Contents lists available at ScienceDirect

# Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

# Synthesis and properties of silsesquioxane-based hybrid urethane acrylate applied to UV-curable flame-retardant coatings

# Xi-e Cheng, Shiyong Liu, Wenfang Shi\*

State Key Laboratory of Fire Science and Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, PR China

#### ARTICLE INFO

Article history: Received 1 August 2008 Received in revised form 21 August 2008 Accepted 23 August 2008

Keywords: UV-curable Organic-inorganic hybrid Flame retardant Silsesquioxane Urethane acrylate

# ABSTRACT

The silsesquioxane-based hybrid urethane acrylate (SHUA) was synthesized by modifying silsesquioxanebased hybrid polyol (SBOH) with the half adduct of isophorone diisocyanate and 2-hydroxyethyl acrylate, and characterized by Fourier transfer infrared (FTIR) and <sup>1</sup>H NMR spectroscopy. The SHUA was mixed with a phosphorus-containing trifunctional acrylate, TAEP, with different ratios to prepare a series of UV-curable organic-inorganic hybrid flame-retardant resins. Both the maximum photopolymerization rate and final unsaturation conversion in the UV-cured films determined by photo-DSC decreased along with SHUA content due to the decrease in functionality density and the increase in viscosity. The limiting oxygen index indicated the flame-retardant property reached to a high level of over 32 even with 40% SHUA addition, while the initial decomposition temperature and the char residue at 850 °C increased. The chemical structure change during the thermal degradation process was monitored by in situ FTIR analysis to demonstrate the condensed-phase flame-retardant mechanism. The dynamic mechanical thermal analysis results showed that the elastic storage modulus on the rubbery plateau region and glass transition temperature of the cured film increased by incorporating a small amount of SHUA, but decrease with over 10 wt.% addition of SHUA. Moreover, the addition of SHUA led to an increase in elongation at break and enhancement in abrasion resistance and hardness of film, even though no enhancement in tensile strength.

© 2008 Elsevier B.V. All rights reserved.

# 1. Introduction

It is a well-known fact that UV-curing technology has widely been used in scientific and industrial fields, because it exhibits many advantages such as few volatile organic compounds (VOC), low energy consuming, reduced cycle time, increased production capacity, superior product quality, and also facilitates the use of heat sensitive substrates [1-4]. In addition to these important features, this technology can offer a broad range of the changes in formulation and curing conditions, and thus final properties. UV-curable organic-inorganic hybrid coatings have attracted great interest in the past years due to the favorable combination of properties resulting from the synergism between organic and inorganic components [5-7]. However, up to now, they are usually prepared from 3-(methacryloyloxy)propyltrimethoxysilane, tetraethyl orthosilicate, and commercial organic oligomers. The cured hybrid coatings possess excellent abrasion resistance and hardness for protecting the underlying substrates [6]. Unfortunately, the processing complexity and instability of these hybrids limited some further applications. Therefore, it is worth to develop new multifunctional oligomers containing both organic and inorganic components used for UV-curable hybrid coatings.

Silsesquioxane complex and silsesquioxane-containing polymers are emerging as new hybrid reagents for developing unique organic-inorganic nanocomposites [8-16]. Silsesquioxane is the term for all structures with the formula of  $R_n Si_n O_{1.5n-x}(OH)_{2x}$ , and usually synthesized by the hydrolytic condensation of organotrialkoxysilane, RSi(OR')3, in the presence of an acid or base as a catalyst. It can form ladder [17-19], cage [16,17], partial cage [20] and polymer structures [14,21]. Among various types of silsesquioxanes, cubic silsesquioxanes (T<sub>8</sub>) with the empirical formula of (R-SiO<sub>1.5</sub>)<sub>8</sub> have become the focus of many studies. The organic-inorganic hybrid materials containing T<sub>8</sub> exhibit dramatic improvements in properties such as higher use temperature [22], heat evolution [23], reduction in flammability [24], processing viscosity [25], mechanical behavior modification [26,27], surface hardness [28], and abrasion resistance [29,30]. However, the synthesis of T<sub>8</sub> complex requires complicated and time-consuming procedures. Several efforts have been directed at the facile synthetic methods for silsesquioxane-based hybrid reagents in order to seek the possibility of large-scale production without tedious process. Notably, Williams and co-workers have reported the synthesis





<sup>\*</sup> Corresponding author. Tel.: +86 551 3606084; fax: +86 551 3606630. *E-mail address*: wfshi@ustc.edu (W. Shi).

<sup>0300-9440/\$ –</sup> see front matter @ 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.porgcoat.2008.08.018

of perfect and imperfect polyhedra bearing secondary hydroxyl groups (OH–SSO) [31–33] or ( $\beta$ -carboxyl)ester groups (COOH–SSO) [34] in the organic branches used as modifiers of epoxy networks [26,34,35]. Mori et al. described the synthetic routes of two kinds of cage-type silsesquioxanes with hydroxyl groups on the outermost surfaces, possessing 12–18 and 6–12 Si atoms, respectively [36–38].

Urethane acrylates are widely used as oligomers in various UV-curable formulations due to the excellent properties of the cured films. To the best of our knowledge, silsesquioxane nanoparticle-based urethane acrylate oligomers have never been synthesized and used in UV-curable formulations. Herein, we report a facile synthesis of an organophilic organic-inorganic hybrid urethane acrylate (SHUA) by the reaction of the half adduct of isophorone diisocyanate and 2-hydroxyethyl acrylate (IPDI-HEA) with a silsesquioxane bearing hydroxyl groups on the outermost surface (silsesquioxane-based hybrid polyol (SBOH)), which can be obtained by hydrolytic condensation of a functionalized precursor, N,N-di-(2,3-dihydroxypropyl)aminopropyltriethoxysilane. Moreover, in contrast to previous reports [6,39], the obtained UV-curable organic-inorganic hybrid urethane acrylate is rather stable and has good miscibility with UV-curable monomers and oligomers. As a part of our continuous efforts to develop UV-curable flame-retardant coatings, SHUA was mixed with a phosphoruscontaining monomer tri(acryloyloxyethyl)phosphate (TAEP) in different ratios. The flame retardancy of the UV-cured film was characterized by the limiting oxygen index (LOI). The thermal degradation process and structural changes at different temperatures were investigated by thermogravimetric analysis (TGA), in situ Fourier transfer infrared (FTIR). The photopolymerization kinetics of the resins, and the dynamic mechanical thermal properties and mechanical behaviors of the cured films were also investigated.

# 2. Experimental

#### 2.1. Materials

Glycidol was purchased from Sigma-Aldrich and used as received. 3-Aminopropyltriethoxysilane, isophorone diisocyanate (IPDI), and 2-hydroxyethylacrylate (HEA), supplied by Sigma-Aldrich, Shanghai First Reagent Co., and Beijing Orient Chemical Co., respectively, were distilled under reduced pressure before use. Hydrofluoric acid (46-48% HF aqueous solution) was used as received. Di-n-butyltindilaurate (DBTDL) as a catalyst was purchased from the Third Reagent Co., Beijing, China. N,N-Dimethylacetamide (DMAc) was used after drying over 4-Å molecular sieves. The detailed synthesis and characterization of the half adduct of isophorone diisocyanate and 2-hydroxyethyl acrylate (IPDI-HEA) were described elsewhere [4,40]. TAEP was synthesized using POCl<sub>3</sub> and HEA in our laboratory [41]. 2-Hydroxy-2-methyl-1-phenyl-1-propanone (Runtecure 1103), used as a photoinitiator, was supplied by Runtec Chemical Co., Changzhou, China. Other chemicals were supplied by Shanghai First Reagent Co. and used as received without further purification.

# 2.2. Synthesis

#### 2.2.1. Silsesquioxane-based polyol

The silsesquioxane-based polyol was prepared according to the procedure developed by Mori et al. [36,37]. One mole of 3-aminopropyltriethoxysilane was dropped slowly into two moles of glycidol under stirring with ice cooling. The addition product, N,N-di(2,3-dihydroxypropyl)-(aminopropyl)triethoxysilane, was obtained after reacted for 1 h at 25 °C. Then an aqueous HF solution

#### Table 1

Viscosity, photopolymerization rates at peak maximum and final unsaturation conversion in the cured films

Sample	Formulation (wt.%)		Viscosity	R <sup>P</sup> <sub>max</sub>	P <sup>f</sup> (%)
	SHUA	TAEP	(mPa s, 25 °C)	$(J g^{-1} s^{-1})$	
TAEP	0	100	95	22.03	80.8
SHUA5 TAEP95	5	95	160	18.56	75.5
SHUA <sub>10</sub> TAEP <sub>90</sub>	10	90	500	14.77	70.0
SHUA20TAEP80	20	80	1250	10.17	67.9
SHUA <sub>30</sub> TAEP <sub>70</sub>	30	70	2850	9.85	65.2
SHUA <sub>40</sub> TAEP <sub>60</sub>	40	60	4950	8.46	62.3

(3.225%, 42.06g) was added into the above addition product (287.82g, 1.558 mol) previously dissolved in 1400 mL of methanol, and stirred for 4 h at 25 °C. After removed methanol, ethanol and water under vacuum, and dried at 60 °C in vacuum for 72 h, the silsesquioxane-based polyol, denominated as SBOH, was obtained in a glassy solid at room temperature (yield 98%).

<sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ (ppm) 0.4–0.9 (–SiCH<sub>2</sub>–), 1.4–1.9 (–SiCH<sub>2</sub>CH<sub>2</sub>–), 2.4–3.2 (–NCH<sub>2</sub>–), 3.4–4.1 (–OCH<sub>2</sub>–, –OCH–). FTIR (NaCl plate, cm<sup>-1</sup>): 3398 (OH), 2940, 2879 (CH), 1119, 1045 (Si–O).

# 2.2.2. Silsesquioxane-based hybrid urethane acrylate (SHUA)

The above-obtained SBOH was dried thoroughly in a vacuum oven at 80 °C for 3 h before use. 10.52 g SBOH (163.03 mol –OH), a proper portion of catalyst (0.1 wt.% DBTDL), *p*-hydroxyanisole (1000 ppm) and 60 mL of DMAc were poured into a dry glass flask which was purged with N<sub>2</sub> before use to eliminate moisture. A given amount of IPDI-HEA previously dissolved in DMAc was slowly dropped into the above vessel at 0 °C under N<sub>2</sub> atmosphere and then stirred continuously at 60 °C until the FTIR absorption peak at 2250 cm<sup>-1</sup> for NCO group disappeared. The resultant mixture was concentrated and then precipitated by being dropped into 500 mL of diethyl ether. The crude product was redissolved in 30 mL of acetone and precipitated into 500 mL of diethyl ether. This procedure was repeated for three times. The resulting white powder was dried in vacuo at 25 °C for 4 days with a yield of 88%, named SHUA.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.3–1.9 (–Si*CH*<sub>2</sub>–, –C(*CH*<sub>3</sub>)*CH*<sub>2</sub>C(*CH*<sub>3</sub>)<sub>2</sub>–), 1.4–2.1 (–Si*CH*<sub>2</sub>*CH*<sub>2</sub>–, –*CH*<sub>2</sub>CH(NHCOO) *CH*<sub>2</sub>–), 2.3–3.2 (–N*CH*<sub>2</sub>–, –*CCH*<sub>2</sub>NHCOO–), 3.3–4.2 (–O*CH*<sub>2</sub>–, –O*CH*–, –CH<sub>2</sub>*CH*(NHCOO)*CH*<sub>2</sub>–), 4.2–4.6 (–NHCOO*CH*<sub>2</sub>*CH*<sub>2</sub>*COO*–), 5.7–6.6 (–COO*CH*=*CH*<sub>2</sub>). FTIR (NaCl plate, cm<sup>-1</sup>): 3340 (OH), 2946, 2872 (CH), 1716 (C=O), 1635, 1409, 810 (CH=CH<sub>2</sub>), 1536 (NH), 1119, 1045 (Si–O).

# 2.3. Sample preparation

The mixtures of SHUA with TAEP in different ratios (Table 1) were stirred until the homogenous blends formed. TAEP and their blends in the presence of 3 wt.% Runtecure 1103 were drawn on a glass plate with a 75  $\mu$ m applicator or pour into a mold with given size, then exposed to a medium pressure mercury lamp (2 kW, Fusion UV systems, USA) in air for 300 s. The distance from the UV lamp to sample is 10 cm.

#### 2.4. Measurements

The <sup>1</sup>H NMR spectrum was recorded with an AVANCE 300 Bruker spectrometer using tetramethylsilane as an internal reference and  $D_2O$  or CDCl<sub>3</sub> as a solvent.

The Fourier transfer infrared spectra were recorded using a Nicolet MAGNA-IR 750 spectrometer. The in situ FTIR spectra were recorded to monitor the thermodegradation process of cured samples in the range of room temperature to 460  $^\circ C$  with a heating rate of 2  $^\circ C$  min^{-1}.

The viscosity at room temperature was measured with a QNX Model rotational viscometer (Tianjin Instrument Co., Tianjin, China).

The photopolymerization rate was monitored in air by a CDR-1 differential scanning calorimeter (DSC) (Shanghai Balance Instrument Co., Shanghai, China) equipped with a UV spot cure system BHG-250 (Mejiro Precision Co., Japan). The incident light intensity at the sample pan was measured to be 2.04 mW cm<sup>-2</sup> with a UV power meter. The unsaturation conversion ( $P_t$ ) was calculated by the formula,  $P_t = H_t/H_{\infty}$ , where  $H_t$  is the heat effect within ts,  $H_{\infty}$  is the heat effect of 100% unsaturation conversion. The DSC curves were normalized by the weight (g) of samples. The polymerization rate is defined by  $Jg^{-1}s^{-1}$ , namely, the heat of polymerization rate and  $H_{\infty}$ , the value  $\Delta H_0 = 86 J \text{ mmol}^{-1}$ , for the heat of polymerization per acrylic unsaturation, was taken.

The limiting oxygen index values were measured using a ZRY-type instrument (made in Jiangning, China) with the sheet of  $120 \text{ mm} \times 6.5 \text{ mm} \times 3 \text{ mm}$  according to ASTM D635-77.

The thermogravimetric analysis was carried out on a Shimadzu TG-50 instrument using a heating rate of 10 °C min<sup>-1</sup> in air.

The tensile storage modulus (*E'*) and tensile loss factors  $(\tan \delta)$  were measured using a dynamic mechanical thermal analyzer (Diamond DMA, PE Co., USA) at a frequency of 2 Hz and a heating rate of 5 °C min<sup>-1</sup> in the range of -50 to 250 °C with the sheet of 25 mm × 5 mm × 1 mm.

The mechanical properties were measured with an Instron Universal tester (model 1185, Japan) at  $25 \,^{\circ}$ C with a crosshead speed of 25 mm min<sup>-1</sup>. The dumb-bell-shaped specimens were prepared according to ASTM D412-87. Five samples were analyzed to determine an average value in order to obtain the reproducible result.

The abrasion resistance was measured with a QMX abrasion apparatus (Tianjin Exp. Apparatus Co., China) in accordance with the corresponding State Standard Testing Method (GB 1731-93). A 250 g load is placed on top of the rubber abrader wheel and allowed to spin for 1 min with a speed of  $60 \text{ r min}^{-1}$ .

The pendulum hardness was determined using a QBY pendulum apparatus (Tianjin Instrument Co., China). The pencil hardness was determined using a QHQ-A pencil hardness apparatus (Tianjin Instrument Co., China).

#### 3. Results and discussion

#### 3.1. Synthesis and architecture characterization

The multifunctional polyol, SBOH, a sphere-shaped nanoparticle with a diameter of about 2.7 nm, was prepared by hydrolysis and condensation of an organic silane, N,N-di(2,3-dihydroxypropyl)-(aminopropyl)triethoxysilane according to the method developed by Mori et al. [36,37]. The number average molecular weight and its polydispersity index of SBOH were reported to be 3760 g mol<sup>-1</sup> and 1.21, respectively. These nanoparticles were found to consist of the species having 12-18 Si atoms with complete and incomplete cagelike structures of Si-O-Si and Si-O-C bonds. Since the molecular weight of a unit with one Si atom is 258.3 g mol<sup>-1</sup>, SBOH contain approximately 14.6 Si atoms or 58 terminal hydroxyl groups [36.37]. Due to the inorganic characteristic of Si–O–Si in the core and a lot of reactive hydroxyl groups on the surface, SBOH was used as a new functional hybrid reagent for the preparation of silsesquioxane-based organic-inorganic hybrid urethane acrylate oligomers (SHUA).

Scheme 1 presents the synthetic route of SHUA. The reaction between the hydroxyl groups of SBOH with IPDI-HEA was followed by FTIR measurement. Fig. 1 shows the FTIR spectra of SBOH and SHUA. In the SBOH spectrum, there is a broad absorption band for hydroxyl group from 3000 to 3800 cm<sup>-1</sup> with a maximum at 3398 cm<sup>-1</sup>. In addition, a sharp peak between 2840 and 2940 cm<sup>-1</sup> due to the C–H stretching vibration in the alkyl chain and a strong absorption band around 1030–1150 cm<sup>-1</sup> corresponding to Si-O-Si stretching on the nanoparticles are present. In the SHUA spectrum, the formation of urethane structure is revealed by the peaks observed at  $1716 \text{ cm}^{-1}$  for C=O and  $1536 \text{ cm}^{-1}$  for N-H. The FTIR spectrum shows the strong absorption bands at 1635, 1409 and 810 cm<sup>-1</sup>, indicating the existence of acrylate groups. There is also an absorption band from 3000 to 3700 cm<sup>-1</sup> but the intensity significantly decreased compared to the benchmark absorption intensity of Si–O at 1046 cm<sup>-1</sup>. This indicates that some hydroxyl groups still existed although most of the hydroxyl groups on the outermost surface reacted with -NCO groups and transformed to terminal double bonds. In fact, due to the steric hindrance, the hydroxyl groups cannot be completely consumed even though much excess molar ratio of IPDI-HEA to -OH group was used. Therefore, in the following steps, SHUA was obtained by fixed the molar ratio of IPDI-HEA to -OH as 0.5.

Fig. 2 represents the <sup>1</sup>H NMR spectra of SBOH and SHUA. The characteristic peaks of SHUA are clearly seen at 0.3-1.9 (-SiCH<sub>2</sub>-, -C(CH<sub>3</sub>)CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>-), 1.4-2.1 (-SiCH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH(NHCOO)CH<sub>2</sub>-), 2.3-3.2 (-NCH<sub>2</sub>-, -CCH<sub>2</sub>NHCOO-), 3.3-4.2 (-OCH<sub>2</sub>-, -OCH-, -CH<sub>2</sub>CH(NHCOO)CH<sub>2</sub>-), 4.2-4.6 (-NHCOOCH<sub>2</sub>CH<sub>2</sub>COO-), and 5.7-6.6 (-COOCH=CH<sub>2</sub>), respectively, indicating the successful synthesis of SHUA. Moreover, the ratio of integration area of the peak corresponding to double bond  $(-COOCH=CH_2, \delta 5.7-6.6, s in Fig. 2(b))$  to that of peak corresponding to the methylene group near Si atom in silsesquioxane core ( $-SiCH_2-$ ,  $\delta$  a in Fig. 2(b)) was 2.91, revealed that about 50% hydroxyl groups in a SBOH molecule were transformed to double bonds, which accords with the initial molar ratio of IPDI-HEA to -OH at the margin of error in the experiment. Because of the globular shape and many residual hydroxyl groups, GPC approach was not used for determining the molecular weight of SHUA. Fortunately, the theoretical molecular weight  $M_{\rm p} = 13.560 \,{\rm g \, mol^{-1}}$ can be calculated according to the molecular weight of SBOH obtained by MALDI-TOF [36,37] and the number of double bond in one SHUA molecule.

# 3.2. Viscosity and photopolymerization kinetics

The viscosity of a UV-curable formulation is considered as one of the most important parameters because it affects the processability, photopolymerization rate and the final properties of the cured film. A suitable viscosity range is required to avoid sagging (in the case of low viscosity) and practical difficulty in applications (encountered with high viscosity). Due to the high molecular weight and the formation of inter/intramolecular hydrogen bond, SHUA is a white powder at room temperature. It is changed easily into a highly viscous transparent material by heating, for example, at 60 °C, which is mostly unsuitable for UV-curable systems. Instead, addition of multifunctional comonomer is a more convenient and common used way to improve the operability. Tri(acryloyloxyethyl)phosphate (TAEP), a phosphorus-containing trifunctional acrylate monomer was chosen as a diluent to mix with SHUA for decreasing the viscosity, and endowing the cured film with flame retardancy. Therefore, a series of UV-curable organic-inorganic hybrid resins with different contents of TAEP were formulated, and their resin compositions are listed in Table 1. In addition, Runtecure 1103 as a photoinitiator was added into each formulation. The viscosity of sample goes down sharply along with the addition of TAEP, reaching to a very low viscosity of 4950 mPas at 25 °C with 60 wt.% addition. Moreover, the



Scheme 1. Synthetic route of SHUA.



**Fig. 1.** FTIR spectra of (a) SBOH, and (b) SHUA.

rapid viscosity reduction further indicates the good miscibility of SHUA with TAEP.

The properties of a UV-cured film are not only related to the resin composition but also to its photopolymerization kinetics. The most important parameters characterizing the curing kinetics of a resin are the rate at the peak maximum  $(R_{max}^p)$  and the final unsaturation conversion (P<sup>f</sup>). The UV-curing kinetics curves of TAEP and the hybrid resins obtained from photo-DSC measurements at room temperature (25 °C) are shown in Figs. 3 and 4, and the data are listed in Table 1. The photopolymerization rates of all hybrid samples show a steep increase at the beginning of irradiation, reaching to  $R_{\text{max}}^{\text{p}}$  value, and then drop rapidly, which appears similarly to that of other conventional acrylate systems reported in the liter-ature [42,43]. Moreover, the  $R_{max}^{p}$  decreases with SHUA content increasing, which can be explained by the fact that the concentration of double bond decreases and the viscosity increases as the SHUA content increases. The double bond concentration of SHUA is  $2.16 \text{ mmol g}^{-1}$  compared with 7.65 mmol g $^{-1}$  for TAEP. The  $P^{\text{f}}$ also decreases systematically with increasing SHUA content from 80.8% for TAEP alone to 62.3% for a SHUA content of 40%. It is attributed to the increase of viscosity when more SHUA is added into the system, which makes the gel effect attained in a lower conversion.



Fig. 2. <sup>1</sup>H NMR spectra of (a) SBOH in D<sub>2</sub>O; and (b) SHUA in CDCl<sub>3</sub>.

# 3.3. Flame retardancy

The flame-retardant properties of the obtained UV-curable organic–inorganic hybrid resins were examined by measuring the LOI values of the cured films. The LOI is the minimum fraction of oxygen in an oxygen–nitrogen mixture that is just sufficient to support combustion of the specimen after ignition. The theoretical phosphorus, nitrogen and silicon contents of the UV-cured samples and their LOI values are given in Table 2. It can be observed that the LOI value decreases from 43.0 to 32.0 by increasing the ratio of SHUA to TAEP. Fig. 5 presents the photographs of samples containing different SHUA contents after combustion. It can be seen that the expanding charred crust was formed after the TAEP/SHUA blend burned, and the degree of expansion increases at first, reaching to the biggest expansion degree, and then decreases with increasing the SHUA content.

As reported in literature [44,45], phosphorus and nitrogen exhibited a synergistic effect on flame retardance through a pro-



Fig. 3. Photopolymerization rate of SHUA/TAEP vs. irradiation time (25 °C).



Fig. 4. Unsaturation conversion in UV-cured SHUA/TAEP films vs. irradiation time (25  $^\circ\text{C}$ ).

posed condensed-phase mechanism, and the degree of expansion greatly influences the flame retardancy. The larger the degree of expansion, the thicker the insulating layer will be formed to protect the underlying material from burning. However, it was found that the LOI value decreases even though the degree of expansion increases. It may be ascribed to the fact that different flame-retardant mechanisms are followed in various systems. It can be supposed that the flame retardancy of a part of TAEP is acting in the gas phase [45], whereas another part of TAEP is acting in condensed phase owing to the synergistic effect between

# Table 2

Theoretical phosphorus, nitrogen and silicon percent in the formulations and the LOI values of the cured films

Sample	Phosphorus (wt.%)	Nitrogen (wt.%)	Silicon (wt.%)	LOI
TAEP	7.90	0	0	43.0
SHUA5 TAEP95	7.51	0.38	0.147	41.0
SHUA <sub>10</sub> TAEP <sub>90</sub>	7.11	0.75	0.29	38.5
SHUA <sub>20</sub> TAEP <sub>80</sub>	6.32	1.50	0.59	35.5
SHUA <sub>30</sub> TAEP <sub>70</sub>	5.53	2.25	0.88	34
SHUA40 TAEP60	4.74	3.00	1.18	32
SHUA	0	7.51	2.94	-



Fig. 5. Photographs of the samples after combustion: (a) TAEP; (b) SHUA<sub>5</sub>TAEP<sub>95</sub>; (c) SHUA<sub>10</sub>TAEP<sub>90</sub>; (d) SHUA<sub>20</sub>TAEP<sub>80</sub>; (e) SHUA<sub>30</sub>TAEP<sub>70</sub>; (f) SHUA<sub>40</sub>TAEP<sub>60</sub>.

phosphorus-nitrogen and phosphorus-silicon [46-48]; and the gas phase mechanism holds the dominant effect. As well known, the gas phase mechanism interrupts the exothermic process and thus suppresses combustion by capturing free radicals through the phosphorus volatiles. Whereas the condensed-phase mechanism facilitates char formation. It can be observed that a thick insulating layer was formed with decreasing the phosphorus content from 7.90 to 6.32% and increasing the nitrogen content to 1.50% owing to the phosphorus-nitrogen synergistic effect. Meanwhile, although the degree of expansion decreases, a high-performance char barrier might be formed when the SHUA content continued to increase due to the increase of silicon content, and thus the enhancement in the phosphorus-silicon synergistic effect [46-48], which can be demonstrated by the following thermal degradation behavior. Two kinds of chars all can prevent the heat transfer, brings down the temperature, and inhibits the release of combustible gases. Simultaneously, some of phosphorus volatiles, such as P<sub>2</sub>, PO, PO<sub>2</sub>, HPO<sub>2</sub>, etc. which can suppress combustion by capturing free radicals, are also prevented emitting from the char layers. Therefore, the effect of gas phase mechanism also weakens with increasing SHUA content, resulting in the LOI value decreased.

# 3.4. Thermal degradation

The thermal stability of a polymeric material is very important when used as a flame-retardant. TGA is one of the most widely used techniques for rapid evaluation of the thermal stability of various polymers. Fig. 6 shows the TGA thermograms of the cured samples from room temperature to 850 °C in air atmosphere. The specific degradation temperatures and the final char yields at 850 °C are listed in Table 3. It is noted that the thermostability of UVcured SHUA/TAEP films at lower temperature first increases and



Fig. 6. TGA curves of the cured films with different SHUA contents.

#### Table 3

Thermogravimetric analysis data of the cured films

Sample	Temperat specific w	ure recorded at reight loss (°C)	Residue (%) (850 °C)	
	10%	50%		
TAEP	294	458	2.1	
SHUA5 TAEP95	308	446	3.5	
SHUA10 TAEP90	316	417	4.4	
SHUA20TAEP80	320	396	6.9	
SHUA <sub>30</sub> TAEP <sub>70</sub>	317	395	7.4	
SHUA40 TAEP60	291	393	11.9	
SHUA	247	384	10.4	



Fig. 7. FTIR spectra of cured SHUA\_{20}TAEP\_{80} during the thermal degradation in the range of RT  $\sim 460\,^\circ\text{C}.$ 

then decreases along with the increase of SHUA content, and the UV-cured SHUA film has the lowest thermostability, which can be verified by the temperature of 10 wt.% loss listed in Table 3. There are mainly two competitive factors which affect the thermostability at lower temperature. On the one hand, the resin with lower phosphorus content possesses higher thermostability at the beginning of degradation due to the decrease of less stable P-O-C bond. On the other hand, the decrease in crosslinking density and the increase of less stable urethane segments with the increase of SHUA content results in weakening in thermostability at lower temperature [49]. At higher temperature, the thermostability weakens with increasing SHUA content. This can also be verified by the data in Table 3, showing that the temperature of 50 wt.% loss reduces along with the increase of SHUA content. It can be explained by the fact that the resin with high phosphorus content is more stable at high temperature owing to the formation of compact char which protects the sample from further degradation and yields more char.

However, it can be seen that the cured TAEP film still shows weight loss at the temperature over 700 °C under air. On the contrary, this weight loss is not observed for the char of SHUA film due to the silicon migration to char surface and the formation of a silicon-protecting layer to char [46,47]. Nevertheless, the weight loss is still observed for UV-cured SHUA/TAEP films at the temperature over 700 °C, which might be owing to the lower silicon content in the resins. It can be observed that the efficiency of protecting the char from further oxidation by silicon enhanced with increasing SHUA content, so the final char yield at 850 °C increases. The SHUA<sub>40</sub>TAEP<sub>60</sub> resin yields most char among the resins, which might come from two reasons: one reason is that silicon favorably provides thermostable char and phosphorus provides a tendency of char formation, and another is that there may be a synergistic effect between phosphorus and nitrogen as reported in literature [43, 44]

The in situ FTIR analysis was used to monitor the chemical structure changes in UV-cured SHUA<sub>20</sub>TAEP<sub>80</sub> films at different degradation temperatures, as shown in Fig. 7. It can be seen that the P–O–C absorption peaks at 1034 and 984 cm<sup>-1</sup> decrease quickly with increasing temperature and then disappear completely above 280 °C, indicating the degradation of P–O–C occurred. Furthermore, four new absorption bands appear. The peaks at 1147 and 1020 cm<sup>-1</sup> are assigned to the stretching vibration of P–O–C and PO<sub>2</sub>/PO<sub>3</sub> in phosphate-carbon complexes, respectively [50]. The



Fig. 8. DMTA curves of the UV-cured films with different SHUA contents.

peaks at 1086 and 885 cm<sup>-1</sup> are attributed to the symmetric and asymmetric stretching vibration of P–O–P band [51,52]. The absorbance at 1264 cm<sup>-1</sup> corresponding to P=O decreases with increasing temperature. Two new absorption bands at 1274 and 1290 cm<sup>-1</sup> assigned to P=O vibration in P–O– $\Phi$  structure appear above 270 °C, where  $\Phi$  represents an aromatic group [53]. All these changes in the FTIR spectra indicate that phosphate group is broken from the aliphatic structure. Some are linked to each other by sharing one oxygen atom, leading to the formation of poly(phosphoric acid) such as  $P_2O_5$  and  $P_4O_{10}$ , and others are linked to the aromatic structures at the temperatures over 280 °C, resulting in the formation of phosphorus-carbon complexes. The formation of aromatic structures is demonstrated by the appearance of new peaks at 755 and 679 cm<sup>-1</sup> in the spectra measured above 270 °C [51]. The absorbance at 1536 cm<sup>-1</sup> for the stretching vibration of N–H bond decreases rapidly from 200 °C and disappears above 300 °C. The same tendency of degradation for C–O–C at 1168 cm<sup>-1</sup> can be observed from Fig. 7, which is also confirmed by the fast decrease and then disappearance of the strong peak at 1731 cm<sup>-1</sup> corresponding to C=O band.

# 3.5. Dynamic mechanical thermal properties

The dynamic mechanical thermal analysis (DMTA) was utilized to investigate the dynamic mechanical behavior of the UV-cured films. Fig. 8 shows the storage modulus of the UV-cured films with different SHUA contents as a function of the temperature from -25 to 200 °C.  $E'_{\text{rubb}}$  is the elastic storage modulus on the rubbery plateau region. It is interesting to note that  $E'_{rubb}$  first increases and then decreases with increasing SHUA content, as shown in Fig. 9. There are mainly two competitive factors which affect the modulus of the networks in the rubbery state. On the one hand, the nanoreinforcement of the SHUA core on the polymer matrix will enhance the modulus in the rubbery state. On the other hand, the decrease of crosslinking density per unit volume will result in the decrease of the storage modulus in the rubbery plateau. It can be seen that the storage modulus for the rubbery state in SHUA/TAEP network with the SHUA content of below 10 wt.% is higher than that of TAEP network, which implies that the significant nanoreinforcement counteracts the effect of reduced crosslinking density on the storage modulus of the rubbery plateau. With continuing to increase the SHUA content, the reduced crosslinking density dominates the negative effect, leading to the tremendous decrease in  $E'_{\rm rubb}$ .

Fig. 8 also shows the plots of loss factor  $(\tan \delta)$  versus temperature. The glass transition temperature  $(T_g)$  of a crosslinked material

Sample	Tensile strength (MPa)	Elongation at break (%)	Abrasion resistance (mg)	Hardness	
				Pendulum (s)	Pencil (H
TAEP	13.4	2.4	_a	271	3
SHUA <sub>5</sub> TAEP <sub>95</sub>	21.6	2.8	19.8	280	3
SHUA10TAEP90	20.2	3.2	18.1	292	3
SHUA <sub>20</sub> TAEP <sub>80</sub>	18.5	4.6	14.5	307	4
SHUA <sub>30</sub> TAEP <sub>70</sub>	16.1	5.9	11.3	320	4
SHUA <sub>40</sub> TAEP <sub>60</sub>	14.4	6.5	9.7	327	4

Table 4Mechanical and physical properties of the cured films

<sup>a</sup> It is too brittle to obtain a good film for abrasion resistance test.

can be determined as the relaxation peak of the tan  $\delta$ . As shown in Fig. 9, the  $T_{\rm g}$  follows the same trends with the  $E'_{\rm rubb}$ . The nanoreinforcement on  $T_{\rm g}$  dominates for the hybrid sample with 5 wt.% SHUA content. The bulky inorganic core could restrict the motion of macromolecular chains, and thus higher temperatures are required to provide the requisite thermal energy for the occurrence of a glass transition in the hybrid materials. When the SHUA content is higher than 5 wt.% in the UV-cured SHUA/TAEP film, the decrease in crosslinking density dominates and results in the decrease of  $T_{\rm g}$ . Moreover, the analysis result on the width of relaxation peaks shows the trend in network homogeneity for the films with different SHUA contents. It can be seen from Fig. 8 that there is no significant difference on the width of relaxation peaks among all the samples, which implies the good miscibility of SHUA with TAEP.

## 3.6. Properties of UV-cured films

The tensile strength and elongation at break are listed in Table 4. The tensile strength first increases and then decreases along with the addition of SHUA to TAEP owing to the two competitive factors: the nanoreinforcement of the SHUA core and the decrease of crosslinking density, which is in agreement with the results obtained by DMTA. However, the elongation at break of the cured film increases progressively. In other words, the rubbery properties of the UV-cured hybrid films are significantly improved, which is attributed to the reduced crosslinking density and the existence of a large number of flexible aliphatic chains.

From Table 4, it can be also found that the abrasion resistance of the UV-cured films is enhanced with increasing SHUA content. As far as the chemical structures of these networks are concerned, this behavior is to be expected since inorganic component has good abrasion resistance. In addition, there are a lot of urethane structures in the network, which is another reason for the enhancement in the abrasion resistance. The pendulum hardness of the UV-cured



**Fig. 9.** The curves for the variations of  $T_g$  and  $E'_{rubb}$  (200 °C) vs. SHUA content.

hybrid films increases with the increase of SHUA content due to the nanoreinforcement. The pencil hardness is 3H for films with the SHUA content of below 10 wt.% and 4H for those with higher SHUA contents, which accords with the results obtained by the pendulum hardness.

# 4. Conclusions

An organophilic organic-inorganic hybrid urethane acrylate (SHUA) was synthesized by the reaction of IPDI-HEA with silsesquioxane bearing terminal hydroxyl groups on the outermost surface (SBOH) which can be obtained by hydrolytic condensation of a functionalized precursor in large-scale production without a tedious and time-consuming process. In contrast to conventional UV-curable organic-inorganic hybrid resins, SHUA/TAEP system is rather stable and the formulating process is convenient.

The viscosity reduced and the photopolymerization rate was enhanced by the incorporation of TAEP into SHUA. The photopolymerization kinetics are significantly affected by the double bond density and viscosity caused by TAEP addition. The elastic storage modulus on the rubbery plateau region and glass transition temperature of the cured films first increased and then decreased along with the content of SHUA in the blend due to the nanoreinforcement by the inorganic core and the decrease of crosslinking density. The char residue at 850 °C increased, whereas the limiting oxygen index decreased with increasing SHUA content. Moreover, it has been found that the flame retardancy of one part of TAEP is acting in the gas phase, while another part of TAEP is acting in condensed phase owing to the synergistic effect between phosphorus-nitrogen and phosphorus-silicon. However, the gas phase mechanism holds the dominant effect during whole degradation process. Better mechanical and physical properties are also observed owing to the synergism between organic and inorganic components.

# Acknowledgement

The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (No. 50633010).

#### References

- [1] C. Decker, Polym. Int. 45 (1998) 133.
- [2] C. Decker, Macromol. Rapid Commun. 23 (2002) 1067.
- [3] Z.G. Chen, D.C. Webster, Polym. Int. 56 (2007) 754.
- [4] X.E. Cheng, Z.G. Huang, J.H. Liu, W.F. Shi, Prog. Org. Coat. 59 (2007) 284.
- [5] M. Avella, M.E. Errico, E. Martuscelli, Nano Lett. 1 (2001) 213.
   [6] M.E.L. Wouters, D.P. Wolfs, M.C. van der Linde, J.H.P. Hovens, A.H.A. Tinnemans,
- Prog. Org. Coat. 51 (2004) 312.
- [7] J.Y. Wen, G.L. Wilkes, Chem. Mater. 8 (1996) 1667.
  [8] G. Li, L. Wang, H. Ni, C.U. Pittman, J. Inorg. Organomet. Polym. 11 (2001) 123.
- [9] Y. Abe, T. Gunji, Prog. Polym. Sci. 29 (2004) 149.
- [10] J.D. Lichtenhan, N.Q. Vu, J.A. Carter, J.W. Gilman, F.J. Feher, Macromolecules 26 (1993) 2141.
- [11] J.D. Lichtenhan, Y.A. Otonari, M.J. Carr, Macromolecules 28 (1995) 8435.

- [12] T.S. Haddad, J.D. Lichtenhan, J. Inorg. Organomet. Polym. 5 (1995) 237.
- R.A. Mantz, P.F. Jones, K.P. Chaffee, J.D. Lichtenhan, J.W. Gilman, I.M.K. Ismail, Ì13Ì M.J. Burmeister, Chem. Mater. 8 (1996) 1250.
- [14] T.S. Haddad, J.D. Lichtenhan, Macromolecules 29 (1996) 7302.
- [15] C. Zhang, R.M. Laine, J. Organomet. Chem. 521 (1996) 199.
- [16] J.D. Lichtenhan, Comments Inorg. Chem. 17 (1995) 115.
- [17] M. Unno, A. Suto, K. Takada, H. Matsumoto, Bull. Chem. Soc. Jpn. 73 (2000) 215.
- [18] P. Xie, R. Zhang, Polym. Adv. Technol. 8 (1997) 649.
- [19] H. Xu, P. Xie, R. Zhang, Eur. Polym. J. 37 (2001) 2397.
- [20] J. Deng, J.T. Polidan, J.R. Hottle, C.E. Farmer-Creely, B.D. Viers, A.R. Esker, J. Am. Chem. Soc. 124 (2002) 15194.
- [21] J. Pyun, K. Matyjaszewski, J. Wu, G.M. Kim, S.B. Chun, P.T. Mather, Polymer 44 (2003) 2739.
- [22] H.Y. Xu, S.W. Kuo, J.Y. Lee, F.C. Chang, Polymer 43 (2002) 5117.
- [23] J.C. Huang, C.B. He, Y. Xiao, K.Y. Mya, J. Dai, Y.P. Siow, Polymer 44 (2003) 4491.
- [24] S.H. Philips, R.I. Gonzalez, K.P. Chaffee, T.S. Haddad, G.B. Hoflund, B.S. Hsiao, B.X. Fu, SAMPE 45 (2000) 1921.
- [25] B.X. Fu, M. Namani, A. Lee, Polymer 44 (2003) 7739.
- [26] S.A. Pellice, D.P. Fasce, R.J.J. Williams, J. Polym. Sci. Part B: Polym. Phys. 41 (2003) 1451
- [27] A. Lee, Mater. Res. Soc. Symp. Proc. 576 (1999) 343.
- [28] S.H. Phillips, R.L. Blanski, S.A. Sveida, T.S. Haddad, A. Lee, I.D. Lichtenhan, F.I. Feher, P.T. Mather, B.S. Hsiao, Mater. Res. Soc. Symp. Proc. 628 (2000), CC4.6.1.
- [29] A. Lee, J.D. Lichtenhan, Macromolecules 31 (1998) 4970.
   [30] L. Zheng, S. Hong, G. Cardoen, E. Burgaz, S.P. Gido, E.B. Coughlin, Macro-
- molecules 37 (2004) 8606.
- [31] D.P. Fasce, R.I.I. Williams, F. Méchin, I.P. Pascault, M.F. Llauro, R. Pétiaud, Macromolecules 32 (1999) 4757.

- [32] D.P. Fasce, R.J.J. Williams, R. Erra-Balsells, Y. Ishikawa, H. Nonami, Macromolecules 34 (2001) 3534.
- [33] I.E. dell'Erba, D.P. Fasce, R.J.J. Williams, R. Erra-Balsells, Y. Fukuyama, H. Nonami, J. Organomet. Chem. 686 (2003) 42.
- [34] I.E. dell'Erba, R.J.J. Williams, Eur. Polym. J. 43 (2007) 2759.
- [35] I.E. dell'Erba, D.P. Fasce, R.J.J. Williams, R. Erra-Balsells, Y. Fukuyama, H. Nonami, Macromol. Mater. Eng. 289 (2004) 315.
- [36] H. Mori, M.G. Lanzendörfer, A.H.E. Müller, Macromolecules 37 (2004) 5228.
- [37] H. Mori, A.H.E. Müller, J.E. Klee, J. Am. Chem. Soc. 125 (2003) 3712.
- [38] H. Mori, Y. Miyamura, T. Endo, Langmuir 23 (2007) 9014.
- [39] J.W. Xu, W.M. Pang, W.F. Shi, Thin Solid Films 514 (2006) 69.
- [40] A. Asif, C.Y. Huang, W.F. Shi, Colloid Polym. Sci. 12 (2004) 200.
- [41] H.B. Liang, W.F. Shi, Polym. Degrad. Stab. 84 (2004) 525.
- [42] A. Asif, W.F. Shi, X.F. Shen, Polymer 46 (2005) 11066.
- [43] Z.G. Huang, W.F. Shi, Eur. Polym. J. 42 (2006) 1506.
- [44] Z.G. Huang, W.F. Shi, Polym. Degrad. Stab. 91 (2006) 1674.
- [45] Z.G. Huang, W.F. Shi, Eur. Polym. J. 43 (2007) 1302.
- [46] G.H. Hsiue, Y.L. Liu, H.H. Liao, J. Polym. Sci. Part A: Polym. Chem. 39 (2001) 986.
- [47] G.H. Hsiue, Y.L. Liu, J. Tsaio, J. Appl. Polym. Sci. 78 (2000) 1.
- [48] C.S. Wu, Y.L. Liu, Y.S. Chiu, Polymer 43 (2002) 4277.
- [49] Z.G. Huang, W.F. Shi, Polym, Degrad, Stab. 92 (2007) 1193.
- [50] S. Bourbigot, M. Le Bras, R. Delobel, J.M. Trémillon, J. Chem. Soc. Faraday Trans. 92 (1996) 3435.
- [51] M. Bugajny, S. Bourbigot, Polym. Int. 48 (1999) 264.
- [52] M. Le Bras, S. Bourigot, B. Revel, J. Mater. Sci. 34 (1999) 5777.
   [53] G.H. Hsiue, S.J. Shiao, H.F. Wei, W.J. Kou, Y.A. Sha, J. Appl. Polym. Sci. 79 (2001) 342