

Polyhedral oligomeric silsesquioxane-based hybrid networks obtained via thiol-epoxy click chemistry

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Abstract A series of hybrid networks based on polyhedral oligomeric silsesquioxane (POSS) were prepared by thiol-epoxy click reaction using commercially available octakisglycidyl-POSS (G-POSS), trimethylolpropane triglycidyl ether, and trimethylolpropane tris(3-mercaptopropionate) as monomers. The click reaction was simply catalyzed by lithium hydroxide which proceeded readily at ambient conditions in very good yields. The incorporation of G-POSS into the network was clearly determined by transmission electron microscopy, FTIR, and ¹H-NMR spectroscopy techniques performed with a model study using 1-butane thiol and G-POSS molecules. The homogeneous distribution of G-POSS up to 5 wt% in the hybrid network was apparently confirmed by morphological investigations. By increasing G-POSS content higher than 5 wt%, the heterogeneous dispersion of G-POSS was determined from the tensile strength measurements. The significant decrease in tensile strength was possible due to the agglomeration of G-POSS. On the other hand, thermal properties of hybrid networks were compared together by thermogravimetric analyses, where all samples exhibited one-step degradation in the range of 220–500 °C. The thermal decomposition of hybrid network led to complete degradation of the organic part and favored the formation of stable carbonaceous and inorganic residues as char. Thus, the char yields of hybrid networks were increased to 6.2, 7.8, 10.1, 12.7, and 15.1% by G-POSS loadings from 0 to 15 wt%. This improvement

was also a proof of the incorporation of G-POSS into the hybrid networks that resulted in high heat-resistant POSS-based hybrid networks compared to a sample without G-POSS.

Keyword Click chemistry · Hybrid networks · Polyhedral oligomeric silsesquioxanes · Thermosets · Thiol-epoxy reaction

Introduction

A combination of inorganic nanofillers and organic polymers may produce desirable properties in a single hybrid material [1]. Compatibility and miscibility of the initial components to control physical characteristics of final products are the most difficult problems in the production of hybrid materials [2]. Because of their hybrid structures, polyhedral oligomeric silsesquioxanes (POSS) are one of the most popular nanofillers having three dimensions ranging from 1 to 3 nm [3]. Hence, these molecules can be easily combined with almost all kinds of thermoplastics [4, 5] or thermosets [6–8] by blending, grafting, crosslinking, or copolymerization processes.

Click chemistry involves synthesis reactions developed to join two molecules rapidly in a single step without generating side products [9]. Due to their simplicity, these reactions can be found in a broad spectrum of applications such as bio-conjugation, radio-labeling of peptides, dendrimer and polymer synthesis, and modification of heterogeneous surfaces [10, 11]. The copper-catalyzed azide-alkyne cycloaddition [12, 13], Diels-Alder cycloaddition [14], oxime/hydrazone formation, and thiol-based [15] reactions have been adopted as click reactions in the literature [16–18]. Among them,

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thiol-based (e.g., thiol-ene, thiol-yne, thiol-epoxy, and thiol-Michael) click reactions [19] provide several advantages such as metal-free catalyst system, reasonable reaction times, using benign or no solvent, and requirement of simple purification techniques.

Because of its distinct characteristics regarding selectivity, controllability, fastness, and high efficiency, thiol-epoxy reaction was considered as “click” chemistry reaction. Thiol-epoxy click reaction has been utilized in several applications [20] such as polymer synthesis [21, 22] and functionalization [23–25], hydrogel [26] and high-performance coatings [27–29], etc. [30, 31]. For example, linear polymers with reactive hydroxyl groups are easily prepared from commercially available 1,4-butanediol diglycidyl ether and 1,2-ethanedithiol monomers using lithium hydroxide as catalyst. The subsequent post-functionalization of this polymer allows a side-functional polymer to be obtained containing photoactive group [22].

In this study, polyhedral oligomeric silsesquioxane (POSS)-based hybrid networks were prepared by thiol-epoxy click chemistry using commercially available multifunctional compounds, trimethylolpropane triglycidyl ether and trimethylolpropane tris(3-mercaptopropionate) as monomers and octakis-glycidyl-POSS (G-POSS) as a hybrid comonomer. The thiol-epoxy crosslinking polymerization was simply conducted under mild conditions (presence of oxygen and moisture at room temperature) using lithium hydroxide as catalyst. The influence of G-POSS concentration on the mechanical and thermal properties of the obtained hybrid networks was also investigated by transmission electron microscopy, thermogravimetric analysis, and a universal test machine. Besides, the incorporation of G-POSS into the network was also confirmed by FTIR and $^1\text{H-NMR}$ spectroscopy techniques which was performed with a model study using 1-butanethiol and G-POSS molecules.

Experimental

Materials

Octakis-glycidyl-POSS (G-POSS, Hybrid Plastic, USA), trimethylolpropane triglycidyl ether (TTE, technical grade, Sigma-Aldrich, Germany), trimethylolpropane tris(3-mercaptopropionate) (TMPMP, $\geq 95.0\%$, Sigma-Aldrich, Germany), 1-butanethiol (99%, Sigma-Aldrich, Germany), and lithium hydroxide monohydrate (LiOH, 99.95%, Sigma-Aldrich, Germany) were used as received. Dimethyl sulfoxide (99.9%, Merck, Germany), tetrahydrofuran (99.9%, Sigma-Aldrich, Germany), and deionized water were used as solvents.

Analysis

The Perkin-Elmer FTIR Spectrum One B spectrometer was used for FTIR analysis. The Agilent NMR System VNMR5 500 spectrometer was used at room temperature in CDCl_3 with $\text{Si}(\text{CH}_3)_4$ as an internal standard for $^1\text{H-NMR}$ analyses. The thermogravimetric analysis was conducted by Perkin-Elmer Diamond TA/TGA with a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen flow (200 mL/min). Transmission electron microscopy (TEM) observation was utilized by an FEI TecnaiTM G² F30 instrument operating at an acceleration voltage of 200 kV. Ultra-thin TEM specimens around 100 nm were cut by a cryo-ultramicrotome (EMUC₆ + EMFC₆, Leica) equipped with a diamond knife. Before TEM analyses, the obtained specimens were placed on porous carbon-coated grids. The tensile properties of samples were determined with a Zwick/Roell Z1.0 universal test machine at room temperature according to the DIN EN ISO 527-1 standard with a crosshead speed of 5 mm/min. For each sample, at least three specimens were tested to provide reproducibility.

Preparation of POSS-based hybrid networks via thiol-epoxy click chemistry

TMPMP (2.51 mmol, 1 g) and TTE (2.51 mmol, 0.76 g) with various G-POSS loadings (0, 2, 5, 10 or 15% by weight) in THF (4.5 mL) were stirred with a magnetic stirrer at room temperature. LiOH (0.55 mmol, 23 mg) dissolved in distilled water (0.5 mL) was added into the resulting solution and the mixture was further stirred for a few minutes to obtain a completely homogeneous mixture. The solutions were poured into glass petri dishes and hybrid network structures were rapidly obtained after 5 min as a result of exothermic reactions. The samples were dried in a vacuum oven for 24 h at room temperature before the characterization.

Results and discussion

The combination of organic and inorganic components at nanoscale not only allows the construction of hybrid networks but also permits the coexistence of competing material properties (mechanical, thermal, optical, chemical resistance, permeability, density, etc.) in one material.

Typically, two different approaches can be used for the formation of hybrid materials: (1) well-defined pre-formed building blocks are reacted with each other to form a hybrid material in which the precursors still, at least partially, keep their original integrity and (2) one or both structural units are formed from the precursors that are transformed into a novel network structure [32].

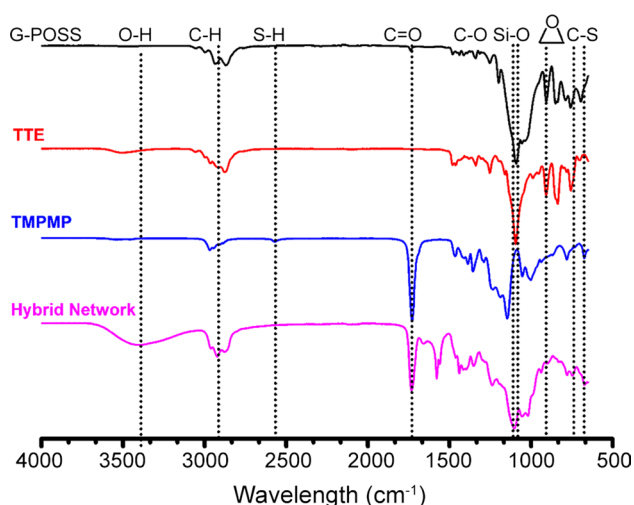
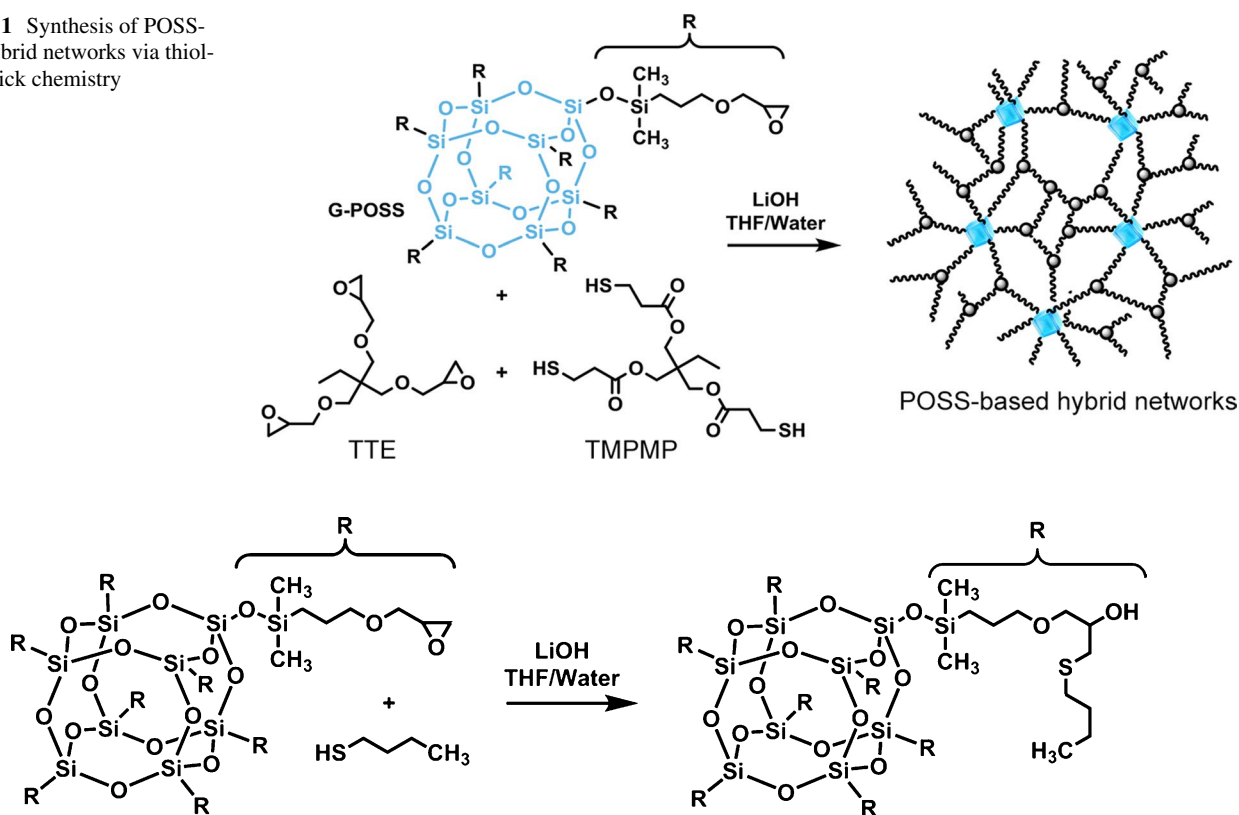


Fig. 1 Monitoring the formation of the hybrid network containing POSS molecules by FTIR spectroscopy

Due to their unique characteristics, the click chemistry reactions (such as CuAAC [33], Diels–Alder [14] and thiol–ene [34] reactions) were utilized for the preparation of organic–inorganic hybrid networks from appropriate nanoparticles (silica, metal, and POSS nanoparticles)

Scheme 1 Synthesis of POSS-based hybrid networks via thiol–epoxy click chemistry



Scheme 2 Ring-opening reaction between G-POSS and 1-butane thiol via thiol–epoxy click reaction

[35]. Recently, thiol–epoxy reaction has been considered as click reaction since this reaction fulfills most of the click chemistry criteria including a simple catalysis, solvent-free conditions, and proceeding rapidly to high yield even at room temperature [20]. To take advantage of these features, a series of hybrid networks containing 2, 5, 10, and 15% G-POSS by weight were prepared by thiol–epoxy type click reaction using commercially available monomers, octakis-glycidyl-POSS, trimethylolpropane triglycidyl ether, and trimethylolpropane tris(3-mercaptopropionate). The LiOH was utilized as an efficient catalyst for the thiol–epoxy reactions at room temperature (Scheme 1).

The FTIR analysis was applied for the characterization of hybrid network formation along with initial compounds via thiol–epoxy click reaction. In the FTIR spectrum of hybrid networks, the characteristic epoxide bands of both G-POSS and TTE at 905 cm^{-1} disappeared completely, whereas a new peak at 3390 cm^{-1} assigned to OH group appeared distinctly (Fig. 1). In addition, the weak absorption band at 2570 cm^{-1} assigned to SH group of TMPMP was not detected after the thiol–epoxide reaction. On the other hand, the C–O, Si–O, C=O, and C–S bands of initial compounds were evidently displayed at 1110, 1080, 740, and 670 cm^{-1} in the FTIR spectrum

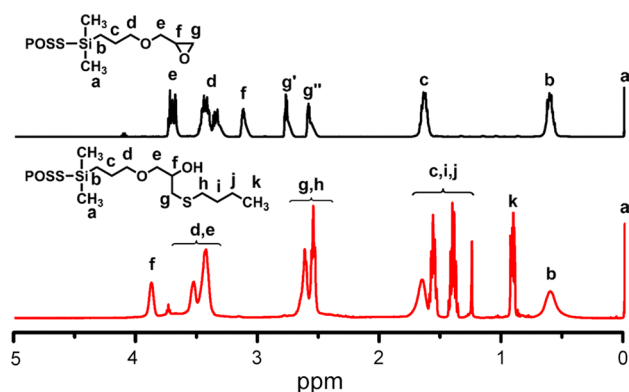


Fig. 2 ^1H -NMR spectrum of the product obtained from the ring-opening reaction between G-POSS and 1-butane thiol

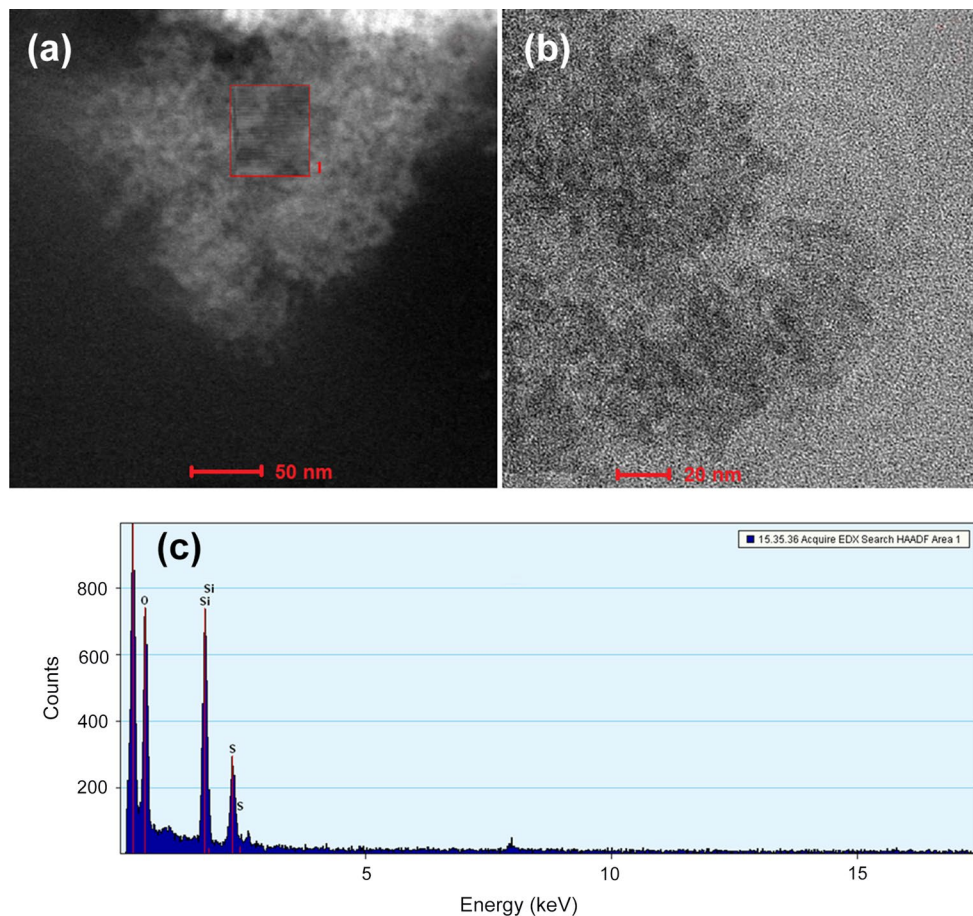
of the hybrid network. As a result, the FTIR analysis of the product provided good assignment to the presence of G-POSS nanoparticles in the hybrid networks. The solubility tests using several solvents including acetone, acetonitrile, chloroform, diethyl ether, *N,N*-dimethylacetamide, dimethyl sulfoxide, 1,4- dioxane, *n*-hexane, methanol, tetrahydrofuran, and water were also carried out to confirm the highly crosslinked structures of

hybrid networks. The results indicated that all samples were insoluble and there were no changes in the color of solutions.

To confirm the chemical bonding of POSS molecules in the network, the model study between G-POSS and 1-butane thiol under identical experimental condition was performed (Scheme 2) and the final product was characterized by ^1H -NMR spectroscopy (Fig. 2). After the ring-opening reaction, the protons of epoxy ring (**f**) were completely shifted to higher frequency from 3.21 to 3.89 ppm, whereas methylene protons (**e**) next to epoxy ring were moved to lower frequency from 3.75 to 3.91–4.12 ppm. In addition, new peaks belonging to methyl and methylene protons (**h**, **i**, **j**, and **k**) of 1-butane thiol appeared at 0.91, 1.21–1.69, and 3.91–4.12 ppm. All these findings undoubtedly confirmed that the G-POSS compound was chemically incorporated into the polymer matrix.

The morphological characterization of the hybrid network (HN-10) was carried out using transmission electron microscopy (TEM). According to the TEM micrograph with lower magnification, it was observed that a high concentration of G-POSS was homogeneously distributed within the hybrid networks without apparent phase

Fig. 3 TEM micrographs of HN-5: **a** in low (scale bar 50 nm); **b** in high (scale bar 20 nm) magnifications; **c** energy-dispersive X-ray (EDX) spectrum



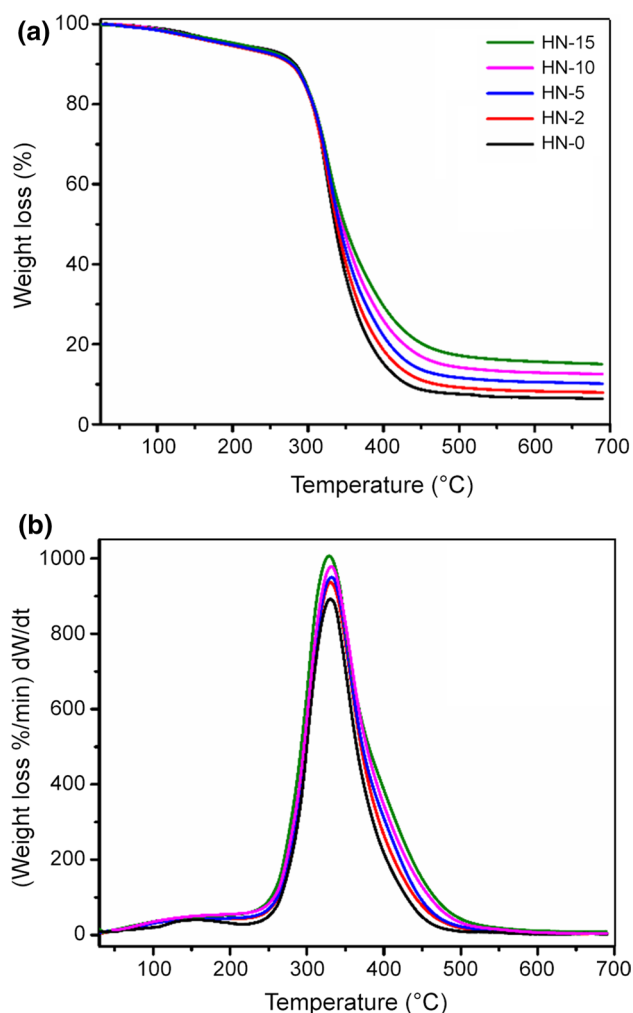


Fig. 4 TGA thermograms of hybrid networks containing G-POSS with various loadings 0, 2, 5, 10, and 15% of monomers by weight

separation. Furthermore, the TEM micrograph with higher magnification confirmed the size of G-POSS falls into the nanometer range of about 2–5 nm. On the other hand, the energy-dispersive X-ray (EDX) detector mapping confirmed the existence of G-POSS as dark domains in the micrograph. Figure 3c displays the EDX image by energy release analysis arising from C K α , O K α , Si K α , and S K α elements at 0.28, 0.53, 1.72, and 2.31 keV, respectively. These results undoubtedly confirm the presence of G-POSS molecules in the hybrid networks. Moreover, the ingredients of the hybrid networks were mainly ensued from C, O, Si, and S elements.

Thermal stability of the hybrid networks was investigated by thermogravimetric (TGA) and difference thermogravimetric (DTG) analyses with a heating rate of 10 °C/min in a nitrogen atmosphere (Fig. 4). All samples exhibited one-step degradation, which was attributed to the bond cleavages of C–O–C, C–S, C–H, and C–C, in the range of

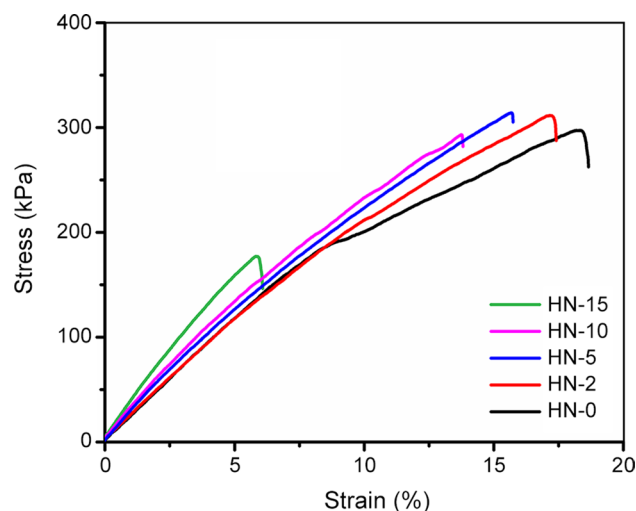


Fig. 5 Stress (%)–strain (kPa) curves of G-POSS-containing hybrid networks

Table 1 Tensile strength (kPa), elongation-at-break (%), and elastic modulus (kPa) values of POSS-containing hybrid networks

Sample	POSS (% by wt)	Tensile strength (kPa)	Elongation-at- break (%)	Elastic modulus (kPa)
HN-0	0	297.6	18.3	2590
HN-2	2	312.4	17.2	2790
HN-5	5	315.2	15.7	3370
HN-10	10	294.1	13.8	3490
HN-15	15	177.7	5.9	3580

220–500 °C. Moreover, these decompositions led to the complete degradation of the organic part of the hybrid networks and favored the formation of stable carbonaceous and inorganic residues as char. The char yields of hybrid networks were increased by G-POSS loadings according to 6.2, 7.8, 10.1, 12.7, and 15.1% for HN-0, HN-2, HN-5, HN-10, and HN-15, respectively. This improvement was also a proof of the incorporation of G-POSS into the hybrid networks that also provided high heat-resistant hybrid samples compared to neat sample in the absence of G-POSS. On the other hand, thermal decomposition behaviors of hybrid networks were completely similar with the result obtained from the neat sample in the absence of G-POSS.

The influence of G-POSS loading on the mechanical properties of hybrid networks was investigated by a universal tensile test machine. The amount of G-POSS in the polymer matrix played a very important role in determining the mechanical properties of final hybrid networks. From the stress–strain curves shown in Fig. 5, the addition of G-POSS up to 5% in the hybrid network made

homogenous distribution as well as efficient interactions between G-POSS and matrix, and consequently, a remarkable enhancement in the tensile strength. By increasing the G-POSS content to 10 and 15% weight ratios, the tensile strength decreased by ~1.2 and 40.3% compared to neat sample (HN-0: 297.6 kPa). This result was also explained by previous studies, in which a large amount of POSS led to the agglomeration as well as its heterogeneous dispersion in the network. The tensile strength values of these hybrid networks significantly decreased due to the structural inhomogeneity. Also shown in Table 1, the increase of POSS weight percentage caused an increase in both rigidity and elastic modulus, but a decrease in elongation-at-break.

Conclusion

In conclusion, thiol-epoxy click reaction was reported as a versatile method for the preparation of POSS-based hybrid networks from commercially available monomers. The crosslinking process was conducted at ambient conditions (presence of oxygen and moisture at room temperature) using lithium hydroxide as catalyst. The presence of G-POSS in the network was clearly determined by both FTIR and TEM analyses. Moreover, the ^1H -NMR result from the model study using G-POSS with 1-butane thiol as monofunctional thiol confirmed the successful thiol-epoxy click reaction. The incorporation of G-POSS improved the mechanical and thermal properties of POSS-based hybrid networks compared to the neat sample in the absence of G-POSS. By increasing G-POSS content higher than 5%, the tensile strength significantly decreased due to the agglomeration and heterogeneous dispersion of G-POSS particles in the hybrid networks. This simple strategy will open new possibilities for the epoxy-based protective coatings where chemical stability, abrasion, and heat resistance are required.

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