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Synthesis and characterization of UV-curable polydimethylsiloxane epoxy acrylate

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Abstract

UV-curable polydimethylsiloxane epoxy acrylate (PSEA) was synthesized by hydrosilylation of allyl glycidyl ether with hydrogen-containing polydimethylsiloxane to give polydimethylsiloxane-type epoxy resin which modified with acrylic acid. The curing speed and the double bond conversion in the UV cured film were influenced by the purity of PSEA with Fourier transform infrared spectroscopy (FT-IR) measurements. The influences of the synthetic process, such as, the reaction temperature, the concentration of reactants and the catalyst which determined the purity and activity of resins were discussed in detail. The structures of this resin were characterized by ^{1}H-NMR and FT-IR spectra. The molecular weight was checked by gel permeation chromatography, and M_n is 45,000. The properties of the cured film were also investigated by thermogravimetric analyzer, dynamical thermal mechanical analysis, and etc. For example, tensile strength (6.9 Mpa), elongation (20%), hardness (A; 18), water absorption (24 h; 2%), weight loss (40 min, 300 °C; 5%) and etc.

Keywords: Polydimethylsiloxane epoxy acrylate; Synthesis; Characterization; UV-curing; Properties

1. Introduction

Polydimethylsiloxanes (PDMSs), which are usually known as “silicone”or “silicone elastomers”, have received widespread attention as a special family of polymers since their commercial introduction in the 1940s and are by far the most important inorganic backbone polymers [1–3]. Their own unique properties, such as, low glass transition temperature (T_g), low surface tension and surface energy, low solubility, low dielectric constant, transparent to visible and UV light, very resistant to ozone, and stable against atomic oxygen even oxygen plasmas. In recent years, PDMSs with different organofunctional substituents are synthesized and used as starting compounds in the preparation of polymeric materials with those properties. Photocrosslinking of functional PDMSs is one of the most efficient methods in rapidly producing siloxane based polymeric networks.

Polydimethylsiloxane epoxy acrylate (PSEA) containing acrylic ester groups, linked to the siloxane chain as pendant units, gives the PSEA reactivity, absorptivity, coupling properties, etc. This compound combines the properties of silicones with the fast crosslinking ability of acrylates. Siloxane-based networks have been used for metal coating and for the protection of glass or optical fibers [4–7] owing to their transparent nature. However, in previous reports, the synthesis of polydimethylsiloxane type epoxy resin (PSE) is complicated and purification is difficult [8,9]. Moreover, further studies of the curing and properties of PSEA are lacking. Thus, the present paper describes a synthesis method of PSEA with high yield, which can be used as a fast curing optical fiber coating. The synthesized polymer is characterized by FT-IR, ^{1}H-NMR, and GPC. The mechanical and thermal properties of the cured film are also investigated.

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2. Experimental

2.1. Materials

Hydrogen-containing polydimethylsiloxane (H-PDMS, hydrogen amount 1.26% per mole chain unit) was supplied by Wuhan University, China. Allyl glycidyl ether (AGE) was obtained from Acros, USA. Benzil dimethyl ketal (BDK) was supplied by Ciba Geigy, Switzerland. Acrylic acid (AA) was purchased from Dongfang Chemical Factory, Beijing. All solvents are reagent grade or are purified by standard methods.

2.2. Synthesis of polydimethylsiloxane type epoxy resin

H-PDMS, AGE (1.05 equivalents of Si–H), 0.8 wt.% of Pt-catalyst and toluene were placed in a 250 ml flask along with a low stream of nitrogen, then the mixture was heated to 130 °C and stirred until the absorption peak of the Si–H peak (2140 cm^{-1}) in the FTIR spectra disappeared. The solvent and the unreacted AGE were removed by distilling at 120 °C in vacuum. The obtained product was a colorless viscous liquid, PSE ($\eta_{25\ ^\circ\mathrm{C}} = 1.6$ Pa s, epoxy value (EV) = 0.5). The molecular structure was confirmed by ^{1}H NMR and FT-IR spectrum. The determination of the epoxy value was carried out using a potentiometric titration as described in the literature [10]. EVs are calculated using the equation:

$$\mathrm{EV(mol/100\ g)} = C(v - v_0)/10W$$

where C is the concentration of $HClO_4$–HAc standard solution (mol/l), v_0 and v are, respectively, the blank and sample consumption of $HClO_4$–HAc standard solution (ml), and W is the weight of sample used (g). The content of active hydrogen is determined by the modified Zerewitinoff method [11].

^{1}H-NMR ($CDCl_3$, ppm,): 0.07 ppm (Si–CH_3); 0.52 ppm (Si–CH_2–); 1.69 ppm (–CH_2–CH_2–CH_2–); 2.52 ppm, 2.95 ppm (epoxyethane); 3.58 ppm (–CH_2–epoxyethane); 3.60 ppm (–OCH_2–CH_2–).

FT-IR (cm^{-1}): 2963, 1409, 1261 (Si–CH_3); 1020–1090 (Si–O–Si); 1289, 2975 (–epoxyethane).

2.3. Synthesis of polydimethylsiloxane epoxy acrylate

PSE, acrylic acid (AA) (mole ratio = 1 : 1.08) were dissolved in toluene and reacted at 110 °C under stirration. After 4 h, the conversion reached 94% by determining the epoxy value or the acid value. The product was cooled to 60 °C, then toluene and unreacted AA were discarded by reduced pressure distillation. The remainder is straw color viscous liquid, PSEA ($\eta_{25\ ^\circ\mathrm{C}} = 3.0$ Pa s).

^{1}H-NMR ($CDCl_3$, ppm,): 0.08 ppm (Si–CH_3); 0.53 ppm (Si–CH_2–); 1.67 ppm (–CH_2–CH_2–CH_2–); 3.53 ppm (–CH_2CH_2–O–); 3.64 ppm (–CH_2–OH); 3.76 ppm (–OCH_2– $\overset{|}{\mathrm{C}}$H–O); 5.10 ppm (CH_2–$\overset{|}{\mathrm{C}}H$–O–); 5.78 ppm (H_2C=C); 6.09 ppm, 6.13 ppm (CH_2=CH–).

FT-IR (cm^{-1}): 3420 (HO–); 2963, 1409, 1261 (Si–CH^3); 1719 (carbonyl), 1020–1090 (Si–O–Si); 1625, 1610, 930 (C=C).

2.4. UV curing of PSEA

PSEA resin with 5 wt.% of BDK (0.2 mm film on glass) was irradiated by a high-pressure mercury lamp (1 kW, HPM 15 from Philips, Belgium) built into an UV-CURE device constructed in our laboratory (Fig. 1), with a distance of 15 cm from lamp to specimen and at room temperature in N_2 atmosphere.

2.5. Measurements

The viscosity of the products was measured with a QNX Model spinning viscometer (Tianjin Instrument Co., Tianjin, China) with the speed of 750 rpm.

The tack-free time was evaluated as the exposure time required to reach a completely tack-free state by touching the surface with a cotton ball under a weight of 200 g for 30 s after UV exposure.

The degree of unsaturation in the UV-cured film was determined with a MAGNA-IR 750 SPECTROMETER

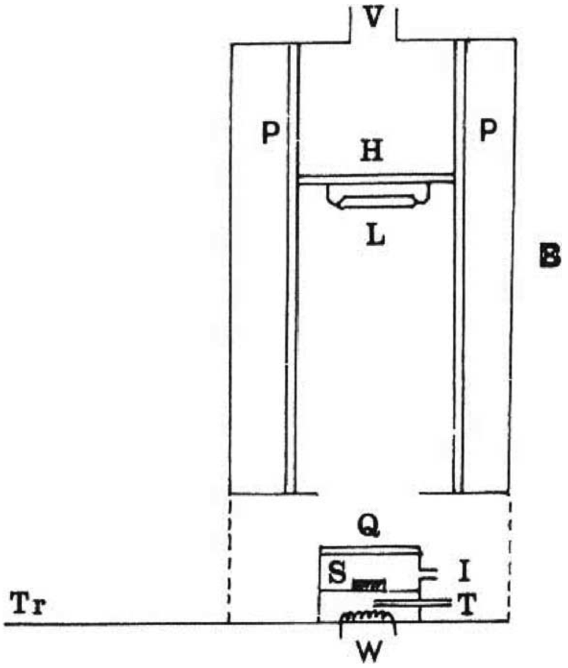


Fig. 1. Schematic diagram of the irradiation device UV-CURE: V, ventilation; P, stands; H, holder; L, lamp; Q, quartz plate; S, sample; I, N_2 entrance; Tr, track; B, shield box; W, heating wire; T, temperature detector.

(Nicolet Instrument Co., USA) using the acrylate double bond at 1610–1625 cm^{-1} by a baseline method. The spectra are normalized with the carbonyl peak at 1719 cm^{-1} as an internal standard to account for variation in sample thickness and instrument recording. The double bond content of the uncured formulation is defined as 100%.

^1H NMR spectra were recorded on a 200 MHz instrument (Bruker AC200) using $CDCl_3$ as solvent and tetramethylsilane as internal standard. GPC data were recorded on a Waters Associated 440 instrument with polystyrene standard for calibration and tetrahydrofuran as the solvent.

Thermal stability was determined with a thermogravimetric analyzer (TGA) (Perkin–Elmer TGA7) over a temperature range of 30–500 °C at a heating rate of 10 °C min^{-1}. Dynamical thermal mechanical analysis (DMA) was carried out on DMTA-IV(USA).

The tensile properties were measured with an Universal Testing Machine (DCS5000, SHIMADZU) at 25 ± 2 °C temperature. The crosshead speed was 50 mm/min. The dumb-bell shaped specimens were prepared according to ASTM D412-87.

3. Results and discussion

3.1. Synthesis of PSE

Two methods for preparing PSE are generally used, they are, copolymerization of cyclosiloxanes by base-catalyzed equilibration and hydrosilylation of allyl glycidyl ether with hydrogen-containing PDMS [10]. However, the conversion percentage of the former one is relatively low. Furthermore, the epoxy rings are easily opened in acidic or basic solution. On the contrary, the high conversion of the later one at similar conditions with fewer by-products can be obtained. Therefore, the later method is selected for preparing PSE in this study (Scheme 1).

3.2. The influence in preparing PSEA

In order to obtain UV curable PSEA, the PSE is modified by AA, which provides acrylated PES with unsaturated double bonds. The reaction rate is affected by the catalyst, reaction temperature and the concentration of reactants.

3.2.1. Effects of catalyst

Fig. 2 shows relationship between the catalyst concentration and the yield of PESA when PSE reacts with AA at 110 °C. It can be seen that the increasing of

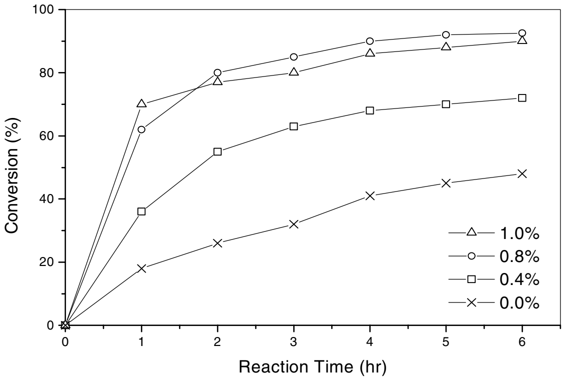
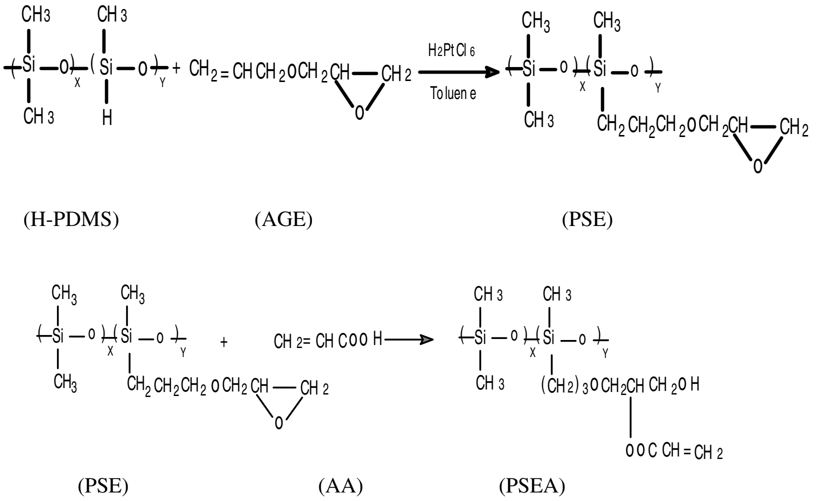


Fig. 2. The concentration of catalyst vs epoxy conversion in hydrosilylation reaction of PSE with AA measured at 110 °C.



Scheme 1.

catalyst has obvious positive influence on the conversion of PSEA. The yield of PSEA is about 65% after reacting for 6 h without catalyst. The yield increases obviously with catalyst increasing, especially at initial stage. The optimistical catalyst concentration is 0.8 wt.% of reactant, because the further increasing of catalyst cannot effectively enhance the yield of PSEA.

3.2.2. Effects of temperature

Fig. 3 shows the effect of reaction temperature on the hydrosilylation of AGE with H-PDMS. It clearly reflects that PDMS with unsaturated epoxy gives yield almost 100% at 130 °C after 2.5 h. It can be proved that Si–H characteristic peak (2140 cm^{-1}) in FT-IR spectra disappears. However, the conversion cannot reach over 80% when the temperature is below 130 °C, even if enhances the time of reaction. For example, the system still can detect active hydrogen after 10 h at 110 °C. On the other hand, excessive high temperature results in the formation of crosslinked structure and even gel. The same results are obtained by chemically titration.

Fig. 4 shows the different yields of PSEA at different reaction temperatures. The reaction rate and the yield are greatly affected by temperature. The yield at 110 °C increases more than 10% than that of at 100 °C. It is proved that improving temperature has positive influence on reaction rate. However, exorbitant temperature will result in gelation because of the reaction between double bonds, such as the reaction at 130 °C.

3.2.3. Effects of the concentration of reactants

With the reaction going on, PSE and AA's concentration will not equal to each other in the end point. It can be found that acid value conversion curve and epoxy value conversion curve do not coincide with each other. Furthermore, the difference increases with the reaction time. At last, rudimental epoxy value is higher than the acid value. This phenomenon can be explained that the acrylic groups react with the –OH groups produced in the reaction of epoxy and acrylic groups. At the beginning of those two competitive reactions, epoxy open loop reaction is chief. With reaction proceeding, hydroxyl group increases sharply and esterification is obvious. Therefore, acid value decreases more quickly than epoxy value. In order to complete epoxy open loop reaction, acrylic acid must be excessive. The optimistical ratio is 1:1.08 (PSE:AA).

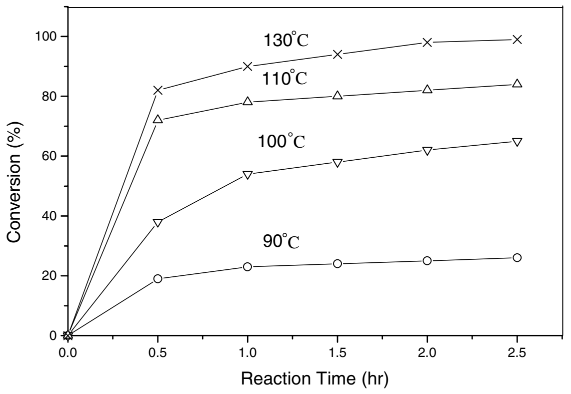


Fig. 3. The effect of reaction temperature on hydrosilylation reaction of AGE with H-PDMS.

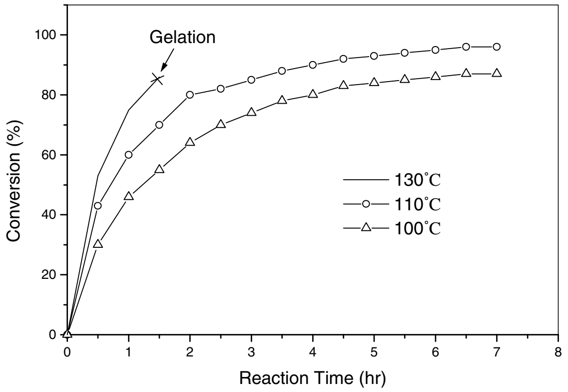


Fig. 4. The effect of reaction temperatures on epoxy conversion in hydrosilylation reaction of PSE with AA.

3.3. Properties of PSEA

3.3.1. The molecular weight distribution of PSEA

The molecular weight distribution of PESA is inspected by GPC as shown in Fig. 5. It can be found that the molecular weight distribution of PSEA is narrow and the coefficient of dispersion (M_w/M_n) is 1.3, the number-average molecular of PSEA is around 45,000 when the PSE preparation reaction occurs at 130 °C. However, the shoulder peak appears when the temper-

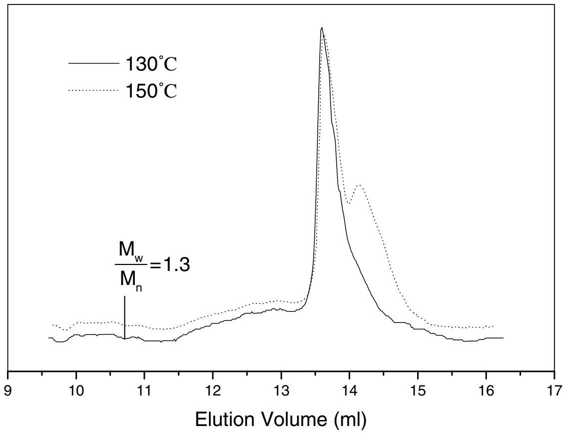


Fig. 5. GPC of PSEA. (THF, 1.0 ml min^{-1}, 308 K).

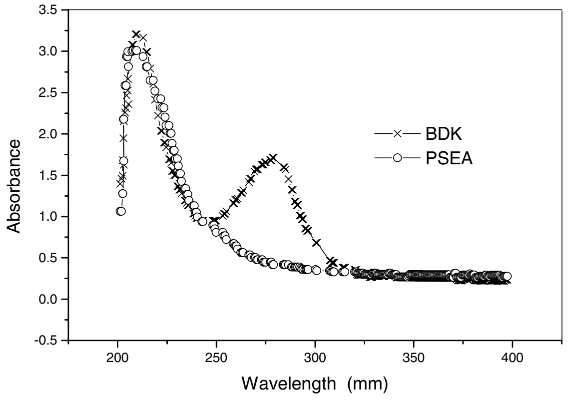


Fig. 6. UV spectra of PSEA and BDK. (BDK: 0.001% w/v in methanol, 1-cm cell).

ature of PSE preparation reaction is higher than 130 °C, which is due to homopolymerization of AGE in hydrosilylation process. This is very harmful to the hydrosilylation and the curing speed of the end product although the amount is very small.

3.3.2. *UV-spectrum of PSEA*

In UV-spectrum (Fig. 6), PSEA has one absorption peak at 208 nm, which attributes to the unsaturated carbon double bond. This kind of structure will not shield the process that BDK absorbs UV-light to form free radical. Therefor, PSEA has high photopolymerization rate in the presence of BDK as a photoinitiator in PSEA curing system. When blending BDK into PSEA, it disappears completely soon, which is due to its good compatibility with PSEA, and sensitive to UV-light as well.

3.3.3. *Photocuring process was inspected by the FT-IR spectrum*

Fig. 7 is FT-IR spectra of PSEA, curve *a* is cured film and curve *b* is non-cured liquid film. We see clearly from curve *b* that $SiCH_3$ (800 cm^{-1}, 1260 cm^{-1}), SiO (1080 cm^{-1}) are characteristic peaks of silicone. At 2140 cm^{-1}, SiH has no peak, which shows the hydrogen of silicon is completely added by AGE. The peak of 910 cm^{-1} is not existence, which is the absorption of epoxy groups formed by AGE and SiH. In the curve *a* and *b*, the common characteristic peaks of SiH_3 (800 cm^{-1}, 1260 cm^{-1}), SiO (1100 cm^{-1}) and COO (1272 cm^{-1}) are obvious. However, the differences are samely obvious. In curve *b*, 1625, 1610 and 930 cm^{-1} are peaks of unsaturated double bond, which show the content of acryloyl oxygen groups ($CH_2{=}CHCOO$–) are large amounts. After curing, we can find from the curve *a* that those peaks disappear completely. It due to curing is almost absoluteness. The double bond is nonexistent. If we calculated the conversion of carbon double bond by absorption, the percent is 87%. This result is accorded to the value which is gained by chemical method. This proved the preparation and structure of PSEA is right.

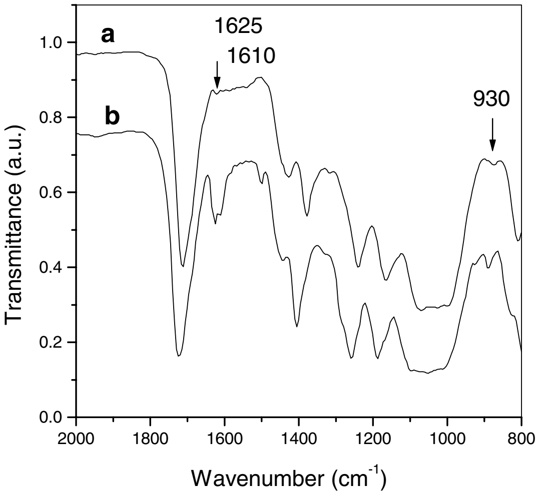


Fig. 7. FT-IR spectra of PSEA, before curing (b) and cured (a).

3.3.4. *Thermal behaviors analyzed by TGA and DMA*

PSEA's thermolysis is shown in Fig. 8. The curve indicates that PSEA has the similar thermal stability to that of silicone rubber, decomposition temperature of PSEA is about 300 °C. This is the result of the somewhat unusual molecular structure of the polymer chains. The (Si–O) bond is one of the most thermally stable bonds formed by silicon and has a bond dissociation energy of 462 kJ/mol compared with 359 kJ/mol for (C–O), 347 kJ/mol for (C–C) and 319 kJ/mol for (Si–C) bond. The thermal stability of siloxanes is thus partly a consequence of the high bond strength. When other organic radicals, such as hydrogen replace methyl groups on silicon atoms, the properties described above are usually

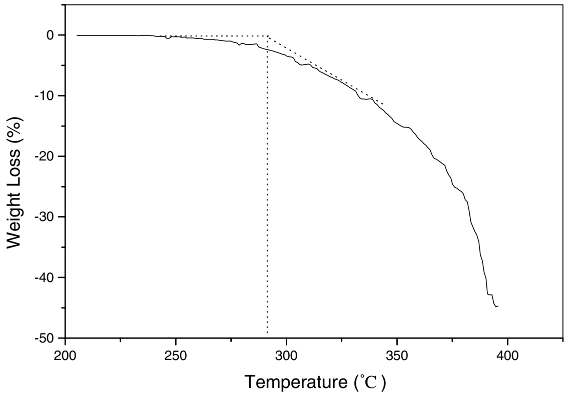


Fig. 8. TGA of PSEA film.

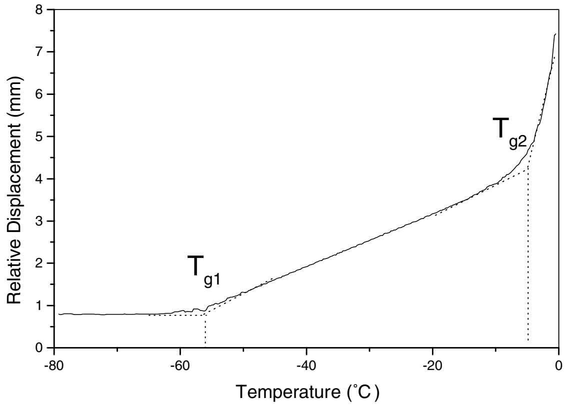


Fig. 9. Relative displacement vs temperature of PSEA cured thin film.

affected to a certain degree. The extent of the change in the properties is a function of the level, type and nature of the substituent. Fig. 9 is the thermal mechanical curve of the PSEA cured film, it is clearly that there are two distinct glass transition temperatures: $T_{g1} = -57$ °C, $T_{g2} = -5$ °C, which declare PSEA has two-phase segregate microstructures. The lower one probably is the characteristics of the siloxane component, and the higher one may be attributed to the crosslinking site which results mainly from acrylates.

3.3.5. *The property of PSEA film*

The properties of PSEA and the UV cured film have been measured as those listed in Table 1 and Table 2. In Table 1, the viscosity of PSEA is 2–3 Pa s at 25 °C. Its appropriate viscosity makes this product suitable for all automatic and manual application without diluent and heater, comparing with the commercial polyether urethane acrylate or polybutadiene urethane acrylate optical fiber coating. Because the optical fiber base is poorly wettable to obtain an adequate thickness when the viscosity of coating is too low. On the other hand, if the viscosity is too high, disadvantages are caused by the moving of air bubbles from the coating layer and the difficulties in obtaining an adequate thickness of the coating layer.

Table 1
Properties of PSEA

Liquid coating (25 °C)	Typical properties
Density (kg/m^3 × 10^3)	1.1131
Viscosity (Pa s)	2–3
Refractive index (25 °C)	1.4698
Molecular (M_n)	45,000
Cured coating (25 °C)	
Density (kg/m^3 × 10^3)	1.2129
Tensile strength (MPa)	6.9
Elongation (%)	20
Tensile modulus (MPa)	3.4
Refractive index (25 °C)	1.4918
Weight loss (40 min, 300 °C)	5%
T_{g1} (°C)	−57
T_{g2} (°C)	−5
Hardness (A)	18
Water absorption (%, 24 h)	2
Electric broken (kV/mm)	50.5
Dielectric constant	6.76
Dielectric loss (50 Hz)	0.006048

Table 2
Resistance to solvents of PSEA film

Solvent	Weight change (%)	Appearance
Toluene	9.0	Good
Xylene	6.9	Good
Acetone	3.6	Good
Ethanol	11	Good
DMF	7.9	Good
THF	6.8	Good
20% H_2SO_4	−0.02	Good
20% HCl	−0.7	Good
20% HNO_3	−7.0	Good
20% Na_2CO_3	−10	Good
20% NaOH	/	Broken
20% KOH	/	Broken

After curing, PSEA film owns flexibility and toughness which was proved by the data of hardness, tensile strength, elongation and tensile modulus. The excellent of ageing and weather resistance are also properties of PSEA film. The thermal weight loss of PSEA is smaller than that of other materials, such as polyether urethane acrylate coatings with thermal weight loss 7–10% after 40 min at 200 °C. It is attributed to the stability of Si–O bond of PDMS. The low T_g of PSEA (−57 °C) decides it can be used in atrocious weather where common optical fiber coating is useless, especially in the winter of north countries. Naked optical fiber is sensitive to water, trace water can cause the defection on fiber or destroy the transmission of light. So, the resistance of water is critical in application, such as marine cables. Comparing with the water absorption (4–6%, 24 h) of polyether urethane acrylate coating, PSEA cured film has low water absorption (2%, 24 h). The electrical data in Table 1 show PSEA film has excellent electrical performance.

In Table 2, PSEA cured film is immerged in different solvents to test the solvent resistance. The results show alkaline liquor completely decomposes the film and the coating cannot protect optical fiber. In other solvents listed in Table 2, PSEA film is perfect but the weight changes are different. In organic solvents, PSEA film absorbs solvent and the weights increase the in order of acetone, THF, xylene, DMF, toluene and ethanol.

However, in inorganic solvents (20% aqueous solution), the weights decrease in order of sulfuric acid, hydrochloric and sodium carbonate.

As discussed above, PSEA not only maintains the properties of PDMS, but also honors fast photocured speed, high tensile modulus, low elongation, low T_g, heat and solvents resistance, and excellent electrical performance. Furthermore, it compatible with others material very well, which does not owned by general PDMS. So, PSEA can be used as a basic rein for optical fiber coating.

4. Conclusion

In this study, photosensitive PSEA are successfully synthesized for multielement composite optical fiber coating. The conclusions are summarized as follows:

1. Hydrosilylation reaction of AGE with H-PDMS at 130 °C gives a nearly 100% yield. The optimistical conditions of acrylic acid modified PSE to prepare PSEA are that the ratio of PSE and AA is 1:1.08, the concentration of H_2PtCL_6 catalyst is 0.8 wt.% of reactants, and the reaction temperature is 110 °C.
2. The Mn of PSEA is 45,000, and the coefficient of dispersion (M_w/M_n) is 1.3.
3. The cured film has two T_g ($T_{g1} = -57$ °C, $T_{g2} = -5$ °C); the decomposition temperature is 280 °C; the conversion percentage of double bond is 87% in cured PSEA film, and the cured film has good solvent resistance.

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