

REINFORCING AND TOUGHENING QF/PSA WITH SILANE COUPLING AGENT CONTAINING POLY(IMIDE SILOXANE)

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ABSTRACT

A novel silane coupling agent containing terminal-alkyne and aromatic amid acid groups(**WS**) for the first time. Then the silane coupling agent containing imide-ring was obtained through ring-closing reaction, which was undergoing by chemical method. The influence of factors including processing temperature and post processing method on the preparation of the coupling agent were studied. Some process factors including the treatment time, the concentration, the pH of the solution with our silane coupling agent(**WS**) and the fiber surface condition were investigated. The composite was heated in a vacuum oven at 65 °C for 2 h; a thermal treatment followed at 170 °C, 210 °C for 2 h and 250 °C for 4 h. It was showed that with the pretreatment method, 1.5 wt% **WS** added to react with the QF for 60 min, the Interlaminar Shear Strength(ILSS) of the composites improved about 43.6 %. However, the flexural strength was increased by 60.6 % with 3.5 wt% **WS** added to react with the QF. So far we have preliminary researched the mechanical properties of composite materials, depth discussion in toughening is still under exploration. The composites fracture morphologies were observed by SEM, which were treated by coupling agent(**WS**) or not.

1 Introduction

Due to excellent heat resistant property, silicon-containing Arylacetylene resin(PSA) has wide application in the field of aeronautics and astronautics^[1]. However, the PSA has similar limitations in their practical use because of its stiff structure^[2]. To improve mechanical properties of composites, many scientists paid attention to modify this kind of composites^[3]. Mechanical parameters are important in application of composites. The mechanical properties of the whole polymer composites highly depend on the mechanical properties of the interface between QFs and matrix resins^[4].

Several modified techniques for surface treatments of QFs have been used to enhanced the interfacial adherence between QFs and matrix resin such as chemical grafting^[5], inorganic fillers treatment^[6-7] and so on. In the case of QF reinforced silicon-containing Arylacetylene resin(PSA), the literature signals the interphase as the feeblest^[8]. In those circumstances the interface strength is limited to the friction between the matrix and the fiber and the mechanical anchorage of the matrix on the fiber surface^[9]. Consequently, there is a huge amount of literature on the enhancement of such interphase, covering fiber surface treatment and coupling agents among others^[10]. The chemical treatments remove part of the sizing agent and extractives of the fiber surface increasing the amounts of OH groups, and then enhancing the chemical bonds with matrix^[11]. So, once a good interface is provided, the mechanical properties of the composites would be better^[12]. However, after chemical treatment on the surface of Quartz Fiber, the mechanical properties decreased quickly^[13]. So, in order to improve its interface performance and high temperature resistant property of the QF/PSA composite, our team designed and synthesized a series of silane coupling agents containing terminal-alkyne and silicon-containing groups. Dong Chao^[14] et al. synthesized a new silane coupling agent alkynyl-containing silicone (AS-1) , and the Interlaminar Shear Strength (ILSS) improved almost by 25.3 %. Liang Xiuhua et al. found a new silane coupling agent containing isocyanate group which the ILSS property has been greatly imcreased by 24. 7 %. Wang Linjing^[15] et al. designed a novel silane coupling agent(CA-K), and the ILSS and Flexual Strength were upgraded by 34.7 % and 40.4 % compared with those unmodified composites at room temperature. In our group, the influence of some small-molecule silane coupling agents on the reinforcement of composites interface has been studied. Small-molecule silane coupling agents can increase the interface compound so that it can reinforce the QF/PSA composites. However, small-molecular silane coupling agent couldn't toughen the QF/PSA composites because it can not absorb so much energy to reduce the force around the surface in the process. To further understand the effect of toughening properties in the composites with the introduction of macromolecules. Recently, silicon-containing polyimides have attracted considerable attention because of their potential to make polyimides more soluble in organic solvents and because of the ability to obtain multiphase morphology^[16-20]. Because of those two reasons, we have synthesized a novel block silane coupling agent including terminal-alkyne groups and poly(imide siloxane) copolymers.

In this paper, the properties of poly(imide siloxane) copolymers (PISs) with crystalline polyimide hard block and PISs with amorphous polysiloxane soft block were introduced in our novel silane coupling agent. Polyimides (PIs) are high-performance macromolecules which are usually obtained via polycondensation of aromatic dianhydride and diamine monomers. And after the synthesis of the macromolecular coupling agents, QF reinforced PSA composites have been formulated, with silane coupling agents contents from 1.5 to 4.5 %. Then, standard specimens were mould injected and tensile tested. Also, the interlaminar shear strength(ILSS) and impact strength of the QF/PSA composites were tested. Finally, a study of some surface morphology was carried on.

2 Materials and methods

2.1 Materials and solubility

The solubility of the PISs were tested by putting 0.01 g of PIS poulder in 1 mL of organic solvents. The results are shown in Table. 1. Because of the soft block of the polysiloxane, the flexibility of the chain would increase and it would be ease to solvent attack. Solubility of PIS is a very important property because polyimides have bad sulubility in solvent which would cause bad intereaction between the surface of the fibers and resins. So we choose some solvents to make sure that this silane coupling agent could be distributed well in THF solvent which would be cored on the fibers.

Table. 1. Solubility of **P1**, **P2**, **WS**
P1

Solvent	Solubility	Solvent	Solubility
Dichloromethane	++	Ethyl Acetate	—
Epichlorohydrin	++	Hexane	—
Dimethyl Sulfoxide	++	Ethanol	—
N,N-Dimethylformamide	++	Pentane	—
1-Methyl-2-Pyrrolidone	++	Ethylene Glycol	—
Chloroform	++	Toluene	—
Tetrahydrofuran	++	Xylene	—

P2

Solvent	Solubility	Solvent	Solubility
Dichloromethane	++	Ethyl Acetate	+—
Epichlorohydrin	++	Hexane	—
Dimethyl Sulfoxide	+—	Ethanol	—
N,N-Dimethylformamide	++	Pentane	—
1-Methyl-2-Pyrrolidone	++	Ethylene Glycol	—
Chloroform	++	Toluene	++
Tetrahydrofuran	++	Xylene	n

WS

Solvent	Solubility	Solvent	Solubility
Dichloromethane	+—	Ethyl Acetate	+—
Epichlorohydrin	+—	Hexane	—
Dimethyl Sulfoxide	+—	Ethanol	—
N,N-Dimethylformamide	++	Pentane	—
1-Methyl-2-Pyrrolidone	++	Ethylene Glycol	—
Chloroform	+—	Toluene	+—
Tetrahydrofuran	++	Xylene	n

Key: ++, soluble at room temperature; +—, soluble on heating; —, insoluble on heating.

The composites were prepared using silicon-containing Arylacetylene resin(PSA), manufactured by our own laboratory. Both, the matrix and the reinforcing fibers were used without any further chemical treatment. **WS** was synthesized in our laboratory.

2.2 Compounding and processing

WS was incorporated into PSA/QF composites in different weight contents(1.5 %, 2.5 %, 3.5 %, 4.5 %). Different weighted amounts of **WS** soluted in 20 mL THF were coated on the fiber and kept for 1 hours. THF was removed by a rotary evaporator at 65 °C to get PSA/QF resins. The composite was degassed, poured into a preheated mold, and cured in the procedure: 170 °C for 2 hours, 210 °C for 2 hours and 250 °C for 4 hours to get the thermosets.

Usually, the transformation of a reactive thermosetting liquid in to a glassy solid involves two distinct macroscopic transitions: molecular gelation and vitrification. Molecular gelation is defined as the time or temperature at which covalent bonds connect across the network to form chemical bonds which gives rise to mechanical properties. Vitrification is when further reaction is prohibited or is dramatically reduced. The relationship between the processing time and mechanical properties is

shown in Table. 2. According to Table. 2, we have found when processing time was 6 minutes, the value of ILSS got the best. So, we choose 6 minutes as our processing time.

Table. 2. Influence of different processing time on ILSS of QF/PSA composites

ILSS(MPa)	Processing Time(min)					
	4	5	6	7	8	9
	14.56±0.34	15.00±0.48	16.07±0.26	15.25±0.72	14.69±0.29	14.27±0.81

2.3 Mechanical properties

Mechanical Measurements were carried out with a Universal Testing Machine DDL100 according to China Standard GB/T 2570-1995 at a crosshead rate of 2 mm/min.

The quartz fiber reinforcements are of type with 7340 MPa tensile strength, 78 GPa tensile modulus, 4.06 % tensile elongation and 2.20 g/cm³ density.

2.3.1 Tensile strength test

We used ISO14125:1998 as our standard for determining the flexural properties of fiber-reinforced plastic composites under three-point(Method A) loading. Composites samples of 45*15*2 mm³ were tested under 23 °C.

Tensile strength is defined as:

$$\sigma_f = \frac{3P * l}{2b * h^2}$$

σ_f : Flexural strength(MPa)

P : Load in newtons(N)

L : Span(mm)

h : Thickness of the specimen(mm)

b : Width of the specimen(mm)

2.3.2 Interlaminar shear strength test

We used ISO14130:1997 as our standard for determining the interlaminar shear strength of fiber-reinforced plastic composites under three-point loading. Composites samples of 20*6*2 mm³ were tested under 23 °C.

Interlaminar shear strength is defined as:

$$\tau_s = \frac{P_b}{b * h}$$

τ_s : Interlaminar shear strength(MPa)

P_b : Load in newtons(N)

h : Thickness of the specimen(mm)

b : Width of the specimen(mm)

2.3.3 Impact strength

We used ISO180:2000 as our standard for determining the impact strength of fiber-reinforced plastic composites. The method is used to investigated the behaviour of specified types of specimen under the impact conditions defined and for estimating the brittleness or toughness of specimens with the limitations inherent in the test conditions. Composites samples of 80*10*4 mm³ were manufactured in our laboratory and we tested those composites with notched.

Impact strength is defined as:

$$\alpha_{iN} = \frac{E_c}{h * b_N} * 10^3$$

E_c :Corrected energy, in joules, absorbed by breaking the test specimen

h : Thickness(mm)

b_N : Remaining width(mm)

2.4 Surface morphology

The surface morphologies of the thermosets were analyzed by S-4800 Scanning Electron Microscopy (SEM) instrument. X-ray Photoelectron Spectroscopy (XPS) were used to analysis elements on different kinds of fibers with a PHI 5000C ESCA System instrument. At first, we mixed **WS** into 20 mL THF and stirred lasted 10 min. And then, the solvent was added onto the surface of the fiber and lasted for 1 hour. After that, we put both treated QF and untreated QF into 100 mL acetone and cleaned it with ultrasonic environment for 15 min. The fiber was dried under vacuum at 45 °C for 1 hour to obtain products.

3 Results and discussion

3.1 Thermal ability

Thermogravimetric analysis(TGA) was utilized in order to investigate the thermal degradation of PIS and composites. The results were shown in Fig. 1. T_{d5} and T_{d10} represented the 5 % and 10 % weight-loss temperatures, respectively, and the results were shown in Table. 2. The T_{d5} value ranged between 387 °C and 625 °C while T_{d10} ranged between 417 °C and 913 °C, and the situation indicated a high degree resistance to thermal degradation. The T_{d5} value of **WS** was down to 387 °C because of polysiloxane-containing chain. The soft block would decrease the thermal stability of poly(imide siloxane). However, the T_{d5} value of PSA/QF-P3 hadn't changed so much in TGA, so it still had a great thermal stability.

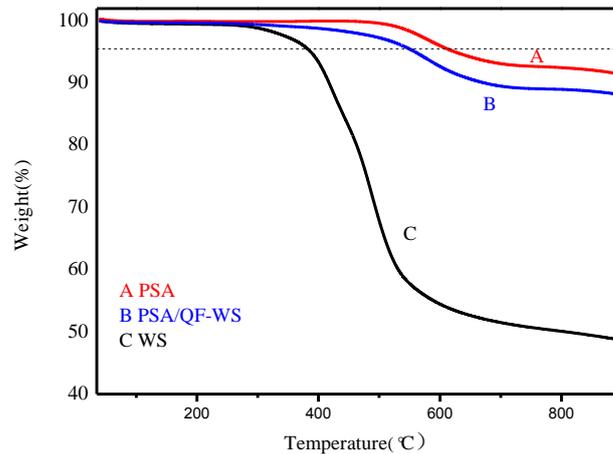


Fig. 1. Thermal Stability of silane coupling agents and its resin

Table. 2. T_{d5} and T_{d10} value of composites

	T_{d5} (°C) ^a	T_{d10} (°C) ^a
PSA	625	913
PSA/QF-WS	559	674
WS	387	417

^a T_{d5} and T_{d10} referring to temperature at 5 % and 10 % weight loss, respectively, which were measured using TGA at a heating rate of 10 °C/min under N₂ atmosphere.

3.2 Contact angles

Contact angles of water and diiodomethane for the PSA/QF and the PSA/QF-P3 composites were shown in Table. 3 and Table. 4.

Table. 3. The surface tensile and their polar, dispersive components of detection reagents

solvent	γ_l	γ_{ld}	γ_{lp}
water	72.80	21.80	51.00
diiodomethane	50.80	48.50	2.30

Table. 4. Contact angles of detective agents and Surface energy parameters of QF

Samples	Contact Angles(deg)		Surface energy parameters(mJ/m ²)			
	θ_w	θ_d	γ_s	γ_{sd}	γ_{sp}	$X_p=\gamma_{sp}/\gamma_s$
PSA/QF	64	29	48.49	37.37	11.12	0.23
PSA/QF- WS	93	40	60.55	39.63	20.92	0.39

The contact angles θ were measured with both polar and nonpolar liquids. The contact angle of water on the surface of untreated fiber was 64 °and then up to 93 °after treated. It means that the surface after treated has a hydrophobic and lipophilic behavior. Wettability was very important in formation of a activity interface and the higher surface energy means that the fiber and the matrix would have a better interaction. Without treated, the surface energy of the fiber is 48.49 mJ/m². However, after 2 % **WS** treated on the surface of the fiber, the value is increased to 60.55 mJ/m² which suggested those treated fibers have a better wettability. They were shown in Fig. 2.

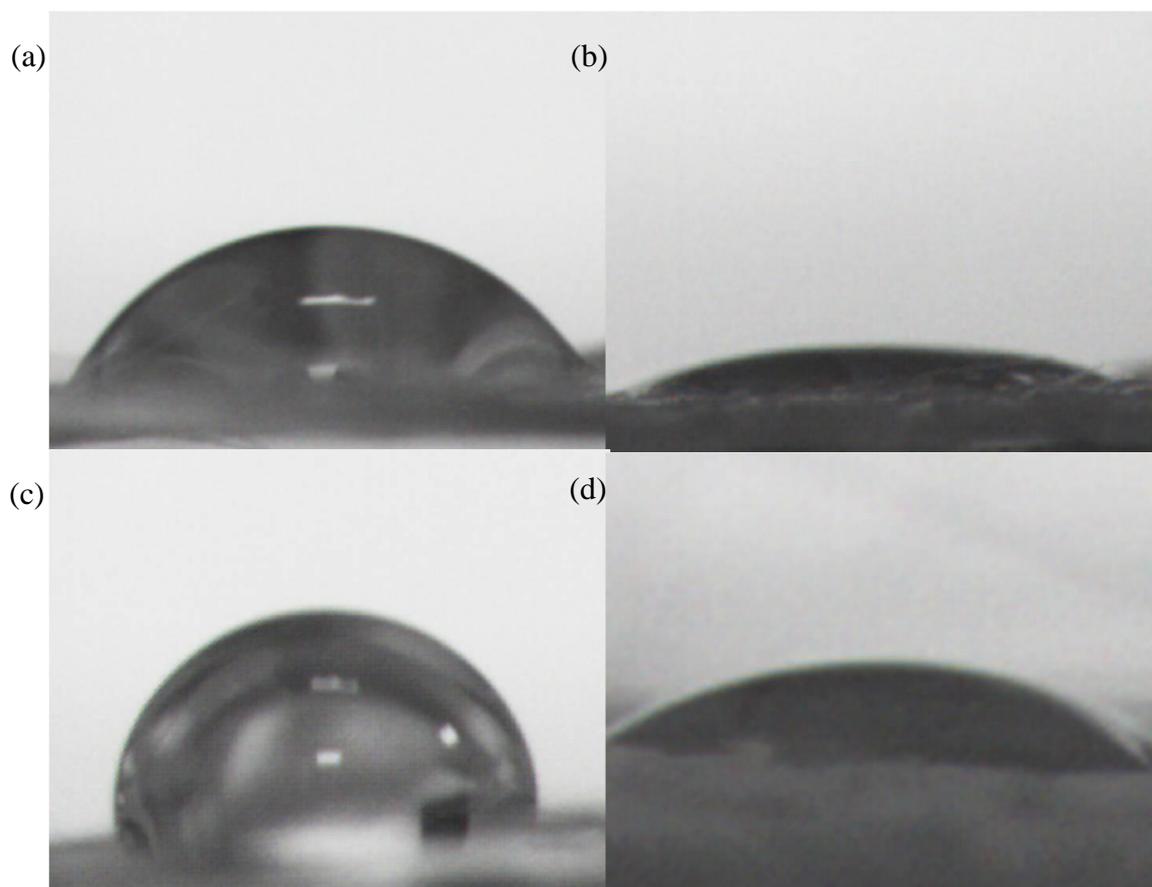


Fig. 2. Contact angles of detective agents on the QF between water and diiodomethane: (a)(b)untreated; (c)(d)treated

3.3 Scanning electron microscope(SEM)

The SEM images of the interphase regions in the PSA/QF composites after ILSS test are shown in Fig. 3. It can be seen that the failure surfaces of quartz fiber composites showed different micromorphology patterns. In Fig. 3 (a), the composites involving silicon-containing Arylacetylene matrix were destroyed from the fiber surface with a weak interface adhesion, and the smooth fiber surface was exposed after material fracture. However, in Fig 3(b), with the addition of silane coupling agent(**WS**) reinforcements, the quartz fibers were well covered with matrix after interlaminar fracture and the surface became rough. We can see that fibers in Fig 3(b) have a better interreaction between each other compared with Fig 3(a) which had been treated with acetone before. So it indicates that there would be an strong interreaction between fiber and matrix after the addition of silane coupling agent(**WS**). An important factor for this phenomenon was the formation of covalent bond in the system.

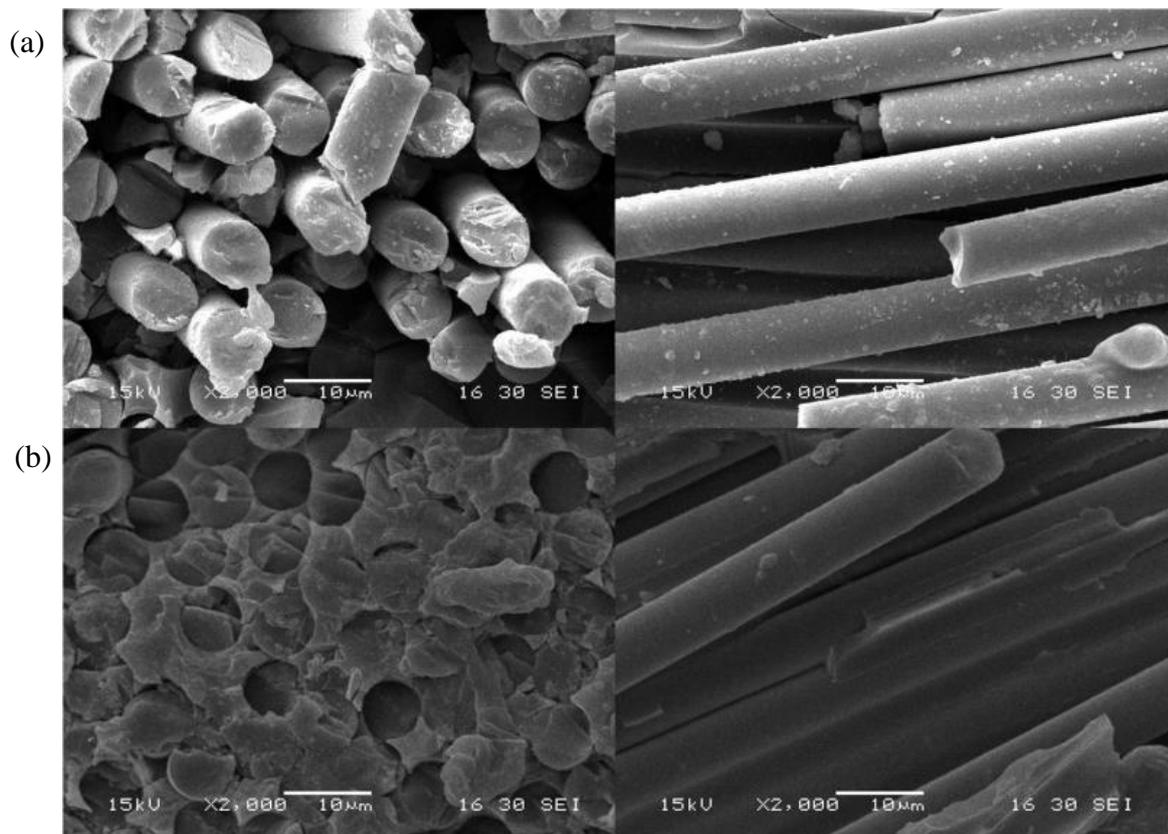


Figure 3. Scanning electron micrographs of fracture cross-sections for QF/PSA composites under room temperature (RT): (a) before **WS** modification; (b) after **WS** modification

3.4 Mechanical characterization

The mechanical properties of the PSA resin was studied below. The influence of the addition of silane coupling agents reinforcements on the mechanical properties were investigated by the measurement of Flexural Strength, Interlaminar Shear Strength(ILSS) and Impact Strength tests.

3.4.1 Pretreatment methods

There are so many aspects which would effect the ILSS of composites such as pretreatment methods, acetic acid and pretreating time.

Pretreatment methods had two ways. One is pretreatment method and the other is migration method. Pretreatment means that we should mix **WS** and THF first, and PSA solvent was added on the surface of fiber later. Migration method means that we could put PSA and **WS** into the solution and then add them onto the surface of the fiber. Differece of the influence of the pretreatment and

migration methods on ILSS of QF/PSA composites were shown in Table. 5. As what we saw in Table. 5, we could find that pretreatment method was better and so we chose pretreatment method.

Table. 5. Influence of the pretreatment and migration methods on ILSS of QF/PSA composites

Concentration/%	Pretreatment(MPa)	Migration(MPa)
0	16.07±0.26	16.03±0.21
1.5	22.97±0.35	22.43±0.39
2.5	22.10±0.64	21.93±0.36
3.5	21.58±1.20	21.30±0.71
4.5	19.49±1.81	19.20±0.30

In our laboratory, we have found that the value of pH would effect the ILSS value of QF/PSA composites. When pH decreased to 4-5, silane coupling agents would hydrolysis more easily in the mixture solvent. And the effect of acetic acid on the treatment effect of silane coupling agents were shown in Table. 6. So, after the mixture stirred for 5 minutes, we added some acetic acid into the mixture to make sure that the value of pH was from 4 to 5.

Table. 6. Effect of acetic acid on the treatment effect of silane coupling agent

Concentration/%	With acetic acid(MPa)	Without acetic acid(MPa)
0	16.07±0.26	15.03±0.24
1.5	22.97±0.35	21.43±0.32
2.5	22.10±0.64	20.93±0.66
3.5	21.58±1.20	20.30±0.21
4.5	19.49±1.81	18.20±0.52

3.4.2 Flexural Strength and Interlaminar Shear Strength(ILSS)

The mechanical properties of the thermosets are shown in Table. 7 and Fig. 4. With the increase of the **WS** content, the flexural strength and the Interlaminar Shear Strength(ILSS) increases first and decreases afterwards. However, they get a head at different maximum values. The introduction of 1.5 % **P3** comes to the maximum value at 22.97 MPa with 42.9 % increment while the introduction of 3.5 % **WS** adds to the maximum value at 321.3 MPa with 60.6 % increment.

Table. 7 Mechanical properties of different concentration of QF/PSA composites

Concentration/%	ILSS(MPa)	Flexural Strength(MPa)
0	16.07±0.26	196.3±10.2
1.5	22.97±0.35	281.4±13.9
2.5	22.10±0.64	306.3±16.3
3.5	21.58±1.20	321.3±13.7
4.5	19.49±1.81	290.0±20.0

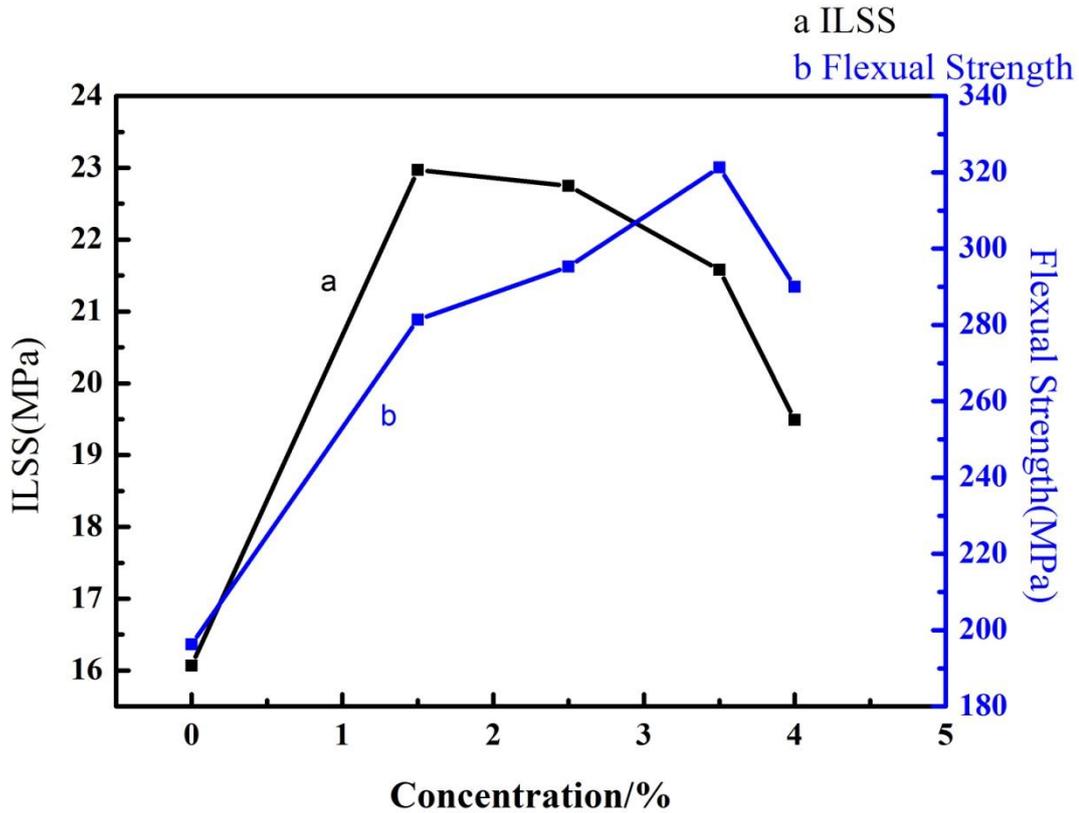


Figure 4. Mechanical properties of different concentration of QF/PSA composites

3.4.3 Impact Fracture energy

Table. 8 Effect of **WS** concentration on Impact Strength of QF/PSA composites

Concentration(wt%)	Impact strength(kJ • m-2)
0.0	104.706±8.425
1.5	106.773±10.492
2.5	144.781±23.875
3.5	162.328±18.735
4.5	186.461±4.664

The mechanical properties of the thermosets are shown in Table. 8. With the increase of the **WS** content, the impact strength increased from 104.706 kJ • m⁻² to 186.461 kJ • m⁻², with 78.1 % increment. It can be clearly seen that the PSA/QF-**WS** composites exhibit both toughening and strengthening in comparison to PSA/QF composites because of the addition by the PDMS chains.

4 Conclusion

In this article, After added **WS** in composites, mechanical properties of the modified composites were increased by charactering with tensile strength tests, Interlaminar Shear Strength(ILSS) and Impact Strength tests. With a small amount addition of **WS**, it show significantly improved toughness, heat resistance, thus completely improving the bottleneck problems like low mechanical properties that exist in PSA/QF composites. These outstanding performances are attributed to the special structure of PIS-containing, including hard and soft block structure, different to PSA/QF composites. These unique characteristics and interactions with PSA resins and QF provide **WS** with efficient and multi-functional roles in modifying PSA resins.

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