
High Performance UV Curing Soybean-Oil Hybrid Systems

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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 silsequioxane (POSS-SH) to prepare UV curable thiol-acrylate and thiol-ene-acrylate soybean-oil hybrid coatings. The photopolymerization process of the coatings was measured and the results showed that the addition of POSS-SH obviously increased the conversion of double bond. The physical and mechanical properties of the 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 the cured samples were increased, and the water resistance was also improved.

KEYWORDS: soybean oil; UV curing; thiol-ene-acrylate; hybrid

1. Introduction

Natural resources like vegetable oils, fatty acids, and lactic acids have been widely attracted attention by researchers because they are environmentally 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]. Jian Hong et al. obtained cross-linked biopolymers from ESO through copper-catalyzed azide-alkyne cycloaddition (CuAAC), the reaction is high-yielding, selective, and devoid of side reactions and has been widely used in producing linear and block copolymers, cyclic and star polymers, and dendrimers^[9-16]. Minghui 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 thiol-ene may be useful to prepare high performance UV curing soy-bean 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]. Xuesong 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 and increased with increasing ratio of acrylate to thiol, while the both thiol and vinyl were almost same level in thiol-ene(vinyl) system^[20]. Hence, incorporating vinyl group into soy bean oil and keeping low molar ratio of thiol to double bond ratio can increase the thiol conversion, which will 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 and ethylene glycol monovinyl ether to 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.

2. Experimental

2.1 Materials

Methanol, acrylic acid, sodium sulfate, hydrochloric acid (37%), butyl acetate and dichloromethane were purchased from HuBei XiLong chemical company. Epoxidized soybean oil (ESO, ShangHai WenHua chemical dyestuff company), 3-(mercaptopropyl)trimethoxysilane(MPTS, Adamas-beta, China) and ethylene glycol monovinyl ether(HuBei XinJing company, ≥99%) were used as received. Isophorone diisocyanate (IPDI) was purchased from Bayer company in Germany. Methoxyphenol (MEHQ) was purchased from Aladdin-reagent in China. The radical photo initiator TPO (2, 4, 6-Trimethyl benzoyl diphenyl phosphine oxide) was supplied by Ciba Company. Pentaerythritol triacrylate was obtained from Eternal chemical company. Triphenyl phosphine was supplied by Sinopharm chemical reagent company. Dibutyltin dilaurate (DBTL) was purchased from ShangHai reagent company. All other chemicals were analytical grade and used without further purification.

2.2. Experimental techniques

The NMR spectra were obtained on a Varian 400 MHz spectrometer with CDCl_3 and TMS as the solvent and internal standard, respectively. 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 intensity of $1.5\text{mW}\cdot\text{cm}^{-2}$ at the surface of the samples (monitored

by a radiometer, type UV-B, Photoelectric Instrument Factory of Beijing normal university).

Tensile strength was conducted by Electromechanical Universal Testing Machine (UTM4203) at tensile test speed of 5mm/min. The film thickness was less than 1mm.

The pencil hardness test uses pencil leads of different hardness grades (6B–6H) as the scratch stylus. The same normal load within dentures 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.

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 pulling away from the metal plate. The diameters of cylinder axis are 2, 3, 4, 5, 6, 8, 10, 12, 14, 18, 25, 32mm.

Adhesion of the coating layer with the substrate was assessed according to the ISO2409-1974 test method.

Variation of Water Contact Angle of the coatings were measured by sessile drop method using a Contact angle analyzer, model EasyDrop, 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 μ L 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 $^{\circ}$ C for 7 d and dried it using filter paper. Conversion rate was calculated by the following formulas:

$$\text{Water absorption wt \%} = \frac{W_1 - W_0}{W_0} \times 100\%$$

$$\text{Water solubility wt \%} = \frac{W_0 - W_2}{W_0} \times 100\%$$

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 7d, W_2 is the weight of the film dried to a constant weight in a dry oven at 75 $^{\circ}$ C after putting it in water for 7d.

2.3 Synthesis of acrylated epoxidized soybean oil (AESO)

Epoxidized soybean oil (30 g, 0.112 mol), triphenyl phosphine (0.447 g, catalyst), and MEHQ (0.112 g, inhibitor) were loaded into a sealed 250-ml three-necked round-bottomed flask with condensate water at 90 $^{\circ}$ C, and acrylic acid (7.271 g, 0.1 mol) was added dropwise into the flask in half an hour. Then the mixture was heated to 120 $^{\circ}$ C for 6 hrs and AESO was obtained as a yellow liquid. $^1\text{H NMR}$ (CDCl_3 , δ): 5.8~6.6 (-HC=CH₂), 4.4~4.5 (-HC-OOC-), 3.33 (-CH(OH)-), 2.8~3.1 (-CH-CH-) IR (cm^{-1}): 3470 (O-H stretch), 1635 cm^{-1} , 810 cm^{-1} (-C=C- stretch, -C=C-rocking), 1746 (O-C=O stretch).

2.4 Synthesis of the vinyl/acrylate ended soybean oil (VASO)

Isophorone diisocyanate (15.709g, 0.07mol), Dibutyltin dilaurate (0.063g) and butyl acetate (15g) were added to the reaction flask while stirring and cooled in an ice bath for 5hrs. Ethylene glycol mono vinyl ether (6.229g, 0.07mol) was added dropwise into the solution. Then the mixture was heated to 30°C and stirred for 1hr, which was further added dropwise into last step's AESO flask in 1 hr. The mixture was stirred at 65°C for 48hrs. The solvent was evaporated and VASO was obtained as a yellow viscous liquid. ¹H NMR (CDCl₃, δ): 5.8~6.6(-C-HC=CH₂, -O-CH=CH₂) IR (cm⁻¹):3373cm⁻¹(-NH stretch).

2.5 Synthesis of POSS-SH

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 MeOH (360 mL) were added dropwise. Then the mixture was stirred at 80°C for 24 hrs produced POSS-SH as a white precipitate. The crude product was washed with cold MeOH three times to remove excess MPTS. The resulting viscous solution was dissolved in CH₂Cl₂ and then washed three times with H₂O. The solution was dried with anhydrous Na₂SO₄ for 24 hrs and concentrated to obtain POSS-SH. IR (cm⁻¹): 2927cm⁻¹, 2853cm⁻¹ (alkyl -CH₂-), 2560cm⁻¹ (S-H stretch), 1260cm⁻¹ (Si-C asymmetric stretch), 1118.7cm⁻¹ and 1033.8cm⁻¹ (Si-O-Si asymmetric stretch), 694cm⁻¹ (Si-C stretch), and 560cm⁻¹ and 475cm⁻¹ (POSS skeletal deformation vibrations).

2.5 Sample Preparations

Two types of films were prepared based on AESO and VASO respectively. In the first case, POSS-SH was mixed in AESO ranging from -C=C- (acrylate):-SH=1:0 to 1:0.5. In the second case, -O-C=C (vinyl): -SH ratio was selected ranging from 1:0 to 1:0.6. All samples were formulated with 1 wt % photo initiator (TPO) and 30 wt % diluents pentaerythritol triacrylate relative to the total reactants content. The different mole ratios of the samples and the wt% of POSS-SH in thiol-acrylate and thiol-ene-acrylate system were shown in Table 1.

Table1 The formulations of all samples

Sample	thiol :acrylate(mol)	thiol: vinyl (mol)	POSS-SH content (wt %)
A0	0: 1		0
A1	0.1:1		3.46
A2	0.2:1		6.72
A3	0.3:1		9.70
A4	0.4:1		12.17
A5	0.5:1		15.18
V0		0:1	0
V1		0.1:1	1.47
V2		0.2:1	2.91

V3	0.4:1	5.64
V4	0.6:1	8.23

3 Results and discussion

3.1 Photopolymerization mechanism of the Hybrid coating

The homo-polymerization and thiol-ene/homo-polymerization hybrid curing mechanisms were measured by FTIR and the results were shown as in Fig.1 to Fig.4, respectively. The peaks at 810 cm^{-1} and 2573 cm^{-1} could be attributed to $\text{C}=\text{C}$ -rocking and $\text{S}-\text{H}$ stretching vibrations, respectively. The double bond thiol conversion were calculated and shown as in Fig.5. As we can see, the peak at 810 cm^{-1} decreased quickly after 10s UV radiation for all four samples and the double bond conversions of 10s radiation for AESO, A3, VASO and V4 were 57.8%, 78.7%, 60.5% and 84.1%, respectively. While, the thiol conversions of A3 and V4 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 was two competitive reaction in thiol-acrylate system: homopolymerization and transfer to thiol. Hence, the thiol conversion is lower than that of acrylate in A3. Meanwhile, the thiol conversion in V3 is higher than that of double bond, which indicated the thiol-ene addition was preferred on homopolymerization with incorporating vinyl end groups. With the further irradiating, the peaks at 810 cm^{-1} and 2573 cm^{-1} were further slowly decreased and the final double bond conversions of AESO, A3, VASO and V4 were 60.5%, 87.8%, 64.1% and 91.5%. After 20s irradiating, the thiol peaks of V4 disappeared and the final thiol conversion of A3 was 71.3%, which further indicated the complete reaction in thiol-acrylate system.

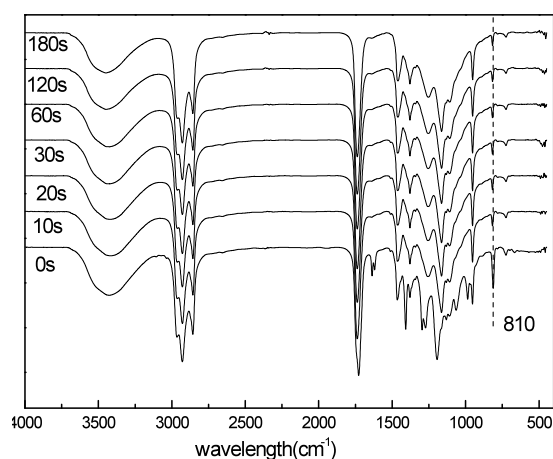


Fig. 1 The FTIR spectra of AESO exposed for various times.

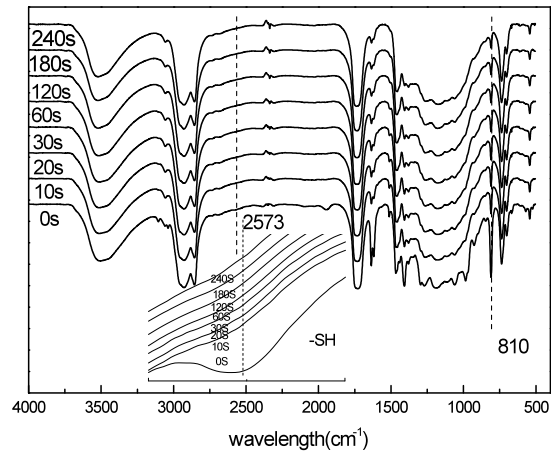


Fig. 2 The FTIR spectra of A3 exposed for various times.

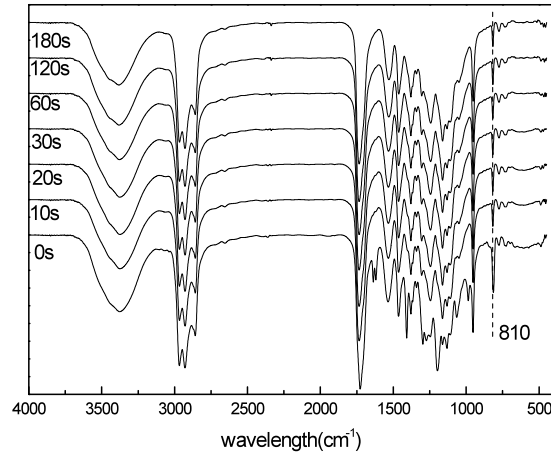


Fig. 3 The FTIR spectra of VASO exposed for various times.

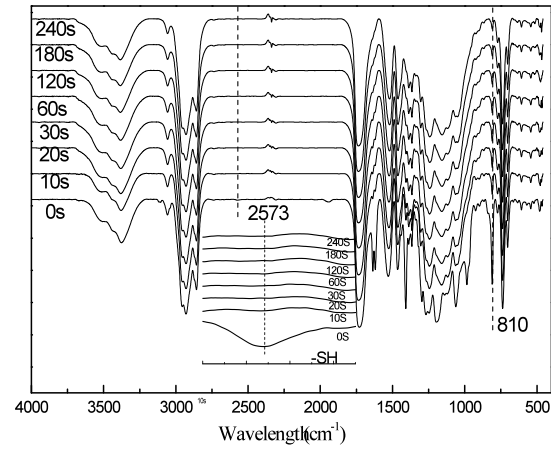


Fig. 4 The FTIR spectra of V4 system exposed for various times.

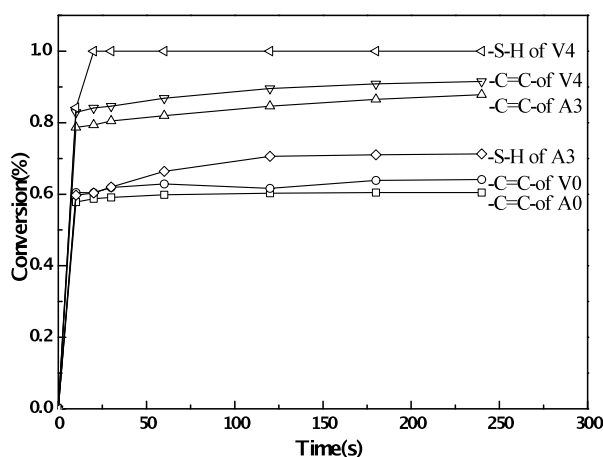


Fig. 5 Thiol and double bond group conversion

3.2 Physical and Mechanical Properties of the hybrid coating

Table 2 and Table 3 were the physical properties of thiol-acrylate and thiol-ene-acrylate systems, 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 A4 and V3. The weight contents of POSS-SH were 12.17 wt% and 5.64 wt%, respectively. The increasing pencil hardness was mainly attributed to the rigid inorganic core of POSS-SH. From the photopolymerization mechanism results, it could be seen that POSS-SH was more effective to improve the $-C=C$ conversion in thiol-ene-acrylate than in thiol-acrylate. As a result, POSS-SH was more effective to improve the thiol-ene-acrylate system's pencil hardness. Meanwhile, the flexibilities of 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.

Table 1 Physical properties of cured thiol-acrylate system.

Sample	-SH : -C=C-(mol)	Pencil Hardness	Flexibility	Adhesion
A0	0: 1	H	2mm	0
A1	0.1: 1	2H	2mm	0
A2	0.2: 1	2H	2mm	0
A3	0.3: 1	2H	2mm	0
A4	0.4: 1	3H	2mm	1
A5	0.5: 1	3H	2mm	4

Table 2 Physical properties of cured thiol-ene-acrylate system

Sample	-SH: -O-C=C-(mol)	Pencil Hardness	Flexibility	Adhesion
V0	0: 1	H	2mm	0
V1	0.1: 1	2H	2mm	0
V2	0.2: 1	2H	2mm	0
V3	0.4: 1	3H	2mm	0
V4	0.6: 1	3H	2mm	0

The strain-stress curves of thiol-acrylate and thiol-ene-acrylate system were shown as Fig. 6 and Fig. 7, respectively. And the tensile strength and fracture toughness were

listed in Table 4 and Table 5. 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 10.28 MPa for A0 to 17.04 MPa for A5, and the fracture toughness increased from 92.0kJ.m⁻³ to 786.1kJ.m⁻³. For thiol-ene-acrylate system, the tensile strength from 15.07 MPa for V0 to 24.38 MPa for V4, and the fracture toughness increased from 95.4 kJ.m⁻³ 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 resist force, and the high functionality of POSS-SH could increase film's crosslink density, which 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 decreasing the molecular weight between two crosslink points. Comparing the thiol-acrylate and thiol-ene-acrylate systems, the incorporation of vinyl end group could obviously increase tensile strength and tensile modulus due to the high crosslink density.

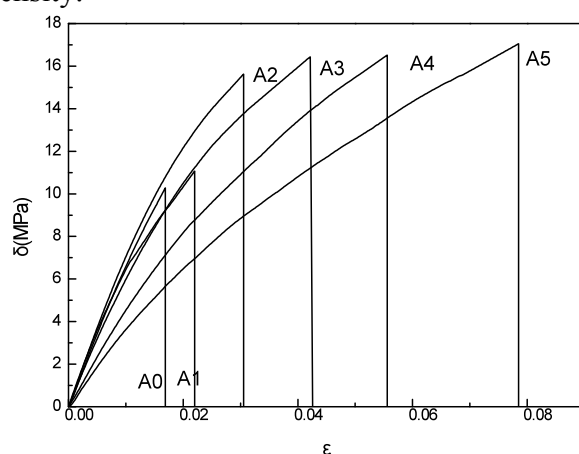


Fig. 6 Strain-stress curves of thiol-acrylate system

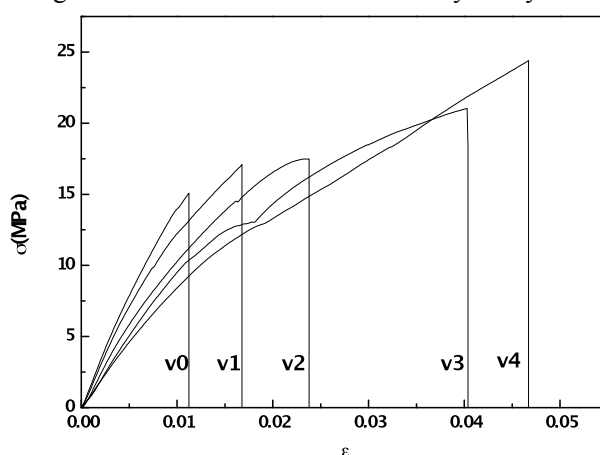


Fig. 7 Strain-stress curves of thiol-ene-acrylate system

Table 3 Mechanical Properties of thiol-acrylate system

Sample	A0	A1	A2	A3	A4	A5
Tensile strength (MPa)	10.28	11.06	15.62	16.43	16.51	17.04

Fracture toughness (kJ.m ⁻³)	92.0	140.4	281.4	422.7	539.1	786.1
Tensile modulus (MPa)	707.4	688.2	655.3	622.1	466.4	375.9

Table 4 Mechanical Properties of thiol-ene-acrylate system

Sample	V0	V1	V2	V3	V4
Tensile strength (MPa)	15.07	17.08	17.48	21.02	24.38
Fracture toughness (kJ.m ⁻³)	95.4	167.8	256.8	542.3	651.9
Tensile modulus (MPa)	1731	1584	1334	1159	961.4

3.3 Surface Properties of the hybrid coating

Surface properties of the coatings were examined by water contact angles, and the images were shown as Fig. 8. The results were listed in Table 6 and Table 7. As we could see, the water contact angle (WCA) was also increased with POSS-SH addition. This was because that the hydrophobic POSS inorganic core among the crosslink 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.

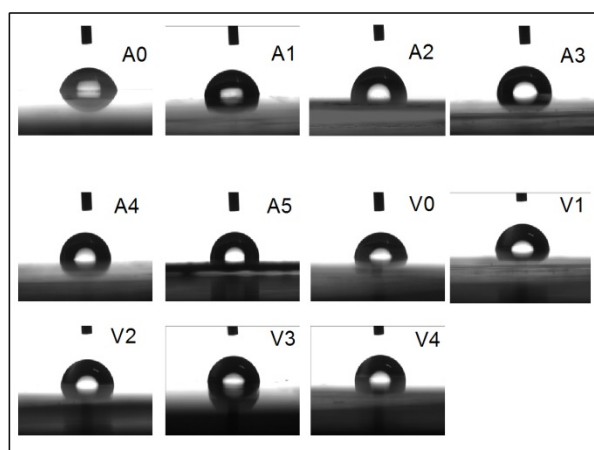


Fig. 8 Water contact angle images of all cured samples

Table 5 Surface Properties of thiol-acrylate system

Sample	A0	A1	A2	A3	A4	A5
water contact angle /°	75.21	81.11	88.76	93.95	95.44	99.17
Water absorption (%)	2.55	1.95	1.83	1.34	1.19	1.09
Water solubility (%)	2.55	2.40	2.19	1.78	1.59	0.93

Table 6 Surface Properties of thiol-ene-acrylate system

Sample	V0	V1	V2	V3	V4
water contact angle /°	85.55	89.73	90.73	92.84	95.14
Water absorption (%)	2.38	2.08	1.93	1.48	1.28
Water solubility (%)	1.97	1.87	1.78	1.48	1.28

4. Conclusions

In this work, two series of high performance of UV curable soy bean 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, especially for thiol-ene-acrylate system. As a result, the sample's pencil hardness was increased from H to 3H with 12.17wt% 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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