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

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ABSTRACT

The silsesquioxane-based hybrid urethane acrylate (SHUA) was synthesized by modifying silsesquioxane-based hybrid polyol (SBOH) with the half adduct of isophorone diisocyanate and 2-hydroxyethyl acrylate, and characterized by Fourier transfer infrared (FTIR) and ^{1}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.

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 $R_nSi_nO_{1.5n-x}(OH)_{2x}$, 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_8) with the empirical formula of $(R–SiO_{1.5})_8$ have become the focus of many studies. The organic–inorganic hybrid materials containing T_8 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_8 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

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of perfect and imperfect polyhedra bearing secondary hydroxyl groups (OH–SSO) [31–33] or (β-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 phosphorus-containing 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 $POCl_3$ 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 (3.225%, 42.06 g) was added into the above addition product (287.82 g, 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%).

Table 1
Viscosity, photopolymerization rates at peak maximum and final unsaturation conversion in the cured films

Sample	Formulation (wt.%)		Viscosity (mPa s, 25 °C)	R^{p}_{max} (J g^{-1} s^{-1})	P^{f} (%)
	SHUA	TAEP			
TAEP	0	100	95	22.03	80.8
$SHUA_5TAEP_{95}$	5	95	160	18.56	75.5
$SHUA_{10}TAEP_{90}$	10	90	500	14.77	70.0
$SHUA_{20}TAEP_{80}$	20	80	1250	10.17	67.9
$SHUA_{30}TAEP_{70}$	30	70	2850	9.85	65.2
$SHUA_{40}TAEP_{60}$	40	60	4950	8.46	62.3

^{1}H NMR (300 MHz, D_2O): δ (ppm) 0.4–0.9 (–SiCH_2–), 1.4–1.9 (–$SiCH_2$$CH_2$–), 2.4–3.2 (–N$CH_2$–), 3.4–4.1 (–O$CH_2$–, –O$CH$–). FTIR (NaCl plate, cm^{-1}): 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_2 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_2 atmosphere and then stirred continuously at 60 °C until the FTIR absorption peak at 2250 cm^{-1} 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.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.3–1.9 (–SiCH_2–, –C(CH_3)CH_2C(CH_3)$_2$–), 1.4–2.1 (–$SiCH_2$$CH_2$–, –$CH_2$CH(NHCOO)$CH_2$–), 2.3–3.2 (–N$CH_2$–, –C$CH_2$NHCOO–), 3.3–4.2 (–O$CH_2$–, –O$CH$–, –$CH_2$$CH$(NHCOO)$CH_2$–), 4.2–4.6 (–NHCOO$CH_2$$CH_2$COO–), 5.7–6.6 (–COO$CH$=$CH_2$). FTIR (NaCl plate, cm^{-1}): 3340 (OH), 2946, 2872 (CH), 1716 (C=O), 1635, 1409, 810 (CH=CH_2), 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 μm 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 ^{1}H NMR spectrum was recorded with an AVANCE 300 Bruker spectrometer using tetramethylsilane as an internal reference and D_2O or $CDCl_3$ 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 sam-