

Synthesis and characterization of silicon-containing arylacetylene ether of bisphenol A resins and their composites

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Abstract. Two novel resins, silicon-containing arylacetylene ether of bisphenol A (PSAP-A) and 1,3-diethynylbenzene-terminated silicon-containing arylacetylene ether of bisphenol A (DPSAP-A), were synthesized from dipropargyl ether of bisphenol A (BADPE) and dimethyldichlorosilane through Grignard reaction. The structures of the resins were characterized by proton nuclear magnetic resonance (¹H-NMR), and thermal properties were explored by thermogravimetric analysis (TGA) and dynamic thermo-mechanical analysis (DMA). In addition, T300 carbon fiber (T300CF) reinforced PSAP-A composite (T300CF/PSAP-A) and T300 carbon fiber reinforced DPSAP-A composite (T300CF/DPSAP-A) were prepared by a solution-impregnation process using tetrahydrofuran as solvent. The results showed that the cured PSAP-A resin and DPSAP-A resin displayed good heat resistance and processing properties. Degradation temperatures of the cured PSAP-A resin and DPSAP-A resin at 5% weight loss (*T*_{5%}) were 421.5°C and 486.3°C, respectively. The flexural strengths of T300CF/PSAP-A and T300CF/DPSAP-A composites reached 458.2 MPa and 287.6 MPa, respectively.

1. Introduction

As the materials with high mechanical properties and excellent high-temperature resistance, high-performance resin matrix composites have been widely studied and applied [1,2]. Silicon-containing acetylene resins (PSA) composed of $[-(R_1)Si(R_2)-C\equiv C-Ar-C\equiv C-]$ units is a class of novel organic-inorganic hybrid thermosetting resins [3,4]. After cured, the PSA resin forms highly cross-linking network structures and exhibits high temperature performance and excellent dielectric properties, which has already shown highly potential application as matrix of advanced polymer composites.

Since 1994, Ito et al. has conducted a series of studies on PSA resins. Representatively, poly(phenylsilyleneethynylene-1,3-phenyleneethynylene) (MSP resin) [5] composed of $[-Si(Ph)HC\equiv C-C_6H_4-C\equiv C-]_n$ was synthesized from arylsilanes and 1,3-diynylbenzenes under the catalysis of magnesium oxide. Although the MSP resin possessed high heat resistance, mechanical properties were poor. Our laboratory has been devoted to the new structures of PSA since 2002. Chen et al. [6] synthesized poly(dimethylsilylene-ethynylene-phenoxyphenoxyphenylene-ethynylene) (PSPE) from 1,4-bis(p-ethynylphenoxy) benzene and dimethyldichlorosilane. The results showed the flexural strength of the cured PSPE resin were 55.0 MPa, which increased by 450%, as compared with the MSP resin. Therefore, studying a new structure of PSA which contains a flexible or polar group can extend its application.

In this paper, silicon-containing arylacetylene ether of bisphenol A (PSAP-A) and 1,3-Diethynylbenzene-terminated silicon-containing arylacetylene ether of bisphenol A (DPSAP-A)



were obtained. The structures of the resins were characterized by $^1\text{H-NMR}$, and thermal properties was explored by TGA and DMA. T300 carbon fiber reinforced PSAP-A composite (T300CF/PSAP-A) and T300 carbon fiber reinforced DPSAP-A composite (T300CF/PSAP-A) were also prepared.

2. Experimental

2.1. Materials

Dipropargyl ether of bisphenol A ether (BADPE) was synthesized according to reference [7], and the purity of it determined by high performance liquid chromatography (HPLC) was 98.7%. Tetrahydrofuran (AR), toluene (AR), magnesium powder (AR), acetic acid (AR), hydrochloric acid (AR), dichlorodimethylsilane (AR), 1,3-diacetylenylbenzene (AR), anhydrous sodium sulphate (AR) were purchased from Shanghai Titan Scientific Co., Ltd. Tetrahydrofuran (THF) was refluxed over sodium filament with benzophenone and freshly distilled under nitrogen before use. Ethyl Bromide (AR) was bought from Shanghai Lingfeng Chemical Reagent Co., Ltd. T300 carbon fiber (T300CF) was obtained from Jiangsu Tianniao High-tech Co., Ltd.

2.2. Synthesis routes

The synthesis route of PSAP-A is shown in Figure 1. The entire synthesis process was carried out in dry nitrogen, magnesium powder (6.6 g, 0.275 mol) and THF (50 mL) were added to a 500-mL four-neck round bottom flask equipped with a condenser, a thermometer, a constant pressure dropping funnel, and a mechanical stirring bar. To the flask, ethyl bromide (28.6 g, 0.263 mol) in THF (50 mL) was added drop wise slowly, and then refluxed for 1 h. Then the reaction system was cooled with ice-water bath, BADPE (38.0 g, 0.125 mol) in THF (50 mL) was added. The mixture was stirred for 2 h at 70°C , a solution of dimethyldichlorosilane (10.76 g, 0.080 mol) and THF (50 mL) was added to the flask at 25°C . The reaction was further refluxed for 2 h. After that the mixed solvent of toluene (100 mL), glacial acetic acid (20 mL) and diluted hydrochloric acid solution (100 mL) were added, then the organic phase was separated off, washed with distilled water, dried with anhydrous sodium sulphate, and distilled off the solvent to obtain a yellow solid with 97.8% yield.

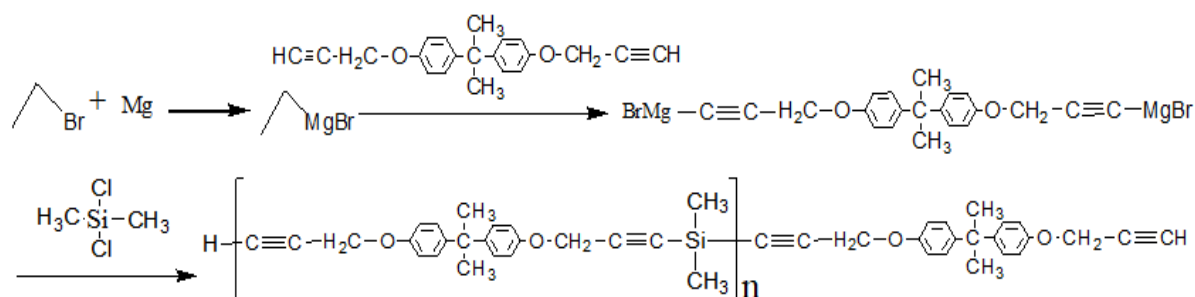


Figure 1. Synthesis route of PSAP-A resin.

The first-step synthesis route of DPSAP-A is shown in Figure 2. The entire synthesis process was carried out in dry nitrogen, magnesium powder (6.6 g, 0.275 mol) and THF (50 mL) were added to a 500-mL four-neck round bottom flask equipped with a condenser, a thermometer, a constant pressure dropping funnel, and a mechanical stirring bar. To the flask, ethyl bromide (28.6 g, 0.263 mol) in THF (50 mL) was added drop wise slowly, and then refluxed for 1 h. Then the reaction system was cooled with ice-water bath, and BADPE (38.0 g, 0.125 mol) in THF (50 mL) was added. The mixture was stirred for 2 h at 70°C , a solution of dimethyldichlorosilane (32.2 g, 0.250 mol) and THF (80 mL) was added to the flask at 25°C . The reaction was further refluxed for 2 h, and filtered at room temperature to obtain the solution of intermediates.

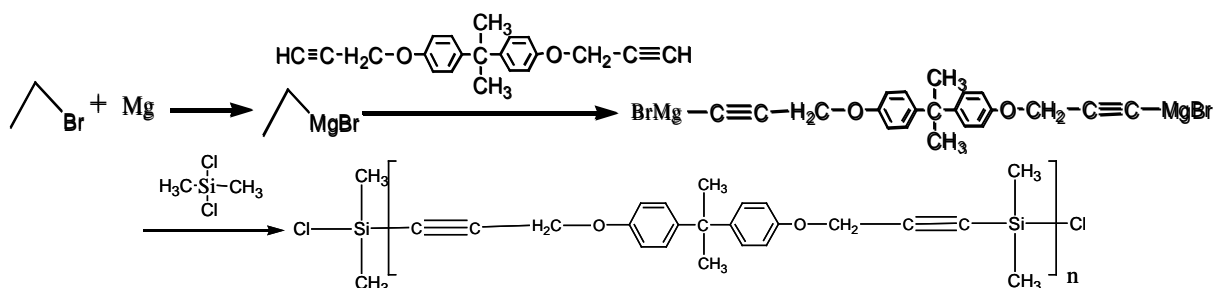


Figure 2. The first step of synthetic route of DPSAP-A resin.

The second-step synthesis route of DPSAP-A is shown in Figure 3. The entire synthesis process was carried out in dry nitrogen, magnesium powder (13.2 g, 0.55 mol) and THF (80 mL) were added to a 1000-mL four-neck round bottom flask equipped with a condenser, a thermometer, a constant pressure dropping funnel, and a mechanical stirring bar. To the flask, ethyl bromide (57.2 g, 0.526 mol) in THF (100 mL) was added drop wise slowly, and then refluxed for 1 h. Then the reaction system was cooled with ice-water bath, and 1, 3-dienynylbenzene (32.2g, 0.250 mol) in THF (80 mL) was added. The mixture was stirred for 2 hat 70°C, the solution of intermediates obtained in the first-step was added to the flask at 25°C. The reaction was further refluxed for 2 h. After thatthe mixed solvent of toluene (200 mL), glacial acetic acid (40mL) and diluted hydrochloric acid solution (200 mL) were added, then the organic phase was separated off, washed with distilled water, dried with anhydrous sodium sulphate, and distilled off the solvent to obtain a tan viscous liquid with 98.6% yield.

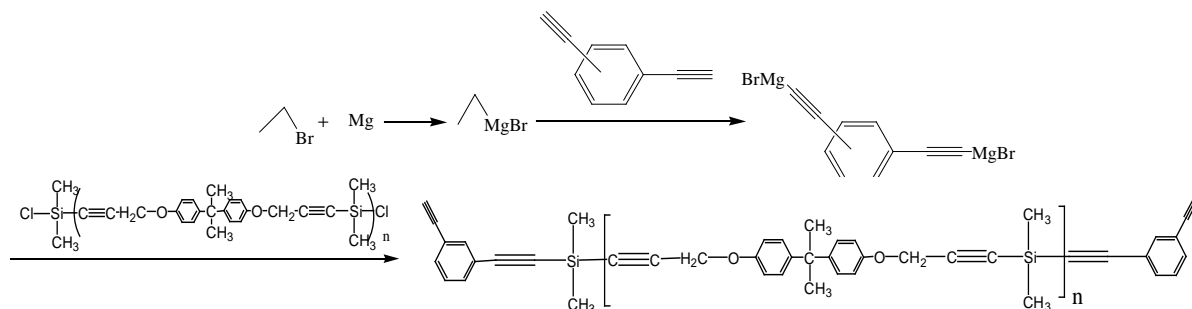


Figure 3. The second step of synthetic route of DPSAP-A resin.

2.3. T300CF/PSAP-A Composite and T300CF/PSAP-A Composite Preparation

Preparation of T300CF/PSAP-A resins and the thermosets: A predetermined amount of PSAP-A resin was dissolved in THF, which then coated on the fiber and kept for 8 h. THF was removed by a rotary evaporator at 65°C to get T300CF/PSAP-A resins. The composite was degassed, poured into a preheated mold, and cured in the procedure: 210°C for 2 h, 250°C for 2 h, 300°C for 2h and 330°C for 4 h to get the thermosets.

Preparation of T300CF/DPSAP-A resins and the thermosets: A predetermined amount of DPSAP-A resin was dissolved in THF, which then was coated on the fiber and kept for 8 h. THF was removed by a rotary evaporator at 65°C to get T300CF/DPSAP-A resins. The composite was degassed, poured into a preheated mold, and cured in the procedure: 170°C for 2 h, 200°C for 2 h, 230°C for 2h, 250°C for 2 h and 300°C for 30 minutes to get the thermosets.

2.4. Characterization

The structures of resins were obtained on the AVANCE 400 spectrometer operating at 400 MHz. Curing behaviors of resins were performed on TA Instruments Q2000 analyses at a heating rate of 10°C/min under nitrogen flow. Properties of cured resins were obtained on TGA/DAC1LF analyzer at a heating rate of 10°C/min under nitrogen flow and DMA1 mechanical analyzer at a heating rate of 3°C/min. Mechanical measurements were carried out with a Universal Testing Machine DDL100

according to China Standard GB/T 2570-1995 at a crosshead rate of 2mm/min.

3. Results and Discussion

3.1. Structural Characterization of PSAP-A Resin and DPSAP-A Resin

The $^1\text{H-NMR}$ (CDCl_3 , ppm) spectras of PSAP-A and DPSAP-A are shown in Figure 4 and Figure 5, respectively. The two resins contain some identical groups with similar resonance peaks. The resonance peak at 4.64 ppm is methylene hydrogen ($-\text{CH}_2-$), the resonance peaks at 6.92-7.48 ppm are the aromatic protons (Ar-H), the resonance peak at 1.63 ppm is methyl hydrogen ($\text{C}-\text{CH}_3$), and the resonance peak at 0.33 ppm is caused by silicon methyl hydrogen ($\text{Si}-\text{CH}_3$). The resonance peak at 2.52 ppm of PSAP-A and the resonance peak at 2.92 ppm of DPSAP-A are assigned to terminal alkyne hydrogen ($\equiv\text{C-H}$).

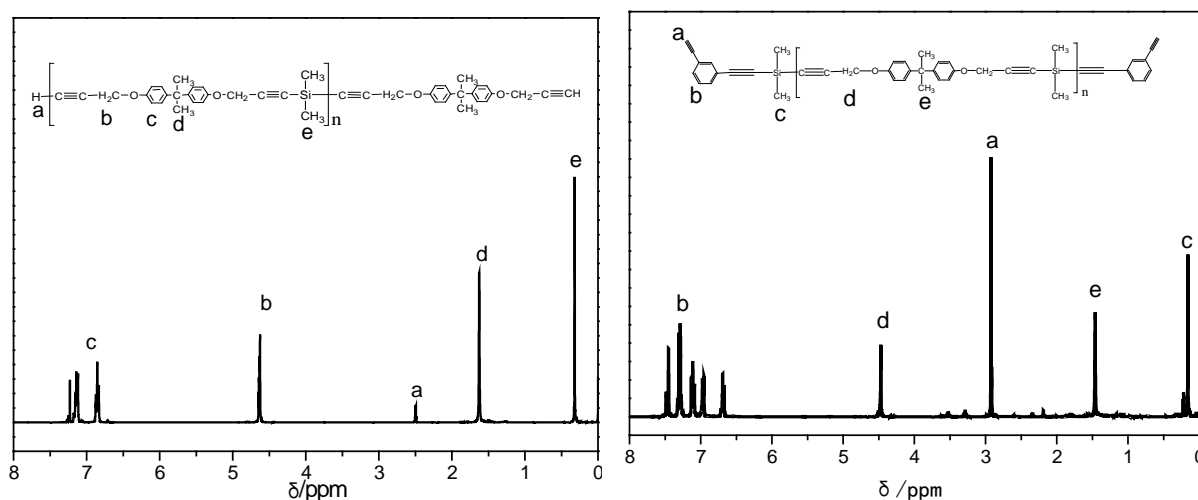


Figure 4. $^1\text{H-NMR}$ spectrum of PSAP-A resin. **Figure 5.** $^1\text{H-NMR}$ spectrum of DPSAP-A resin.

3.2. Curing Behaviors of PSAP-A Resin and DPSAP-A Resin

The curing behaviors of PSAP-A resin and DPSAP-A resin are shown in Figure 6, analysis results are shown in Table 1. There are two exothermic peaks in the curves of PSAP-A resin and DPSAP-A resin, corresponding to the curing cross-linking of the end alkyne and the internal alkyne. The initial temperatures of PSAP-A resin and DPSAP-A resin are 244.2°C and 203.5°C, respectively, the first peak temperatures were 291.1°C and 234.1°C, respectively, which is due to the difference of the terminal alkynes. In contrast with the molecular weight of 1, 3-diacetylenylbenzene, BADPE is greater. Accordingly, the terminal alkyne content of the DPSAP-A resin is more, which illustrates DPSAP-A has higher activity.

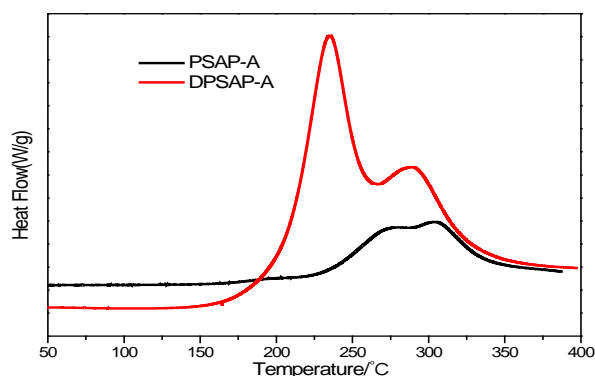


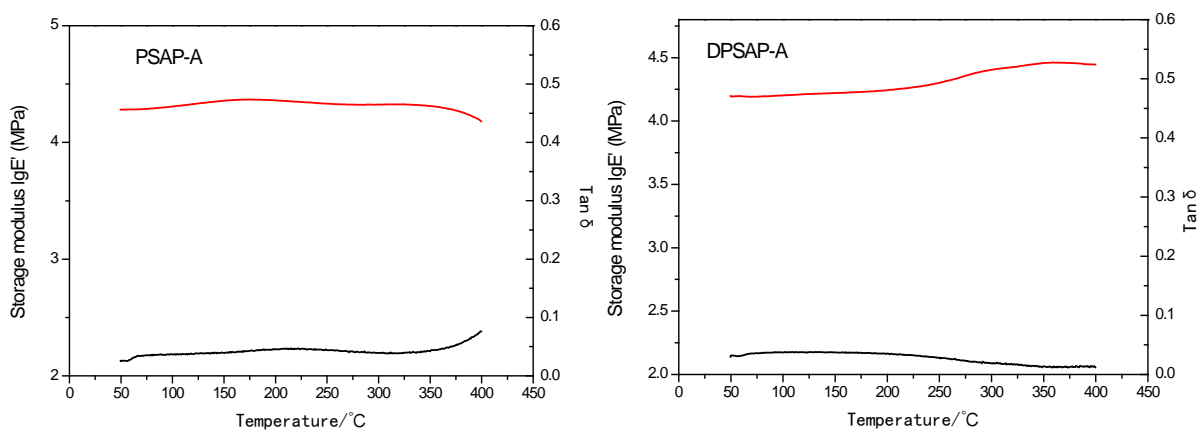
Figure 6. DSC curves of PSAP-A resin and DPSAP-A resin.

Table 1. DSC analysis results of PSAP-A resin and DPSAP-A resin.

Sample	$T_i(^{\circ}\text{C})$	$T_{p1}(^{\circ}\text{C})$	$T_{p2}(^{\circ}\text{C})$	$\Delta H(\text{J/g})$
PSAP-A	244.2	291.1	316.4	793.9
DPSAP-A	203.5	234.1	310.6	1038.0

3.3. Properties of Cured PSAP-A Resin And Cured DPSAP-A Resin

Glass transition temperature (T_g) of the cured PSAP-A resin and DPSAP-A resin were detected by DMA. Generally, the damping on a DMA curve is identified as the glass transition because a large decrease in modulus occurred at this point. As shown in the Figure 7, it can be seen that the storage modulus and loss tangents of the cured PSAP-A resin and DPSAP-A resin are not changed significantly in the temperature range of 50~400 $^{\circ}\text{C}$. what's more, there appears no glass transition temperature, so PSAP-A resin and DPSAP-A resin exhibit excellent high temperature resistance.

**Figure 7.** DMA curve of cured PSAP-A resin and DPSAP-A resin.

The TGA curves of cured PSAP-A resin and DPSAP-A resin are shown in Figure 8, and the analysis results are shown in Table 2. It can be seen that they possess high initial degradation temperature, and the degradation temperature of the cured PSAP-A at 5% weight loss (T_{d5}) is 421.5 $^{\circ}\text{C}$, and the decomposition residue (Y_c) of the cured PSAP-A resin at 800 $^{\circ}\text{C}$ is 58.7%, while the T_{d5} of the cured DPSAP-A resin is 486.3 $^{\circ}\text{C}$, $Y_{c800^{\circ}\text{C}}$ is 75.11%. This is due to the benzene ring structure formed by the cyclic tripolymerization[8] during the curing process of DPSAP-A resin, whereas the network structure [9] formed by alkyne coupling reactions during the curing process of PSAP-A resin. Obviously the thermal stability of the benzene ring structure is better than the network structure.

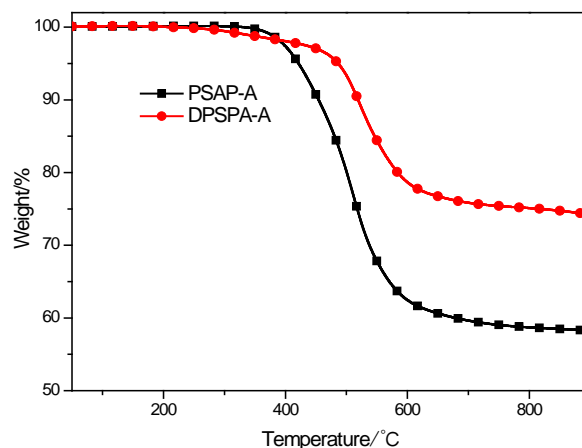
**Figure 8.** TGA curve of cured PSAP-A resin and DPSAP-A resin.

Table 2. TGA analysis results of cured PSAP-A resin and DPSAP-A resin.

Sample	$T_{d5}/^{\circ}\text{C}$	$Y_{c800^{\circ}\text{C}}/\%$
PSAP-A	421.5	58.7
DPSAP-A	486.3	75.1

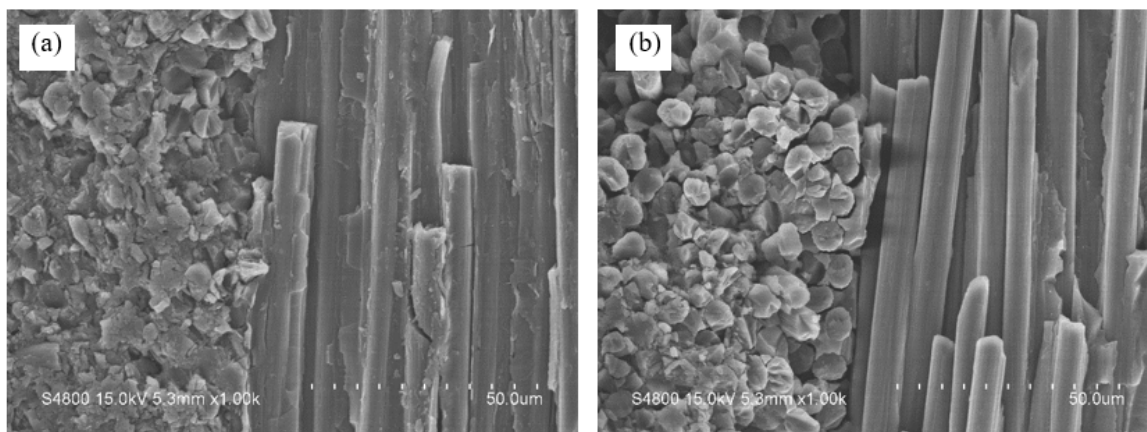
3.4. Mechanical Properties

The mechanical properties of the thermoset are listed in Table 3. As can be seen the flexural strength and interlaminar shear strength (ILSS) of T300CF/PSAP-A are much superior to T300CF/DPSAP-A. Because the benzene ring structure formed by the cyclic tripolymerization of DPSAP-A resin is much more rigid than the network structure of PSAP-A resin. In addition, due to the terminal alkyne content of the PSAP-A resin is less, the cross linking density of PSAP-A is lower.

Table 3. TGA analysis results of cured PSAP-A resin and DPSAP-A resin

Sample	Flexural strength/MPa	Flexural modulus/GPa	ILSS/MPa
T300CF/PSAP-A	458.2±10.6	48.1±2.3	32.1±1.0
T300CF/DPSAP-A	287.6±8.5	29.3±1.2	20.2±1.1

The SEM images of fracture surface of T300CF/PSAP-A composite and T300CF/DPSAP-A composite are shown in the Figure 9. The two composites exhibit different micromorphology patterns. In Figure 9 (b), the T300CF/DPSAP-A composite has a weak interface adhesion, and the smooth fiber surface is exposed after material fracture. However, the T300CF/PSAP-A composite covered with matrix after interlaminar fracture and the surface became rough, which corresponds to better mechanical properties of the T300CF/PSAP-A composite.

**Figure 9.** The micrographs of the profile and fracture surface of T300CF/PSAP-A (a) and T300CF/DPSAP-A (b)

4. Conclusions

Two new silicon-containing arylacetylene ether of bisphenol A were synthesized from bisphenol A dipropargyl ether and dimethyldichlorosilane through Grignard reaction. The cured PSAP-A resin and DPSAP-A resin show good heat resistance. The resin with 1,3-diethynylbenzene-terminated can be cured at lower temperature and has higher initial decomposition temperature. T_{d5} of cured PSAP-A resin and DPSAP-A resin are 421.5°C and 486.3°C, respectively. There is no glass transition temperature from room temperature to 400°C. T300CF/PSAP-A composite has better mechanical properties than the T300CF/DPSAP-A composite, The flexural strength are 458.2 MPa and 287.6 MPa, respectively, and the Interlaminar Shear Strength are 32.1 MPa and 20.2 MPa, respectively. With the

excellent Properties, the resins are expected to be used in aerospace materials.

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