

Synthesis and characterization of sustainable polyurethane based on epoxy soybean oil and modified by double-decker silsesquioxane

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Abstract A series of environmentally friendly and sustainable polyurethanes using epoxy soybean oil as feedstock were synthesized with the introduction of double-decker silsesquioxane. Feature is that through the two-step polymerization, double-decker octaphenylsilsesquioxanetetraol was added to partially replace 1,4-butanediol acting as chain extender, and petroleum-based polyol was effectively replaced for polyurethane synthesis. On top of that, POSS tetraol was prepared and characterized by ¹H NMR and MALDI-TOF MS. As for the organic–inorganic hybrid nanocomposites, their structures and properties were investigated by FTIR, DSC, TGA, SEM, tensile test techniques, and static contact angle. DSC analysis showed that covalent incorporation of POSS into the PU network would increase the glass transition temperature (T_g) of the systems. TG analysis demonstrated that the hybrid nanocomposites were indeed more oxidative thermal stable, compared to virgin polyurethane especially at high temperature. SEM revealed that both nano- and micro-sized POSS aggregates were shown to be dispersed heterogeneously in the polyurethane matrix, despite the expectation to be dispersed or incorporate into molecular chains by chemical bonding between OH and NCO. According to the tensile test results, POSS-containing nanocomposites exhibited an increased modulus with an increasing POSS concentration at low POSS content, and with high loading, these values would decline. The results of the static contact angles revealed that the hydrophobicity

of the hybrid material was significantly improved with the inclusion of POSS.

Introduction

Polyhedral oligomeric silsesquioxanes (POSSs), having the empirical formula $(\text{RSiO}_{1.5})_n$, represent a class of rather versatile building blocks with the three-dimensional structure, which are characterized by the inner inorganic cage-like Si–O framework and external organic substituents that can feature a range of polar or nonpolar functional groups [1]. Generally, the synthetic strategies of POSS are based on the hydrolysis and condensation of trifunctional silsesquioxanes, substitution reactions with retention of the siloxane cage, corner-capping reactions, and the functionalization of the performed POSS cage [2]. In addition, attributing to the readily functionalized approach to POSS [3–7], derivatives possessing various actively functional groups and unique performance can be prepared with one or more reactive functional groups. The enhancement at molecular level through maximizing the surface area and chemical interaction with polymer matrix make POSS widely applied in the design and synthesis of novel organic–inorganic hybrid nanomaterials exhibiting enhanced thermal [8, 9], mechanical properties (e.g., strength, modulus, rigidity), nonflammability [10–12], oxidative resistance [13], and excellent dielectric properties [14–16] via the synergism of organic and inorganic components. For such nanocomposites, currently, synthetic procedures are mainly based on simple physical blending or copolymerization of POSS into polymer matrix. For the latter, it is widespread to introduce POSS into a polymer matrix by covalently bonding as a pendent group [17–20] or a nanocross-linker [21–23]. As a result, a series of

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POSS-containing nanocomposites were achieved like polystyrene–POSS copolymers [24], polymethacrylate–POSS copolymers [21, 25], norbornyl–POSS copolymers [26], polyethylene–POSS copolymers [27], polypropylene–POSS copolymers [28, 29], poly(ethylene oxide)–POSS copolymers [30], epoxy resin–POSS copolymers [31, 32], polyamide–POSS copolymers [33, 34], polyurethane–POSS copolymers [11, 35, 36], polyimide–POSS copolymers [37, 38], and phenolic–POSS copolymers [2, 39].

Due to their versatility, polyurethanes have been tailored to meet significant applications in coatings, adhesives, sealants, elastomers as well as other fields. However, to endow these materials with excellent and special performance for extraordinary application, a growing number of work have been conducted such as modification with silicon-containing compounds including polysiloxanes and POSS. Raftopoulos and coauthors [36] prepared PU/POSS nanocomposites with 1,2-propanediol isobutyl POSS (PHIPOSS) and aminoethylaminopropyl isobutyl POSS (DIAPOSS) tethered by urethane or urea linkages on the hard segments of polyurethane chains to achieve T_g increasing materials. Markovic et al. [40] synthesized a series of polyurethane hybrids octakis (*m*-isoprenyl- α,α -dimethylbenzylisocyanato dimethylsiloxy) octasilsesquioxane (Q8M8) as a crosslinking agent. Mather and coauthors [41] controlled the molar ratio of PCL:POSS to obtain poly(ϵ -caprolactone)-POSS multiblock thermoplastic polyurethanes. To my best knowledge, other POSSs with active groups such as amino-group and hydroxyl-group were also successfully introduced to polyurethane chains to acquire high-performance materials [5, 42–44].

In recent years, few investigations have been done on the polyurethane/POSS hybrids with respect to sustainable resources. In order to better solve global emergency problems and the shortcoming of pure nature-based polyurethane, further studies are necessary to be conducted. Therefore, the purpose of this paper is to propose a synthetic method of novel sustainable polyurethanes modified by POSS. Moreover, we also discussed the thermal and mechanical properties as well as the morphology and surface hydrophobicity of these hybrids after modification. The strategy may hold great promise for future high-end uses of soybean oil-based polyurethane.

Materials and methods

Materials

Phenyltrimethoxysilane (98 %) was purchased from Xiya Reagent Co. (Chengdu China) and used without further purification. Epoxy soybean oil (ESO) was obtained from Hairma Chemical (GZ) Ltd., China. Isophorone diisocyanate

(IPDI; Wuxi East Grace Electronic Material Technology Co., Ltd.), stannous octoate (Shanghai Reagent Co.), and 1,4-butanediol (BDO; Aldrich) were purchased to prepare polyurethanes. Prior to use, reagents such as ethyl acetate (EtAc), tetrahydrofuran (THF), and 1,4-butanediol (BDO) need to be dehydrated and stored in the presence of 4A molecular sieves. Unless specially indicated, other reagents in this article were purchased from Shanghai Reagent Co., China and used as received.

Synthesis

Synthesis of double-decker octaphenylsilsesquioxanetetraol (DDT₈OH)

The synthesis of octaphenylsilsesquioxane underwent a two-step procedure. Firstly, Octaphenyldicyclooctasiloxane tetrasodium silanolate ($\text{Na}_4\text{O}_{14}\text{Si}_8(\text{C}_6\text{H}_5)_8$) was prepared according to the method reported by Kakimoto and coauthors [45]. To prepare DDT₈OH, the hydrolysis reaction of $\text{Na}_4\text{O}_{14}\text{Si}_8(\text{C}_6\text{H}_5)_8$ was carried out by following the literature reported by Kazuhiro Yoshida et al. with slight modification. Typically, $\text{Na}_4\text{O}_{14}\text{Si}_8(\text{C}_6\text{H}_5)_8$ (3 g, 2.6 mmol) and tetrahydrofuran (30 mL) were charged into a flask equipped with magnetic stirrer and a nitrogen bubbler. Thereafter, acetic acid (2.4 g) was quickly added to maintain a small nitrogen flow and temperature below 30 °C. After stirring for 3.5 h, deionized water (20 g) was added and the stirring was kept for another 1 h. Remove the solvent with the rotary evaporation and then add 20 mL chloroform. Then the solution was transferred into a separating funnel and washed with the saturated sodium hydrogen carbonate solution and deionized water to obtain a neutral solution. After all the programs, the organic layer was dried on anhydrous magnesium sulfate and condensed under reduced pressure. The crude resultant was purified by passing through a silica gel column to afford white solids.

Prepare and synthesis of soybean oil-based polyurethane

To synthesized sustainable polyurethane, ESO as feedstock needs to be converted into polyol firstly. In our method, epoxy groups were opened with methanol using tetrafluoroboric acid as catalyst according to the literature reported by Petrovic [46]. Finally, a light-yellow viscous SBO polyol with a OH number 177 mg KOH/g was obtained.

Polyurethanes were synthesized by a standard two-step prepolymer method and a typically synthetic procedure as follows: SBO polyol (4 g, 12.62 mmol OH), EtAc (20 mL), stannous octoate (100 μL), and IPDI (1.98 mL) were charged into a flask equipped with a magnetic stirrer, a condenser, and a nitrogen bubbler. Under a high pure nitrogen atmosphere, the pre-polymerization was

performed at 80 °C for 2 h with vigorous stirring. After determining the isocyanate (NCO) content according to ASTM D5155-96, stoichiometric amount of chain extender 1,4-butanediol (BDO) was added and the reaction mixture was kept stirring for another 2 h at 80 °C. Finally, the resultant mixture was poured into a Teflon plate, allowed to evaporate the solvent, and then cured at 50 °C for 12 h.

Synthesis of hybrid polyurethane with DDT₈OH as a chain extender

The synthesis of hybrid polyurethane was similar to pure polyurethane at the stage of prepolymer. However, different contents of DDT₈OH (See Table 1) dissolved in ethyl acetate were added into the prepolymer solution in the chain extending stage, maintaining stirring and ultrasonic dispersion for 30 min. Thereafter, stoichiometric amount of chain extender 1,4-butanediol (BDO) was added to control the overall molar ratio of hydroxyl groups to isocyanate functional groups to be 1:1.05, followed by determining the isocyanate (NCO) content of the above mixture. The chain extension reaction was also performed at 80 °C for 2 h, and the products were poured into a Teflon plate, allowed to evaporate the solvent, and then cured at 50 °C for 12 h. Consequently, a series of sustainable hybrid polyurethanes were successfully synthesized.

Measurements

¹H nuclear magnetic resonance (NMR) spectra were recorded on a 400 MHz Bruker Instruments (model Avance 400, Germany) using Acetone-d₆ as solvent and tetramethylsilane (TMS) as internal reference. Matrix-assisted ultraviolet laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) experiment was carried out on an ultrafleXtreme MALDI-TOF/TOF mass spectrometer. For analysis, the matrix 2,5-dihydroxybenzoic acid dissolved in THF (50 mg/mL) was mixed with double-decker POSS solution (0.1 mg/mL in 1:1 v/v ratio). The ATR-FTIR spectra were obtained with a Nicolet 6700 infrared spectrometer using a DL_aTGS detector. All spectra

were carried out between 4000 and 500 cm⁻¹ with averaging 32 scans at a resolution of 4 cm⁻¹. The morphology of the samples was observed by Scanning Electron Microscopy (S-4800, Hitachi), and the samples were fractured with liquid nitrogen and coated with gold prior to use for observation, and to avoid carbonizing organic molecular, the accelerating voltage should be chosen as 1 kV. Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) of the hybrids were performed using TA Instruments (TGA/1100SF) and (TA-DSC822e), respectively. The thermogravimetric analysis (TGA) was ramped at 20 °C/min under a nitrogen flow rate of 50 mL/min from 25 to 600 °C. While for DSC analysis, samples (5–10 mg) were loaded in alumina pans and cycled twice through a temperature range of 0–150 °C at a nitrogen flow rate of 50 mL/min. The tensile properties were measured according to ASTM D 882-97 on a tensile tester model and the gage length was 4 mm. The extension rate was 10 mm/min, and five specimens were used for each sample.

Results and discussion

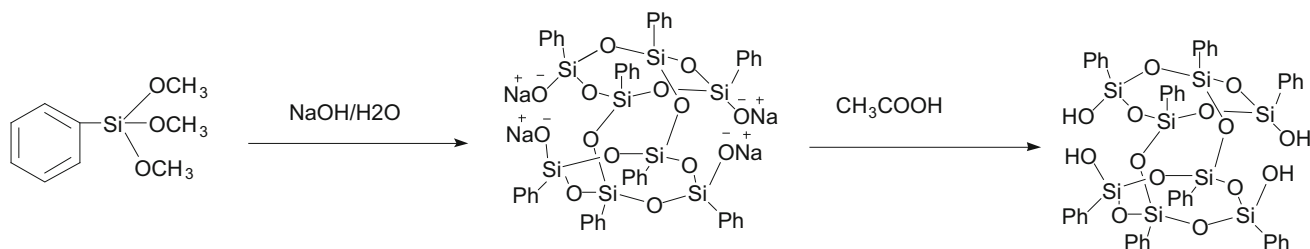
Synthesis

Synthesis of double-decker octaphenylsilsesquioxanetetraol (DDT₈OH)

Toward our final research, DDT₈OH was synthesized firstly as shown in Scheme 1. According to the literature reported by Kakimoto and coauthors [45], octaphenyldicyclooctasiloxane tetrasodium silanolate [Na₄O₁₄Si₈(C₆H₅)₈] was synthesized. Thereafter, the hydrolysis reaction between [Na₄O₁₄Si₈(C₆H₅)₈] and acetic acid was carried out to afford DDT₈OH. To verify the successful synthesis of DDT₈OH, ¹H NMR and MALDI-TOF MS were taken into analysis. In the ¹H NMR spectra shown in Fig. 1, the resonance at 2.90 ppm was attributed to the protons of hydroxyl groups, whereas the signals of resonance in the range of 6.60–7.90 ppm were ascribed to the protons of benzene, and

Table 1 Chemical composition of polyurethanes

Samples	SOB polyol mass (g)	IPDI vol. (ml)	Stannous octoate vol. (μl)	DDT ₈ OH mass (g)	DDT ₈ OH (wt%)
Pure PU	4	1.98	100	0	0
Hybrid-1	4	1.98	100	0.10	1.56
Hybrid-2	4	1.98	100	0.30	4.48
Hybrid-3	4	1.98	100	0.50	7.20
Hybrid-4	4	1.98	100	0.70	9.75
Hybrid-5	4	1.98	100	0.90	12.59



Scheme 1 Synthetic route of DDT₈OH

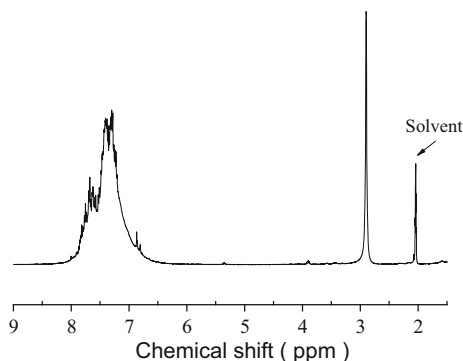


Fig. 1 ¹H NMR of DDT₈OH

the ratio of integral intensity for these protons was measured to be 1:10, which were successfully consistent with the value calculated according to the structure formula. The molecular weight of DDT₈OH was measured by MALDI-TOF MS (shown in Fig. 2). It was seen that DDT₈OH possessed the molecular weight of 1068 [1091.08–23], which fully agrees with the value calculated according to the structure formula.

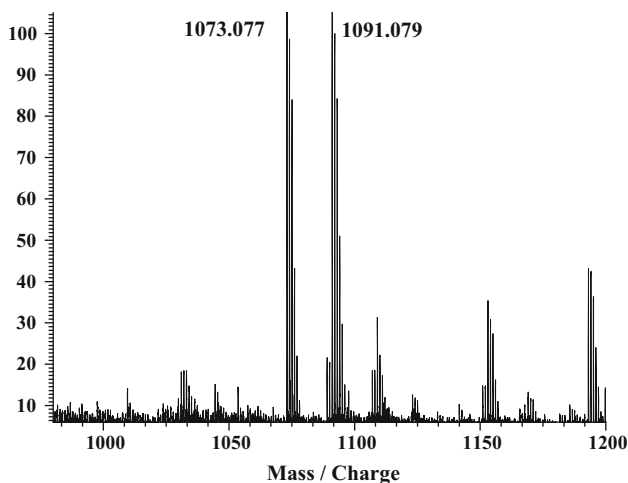


Fig. 2 MALDI-TOF MS of DDT₈OH

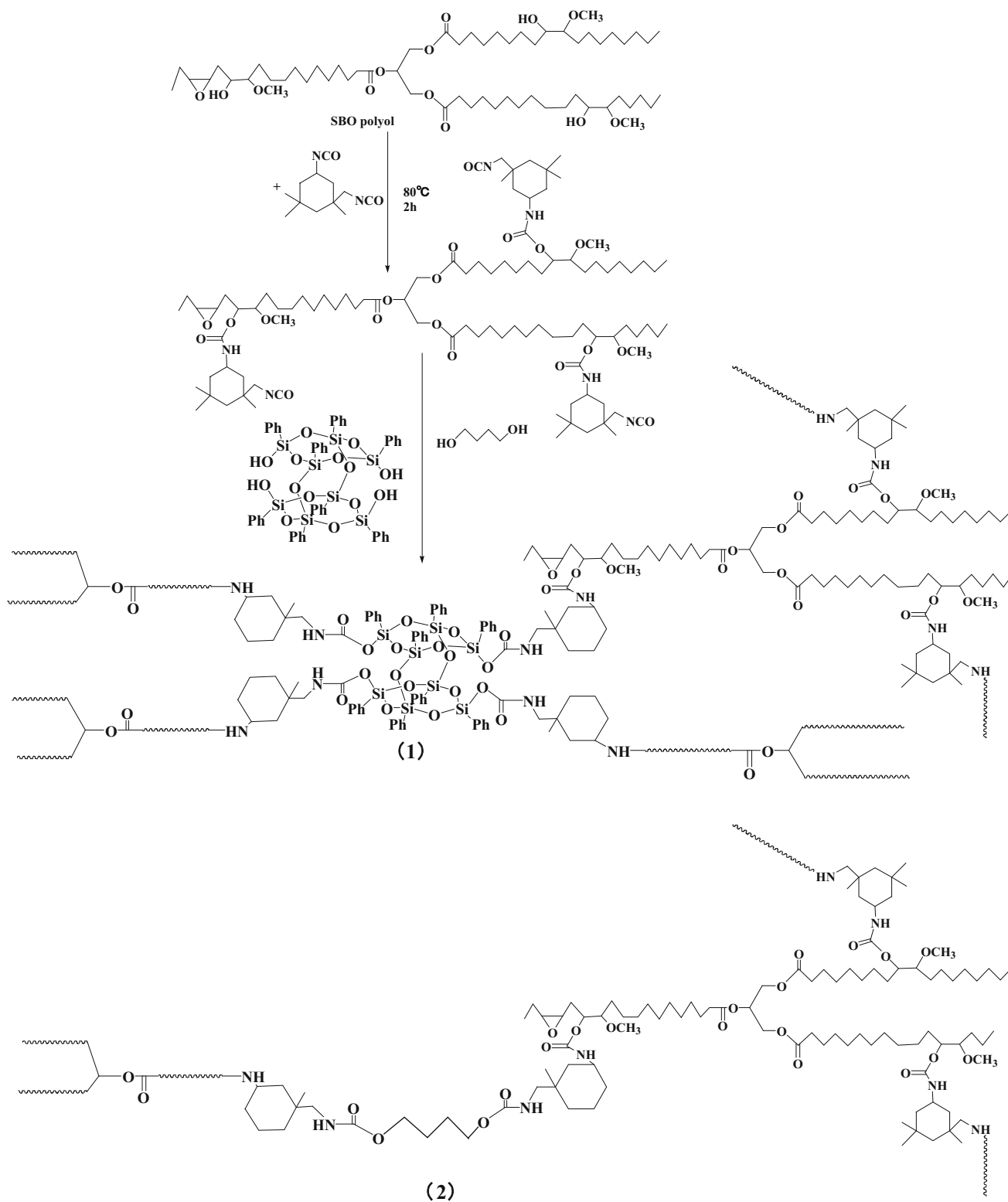
In short, the results of ¹H NMR and MALDI-TOF MS indicate the successful synthesis of DDT₈OH.

Synthesis of sustainable polyurethane and hybrid polyurethanes

Hybrid polyurethanes with double-decker POSS in the main chains were synthesized through the reaction between soybean oil polyol and IPDI using DDT₈OH and BDO as chain extenders (See Scheme 2). A series of ATR-FTIR were taken to identify the chemical structures of the polyurethanes as shown in Fig. 3. All PUs exhibit absorption peaks around 3340 cm⁻¹ ascribed to the stretching vibration of NH. For Si–O–Si groups in the silsesquioxane cages, the stretching vibration occurred around 1100 cm⁻¹. However, for the PU–POSS hybrids, perhaps the unfortunate overlap between Si–O–Si groups and that of the aliphatic ether lead to small difference among the IR spectra [47].

DSC analysis

DSC analyses of all samples were conducted to evaluate the effect of POSS on the motion of the macromolecular chains, and all T_g (the midpoint of the stepwise decrease of the heat flow trace observed during heating) values are reported in Table 2. With the increasing of POSS fraction in the polymer, the T_g was slightly shifted to higher temperatures from a $T_g = 38$ °C (pure PU) to a $T_g = 65$ °C (PU/POSS with 12.59 wt% POSS). It was convinced that the relatively rigid structure of the bulky POSS cages would restrict the chain motion, thereby decreasing the free volume, and consequently, higher temperatures were required to provide the requisite thermal energy to cause a glass transition in the hybrids [48]. Besides, according to other reports, with high POSS content, a serious aggregation occurred, which would increase the free volume since the aggregation particles acted as solid lubricant and resulted in the decrease of the T_g . Both the two opposite factors contributed to the change of T_g , but in the current system, perhaps the former played a leading role (Fig. 4).



Scheme 2 Synthetic route of PU-DDT₈OH

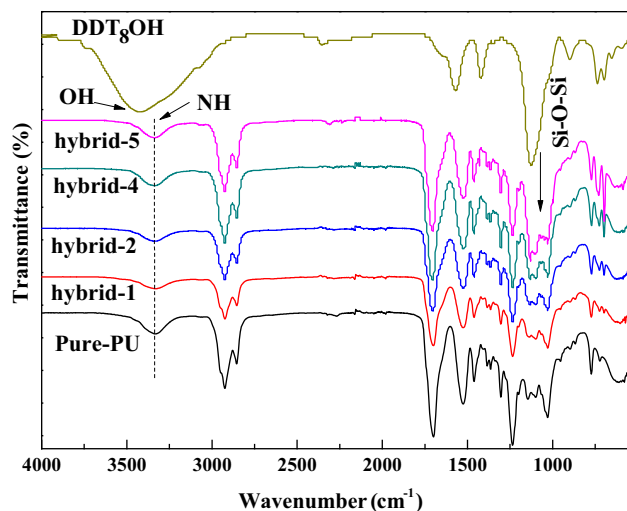


Fig. 3 FTIR spectra of PU hybrids and DDT₈OH

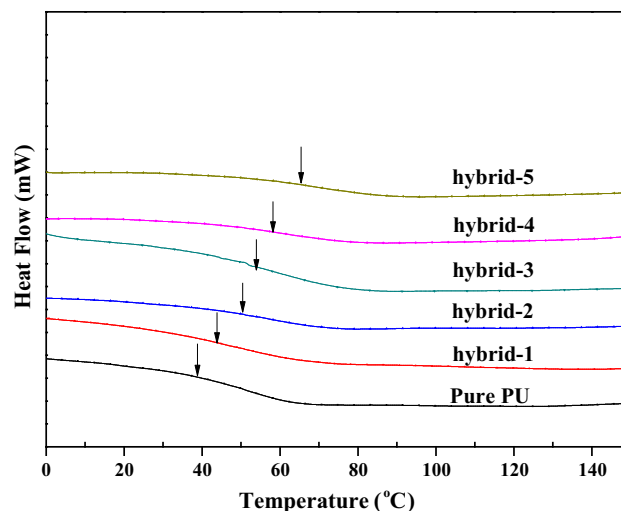


Fig. 4 DSC curves of all PUs

Thermal decomposition behavior

Thermal decomposition behaviors of the hybrids were examined with TGA (see Fig. 5) at a heating rate of 20 °C/min in a nitrogen atmosphere. For analysis, we defined T_{d5} as the onset of decomposition temperature, where the samples showed 5 % weight loss. As it can be seen, the thermal decomposition of PU hybrid was a two-step process. The initial thermal decomposition (5 wt% weight loss) of PU hybrid due to the decomposition of urethane bonds took place above 200 °C, while the second decomposition process attributed to soybean oil chain scission occurred later on at 340 °C [49–51]. It can be noted that all polyurethanes show a similar TGA decomposition trend, which demonstrated that the degradation mechanism does not significantly alter despite the introduction of DDT₈OH. Clearly, the 5 % weight loss temperatures (T_{d5}) for hybrids were significantly higher than pure polyurethane, especially with 4.48 % POSS content, whose T_{d5} can be as high as 250 °C, almost 37 °C higher than pure polyurethane. However, beyond 4.48 %, with the increasing concentration of DDT₈OH, the onset of decomposition temperature gradually decreased. In this context, two possible facts could be envisaged about this thermal phenomenon.

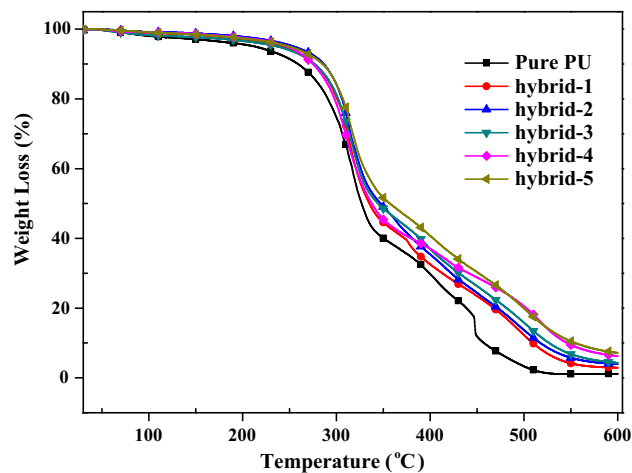


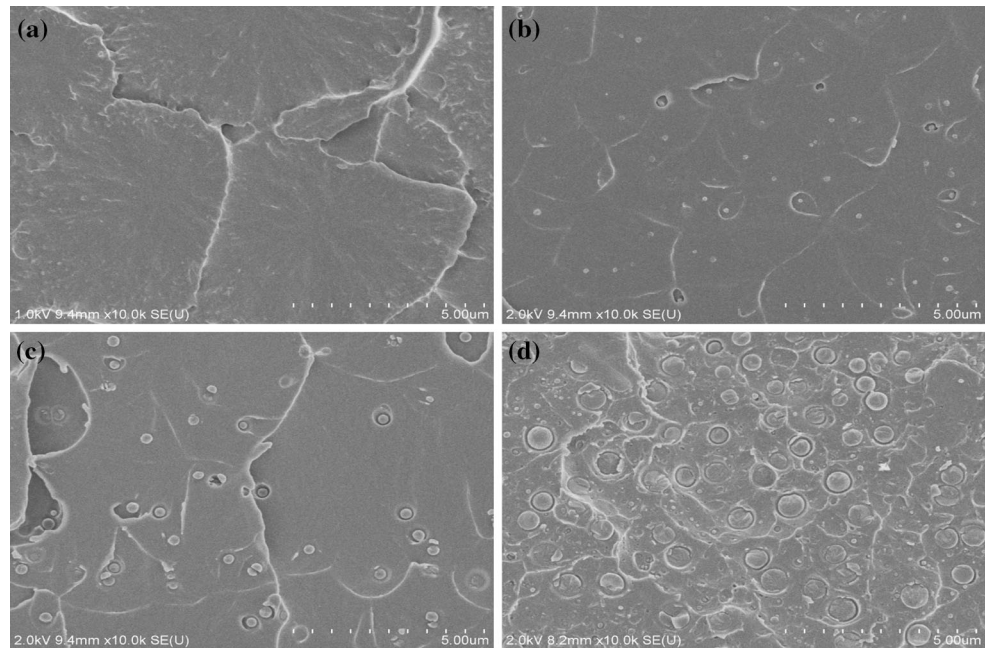
Fig. 5 TGA curves of polyurethanes POSS nanocomposites

Firstly, the incorporation of DDT₈OH, which displayed excellent thermal stability, into polyurethane chains through chemical bonds could significantly retard the movement and scission of molecular chains, consequently improving T_{d5} . Secondly, when POSS content was beyond 4.48 wt%, aggregation between POSS became serious, which would reduce the overall effectiveness in inhibiting chain scission. In fact, both the two opposite effects

Table 2 TGA results of pure and hybrid polyurethanes

Samples	DDT ₈ OH (wt%)	T_{d5} (°C)	Char residue (wt%)	T_g (°C)
Pure PU	0	213	1.18	38
Hybrid-1	1.56	248	2.94	43
Hybrid-2	4.48	250	3.94	50
Hybrid-3	7.20	242	4.33	54
Hybrid-4	9.75	237	6.26	58
Hybrid-5	12.59	231	7.19	65

Fig. 6 SEM images of polyurethanes POSS nanocomposites with 4.48, 7.20, 9.75, and 12.59 wt% poss.
a Hybrid-2 (4.48 wt% poss).
b Hybrid-3 (7.20 wt% poss).
c hybrid-4 (9.75 wt% poss).
d Hybrid-5 (12.59 wt% poss)



determined the change of T_{d5} together. In addition, with high POSS content, TGA curves above 350 °C became flatter which indicated that the decomposition rates during the second decomposition process of the hybrids were slower. It was convinced that the silicon dioxide from the oxidation of POSS at high temperature would be coated on the surface and suppress the release of gaseous products from segmental decomposition, which made the material heat insulating and flame resistance [52, 53]. The fact that superior thermal stability was in accordance with higher char residual (see Table 2) was also proved above conclusion.

Morphology

Scanning electron microscopy (SEM) was performed to identify changes in surface morphology related to the POSS contents. Figure 6 displays a group of SEM images of the samples with 4.48, 7.20, 9.75, and 12.59 wt% POSS, and it could be seen that the images of the composites displayed numerous micron-sized particles on the fracture surfaces. The number as well as the size of particles increased as POSS loading increased. At low POSS content, the morphology of the PU hybrid still displayed relatively smooth structure, except for numerous micron-sized particles about 200 nm dispersing on. However, as POSS loading increased, the dispersed particles gradually seeped into the organic matrix and small particles gradually aggregated into larger ones with a size of 650 nm. The phenomenon occurred because POSS had a strong aggregation effect through physical interactions similar to the

reports by A. Strachota et al. [54, 55]. For these strong physical interactions, it might be interpreted that due to benzene ring being hydrophobic and inert to PU chains, the only direction of the nano-cages interacting with the matrix would be the hydroxyls hung on the open face of the POSS cage. In addition, the incorporation of POSS could also change the material morphology as numerous detachment regions and holes appeared (Fig. 6d). On increasing POSS content, particles with relatively large size fell into corresponding holes, which might be derived from the removal of the solvent EtAc enveloped to the space between particles and polymers.

Mechanical properties of PU–POSS hybrids

Tensile tests were carried out at room temperature to evaluate the static mechanical properties of PU/POSS hybrids, and the results are shown in Fig. 7. With low POSS content (not above 7.20 wt%), hybrid polyurethanes displayed brittle fracture, which was attributed to the changes of macromolecular bonds and angles. However, in the case of hybrid PU containing 12.59 wt% of POSS, there existed an unexpected yield point and ductile fracture manifested in the movement and rearrangement of polymer chain segment started. The tensile tests indicated that all of the POSS-containing hybrid polyurethanes behaved like glassy polymer. Compared to pure PU, POSS-containing nanocomposites exhibited an increased modulus with an increasing POSS concentration at low content, but with high loading, this value would drastically decline. This trend could be interpreted on the basis of two factors: 1.

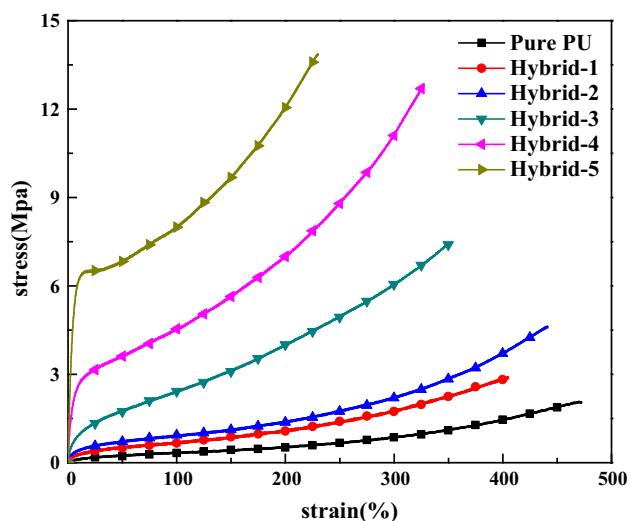


Fig. 7 Stress–strain curves of all PUs

Table 3 Static contact angles of pure PU and the hybrid polyurethanes

Samples	DDT ₈ OH (wt%)	Static contact angle	
		$\theta_{\text{H}_2\text{O}}$ (°)	$\theta_{\text{ethylene glycol}}$ (°)
Pure PU	0	74.2 ± 1.10	57.4 ± 0.40
Hybrid-1	1.56	88.5 ± 0.80	61.4 ± 0.10
Hybrid-2	4.48	91.7 ± 1.30	63.5 ± 0.10
Hybrid-3	7.20	92.6 ± 0.20	72.8 ± 0.80
Hybrid-4	9.75	95.2 ± 0.20	78.1 ± 0.50
Hybrid-5	12.59	103.7 ± 0.3	81.0 ± 0.20

The nano-reinforcement of POSS cages on the polymeric matrices and the increase in cross-link density of the networks by chemical introduction of POSS led to mechanical enhancement. 2. At higher POSS content, there was a possibility of over-crosslinking and serious aggregation, which resulted in mechanical impairment.

Surface hydrophobicity

The surface hydrophobicity of the organic–inorganic hybrid polyurethanes was investigated, since the DDT₈OH cages in the hybrid polyurethanes were the derivatives of organosilicon compound which was famous for low free energy. In order to certify the effect of DDT₈OH on surface wettability, all hybrid polyurethanes were studied by means of static contact angle measurements. Water and ethylene glycol were used as probe liquids to obtain the static contact angles, respectively. The static contact angles of pure PU and the hybrid polyurethanes are shown in Table 3. From Table 3, a conclusion that both the water and ethylene glycol contact angles of the hybrid

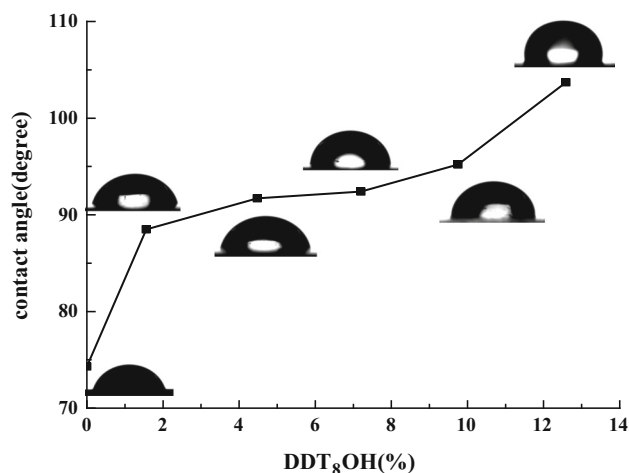


Fig. 8 Plot of surface water contact angles as a function of the content of all PUs

polyurethanes were mildly heightened with the increasing concentration of DDT₈OH in the copolymers (see Fig. 8) in comparison with the pure PU could be drawn. For hybrid 5, the water contact angle reached 103.5°, illustrating that the hydrophobicity of the hybrid material was significantly improved.

Conclusions

In this work, a series hybrid polyurethanes based on sustainable epoxy soybean oil were synthesized using double-decker octaphenylsilsesquioxanetetraol (DDT₈OH) to replace 1,4-butanediol (BDO) as chain extender. According to the analysis of ¹H NMR and IR, the DDT₈OH was successfully synthesized and introduced into the molecular chains. By controlling the adding amounts of inorganic constitutes, the mass percentage of DDT₈OH could reach up to 12.59 wt%. Thereafter, a series of characterizations were conducted to evaluate the quality of the material. TGA revealed that the thermal stabilities of the nanocomposites were enhanced, especially for the thermal decomposition at high temperature. The DSC results suggested that the nanocomposites displayed increased glass transition temperatures (T_g), making molecular chains more rigid. SEM indicated that POSS was homogeneously dispersed in the polymer matrix at low DDT₈OH concentration; however, serious aggregation would occur with high loading. In terms of tensile tests, the nanocomposites showed enhanced mechanical performance to some extent. The hydrophobicity of the hybrid material was significantly enhanced as the static contact angle displayed. Overall, the results of the present work confirm that the incorporation of double-decker silsesquioxane into sustainable polyurethane molecular chains can make it possible to prepare hybrids

with relatively perfect physical properties and will open up new pathways for the development of environmentally friendly polymer finally.

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