Research Article

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Polytriazole resins toughened by an azide-terminated polyhedral oligomeric silsesquioxane (OADTP)

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Abstract: An azido-terminated polyhedral oligomeric silsesquioxane (POSS) compound, octakis(azidopropyl-3-oxycarbonyl-1-decyl-10-thiopropyl-3-)POSS (OADTP), is synthesized and characterized. POSS-polytriazole (PTA) resins are prepared from an azide, an alkyne monomer, and OADTP. The toughening effect of OADTP on PTA resins is analyzed by impact performance test and electronic microscope characterization, and the thermal performance of resins is measured by thermogravimetric analysis and dynamic mechanical analysis. The results show that the addition of the POSS can improve the mechanical properties of PTA resins. The impact strength of POSS-PTA resins first increases and then decreases with the increase in the POSS compound, and the maximum one arrives at 54.8 kJ m^{-2} which increases by 44.2% as compared to 38 kJ m^{-2} of the PTA resin. A good thermal stability remains in POSS-PTA resins.

Keywords: POSS-modified resin, polytriazole resin, nanocomposites, toughening of a resin

1 Introduction

Polytriazole (PTA) resins have shown potential application as matrices in advanced composites owing to their good thermal performance and mechanical properties. The PTA resins could be cured at low temperature through

Click reaction of alkyne and azide compounds without curing agent (1), which has good designability and effectiveness to prepare various triazole polymers (2–7). Huang group (8–11) had developed a series of thermosetting PTA resins by 1,3-dipolar cycloaddition reaction of azides and alkynes since 2002. Wan's investigation (12) showed that the glass transition temperature and thermal decomposition temperature of the cured PTA resin prepared from *p*-xylylene diazide and *N,N,N',N'*-tetrapropargyl-*p,p'*-diaminodiphenylmethane (TPDDM) are 218°C and 350°C, respectively. Chisca et al. (13) reported the synthesis of organic solvent resistant PTA membranes using a sustainable process and investigated the mechanical properties by measuring the creep recovery. Tang et al. (14) successfully synthesized hyperbranched PTAs with excellent adhesive properties on copper, aluminum, and iron. In recent years, with the rapid development in the aeronautics and astronautics fields, there are great requirements of advanced polymeric composites with high toughness. Ma et al. (15) modified the PTA resins with PEGs to prepare the EPTA resins and the impact strength of EPTA resins increased by 100.8%, but the flexural strength and thermal stability decreased.

Polyhedral oligomeric silsesquioxane (POSS) is an organic–inorganic cage-like structure containing Si and O elements. Each silicon atom can be connected to an organic functional group. The three-dimensional size of a POSS is about 1–3 nm (16,17), and the nanoscale structure with functional organic groups makes POSS well integrated into the resin matrix through chemical action. Laine et al. (18,19) found that POSS with different organic groups have influence on the dynamic mechanical properties, fracture toughness, and thermal stability of the material produced from POSS. New organic–inorganic hybrid functional materials could be obtained using POSS as a nano-structured unit to modify polymers. Mohamed et al. (20) reported some prepared mono-functionalized BZ ring-containing hybrid organic/inorganic (POSS) materials, and this polybenzoxazines (PBZ-POSS) displayed a higher value of T_g and a higher char yield. Nie et al. (21) synthesized unsaturated polyester resins (UPR) containing

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[(6-oxide-6H-dibenz(c,e)(1,2)oxaphosphorin-6-yl)methyl] butanedioic (DDP) (DDP-UPR) and UPR containing both DDP and (2,3-propanediol)propoxy-heptaisobutyl substituted-POSS (PSS-POSS) (DDP-PSS-POSS-UPR series) and showed that the PSS-POSS enhanced the flame retardance of DDP-UPR. Nowadays, POSS has been combined with several resins as a toughening agent to prepare a new material, such as epoxy resin (22,23), poly(methyl methacrylate) (24), polyimide (25), and poly(lactic acid) (26,27). Song et al. (28) successfully synthesized a series of hybrid thermoplastic polyurethanes by incorporation of bi-functional POSS with the polyurethanes. Fan's group (29) blended POSS-(PDMAEMA-*b*-PDLA)₈ with polylactic acid (PLLA) and the blend showed high mechanical properties when appropriate amount of POSS-(PDMAEMA-*b*-PDLA)₈ was added. Bu et al. (30) modified poly(silicane arylacetylene) (PSA) resin with octa(propargyl propyl sulfide) POSS (OPPSP) and the flexural and impact strength of OPPSP-PSA thermosets are increased by 80.5% and 92.8%, respectively.

The addition of POSS nanoparticles into a resin can improve the mechanical properties of the produced resin while maintaining thermal properties of the resin. In this paper, a new kind of POSS attached flexible organic chain (OADTP) is synthesized and incorporated into a PTA resin to produce OADTP-PTA resins. The structure, mechanical properties, and thermal properties of the OADTP-PTA resins are investigated.

2 Experimental

2.1 Materials

3-Merraptnpropyltrimethoxysilane, 1-chloropropanol, azodisobutyronitrile (AIBN), 4-dimethylaminopyridine (DMAP), *N,N*-dimethylformamide (DMF), hydrochloric acid, methanol, and magnesium sulfate are purchased from Shanghai Titan Technology Co. Ltd. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCl) is purchased from Diba Co. Ltd. 10-Undecenioc acid is purchased from Acros Co., Ltd. 1,1-Bisazidomethyl-4,4'-biphenyl (BAMBP), and TPDDM are synthesized in our lab.

2.2 Synthesis of octakis(azidopropyl-3-oxy carbonyl-1-decyl-10-thiopropyl) POSS (OADTP)

The reaction process for the synthesis of OADTP is shown in Figure 1. Octakis(mercaptopropyl) POSS (POSS-SH)

was synthesized by the similar procedure reported by Lin et al. (31). 3-Merraptnpropyltrimethoxysilane (30 g, 0.15 mol) was added into a mixed solution of concentrated HCl (40 mL) and methanol (700 mL) and stirred at 65°C for 24 h to obtain a white paste precipitate. After washing thrice with methanol, the precipitate was dissolved in dichloromethane and washed with water. The organic phase separated and dried over MgSO₄ was concentrated by distillation and POSS-SH was obtained in 83% yield. FT-IR (KBr): 2,560 (ms, ν_s(S-H)); 2,924 (s, ν_s(C-H)); ¹H NMR (400 MHz, CDCl₃, δ): 0.7 (t, 2H, Si-CH₂-), 1.3 (t, H, S-H), 1.6 (m, 2H, -CH₂-), 2.5 (q, 2H, -CH₂-S-).

AIBN (0.1 g, 0.6 mmol) and 10-undecenioc acid (1.84 g, 0.01 mol) dissolved in tetrahydrofuran (25 mL) and POSS-SH (1.02 g, 1 mmol) were poured into a three-necked round bottom flask. The mixture was kept at room temperature for 1 day under vigorous stirring, followed by vacuum distillation and a white paste was obtained. The paste was poured into methanol, and then a solid precipitated out, filtered under reduced pressure to obtain octakis(carboxylic acid-1-decyl-10-thiopropyl) POSS (POSS-COOH) as a white solid (yield: 53%). FT-IR (KBr): 1,099 (s, ν_s(SiOSi)), 1,705 (s, ν_s(C=O)), 2,930 (s, ν_s(C-H)); ¹H NMR (400 MHz, DMSO, δ): 0.8 (t, 2H, Si-CH₂-), 1.3 (m, 16H, -CH₂-), 1.5 (m, 2H, -CH₂-), 1.6 (m, 2H, S-CH₂-), 2.6 (q, 2H, -CH₂-S-), 3.4 (s, 2H, CH₂-C), 12 (s, H, -OH).

POSS-COOH (2.49 g, 1 mmol), 1-chloropropanol (0.95 g, 0.01 mol), DMAP (1.22 g, 0.01 mol), and dichloromethane (15 mL) were charged in a 100 mL four-necked flask; then, EDCl (1.92 g, 0.01 mol) was slowly added in a drop-wise manner within 30 min at 0°C. The mixture was kept at room temperature for 24 h. Then, the organic product was washed with deionized water several times until pH value of the washed water solution is near 7. After the mixture was dried over MgSO₄, the organic phase was concentrated by distillation and octakis(chloropropyl-3-oxy carbonyl-1-decyl-10-thiopropyl) POSS (POSS-Cl) was obtained in 48% yield. FT-IR (KBr): 1,099 (s, ν_s(SiOSi)), 1,735 (s, ν_s(C=O)), 2,930 (s, ν_s(C-H)); ¹H NMR (400 MHz, CDCl₃, δ): 0.7 (t, 2H, Si-CH₂-), 1.2 (m, 16H, -CH₂-), 1.5 (m, 2H, -CH₂-), 2.0 (m, 2H, -CH₂-), 2.2 (t, 2H, -S-CH₂-), 2.4 (q, 4H, -CH₂-S-, -CH₂-C=O), 3.5 (t, 2H, CH₂-Cl), 4.1 (t, 2H, -O-CH₂-).

POSS-Cl (12.5 g, 4 mmol), sodium azide (5.2 g, 0.08 mol), and DMF (200 mL) were mixed in a three-necked flask and then kept at 80°C for 24 h with vigorous stirring. The mixture was poured into water and extracted with ethyl acetate (200 mL). Organic layer was washed with water for several times. After the mixture dried over MgSO₄, the organic phase was concentrated by distillation and the product OADTP was obtained in the yield of 40%.

Figure 1: Synthesis of octakis(azidopropyl-3-oxycarbonyl-1-decyl-10-thiopropyl-3-)POSS (OADTP).

2.3 Preparation of OADTP-PTA resins

The OADTP-PTA resins were prepared by the reaction of TPDDM with BAMBP and OADTP. OADTP was incorporated into the resins in different molar ratios. TPDDM and BAMBP together with OADTP with the molar ratio 1.02:1.00 of alkyne group to azide group ($[C\equiv C]/[N_3]$) were mixed in acetone with a solid content of 70% and stirred at 60°C for 6 h. Acetone was removed by a rotary evaporator at 60°C and then the light yellow resins were dried in vacuum. The obtained resins were cured in the following procedure: 80°C/6 h + 120°C/2 h + 150°C/2 h + 180°C/2 h + 210°C/2 h. The synthesis reactions of OADTP-PTA resins are shown in Figure 2. The names of the resins with various content of OADTP are listed in Table 1.

2.4 Instrumentation and characterization

Nuclear magnetic resonance (NMR) measurements were carried out on a Bruker Advance 400 MHz Spectrometer (Bruker, USA) using tetramethylsilane as an internal standard in DMSO or $CDCl_3$. FT-IR spectrum measurements were carried out on a Nicolet iS10 infrared spectrometer (Madison, USA) in the region of 4,000–400 cm^{-1} using KBr pallets. Differential scanning calorimetry (DSC) analyses were performed with a Q2000 (TA, USA) at a heating rate of 10°C min^{-1} in a nitrogen atmosphere. Dynamic mechanical analysis (DMA) was carried out on

a DMA1 (Mettler Toledo, Switzerland) in the dual cantilever clamp mode under nitrogen at the frequency of 11 Hz with a programmed heating rate of 3°C min^{-1} from room temperature to 350°C. Thermogravimetric analysis (TGA) was conducted on a TGA/DSC 1 (Mettler Toledo, Switzerland) under nitrogen at a heating rate of 10°C min^{-1} from RT to 800°C, and the gas flow rate was 60 mL min^{-1} . The impact test was carried out on the Italy CEAST9050 cantilever beam impact testing machine, and the pendulum energy impact range was 0.55–22.5 J. No notch impact was tested when the pendulum energy was 4 J with the sample size of 80 × 10 × 4 mm on reference to GB/T2571-1995 standard. Scanning electron microscopy (SEM) observation was performed using the S-4800 scanning electron microscope (Hitachi, Japan) with an acceleration voltage of 15 kV.

3 Results and discussion

3.1 Synthesis and characterization of octakis(azidopropyl-3-oxycarbonyl-1-decyl-10-thiopropyl-3-)POSS

Figure 3 shows the FT-IR and 1H -NMR spectra of the POSS-Cl and OADTPs. In Figure 3a, the strong absorption at 1,092 cm^{-1} is the characteristic mode of Si–O–Si in the silsesquioxane cage (32,33). The stretching absorption at

Figure 2: Schematic route of synthesis and curing reactions of OADTP-PTA resins.

Table 1: The formulation of reactants for the synthesis of POSS-PTA

Resin	OADTP (mmol)	BAMBP (mmol)	TPDDM (mmol)
PTA	—	4.00	2.04
OADTP-PTA-03	0.03	3.88	2.04
OADTP-PTA-06	0.06	3.76	2.04
OADTP-PTA-10	0.10	3.60	2.04
OADTP-PTA-13	0.13	3.48	2.04
OADTP-PTA-16	0.16	3.36	2.04
OADTP-PTA-22	0.22	3.12	2.04
OADTP-PTA-34	0.34	2.64	2.04
OADTP-PTA-46	0.46	2.16	2.04

Figure 3: The FT-IR (a) and ^1H -NMR (b) spectra of POSS-Cl and OADTP.

$1,735\text{ cm}^{-1}$ belongs to the characteristic absorptions of the ester group $\text{C}=\text{O}$ and the azide $-\text{N}_3$ stretching vibration is located at $2,095\text{ cm}^{-1}$. The $\text{C}-\text{H}$ asymmetric stretching vibration of the CH_2 is at $2,853$ and $2,930\text{ cm}^{-1}$. In Figure 3b, for POSS-Cl, the signals of resonance at 0.65 , 1.53 , and 2.42 ppm are, respectively, assignable to methylene protons at positions a, b, and c. The strong signal of resonance at 1.21 ppm is assigned to the methylene protons marked e, and the resonances at 2.42 (d) and 2.24 (f) ppm correspond to the methylene protons of $\text{S}-\text{CH}_2$ and $\text{CH}_2-\text{C}=\text{O}$. The protons marked c and d are in similar circumstance so that the signal appeared at same position. The characteristic signal appearing at 2.04 , 3.55 , and 4.14 ppm corresponds to protons in chloropropyl marked h, i, and g, respectively. As shown in Figure 3b, the resonance signals for most protons of OADTP are similar with those of POSS-Cl, except that the h' , i' , and g' shift to 1.83 ,

3.32 , and 4.00 ppm because of the different electron attracting effect of chlorine atom and azide group.

3.2 Solubility of OADTP-PTA resins

For thermosetting resins, solubility has an impact on the process of the resin. The test for solubility is to place 10 mg resin in 1 mL solvent and then the mixture is stirred at room temperature. The results show that the resin has good solubility. The resin can be dissolved in solvents such as acetone, ethyl acetate, chloroform, dichloromethane, dimethyl sulfoxide, and ethyl acetate except for non-polar solvents, which is beneficial to the subsequent processing of the resin.

3.3 Curing behavior of OADTP-PTA resin

The curing behavior of OADTP-PTA resins was investigated by DSC at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere, and the obtained DSC curves of the OADTP-PTA-16 and PTA are shown in Figure 4. The results of DSC analyses for all OADTP-PTA resins are tabulated in Table 2.

As shown in Figure 4 and Table 2, the DSC curves show two exothermic peaks: one big peak between 70°C and 195°C and one small peak between 200°C and 215°C . The initial exothermal temperature (T_i) of the big peaks for all resins is around 70°C , the top peak temperature is around 142°C , and the end exothermal temperature is around 195°C . This indicates that the “Click” reaction of

Figure 4: DSC curve of PTA and OADTP-PTA.

Table 2: DSC analysis results of OADTP-resins

Resin	T_i (°C)	T_p (°C)	T_e (°C)	ΔH (J/g)
PTA	80	141	189	826.0
OADTP-PTA-03	69	141	196	822.9
OADTP-PTA-06	74	145	196	597.9
OADTP-PTA-10	72	145	198	552.4
OADTP-PTA-13	68	142	196	859.4
OADTP-PTA-16	74	143	199	781.0
OADTP-PTA-22	66	142	193	777.8
OADTP-PTA-34	71	144	194	758.8
OADTP-PTA-46	69	142	205	904.1

alkyne and azide is less affected by OADTP. The first exothermic heat ΔH of the resins is high. The initial curing reaction temperature should be determined around T_i to avoid explosive polymerization during curing process. A small exothermic peak from 200°C to 215°C is

probably the exothermic peak of self-polymerization of alkyne groups because of a bit excessive addition of alkyne monomer.

The curing process of OADTP-PTA-16 resin is studied by FT-IR analysis. The absorption of the characteristic functional group of OADTP-PTA-16 resin changes at different curing stages in the FT-IR spectra during the process of polymerization as shown in Figure 5. The azide $-N_3$ and alkynyl $-C\equiv C-$ stretching vibration are near $2,095\text{ cm}^{-1}$. The absorption peak gradually becomes weak with the curing process, and the absorption disappears after curing temperature reaches 210°C, indicating that the curing of OADTP-PTA resin is completed.

According to DSC and FT-IR analyses, the curing procedure is determined: 80°C/6 h + 120°C/2 h + 150°C/2 h + 180°C/2 h + 210°C/2 h.

3.4 Mechanical properties of cured OADTP-PTA resins

The mechanical properties of cured resins are listed in Table 3 and shown in Figure 6. The impact strength of OADTP-PTA resins increases at first, then reaches maximum, and finally decreases with the increase in the amount of OADTP. The flexural strength of OADTP-PTA resins is slightly higher than that of PTA resin. It can be clearly seen that the OADTP-PTA thermoset exhibits both toughening and strengthening in comparison with PTA thermoset.

From Figure 6, it is clearly shown that the impact strength peaks and reaches to 54.8 kJ m^{-2} when the molar content of OADTP is 0.16 mmol. The impact strength of OADTP-PTA-16 resin increases by 44.2% compared with 38 kJ m^{-2} of the PTA resin. Then, as the content of POSS compound continues to increase after exceeding 0.16 mmol

Figure 5: FT-IR spectra of OADTP-PTA-16 resin at different curing stages.**Table 3:** Mechanical properties of cured OADTP-PTA resins

Resins	Impact strength (kJ m^{-2})	Flexural strength (MPa)	Flexural modulus (GPa)
PTA	38.0 ± 2.8	124.8 ± 1.1	2.89 ± 0.02
OADTP-PTA-03	40.2 ± 2.4	133.5 ± 4.3	2.80 ± 0.06
OADTP-PTA-06	42.9 ± 1.7	135.6 ± 1.8	2.73 ± 0.06
OADTP-PTA-10	43.7 ± 2.3	136.5 ± 1.7	2.79 ± 0.08
OADTP-PTA-13	48.8 ± 2.6	138.6 ± 3.0	2.77 ± 0.04
OADTP-PTA-16	54.8 ± 2.1	138.6 ± 3.6	2.92 ± 0.08
OADTP-PTA-22	52.0 ± 1.4	134.7 ± 1.8	2.90 ± 0.12
OADTP-PTA-34	44.6 ± 1.3	127.2 ± 2.3	2.69 ± 0.04
OADTP-PTA-46	33.5 ± 0.7	130.8 ± 2.4	2.68 ± 0.05

Figure 6: The mechanical properties of cured OADTP-PTA resins.

the impact strength begins to decrease slowly and is lower than that of PTA resin at 0.46 mmol.

The result indicates that the POSS compound could increase the impact strength of PTA resin. On one hand, the POSS is organically combined with PTA resin through covalent bonds. OADTP contains eight active functional groups, which increases the crosslinking density of the material and improves the mechanical properties of the materials. POSS is a hollow inorganic nanoscale particle. When the cured OADTP-PTA resins are damaged, the silver streak caused by the impact will deflect when it

encounters the POSS nanoparticles in the resin, thereby absorbing a large amount of fracture energy. Uniformly distributed nanoparticles can produce micro-cracks in the resin when subjected to a force, triggering a stress concentration effect, and absorbing part of the energy to toughen the resin. On the other hand, OADTP has long flexible chains, which also could absorb and dissipate energy more efficiently than that with a rigid chain. Thereby, the toughness of the cured OADTP-PTA resins is improved. The increase in the amount of the addition leads to the decrease in performance, which is because too many nanoparticles will lead micro-cracks to crack, which has the opposite effect. Therefore, the amount of OADTP needs to be controlled within a certain range.

3.5 Microstructure analysis of cured POSS-PTA resins

The fracture morphology of resins observed by SEM could provide necessary information for the properties and modification of the resins. The SEM images for the fracture surfaces of the cured resins are shown in Figure 7. Figure 7a shows that the fracture surface of the cured PTA resin is smooth, and there are few shallow stress streaks,

Figure 7: SEM images of PTA resin and POSS-PTA resins: (a) PTA, (b) OADTP-PTA-16, (c) OADTP-PTA-46.

which presents a bit brittle fracture of the thermosetting materials. Figure 7b shows that the cracks possess branches, increasing the energy dissipation pathway of the matrix resin. With the high-speed impact, more energy could be absorbed and effectively disperses the stress concentration which demonstrates that the addition of OADTP gives the OADTP-PTA resin better toughness. However, when the addition OADTP exceeds a certain amount, the fracture surface of the OADTP-PTA-46 resin becomes smooth again with few stress streaks, as shown in Figure 7c, which supports that the impact strength decreases.

3.6 Thermal properties of cured OADTP-PTA resins

The effect of OADTP content on the thermal properties of cured POSS-PTA resins was evaluated with DMA and TGA, and the typical DMA and TGA curves are shown in Figures 8 and 9. All analysis results are tabulated in Table 4. The glass transition temperatures (T_g) of the cured resins were determined from the peak of $\tan \delta$. The result shows that the T_g of OADTP-PTA resins are slightly lower and decreased by 5–20°C, compared with PTA resin. With the addition of OADTP, the network has more flexible chain segment, so that the glass transition temperature of the OADTP-PTA resins reduces a little.

The thermal stability of the cured OADTP-PTA resins with different contents of OADTP was investigated by TGA, as shown in Figure 9 and summarized in Table 4. The char yield at 800°C first increases to 49.34% and then decreases to 38.40% because of the organic chain of the

Figure 9: TGA curves of cured PTA and OADTP-PTA resins.

Table 4: Thermal properties of cured PTA and OADTP-PTA resins

Cured resin	T_g (°C)	T_{d5} (°C)	Y_{800} (%)
PTA	235	355	40.25
OADTP-PTA-03	228	345	49.34
OADTP-PTA-06	221	356	42.54
OADTP-PTA-10	226	359	39.42
OADTP-PTA-13	229	357	39.72
OADTP-PTA-16	224	355	38.40
OADTP-PTA-22	221	357	39.27
OADTP-PTA-34	217	355	40.90
OADTP-PTA-46	207	354	37.81

POSS. The temperature at 5% weight loss (T_{d5}) of OADTP-PTA resins is almost the same as PTA resin. The OADTP-PTA resin maintains thermal stability of PTA because of the thermal stability of POSS.

Figure 8: DMA curves of cured PTA and OADTP-PTA-16 resin.

4 Conclusion

A new kind of N_3 -terminated POSS (OADTP) is synthesized and characterized, and related OADTP-PTA resins with different amount of OADTP are prepared via thermal reaction. The addition of OADTP can improve the mechanical properties. The mechanical properties of OADTP-PTA resins reach a maximum when the content of OADTP arrives at 0.16 mmol. The impact strength of OADTP-PTA resins increases first and then decreases with the increase in the amount of OADTP. The impact strength and flexural strength of OADTP-PTA-16 resin reach 54.8 kJ m⁻² and 138.6 MPa, increased by 44.2% and 11.1%, respectively.

Simultaneously, the OADTP-PTA resins maintain a good thermal stability of PTA resin. The temperature at 5% weight loss (T_{d5}) and the char yield at 800°C (Y_{800}) of OADTP-PTA-16 resin are 355°C and 38.40%, respectively.

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References

- Wan L, Luo Y, Xue L, Tian J, Chen X. Preparation and properties of a novel polytriazole resin. *J Appl Polym Sci*. 2010;104(2):1038–42. doi: 10.1002/app.24849.
- Rostovtsev VV, Green LG, Fokin VV, Sharpless KB. A stepwise Huisgen cycloaddition process: copper(I)-catalyzed regio-selective “ligation” of azides and terminal alkynes. *ChemInform*. 2002;41(14):2596–9. doi: 10.1002/chin.200243045.
- Ponce ML, Roeder J, Gomes D, Nunes SP. Stability of sulfonated polytriazole and polyoxadiazole membranes. *Asia-Pacific J Chem Eng*. 2010;5(1):235–41. doi: 10.1002/apj.370.
- Thibault RJ, Takizawa K, Lowenheilm L, Helms B, Hawker CJ. A versatile new monomer family: functionalized 4-vinyl-1,2,3-triazoles via click chemistry. *J Am Chem Soc*. 2006;128(37):12084–85. doi: 10.1021/ja0648209.
- Li H, Li L, Wu H, Lam JWY, Sun JZ, Qin A, et al. Ferrocene-based poly(aroxycarbonyltriazole)s: synthesis by metal-free click polymerization and use as precursors to magnetic ceramics. *Polym Chem*. 2013;4(22):5537–41. doi: 10.1039/c3py00892d.
- Tang J, Wan L, Zhou Y, Pan H, Huang F. Strong and efficient self-healing adhesives based on dynamic quaternization cross-links. *J Mater Chem A*. 2017;5(40):21169–77. doi: 10.1039/C7TA06650C.
- Austin B, Byul SH, Mathew M, Patricia F, Christopher N. Thermomechanical formation-structure-property relationships in photopolymerized copper-catalyzed azide-alkyne (CuAAC) networks. *Macromolecules*. 2016;49(4):1191–200. doi: 10.1021/acs.macromol.6b00137.
- Li Y, Zhou HEY, Wan L, Huang F, Du L. Synthesis and characterization of a new series of rigid polytriazole resins. *Des Monomers Polym*. 2013;16(6):556–63. doi: 10.1080/15685551.2013.771308.
- Wang Y, Wan L, Han D, Ye L, Huang F. Investigation of novel polytriazole resins. *Des Monomers Polym*. 2016;19(7):688–95. doi: 10.1080/15685551.2016.1209628.
- Huang F, Wan L, Du L, Li Y. The effects of structures on properties of new polytriazole resins. *High performance polymers and engineering plastics*. Hoboken, NJ: John Wiley & Sons, Ltd; 2011.
- Xue L, Wan L, Hu Y, Shen X, Huang F, Du L. Thermal stability of a novel polytriazole resin. *Thermochim Acta*. 2006;448(2):147–53. doi: 10.1016/j.tca.2006.07.012.
- Wan L, Luo Y, Lian X, Tian J, Chen X. Preparation and properties of a novel polytriazole resin. *J Appl Polym Sci*. 2010;104(2):1038–42. doi: 10.1002/app.24849.
- Chisca S, Marchesi T, Falca G, Musteata V, Huang T, Abou-Hamad E, et al. Organic solvent and thermal resistant polytriazole membranes with enhanced mechanical properties cast from solutions in non-toxic solvents. *J Membr Sci*. 2020;597(C):117634. doi: 10.1016/j.memsci.2019.117634.
- Tang Y, Jim CKW, Liu Y, Ye L, Qin A, Lam JWY, et al. Synthesis and curing of hyperbranched poly(triazole)s with click polymerization for improved adhesion strength. *ACS Appl Mater Inter*. 2010;2(2):566–74. doi: 10.1021/am9008727.
- Ma M, Wang X, Yu Z, Wan L, Huang F. High impact polytriazole resins for advanced composites. *Des Monomers Polym*. 2020;23:50–8. doi: 10.1080/15685551.2020.1761584.
- Laine RM. Nanobuilding blocks based on the $[\text{OSiO}_{1.5}]_x$ ($x = 6, 8, 10$) octasilsesquioxanes. *J Mater Chem*. 2005;15(15):3725–44. doi: 10.1039/b506815k.
- Pielichowski K, Njuguna J, Janowski B, Pielichowski J. Polyhedral oligomeric silsesquioxanes (POSS)-containing nanohybrid polymers. *Adv Polym Sci*. 2006;201:225–96. doi: 10.1007/12_077.
- Choi J, Harcup J, Yee AF, Zhu Q, Laine RM. Organic/inorganic hybrid composites from cubic silsesquioxanes. *J Am Chem Soc*. 2001;123(46):11420–30. doi: 10.1021/ja010720l.
- Choi J, Kim SG, Laine RM. Organic/inorganic hybrid epoxy nanocomposites from aminophenylsilsesquioxanes. *Macromolecules*. 2004;37(1):48–55. doi: 10.1021/ma030172r.
- Mohamed M, Kuo SW. Functional silica and carbon nanocomposites based on polybenzoxazines. *Macromol Chem Phys*. 2018;220(1). doi: 10.1002/macp.201800306.
- Nie Y, Leng X, Jiang Y, Chai S, Zhang J, Zou Q. Influence of reactive POSS and DDP on thermal stability and flame retardance of UPR nanocomposites. *e-Polymers*. 2017;17(6):463–70. doi: 10.1515/epoly-2016-0316.
- Chandramohan A, Alagar M. Preparation and characterization of cyclohexyl moiety toughened POSS-reinforced epoxy nanocomposites. *Int J Polym Anal Char*. 2013;18(1):73–81. doi: 10.1080/1023666X.2013.747253.

- (23) Kim GM, Qin H, Fang X, Sun FC, Mather PT. Hybrid epoxy-based thermosets based on polyhedral oligosilsesquioxane: Cure behavior and toughening mechanisms. *J Polym Sci Part B Polym Phys*. 2003;41(24):3299–313. doi: 10.1002/polb.10703.
- (24) Kopesky ET, McKinley GH, Cohen RE. Toughened poly(methyl methacrylate) nanocomposites by incorporating polyhedral oligomeric silsesquioxanes. *Polymer*. 2007;48:530–41. doi: 10.1016/j.polymer.2005.10.143.
- (25) Mohamed MG, Kuo SW. Functional polyimide/polyhedral oligomeric silsesquioxane nanocomposites. *Polymers*. 2019;11(1):26. doi: 10.3390/polym11010026.
- (26) Yilmaz S, Kodal M, Yilmaz T, Ozkoz G. Fracture toughness analysis of O-POSS/PLA composites assessed by essential work of fracture method. *Compos Part B Eng*. 2014;56:527–35. doi: 10.1016/j.compositesb.2013.08.081.
- (27) Kulinski Z, Piorkowska E. Crystallization, structure and properties of plasticized poly(l-lactide). *Polymer*. 2005;46:10290–300. doi: 10.1016/j.polymer.2005.07.101.
- (28) Song X, Zhang X, Li T, Li Z, Chi H. Mechanically robust hybrid POSS thermoplastic polyurethanes with enhanced surface hydrophobicity. *Polymers*. 2019;11(2):373. doi: 10.3390/polym11020373.
- (29) Fan X, Cao M, Zhang X, Li Z. Synthesis of star-like hybrid POSS-(PDMAEMA-*b*-PDLA)₈ copolymer and its stereocomplex properties with PLLA. *Mater Sci Eng*. 2017;76(Jul):211–6. doi: 10.1016/j.msec.2017.03.108.
- (30) Bu X, Zhou Y, Huang F. The strengthening and toughening effects of a novel octa(propargyl propyl sulfide) POSS (OPPSP) on silicon-containing arylacetylene (PSA). *Mater Lett*. 2016;174:21–3. doi: 10.1016/j.matlet.2016.03.067.
- (31) Lin H, Wan X, Jiang X, Wang Q, Yin J. A nanoimprint lithography hybrid photoresist based on the thiol–ene system. *Adv Funct Mater*. 2011;21(15):2960–7. doi: 10.1002/adfm.201100692.
- (32) Zhang W, Müller AHE. A “click chemistry” approach to linear and star-shaped telechelic POSS-containing hybrid polymers. *Macromolecules*. 2010;43(7):3148–52. doi: 10.1021/ma902830f.
- (33) Niu M, Li T, Xu R, Gu X, Yu D. Synthesis of PS-*g*-POSS hybrid graft copolymer by click coupling via “graft onto” strategy. *J Appl Polym Sci*. 2013;129(4):1833–44. doi: 10.1002/app.38877.