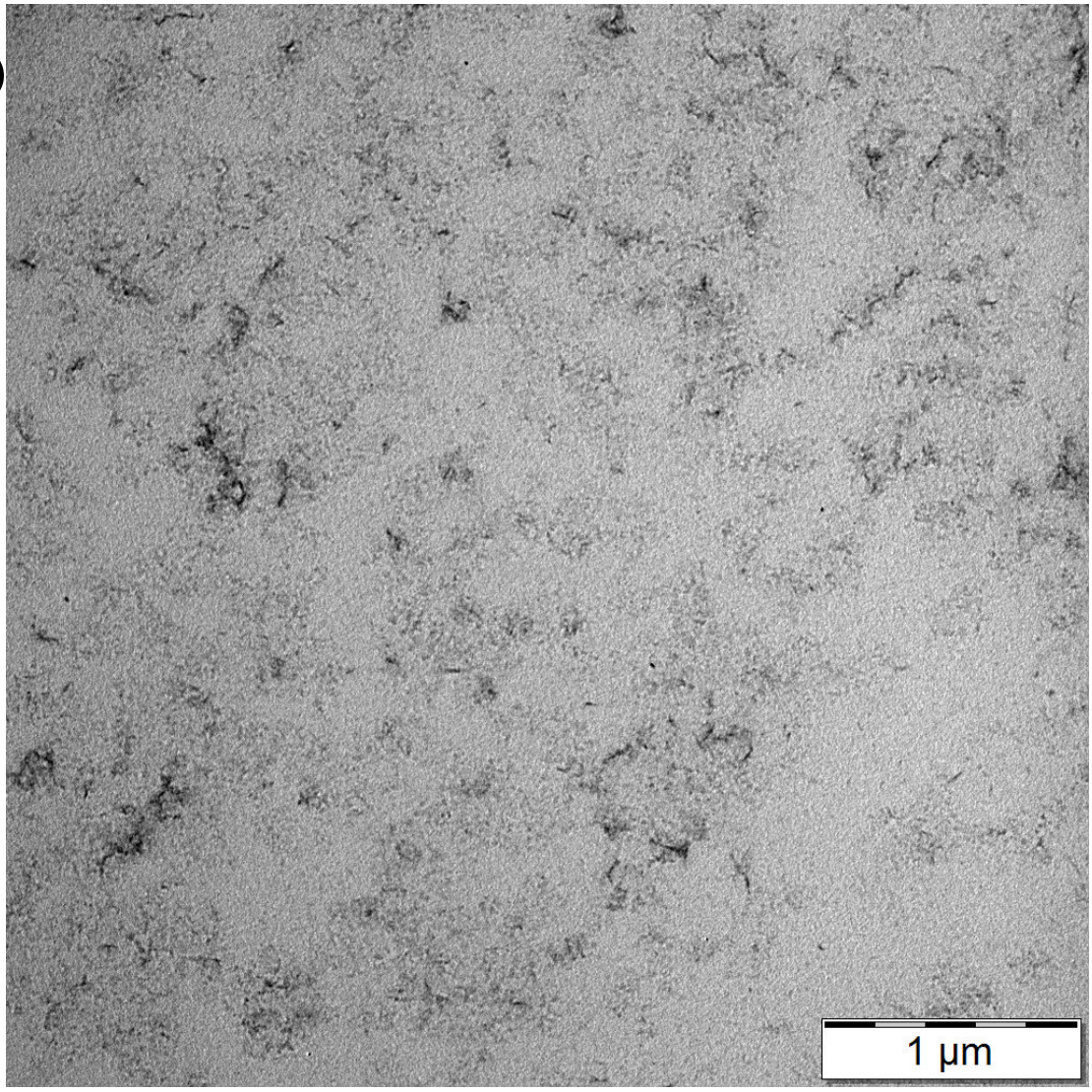


SI-Figure S2 – multi-page (continued): *(d) High-resolution version of the TEM image of 4R-0T.*

SI-Figure S2 – multi-page (continued):

4R-0T, **larger-scale-view**

(d2)

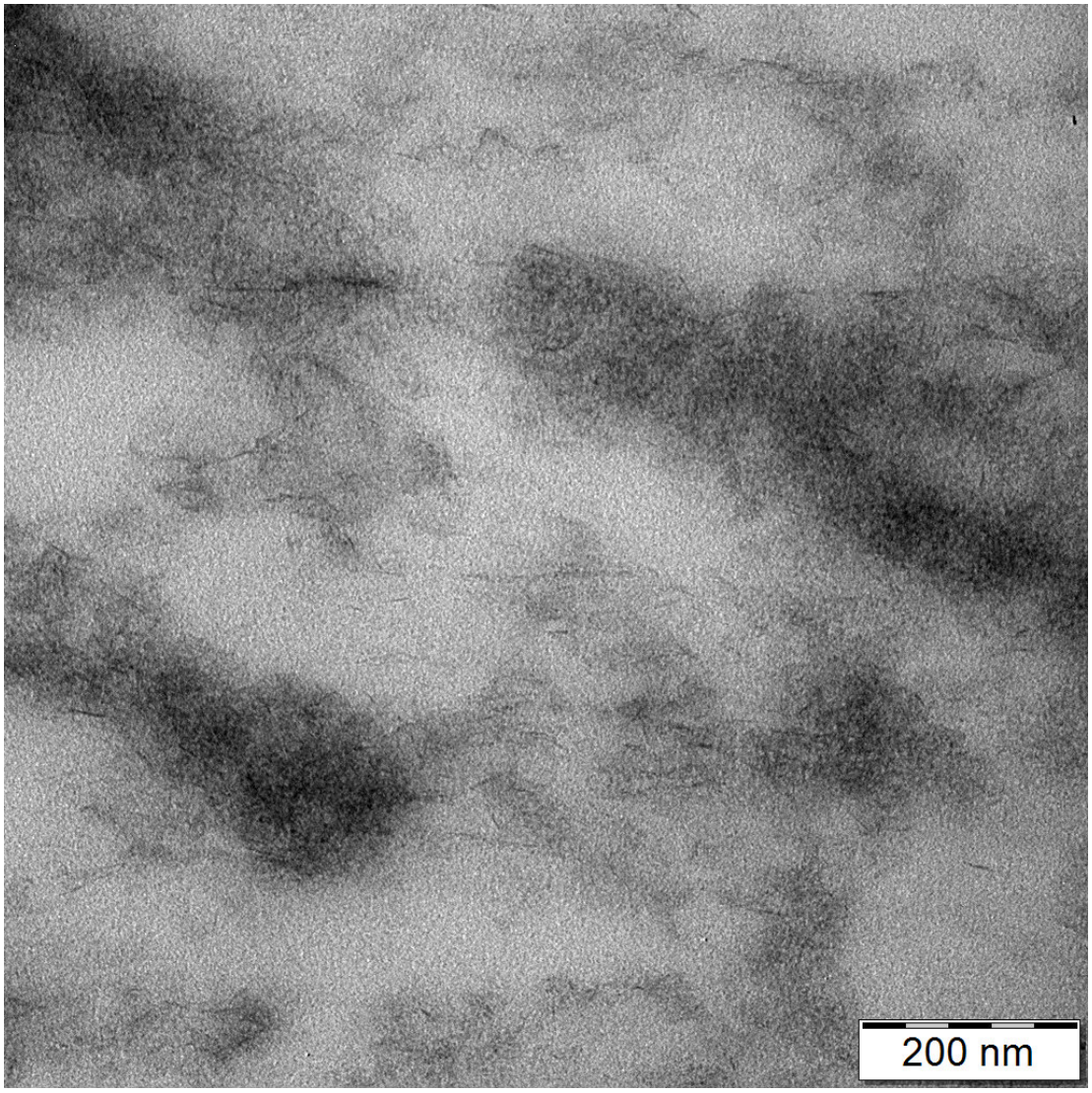


SI-Figure S2 – multi-page (continued): *(d2) TEM: larger-scale-view of 4R-0T.*

SI-Figure S2 – multi-page (continued):

4R-5T

(e)

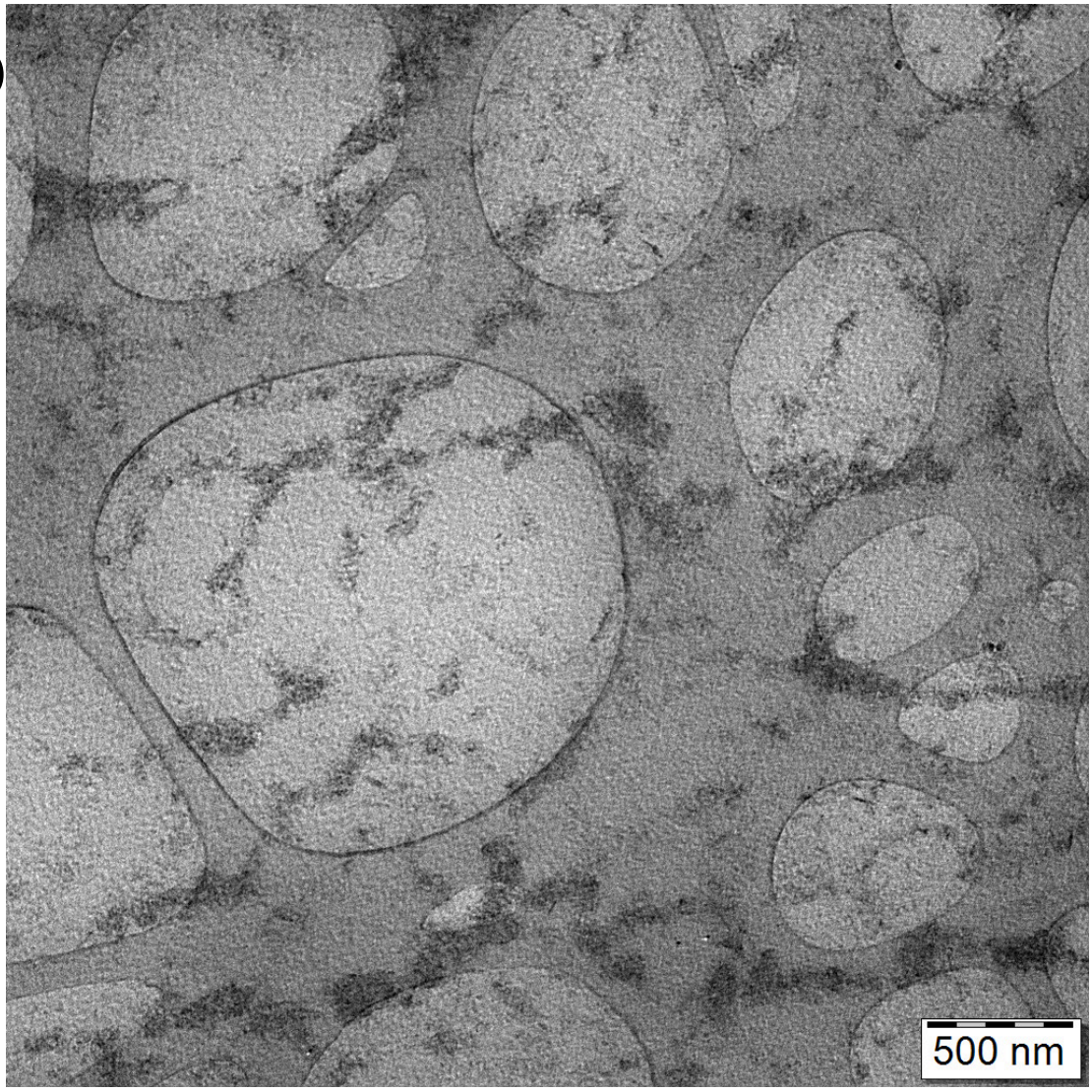


SI-Figure S2 – multi-page (continued): *(e) High-resolution version of the TEM image of 4R-5T.*

SI-Figure S2 – multi-page (continued):

4R-5T, **larger-scale-view**

(e2)

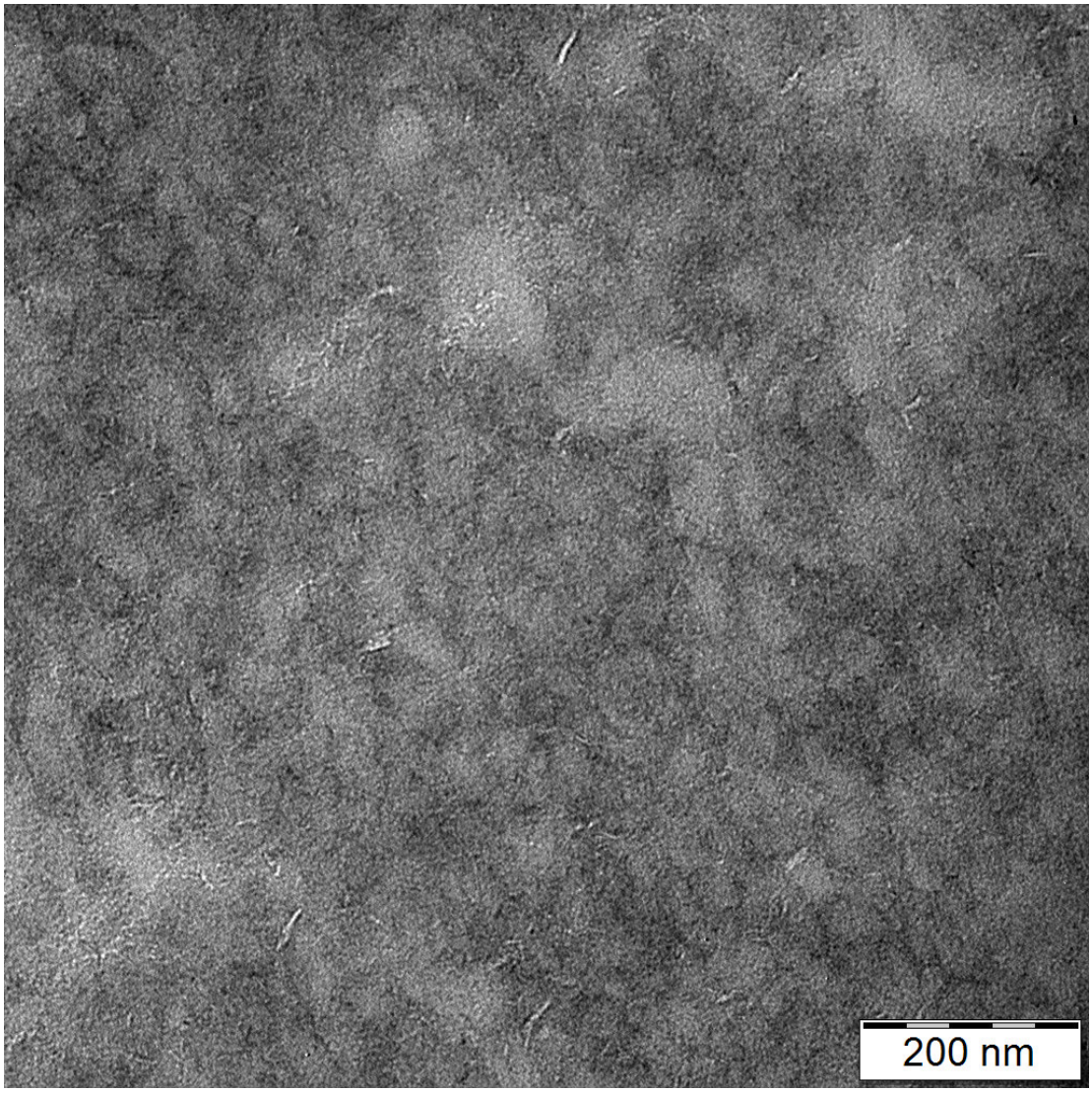


SI-Figure S2 – multi-page (continued): *(e2) TEM: larger-scale-view of 4R-5T; note (!): the visible large 'pores' or 'bubbles' are not related to the sample itself: this are pores in the graphite substrate which was used to support the observed specimen.*

SI-Figure S2 – multi-page (continued):

4R-15T

(f)

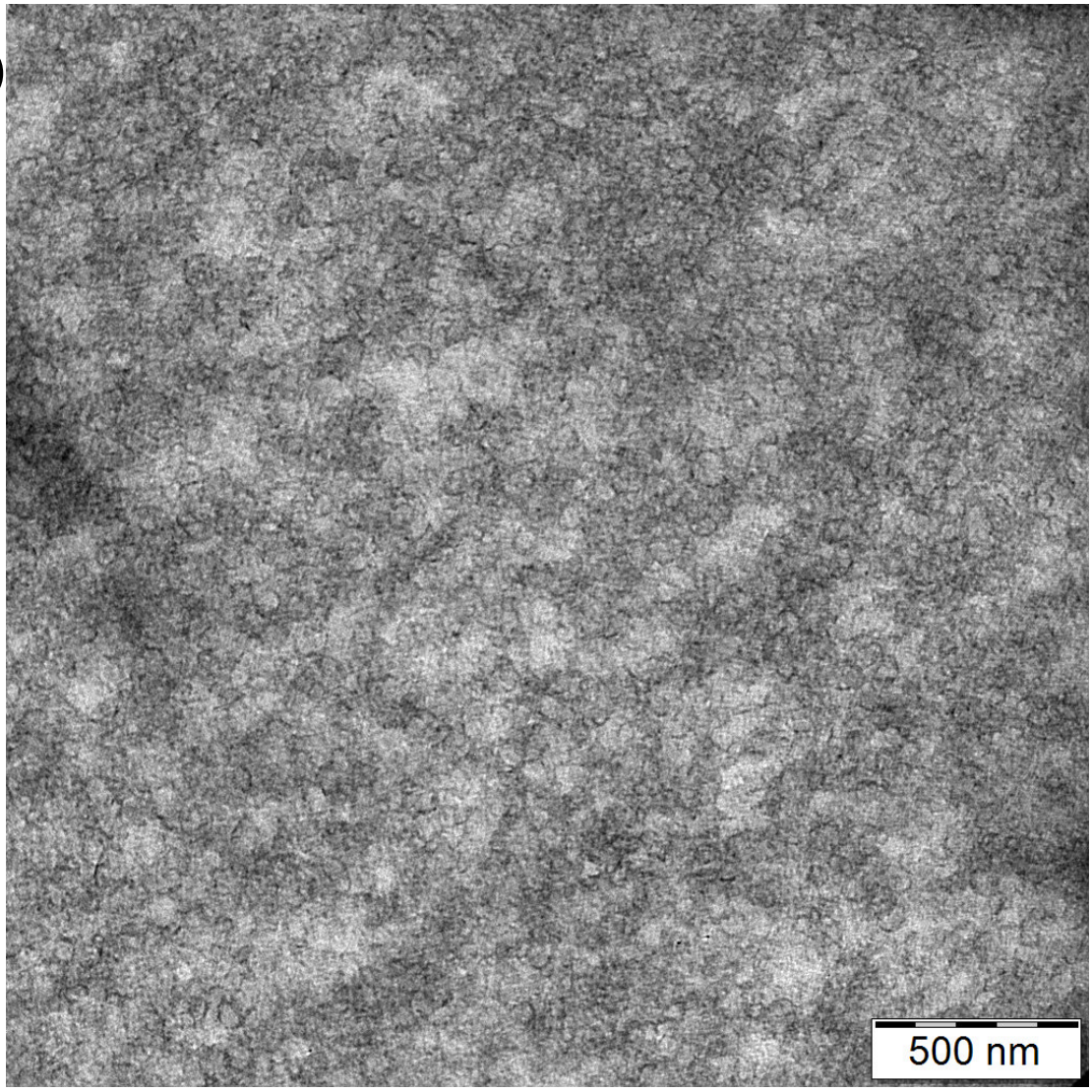


SI-Figure S2 – multi-page (continued): *(f) High-resolution version of the TEM image of 4R-15T.*

SI-Figure S2 – multi-page (continued, last image):

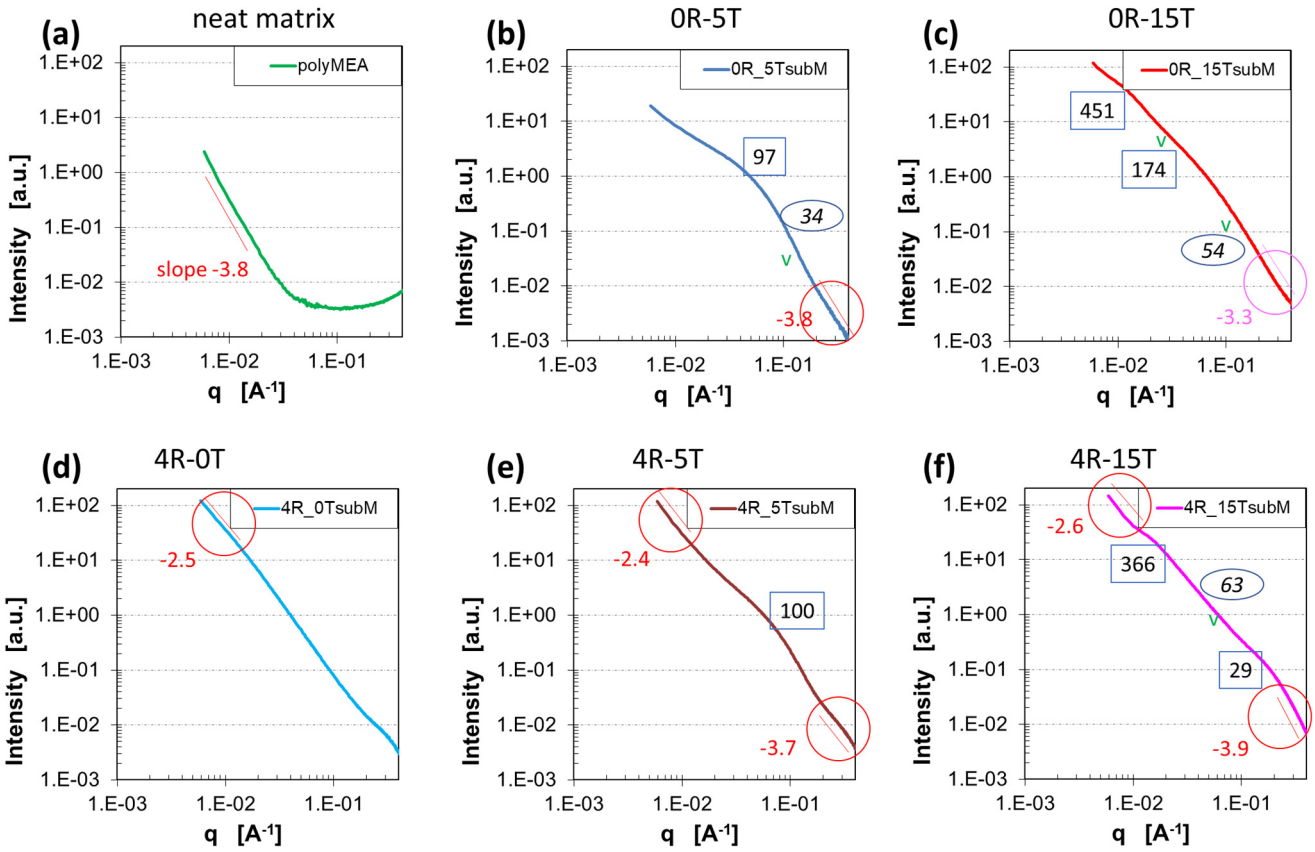
4R-15T, **larger-scale-view**

(f2)

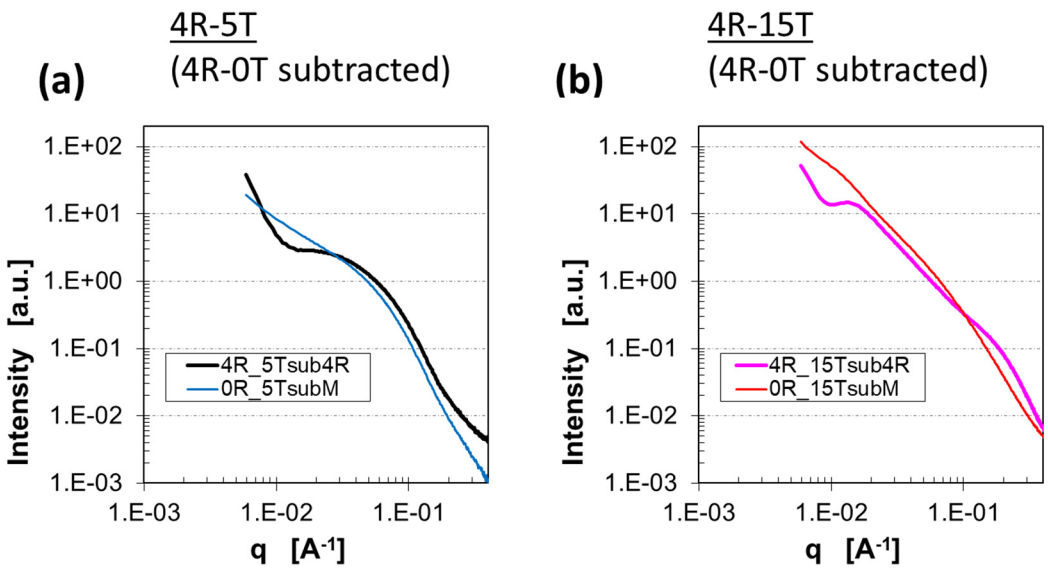


SI-Figure S2 – multi-page (continued, last image): *(f2)) TEM: larger-scale-view of 4R-15T.*

X-ray diffraction (Morphology): detailse view of SAXS region



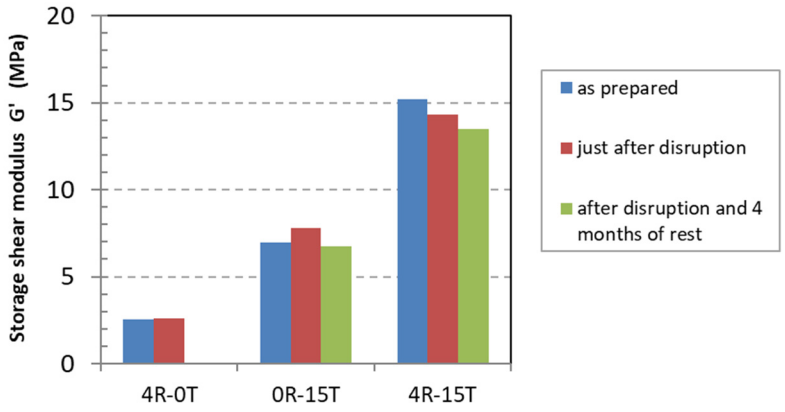
SI-Figure S3: *Details of X-Ray scattering patterns after subtraction of matrix intensity: (a) neat polyMEA; (b) polyMEA + 5% of SiO2; (c) with 15% of SiO2; (d) with 4% of clay; (e) with 4% of clay + 5% of SiO2; (f) with 4% of clay + 15% of SiO2; labels: calculated characteristic distances (attempted subtraction of both polyMEA and Clay is illustrated below, in* ***SI-Figure S4****).*



SI-Figure S4: *Patterns of the SAXS region of the doubly filled samples 4R-5T and 4R-15T obtained by subtraction of the curve of the clay-containing matrix (4R-0T) from the original curves of the mentioned samples; the results suggest, that the fillers are not distributed independently of each other, which leads to strange shapes of the curves after subtraction.*

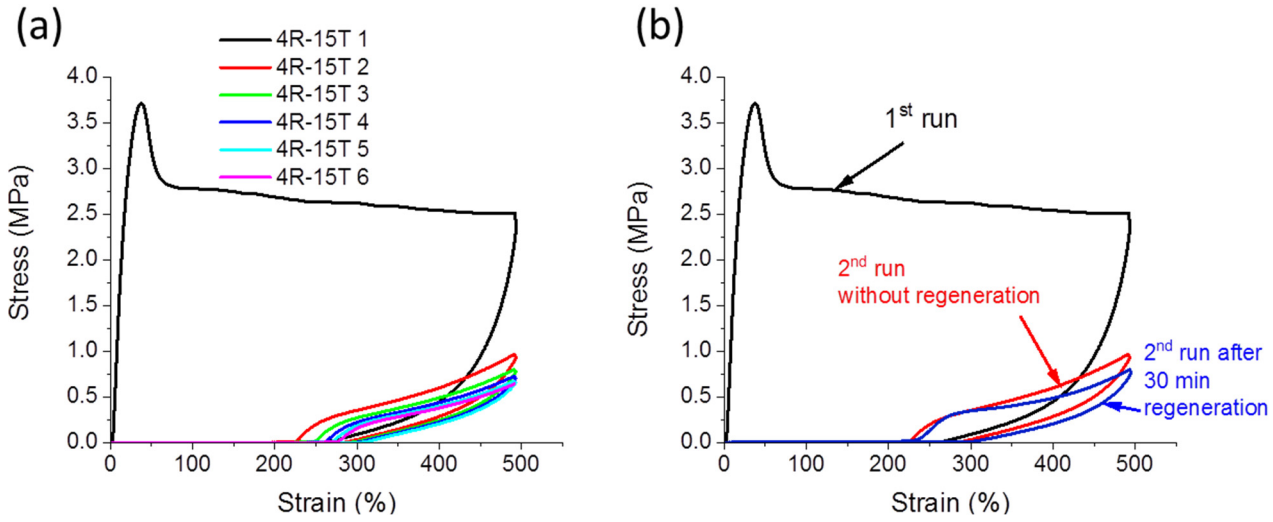
2. Tensile properties

Shear moduli at small deformation after preparation and different treatment

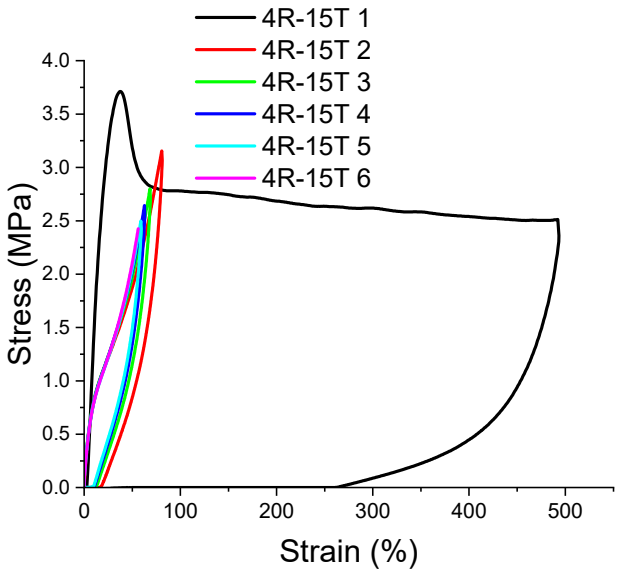


SI-Figure S5: *Shear moduli at small deformation (as determined in torsion experiments), for the most important nanocomposite samples, in different states: (blue columns) as prepared; (red columns) just after disruption in tensile experiment; (green columns) after tensile disruption and subsequent 4-month-rest; corresponding Young's moduli can be calculated as E = 3 G.*

Hysteresis tests in the as prepared state

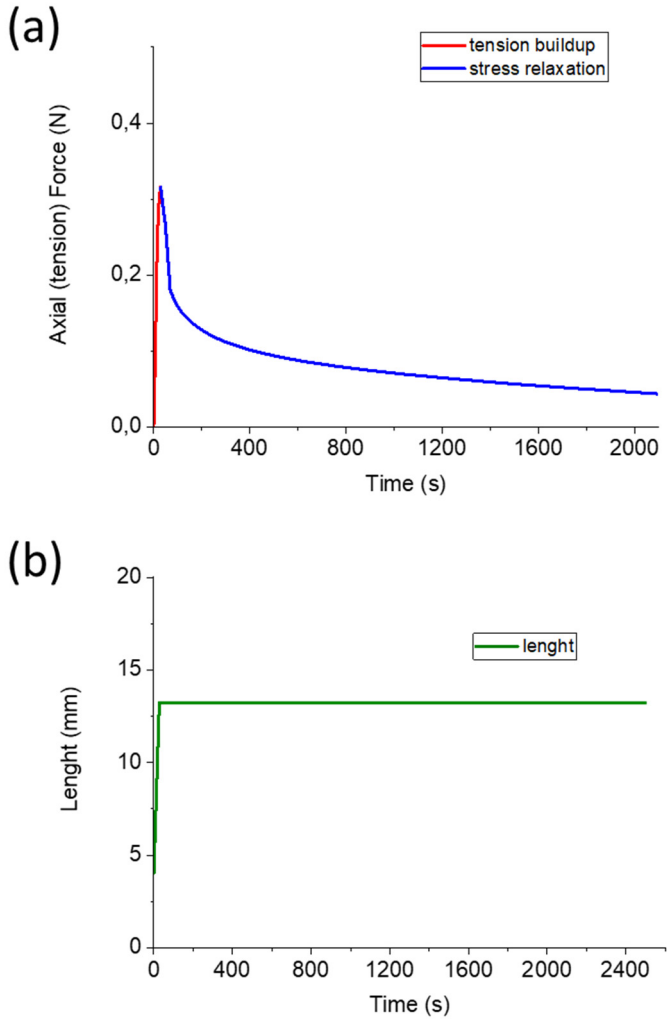


SI-Figure S6: *Behaviour of the nanocomposite 4R-15T (a) upon repeated cyclic loading; (b) after a 30 min rest time following the first loading cycle.*

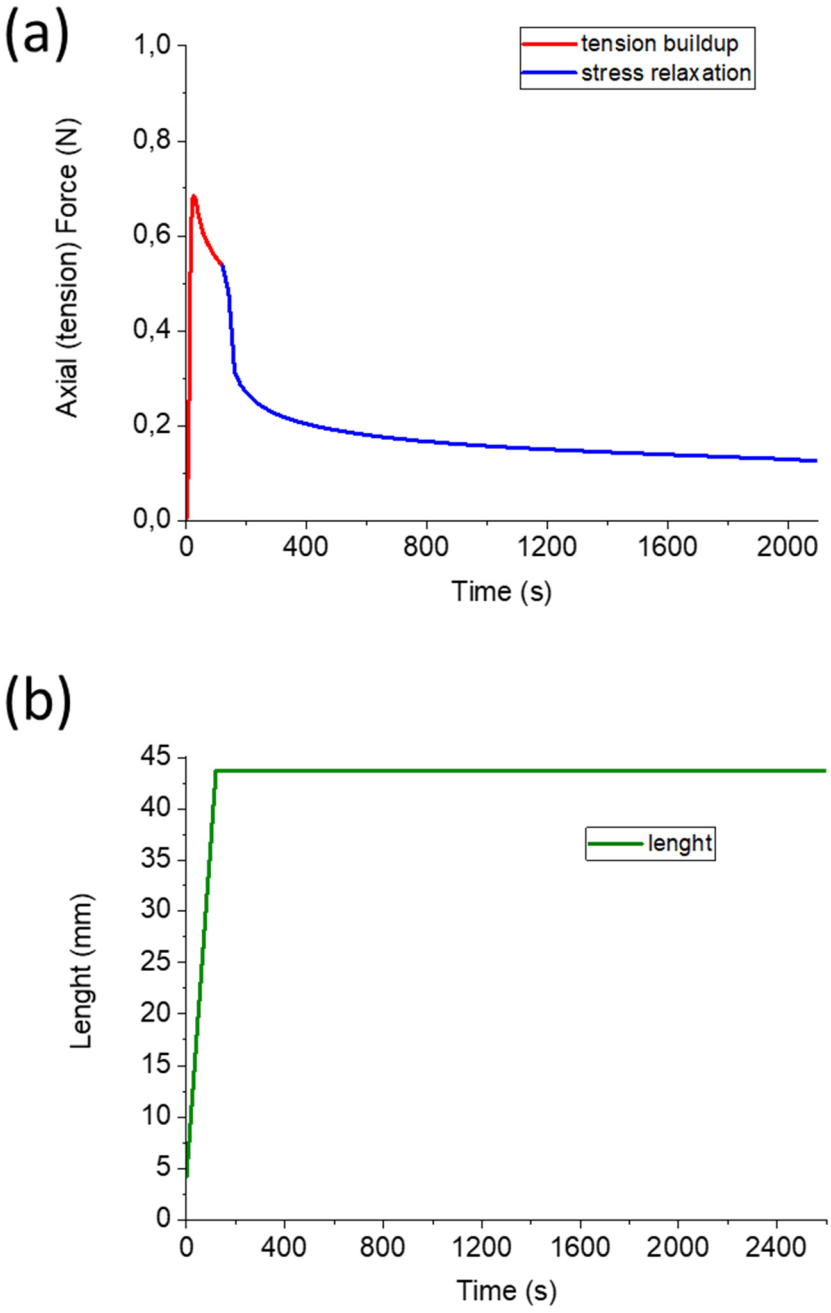


SI-Figure S7: *Hysteresis behaviour of the nanocomposite 4R-15T upon repeated cyclic loading with evaluation of each cycle as a new specimen with a new initial geometry.*

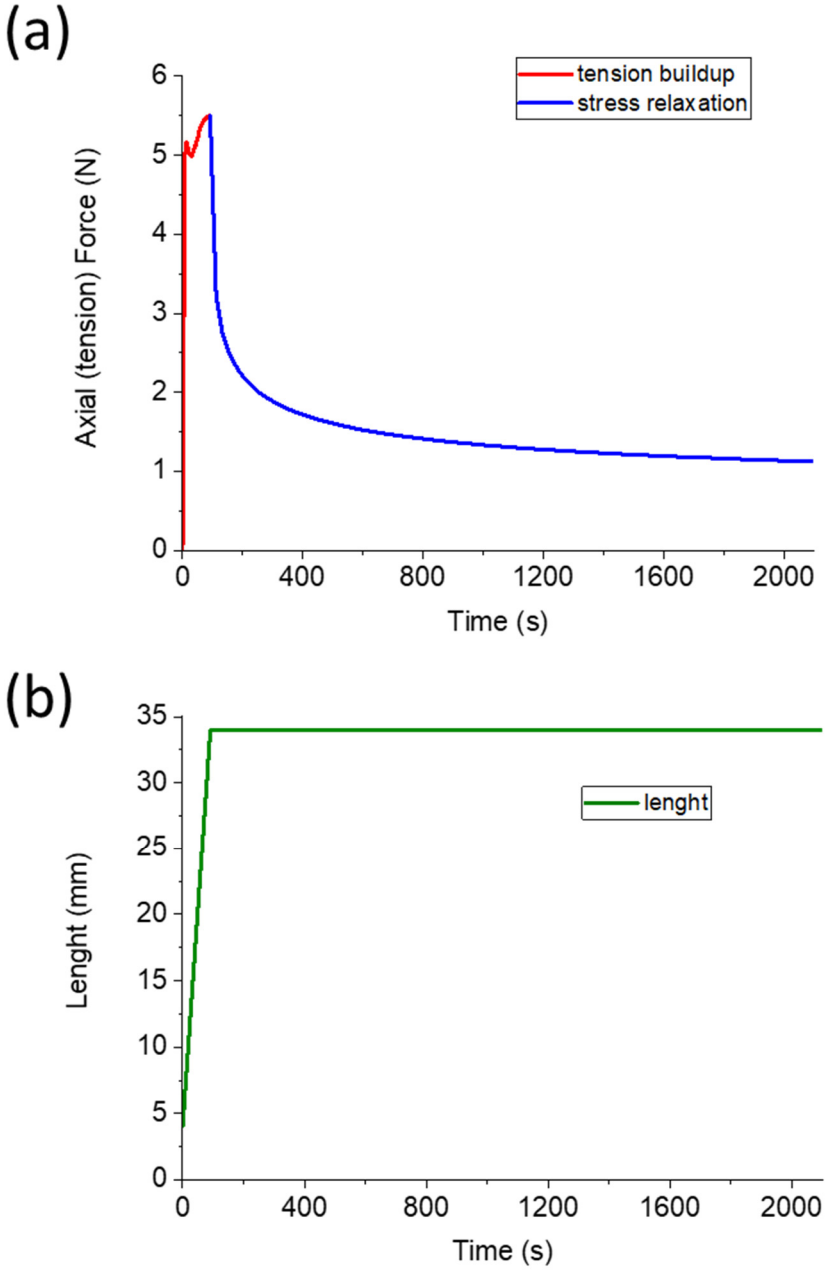
Relaxation tests



SI-Figure S8: *Neat polyMEA: Stress relaxation experiment: (a) graph of stress build-up (as consequence of mechanical stretching, red line) and of subsequent relaxation (during the rest period, blue line); (b) length of the specimen between the clamps of the analysing machine during this experiment.*



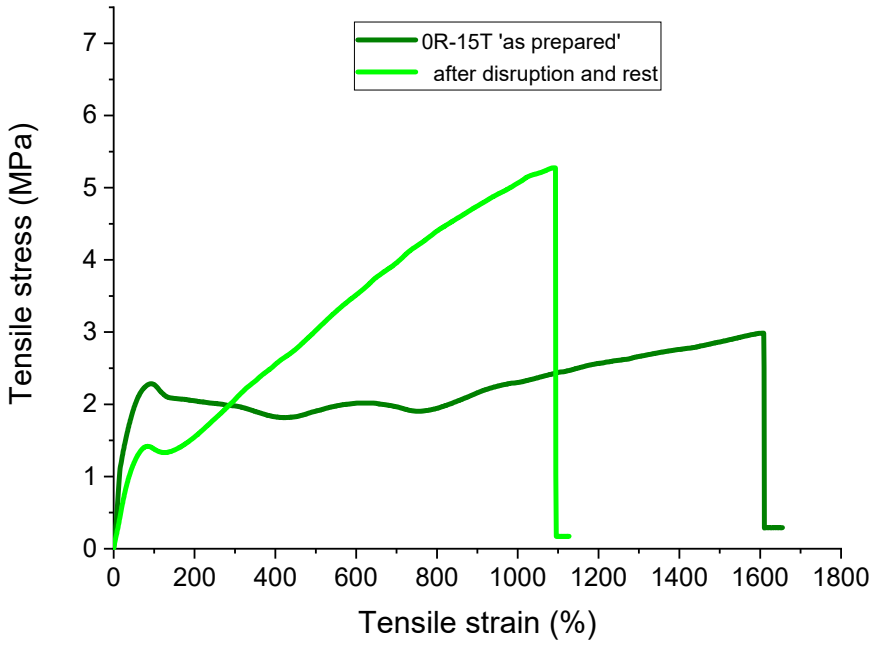
SI-Figure S9: *4R-0T: Stress relaxation experiment: (a) graph of stress build-up (as consequence of mechanical stretching, red line) and of subsequent relaxation (during the rest period, blue line); (b) length of the specimen between the clamps of the analysing machine during this experiment.*



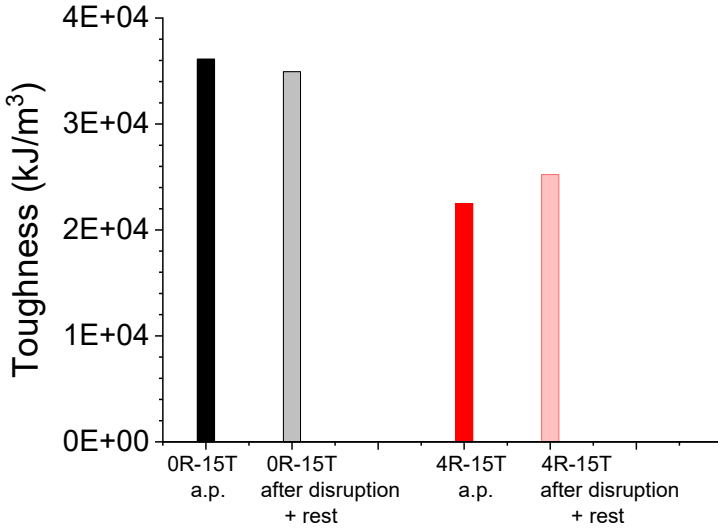
SI-Figure S10: *0R-15T: Stress relaxation experiment: (a) graph of stress build-up (as consequence of mechanical stretching, red line) and of subsequent relaxation (during the rest period, blue line); (b) length of the specimen between the clamps of the analysing machine during this experiment.*

3. Changes after enduring very large deformations

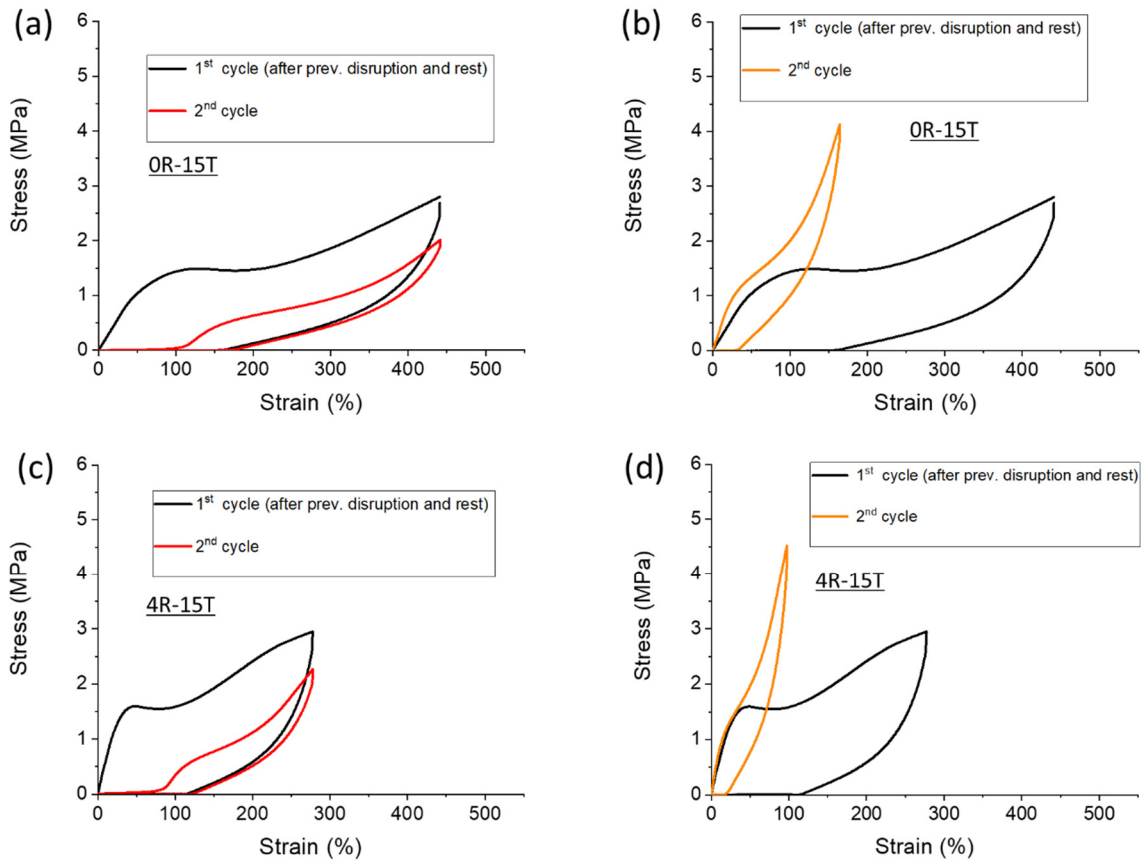
Tensile tests after enduring deformation until disruption



SI-Figure S11: *0R-15T: successive tensile tests until disruption, first with an 'as prepared' sample, thereafter with one of the 'stretching-treated' pieces obtained by the disruption after 4 months of rest preceding the second test.*



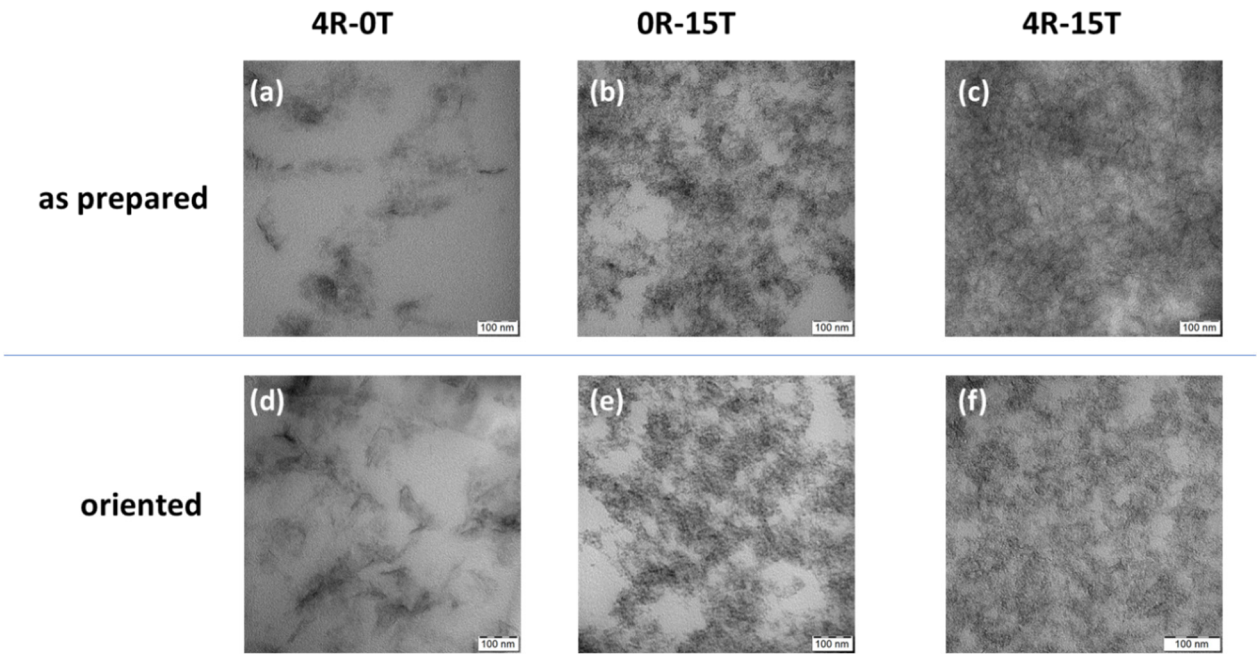
SI-Figure S12: *0R-15T and 4R-15T: tensile toughness values of the nanocomposites in the 'as prepared' state (label "a.p."), and after destructive stretching and subsequent rest time of 4 months (label "after disruption + rest").*



SI-Figure S13: *Hysteresis curves up to large deformations of the silica-filled nanocomposites which underwent previous stretching until disruption, as well as a period of subsequent rest: (a, b) polyMEA / 15% SiO2; and (c, d) polyMEA / 4% clay / 15% SiO2: 'normal' depiction in engineering mode – second cycle evaluated using original geometry prior to first cycle (a, c); as well as evaluation of the second cycles as new specimens with new initial geometry (b, d).*

TEM analysis of morphology changes

SI-Figure S14 – multi-page:

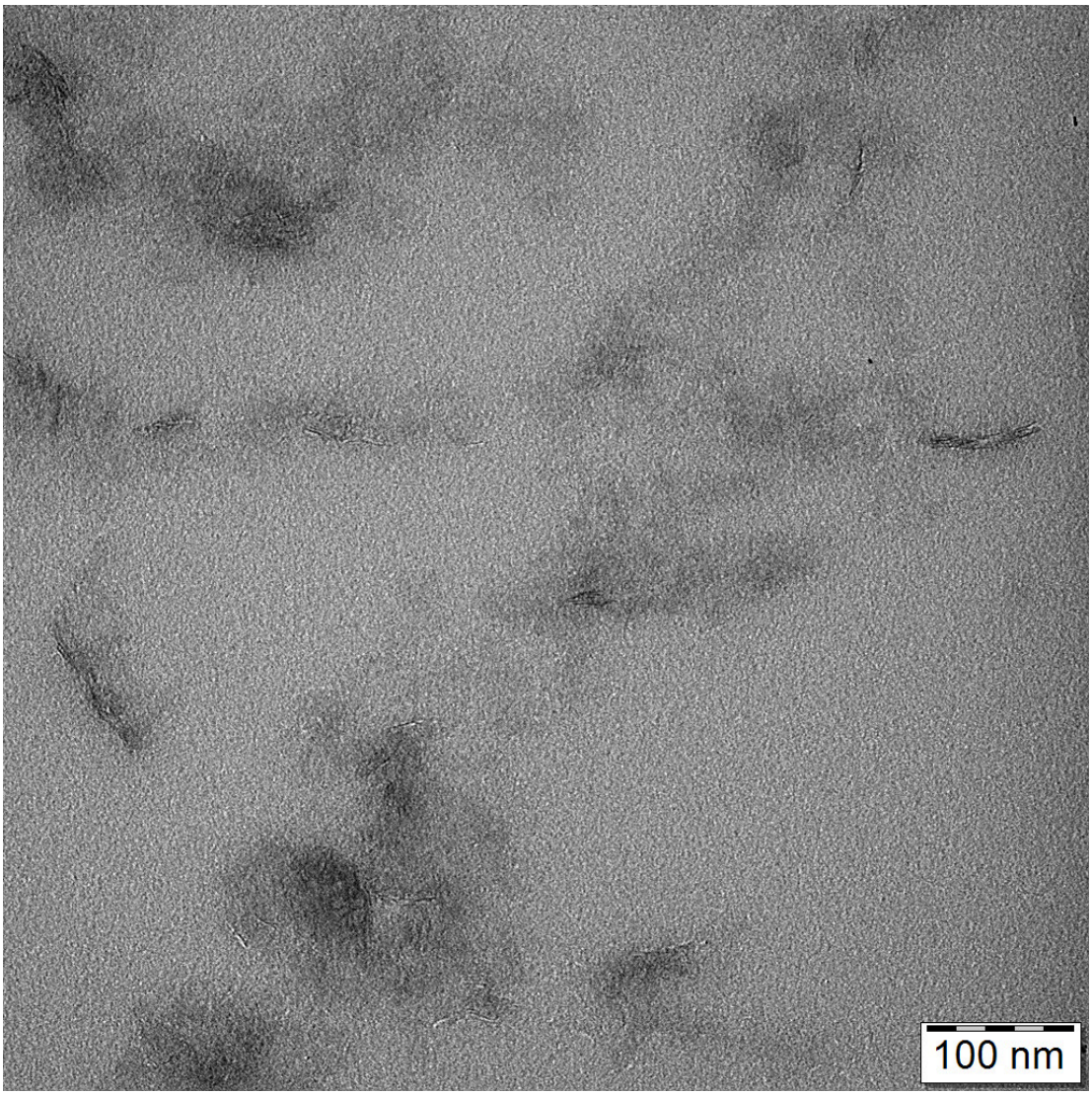


SI-Figure S14 – multi-page: ***Overview:*** *Effect of the endured very extensive stretching (until disruption) on the morphology (TEM) of the most important nanocomposite samples (scalebar: 100 nm): (a-c) morphology in the 'as prepared' state; (d–f) morphology after a endured elongation until rupture – the elongation axis was in the image plane.*

SI-Figure S14 – multi-page (continued):

4R-0T, as prepared, intact

(g)

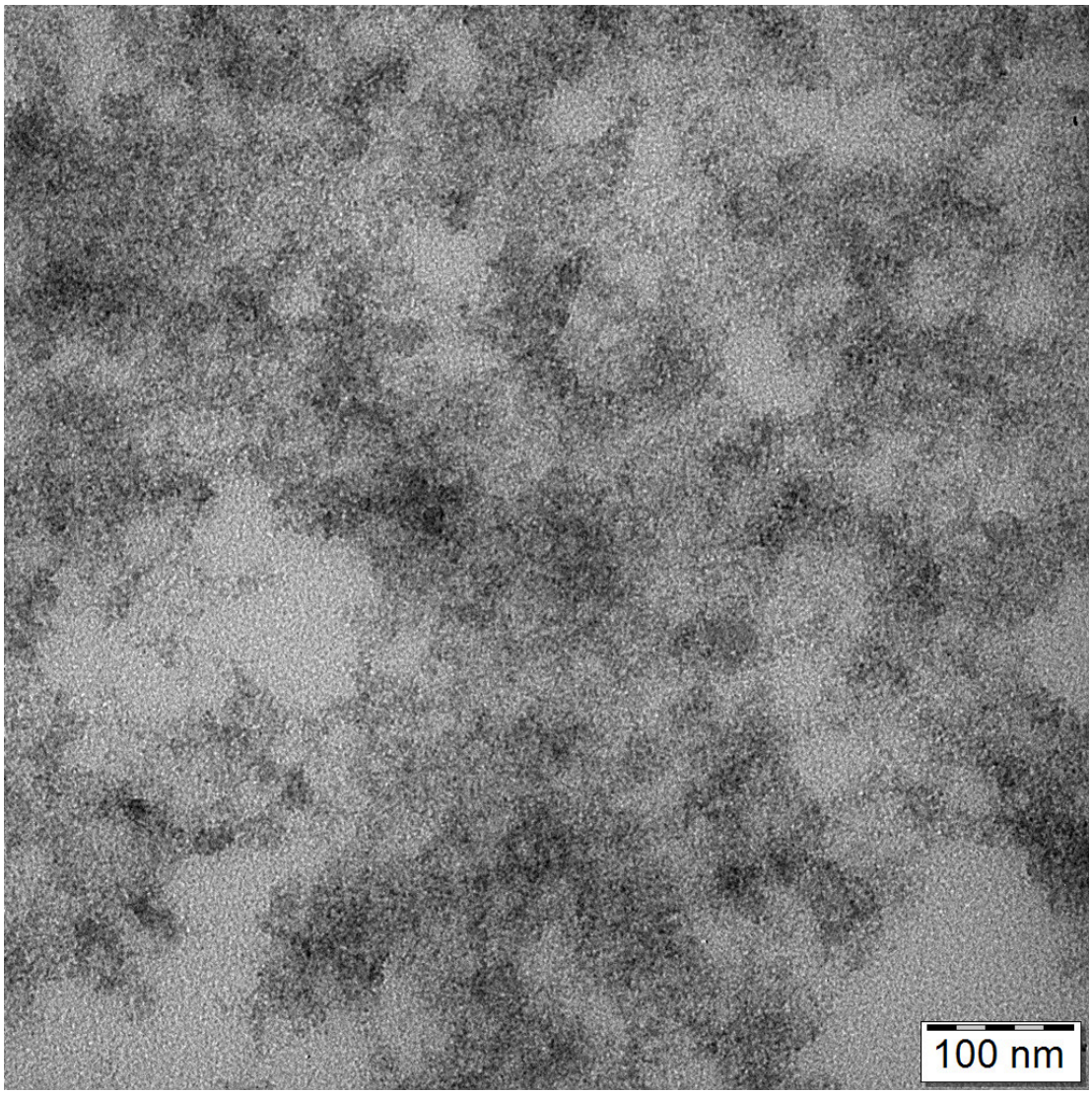


SI-Figure S14 – multi-page (continued): *(g) High-resolution TEM image of* 4R-0T*, 'as prepared', intact.*

SI-Figure S14 – multi-page (continued):

0R-15T, as prepared, intact

(h)

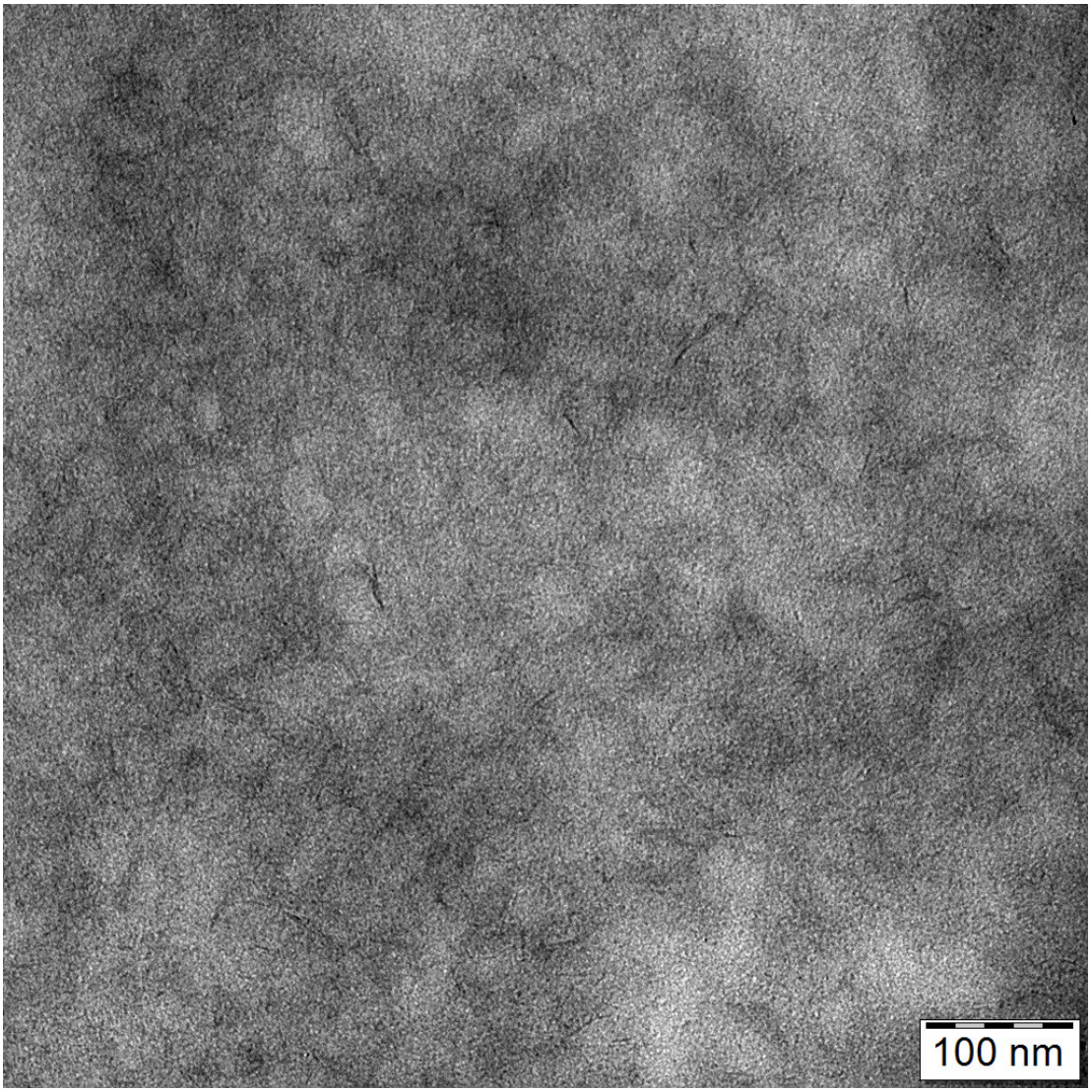


SI-Figure S14 – multi-page (continued): *(h) High-resolution TEM image of* 0R-15T*, 'as prepared', intact.*

SI-Figure S14 – multi-page (continued):

4R-15T, as prepared, intact

(i)

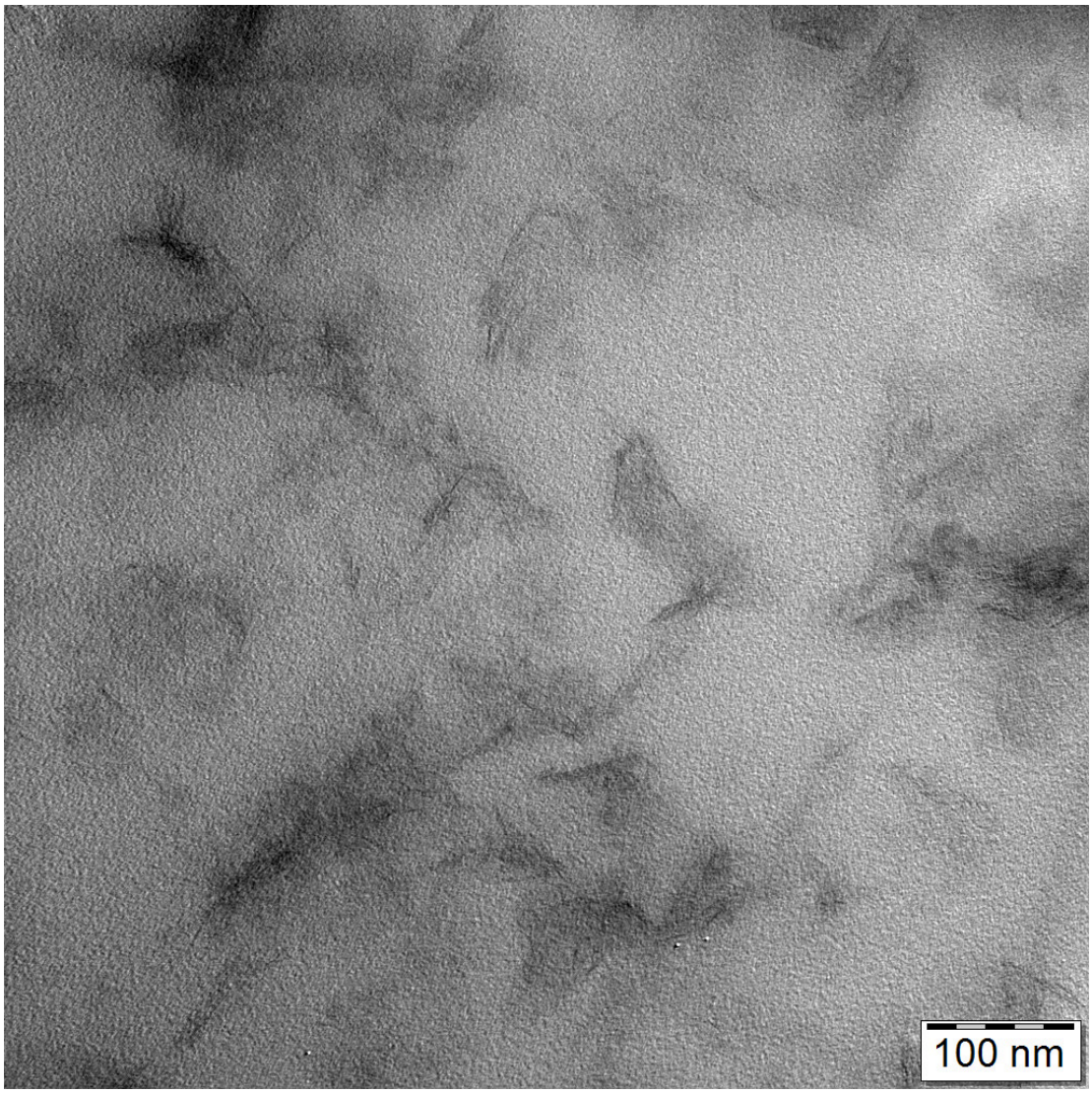


SI-Figure S14 – multi-page (continued): *(i) High-resolution TEM image of* 4R-15T*, as prepared, intact.*

SI-Figure S14 – multi-page (continued):

4R-0T, after stretching until disruption

(j)

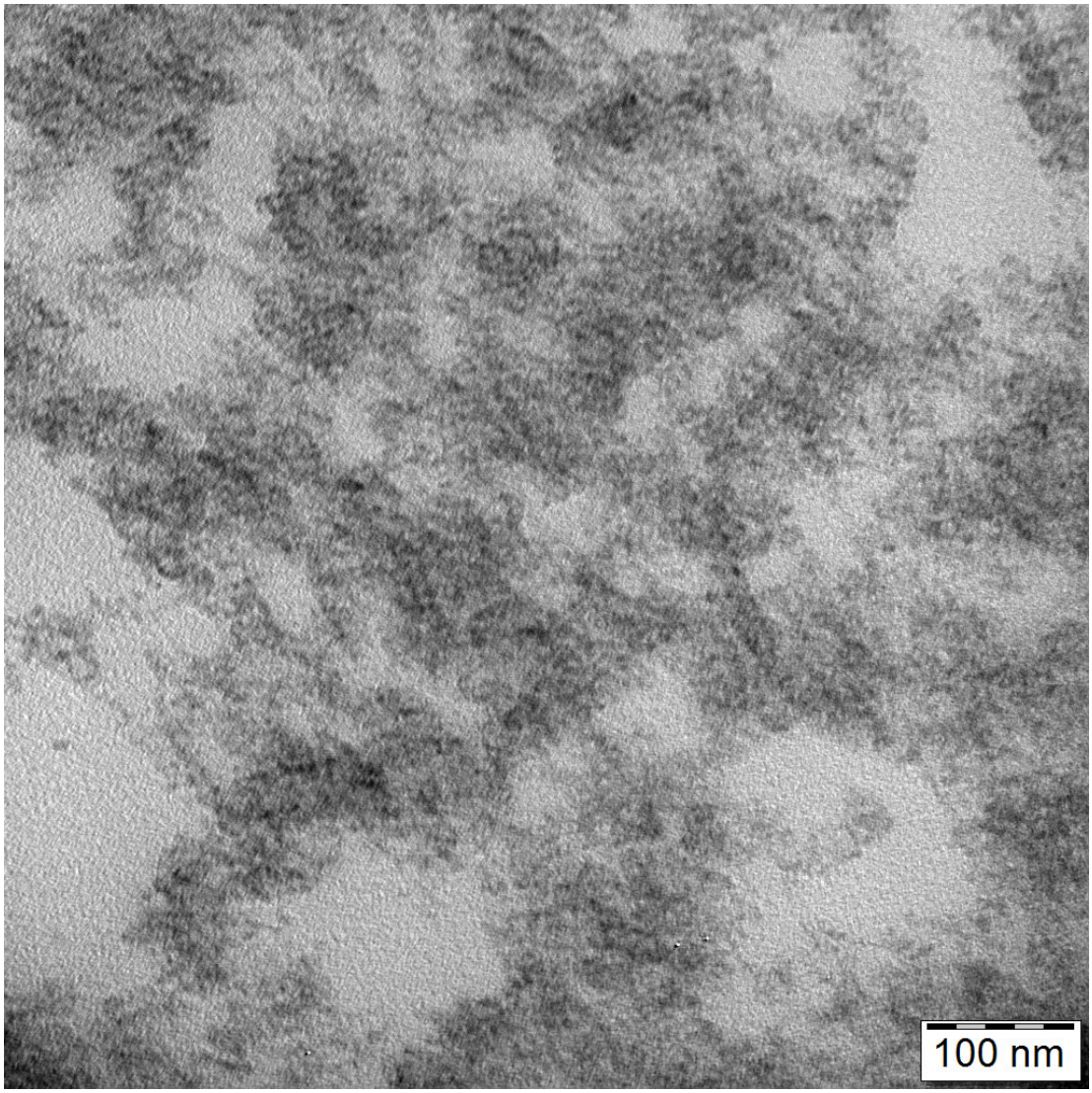


SI-Figure S14 – multi-page (continued): *(j) High-resolution TEM image of* 4R-0T *after stretching until disruption – the elongation axis was in the image plane.*

SI-Figure S14 – multi-page (continued):

0R-15T, after stretching until disruption

(k)

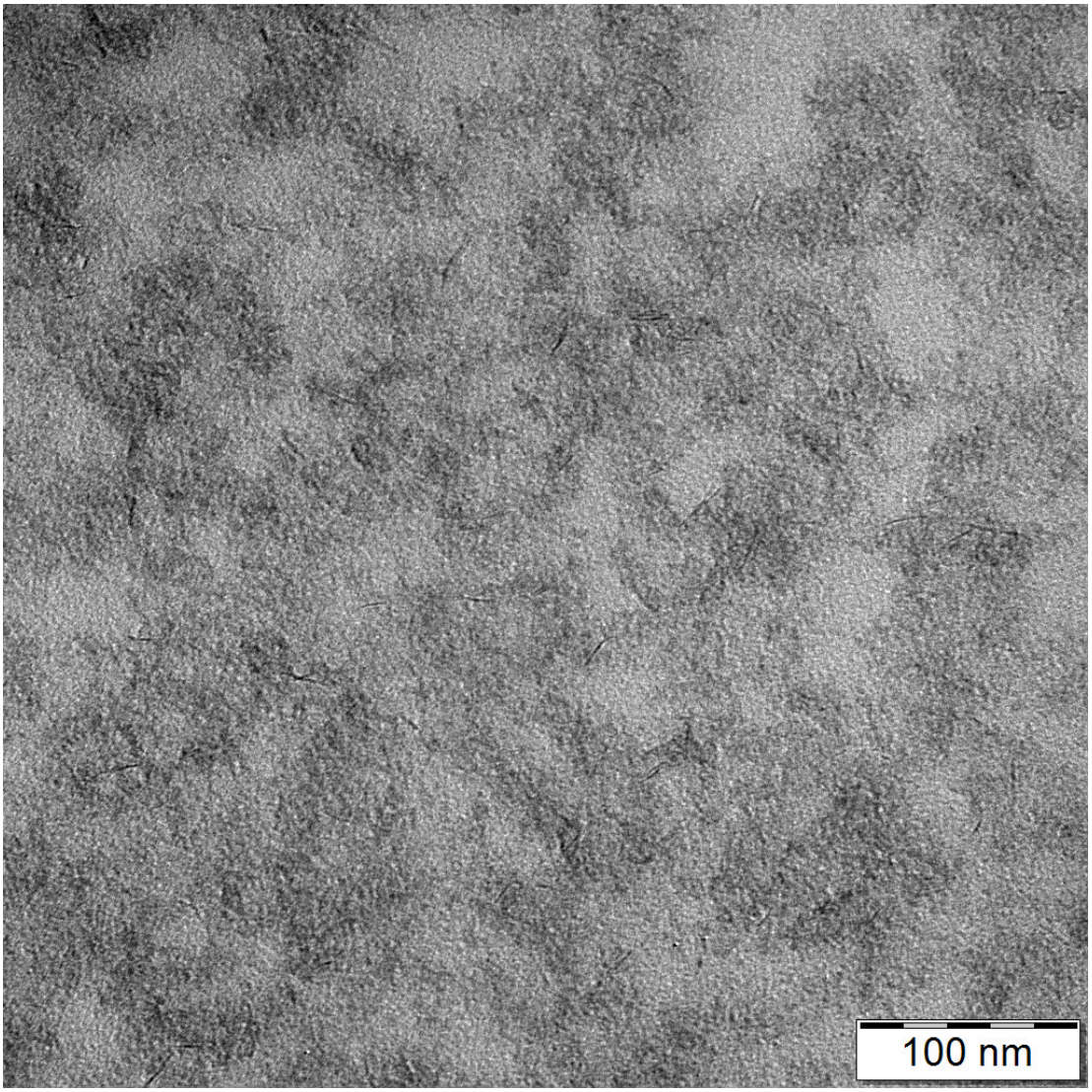


SI-Figure S14 – multi-page (continued): *(k) High-resolution TEM image of* 0R-15T *after stretching until disruption – the elongation axis was in the image plane.*

SI-Figure S14 – multi-page (continued, last image):

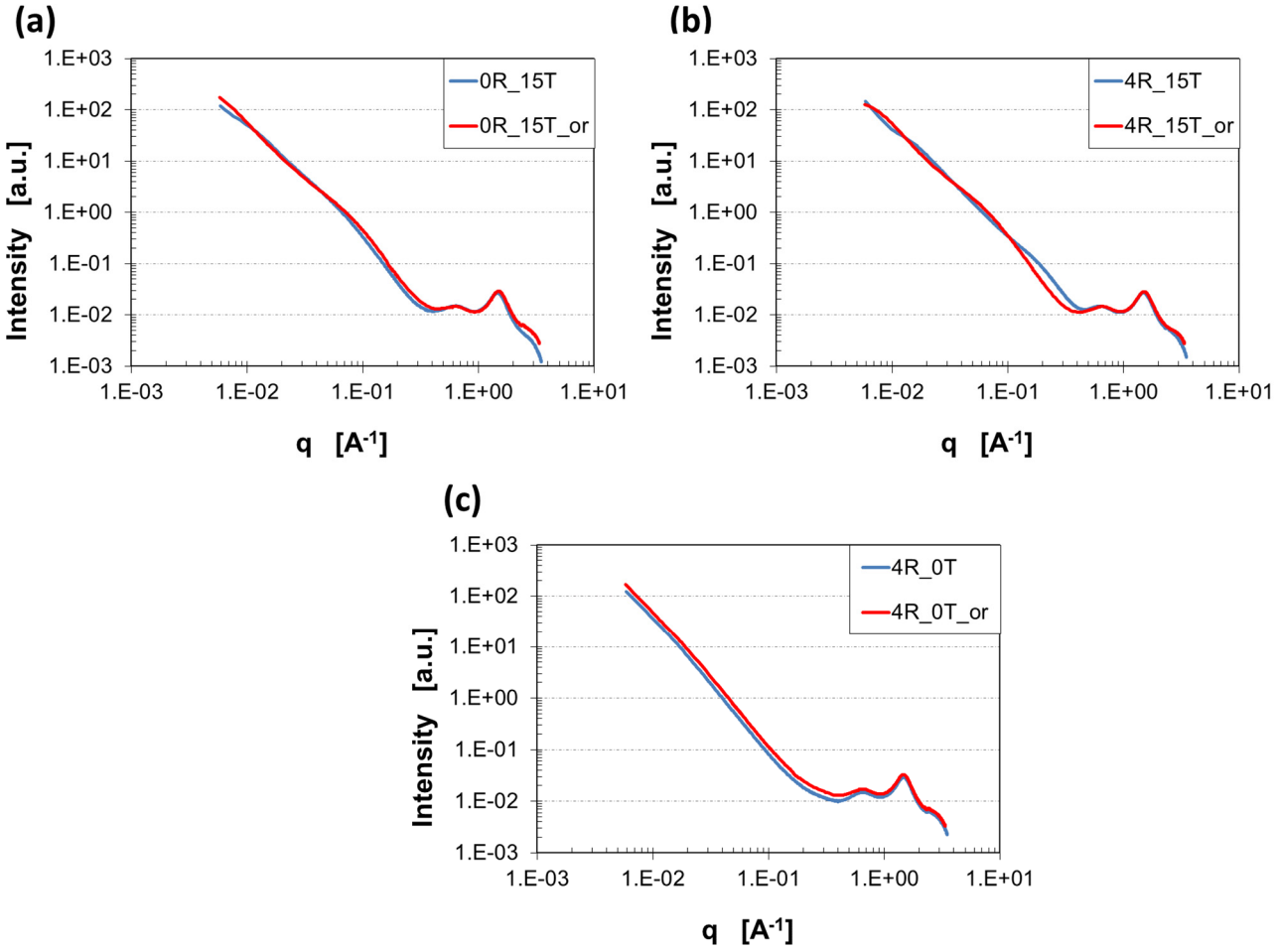
4R-15T, after stretching until disruption

(l)



SI-Figure S14 – multi-page (continued, last image): *(l) High-resolution TEM image of* 4R-15T after stretching until disruption – the elongation axis was in the image plane.

X-ray scattering analysis of morphology changes

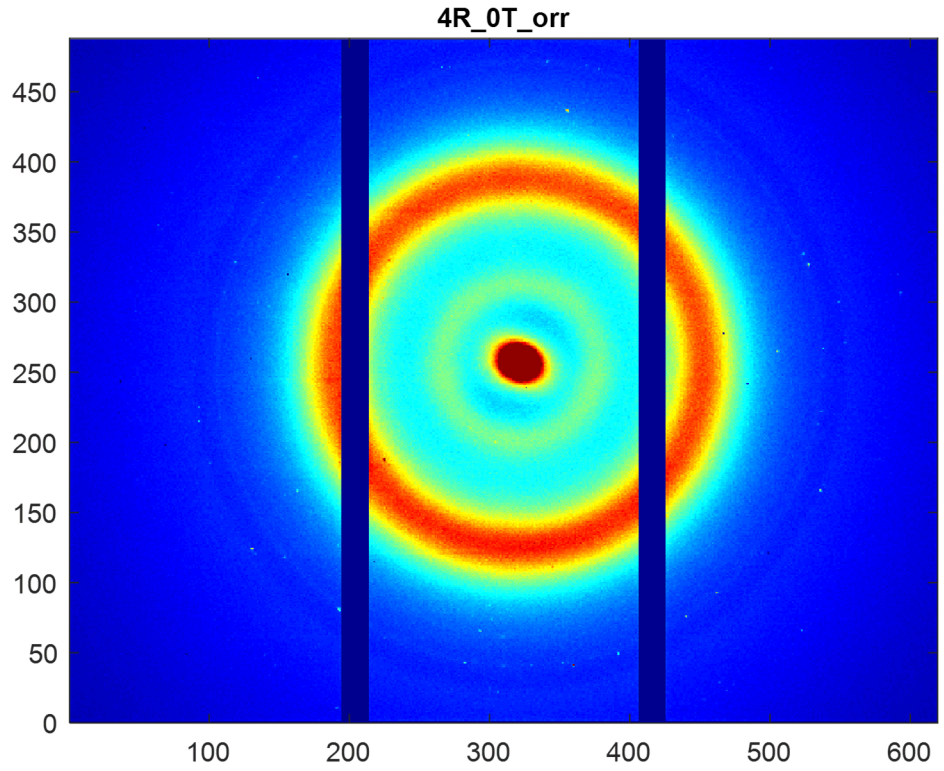


SI-Figure S15: *Effect of previous elongation until destruction on some of the X-ray diffraction patterns of the most important among the studied elastomers: (a) sample with 15 wt.% of nano-SiO2*

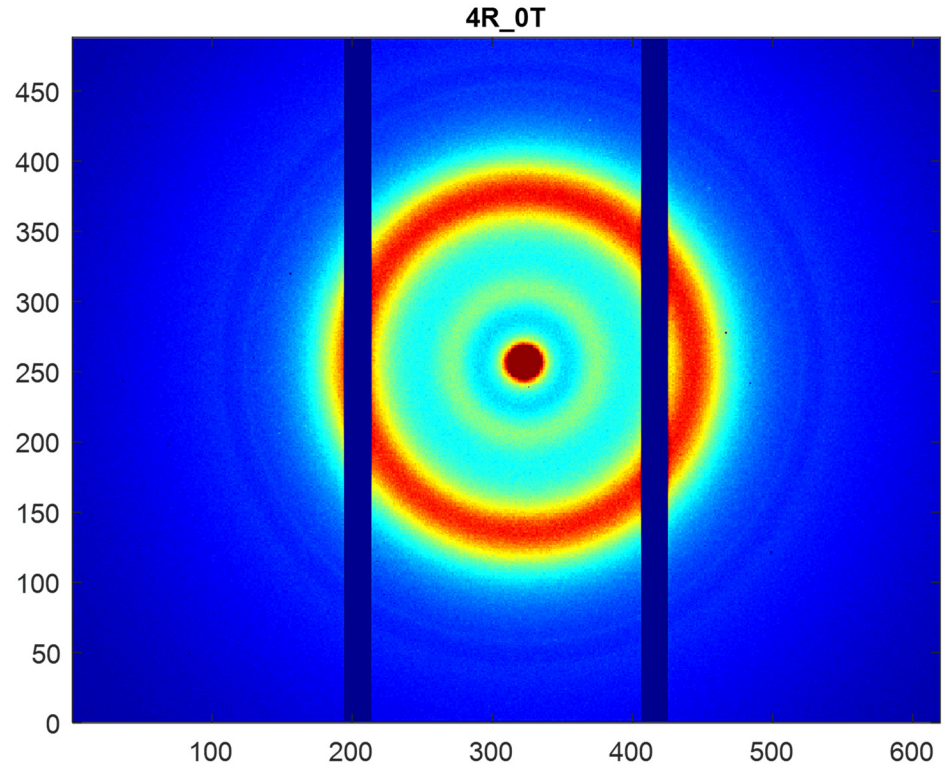
2-dimensional X-ray diffractograms before and after disruption test

SI-Figure S16 – multi-page:

(a)



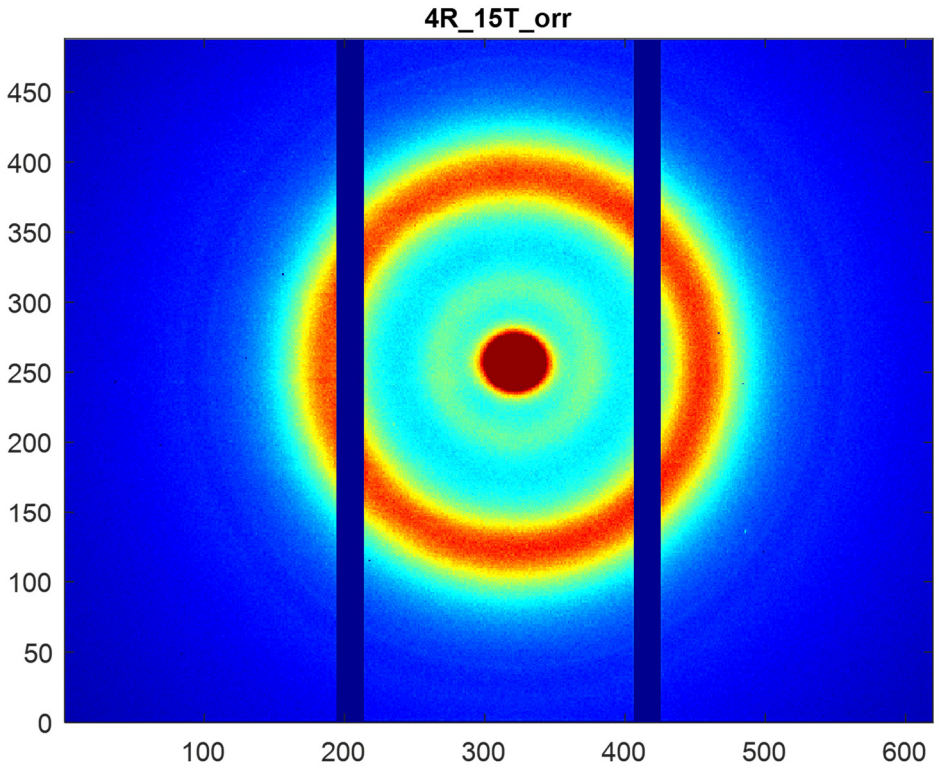
(b)



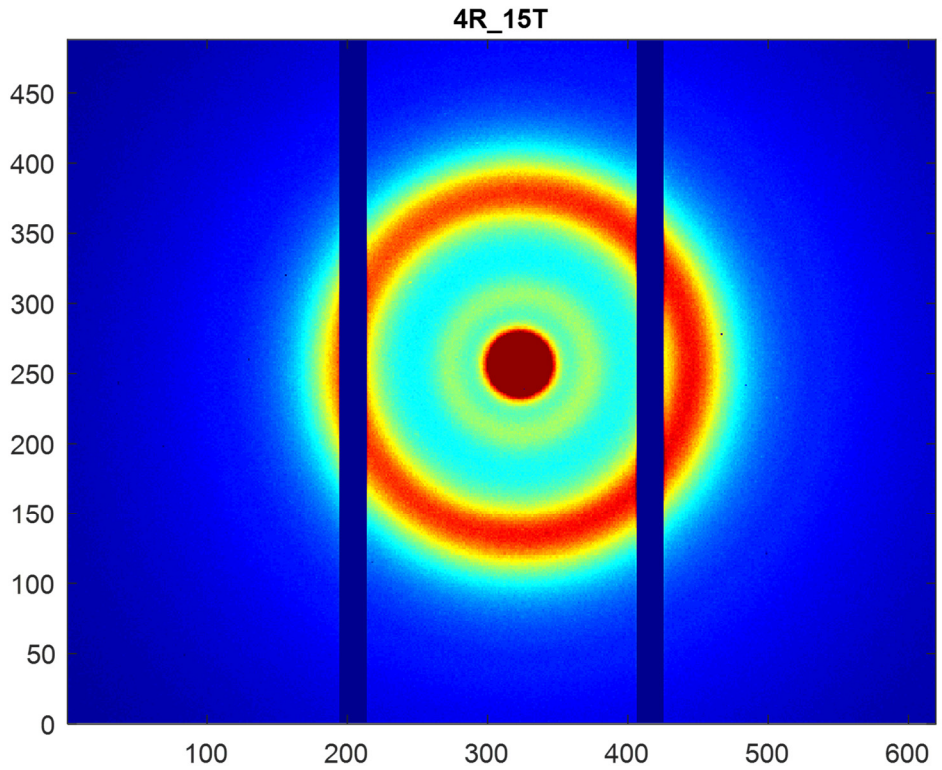
SI-Figure S16 – multi-page: *2D diffractograms of the nanocomposite 4R-0T (4 wt.% of clay as the exclusive filler): (a) in partly aligned state ca. 30 min after tensile test until disruption; (b) in the intact 'as prepared' state.*

SI-Figure S16 – multi-page (continued):

(c)



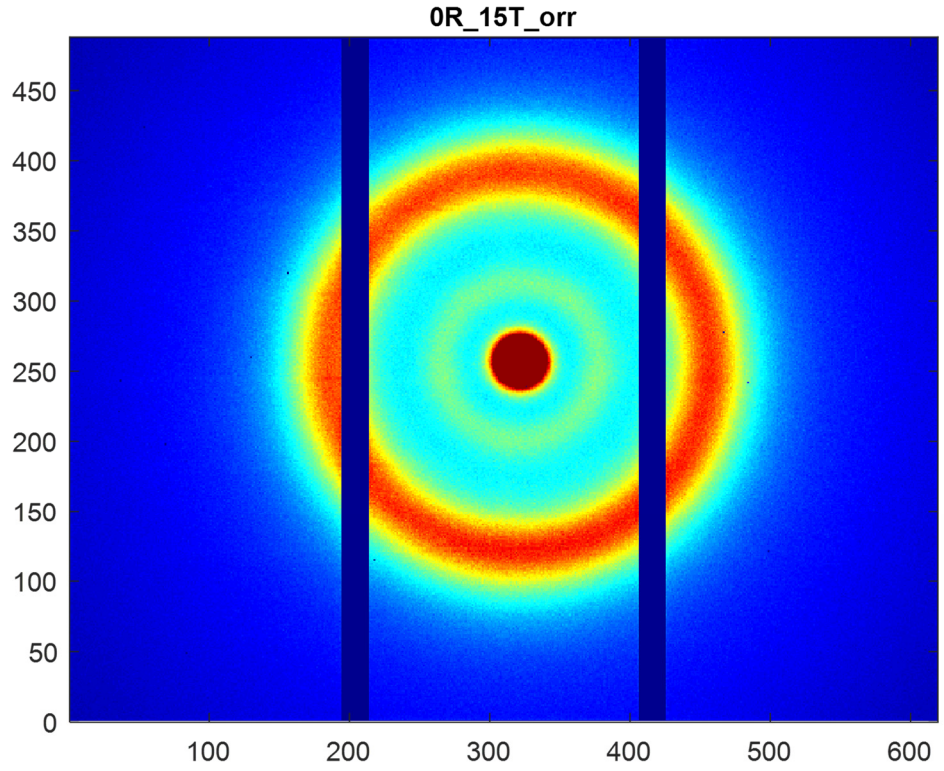
(d)



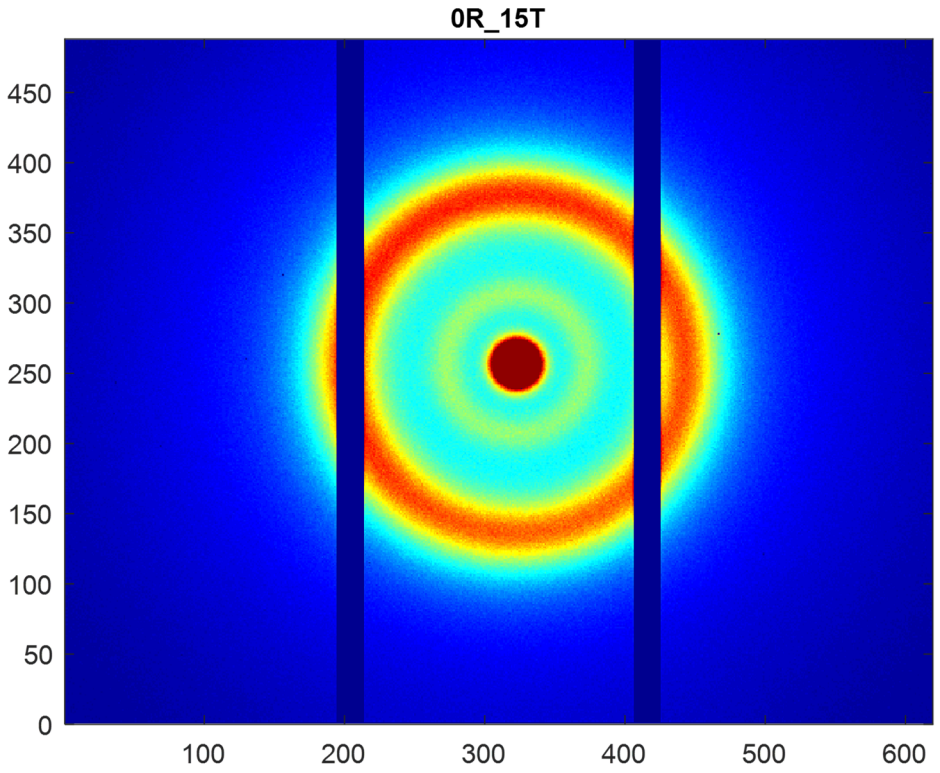
SI-Figure S16 – multi-page (continued): *2D diffractograms of the nanocomposite 4R-15T (4 wt.% of clay + 15 wt.% of silica): (c) in slightly anisotropic state ca. 30 min after tensile test until disruption; (d) in the intact 'as prepared' state.*

SI-Figure S16 – multi-page (continued):

(e)



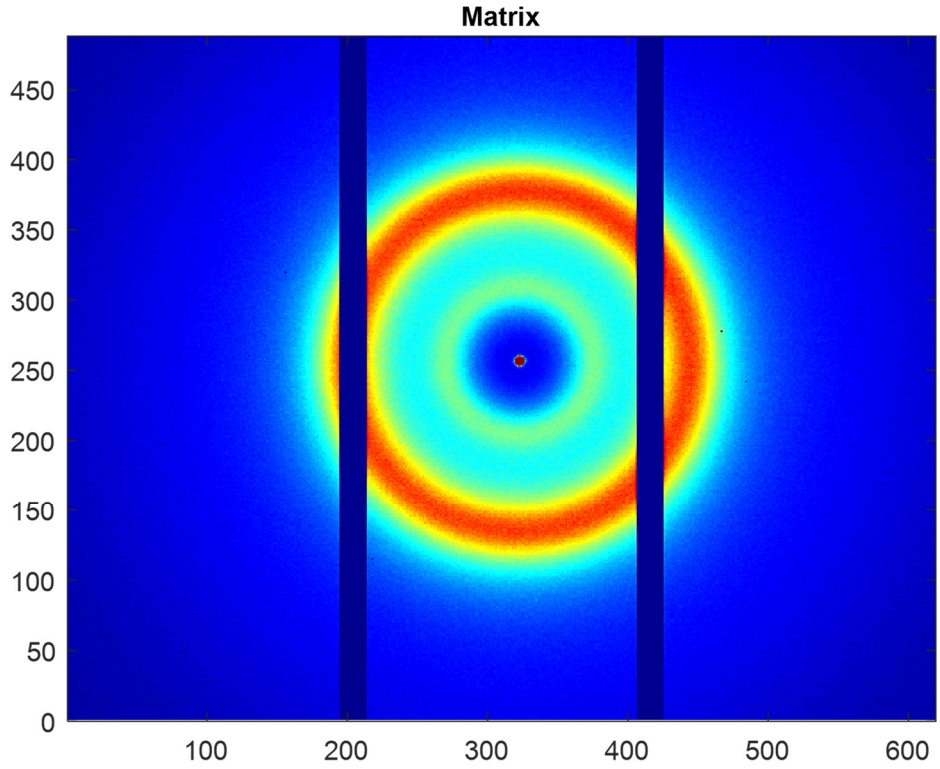
(f)



SI-Figure S16 – multi-page (continued): *2D diffractograms of the nanocomposite 0R-15T (15 wt.% of silica as exclusive filler): (e) in isotropic, non-oriented state ca. 30 min after tensile test until disruption; (f) in the intact 'as prepared' state.*

SI-Figure S16 – multi-page (continued, last image):

(g)



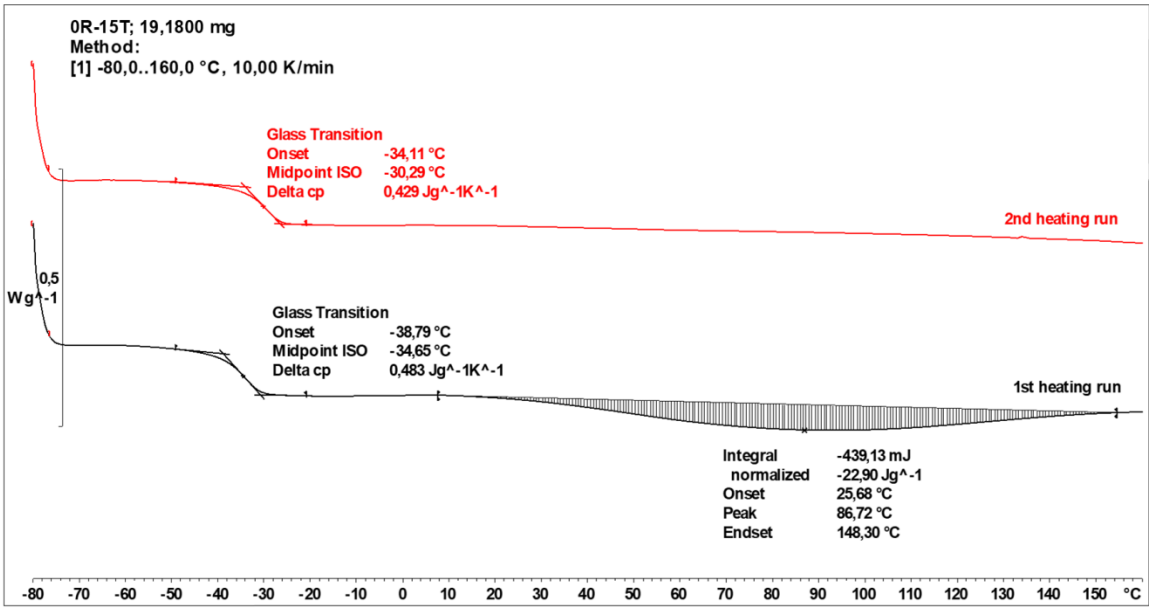
SI-Figure S16 – multi-page (continued, last image): *(g) 2D diffractogram of neat polyMEA in the 'as prepared' state (as reference).*

4. Thermal properties (DSC)

SI-Figure S17 – multi-page:

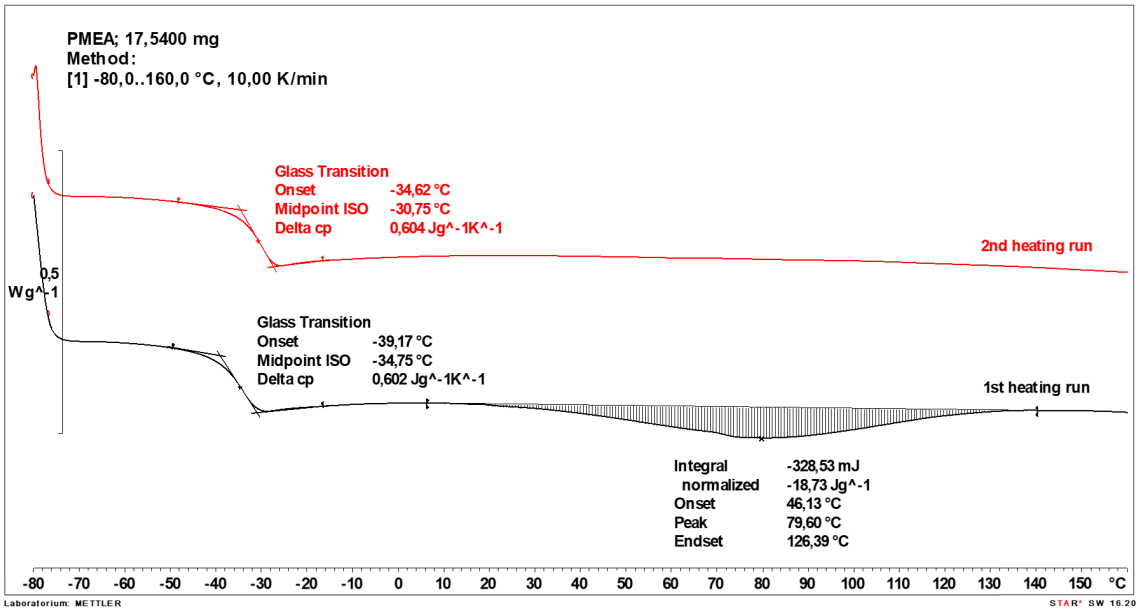
0R-15T

(a)



neat polyMEA

(b)

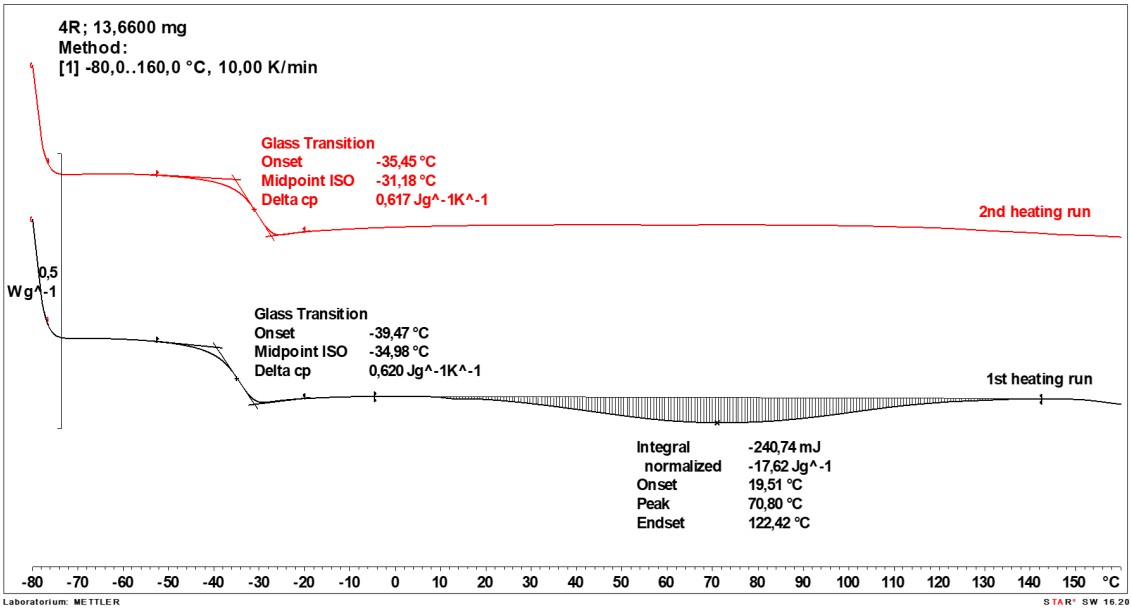


SI-Figure S17 – multi-page: *DSC trace of (a) 0R-15T (polyMEA with 15 wt.% of nano-SiO2); (b) neat polyMEA matrix.*

SI-Figure S17 – multi-page (continued):

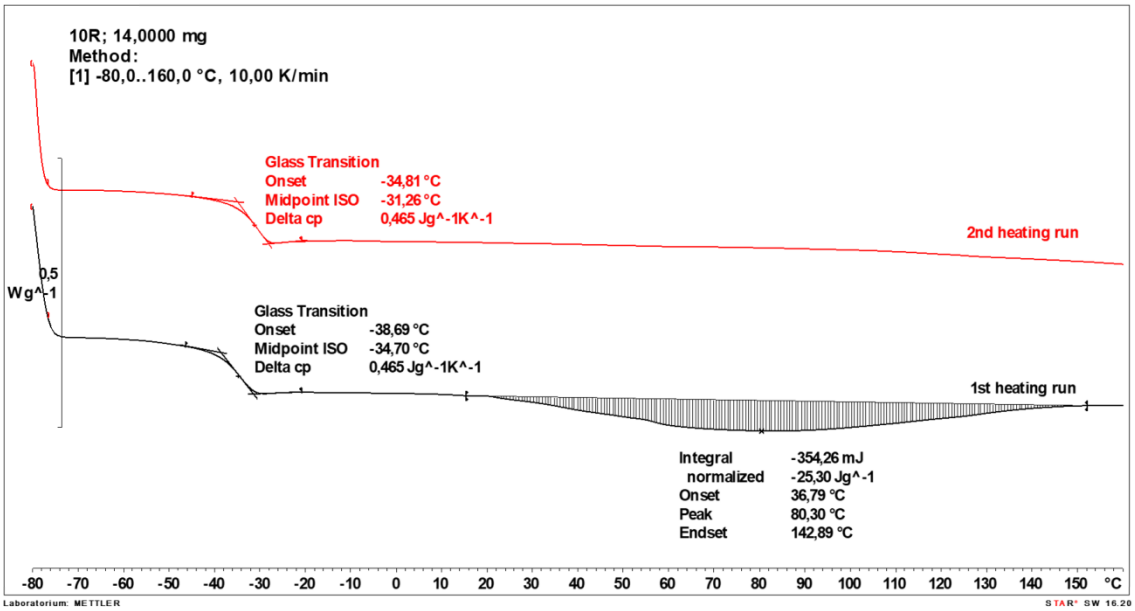
4R-0T

(c)



10R-0T

(d)

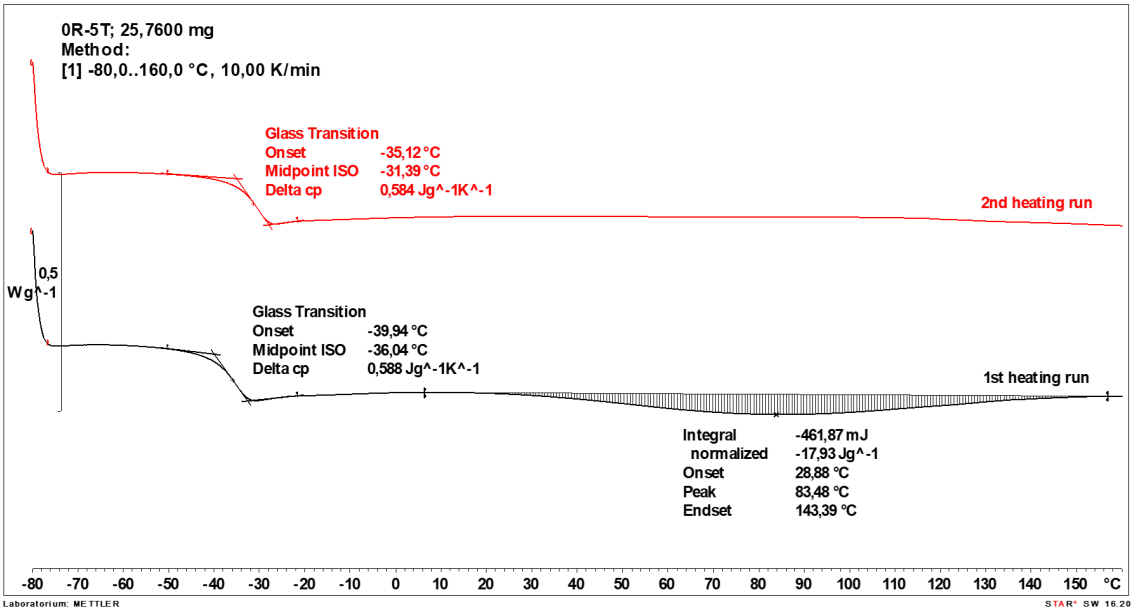


SI-Figure S17 – multi-page: *DSC trace of (c) 4R-0T (polyMEA with 4 wt.% of clay); (d) 10R-0T (polyMEA with 10 wt.% of clay).*

SI-Figure S17 – multi-page (continued):

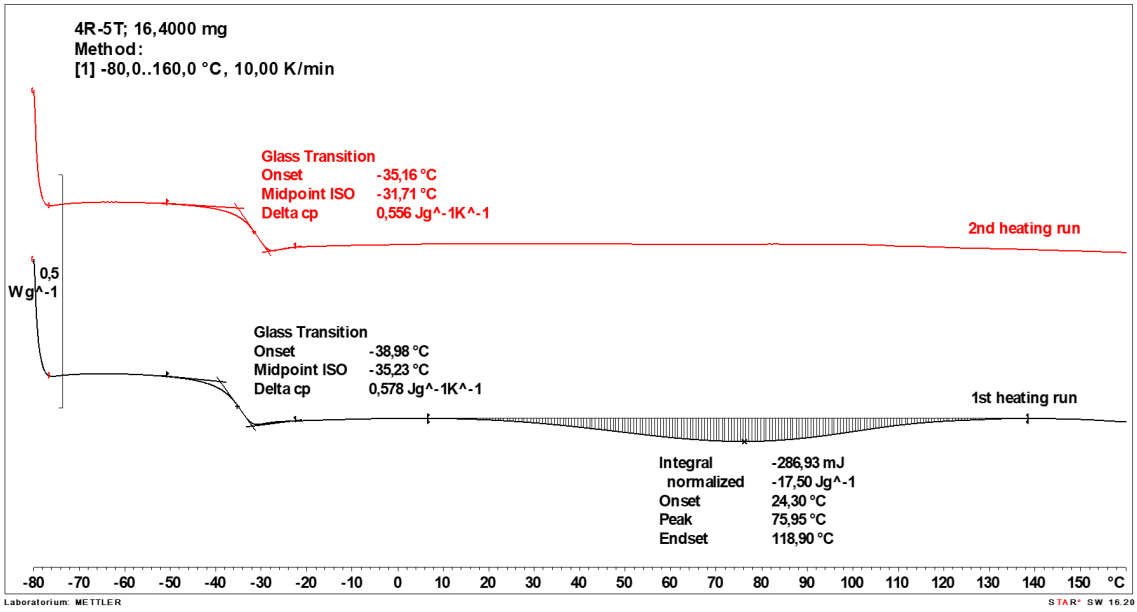
0R-5T

(e)



4R-5T

(f)

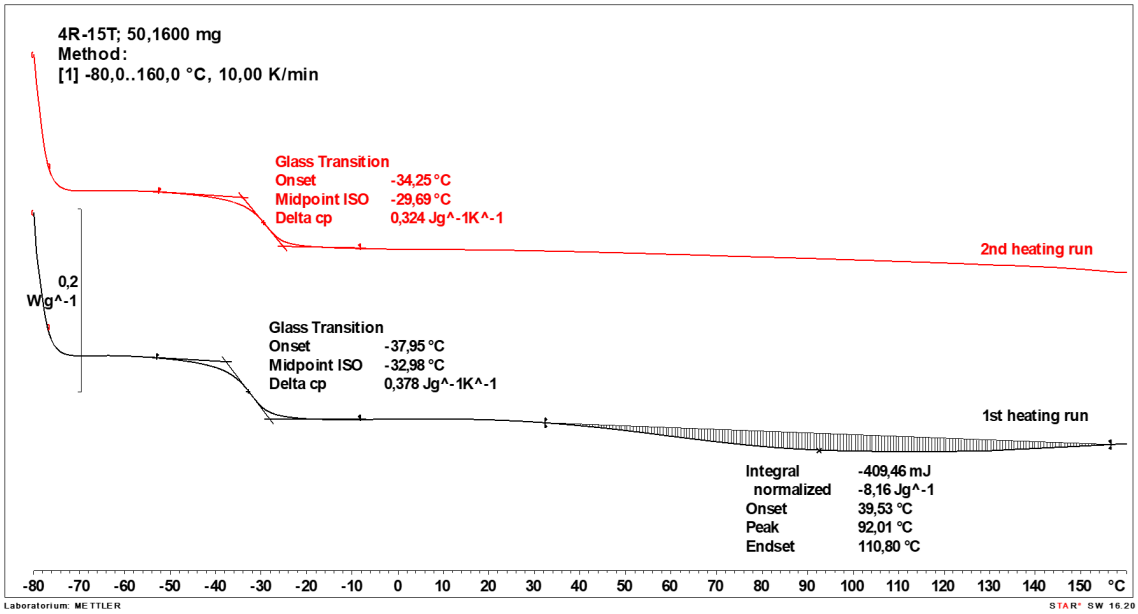


SI-Figure S17 – multi-page: *DSC trace of (e) 0R-5T (polyMEA with 5 wt.% of nano-silica); (f) 4R-5T (polyMEA with 4 wt.% of clay and 5 wt.% of nano-silica).*

SI-Figure S17 – multi-page (continued, last image):

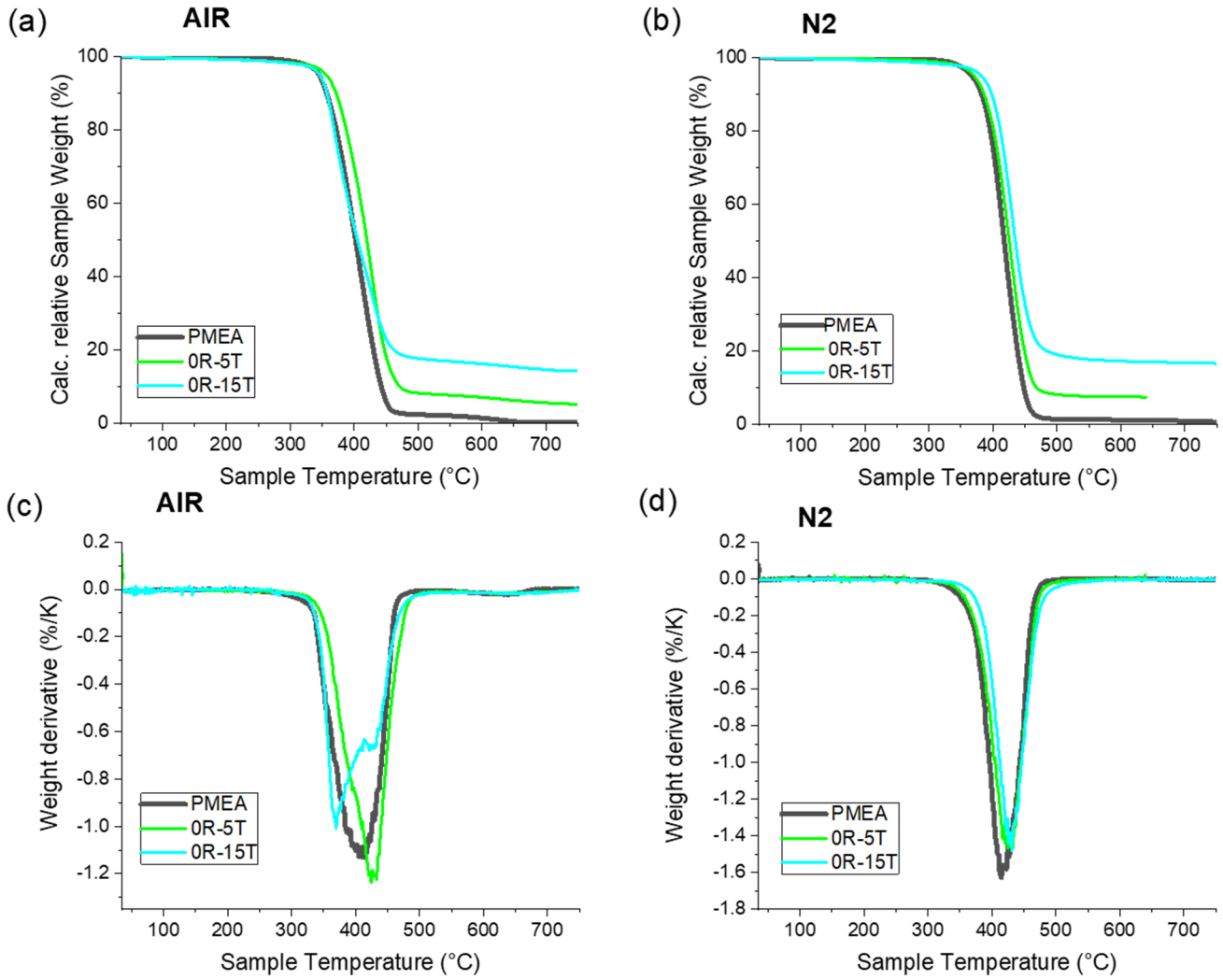
4R-15T

(g)

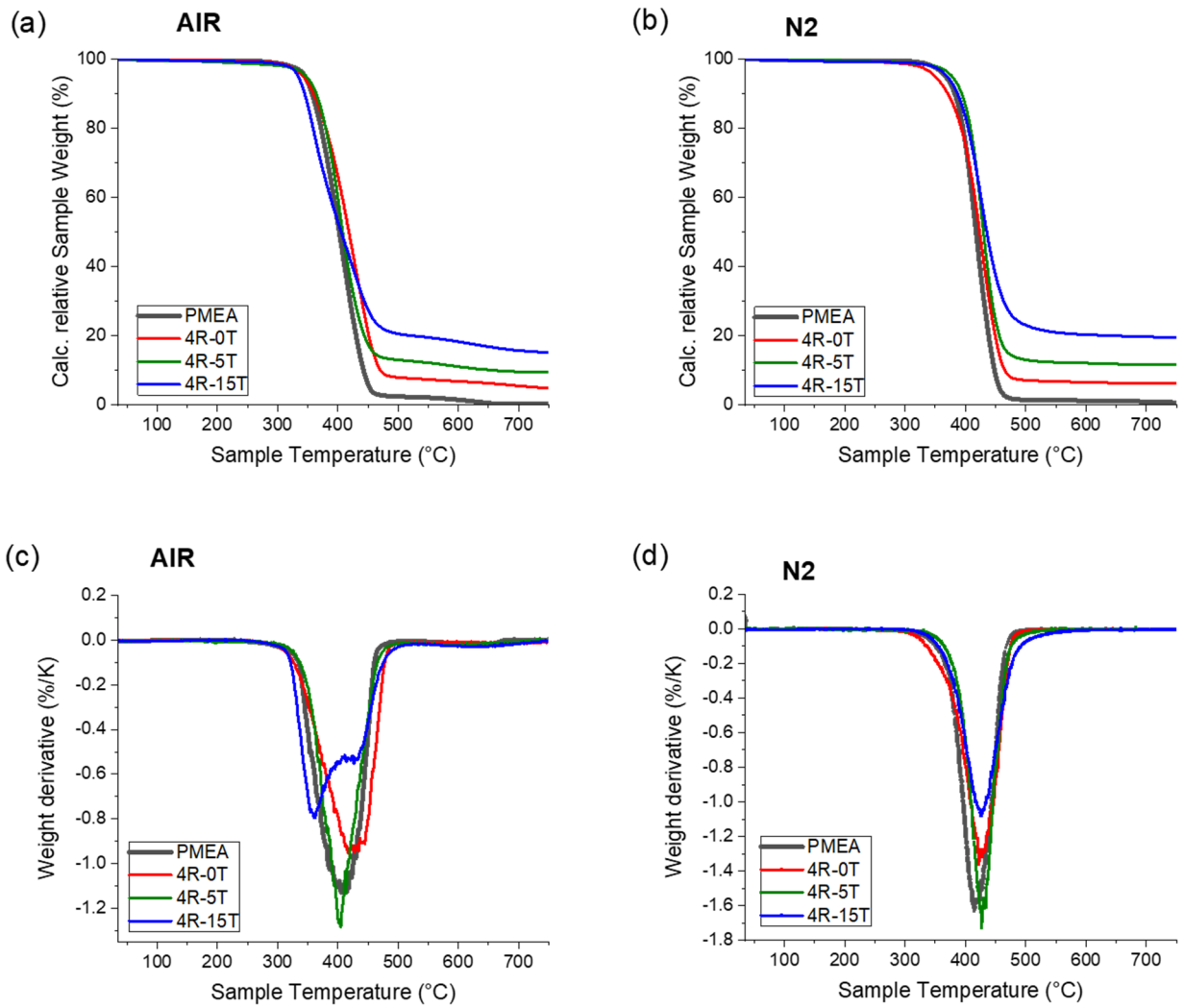


SI-Figure S17: – multi-page (continued, last image): *(g) DSC trace of 4R-15T (polyMEA with 4 wt.% of clay and 15 wt.% of nano-silica).*

5. Stability against oxidative and thermal degradation (TGA)



SI-Figure S18: *TGA traces of the doubly filled polyMEA/clay/silica nanocomposite elastomers: Effect of the silica content (0, 5, 15 wt.%) in combination with 4 wt.% of clay: (a, c) in air; (b, d) in nitrogen atmosphere; (a,b) temperature-dependent relative weight; (c, d) derivative of the relative weight (dTG, decomposition peaks).*



SI-Figure S19: *TGA traces of the polyMEA/clay/silica nanocomposite elastomers: Effect of the silica content (0, 5, 15 wt.%): (a, c) in air; (b, d) in nitrogen atmosphere; (a,b) temperature-dependent relative weight; (c, d) derivative of the relative weight (dTGA, decomposition peaks).*