

## Synthesis and Characterization of Sustainable Polyurethane Modified by Cyclic Polysiloxane

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**ABSTRACT:** In this article, a series of sustainable polyurethanes are prepared by introducing different content of cyclic polysilanol, which may act as a chain extender to replace 1, 4-butanediol (BDO). Consequently, cyclic polysiloxanes are successfully incorporated into the molecular chains to afford organic–inorganic polyurethanes and then their effects on polyurethanes thermal properties and surface hydrophilicity are fully characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and contact angle testing. Results show that the hybrid polyurethanes display enhanced glass transition temperatures ( $T_g$ ). While in terms of TGA, the effects of cyclic polysilanol on thermal properties seem complex, which would reduce the thermal stability in the first degradation process but enhance in the second process. The morphology observed by scanning electron microscopy (SEM) show that the inorganic constitutions, namely, cyclic polysilanol, may occur to self-condensation or aggregation, which can help to explain the uncommon thermal phenomenon above. Thus, an opportunity of future applicability in the areas of sustainable polymer with improved properties can be envisioned in our research method of hybrid polyurethanes. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 41277.

**KEYWORDS:** biopolymers and renewable polymers; functionalization of polymers; morphology; polyurethanes; thermogravimetric analysis

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### INTRODUCTION

Because of their versatility, polyurethanes have been tailored to meet significant applications in coatings, adhesives, sealants, elastomers as well as other fields. Conventionally, the widespread synthetic route of polyurethane is to react a petroleum-based polyol with a diisocyanate. However, during this process, problems of the depletion of petroleum resources, environmental pollution, and waste disposal have become increasingly prominent.<sup>1</sup> Recently, efforts of searching for renewable and environment friendly feed stocks to substitute petroleum resource have been made globally. During all these researches, nature oils are supposed to be the ideal candidates and consequently attracted considerable attentions with regard to their relatively low cost, readily availability, renewable, biodegradable, and eco-friendly properties. All of these advantages of nature oils can provide an excellent platform for both the synthesis and application of polymeric materials. With these in mind, the polyurethane industry may benefit most from the research and development of natural triglyceride oils such as soybean oil, castor oil, palm oil, and rapeseed oil.<sup>2</sup> Despite for the excellent development prospects of these oil, shortcomings of their derivatives still exist especially from the hydroxyl value as well as the

length of the molecular chains of corresponding triglyceride oils derivatives.<sup>3</sup> To make them available, researchers have devoted to modify these nature triglyceride oils with the introduction of multiple hydroxyl functionalities and to date, several strategies such as air oxidation, ozonolysis/reduction, epoxidation/hydroxylation, hydroformylation have been developed successfully in this field.<sup>4–8</sup> Among them, polyols synthesized from ring opening reaction of epoxidized triglyceride oils in the presence of acid catalysts is one of the most exploited process. For example, Petrovic et al. synthesized four polyols by oxirane ring opening with HCl, HBr, methanol, and hydrogen.<sup>9</sup> Other ring opening reagents such as lactic acid, 1,2-propanediol, ethylene glycol, ethylene oxide, and different catalysts were also applied to convert plant oil into a polyol.<sup>10–13</sup>

As novel materials, organic–inorganic hybrids have drawn immense attentions due to their excellent and comprehensive properties. To date, scientists have been successfully incorporated inorganic constituents into the macromolecular structure both by physical intermixing and chemical bonding methods to obtain high performance polymers. It is commonly believed that precise control of the dispersion of inorganic compounds in organic matrices and their spatial distribution may dominate

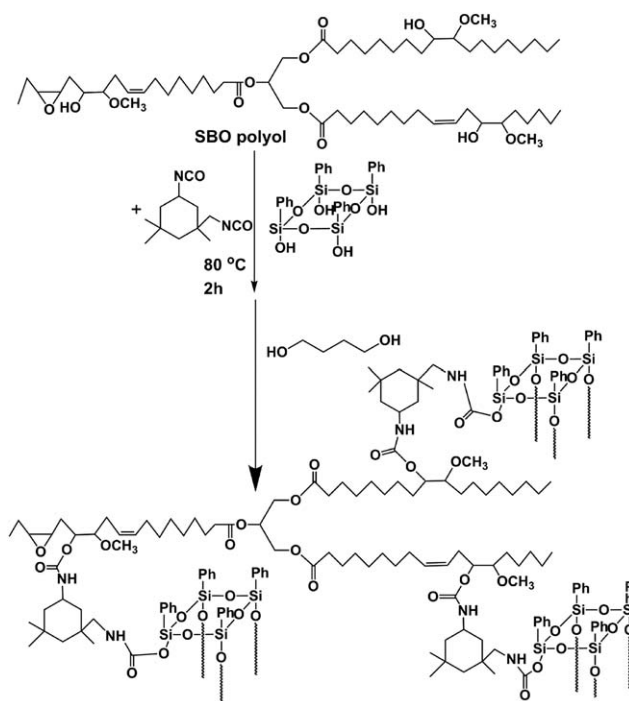
the design and synthesis of novel polymers. For uniformly dispersion, covalently incorporation is proved to be a good solution and consequently lead to enhanced performance. According to the results of previous work by others, organic siloxanes and their derivatives can be ideal candidates for the implementation of this approach, which not only possess reactive functional groups themselves but also can be easily modified to introduce into polymer chains. To accommodate the rapid development of society, it is imperative to prepare polyurethanes possessing the following two characteristics: First, raw materials should be readily availability, renewable, biodegradable, and eco-friendly properties; Second, optimal process could endow them with excellent performance to make them with practical application. So far, growing number of work has been conducted on petroleum-based polyurethanes modified with silicon-containing compounds including polysiloxanes, polysilsesquioxanes, but very limited attention has been attached to the nature oil-based polyurethanes.<sup>14–21</sup> Despite there are some scientific and patent literature on the plant oil-silica hybrids, these modifications merely focus on the hydroxylated or epoxidized oil for simple processing and no polymers such as polyurethane were synthesized.<sup>22,23</sup> Therefore, it is imminent to obtain high performance materials efficiently using organic–inorganic hybrid technology to modify nature oil-based polyurethane.

With these in mind, in this contribution, we focused on the synthesis of hybrid polyurethanes with polysiloxane into polyurethanes chains by the use of tetrafunctional polysiloxane. To the best of our knowledge, these sustainable polyurethanes with cyclic tetramer siloxane anchored to the chain backbone have not been reported up to now and in our opinion, with the excellent thermal oxidation resistance of polysiloxane and low surface energy of silicon atoms, such modification may lead to significant thermal property enhancement, while simultaneously improving other physical properties such as surface hydrophobicity. Toward this end, polysiloxane tetraol used as a chain extender to partially replace 1,4-butanediol (BDO) was synthesized in the first place. In particular, The PU hybrids were characterized by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) and surface contact angles testing. Furthermore, a strange and interesting phenomenon-micrometer aggregates-was investigated, which may result from the self-condensation or aggregation of polysiloxane tetraol. The reason remains unclear, which requires further study.

## EXPERIMENTAL

### Materials

Epoxy soybean oil (ESO) with nominal number-average molecular weights ( $M_n$ ) of 1285 (determined by GPC) were obtained from Hairma Chemical (GZ), China. Phenyltrichlorosilane (98%) was purchased from Shanghai Darui Fine Chemical and used without further purification. Isophorone diisocyanate (IPDI) and stannous octoate were purchased from Wuxi East Grace Electronic Material Technology and Shanghai Reagent Company, respectively. Without special explanation, all other reagents for this research were purchased from Shanghai Re-



**Scheme 1.** Synthesis route of the hybrid polyurethanes.

gent, China. The reagents such as acetone, isopropyl alcohol, methanol, tetrafluoroboric acid, carbon disulfide were of chemically pure grade and used as received. Tetrahydrofuran (THF) were distilled with metal sodium and stored in the presence of a molecular sieve of 4A before use. BDO was distilled under reduced pressure prior to use.

### Synthesis of Soybean Oil Polyol (SBO Polyol), Cyclic Polysilanol, and Hybrid Polyurethanes

Polyol was synthesized according to the literature reported by Petrovic et al.<sup>24</sup> The epoxy groups in the ESO were opened by methanol using tetrafluoroboric acid as catalyst. Consequently, ESO is converted to a light-yellow viscous SBO polyol with an OH number of 159 mg of KOH/g, which were carried out following ASTM D4274.

*Cis*-(1,3,5,7-tetrahydroxy)-1,3,5,7-tetraphenylcyclooctasiloxane (*cis*-[PhSi(O)OH]<sub>4</sub>) was synthesized through the hydrolysis of phenyltrichlorosilane in aqueous acetone following the method reported by Brown and Yamamoto et al.<sup>25,26</sup>

The chemical synthesis of hybrid polyurethanes was carried out using SBO polyol, cyclic polysilanol (*cis*-[PhSi(O)OH]<sub>4</sub>), BDO, IPDI, and stannous octoate using a two-step polymerization procedure, where both BDO and *cis*-[PhSi(O)OH]<sub>4</sub> were set as the chain extenders. The synthetic procedure was illustrated in Scheme 1. To control the content of *cis*-(1,3,5,7-tetrahydroxy)-1,3,5,7-tetraphenylcyclooctasiloxane in these work, a series of hybrid polyurethanes (inorganic constituent mass content ranges from 0 to 15.00 wt %) were prepared. Here we describe the detailed procedure to prepare hybrid polyurethane with a mass content of 10.44 wt % as a representative example. First, to a flask equipped with a magnetic stirrer, a condenser and a nitrogen bubbler, SBO polyol (2.00 g, 5.66 mmol OH),

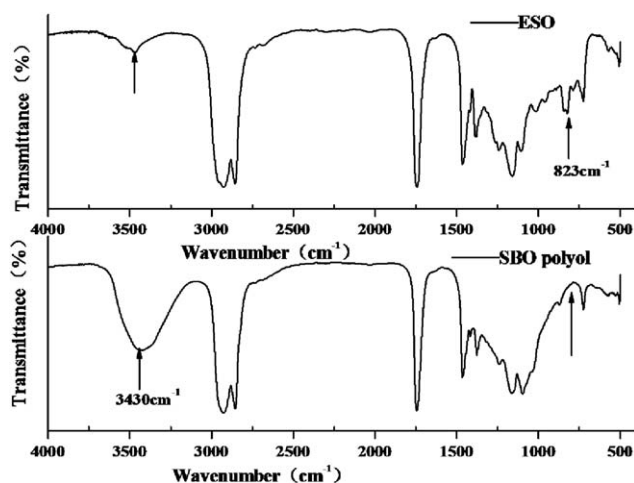


Figure 1. FTIR spectra of ESO and SBO polyol.

stannous octoate (160  $\mu\text{L}$ ), IPDI (1.8 mL), THF (20 mL), and 0.5 g *cis*-[PhSi(O)OH]<sub>4</sub> dissolved in 5 mL THF were charged with vigorous stirring and nitrogen purge at 80°C. The reaction was performed for 2 h to obtain the prepolymer. Next, the isocyanate (NCO) content was determined according to ASTM D5155-96 and the prepolymer were mixed with a stoichiometric amount of BDO as chain extender to control the overall molar ratio of hydroxyl to isocyanate functional groups to be 1 : 1.05. After stirring for another 30 min, the resultant mixture were cast on Teflon plates, cured at 120°C for 2 h and finally post-cured at 80°C for 6 h to obtain final products. The synthesis of other hybrid polyurethanes were followed the above procedure except for the different *cis*-[PhSi(O)OH]<sub>4</sub> content.

### Measurements

To identify molecular bond of polyurethanes, the ATR-FTIR spectra were performed with a Nicolet 6700 infrared spectrometer using a DLATGS detector. All spectra were carried out between 4000 and 500  $\text{cm}^{-1}$  with averaging 32 scans at a resolution of 4  $\text{cm}^{-1}$ .

<sup>1</sup>H nuclear magnetic resonance (NMR) spectra were recorded on a 400 MHz Bruker Instruments (model Avance 400, Ger-

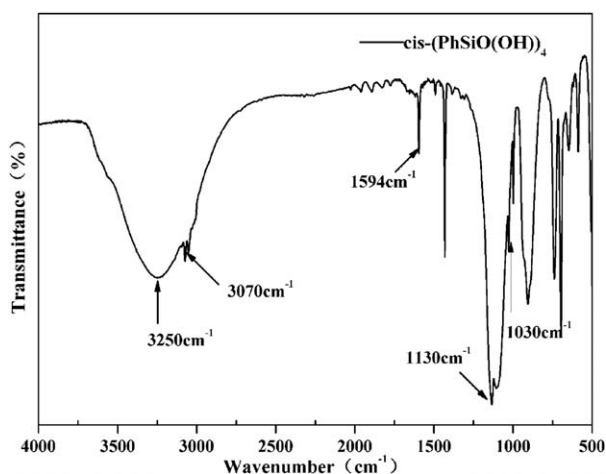


Figure 2. FTIR spectra of *cis*-[PhSi(O)OH]<sub>4</sub>.

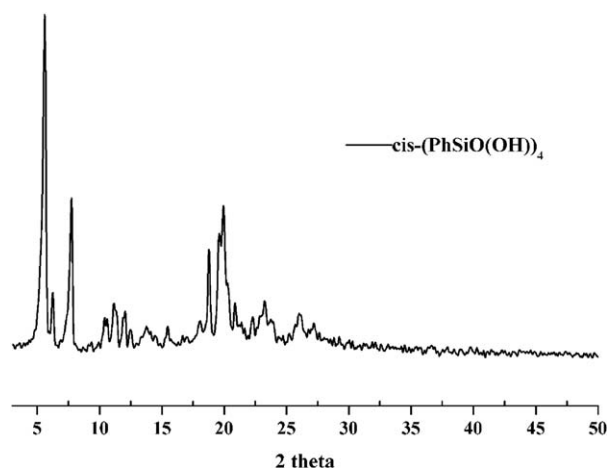


Figure 3. X-ray spectra of *cis*-[PhSi(O)OH]<sub>4</sub>.

many) using Acetone-d<sub>6</sub> as solvent and tetramethylsilane (TMS) as internal reference at room temperature.

X-ray diffraction (XRD) analyses of the samples were carried out on a X-ray diffractometer (D8 Advance, Bruker AXS) using Cu-K $\alpha$  radiation. The  $2\theta$  angle ranged from 3° to 50° at the scanning rate of 4°  $\text{min}^{-1}$ .

The morphology of the samples was observed by Scanning Electron Microscopy (S-4800, Hitachi). The samples were fractured with liquid nitrogen and coated with gold prior to use for observation. To avoid carbonizing organic molecular, the accelerating voltage should choose to be 1 kV.

TGA and DSC of the hybrids were performed using TA Instruments (TGA/1100SF) and (TA-DSC822e), respectively. The TGA was ramped at 20°C  $\text{min}^{-1}$  under a nitrogen flow rate of 50 mL  $\text{min}^{-1}$  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 -20 to 150°C at a nitrogen flow rate of 50 mL  $\text{min}^{-1}$ .

The surface for hydrophobicity test were prepared by quickly spinning the mixture of prepolymer, BDO, and *cis*-

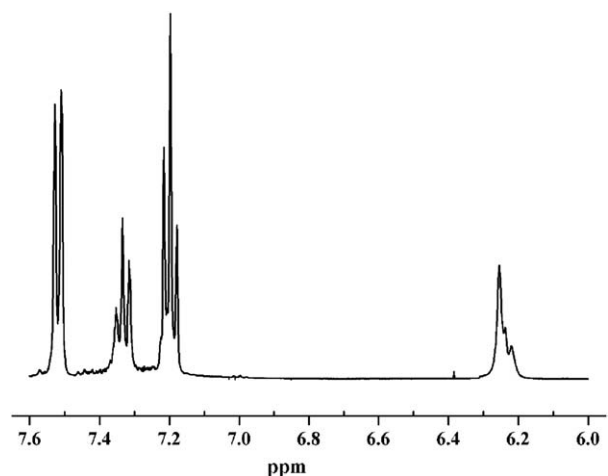


Figure 4. <sup>1</sup>H NMR of *cis*-[PhSi(O)OH]<sub>4</sub>.

**Table I.** Chemical Composition of All Polyurethanes

Samples	SOB polyol mass (g)	IPDI vol. (mL)	Stannous octoate vol. ( $\mu\text{L}$ )	<i>cis</i> -[PhSi(O)OH] <sub>4</sub> mass (g)	<i>cis</i> -[PhSi(O)OH] <sub>4</sub> (wt %)
Pure PU	2	1.80	160	0	0
PU-1	2	1.80	160	0.25	5.47
PU-2	2	1.80	160	0.40	8.51
PU-3	2	1.80	160	0.50	10.44
PU-4	2	1.80	160	0.75	15.00

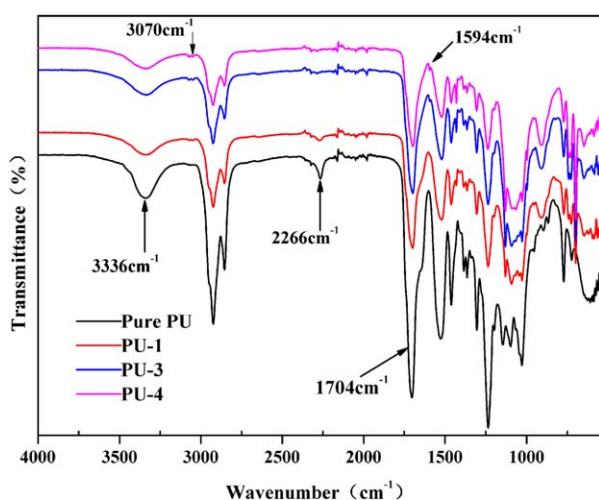
[PhSi(O)OH]<sub>4</sub> onto the clean silicon wafers, followed by curing at 120°C for 4 h. Tests were carried out on a DCA-315 contact angle measurement apparatus with ultrapure water and hexane as probe liquids at room temperature. Contact angles were measured at three different positions for one sample and the results were expressed as mean value.

## RESULTS AND DISCUSSION

### Synthesis

**Synthesis of SBO Polyol.** The IR spectra of ESO and soy-based polyol were shown in Figure 1. The epoxy groups in the ESO were characterized by the peaks around 823 cm<sup>-1</sup> (indicated by the arrow). However, after ring opening reaction with methanol, the peak almost disappeared and new characteristic broad absorption peaks around 3430 cm<sup>-1</sup> appeared, which were attributed to the hydroxy groups. In conclusion, all these results indicated the successful conversion of ESO to SBO polyol.

**Synthesis of Cyclic Polysilanol.** Figure 2 showed the IR spectra of *cis*-(1,3,5,7-tetrahydroxy)-1,3,5, 7-tetraphenyl-cyclooctasiloxane. It was well established that the two peaks around 1130 and 1030 cm<sup>-1</sup> were derived from the antisymmetric stretching vibrations and asymmetric stretching vibrations of Si—O—Si bonds, respectively.<sup>27</sup> Besides, a broad intense absorption peak was observed at 3250 cm<sup>-1</sup>, which was corresponded to the O—H stretching vibration of the hydroxy attached to Si. As for



**Figure 5.** FTIR spectra of hybrid polyurethanes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

the benzene ring, the characteristic absorption peaks were exhibited at 3073, 1594, 1700–2000 cm<sup>-1</sup>.

Powder X-ray diffraction (XRD) spectra of *cis*-(1,3,5,7-tetrahydroxy)-1,3,5,7-tetraphenyl-cyclooctasiloxane was presented in Figure 3. The data were collected with a scanning step of 4° min<sup>-1</sup> from 2 $\theta$  = 3° to 2 $\theta$  = 50°. The typical XRD curve exhibited a series of prominent peaks at 2 $\theta$  = 5.6°, 6.2°, 7.7°, 11.2°, 18.8°, and 19.9°, well consistent with the literature published before by Brown in 1965.<sup>25</sup>

Figure 4 showed the <sup>1</sup>H NMR of *cis*-[PhSi(O)OH]<sub>4</sub> and the chemical shifts of hydrogen protons were successfully confirmed with the previous reports.<sup>28</sup> The attributions of protons can be described as follow: 7.49–7.54 (d, 2H,  $\sigma$ -Ph), 7.30–7.36 (t, 1H, *p*-Ph), 7.17–7.22 (t, 2H, *m*-Ph), 6.20–6.27 (s, 1H, SiOH). The intensity of phenyl protons relative to the OH protons is 5:1, which was consistent with the structure of *cis*-[PhSi(O)OH]<sub>4</sub> successfully.

**Synthesis of Hybrid Polyurethanes.** A series of polyurethanes were synthesized according to the chemical composition listed in Table I and Table II. The IR spectra of both pure polyurethane and hybrids polyurethanes were shown in Figure 5 and the assignments of some major bands were given in Table III. It was well established that the strong broad peak around 3336 cm<sup>-1</sup>, derived from the N—H stretching vibration, and the stretching vibration of carbonyl at 1704 cm<sup>-1</sup> were actually exhibited in all IR spectra.<sup>24,29</sup> However, the additional weak peak appeared in the pure PU around 2266 cm<sup>-1</sup> were attributed to the residual N=C=O groups. With high *cis*-[PhSi(O)OH]<sub>4</sub> content, like PU-4, two weak peaks around 3070 and 1594 cm<sup>-1</sup> (indicated by the arrows) were formed, ascribed to the stretching vibration of benzene rings formed at by the introduction of *cis*-[PhSi(O)OH]<sub>4</sub> in polyurethane molecular chains. Meanwhile,

**Table II.** NCO Values and the Addition Amount of 1, 4-butanediol for PU Prepolymers

Samples	<i>cis</i> -[PhSi(O)OH] <sub>4</sub> (wt %)	NCO (wt %)	1,4-butanediol (g)
Pure PU	0	1.12	0.2391
PU-1	5.47	1.09	0.2219
PU-2	8.51	1.01	0.1982
PU-3	10.44	0.90	0.1899
PU-4	15.00	0.70	0.1487



**Table III.** Assignment of Major Different Peaks of Hybrid Polyurethanes

Peak location (cm <sup>-1</sup> )	Chemical structure	Motion
3336	NH	N—H stretching vibration
2924	CH <sub>3</sub>	C—H stretching vibration
2854	CH <sub>2</sub>	C—H symmetric stretching
2266	NCO	N=C=O stretching vibration
1704	C=O	Carbonyl stretching vibration
3050	C=CH	C—H stretching vibration from C=CH group
1590	C=C	C=C stretching vibration

the broad peak around 3250 cm<sup>-1</sup> resulted from the strong intermolecular hydrogen bond between silanol groups almost disappeared may result from the successful dispersion of *cis*-[PhSi(O)OH]<sub>4</sub> into the hybrids and the reaction between IPDI and silanol. Obviously, this set of IR spectra indicates the successful synthesis of soy-based polyurethanes and introduction of cyclic polysilanol in molecular chains.

### Thermal Properties

Thermal properties of polyurethanes were detected by TGA and DSC, and the results were summarized in Table IV. In the present work, TGA has been investigated as a function of *cis*-[PhSi(O)OH]<sub>4</sub> concentration over a wide temperature range from 25 to 600°C. Meanwhile, to compare the decomposition rates, DTG curves (the derivatives of thermogravimetric curves) of different polyurethanes are also presented in Figure 6. Within the experimental temperature range, the TGA curves of all samples displayed similar degradation profiles, revealing that the degradation mechanism of PU networks did not significantly alter with the addition of *cis*-[PhSi(O)OH]<sub>4</sub>. From the figure, it could be found that all samples decomposed mainly in two steps: The first step connected with the degradation of the urethane bonds took place above 250°C, while the second decomposition step related to soybean oil chain scission occurred later at 340°C.<sup>29–31</sup> Clearly, from Table IV,  $T_{\text{onset}}$  (defined as the initial thermal decomposition temperature) of hybrids were lower than pure polyurethane and decreased with increasing concentration of cyclic polysilanol. These could be related to the consolidation effects, which could be interpreted on the following factors. First, urethane bonds synthesized from IPDI and *cis*-[PhSi(O)OH]<sub>4</sub> may be more unstable, leading to a fast decom-

**Table IV.** TGA Results of Pure and Hybrid Polyurethanes

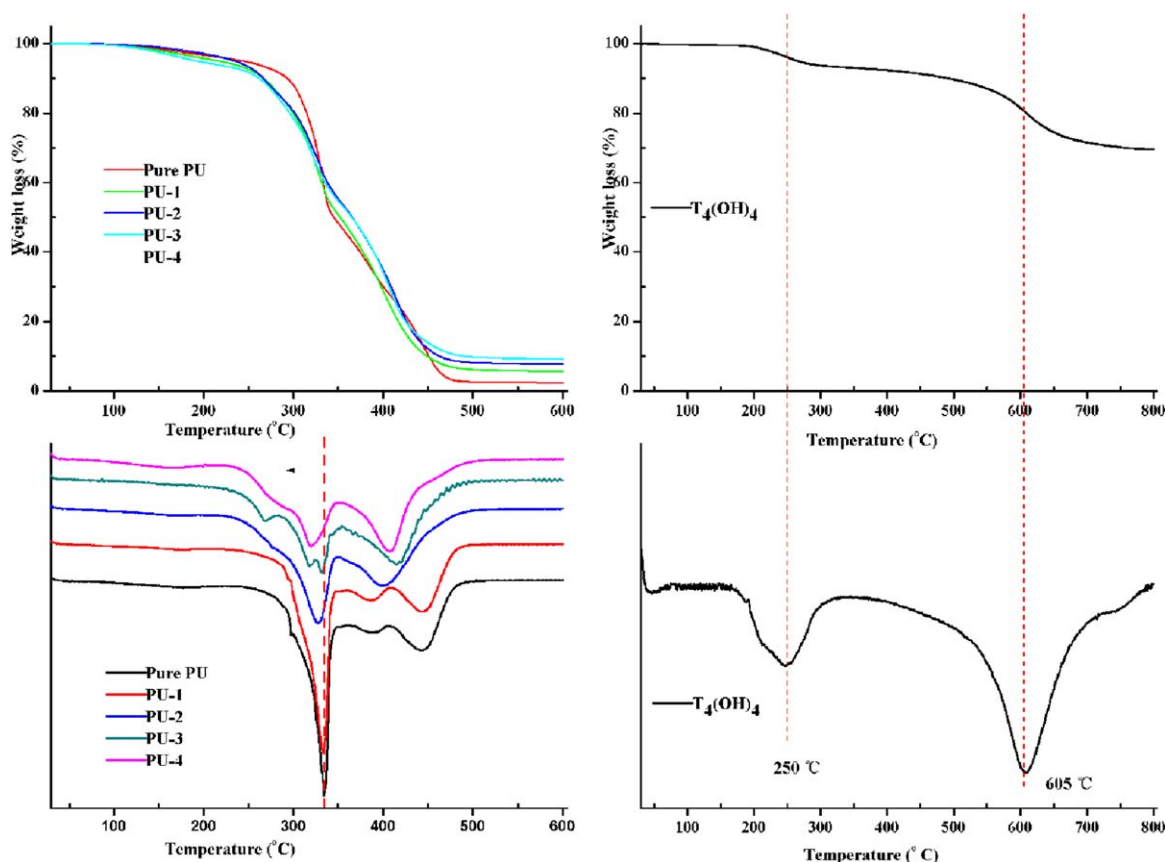
Samples	<i>cis</i> -(PhSiO(OH)) <sub>4</sub> (wt %)	$T_{\text{onset}}$ (°C)	$T_{\text{DTGmax}}$ (°C)	Residue at 600°C (wt %)
Pure PU	0	318.90	335	1.97
PU-1	5.47	313.93	332	2.31
PU-2	8.51	291.15	328	5.66
PU-3	10.44	293.82	323	7.70
PU-4	15.00	294.68	319	9.12

position upon heating. As polysilanol loading increased, the amount of weaker urethane linkage increased, thus the  $T_{\text{onset}}$  of the networks decreased. Second, the large steric resistance of cyclic rigid structure of benzene rings in *cis*-[PhSi(O)OH]<sub>4</sub> hindered the formation of urethane bonds and restricted the mobility of molecules, and finally the chain extension reaction was hindered.  $T_{\text{DTGmax}}$  (temperature corresponding to the fastest rate of thermal decomposition) of hybrids also have the same trends and decreased with high polysilanol loading:  $T_{\text{DTGmax}}$  s of PU-1, PU-2, PU-3, and PU-4 were 3, 7, 12, and 16°C, respectively, lower than that of pristine PU. Compared with pure polyurethane, thermal decomposition of hybrids shifted to lower temperatures (see 200°C) with the incorporation of polysilanol, which can be explained by the poor thermal stability of polysilanol. The weight loss of polysilanol started at about 200°C, with a more pronounced weight loss at 250°C and ending point of about 750°C. Getting inspired from that, the decomposition of hybrids polyurethanes began at 200°C was related to the initial decomposition of polysilanol. In addition, the char residues of POSS-PU hybrids were higher than that of neat PU, and increased monotonously with the increase of polysilanol loadings. Residues of PU-1, PU-2, PU-3, and PU-4 were 1.97, 2.31, 5.66, 7.70, and 9.12 wt %, respectively. It was reasonable that there were less volatiles released from the hybrid materials during heating because of the incorporation of polysilanol. Meanwhile, silica oxide coating on the surface upon heating, make material heat insulating and flame retardance enhanced. In conclusion, the thermal decomposition performances of hybrid polyurethanes suggest whether incorporate of *cis*-[PhSi(O)OH]<sub>4</sub> by chemical bonds or not would make a little difference on polyurethane thermal stability.

DSC analyses were conducted to observe the change of glass transition temperature ( $T_g$ ) of various polyurethane products so as to evaluate the effect of cyclic polysilanol on the mobility of the molecular chain. The measurements were performed in the temperature range of 0 to 150°C as shown in Figure 7. DSC analysis revealed different performance of the hybrid PU materials when contrasted to neat polyurethane. It is noteworthy that all curves displayed a single glass transition, and the result of increasing concentration of inorganic constituents is an upward shift in the  $T_g$ . Notably, the  $T_g$  of hybrid PU-4 can be increased about 16°C as compared with pure counterpart. In our opinion, the large steric resistance from benzene ring as well as the rigid structure of the eight-member ring in polysiloxane would forbid PU chains to move freely. Besides, the high strength of the rigid networks with the cyclic structure of polysilanol was another reason that caused the segmental mobility to be restricted. In fact, both the two reasons result in an increasing of  $T_g$  values.

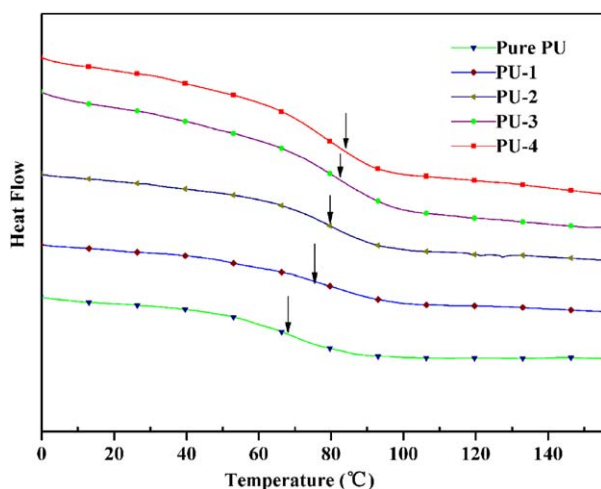
### Morphology

Figure 8 displayed a group of SEM images of the samples with 0, 5.47, 8.51, and 15.00 wt % polysilanol, showing the relationship between diameter and the number density of dispersed phase particles and the polysilanol loading. It can be seen that the images of the composites displayed numerous micron-sized particles on the fracture surfaces and the number as well as the size of particles increased as polysilanol loading increased. Figure 8(a) showed that pure PU has a smooth structure, while for



**Figure 6.** TGA curves of pure polyurethane and hybrid polyurethanes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

the hybrid film series [Figure 8(b–d)], the incorporation of polysilanol changed the material morphology and more detachment regions were showed than those observed for pure PU. Besides, with the increase of polysilanol content the particles have gradually seeped into the organic matrix just as Figure 8(b–d) showed. When inorganic pattern mass content is below 8.51 wt %, numerous micron-sized particles about

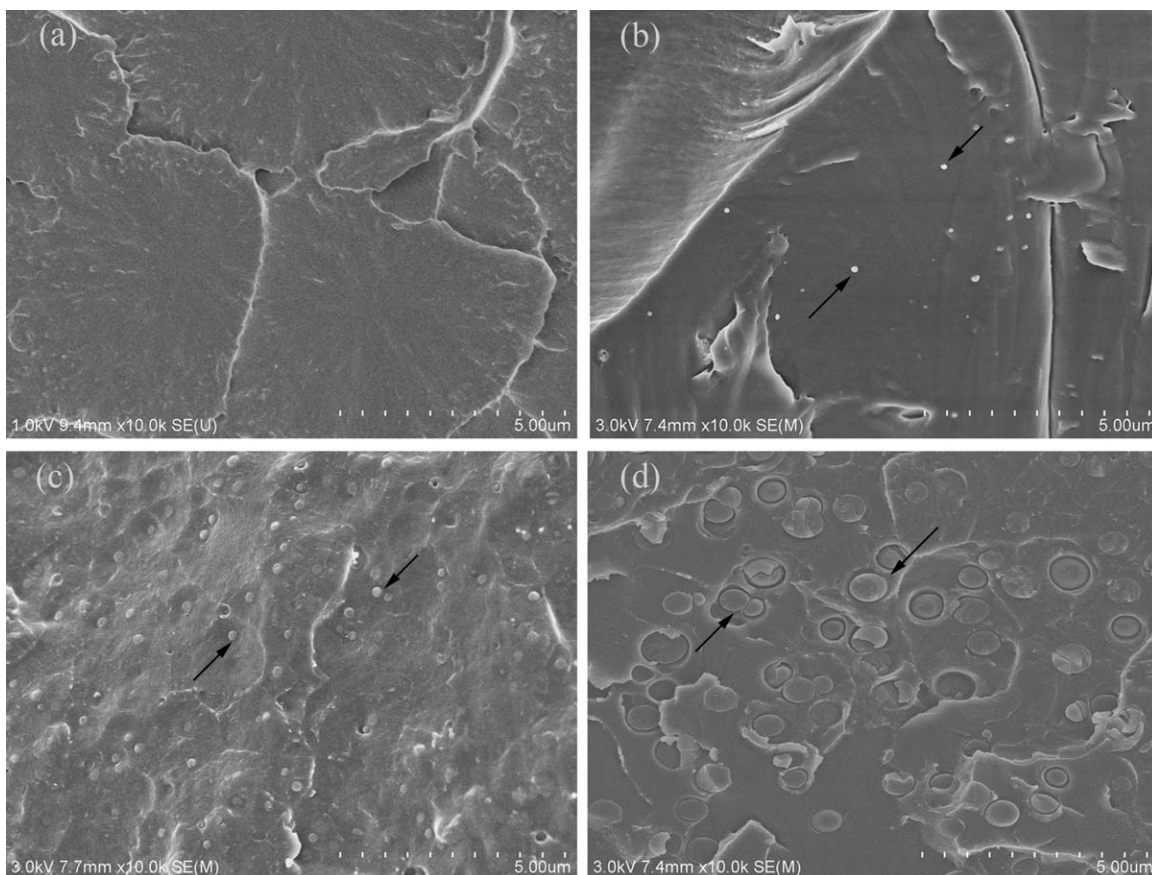


**Figure 7.** DSC curves of hybrid polyurethanes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

200 nm were dispersed on PU fracture surfaces. The number density of these dispersed phase particles was enhanced from 5.47 to 8.51 wt %. As for PU-4, the dispersed particles increased to 650 nm resulted from the decrease of small particles and their aggregation to larger ones. In our opinion, the phenomenon occurred because polysilanol has a strong aggregation effect through physical interactions as well as their chemical instability, which may occurred self-condensation under mild conditions.<sup>25,27</sup> As for the strong physical aggregation effect, it may be due to benzene ring being hydrophobic, while the other four hydroxyls opposite to the benzene ring direction are hydrophilic in character, which would have chemical interactions with the PU. In this way, the only direction of the polysilanol interacting with the matrix would be the hydroxyls on the opposite face to benzene ring. Finally, the hydrophilic hydroxyl aggregate together. Considering that, precise control of the aggregation and self-condensation will enable the mechanical and thermal properties of these materials to be improved, consequently paving the way for their practical use.

#### Surface Hydrophobicity

It turns out by both theoretical and experimental evidence that organosilicon is a low free energy compound, which can influence the surface dewettability of hybrid polymers. To estimate the effect of *cis*-[PhSi(O)OH]<sub>4</sub> on the surface wettability, all polyurethanes were investigated by static contact angle measurements. Figure 9 showed experimental dates of pure PU and the



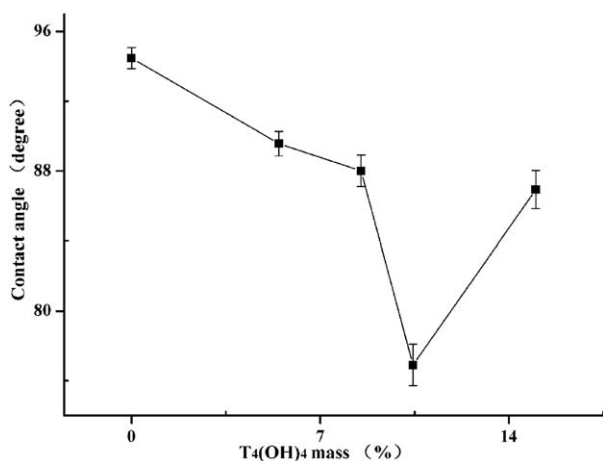
**Figure 8.** SEM images of (a) pure PU, (b) PU-1, (c) PU-3, (d) PU-4.

hybrid polyurethanes. Compared with pure PU, the water contact angles of the hybrid polyurethanes were decreased, strangely being not consistent with precious reports of the hydrophobicity of organosilicon. The water static contact angle was decreased to  $76.90 \pm 1.18$  with the inorganic constituent mass percentage being 10.44 wt % and increased at a higher polysilanol content. In our opinion, this phenomenon may mainly attribute to the dispersion or aggregation of polysilanol and can be explained as follow: At low polysilanol content, say 10.44 wt %, polysilanol

were dispersed relatively uniform in polymer matrix by chemical bonds and no obvious aggregation occurred. On this occasion, hydrophilic hydroxyl and hydrophobic benzene ring of polysilanol may be messily arranged on the material surface and consequently lead to low contact angle value. With high mass content, particles were inclined to aggregate to big ones with hydrophobic benzene ring outside, which may be contributed to improve the hydrophobicity.

## CONCLUSIONS

In this work, a series hybrid polyurethanes were synthesized using *cis*-[PhSi(O)OH]<sub>4</sub> replacing BDO as chain extender. According to the analysis of <sup>1</sup>H NMR and IR, the *cis*-[PhSi(O)OH]<sub>4</sub> were successfully introduced into the molecular chains. By controlling the adding amounts of inorganic constituents, the mass percentage of *cis*-[PhSi(O)OH]<sub>4</sub> can reach up to 15 wt %. Thereafter, a series of characterizations were conducted to evaluate the quality of the material. TGA reveals that the PUs experience two thermal decomposition processes and *cis*-[PhSi(O)OH]<sub>4</sub> have little effects on the decomposition of the hybrids. While the glass transition temperature dates suggest that the incorporation of *cis*-[PhSi(O)OH]<sub>4</sub> to the hard segments of PU would enhance *T<sub>g</sub>*, making molecular chains more rigid as confirmed by the DSC. Microscopic phase separation occurred in hybrid film due to the self-condensation and aggregation among *cis*-[PhSi(O)OH]<sub>4</sub> through SEM. Despite having a little impact on the thermal stability of the composite



**Figure 9.** Static contact angle of pure PU, PU-1, PU-3, and PU-4.

material, cyclic polysilanol can influence the surface hydrophobicity of polyurethanes, which show a trend of first increase and then decrease. Overall, the results of the present study confirm that the incorporation of cyclic polysilanol into polyurethane molecular chains can make it possible to prepare hybrid polyurethanes with relatively perfect physical properties.

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