

UV curable soybean-oil hybrid systems based on thiol-acrylate and thiol-ene-acrylate chemistry

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ABSTRACT: In this study, epoxidized soybean oil was modified to prepare acrylated epoxidized soybean oil (AESO) and vinyl/acrylate ended soybean oil (VASO), which were blended with mercaptopropyl polyhedral oligomeric silsesquioxane (POSS-SH) to prepare UV curable thiol-acrylate and thiol-ene-acrylate hybrid coatings. Photopolymerization processes of the coatings were measured and the results showed that addition of POSS-SH obviously increased the conversion of double bond. The physical and mechanical properties of all cured samples were investigated, which indicated that the pencil hardness, tensile strength, and fracture toughness were significantly improved by POSS-SH. Moreover, with increasing POSS-SH content, the water contact angles of cured samples were increased, and the water resistance was greatly improved. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42095.

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INTRODUCTION

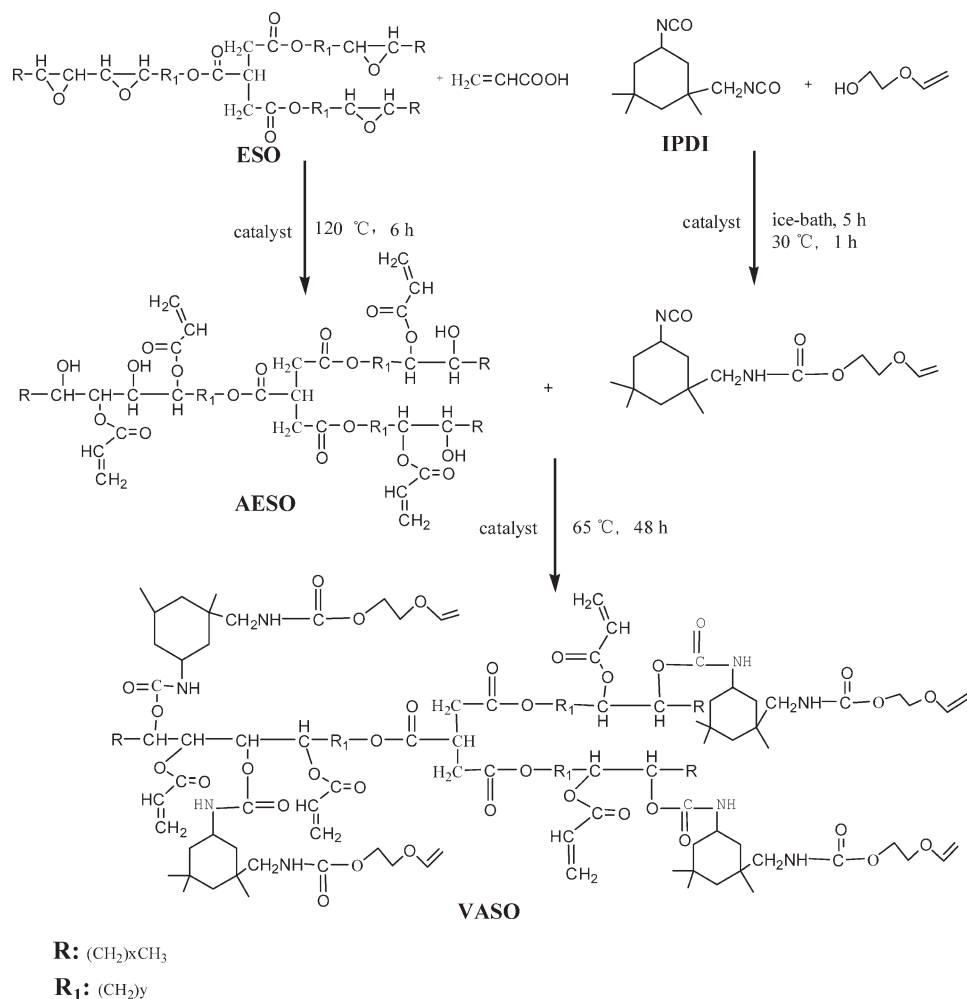
Natural resources like vegetable oils, fatty acids, and lactic acids have been widely attracted attention by researchers because they are environmental friendly and can be molecular-engineered into renewable polymers in a way similar to many petroleum-derived chemicals.^{1–3} Soybean oil is one of the most widely used vegetable oils in coatings and considered as abundant and low-cost feedstock. However, soybean oil must be chemically modified (i.e., introduction of more reactive functional groups) to be useful for applications in industrial products for the low reactivity of the double bonds within the soybean oil molecule and the flexibility of the triglyceride fatty acid structure.

Epoxidized soybean oil (ESO) as an important starting material for the development of soybean oil-based materials such as coatings, adhesives, plasticizers, and lubricants has been reported in many articles.^{4–7} Baipai *et al.* synthesized acrylated epoxidized soybean oil (AESO) and used for UV curable coatings.⁸ Hong *et al.* obtained cross-linked biopolymers from ESO through copper-catalyzed azide-alkyne cycloaddition (CuAAC), which was high-yielding, selective, and devoid of side reactions and had been widely used in producing linear and block copolymers, cyclic and star polymers, and dendrimers.^{9–16} He *et al.* provided a rapid and highly efficient strategy for the synthesis of soybean oil-based acrylate via photoclick thiol-ene reaction.¹⁷ The photoclick thiol-ene system leads to high monomer conversions,¹⁸ low shrinkage,^{19,20} homogeneous mechanical

properties, very little oxygen inhibition, and no metal residue.^{21,22} Thus, photoclick thiolene may be useful to prepare high performance UV curing soybean hybrid systems by incorporating inorganic particle into the soybean-oil networks.

The polyhedral oligomeric silsesquioxane (POSS) is a new kind of unique inorganic particles with definite structure possessing many advantages over other inorganic agents, such as, definite size, easy modified with different function group, high thermal stability, and high mechanical properties.²³ Jiang *et al.* synthesized POSS with thiol and alkyl (POSS-OA/SH) groups using for acrylated castor oil by thiol-acrylate photopolymerization method.²⁴ The results showed that the addition of POSS-OA/SH could effectively improve the acrylate conversion and the cured film's thermal stability. However, the Young's modulus and hardness were decreased, especially for high POSS content. Neil N. Cramer and Christopher N. Bowman have reported that the thiol conversion was greatly lower than that of acrylate in thiol-acrylate system, which increased with increasing ratio of acrylate to thiol, while both thiol and vinyl conversions were almost the same level in thiol-ene (vinyl) system.²⁰ Hence, incorporating vinyl group into soybean oil and keeping low molar ratio of thiol to double bond ratio may increase the thiol conversion, which may further improve the hybrid's properties.

In this work, AESO, which was obtained by ring opening of ESO with acrylic acid, was further modified by isophorone diisocyanate (IPDI) and ethylene glycol monovinyl ether to



Scheme 1. Chemical route for the synthesis of AESO and VASO.

prepare vinyl/acrylate ended soybean oil (VASO). AESO and VASO were blend with POSS-SH in different ratios to prepare UV curable thiol-acrylate and thiol-ene-acrylate soy bean hybrids, which photopolymerization processes were measured. The physical properties, mechanical properties, and surface properties of samples were investigated.

EXPERIMENTAL

Materials

Epoxidized soybean oil (ESO, epoxide content 3.7 mol/kg, industrial grade) was obtained from Wenhua chemical dyestuff company (Shanghai, China) Isophorone diisocyanate (IPDI, industrial grade) and 3-(mercaptopropyl) trimethoxysilane (MPTS, analytical grade) were purchased from Adamas-beta. Methoxyphenol (MEHQ, chemical grade) that used as polymerization inhibitor was supplied by Aladdin-Chemical. Radical photoinitiator 2,4,6-trimethyl benzoyldiphenyl phosphine oxide (TPO, chemical grade) was obtained from Ciba. Pentaerythritol triacrylate (PETA, chemical grade) was purchased from Eternal-Chemical that used as diluents. Triphenylphosphine (chemical grade) was purchased from Sinopharm-Chemical. Dibutyltindilaurate (DBTDL, analytical grade) that used as catalyst was obtained from Shanghai reagent company. Methanol, acrylic

acid, sodium sulfate, petroleum ether, butanone, hydrochloric acid (Purity: 37%), butyl acetate and dichloromethane were purchased from Xilong chemical company (analytical grade, Hubei, China). All above mentioned chemicals were used as received. Ethylene glycol monovinyl ether (Purity: $\geq 99\%$, industrial grade) was purchased from Xinjing Company (Hubei, China) and treated with 3 Å molecular sieves to dehydrate.

Experimental Techniques

The $^1\text{H-NMR}$ spectra were obtained on a 400 MHz Varian Gemini spectrometer from CDCl_3 solutions with tetramethylsilane (TMS) as the internal standard at ambient temperature.

Real-time infrared spectroscopy (FTIR) was conducted to monitor the conversion of $-\text{S}-\text{H}$ and $-\text{C}=\text{C}$, which were conducted by sandwiching the samples between two NaCl salt windows with an irradiation at the surface of the samples in the range of $4000\text{--}400\text{ cm}^{-1}$. A UV-light source (RW-UVA- φ 200U, Runwing, China) with a 250–400 nm bandpass filter was used for photopolymerization.

The acid value is the number that expresses, in milligrams the quantity of potassium hydroxide required to neutralise the free acids present in 1 g of the substance. The acid value was

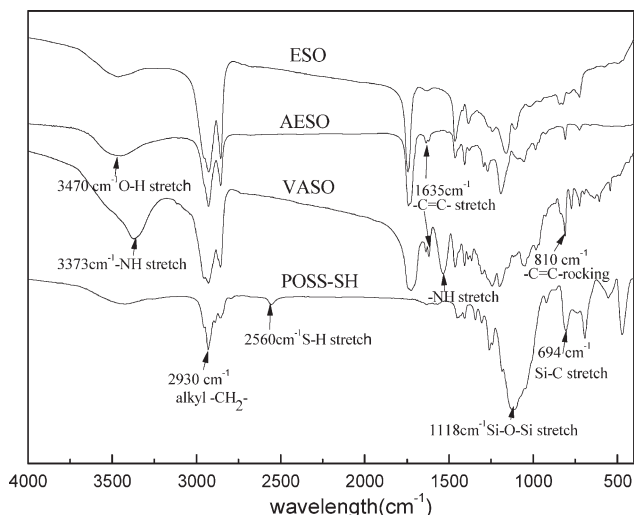


Figure 1. The FTIR spectra of ESO, AESO, VASO, and POSS-SH.

conducted to monitor the process of the reaction according to GB/T 668—2008.

Tensile strength was conducted by Electromechanical Universal Testing Machine (WD-1, Sansi Company, China) at tensile test speed of 5 mm/min. The tested specimens were cut into rectangle strips (dimensions $150 \times 10 \times 1 \text{ mm}^3$) according to ISO 527-3-1995 test method and the distance between testing marks was 50 mm. The average value of at least five replicates of each sample was taken.

The pencil hardness test uses pencil leads of different hardness grades (6B–6H) as the scratch stylus. The same normal load with indenters of different hardness is applied on the samples. The hardest pencil grade that does not cause damage to the coated specimen is considered as the pencil hardness of the coating according to GB/T 6739—1986.

The type of QTY-32 Flexibility test is the evaluation of paint, varnish, and coatings bending resistant around the cylinder axis or the ability of peeling off from the metal plate. The diameters of cylinder axis are 2, 3, 4, 5, 6, 8, 10, 12, 14, 18, 25, 32 mm according to GB/T 1731—1993.

Adhesion of the coating layer with the substrate was assessed according to the ISO2409—1974 test method. In this test, eleven cuts are made in two directions using the cutter at right angles to each other to form a grid of small squares. A pressure-sensitive adhesive tape is applied over the lattice and removed by pulling in a single smooth action. Adhesion is then assessed by comparing the fraction of coating removed from grid of squares against the ISO2409—1974 standard ratings (0–5).

Variation of Water Contact Angle of the coatings were measured by sessile drop method using a contact angle analyzer, model Easy Drop, Germany. All measurements made were static contact angles using tangent line fitting mode. The angle at which the drop with a drop volume of 4 μL slides down can be measured by means of a protractor attached to the instrument.

Water absorption and solubility were measured by gravimetric analysis. At regular time intervals a certain quantity of the film

was put into water at 25°C for 7 days and dried it using filter paper. Conversion rate was calculated by the following formulas:

$$\text{Waterabsorption (wt \%)} = \frac{W_1 - W_0}{W_0} \times 100\%$$

$$\text{Waterabsorption (wt \%)} = \frac{W_0 - W_2}{W_0} \times 100\%$$

where W_0 is the weight of a certain amount of film, W_1 is the weight of the film after putting it in water for 7 days, W_2 is the weight of the film dried to a constant weight in a dry oven at 75°C after putting it in water for 7 days.

The SEM of hybrid films was obtained using Nova Nano SEM-450 Field emission scanning electron microscope.

Synthesis of Acrylated Epoxidized Soybean Oil

AESO was synthesized according to Scheme 1. Epoxidized soybean oil (30 g, epoxy mole:0.112 mol), triphenylphosphine(0.447 g,

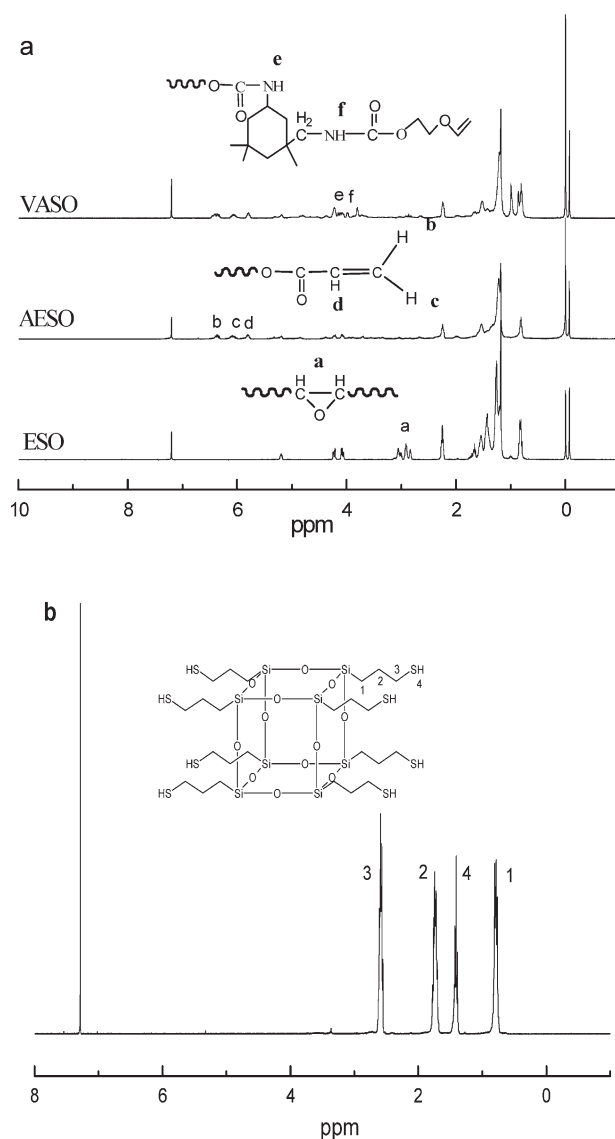


Figure 2. The $^1\text{H-NMR}$ spectra of (a) ESO, AESO, VASO and (b) POSS-SH in the CDCl_3 solvent.

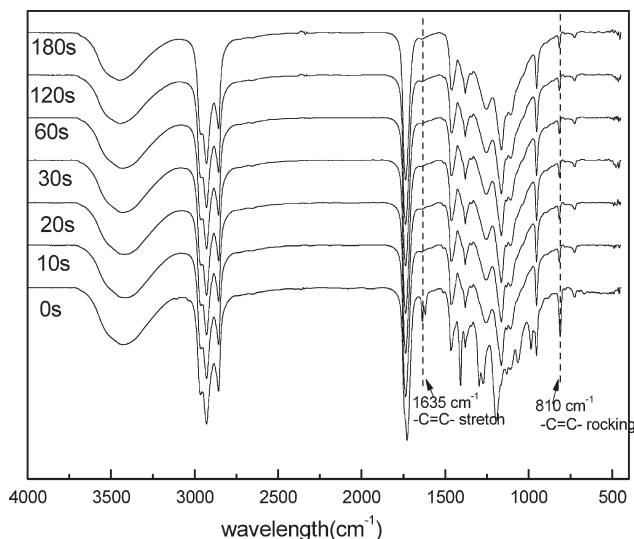


Figure 3. The FTIR spectra for the photopolymerization of AESO/0POSS-SH with different irradiation time.

catalyst), and MEHQ (0.112 g, inhibitor) were placed in a sealed 250 mL three-necked round-bottomed flask with condensate water at 90°C, and acrylic acid (7.271 g, 0.1 mol) was added by dropwise into the flask in half an hour. Then the mixture was heated to 120°C and mechanically stirred until acid value decreased to 5 mg KOH/g. Finally, the resulting viscous yellow liquid was dissolved in butanone and then washed three times with petroleum ether to remove excess acrylic and separate sediment and concentrated to obtain AESO. The FTIR spectra and ¹H-NMR spectra of ESO, AESO were shown in Figures 1 and 2(a).

¹H-NMR (CDCl₃, δ): 5.8–6.6 (–HC=CH₂), 4.4–4.5 (–HC–OOC–), 3.9–4.21 (–O–CH₂–), 3.33 (–CH (OH) –), 2.8–3.1 (–CH–CH–)

IR (cm⁻¹): 3470 cm⁻¹ (O–H stretch), 1635 cm⁻¹ and 810 cm⁻¹ (–C=C– stretch, –C=C–rocking), 1746 cm⁻¹ (O=C=O stretch).

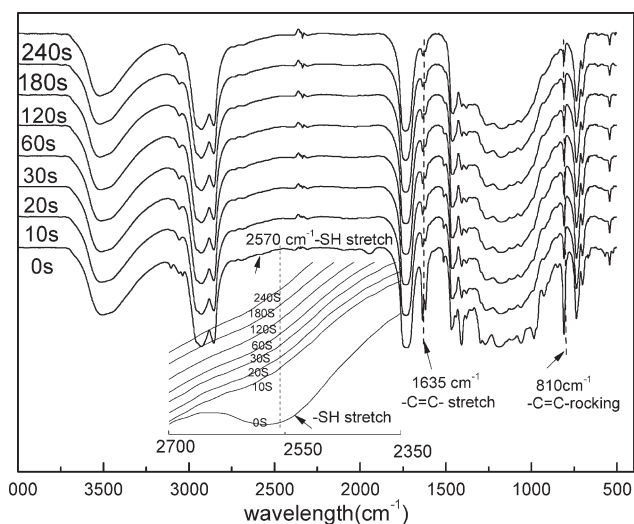


Figure 4. The FTIR spectra for the photopolymerization of AESO/0.3POSS-SH with different irradiation time.

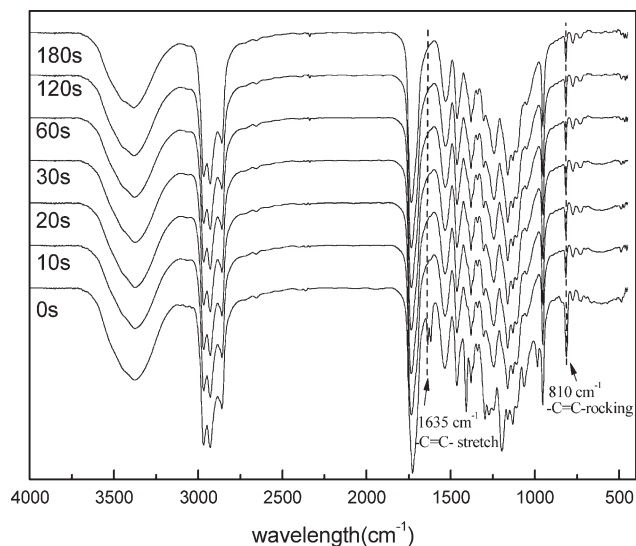


Figure 5. The FTIR spectra for the photopolymerization of VASO/0POSS-SH with different irradiation time.

Synthesis of the Vinyl/Acrylate Ended Soybean Oil

VASO was synthesized according to Scheme 1. Isophorone diisocyanate (15.709 g, 0.07 mol), dibutyltin dilaurate (0.063 g), and butyl acetate (15 g) were added to the reaction flask and ethylene glycol monovinyl ether (6.229 g, 0.07 mol) was added by dropwise into the solution equipped with a magnetic stirrer and cooled in an ice bath for 5 h. After that, it was then stirred at 30°C for 1 h, which was further added drop wise into AESO flask and stirred at 65°C for 48 h. Then the solvent was removed under vacuum and the resulting viscous yellow liquid was redissolved in butanone, which was washed three times with petroleum ether to remove excess acrylic and separate sediment. Finally, VASO was obtained by removed the butanone under vacuum. The FTIR spectra and ¹H-NMR spectra of VASO were shown in Figures 1 and 2(a).

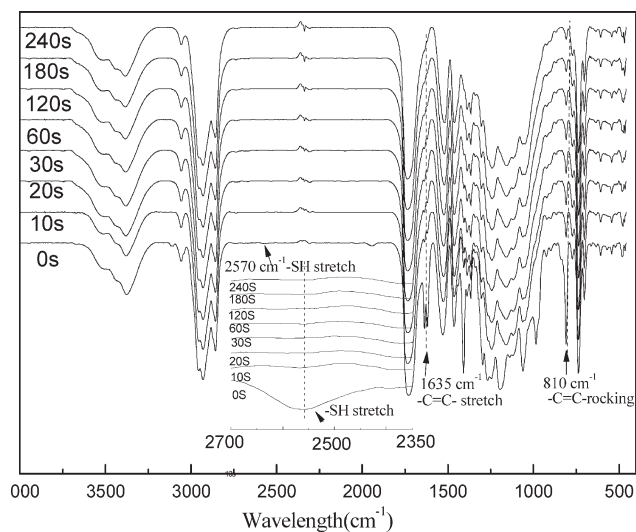


Figure 6. The FTIR spectra for the photopolymerization of the VASO/0.6POSS-SH with different irradiation time.

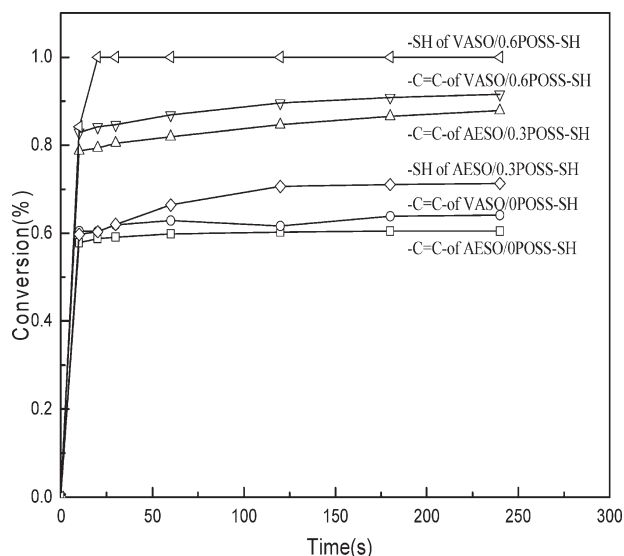


Figure 7. The thiol and double bond group conversion vs. time for AESO, AESO/0.3POSS-SH, VASO, and VASO/0.6POSS-SH.

$^1\text{H-NMR}$ (CDCl_3 , δ): 5.8–6.6 ($-\text{C}-\text{HC}=\text{CH}_2$, $-\text{O}-\text{CH}=\text{CH}_2$), 3.9–4.21 ($-\text{NH}-\text{CO}-\text{O}-\text{CH}_2-$), 2.9 ($-\text{C}-\text{CH}_2-\text{NH}-\text{CO}-$).

IR (cm^{-1}): 3373 cm^{-1} , 1536 cm^{-1} ($-\text{NH}$ stretch), 1635 cm^{-1} and 810 cm^{-1} ($-\text{C}=\text{C}-$ stretch, $-\text{C}=\text{C}$ -rocking).

Synthesis of POSS-SH

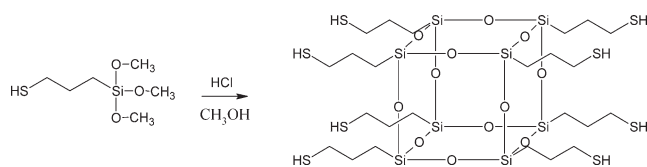
As is shown in Scheme 2, POSS-SH was synthesized according to literature method.²⁴ MPTS (15 mL) was loaded into a sealed 500 mL three-necked round-bottomed flask with condensate water, while stirring concentrated HCl (37%, 30 mL) in methanol (360 mL) were added by dropwise. Then the mixture was stirred at 80°C for 24 h and produced POSS-SH as a white precipitate. The crude product was washed with cold methanol three times to remove excess MPTS. The resulting viscous solution was dissolved in CH_2Cl_2 and then washed three times with H_2O . The solution was dried with anhydrous Na_2SO_4 for 24 h and concentrated to obtain POSS-SH. The FTIR spectra and $^1\text{H-NMR}$ spectra of POSS-SH was shown in Figure 1 and 2(b).

$^1\text{H-NMR}$ (CDCl_3 , δ): 0.7–0.87 ($-\text{Si}-\text{CH}_2-$), 1.35–1.5 ($-\text{SH}$), 2.5–2.6 ($-\text{CH}_2-\text{SH}$), 1.75 ($-\text{CH}_2-\text{CH}_2-\text{SH}$).

IR (cm^{-1}): 2930 cm^{-1} , 2853 cm^{-1} (alkyl $-\text{CH}_2-$), 2560 cm^{-1} ($\text{S}-\text{H}$ stretch), 1260 cm^{-1} ($\text{Si}-\text{C}$ asymmetric stretch), 1118.7 cm^{-1} ($\text{Si}-\text{O}-\text{Si}$ a symmetric stretch), 694 cm^{-1} ($\text{Si}-\text{C}$ stretch), 560 and 475 cm^{-1} (POSS skeletal deformation vibrations).

Sample Preparations

Two types of films were prepared based on AESO and VASO, respectively. In the first case, POSS-SH was mixed with AESO ranging from $-\text{C}=\text{C}-$ (acrylate): $-\text{SH} = 1 : 0$ to $1 : 0.5$ and



Scheme 2. Chemical route for the synthesis of POSS-SH.

Table I. The Formulations of All Samples

Sample	Thiol : acrylate (mol ratio)	Thiol : vinyl (mol ratio)	POSS-SH content (wt %)
AESO/0POSS-SH	0 : 1		0
AESO/0.1POSS-SH	0.1 : 1		3.46
AESO/0.2POSS-SH	0.2 : 1		6.72
AESO/0.3POSS-SH	0.3 : 1		9.70
AESO/0.4POSS-SH	0.4 : 1		12.17
AESO/0.5POSS-SH	0.5 : 1		15.18
VASO/0POSS-SH		0 : 1	0
VASO/0.1POSS-SH		0.1 : 1	1.47
VASO/0.2POSS-SH		0.2 : 1	2.91
VASO/0.4POSS-SH		0.4 : 1	5.64
VASO/0.6POSS-SH		0.6 : 1	8.23

Table II. Physical Properties of Cured Thiol-Acrylate Hybrid System:

AESO/0.1POSS-SH, AESO/0.2POSS-SH, AESO/0.3POSS-SH, AESO/0.4POSS-SH, and AESO/0.6POSS-SH as Well as Neat AESO

Sample	$-\text{SH}:-$ $\text{C}=\text{C}-$ (mol)	Pencil hardness	Flexibility	Adhesion
AESO/0POSS-SH	0 : 1	H	2 mm	0
AESO/0.1POSS-SH	0.1 : 1	2H	2 mm	0
AESO/0.2POSS-SH	0.2 : 1	2H	2 mm	0
AESO/0.3POSS-SH	0.3 : 1	2H	2 mm	0
AESO/0.4POSS-SH	0.4 : 1	3H	2 mm	0
AESO/0.5POSS-SH	0.5 : 1	3H	2 mm	1

resultant films were coded as AESO/0POSS-SH, AESO/0.1POSS-SH, AESO/0.2POSS-SH, AESO/0.3POSS-SH, AESO/0.4POSS-SH, AESO/0.5POSS-SH. In the second case, $-\text{O}-\text{C}=\text{C}$ (vinyl): $-\text{SH}$ ratio was selected ranging from 1 : 0 to 1 : 0.6 that named VASO/0POSS-SH, VASO/0.1POSS-SH, VASO/0.2POSS-SH, VASO/0.4POSS-SH, VASO/0.6POSS-SH. All samples were formulated with 1 wt % photoinitiator (TPO) and 30 wt % diluents pentaerythritol triacrylate relative to the total reactants

Table III. Physical Properties of Cured Thiol-ene-acrylate Hybrid System:

VasO/0.1POSS-SH, VasO/0.2POSS-SH, VasO/0.4POSS-SH, and VasO/0.6POSS-SH as Well as Neat VasO

Sample	$-\text{SH}:-$ $-\text{O}-\text{C}=\text{C}-$ (mol)	Pencil hardness	Flexibility	Adhesion
VASO/0POSS-SH	0 : 1	H	2 mm	0
VASO/0.1POSS-SH	0.1 : 1	2H	2 mm	0
VASO/0.2POSS-SH	0.2 : 1	2H	2 mm	0
VASO/0.4POSS-SH	0.4 : 1	3H	2 mm	0
VASO/0.6POSS-SH	0.6 : 1	3H	2 mm	0

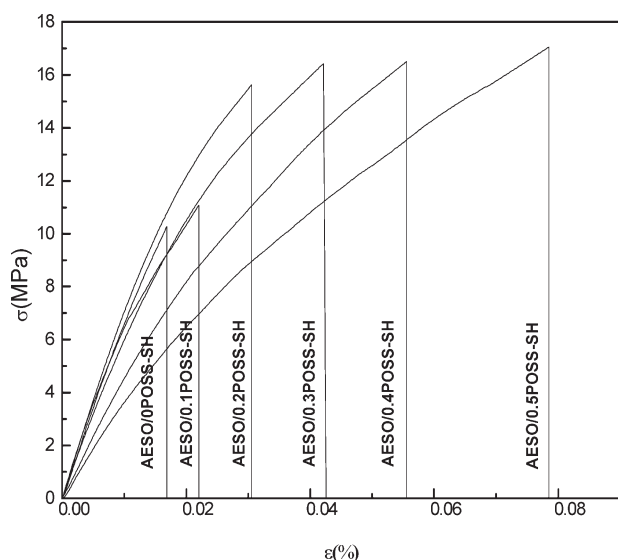


Figure 8. Stress–strain curves of thiol-acrylate hybrid system: AESO/0.1POSS-SH, AESO/0.2POSS-SH, AESO/0.3POSS-SH, AESO/0.4POSS-SH, and AESO/0.6POSS-SH as well as neat AESO.

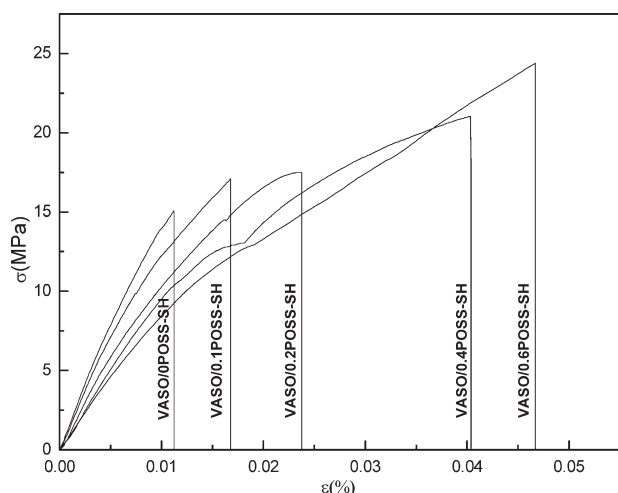


Figure 9. Stress–strain curves of thiol-ene-acrylate hybrid system: VASO/0.1POSS-SH, VASO/0.2POSS-SH, VASO/0.4POSS-SH, and VASO/0.6POSS-SH as well as neat VASO.

content. The different mole ratios of the samples and the wt % of POSS-SH in thiol-acrylate and thiol-ene-acrylate system were listed in Table I.

Table IV. Mechanical Properties of Thiol-acrylate Hybrid System: AESO/0.1POSS-SH, AESO/0.2POSS-SH, AESO/0.3POSS-SH, AESO/0.4POSS-SH, and AESO/0.6POSS-SH as Well as Neat AESO

Sample	Tensile strength (MPa)	Fracture toughness (kJ m^{-3})	Tensile modulus (MPa)
AESO/0POSS-SH	10.3 ± 1.2	92.0 ± 8.7	707.4 ± 37.5
AESO/0.1POSS-SH	11.1 ± 1.1	140.4 ± 18.4	688.2 ± 34.8
AESO/0.2POSS-SH	15.6 ± 0.9	281.4 ± 17.3	655.3 ± 31.6
AESO/0.3POSS-SH	16.4 ± 0.8	422.7 ± 27.2	622.1 ± 30.3
AESO/0.4POSS-SH	16.5 ± 0.5	539.1 ± 15.8	466.4 ± 20.8
AESO/0.6POSS-SH	17.0 ± 1.0	786.1 ± 19.7	375.9 ± 35.3

RESULTS AND DISCUSSION

Photopolymerization Mechanism of the Hybrid Systems

The homo-polymerization and thiol-ene/homo-polymerization hybrid curing mechanisms were measured by FTIR and the results were shown as Figures 3–6, respectively. The peaks at 810 and 2573 cm^{-1} could be attributed to —C=C rocking and —S—H stretching vibrations, respectively. The double bond and thiol conversion were calculated and shown as in Figure 7. As we can see, the peak at 810 cm^{-1} decreased quickly after 10 s UV radiation for all four samples and the double bond conversions of 10 s radiation for AESO/0POSS-SH, AESO/0.3POSS-SH, VASO/0POSS-SH, and VASO/0.6POSS-SH were 57.8%, 78.7%, 60.5%, and 84.1%, respectively. While, the thiol conversions of AESO/0.3POSS-SH and VASO/0.6POSS-SH were 59.7% and 84.2%, respectively. The results indicated that the addition of POSS-SH could significantly improve the conversion of double bond. Moreover, as mentioned in Neil's work,²⁰ there were two competitive reactions in thiol-acrylate system: homopolymerization and transfer to thiol. Hence, the thiol conversion is lower than that of acrylate in AESO/0.3POSS-SH. Meanwhile, the thiol conversion in VASO/0.6POSS-SH is higher than that of double bond, which indicated the thiol-ene addition was preferred on homopolymerization with incorporating vinyl end groups. With further irradiating, the peaks at 810 and 2573 cm^{-1} were further slowly decreased and the final double bond conversions of AESO/0POSS-SH, AESO/0.3POSS-SH, VASO/0POSS-SH, and VASO/0.6POSS-SH were 60.5%, 87.8%, 64.1%, and 91.5%. After 20 s irradiating, the thiol peaks of VASO/0.6POSS-SH disappeared and the final thiol conversion of AESO/0.3POSS-SH was 71.3%, which further indicated the complete reaction in thiol-acrylate system.

Physical and Mechanical Properties of the Hybrid Systems

The physical properties of thiol-acrylate and thiol-ene-acrylate systems were listed in Tables II and III, respectively. The cured films of AESO and VASO possessed the same level pencil hardness, flexibility, and adhesion properties. The pencil hardness increased from H without POSS-SH addition to 3H for AESO/0.4POSS-SH and VASO/0.4 (O=C=C) with 12.17 and 5.64 wt % POSS-SH addition, which was mainly attributed to the rigid inorganic core of POSS-SH. As shown in the photopolymerization mechanism results, thiol conversion was obviously improved by incorporating vinyl group in thiol-ene-acrylate systems. As a result, POSS-SH was more effective to improve the thiol-ene-acrylate system's pencil hardness. Meanwhile, the flexibilities of

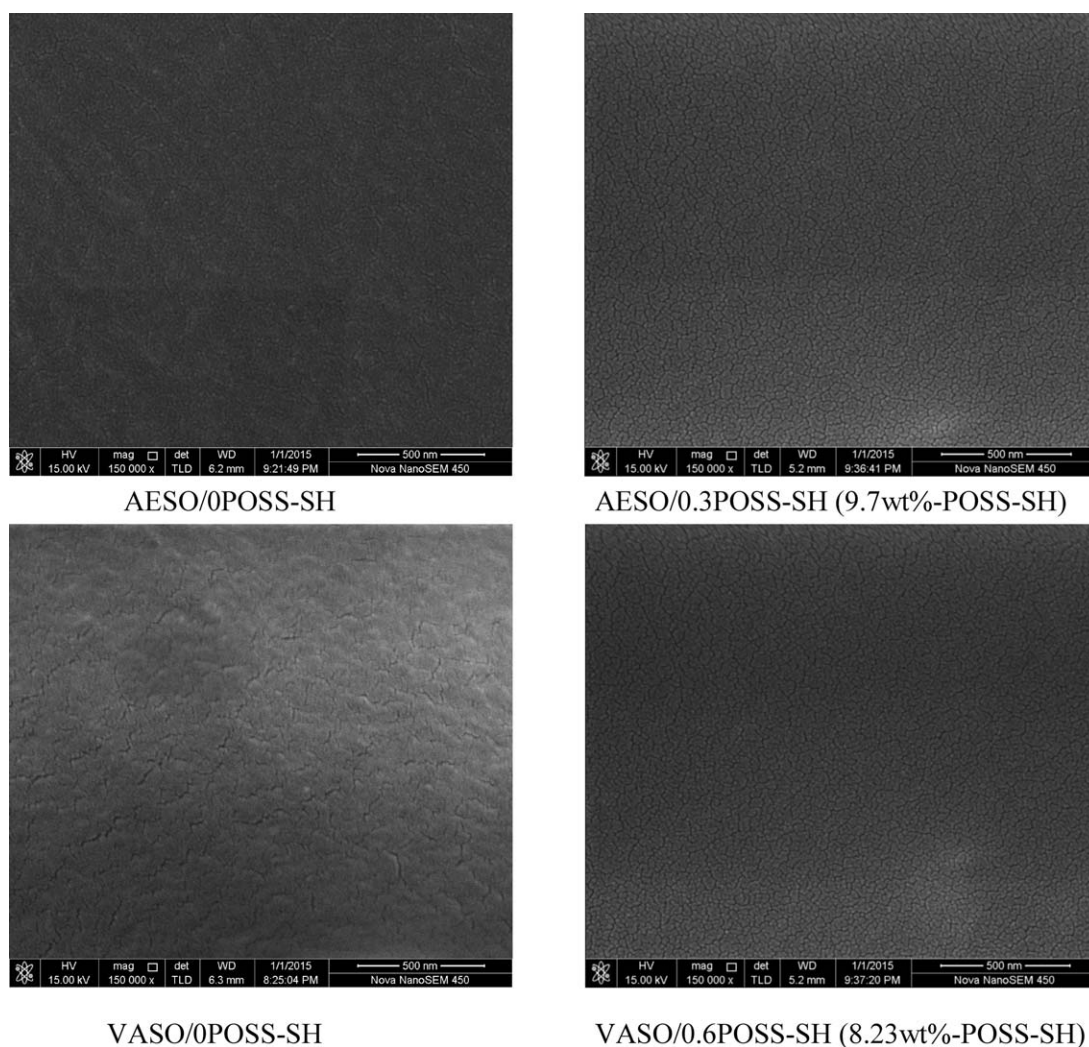
Table V. Mechanical Properties of Thiol-ene-acrylate Hybrid System: VasO/0.1POSS-SH, VasO/0.2POSS-SH, VasO/0.4POSS-SH, and VasO/0.6POSS-SH as Well as Neat VasO

Sample	Tensile strength (MPa)	Fracture toughness (kJ m^{-3})	Tensile modulus (MPa)
VASO/0POSS-SH	15.1 ± 1.3	95.4 ± 12.3	1731 ± 92.6
VASO/0.1POSS-SH	17.1 ± 1.1	167.8 ± 18.4	1584 ± 75.7
VASO/0.2POSS-SH	17.5 ± 0.8	256.8 ± 20.5	1334 ± 89.4
VASO/0.4POSS-SH	21.0 ± 1.3	542.3 ± 50.4	1159 ± 70.7
VASO/0.6POSS-SH	24.4 ± 1.5	651.9 ± 62.6	961.4 ± 88.5

the films were maintained due to the small size and good compatibility of POSS-SH. Moreover, thiol-ene-acrylate system showed better performance for maintaining the adhesion than thiol-acrylate system.

The strain–stress curves of thiol-acrylate and thiol-ene-acrylate system were shown as Figures 8 and 9, respectively. And the tensile strength and fracture toughness were listed in Tables IV and V. It could be seen that both tensile strength and fracture toughness were increased significantly with POSS-SH

addition. For thiol-acrylate system, the tensile strength increased from 10.3 MPa for AESO/0POSS-SH to 17.0 MPa for AESO/0.5POSS-SH, and the fracture toughness increased from 92.0 to 786.1 kJ m^{-3} . For thiol-ene-acrylate system, the tensile strength increased from 15.1 MPa for VASO/0POSS-SH to 24.4 MPa for VASO/0.6POSS-SH, and the fracture toughness increased from 95.4 to 651.9 kJ m^{-3} . These were mainly because that the POSS-SH addition incorporated rigid inorganic core into the networks by chemical bond, which could

**Figure 10.** SEM micrographs of the fractured surface of (a) AESO/0POSS-SH, (b) AESO/0.3 POSS-SH, (c) VASO/0POSS-SH, and (d) VASO/0.4POSS-SH.

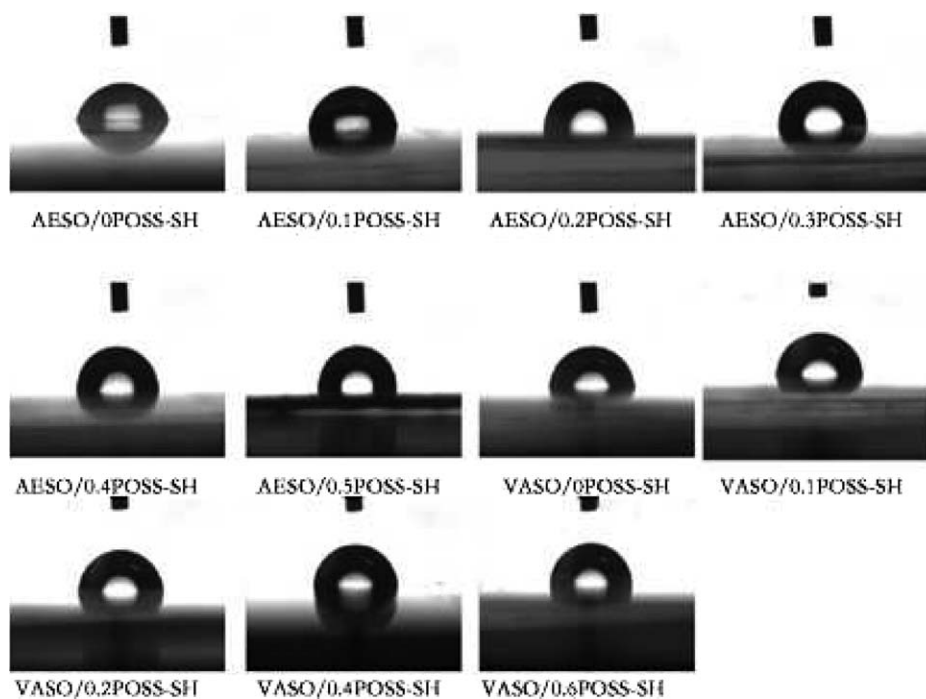


Figure 11. Digital photographs of water contact angles for all hybrid films at room temperature.

Table VI. Surface Properties of Thiol-acrylate Hybrid System: AESO/0.1POSS-SH, AESO/0.2POSS-SH, AESO/0.3POSS-SH, AESO/0.4POSS-SH, and AESO/0.6POSS-SH as Well as Neat AESO

Sample	Water contact angle (°)	Water absorption (%)	Water solubility (%)
AESO/0POSS-SH	75.2 ± 0.9	2.6 ± 0.20	2.6 ± 0.20
AESO/0.1POSS-SH	81.1 ± 1.2	2.0 ± 0.25	2.4 ± 0.21
AESO/0.2POSS-SH	88.8 ± 0.7	1.8 ± 0.14	2.2 ± 0.13
AESO/0.3POSS-SH	94.0 ± 0.8	1.3 ± 0.17	1.8 ± 0.15
AESO/0.4POSS-SH	95.1 ± 1.0	1.2 ± 0.19	1.6 ± 0.17
AESO/0.5POSS-SH	99.2 ± 0.6	1.1 ± 0.09	0.9 ± 0.06

resist force, and the high functionality of POSS-SH also could help to resist force. Thus the tensile strength was improved obviously. Moreover, the small size, good compatibility and the flexibility of $-C-S-C-$ bond could increase the fracture toughness. However, the addition of POSS-SH decreased the tensile modulus, which was mainly attributed to three reasons: increasing free volume, formation of $-C-S-C-$ and slightly increasing the molecular weight between two crosslink points.

Comparing thiol-acrylate systems with thiol-ene-acrylate systems, the incorporation of vinyl end group could obviously increase tensile strength and tensile modulus due to the high crosslink density.

The Micrographs of the Hybrid Films

The homogeneity of the POSS nanoparticles dispersion was studied by Field emission scanning electron microscopy. As

Table VII. Surface Properties of Thiol-ene-acrylate Hybrid System: VasO/0.1POSS-SH, VasO/0.2POSS-SH, VasO/0.4POSS-SH, and VasO/0.6POSS-SH as Well as Neat VasO

Sample	Water contact angle (°)	Water absorption (%)	Water solubility (%)
VASO/0POSS-SH	85.6 ± 1.3	2.4 ± 0.23	2.0 ± 0.19
VASO/0.1POSS-SH	89.7 ± 0.5	2.1 ± 0.11	1.9 ± 0.13
VASO/0.2POSS-SH	90.7 ± 0.9	1.9 ± 0.17	1.8 ± 0.18
VASO/0.4POSS-SH	92.8 ± 0.8	1.5 ± 0.19	1.5 ± 0.16
VASO/0.6POSS-SH	95.1 ± 1.1	1.3 ± 0.21	1.3 ± 0.20

shown in Figure 10, no aggregation was observed in the SEM image, indicating no phase separation and homogenous dispersion between POSS nanoparticles and the soybean oil resin. POSS functionalized with thiol groups is cross-linked in the soybean oil matrix at a molecular level and well-dispersed in the oil.

Surface Properties of the Hybrid Systems

Surface properties of the coatings were examined by water contact angles, and the digital photographs were shown as Figure 11. The results were listed in Tables VI and VII. As we could see, the water contact angle (WCA) was increased with POSS-SH addition. This was because that the hydrophobic POSS inorganic core among the crosslinked networks could improve the film surface's hydrophobic property. As a result, the water absorption and water solubility of the samples were decreased with POSS-SH addition.

CONCLUSIONS

In this work, two series of UV curable soybean hybrid coatings were studied based on thiol-acrylate and thiol-ene-acrylate system. The former one contained acrylated soybean resin and POSS-SH, and the latter one contained vinyl/acrylate ended soybean resin and POSS-SH. The addition of POSS-SH could increase the double bond conversion, and thiol conversion could also be improved by incorporating vinyl group. As a result, the sample's pencil hardness was increased from H to 3H with 12.17 and 5.64 wt % content of POSS-SH for thiol-acrylate and thiol-ene-acrylate system, respectively. Both tensile strength and fracture toughness were increased significantly with POSS-SH addition. Moreover, the cured film's hydrophobic properties were also increased with POSS-SH addition.

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