

Electronic Supplementary Information:

Nanocomposite preparation *via in-situ* polymerization of quaternary ammonium salt ion-bonded to graphite platelets

L. Poláková, H. Beneš, P. Ecorchard, E. Pavlová, Z. Sedláková, J. Kredatusová and V. Štengl

Materials

N-[3-(dimethylamino)propyl] methacrylamide (DMAPMA) and *n*-butyl methacrylate (BuMA) were obtained from Sigma-Aldrich and distilled prior to use. Natural graphite with carbon content of 96 wt.% was obtained from Koh-i-noor Grafite, Ltd., Czech Republic; diameter of graphite flakes was in the range of 3-30 μm . 2,2'-Azobis(2-methylpropionitrile) (Fluka) was recrystallized from methanol. Sodium metal (99.9%), *n*-hexadecyl iodide (95%) and ethylenediamine (en, 99.5%) were obtained from Sigma-Aldrich and used as received. Acetone (p.a., Lach-Ner) and *n*-hexane (p.a., Lach-Ner) were dried over molecular sieves.

Methods of measurements

Thermogravimetric analysis (TGA) coupled with Fourier transform infrared spectroscopy (FTIR) of released gases was performed using a Pyris 1 TGA analyzer (PerkinElmer) coupled with an IR spectrometer Spectrum 100T FT-IR (PerkinElmer) through a transfer line TL 8000 (PerkinElmer). The sample was heated from 35 °C to 800 °C with the heating rate 10 °C/min under flowing nitrogen at 20 mL/min. The infrared spectroscopic cell and the coupling system to TGA were kept at 260 and 250 °C, respectively, to prevent condensation of evolved gases or vapors. FTIR spectra were continuously collected during the whole analysis, and they were recorded in the range of 650–4000 cm^{-1} , at 2 scans per spectrum at 4 cm^{-1} resolution.

FTIR spectra of samples were measured using the attenuated total reflectance (ATR) technique on an IR spectrometer Spectrum 100T FT-IR (PerkinElmer) with a DTSG detector fitted with an Universal ATR accessory with a diamond/ZnSe crystal. All spectra were recorded

in the range of 650-4000 cm^{-1} at 16 scans per spectrum at 4 cm^{-1} resolution. Software Spectrum v2.00 was used for processing the spectra. The samples were directly put on the diamond crystal and measured.

Diffraction patterns of the samples were collected with diffractometer Bruker D2 equipped with conventional X-ray tube (Cu $K\alpha$ radiation, 30 kV, 10 mA). The primary divergence slit module width 0.6 mm, Soller Module 2.5, Air scatter screen module 2 mm, Ni $K\beta$ -filter 0.5 mm, step 0.00405° and time per step 0.3 s and the LYNXEYE 1-dimensional detector were used.

Transmission electron microscopy (TEM) was performed using Tecnai G2 Spirit Twin 12, FEI, Czech Republic. The thin sections of the samples were prepared by an ultramicrotome (Ultracut UCT, Leica, Germany) under cryo-conditions (the sample and knife temperatures were -60 and -40 °C, respectively). Then the ultrathin sections were transferred to a copper TEM grid (300 mesh). All of the micrographs were captured in the bright field mode at an accelerating voltage of 120 kV.

Scanning electron microscopy (SEM) of the pristine graphite, G1 and G2 intercalates was performed using Vega Plus TS 5135 (Tescan, Czech Republic) with secondary electron imaging at 30 kV. The powder samples were fixed on a metallic support using conductive double-adhesive carbon tape (Christine Groepl, Austria).

Electron microscopy images of polymer composites with pristine graphite (PG) and with G2 intercalate (PG2) were collected on FEI NOVA NanoSEM450 in a high-vacuum mode using acceleration voltage 10-30 kV (SEM images) and with using STEM I two segment solid-state diode (STEM images). The samples were dissolved in THF and the solutions were deposited on the Formvar coated grids.

Heat capacity and thermal conductivity of the prepared composites were measured according to ASTM E1952-11 on a calorimeter Q 2000 (TA Instruments, USA) using modulated temperature DSC.

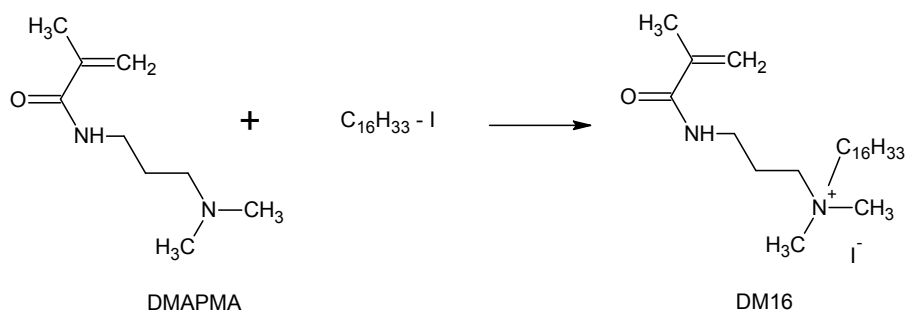
Tensile tests were carried out at 50 °C using an Instron 5800 apparatus at a crosshead speed of 10 $\text{mm}\cdot\text{min}^{-1}$. Samples were first dissolved in THF, poured into open teflon molds and then dried under vacuum. The dried films were cut into the dumb-bell shape (specimen type 5B) with a razor blade. At least five specimens were tested for each sample. The Young's modulus, the stress to break and elongation to break were evaluated. In addition, the energy to break

obtained from the area under the stress–strain curve was determined as a standard measure of the elastomer toughness.

Synthesis

a. DM16 monomer

The reaction proceeded according to the Scheme S1. In a round-bottom flask equipped with magnetic stirrer, thermometer and dropping funnel, DMAPMA monomer (3.2 mL, 17.6 mmol) was mixed with dry acetone (10 mL). The flask was placed into a cooling bath (-5 to 0 °C). Upon stirring and cooling, *n*-hexadecyl iodide (8.3 mL, 26.4 mmol) in dry acetone (25 mL) was added dropwise. The flask was then kept in a refrigerator. After 6 hours the precipitate was filtered off and extracted with dry hexane (2×50 mL). White crystals were filtered off and dried over P₂O₅ in vacuum to a constant weight. *M.p.*: 68-70 °C. *Yield*: 92 %. *Elemental analysis* (% theoretical/found): C (57.46/57.17); H (9.84/9.90); N (5.36/4.58); O (3.06/5.99); I (24.28/22.36). ¹H NMR data (300.1 MHz, MeOD): δ 5.75+5.40 (s+s, 2H, CH₂=), 3.35 (m, 6H, -CH₂N-), 3.1 [s, 6H, -N(CH₃)₂], 2.03 (m, 2H, -CH₂-), 2.00 (s, 3H, -CH₃), 1.73 (m, 2H, -CH₂-), 1.37–1.28 (m, 26H, aliph.), 0.90 (t, 3H, -CH₃). ¹³C NMR data (150 MHz, MeOD): δ 171.4, 141.0, 121.1, 65.5, 63.1, 51.6, 49.7, 37.6, 33.1, 30.7, 27.4, 23.8, 18.9, 14.5, 7.1, 2.0.



Scheme S1 Synthetic route for the preparation of DM16 monomer.

b. G1 intercalate

Graphite intercalated with sodium-ethylenediamine complex (GIC G1) was synthesized using a slightly modified procedure described in literature.⁴⁻⁵ Graphite (500 mg) and

freshly cut sodium (100 mg) were dispersed in ethylenediamine (en; 6 mL). The mixture was bubbled thoroughly with nitrogen and sealed. The reaction proceeded upon stirring for 24 h at 60 °C. Subsequently, 20 mL of en was added to dissolve unreacted sodium, supernatant was then separated by centrifugation and the solid was dried in vacuum to a constant weight.

c. *G2 intercalate*

G1 (79 mg) was dispersed in a solution of DM16 monomer (915 mg) in DMF (2 mL), reaction mixture was bubbled with nitrogen and sealed. The reaction was carried out upon stirring overnight at 25 °C. The product was filtered off, washed carefully three times with acetonitrile and methanol and dried in vacuum to a constant weight.

d. *G3 intercalate*

G1 (79 mg) was dispersed in a solution of *n*-hexadecyl iodide (617 mg) in DMF (2 mL), reaction mixture was bubbled with nitrogen and sealed. The reaction was carried out upon stirring overnight at 25 °C. The product was filtered off, washed carefully three times with acetonitrile and methanol and dried in vacuum to a constant weight.

e. *polymer composites PG, PG1, PG2 and PG3*

In a typical experiment, G2 (1 mg, 0.1 wt.%), *n*-butyl methacrylate (BuMA; 999 mg, 99.9 wt.%) and DMSO (2 mL) were placed into a 5 mL ampoule, the ampoule was closed and placed into refrigerator overnight to allow the intercalate to “swell” in the liquid medium. Prior to polymerization, the mixture was gently stirred for 1 h at room temperature, then 2,2'-azobis(2-methylpropionitrile) (5.7 mg, 0.5 mol.%) was added. The polymerization proceeded under inert atmosphere for 2.5 h at 60 °C. The resulting grey polymer PG2 was immersed in methanol several times and the precipitate was dried in vacuum. Homopolymer polyBuMA as well as polymer composites PG1, PG2 (with 0.05 wt.%, 0.25 wt.% and 0.5 wt.% of G2), PG3 and PG filled with G1, G3 and pristine graphite, respectively, were also synthesized under similar conditions.

FTIR spectroscopic measurements of gases evolved during TGA

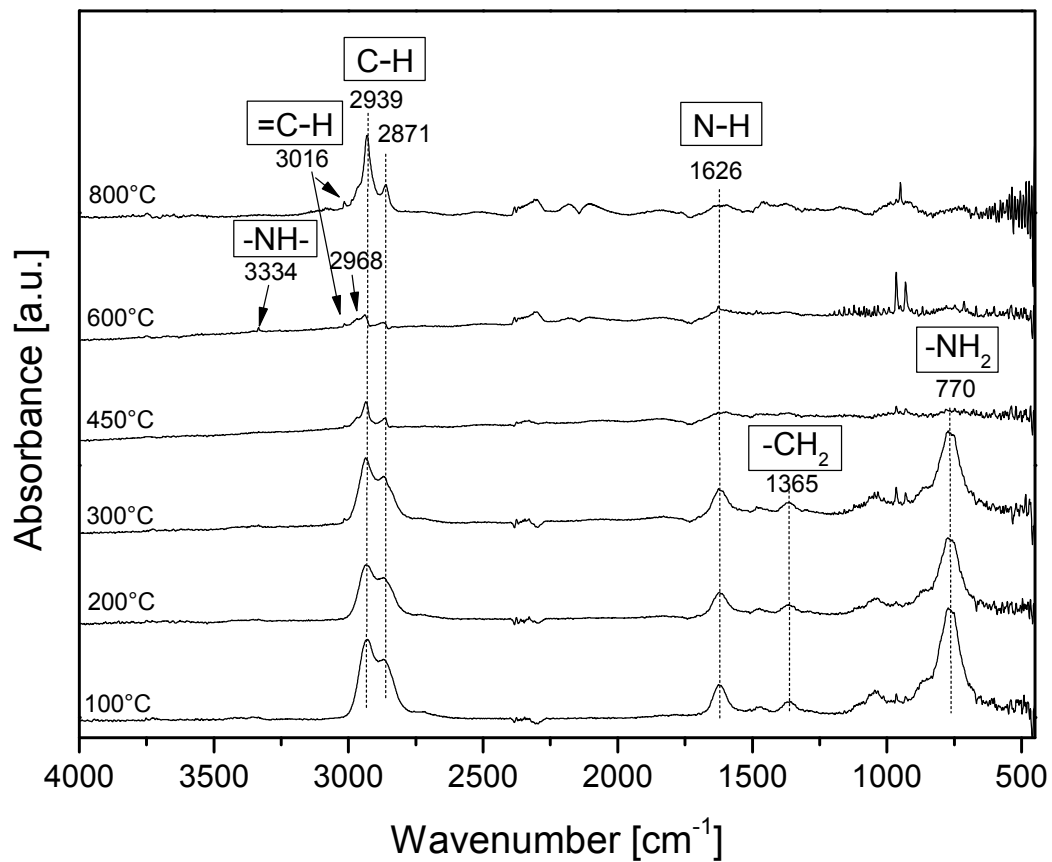


Fig. S1: TGA coupled with FTIR spectroscopic measurements: FTIR spectra of the gases released during TGA of G2 intercalate at different temperatures.

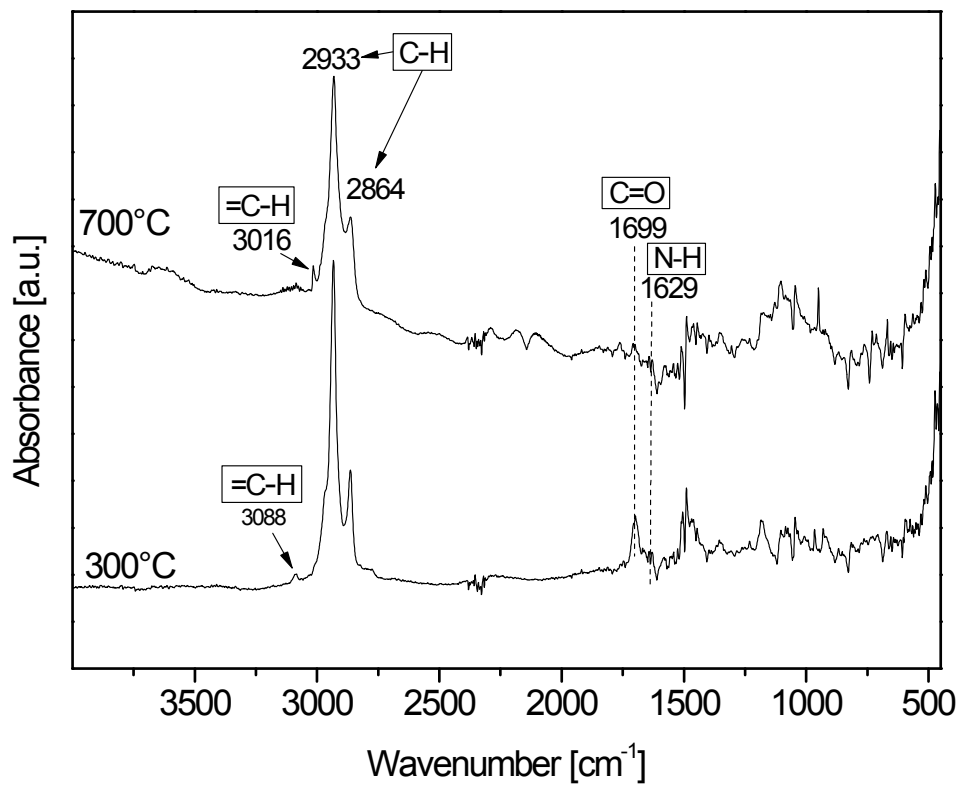


Fig. S2: TGA coupled with FTIR spectroscopic measurements: FTIR spectra of the gases released during TGA of DM16 at different temperatures.

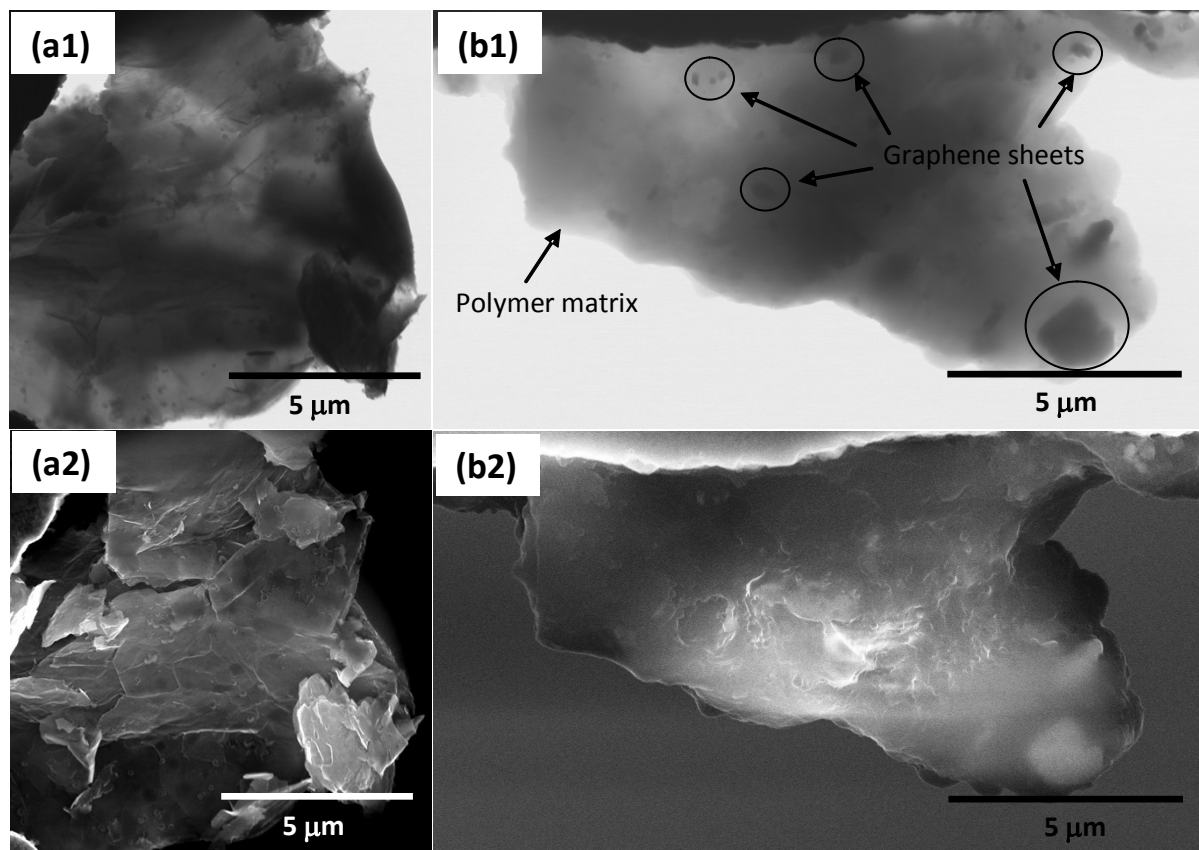


Fig. S3: STEM (a1 and b1) and SEM (a2 and b2) images of polymer composites filled with 0.1 wt.% of (a) pristine graphite (PG) and (b) G2 intercalate (PG2).

PG3 polymer composite

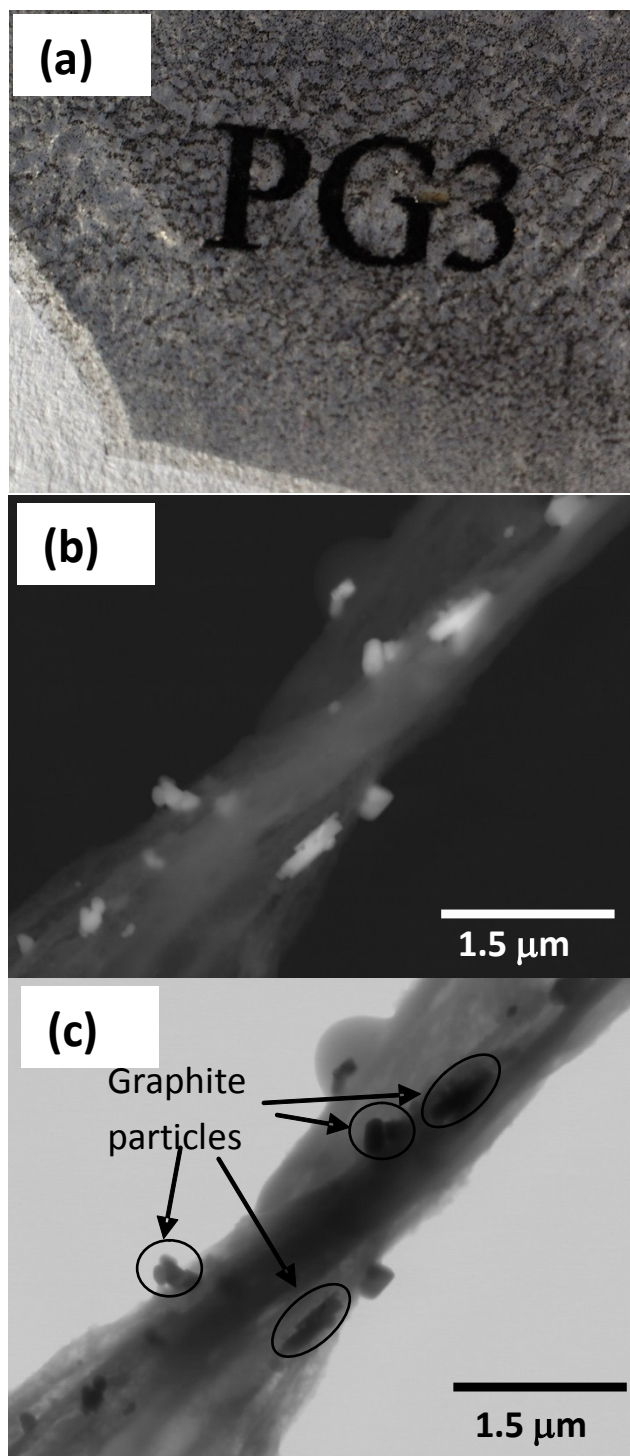


Fig. S4: Photo of PG3 polymer membrane (200 μm thick) (a). SEM (b) and STEM (c) images of PG3 polymer composite.

Table S1: Radii of the atoms involved in tetrahedral conformation (DM16 monomer) for calculation of the layer thickness in the G2 intercalate.

Element	Type of the radius	Value of the radius (pm)
nitrogen	ionic	65
carbon	covalent	77
hydrogen	covalent	37

Tensile test

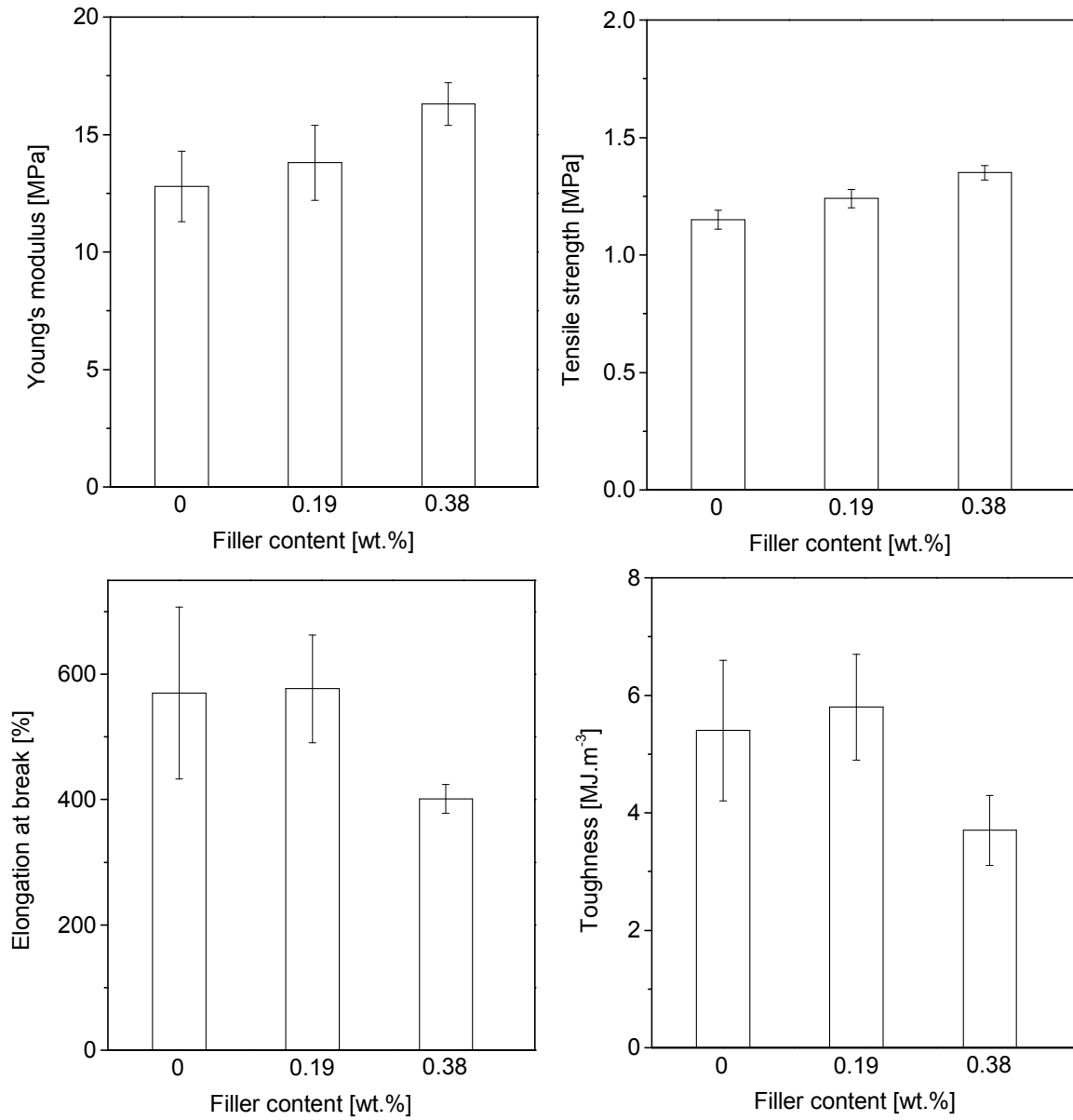


Fig. S5: Mechanical properties of the neat polymer matrix (polyBuMA) and PG2 polymer nanocomposites. The filler content stands for the total content of graphite/graphene in the composite.