

In situ preparation of thermoset/clay nanocomposites via thiol-epoxy click chemistry

Ozlem Purut Koc¹ · Seda Bekin Acar¹ · Tamer Uyar² · Mehmet Atilla Tasdelen¹ 

Received: 20 December 2017 / Accepted: 5 March 2018 / Published online: 8 March 2018
© Springer-Verlag GmbH Germany, part of Springer Nature 2018

Abstract A series of thermoset/clay nanocomposites are prepared by thiol-epoxy click reaction using commercially available starting compounds at ambient conditions in very good yields. The incorporation and exfoliation of clay nanolayers in the thermoset matrix are confirmed by FT-IR, XRD and TEM analyses. The influence of clay loadings on the thermal and mechanical analyses is investigated and all nanocomposites exhibit improved properties than that of the pristine thermoset. The nanocomposite containing 1% montmorillonite by weight has the most improved mechanical properties due to its highly exfoliated structure resulting in efficient interactions between clay and polymer matrix. A further increase of the clay loading results in the aggregation of clay plates to form intercalated structures leading to deteriorated thermal and mechanical properties of nanocomposites.

Keywords Click chemistry · Nanocomposites · Nanoclay · Thermoset · Thiol-epoxy reaction

Introduction

Polymer/clay nanocomposites are one kind of composite materials containing nanometer-sized inorganic nanoparticles, typically in the range of 1–100 nm, which are uniformly dispersed in and fixed to a polymer matrix [1]. Because of their superior physical properties such as high dimensional stability, gas barrier

✉ Mehmet Atilla Tasdelen
tasdelen@yalova.edu.tr

¹ Department of Polymer Engineering, Faculty of Engineering, Yalova University, 77200 Yalova, Turkey

² UNAM-Institute of Materials Science and Nanotechnology, Bilkent University, 06800 Ankara, Turkey

performance, flame retardancy, and mechanical strength, their applications have been expanded continuously in the fields of automotive, cable packaging and coating [2]. The inclusion of inorganic nanoclays into a polymer matrix not only combines their properties but also brings advanced new functions in many industrial applications. Depending on the starting materials and processing techniques, there are three approaches for the preparation of polymer/clay nanocomposites: (i) solution mixing, (ii) melt blending and (iii) in situ polymerization. By applying these methods, three distinct morphologies can be possibly obtained; exfoliated (delaminated), intercalated (floculated) and unintercalated (microcomposite) [3]. Compared to the first two approaches, the in situ polymerization method is an effective method to obtain nanocomposites with exfoliated structures that are responsible for the dramatic improvements in the physical properties [4]. In this method, the organo-modified clay containing either monomer [5, 6] or initiator [7–9] functionalities are mixed with a suitable liquid monomer solution prior to polymerization [10–12]. By applying appropriate stimulus, such as heat, light or chemical activation, the chain growth as well as the delamination of the clay galleries can be triggered and hence the corresponding nanocomposite is formed [13]. Click chemistry is a general term that identifies a class of chemical reactions to generate substances rapidly and reliably by connecting molecules from reactive groups that will only connect with one another [14]. Due to its unique features including simplicity, efficiency and orthogonally, it has been widely used in the diverse applications from organic chemistry to polymer and material science [15, 16]. The well-known click chemistry reactions are: (i) cycloaddition reactions [copper (I)-catalyzed azide-alkyne (CuAAC) and Diels–Alder], (ii) ring-opening reactions (epoxides and aziridines), (iii) non-aldol reactions (ureas, oximes, and hydrazones) and (iv) addition reactions (thiol-ene/yne and Michael). Recently, base-catalyzed ring-opening reaction of an epoxide with a thiol is classified as click chemistry reaction due to its exceptional features such as selectivity, controllability, simplicity, fastness, and high efficiency [17]. Compared to other click reactions, it has additional advantages such as metal-free catalyst system and resulting product containing reactive hydroxyl groups that enable further functionalization. This click reaction is utilized not only in polymer synthesis [18, 19] such as synthesis of thermosets [20, 21], hybrid network [22–24], hydrogels [25] and high-performance coatings [26–28], but also in functionalization of polymers [29–31]. For the preparation of polymer/clay nanocomposites, only used click reaction is CuAAC click reaction, in which alkyne-functionalized monomers or prepolymers [32, 33] are clicked azido-functionalized nanoclay, independently [34].

Thermoset polymers are bonded covalently and cannot be melted by heating or dissolved completely in any solvent because of their three-dimensional cross-linked structures [35]. They have been utilized for the preparation of many important advanced materials, such as protective coatings, aerospace composites and computer chip packaging due to their attractive properties (good strength, well chemical resistance and high temperature stability) [36]. On the other hand, thermoset materials can have brittleness and lack of durability in their final properties. So, thermoset nanocomposites have been evolved to eliminate these shortcomings. Because of its desirable characteristics, thiol-epoxy click reaction has

been utilized for the preparation of hyper-branched epoxy [37] and polyester [38] and complex multi-layered microdevices [39] using commercially available monomers. A facile way to improve physical properties of thermoset is to produce their composites or nanocomposites using appropriate reinforcements. The use of nanosized fillers with high aspect ratio such as clays, nanotubes and nanoparticles has intensively developed due to their unique multifunctional and highly enhanced properties.

In this study, clay-based thermoset nanocomposites have been prepared by thiol-epoxy click chemistry using trimethylolpropane triglycidyl ether and trimethylolpropane tris(3-mercaptopropionate) as commercially available monomers and montmorillonite (Cloisite 30B) as nanofiller. The thiol-epoxy click reaction can be simply catalyzed by lithium hydroxide and conducted in the presence of air and water at ambient temperature and pressure. The obtained polymer/clay nanocomposites have been characterized by Fourier-transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) spectroscopy, transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). The influence of clay loadings on thermal and mechanical properties of the resulting polymer/clay nanocomposites is also investigated.

Experimental

Materials

The organo-modified montmorillonite (Cloisite 30B was an alkyl quaternary ammonium salt bentonite) was purchased from Southern Clay Products and kept in a vacuum oven for 1 h at 110 °C before using as nanofiller. Trimethylolpropane triglycidyl ether (TTE, technical grade, Aldrich), trimethylolpropane tris(3-mercaptopropionate) (TMPMP \geq 95.0%, Aldrich), and lithium hydroxide monohydrate (LiOH 99.95%, Aldrich) were used as received. Tetrahydrofuran (THF, 99.9%, Aldrich) and deionized water were used as solvents.

Preparation of thermoset/clay nanocomposites via thiol-epoxy click chemistry

The TMPMP (1.52 mmol, 0.605 g) and TTE (1.52 mmol, 0.46 g) with various clay loadings (0, 1, 5 or 10% 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 to the resulting solution by stirring according to a modified procedure [25]. To obtain completely homogeneous mixture, the solution was further stirred for few minutes. The solutions containing 1, 5 or 10% clay were poured into glass Petri dishes and nanocomposite structures were rapidly obtained after 5 min as a result of exothermic reactions. The samples (NC-1, NC-5 or NC-10) were dried in a vacuum oven for 24 h at 50 °C before the characterization to eliminate the remaining water and THF on the determined properties.

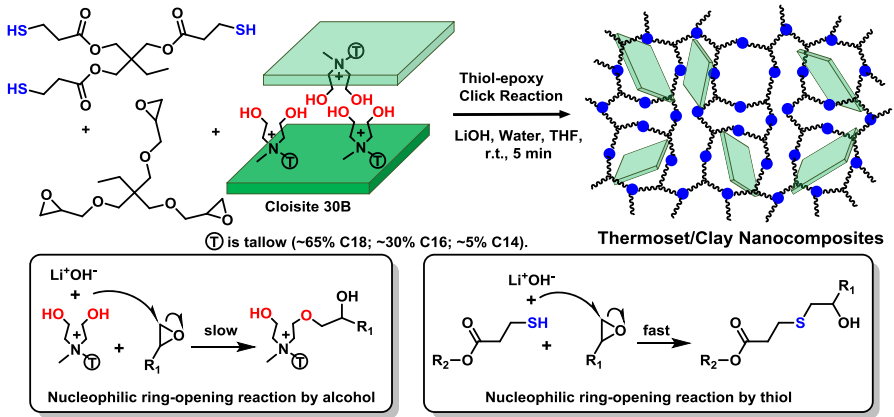
Instrumentation

Fourier-transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer FT-IR Spectrum One B spectrometer. The powder XRD measurements were performed on a PANalytical X'Pert PRO X-ray diffractometer equipped with graphite-monochromatized Cu K-alpha radiation ($\lambda = 0.115$ nm). The thermogravimetric analysis was conducted by Perkin-Elmer Diamond TA/TGA with a heating rate of 10 °C/min under nitrogen flow (200 mL/min). Transmission electron microscopy (TEM) observation was utilized by a FEI TecnaiTM G² F30 instrument operating at an acceleration voltage of 200 kV. The ultrathin 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 located on holey carbon-coated grid. 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 the crosshead speed of 5 mm/min. The sample specimens were cut into rectangular bars with 7.4 mm × 20 mm × 10 mm dimensions. For each sample, at least three specimens were tested to provide reproducibility.

Results and discussion

To take advantages of thiol-epoxy click reaction, a series of thermoset nanocomposites containing 1, 5 and 10% nanoclay by weight were prepared using Cloisite 30B as organo-modified nanoclay with TMPMP and TTE as commercially available monomers. All reactions were activated by LiOH as a base-catalyst and carried out at room temperature. Due to their highly strained three-membered rings, epoxides are very reactive towards a large range of nucleophiles, alcohols, alkoxides, amines and thiols, and easily converted corresponding compounds in basic and acidic conditions. To benefit from this chemistry, a series of thermoset/clay nanocomposites were simply prepared by simultaneous base-catalyzed thiol-epoxy and alcohol-epoxy ring-opening reactions. The epoxy rings of TTE were opened via two competitive reactions by either thiol groups of TMPMP or alcohol groups of Cloisite 30B (containing one methyl and tallow groups, and two pendant alcohol groups ($-\text{CH}_2\text{CH}_2\text{OH}$) on the quaternary ammonium ions) in the presence of LiOH (Scheme 1).

The formation of nanocomposites was monitored by FT-IR analysis by following their characteristic bands of epoxide and thiol groups of initial compounds, which were assigned at 910 and 2680 cm^{-1} . After ring-opening reactions, these bands were completely disappeared, whereas a new peak, appeared at 3400 cm^{-1} , was attributed to O–H bond closest to thioether group. Furthermore, the weak absorption band at 2570 cm^{-1} assigned to S–H bond of TMPMP was not detected in the nanocomposite's spectrum (Fig. 1). Additionally, the peaks at 2890 , 1740 and 1100 cm^{-1} were assigned to C–H, C=O and C–O–C bonds, clearly indicating the presence of initial compounds in the nanocomposites. Overall, the successful thiol-epoxy click reaction in the presence of organo-modified clays yielded to thermoset



Scheme 1 Thermoset/clay nanocomposites by simultaneous base-catalyzed thiol-epoxy and alcohol-epoxy ring-opening reactions using Cloisite 30B as nanoclay and TTE and TMPMP as monomers

Fig. 1 FT-IR spectra of initial TTE and TMPMP compounds and resulting nanocomposites (NC-10 containing 10% clay by weight)

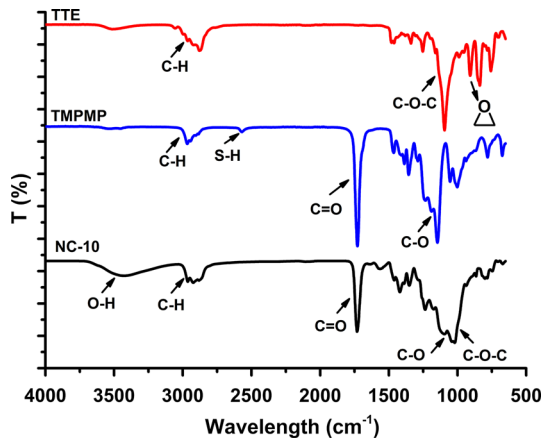
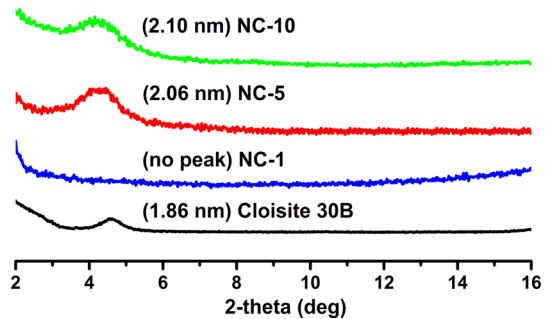


Fig. 2 XRD spectra of Cloisite 30B and resulting nanocomposites (NC-1, NC-5 and NC-10)



networks containing aliphatic (C–H), thioether (C–S–C), ester [(C=O)–O] and alcohol (O–H) groups according to FT-IR analysis.

The X-ray diffraction patterns of commercial clay (Cloisite 30B) and obtained nanocomposites with various clay loadings (1, 5 and 10% by weight) are shown in Fig. 2. In the XRD pattern of Cloisite 30B, there was a weak peak at $2\theta = 4.81^\circ$, and it indicated that the distance between clay layers was about 1.86 nm. However, there was no peak in the X-ray diffractogram of NC-1, so it was estimated that almost all clay layers were exfoliated and dispersed randomly in thermoset matrix. When the clay loadings were over 1%, a similar peak at low angle was detected for both NC-5 and NC-10 samples. There was no apparent difference between the XRD patterns of NC-5 and NC-10, and the distances between clay plates were calculated as 2.06 and 2.10 nm, respectively. This observation indicated a coexistence of intercalated or intercalated/exfoliated clay layers in the nanocomposites. In the polymer/clay nanocomposite preparation, the clay layers exhibited strong polar interactions that were critical to the formation of intercalated and exfoliated morphologies [40–42]. By increasing clay loadings, the silicate layers were stacked on each other and held together through intensive ionic attractions and, therefore, intercalated or mixed intercalated/exfoliated structures were formed in the thermoset matrix.

To get more detailed information on the clay dispersions, the morphologies of NC-1 and NC-5 samples were investigated by transmission electron microscopy. In Fig. 3, the dark lines were assigned as clay layers, whereas the bright areas represented thermoset matrix. In the both samples, TEM analysis revealed that mixed exfoliated/intercalated morphologies were attained upon addition of nanoclay. The observed individual clay layers (highlighted by yellow circles) were well dispersed (delaminated) in the polymer matrix, while the large intercalated tactoids (highlighted by red rectangles) were visible in NC-1 and NC-5. Although the most of the clay layers were locally stacked, some of them were isolated from

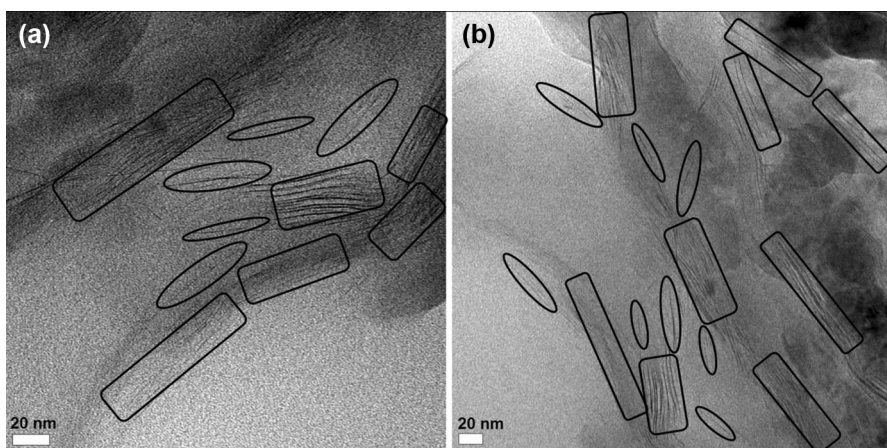


Fig. 3 TEM micrographs of NC-1 (a) and NC-5 (b) in low magnifications (circle as exfoliated layers and rectangles layers as intercalated, scale bar: 20 nm)

any stack and randomly dispersed in the polymer matrix [43–45]. The coexistence of partially exfoliated/intercalated structures proposed that the van der Waals and Coulombic forces between silicate layers as well as their high specific surface area and surface energy tending to keep them tightly rather than to disperse homogeneously. Overall, combined XRD and TEM results confirmed that the resulting nanocomposites had partially mixed exfoliated/intercalated morphologies.

Thermal behaviors of nanocomposites were investigated by thermogravimetric (TGA) and derivative thermogravimetry (DTG) analyses and compared with neat thermoset sample that was prepared in the absence of Cloisite 30B under identical conditions (Fig. 4). All samples showed one-step degradation implying the bond cleavages of C–O–C, C–S, C–H and C–C in the range of 220–500 °C. In addition, this decomposition caused an entire degradation of the organic part of nanocomposites and provided the formation of stable, carbonaceous and inorganic residues as a char. The amounts of residual char yields were 3.9, 5.6, 11.8 and 17.5% for neat thermoset polymer, NC-1, NC-5 and NC-10, respectively. This increment was attributed to the incorporation of inorganic clays in thermoset matrix causing the restriction of movement of polymer chains. According to the TGA and DTG results, the maximum decomposition temperature was first increased from 323 °C (neat thermoset) to 339 °C (NC-1) and then was decreased to 327 °C (NC-5) and 328 °C (NC-10). This trend could be explained by morphologies of the nanocomposites, in which NC-1 had highest exfoliated structures according to TEM and XRD analyses. On the other hand, the increase of intercalated structures in the nanocomposites could slightly reduce the thermal stabilities of nanocomposite (NC-5 and NC-10). However, all nanocomposites exhibited improved thermal stabilities compared to neat thermoset sample.

The influence of clay loadings on the mechanical properties of nanocomposites was also investigated by a universal tensile test machine. The amount of clay nanoparticles in the polymer matrix played a crucial role in determining the mechanical properties of prepared nanocomposite structures. As expected from previous studies, there was a tendency that tensile modulus was increased by

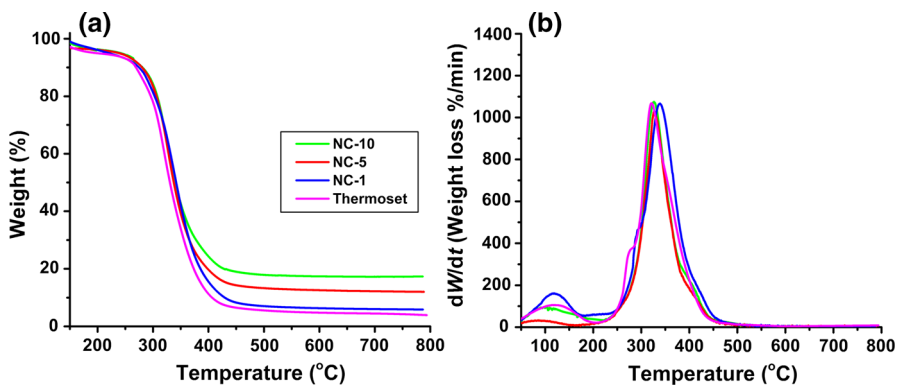


Fig. 4 TGA (a) and DTG (b) thermograms of neat thermoset and resulting nanocomposites (NC-1, NC-5 and NC-10)

increasing clay contents, whereas elongation at break was conversely decreased [41, 42, 46]. This decrease could be also associated with the plasticization effects of residual water on the clay layers. From the stress–strain curves shown in Fig. 5, the tensile strength and elongation at break values of nanocomposites were significantly increased in comparison with the neat thermoset sample. Among the nanocomposite samples, the NC-1 was the most improved mechanical properties due to its high-exfoliated structures providing efficient interactions between clay and polymer matrix. For high clay contents, mechanical properties of nanocomposites were deteriorated in both cases, but still higher than that of the neat thermoset sample in the absence of clay. It was consistent with the literature findings that a large amount of clay gave rise to a decrease in the mechanical properties due to heterogeneous dispersion and aggregation of clay resulting in poor interfacial interactions between clay layers and thermoset network. Consequently, the increase in clay contents not only resulted in an improvement on rigidity and elastic modulus, but also lowered elongation at break.

Conclusions

In conclusion, thermoset/clay nanocomposites from commercially available monomers and organoclay were prepared via thiol-epoxy click reaction under ambient conditions using lithium hydroxide as catalyst at room temperature. The combined XRD and TEM analyses indicated that the obtained nanocomposites had a mixed exfoliated/intercalated morphology. In addition, the thermal and mechanical properties of these nanocomposites were considerably improved compared to the pristine thermoset polymer. Among them, the NC-1 had the most improved

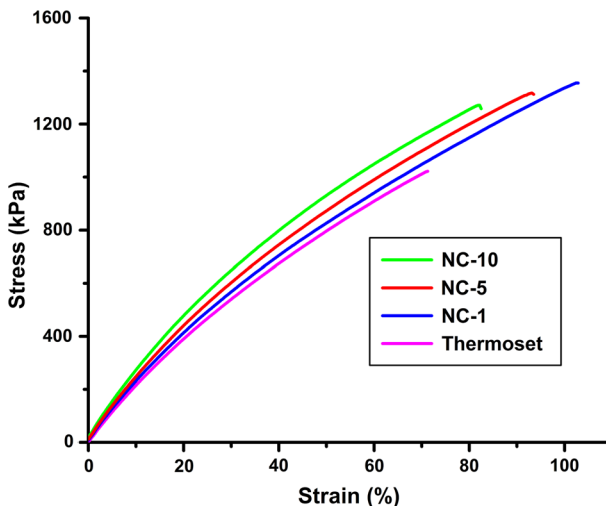


Fig. 5 Stress (%)–strain (kPa) curves of neat thermoset and resulting nanocomposites (NC-1, NC-5 and NC-10)

mechanical properties due to its highly exfoliated structures resulting in efficient interactions between clay and polymer matrix.

Acknowledgements The authors would like to thank Yalova University Research Fund (Project no: 2015/YL/055) for financial supports.

References

1. Ray SS, Okamoto M (2003) Polymer/layered silicate nanocomposites: a review from preparation to processing. *Prog Polym Sci* 28(11):1539–1641. <https://doi.org/10.1016/j.progpolymsci.2003.08.002>
2. Pavlidou S, Papaspyrides C (2008) A review on polymer-layered silicate nanocomposites. *Prog Polym Sci* 33(12):1119–1198. <https://doi.org/10.1016/j.progpolymsci.2008.07.008>
3. Kotal M, Bhowmick AK (2015) Polymer nanocomposites from modified clays: recent advances and challenges. *Prog Polym Sci* 51:127–187. <https://doi.org/10.1016/j.progpolymsci.2015.10.001>
4. Tasdelen MA, Kreutzer J, Yagci Y (2010) In situ synthesis of polymer/clay nanocomposites by living and controlled/living polymerization. *Macromol Chem Phys* 211(3):279–285. <https://doi.org/10.1002/macp.200900590>
5. Dizman C, Ates S, Uyar T, Tasdelen MA, Torun L, Yagci Y (2011) Polysulfone/clay nanocomposites by in situ photoinduced crosslinking polymerization. *Macromol Mater Eng* 296(12):1101–1106. <https://doi.org/10.1002/mame.201100114>
6. Karamane M, Raihane M, Tasdelen MA, Uyar T, Lahcini M, Ilsouk M, Yagci Y (2017) Preparation of fluorinated methacrylate/clay nanocomposite via in situ polymerization: characterization, structure, and properties. *J Polym Sci A* 55(3):411–418. <https://doi.org/10.1002/pola.28403>
7. Altinkok C, Uyar T, Tasdelen MA, Yagci Y (2011) In situ synthesis of polymer/clay nanocomposites by type II photoinitiated free radical polymerization. *J Polym Sci A* 49(16):3658–3663. <https://doi.org/10.1002/pola.24788>
8. Aydin M, Atilla Tasdelen M, Uyar T, Yagci Y (2013) In situ synthesis of A3-type star polymer/clay nanocomposites by atom transfer radical polymerization. *J Polym Sci A* 51(24):5257–5262. <https://doi.org/10.1002/pola.26957>
9. Ozkose UU, Altinkok C, Yilmaz O, Alpturk O, Tasdelen MA (2017) In-situ preparation of poly (2-ethyl-2-oxazoline)/clay nanocomposites via living cationic ring-opening polymerization. *Eur Polym J* 88:586–593. <https://doi.org/10.1016/j.eurpolymj.2016.07.004>
10. Wang X, Su Q, Shan JH, Zheng JP (2016) The effect of clay modification on the mechanical properties of poly(methyl methacrylate)/organomodified montmorillonite nanocomposites prepared by in situ suspension polymerization. *Polym Compos* 37(6):1705–1714. <https://doi.org/10.1002/pc.23343>
11. Assem Y, Khalaf AI, Rabia AM, Yehia AA, Zidan TA (2016) Synthesis and characterization of hybrid clay/poly (*N,N*-dimethylaminoethyl methacrylate) nanocomposites. *Polym Compos* 37(10):2950–2959. <https://doi.org/10.1002/pc.23492>
12. Oral A, Tasdelen MA, Demirel AL, Yagci Y (2009) Poly(cyclohexene oxide)/clay nanocomposites by photoinitiated cationic polymerization via activated monomer mechanism. *J Polym Sci A* 47(20):5328–5335. <https://doi.org/10.1002/pola.23581>
13. Aydin M, Uyar T, Tasdelen MA, Yagci Y (2015) Polymer/clay nanocomposites through multiple hydrogen-bonding interactions. *J Polym Sci A* 53(5):650–658. <https://doi.org/10.1002/pola.27487>
14. Kolb HC, Finn MG, Sharpless KB (2001) Click chemistry: diverse chemical function from a few good reactions. *Angew Chem Int Ed* 40(11):2004–2021. [https://doi.org/10.1002/1521-3773\(20010601\)40:11<2004:AID-ANIE2004>3.0.CO;2-5](https://doi.org/10.1002/1521-3773(20010601)40:11<2004:AID-ANIE2004>3.0.CO;2-5)
15. Nandivada H, Jiang XW, Lahann J (2007) Click chemistry: versatility and control in the hands of materials scientists. *Adv Mater* 19(17):2197–2208. <https://doi.org/10.1002/adma.200602739>
16. Binder WH, Sachsenhofer R (2008) ‘Click’ chemistry in polymer and material science: an update. *Macromol Rapid Commun* 29(12–13):952–981. <https://doi.org/10.1002/marc.200800089>
17. Stuparu MC, Khan A (2016) Thiol-epoxy “click” chemistry: application in preparation and post-polymerization modification of polymers. *J Polym Sci A* 54(19):3057–3070. <https://doi.org/10.1002/pola.28195>

18. De S, Khan A (2012) Efficient synthesis of multifunctional polymers via thiol-epoxy “click” chemistry. *Chem Commun* 48(25):3130–3132. <https://doi.org/10.1039/c2cc30434a>
19. Binder S, Gadwal I, Biemann A, Khan A (2014) Thiol-epoxy polymerization via an AB monomer: synthetic access to high molecular weight poly(beta-hydroxythio-ether)s. *J Polym Sci A* 52(14):2040–2046. <https://doi.org/10.1002/pola.27212>
20. Guzman D, Ramis X, Fernandez-Francos X, Serra A (2015) Enhancement in the glass transition temperature in latent thiol-epoxy click cured thermosets. *Polymers* 7(4):680–694. <https://doi.org/10.3390/polym7040680>
21. Acebo C, Fernandez-Francos X, Ramis X, Serra A (2016) Thiol-yne/thiol-epoxy hybrid crosslinked materials based on propargyl modified hyperbranched poly(ethyleneimine) and diglycidylether of bisphenol A resins. *RSC Adv* 6(66):61576–61584. <https://doi.org/10.1039/c6ra13158a>
22. Acar SB, Ozcelik M, Uyar T, Tasdelen MA (2017) Polyhedral oligomeric silsesquioxane-based hybrid networks obtained via thiol-epoxy click chemistry. *Iran Polym J* 26(6):405–411. <https://doi.org/10.1007/s13726-017-0529-x>
23. Gorkem Sencevik R, Atilla Tasdelen M (2014) Poly (methyl methacrylate)/POSS hybrid networks by type II photoinitiated free radical polymerization. *Polym Compos* 35(8):1614–1620. <https://doi.org/10.1002/pola.27487>
24. Arslan I, Tasdelen MA (2016) POSS-based hybrid thermosets via photoinduced copper-catalyzed azide–alkyne cycloaddition click chemistry. *Des Monomers Polym* 19(2):155–160. <https://doi.org/10.1080/15685551.2015.1124323>
25. Cengiz N, Rao JY, Sanyal A, Khan A (2013) Designing functionalizable hydrogels through thiol-epoxy coupling chemistry. *Chem Commun* 49(95):11191–11193. <https://doi.org/10.1039/c3cc45859h>
26. Fernandez-Francos X, Konuray AO, Belmonte A, De la Flor S, Serra A, Ramis X (2016) Sequential curing of off-stoichiometric thiol-epoxy thermosets with a custom-tailored structure. *Polym Chem* 7(12):2280–2290. <https://doi.org/10.1039/c6py00099a>
27. Guzman D, Ramis X, Fernandez-Francos X, Serra A (2015) Preparation of click thiol-ene/thiol-epoxy thermosets by controlled photo/thermal dual curing sequence. *RSC Adv* 5(123):101623–101633. <https://doi.org/10.1039/c5ra22055f>
28. Guzman D, Ramis X, Fernandez-Francos X, Serra A (2014) New catalysts for diglycidyl ether of bisphenol A curing based on thiol-epoxy click reaction. *Eur Polym J* 59:377–386. <https://doi.org/10.1016/j.eurpolymj.2014.08.001>
29. Brandle A, Khan A (2012) Thiol-epoxy ‘click’ polymerization: efficient construction of reactive and functional polymers. *Polym Chem* 3(12):3224–3227. <https://doi.org/10.1039/c2py20591b>
30. Gadwal I, Khan A (2013) Protecting-group-free synthesis of chain-end multifunctional polymers by combining ATRP with thiol-epoxy ‘click’ chemistry. *Polym Chem* 4(8):2440–2444. <https://doi.org/10.1039/c3py00136a>
31. Acebo C, Fernandez-Francos X, Ramis X, Serra A (2016) Multifunctional allyl-terminated hyperbranched poly(ethyleneimine) as component of new thiol-ene/thiol-epoxy materials. *React Funct Polym* 99:17–25. <https://doi.org/10.1016/j.reactfunctpolym.2015.12.003>
32. Tasdelen MA (2011) Poly(epsilon-caprolactone)/clay nanocomposites via “click” chemistry. *Eur Polym J* 47(5):937–941. <https://doi.org/10.1016/j.eurpolymj.2011.01.004>
33. Tasdelen MA, Van Camp W, Goethals E, Dubois P, Du Prez F, Yagci Y (2008) Polytetrahydrofuran/clay nanocomposites by in situ polymerization and “click” chemistry processes. *Macromolecules* 41(16):6035–6040. <https://doi.org/10.1021/ma801149x>
34. Arslan M, Tasdelen MA (2017) Polymer nanocomposites via click chemistry reactions. *Polymers* 9(10):499. <https://doi.org/10.3390/polym9100499>
35. Raquez JM, Deleglise M, Lacrampe MF, Krawczak P (2010) Thermosetting (bio)materials derived from renewable resources: a critical review. *Prog Polym Sci* 35(4):487–509. <https://doi.org/10.1016/j.progpolymsci.2010.01.001>
36. Yousefi A, Laffleur PG, Gauvin R (1997) Kinetic studies of thermoset cure reactions: a review. *Polym Compos* 18(2):157–168. <https://doi.org/10.1002/pc.10270>
37. Zhang DH, Liu CH, Chen SF, Zhang JH, Cheng J, Miao MH (2016) Highly efficient preparation of hyperbranched epoxy resins by UV-initiated thiol-ene click reaction. *Prog Org Coat* 101:178–185. <https://doi.org/10.1016/j.porgcoat.2016.08.010>
38. Flores M, Tomuta AM, Fernandez-Francos X, Ramis X, Sangermano M, Serra A (2013) A new two-stage curing system: thiol-ene/epoxy homopolymerization using an allyl terminated hyperbranched

- polyester as reactive modifier. *Polymer* 54(21):5473–5481. <https://doi.org/10.1016/j.polymer.2013.07.056>
39. Sticker D, Rothbauer M, Lechner S, Hehenberger MT, Ertl P (2015) Multi-layered, membrane-integrated microfluidics based on replica molding of a thiol-ene epoxy thermoset for organ-on-a-chip applications. *Lab Chip* 15(24):4542–4554. <https://doi.org/10.1039/c5lc01028d>
 40. Mohan T, Ramesh Kumar M, Velmurugan R (2005) Rheology and curing characteristics of epoxy–clay nanocomposites. *Polym Int* 54(12):1653–1659. <https://doi.org/10.1002/pi.1897>
 41. Piscitelli F, Scamardella AM, Romeo V, Lavorgna M, Barra G, Amendola E (2012) Epoxy composites based on amino-silylated MMT: the role of interfaces and clay morphology. *J Appl Polym Sci* 124(1):616–628. <https://doi.org/10.1002/app.35015>
 42. Lan T, Kaviratna PD, Pinnavaia TJ (1995) Mechanism of clay tactoid exfoliation in epoxy–clay nanocomposites. *Chem Mater* 7(11):2144–2150. <https://doi.org/10.1021/cm00059a023>
 43. Osman MA, Mittal V, Morbidelli M, Suter UW (2004) Epoxy–layered silicate nanocomposites and their gas permeation properties. *Macromolecules* 37(19):7250–7257. <https://doi.org/10.1002/pc.23397>
 44. Brown JM, Curliss D, Vaia RA (2000) Thermoset–layered silicate nanocomposites. Quaternary ammonium montmorillonite with primary diamine cured epoxies. *Chem Mater* 12(11):3376–3384. <https://doi.org/10.1021/cm000477+>
 45. Morgan AB, Gilman JW (2003) Characterization of polymer-layered silicate (clay) nanocomposites by transmission electron microscopy and X-ray diffraction: a comparative study. *J Appl Polym Sci* 87(8):1329–1338. <https://doi.org/10.1002/app.11884>
 46. Sanchez-Cabezudo M, Prolongo MG, Salom C, del Cid MAG, Masegosa RM (2016) Ternary nanocomposites: curing, morphology, and mechanical properties of epoxy/thermoplastic/organoclay systems. *Polym Compos* 37(7):2184–2195. <https://doi.org/10.1002/pc.23397>