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The synthesis and characterization of a heat-resistant Si-containing aryl ether arylacetylene resin

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Abstract

A Si-containing arylether arylacetylene resin, poly(dimethylsilyene-ethynylene-phenyleneetherene-ethynylene) (PSEE), was synthesized from diethynyldiphenyl ether and dichlorosilane through Grignard reactions. The structures and properties of PSEE resin were characterized by NMR, FT-IR, DSC, TGA analysis techniques. PSEE resin can be crosslinked to form a thermoset at a temperature less than 200^0C. There is no glass transition in the temperature range of RT~500^0C and T_{d5} is 568^0C in N_2 for PSEE thermoset. The thermoset shows good dielectric properties and its glass fiber reinforced composite exhibits high mechanical properties. Copyright © 2017 VBRI Press.

Keywords: Si-containing arylacetylene resin, high performance thermosetting resin, heat resistance, advanced composite.

Introduction

High performance resins are widely used in advanced resin matrix composites, in which a series of thermosetting resins with specialty properties have been developed like epoxy resins, phenolic resins, bismaleimide resins, polyimide resins, cyanate ester resins, and so on[1]. Recently developed silicon-containing arylacetylene resins are a kind of inorganic-organic hybrid thermosetting resins which possess excellent thermal stability[2-3]. In 1994, Itoh's research group[4-5] reported one of silicon-containing arylacetylene resins, called MSP resin, which is a highly heat-resistant thermosetting resin. The thermal decomposition temperature of the cured MSP resin arrives at 860 ^{0}C (T_{d5}) in inert atmosphere. Keller[6-7], Corriu[8] and Joji[9] groups have separately done a lot of researches and developed a series of silicon-containing polymers. Up to now, there have been many reports on silicon-containing arylacetylene resins [10-14].

Since 2002, our research group[12-19] has focused on the synthesis and modification of new series of poly (silyene arylacetylene) (PSA) resins, e.g., poly (methylsilyene-ethynylene-phenylene-ethynylene), poly (dimethylsilene-ethynylene-phenylene-ethynylene), and poly (methylvinylsilyene-ethynylene-phenylene-ethynylene). Their rheological character, cure kinetics, and thermal properties have been investigated. PSA resins exhibit extremely high heat resistance but a bit brittleness which limits their extensive applications. A number of modification approaches have been made with good achievements, including blending with acetylene-terminated polyetherimide, propargyl-terminated benzoxazine, and acetylene-terminated benzoxazines. Our group[20-22] reported the preliminary synthesis and properties of diethynylphenyl ether, dipropargyloxy aromatic monomer, and their silicon-containing polymers. The introduction of aromatic/aliphatic ether structure to the polymer chains could increase the polarity and flexibility of the main chain. The produced polymers exhibit high thermal stability and mechanical properties.

In this work, poly(dimethylsilyene-ethynylene-phenyleneetherene-ethynylene) (PSEE) resin was synthesized from 4,4'-diethynyldiphenyl ether and dichlorosilane through Grinard reactions. The structures and properties of PSEE resin are further characterized.

Experimental

Raw materials

Bis(4-bromophenyl) ether, 2-methyl-3-butyn-2-ol, copper iodide, bis(triphenylphosphine) palladium(Ⅱ) chloride, and dichlorodimethylsilane were purchased from Aldrich Co., Ltd. Triethylamine, toluene and tetrahydrofuran (THF) were freshly distilled before use. Acetic acid, hydrochloride, anhydrous sodium sulfate, ethyl bromide, ethyl acetate, petroleum ether, magnesium powder, and potassium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd. PSA resin was made in our laboratory[13].

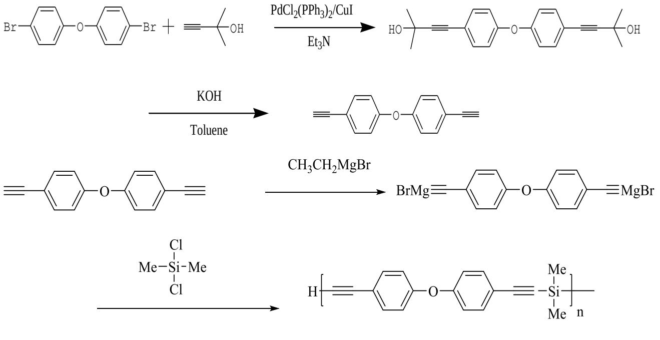
Quartz fiber (QF) cloth(0.14 mm thickness, plain weave) was purchased from Hubei Feilihua Quartz Glass Co., Ltd.

Instrumentation

Nuclear Magnetic Resonance (NMR) analyses were carried out on a BRUKER AVANCE 500 nuclear magnetic resonance spectrometer with chloroform-d as a solvent and tetramethylsilane as an internal standard. Fourier Transform Infrared (FT-IR) spectra were obtained on a Nicolet 5700 spectrometer and samples were prepared by the KBr powder method. Gel Permeation Chromatography (GPC) was conducted on AMERICAN Waters 1515 chromatography instrument and terahydrofuran (THF) as an eluent. Differential Scanning Calorimetric analyses (DSC) were performed on a AMERICAN TA Instruments Q2000 analyzer at a heating rate of 10^0C/min under N_2 flow. Thermogravimetric Analyses (TGA) were performed on a METTLER TOLEDO Instruments TGA/DSC 1 analyzer at a heating rate of 10^0C/min in nitrogen atmosphere. Dynamic Mechanical analyses (DMA) were performed on a METTLER DMA 1 thermomechanical analyzer and the dimension of sample is 35x8x3 mm^3. Rheological analysis was carried out on a Thermo Haake RS600 Rheometer system in the range of 120-200^0C. The shear rate and heating rate for the viscosity measurements were 0.01 s^{-1} and 2^0C/min respectively. Dielectric property measurements were performed on NOVOCONTROL Concept 40 Broadband Dielectric Impedance Spectrometer and the size of specimen is ϕ30.0 x 2.0 mm. The hardness of thermoset was measured with a 934-1 Barker Hardness Tester. The flexural properties were measured with a Shimadzu AG-50kNE universal tester and MTS Alliance RF/100 tester (USA). The crosshead speed for the tests is 2 mm/min. The dimension of thermoset samples is 80x15x4 mm^3. The dimension of composite sample is 45x15x2 mm^3. The testing number of samples is 5 at least. Scanning Electron Microscopy (SEM) images were obtained on a Hitachi S4800 field emission scanning electron microscope operating at 15 kV. The fracture surfaces of the samples were sputtered with gold before observation. The gelation time was determined according to the literature procedure on a heating platform[23-24].

Synthesis of poly(dimethylsilyene-ethynylene-phenyleneetherene- ethynylene) (PSEE)

The synthetic route for PSEE resin is shown in **Scheme 1**.



Scheme 1. The synthetic route for PSEE resin.

Synthesis of 4,4'-diethynyldiphenyl ether (DEDPE)

A 500 ml three-necked flask installed with a thermometer, a magnetic stirrer and a condenser was flame-dried and deoxidized before use. Bis(4-bromophenyl) ether (26.24 g, 80 mmol) and triethylamine (300 ml) were added into the flask and the mixture was stirred for 10 min. And then $PdCl_2(PPh_3)_2$ (1.68 g, 2.4 mmol), CuI (0.76g, 4.0 mmol) and 2-methyl-3-butyl-2-ol (20.19 g, 240 mmol) were added into the flask in sequence. The reaction mixture was heated to 90^0C and stirred for 12 h at 90^0C. The mixture was cooled to room temperature and followed by filtration. The filtrate was evaporated under reduced pressure and then a light yellow solid was gotten. The solid product was recrystallized with ethyl acetate to get a colorless crystalline product, 4,4'-bis(2-methyl-3-butyn-2-ol) diphenylether (BDPE), of 24.47 g with yield of 91.6% and m.p. 136~137^0C. ^{1}H NMR ($CDCl_3$, ppm) δ: 6.92~7.41 (s, 8H, aromatic), 1.62 (s, 12H, CH_3). ^{13}C NMR ($CDCl_3$, ppm) δ: 156.7, 133.2, 118.8, 117.7 (C_{ar}), 93.3 (**C**≡C–Ar), 83.6 (–C≡**C**–Ar), 66.8 (C–OH), 32.1 (–CH_3). IR (KBr, cm^{-1}): 3344 (–OH), 3070 (Ar–H), 2982 (–CH_3), 2224 (C≡C), 1596, 1500 (Ar), 1246 (Ar–O–Ar), 1162 (C–O).

A 500 ml three-necked flask installed with a thermometer, a magnetic stirrer and a condenser was flame-dried and deoxidized before use. BDPE (23.38 g, 70 mmol), toluene (300 ml), and potassium hydroxide (5 g) were added into the flask in turn and the mixture in the flask was heated to reflux for 12 h. Then the flask was cooled to room temperature and the product was obtained by filtration. The obtained solid product was recrystallized with petroleum ether to get light yellow crystalline 4,4'-diethynyldiphenyl ether (DEDPE) of 14.2 g with yield of 93.1% and m.p. 63~64^0C. ^{1}H NMR ($CDCl_3$, ppm) δ: 6.92~7.41 (s, 8H, aromatic), 3.04 (s, 2H, C≡CH). ^{13}C NMR ($CDCl_3$, ppm) δ: 157.1, 134.0, 118.9, 117.3(C_{ar}), 83.0(**C**≡C–Ar), 76.6(C≡**C**–Ar). IR(KBr, cm^{-1}): 3282 (≡CH), 3057 (Ar–H), 2152 (C≡C), 1595, 1496 (Ar), 1241 (Ar–O–Ar).

Synthesis of PSEE resin

A 250 ml three-necked flask equipped with a thermometer, a stirrer and a condenser were flame-dried and deoxidized before use. Magnesium powder (1.44 g, 60 mmol) and tetrahydrofuran (20 ml) were added into the flask and then the mixed liquor of ethyl bromide (5.45 g, 50 mmol) and tetrahydrofuran (20 ml) was added dropwise within 15 min. The reaction mixture was heated to 40^0C for 1 h and then a gray black mixture was produced. After the mixture was cooled to 25^0C by ice water, the mixed liquor of DEDPE (5.45 g, 25 mmol) and tetrahydrofuran (20 ml) was dropwise added for 15 min. The reaction mixture was heated to reflux for 1 h and then the mixture became maroon. After the mixture was again cooled to 25^0C by ice water, the mixed liquor of dichlorodimethylsilane (2.20g, 16.6 mmol) and tetrahydrofuran (20 ml) was dropwise added for 15 min. Thereafter, the mixture was heated to reflux for 2 h. After most of tetrahydrofuran was removed by distillation, toluene (50 ml) was added into the flask. Acetic acid (3 g) and 0.1 M HCl (50 ml) was sequentially added into the flask. The reaction mixture was transferred into a 500 ml separatory funnel and separated. The organic layer was washed with deionized water until the washing water approached to neutral. The organic phase was isolated and dried with anhydrous sodium sulfate. The liquor was separated and distilled under reduced pressure to get 5.47 g yellow solid PSEE with the yield of 85.5%.

Preparation of PSEE and PSA thermosets

PSEE and PSA resins were separately weighted and heated to 150^{0}C for 1 h, 170^{0}C for 1 h，210^{0}C for 2 h, and 250^{0}C for 4 h for curing. Then the cured products were cooled to ambient temperature and dark brown PSEE and PSA thermosets were respectively obtained.

Preparation of QF/PSEE and QF/PSA composites

12.20 g PSEE resin or PSA resin was dissolved in 20 ml tetrahydrofuran to make a resin solution. 18 Pieces of quartz fiber (QF) clothes with a size of 80x100 mm^2 were soaked in the resin solution uniformly and then dried to get a prepreg. The prepreg was placed in a mould and pressed at 170^{0}C for 2 h, 210^{0}C for 2 h and 250^{0}C for 4 h under the pressure of 0.5~0.7 MPa. QF/PSEE or QF/PSA composite laminate was gotten and the content of the resin in the composite is 30.4 wt% (ca).

Results and discussion

Characterization of PSEE resin

Structural characterization of PSEE resin

The ^{1}H NMR and ^{29}Si NMR spectra of PSEE resin are presented in **Fig. 1**. In **Fig. 1(a),** the resonances at 6.8~7.5 ppm are assigned to the aromatic hydrogen, that at 3.0 ppm corresponds to the ethynyl protons and that at 0.5 ppm is assigned to the protons in the methyl groups. In **Fig. 1(b),** the resonance at -39.4 ppm is contributed by the silicon atom in the PSEE chain backbone.

FT-IR spectra of PSEE resin are shown in **Fig. 2(a)**. As shown in the figure, the absorption peaks at 3285 cm^{-1} and 2152 cm^{-1} are assigned to the stretching vibrations of ≡C–H and C≡C bonds, respectively. The absorption at 3025 cm^{-1} is for the stretching vibrations of C–H on benzene ring. The band at 1592 and 1498 cm^{-1} are associated with the C=C stretching vibrations of the aromatic ring. The absorption at 2955 cm^{-1} and 1251 cm^{-1} are respectively attributed to –C–H(CH_3) and Si–C stretching vibrations. The absorption at 1218 cm^{-1} belongs to the stretching vibration of C–O–C. All results demonstrate that the PSEE resin with designed structure is successfully synthesized.

Molecular weights of PSEE resin are determined by gel permeation chromatography (GPC) and the data are presented in **Table 1**. As shown in the table, the average number molecular weight $\overline{M_n}$ of PSEE resin is 1972.

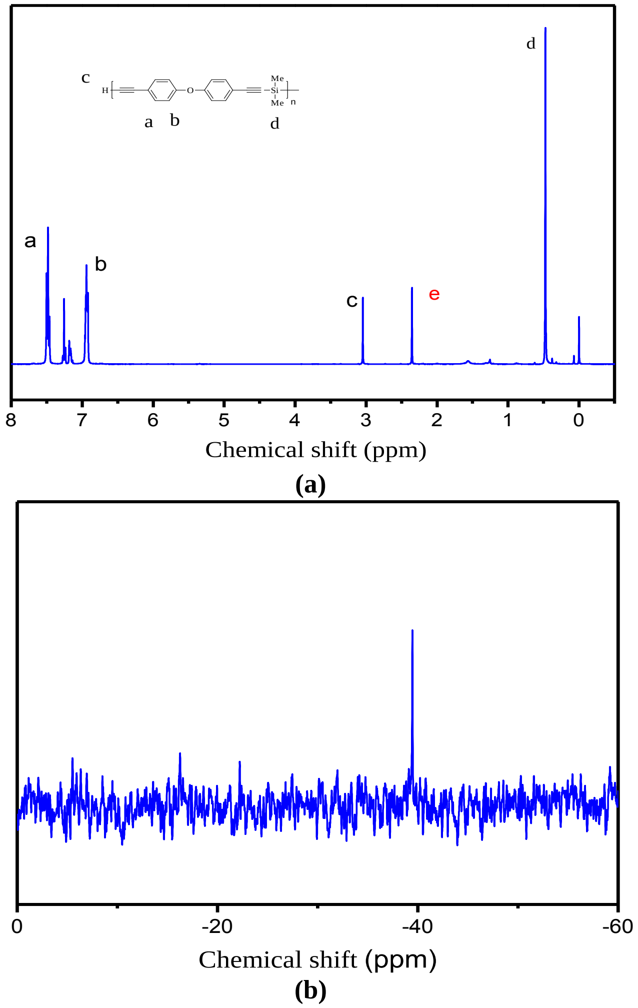


Fig. 1. ^{1}H-NMR(a) and ^{29}Si-NMR(b) spectra of PSEE resin.

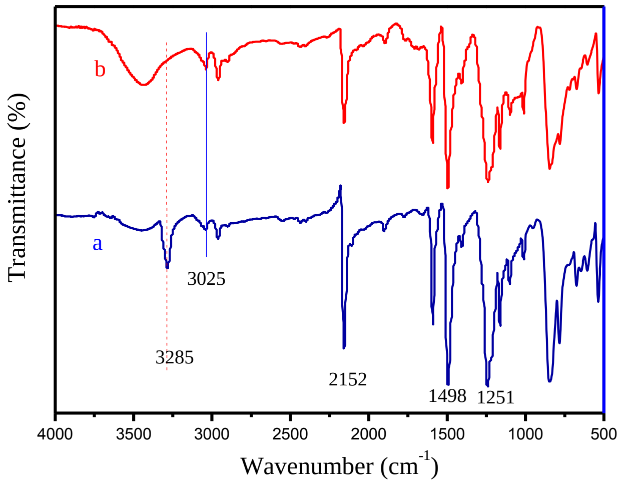


Fig. 2. FT-IR spectra of PSEE resin and its thermoset a: PSEE resin, b: PSEE thermoset.

Table 1. Molecular weight and its distribution of PSEE resin.

Resin	$\overline{M_n}$	$\overline{M_w}$	Polydispersity index
PSEE	1972	2848	1.44

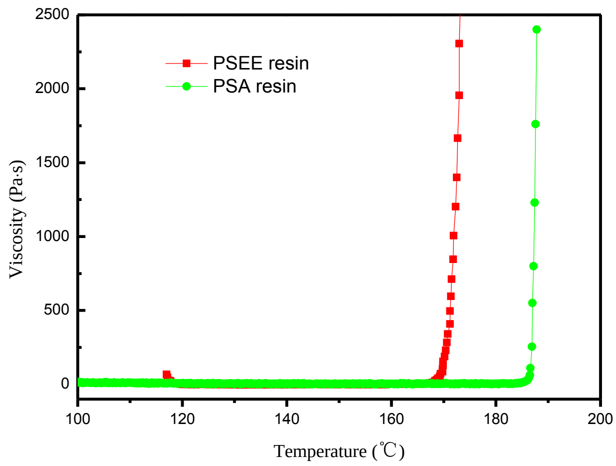


Fig. 3. The viscosity of PSEE and PSA resins as a function of temperature.

Processability of PSEE resin

The viscosity of PSEE resin was measured in the temperature range from 100^{0}C to 200^{0}C and the change of the viscosity with the temperature is shown in **Fig. 3**. As shown in the figure, PSEE resin keeps a stable and low viscosity in the temperature range of 118~168^{0}C. PSEE resin has a processing window of 50^{0}C (ca) which is a little narrow compared with that of PSA resin. When the temperature arrives at above 168^{0}C, the viscosity increases rapidly due to the start of thermal crosslinking reactions of PSEE resin.

The curing behavior of PSEE resin is determined by DSC analysis and the result is shown in **Fig. 4** and listed in **Table 2**. As shown in **Fig. 4,** there is a small endothermic peak at 120^{0}C (ca) in which the melting of PSEE resin results. There is an exothermic peak in the range from 170^{0}C to 300^{0}C and the exothermic enthalpy is 378.1 J/g due to the curing reactions of PSEE resin. The gelation time of PSEE resin at 170^{0}C is about 27 min. PSEE resin could be cured at the temperature lower than 200^{0}C although the curing temperature of PSEE resin is a little higher than that of PSA resin. PSEE resin exhibits good processability.

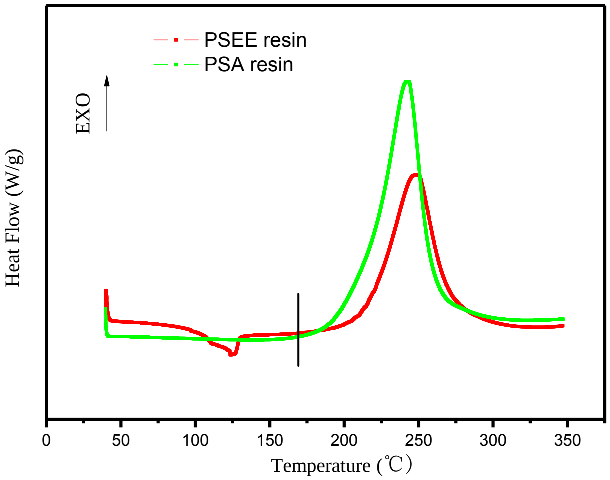


Fig. 4. DSC curves of PSEE and PSA resins.

Table 2. DSC analyses results of PSEE and PSA resins.

Resin	Exothermic peak temperature (℃)			ΔH(J/g)
	T_i	T_p	T_f	
PSEE	200	249	300	378.1
PSA	190	230	280	482.5

Characterization of PSEE thermoset

Structural characterization of PSEE thermoset

The FT-IR spectrum of PSEE thermoset is shown in Figure 2(b). As shown in the figure, the absorption at 3285 cm^{-1} for ≡C–H group greatly decreased and that at 2152 cm^{-1} for the stretching vibration of -C≡C- group is also decreased. The other bands at 3025, 2955, 1592, 1498, 1251, 1218 cm^{-1} don't change obviously. Thereby, the terminal ethynyl and internal ethynylene of PSEE resin reacts with each other and a cross-linked stucture is formed. The presence of the peak at 2152 cm^{-1} for PSEE thermoset indicates the internal ethynylene group does not compleltely react in the curing conditions.

Mechanical properties of PSEE thermoset

Mechanical properties of PSEE thermoset are shown in **Table 3.** As shown in **Table 3**, the flexural strength of PSEE thermoset reaches 40 MPa and the flexural modulus 3.4 GPa. PSEE thermoset exhibits better mechanical properties as compared with PSA thermoset. The Barcol hardness of PSEE thermoset arrives at 43 HBa, which is lower than that of PSA thermoset. This illustrates the PSEE thermoset has a better toughness. SEM observation also confirms this point. **Fig. 5** shows SEM photographs of fracture surface of PSEE and PSA thermosets. As shown in **Fig. 5,** there are some streaks on the fracture surface of PSEE thermoset which is the toughness character, but there are no streaks on the fracture surface of PSA thermoset.

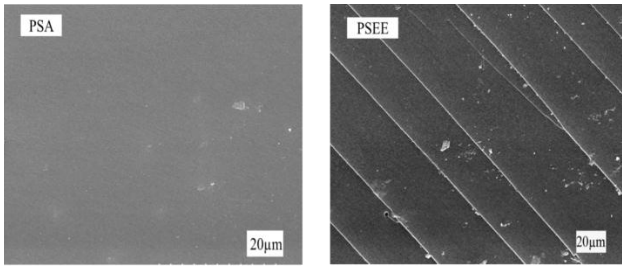


Fig. 5. SEM photos of PSEE and PSA thermosets.

Table 3. Mechanical properties of PSEE and PSA thermosets.

Thermoset	Flexural strength (MPa)	Flexural modulus (GPa)	Barcol Hardness (HBa)
PSEE	40±3	3.4±0.2	43±2
PSA	23±1	3.0±0.3	58±2

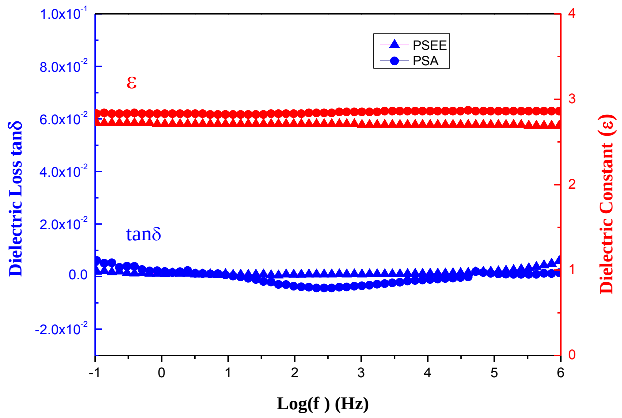


Fig. 6. Dielectric properties as a function of frequency for PSEE and PSA thermosets

Dielectric property of PSEE thermoset

The relationship between dielectric property and frequency for PSEE and PSA thermosets is shown in **Fig. 6**. As shown in **Fig. 6,** the dielectric constant and dielectric loss have no much change with the increase in frequency for PSEE and PSA thermosets. The dielectric constant is about 2.71 and the dielectric loss tanδ is less than 1.0×10^{-2} for PSEE thermoset in the frequency range of 1~10^{6} Hz. This indicates the PSEE thermoset possesses good dielectric properties like PSA thermoset.

Thermal properties of PSEE thermoset

DMA technique is used to determine the glass transition temperature (T_g) of PSEE thermoset and the result is shown in **Fig. 7.** As shown in **Fig. 7,** the storage modulus E' first has a little decrease and then a little rise with the rise of temperature. There is no big decrease for the curve of E'. The rise of storage modulus is possibly due to the further crosslinking reactions of the internal alkynylene at above 350^{0}C. There is no peak on the curve of loss tanδ. This means that there is no glass transition in the temperature range from RT to 500^{0}C. In other words, PSEE thermoset has no T_g in the temperature range of RT ~ 500^{0}C.

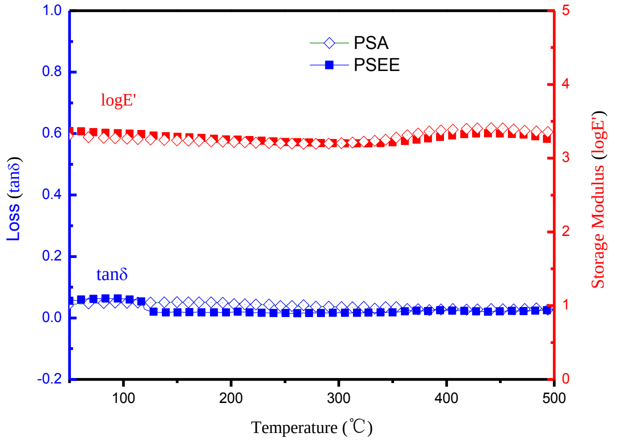


Fig. 7. DMA curves of PSEE and PSA thermosets.

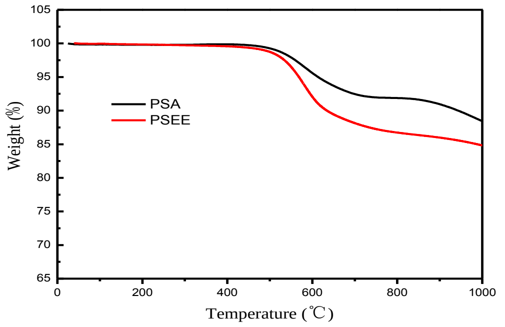


Fig. 8. TGA curves of PSEE and PSA thermosets.

The thermal stability of PSEE and PSA thermosets is investigated by TGA analysis and the results are shown in **Fig. 8** and the data are listed in **Table 4**. As shown in **Fig. 8,** there is almost a smooth line in the temperature range from RT to 470^{0}C for both PSEE and PSA thermosets. T_{d5} (5% weight loss temperature) and the residue yield Y_r at 800^{0}C are 568^{0}C and 86.7% for PSEE thermoset, respectively. This indicates PSEE thermoset has good thermal stability in nitrogen atmosphere although T_{d5} and Y_r values are a little lower than those for PSA thermoset. A rapid decomposition would take place at above 470℃. The decomposition probably results from to the C–O and/or C–Si bond cleavages[25].

Composite property of PSEE thermoset to quartz fibers

Mechanical properties of quartz fiber reinforced PSEE and PSA matrix (QF/PSEE and QF/PSA) composites are characterized by three-point bending test. The flexural properties of QF/PSEE composites were measured at room temperature (RT) and 250^{0}C respectively. The results are shown in **Table 5**. As shown in **Table 5**, QF/PSEE composites have high mechanical properties. The flexural strength and modulus arrive respectively at 300 MPa and 21.3 GPa, and the shear strength reaches 26.5 MPa at room temperature. All of these properties decrease but still keep in a higher level at 250^{0}C. The mechanical properties of QF/PSEE are much higher as compared with those of QF/PSA composite due to the introduction of phenyl ether unit into the resin chain.

Table 4. TGA data of PSEE and PSA thermosets in nitrogen.

Thermoset	T_{d5}(^{0}C)	Y_r(800^{0}C) (%)
PSEE	568	86.7
PSA	608	92.1

Table 5. Mechanical properties of quartz fiber reinforced composites.

Sample	Measured Temperature (℃)	Flexural strength (MPa)	Flexural modulus (GPa)	Shear strength (MPa)
QF/PSEE	RT	300±10	21.3±0.5	26.5±2.4
	250	210±10	20.5±2.1	15.6±2.9
QF/PSA	RT	197±9	18.7±1.5	14.4±0.6
	250	141±8	18.5±3.1	8.7±1.1

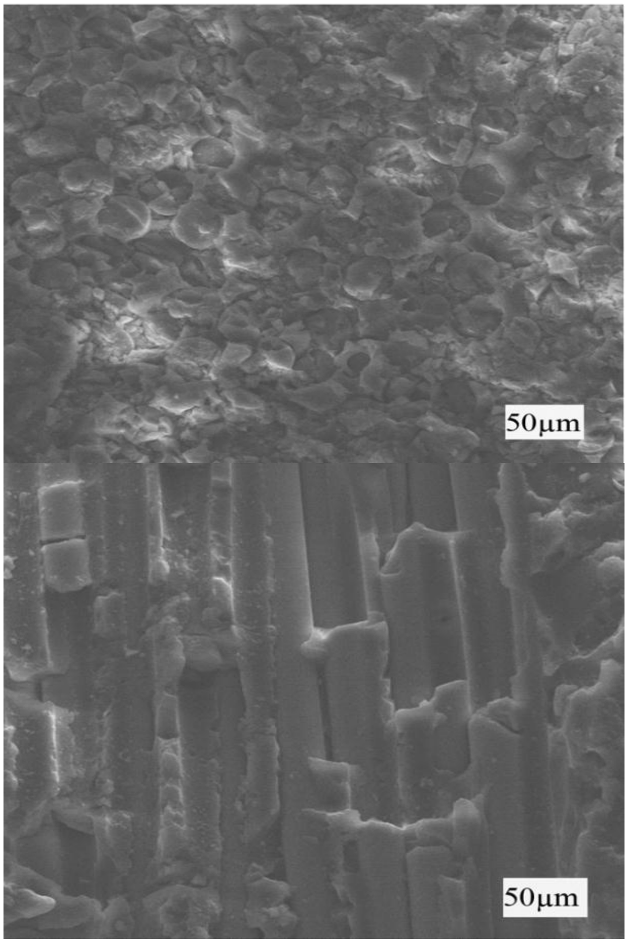


Fig. 9. SEM photos of the fracture surface of QF/PSEE composite.

SEM is used to observe the fracture surface of composites and the photos are shown in **Fig. 9**. As shown in the figure, the PSEE resin is well and uniformly filled between the quartz fibers. This supports the high mechanical properties of QF/PSEE composite.

Conclusions

Poly(dimethylsilyene ethynylene phenyleneetherene ethynylene) (PSEE) resin was prepared from diethynyldiphenyl ether and dimethyldichlorosilane. The obtained PSEE resin was characterized by NMR, FT-IR, GPC, DSC, TGA, etc. The PSEE resin is solid at room temperature and melts at 120^0C(ca). The melted PSEE resin has a low viscosity with a processing window of 50^0C and can be cured at the temperature lower than 200^0C. As for PSEE thermoset, there is no glass transition in the temperature range of RT ~ 500^0C. T_{d5} and the residue yield Y_r at 800℃ reaches 568^0C and 86.7%, respectively. The flexural strength and modulus arrive at 40 MPa and 3.4 GPa, respectively. QF/PSEE composite also exhibits high mechanical properties. As compared with PSA resin, PSEE resin exhibits superior mechanical properties. The PSEE resin is expected to be used as a high-performance resin matrix for advanced composites.

Acknowledgements

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