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Hybrid cyclotriphosphazene–polysiloxane–nano-SiO_2 composites with improved mechanical properties

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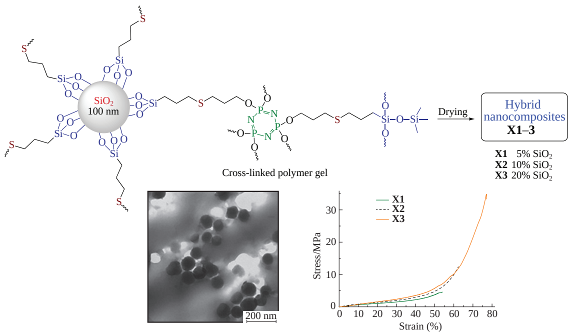
Starting from the functional cyclotriphosphazene, polysiloxane and nano-SiO_2 precursors, three new hybrid nanocomposites with reinforced mechanical properties were prepared. Young's modulus values for all the composite samples are similar in the range of 7–11 MPa, stress at fracture increases with the nano-SiO_2 content increase in the material and reaches a maximum value of 36 MPa for the composite with 20% nano-SiO_2. The nanocomposites investigated are elastic and demonstrate the ability to be deformed without failure up to 54% strain.



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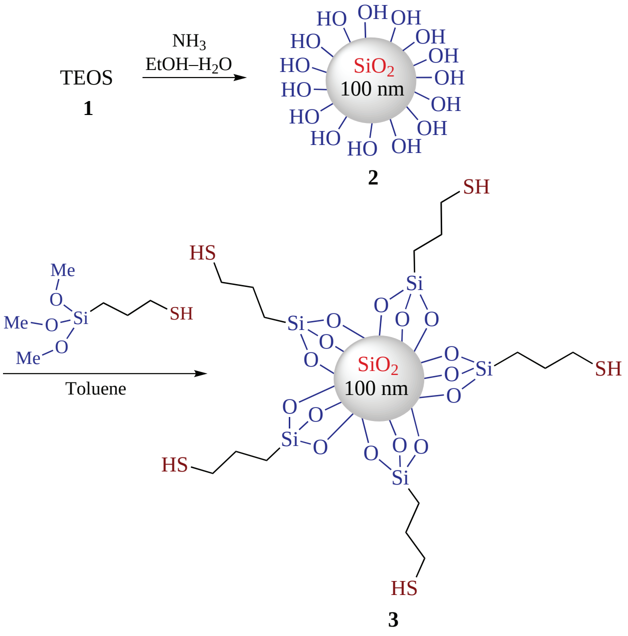
Hybrid polymer systems that combine organic and inorganic components at the molecular level attract attention due to their unusual fine-tunable properties that allow one to develop new-generation materials with improved physical and mechanical properties for different areas of polymer chemistry and materials science.[1–3] Functional phosphazenes[4–6] and siloxanes[7–16] as promising precursors for the preparation of hybrid organoelement polymers possess low toxicity, biocompatibility, biodegradability and nonflammability. For the preparation of hybrid polymers, traditional organic or inorganic solvents,[17] supercritical fluids[18–21] or solvent-free media are used.[22] As an example, new cross-linked polymers with various structures based on the (3-mercaptopropyl)polysiloxane and cyclic allyloxyphosphazene precursors prepared by thiol–ene 'click' reactions[4] exhibited good mechanical properties and thermal stability. To improve the properties of polymers such as tensile strength, elongation at break and Young's modulus, addition of inorganic particles is typically employed resulting in a composite material. Compared with single materials, the composite ones can have a unique combination of properties. Thus, addition of nanoparticles is known to improve mechanical, thermal, electrical, optical and magnetic properties of the corresponding nanocomposites.[23] The composites were obtained from various combinations of polymers and inorganic nanoparticles such as poly(glycidyl methacrylate)–SiO_2,[24] polydimethylsiloxane–TiO_2,[25] polylactide–SiO_2,[26] poly(trimethylolpropane triacrylate)–SiO_2,[27] polydimethylsiloxane–nanodiamond[28] and polystyrene–hematite.[29] Nanocomposites find numerous applications as materials with exceptional physical, catalytic, biomedical[30] and antibacterial[25] properties as well as are employed for packaging[31] and coating.[32,33] Based on poly(propylene oxide)–poly(ethylene oxide)–poly(propylene oxide) triblock chains and surface-modified SiO_2 nanoparticles, a cross-linked nanocomposite polymer electrolyte (CNPE) was developed.[34] The preparation of homogeneous nanocomposites is hampered by spontaneous aggregation of nanoparticles in the matrix leading to a reduction of the mutual specific contact area and deterioration of the expected properties.[35] To reduce the aggregation and to improve the dispersion of nanoparticles in the matrix, grafting the polymers onto the nanoparticles surface is used.[24,36]

In this work, we synthesized a series of new hybrid nanocomposite materials with reinforced mechanical properties, starting from 2,2,4,4,6,6-hexa(2-propen-1-yloxy)cyclotriphosphazene, thiol-containing oligosiloxane and SH-functionalized SiO_2 nanoparticles using the method similar to that described by us.[4] The required distribution of SiO_2 nanoparticles was achieved through their SH-functionalization (Scheme 1). Spherical nano-SiO_2 **2** was prepared by the Stöber method from tetraethoxysilane (TEOS) **1**. Then, SH-functionalized nano-SiO_2 **3** was obtained from particles **2** after treatment with (3-mercaptopropyl)trimethoxysilane in toluene. Dispersity and size of particles **3** were determined using SEM, they kept almost the same mean diameter of ~100 nm (Figure S1, Online Supplementary Materials).

2,2,4,4,6,6-Hexa(2-propen-1-yloxy)cyclotriphosphazene **4** (Scheme 2) was obtained by the known method.[37] Low-molecular-weight branchy 3-mercaptopropylsilsesquioxane **5** with terminal trimethylsilyl groups, having $M_n = 780$ Da, $M_w = 840$ Da and PDI = 1.08 corresponding to oligomer with average four 3-mercaptopropylsiloxy groups, was synthesized employing the method described by us.[7] The final composite materials were prepared by the hydrothiolation 'click' reaction using DMPA as an initiator under the 365 nm UV lamp irradiation for 30 min with subsequent slow evaporation of solvent from the resulting cross-linked polymer gel **6** (see Scheme 2). Thus, three



Scheme 1

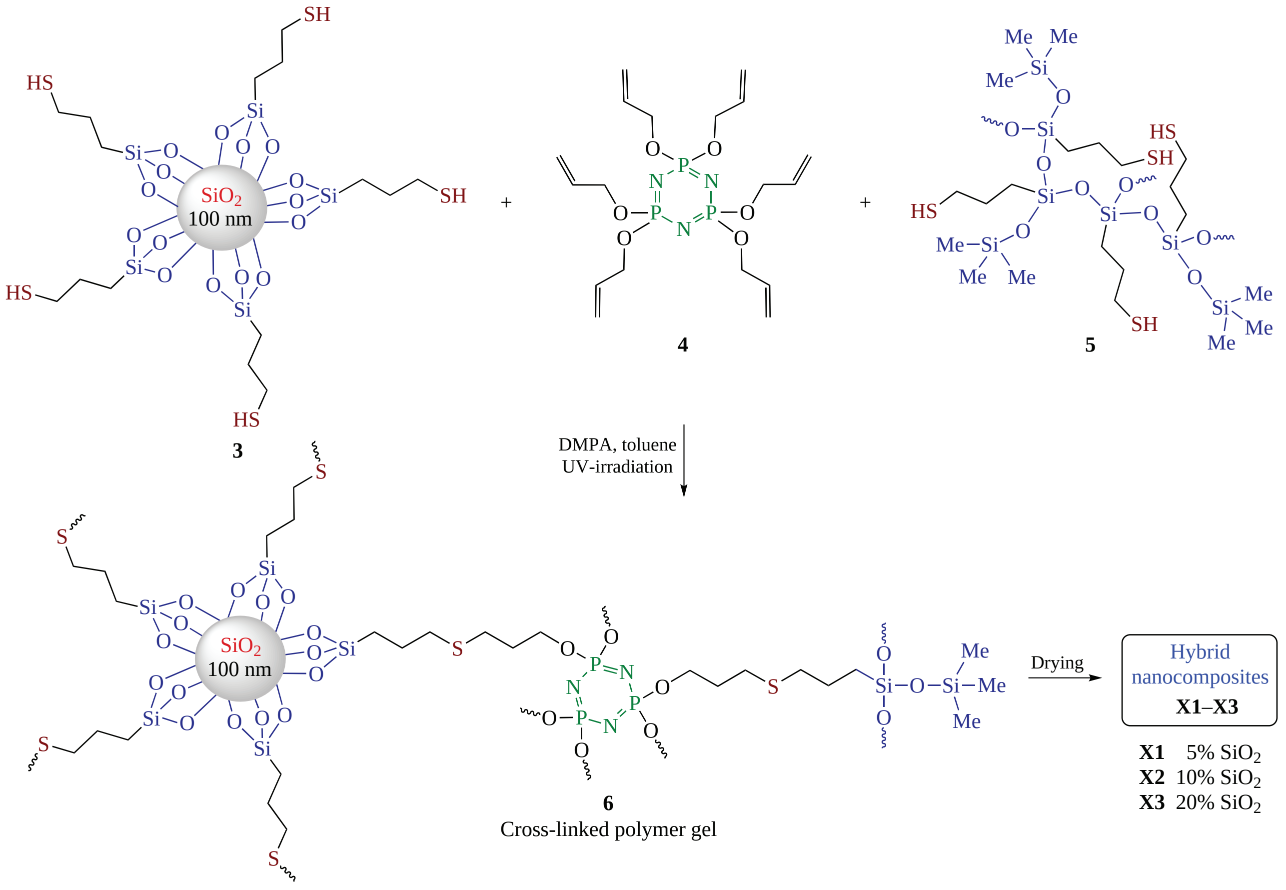
slightly springy opaque samples with equimolar ratio of transformed precursors **4** and **5** as well as various content of nano-SiO_2, namely 5, 10 and 20% for the samples **X1**, **X2** and **X3**, respectively, were obtained (for details, see Online Supplementary Materials).

Morphological investigation of the nanocomposites was carried out with their slices using transmission electron microscopy (TEM). Microstructure of all the composites is homogeneous with almost identical nano-SiO_2 inclusions having mean diameter ~100 nm (Figure S2). As follows from the micrographs, the content of nano-SiO_2 in samples **X2** and **X3** is much higher compared with composite **X1**, conglomeration of nanoparticles being observed for all the samples.

The mechanical properties of the nanocomposites were explored by compression test (Figure 1, Table 1). Composites **X1**, **X2** and **X3** have similar behavior under compression up to 50% of the original size (see Figure 1). Until 50% deformation, no cracking was observed. However, further deformation of the samples demonstrated the difference in their strength, their stress at fracture increased with the content of nano-SiO_2. The lowest stress at fracture 4.6 MPa was revealed for composite **X1** with 5% nano-SiO_2. It is interesting, that this value is lower than the one for the hybrid material without nano-SiO_2 (11.6 MPa) obtained in our work.[4] Increase in the nano-SiO_2 amount to 10% resulted in the stress at fracture value of 12.6 MPa, which indicated reduction of the nanocomposite robustness after introduction of up to 10% nano-SiO_2. When the content of nano-SiO_2 reached 20%, the sample robustness increased drastically and the material was destroyed at the stress value of 36 MPa. At the same time, strain at fracture also increased from 54 to 77% with the elevation of nano-SiO_2 content in the sample from 5 to 20%. Young's modulus values for composites **X1**–**X3** are similar in the range of 7–11 MPa.

The prepared samples demonstrated the ability to be deformed without failure. Therefore, cyclic tests were carried out comprising 10 cycles with a maximum strain of 10% for composites **X1** and **X2**. The character of resulting stress–strain curves for both materials is very close, which indicates the same type of polymer network (Figure 2).

In summary, new hybrid cross-linked polymers with reinforced mechanical properties were prepared from the cyclotriphosphazene, oligosiloxane and nano-SiO_2 precursors by the hydrothiolation 'click' reaction, their mechanical properties were investigated by compression test. Young's



Scheme 2

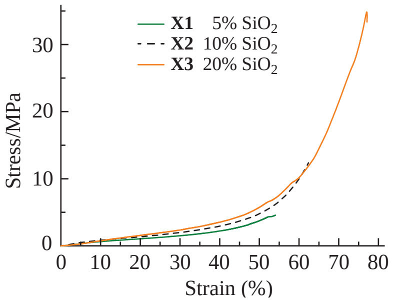


Figure 1 Stress–strain curves of nanocomposites **X1**–**X3**.

Table 1 Mechanical properties of nanocomposites **X1**–**X3**.

Sample	Stress at fracture/MPa	Strain at fracture (%)	Young’s modulus/MPa
X1	4.6	54	7
X2	12.6	63	11
X3	36	77	9
Without SiO_2 (from our work[4])	11.6	53	14

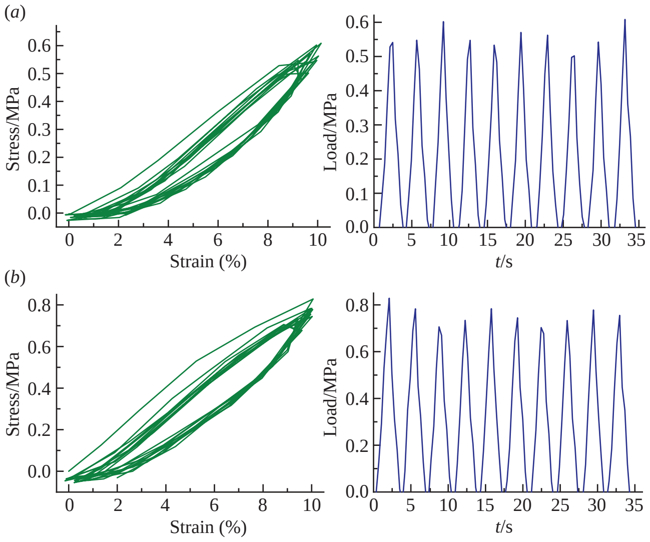


Figure 2 Stress–strain and load–time cyclic curves of nanocomposites (*a*) **X1** and (*b*) **X2**.

modulus values for all the samples are similar in the range of 7–11 MPa. Stress at fracture increases with the nano-SiO_2 content increase and reaches a maximum value of 36 MPa for the nanocomposite with 20% SiO_2. The materials prepared demonstrated the ability to be deformed without failure, which was estimated using cyclic compression tests.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.03.027.

References

1 M. Faustini, L. Nicole, E. Ruiz-Hitzky and C. Sanchez, *Adv. Funct. Mater.*, 2018, **28**, 1704158.
2 S. H. Mir, L. A. Nagahara, T. Thundat, P. Mokarian-Tabari, H. Furukawa and A. Khosla, *J. Electrochem. Soc.*, 2018, **165**, B3137.
3 G. A. Abakumov, A. V. Piskunov, V. K. Cherkasov, I. L. Fedushkin, V. P. Ananikov, D. B. Eremin, E. G. Gordeev, I. P. Beletskaya, A. D. Averin, M. N. Bochkarev, A. A. Trifonov, U. M. Dzhemilev, V. A. D’yakonov, M. P. Egorov, A. N. Vereshchagin, M. A. Syroeshkin, V. V. Jouikov, A. M. Muzafarov, A. A. Anisimov, A. V. Arzumanyan, Yu. N. Kononevich, M. N. Temnikov, O. G. Sinyashin, Yu. H. Budnikova, A. R. Burilov, A. A. Karasik, V. F. Mironov, P. A. Storozhenko, G. I. Shcherbakova, B. A. Trofimov, S. V. Amosova, N. K. Gusarova, V. A. Potapov, V. B. Shur, V. V. Burlakov, V. S. Bogdanov and M. V. Andreev, *Russ. Chem. Rev.*, 2018, **87**, 393.
4 D. A. Khanin, Y. N. Kononevich, M. N. Temnikov, V. P. Morgalyuk, V. G. Vasil’ev, A. Y. Popov, V. K. Brel, V. S. Papkov and A. M. Muzafarov, *Polymer*, 2020, **186**, 122011.
5 H. R. Allcock, *Appl. Organomet. Chem.*, 2010, **24**, 600.
6 H. R. Allcock, *Appl. Organomet. Chem.*, 2013, **27**, 620.
7 M. N. Temnikov, Y. N. Kononevich, I. B. Meshkov, M. I. Buzin, V. G. Vasil’ev, G. G. Nikiforova and A. M. Muzafarov, *Polymer*, 2018, **138**, 255.
8 C. Sanchez, P. Belleville, M. Popall and L. Nicole, *Chem. Soc. Rev.*, 2011, **40**, 696.
9 A. Mehdi, C. Reye and R. Corriu, *Chem. Soc. Rev.*, 2011, **40**, 563.
10 I. Tkachenko, Y. Kononevich, Y. Kobzar, O. Purikova, Y. Yakovlev, I. Khalakhan, A. Muzafarov and V. Shevchenko, *Polymer*, 2018, **157**, 131.
11 *Organic–Inorganic Hybrid Nanomaterials*, eds. S. Kalia and Y. Haldorai (*Advances in Polymer Science*, eds. A. Abe, A.-C. Albertsson, G. W. Coates, J. Genzer, S. Kobayashi, K.-S. Lee, L. Leibler, T. E. Long, M. Möller, O. Okay, V. Percec, B. Z. Tang, E. M. Terentjev, P. Theato, B. Voit, U. Wiesner and X. Zhang, vol. 267), Springer, Cham, 2015.
12 M. N. Temnikov, Y. N. Kononevich, A. Y. Popov, V. G. Vasil’ev and A. M. Muzafarov, *ChemistrySelect*, 2020, **5**, 5014.
13 E. E. Kim, Y. N. Kononevich, A. A. Anisimov, M. I. Buzin, V. G. Vasil’ev, A. A. Korlyukov, D. S. Ionov, D. A. Khanin, E. V. Shtykova, V. V. Volkov and A. M. Muzafarov, *React. Funct. Polym.*, 2021, **164**, 104896.
14 E. Yu. Katarzhnova, E. A. Tatarinova, G. M. Ignat’eva, N. G. Vasilenko, I. B. Meshkov and A. M. Muzafarov, *Mendeleev Commun.*, 2021, **31**, 393.
15 M. A. Obrezkova, I. I. Saraeva, G. M. Ignat’eva, N. G. Vasilenko and A. M. Muzafarov, *Mendeleev Commun.*, 2021, **31**, 704.
16 V. A. Vasnev, B. A. Izmaylov, V. V. Istratov, G. D. Markova and O. V. Baranov, *Russ. Chem. Bull.*, 2021, **70**, 1471.
17 M. M. Adnan, A. R. M. Dalod, M. H. Balci, J. Glaum and M.-A. Einarsrud, *Polymers*, 2018, **10**, 1129.
18 C. A. García-González, J.-M. Andanson, S. G. Kazarian, J. Saurina and C. Domingo, *Compos. Interfaces*, 2009, **16**, 143.
19 T. Mousavand, S. Takami, M. Umetsu, S. Ohara and T. Adschiri, *J. Mater. Sci.*, 2006, **41**, 1445.
20 E. S. Alekseev, A. Yu. Alentiev, A. S. Belova, V. I. Bogdan, T. V. Bogdan, A. V. Bystrova, E. R. Gafarova, E. N. Golubeva, E. A. Grebenik, O. I. Gromov, V. A. Davankov, S. G. Zlotin, M. G. Kiselev, A. E. Koklin, Yu. N. Kononevich, A. E. Lazhko, V. V. Lunin, S. E. Lyubimov, O. N. Martyanov, I. I. Mishanin, A. M. Muzafarov, N. S. Nesterov, A. Yu. Nikolaev, R. D. Oparin, O. O. Parenago, O. P. Parenago, Ya. A. Pokusaeva, I. A. Ronova, A. B. Solovieva, M. N. Temnikov, P. S. Timashev, O. V. Turova, E. V. Filatova, A. A. Philippov, A. M. Chibiryaev and A. S. Shalygin, *Russ. Chem. Rev.*, 2020, **89**, 1337.
21 M. A. Pigaleva, I. V. Elmanovich, Y. N. Kononevich, M. O. Gallyamov and A. M. Muzafarov, *RSC Adv.*, 2015, **5**, 103573.
22 L. C. E. da Silva, L. G. L. Germiniani, T. S. Plivelic and M. C. Gonçalves, *Soft Matter*, 2018, **14**, 1709.
23 S. Mallakpour and M. Naghdi, *Prog. Mater. Sci.*, 2018, **97**, 409.
24 J. M. Kubiak and R. J. Macfarlane, *Adv. Funct. Mater.*, 2019, **29**, 1905168.
25 N. K. Sethy, Z. Arif, P. K. Mishra and P. Kumar, *J. Polym. Eng.*, 2020, **40**, 211.
26 F. Hedayati, N. Moshiri-Gomchi, M. Assaran-Ghomi, S. Sabahi, N. Bahri-Laleh, S. Mehdipour-Ataei, J. Mokhtari-Aliabad and S. A. Mirmohammadi, *Polym. Adv. Technol.*, 2020, **31**, 566.
27 C. I. Jo, J. Ko, Z. Yin, Y.-J. Kim and Y. S. Kim, *Ind. Eng. Chem. Res.*, 2016, **55**, 9433.
28 A. Kausar, *Polym.-Plast. Technol. Mater.*, 2020, **59**, 1148.
29 A. Kausar, *Polym.-Plast. Technol. Mater.*, 2020, **59**, 323.

30 D. Ponnamma, J.-J. Cabibihan, M. Rajan, S. S. Pethaiah, K. Deshmukh, J. P. Gogoi, S. K. K. Pasha, M. B. Ahamed, J. Krishnegowda, B. N. Chandrashekar, A. R. Polu and C. Cheng, *Mater. Sci. Eng., C*, 2019, **98**, 1210.
31 A. Kausar, *J. Plast. Film Sheeting*, 2020, **36**, 94.
32 T. M. A. Bui, T. V. Nguyen, T. M. Nguyen, T. H. Hoang, T. T. H. Nguyen, T. H. Lai, T. N. Tran, V. H. Nguyen, V. H. Hoang, T. L. Le, D. L. Tran, T. C. Dang, Q. T. Vu and P. Nguyen-Tri, *Mater. Chem. Phys.*, 2020, **241**, 122445.
33 M. D'Arienzo, S. Dirè, E. Cobani, S. Orsini, B. Di Credico, C. Antonini, E. Callone, F. Parrino, S. Dalle Vacche, G. Trusiano, R. Bongiovanni and R. Scotti, *Coatings*, 2020, **10**, 913.
34 S. Tang, Q. Lan, L. Xu, J. Liang, P. Lou, C. Liu, L. Mai, Y.-C. Cao and S. Cheng, *Nano Energy*, 2020, **71**, 104600.
35 D. W. Schaefer and R. S. Justice, *Macromolecules*, 2007, **40**, 8501.
36 M. Bonnevide, T. N. T. Phan, N. Malicki, S. K. Kumar, M. Couty, D. Gigmes and J. Jestin, *Polymer*, 2020, **190**, 122190.
37 M. Dutkiewicz, M. Przybylak, R. Januszewski and H. Maciejewski, *Polym. Degrad. Stab.*, 2018, **148**, 10.

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