Reinforcement of Silicon-Containing Arylacetylene/Quarts Fiber composites by poly(imide-co-siloxane) macromolecular coupling agent

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Abstract. In this paper, poly(imide siloxane) copolymers (PISs) with crystalline polyimide hard block and PISs with amorphous polysiloxane soft block were introduced into a novel macromolecular silane coupling agent. The result showed that the interlaminar shear strength (ILSS), flexural strength and notched impact strength increased by 47.0%, 60.6% and 78.1%, respectively. At 250 ^{o}C, the retention rate of ILSS and flexural strength reached 81.9% and 85.1%. The retention rate of ILSS and flexural strength reached 57.9% and 59.3% at 500 ^{o}C, respectively. The surface morphology was explored by X-ray photoelectron spectroscopy (XPS), and the data revealed that chemical bonding was tight between fiber and P3. Finally, the mechanism of reinforcement and toughness extracted from interphase morphologies of scanning electron microscopy (SEM) suggested that soft and moderate macromolecule layers were constructed between the matrix and the fiber when treated with P3, which improved the mechanical strength and toughness of the Silicon-Containing Arylacetylene/Quarts Fiber (PSA/QF) composites. Overall, these findings look promising for future in reinforcement and heat-resistance.

1. Introduction

The excellent properties combined with the superior chemical resistance and outstanding thermal stability of PSA/QF composites made it ideal for use as structural material in aerospace industry[1]. However, PSA resin composed of [-(R$_1$)Si(R$_2$)-C≡C-Ar-C≡C-]showed moderatemechanical properties after solidification [2]. The mechanical properties of polymer composites depend highly on the interface between QF and matrix resin. To satisfy the demands of high mechanical properties and application sin high-temperature environments, many studies focused on modification of these composites by other materials [3].

Macromolecular coupling agent [4] is an effective method to improve the interfacial bonding strength of materials. For instance, Gu et al. [5] designed and synthesized a polyimide macromolecular coupling agent, and found it effectively improve heat resistance and mechanical strength of the composite. However, polyimide resin and PSA resin may also produce distinct phase separation, which can be overcome by dispersion of block copolymer into nano-scale of thermosetting resin[6]. Grubbs et al. [7] and Hameed et al. [8] introduced block copolymers having glycidyl methacrylate into epoxy resin to obtain thermosetting resin with nanostructures. George et al. [9] dispersed polystyrene-b-polybutadiene-b-polystyrene(SBS) triblock copolymers in epoxy resins by epoxidation of polybutadiene(PB) to guarantee compatibility. However, these macromolecule coupling agents have

limited in heat resistance. This incorporated high-temperature-resistant polyimide[10] hard segment and good-adhesive[11] polysiloxane soft segment into block copolymer macromolecular coupling agent to improve the interfacial compatibility of the composite material, as well as ensure better composite mechanical properties and high-temperature performance.

In this paper, poly(imide siloxane) copolymers(PISs) with crystalline polyimide hard block and amorphous polysiloxane soft block were introduced into novel macromolecularsilane coupling agent. Polyimides(PIs) are high-performance macromolecules, which can be obtained by polycondensation of aromatic dianhydride and diamine monomers[12].The effects on PSA composite matrix fibers were investigated. The surface morphology and mechanical properties of the as-prepared PSA/QF were characterized byX-ray photoelectron spectroscopy(XPS), contact angle, scanning electron microscopy(SEM), and tensile tests. The results indicated that PSA/QF composites will not only maintain good interfacial bonding at high temperature, but also play an important role in reinforcement and toughness.

2. Experimental

2.1. Materials
Bis(γ-aminopropyl) polydimethylsiloxane(APPS) was purchased from Micxy Reagents, and itsnumerical average molecular weight determined by ^{1}H-NMR spectrum was 995 g/mol. 4,4'-(4,4'-isopropylidenediphenoxy)-bis-(phthalic anhydride), 2,2-Bis-(3-amino-4-hydroxylphenyl) propane, propargyl bromide and (3-aminopropyl) triethoxysilane were obtained from Adamas Reagents and sublimated before use. Potassium carbonate(AR), triethylamine(AR), acetic anhydride(AR), acetone(AR) and N,N-dimethyl formamide(AR) were purchased from General Reagents and used as received without further purification. Tetrahydrofuran was refluxed with sodium and benzophenone until the blue color of ketyl of benzophenone was well established, and was then distilled. Silicon-containing aryacetyleneresin(PSA) was synthesized in our laboratory and Quartz Fiber(QF) was obtained from Feilihua Quartz Fiber.

2.2. Synthesis Routes
4,4'-(4,4'-isopropylidenediphenoxy)bis (phthalic anhydride)(BPADA)(2.10g, 8mmol) and APPS(1.0g, 1mmol) were mixed with 100 mL DMF/THF(1:1) under nitrogen atmosphere at room temperature for 2 hours. Next, 2, 2-bis (3-amino-4-hydroxylphenyl) propane(0.36g, 1mmol) was added into the mixture. After 4 hours stirring, triethylamine and acetic anhydride were added to the solution and reaction temperature was raised to 80°C for 6 hours. The solution was then washed thoroughly with hot ethanol and water, then dried under vacuum at 65°Cfor 6 hours.

A three-necked 100 mLflask containing a magnetic stirrer and nitrogen inlet fitted with a condenser was charged with 5. 24g(2.5mmol) P1, 0.5g potassium carbonate and 50mL DMF under nitrogen atmosphere. The mixture was stirred for 2 hours at 70°C to ensure complete dissolution and then 0.6g(5mmol) propargyl bromide was added dropwise to the flask and reacted within 6 hours.The resulting precipitate was then collected, washed three times with hot ethanol: water(1:1), and dried under vacuum at 65°C for 6 hours to yieldalalkyne-containing poly(imide-co-siloxane).

Alalkyne-containing poly(imide siloxane),(3-aminopropyl)triethoxysilaneand acetone(30 mL) were mixed in a three-necked 100 mL flask under nitrogen atmosphere at 50°Cand stirred for 3 hours. The mixture P3was then put in ethanol under constant stirring to form a precipitate, which was then dried under vacuum at 45°C for 4 hours.

2.3. PSA/QF Composites Preparation
To prepare PSA/QF resins and thermosets, P3 was incorporated into PSA/QF composites at different weight ratios of 1.5%, 2%, 2.5%, 3%, 3.5%, and 4%. Different weighted amounts of P3 were dissolved in 20mL THF, which then were coated on the fiber and kept for 1 hour. THF was removed by a rotary evaporator at 65°C to obtain PSA/QF resins. The composite was degassed, poured into a preheated mold, and cured at 170°C for 2 hours, 210°Cfor 2 hours, and 250°C for 4 hours to form the thermoset.

2.4.Characterization

The surface morphologies of the thermosets were analyzed by S-4800 scanning electron microscopy (SEM) instrument. X-ray photoelectron spectroscopy (XPS, PHI 5000C ESCA) was used for elemental analysis. The mechanical measurements were carried out with a Universal Testing Machine CCSS-44100 and PTM7501-B, the interlaminar shear strength test was performed according to the JC/T773-1996[13] standard; the flexural strength test was performed according to the GB/T9341-2000[14] standard; notched impact strength test was performed according to ISO 180:2000[15] standard, notch type: Type A.

## 3. Results and Discussion

3.1. Mechanical Properties

The mechanical properties of PSA resins were studied by evaluating the influence of added silane coupling agents. The testing was carried out by Interlaminar Shear Strength(ILSS), Flexural Strength, and notched impact strength.

3.1.1. Flexural strength and ILSS

The mechanical properties of the thermosets are gathered in Table 1 and Figure1. As P3 content rose, the introduction of 1.5% P3 increased the maximum value to24.00MPa with 47.0% increment, while introduction of 3.5% P3 raised maximum value to 321.3MPa with 60.6% increment. P3 played an important role in composite by adsorbing on the fiber surface, resulting in weak interface layer[16]. This lowered the interfacial bond strength of PSA/QF and affected the mechanical properties. The presence of polysiloxane on the main chain of macromolecule alkane structure reacted with QF. Hence, the physical winding of many molecules improved the bending strength of the composite material, inducing good reinforcing effects on the composites.

Table1. Mechanical properties using different amounts of PSA/QF-P3 composites.

| Concentration/%	ILSS(MPa)	Flexual Strength(MPa)
0	16.07±0.26	196.3±10.2
1.5	24.00±0.35	281.4±13.9
2.0	23.62±0.17	289.7±11.6
2.5	22.75±0.34	295.3±16.3
3.0	22.10±0.64	310.6±12.9
3.5	21.58±1.20	321.3±13.7
4.0	19.49±1.81	290.0±20.0
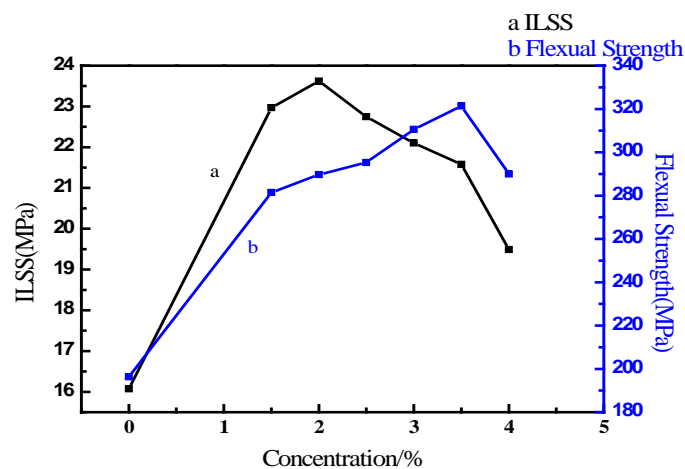
Figure 1. Mechanical properties using different amounts of PSA/QF-P3 composites.

3.1.2. Impact fracture energy

The mechanical properties of the thermoset are shown in Table 2 and Figure 2. As P3 content raised, the impact strength increased from 104.7 kJ·m^{-2} to 186.5 kJ·m^{-2}, corresponding to about 78.1% increment. It can clearly be seen that PSA/QF-P3 composites exhibited both toughening and strengthening effects when compared to PSA/QF composites thanks to added PDMS chains. The block polymer improved compatibility of the composite interface due to introduced polysiloxane[17]. It also promoted the macromolecular block coupling agent P3 to enhance the interface.

Table2. Effect of P3 concentration on Impact Strength of PSA/QF composites.

Concentration(wt%)	Impact strength(kJ·m^{-2})
0.0	104.7±8.4
1.5	106.8±10.5
2.0	121.9±20.8
2.5	144.8±23.9
3.0	157.0±9.6
3.5	162.3±18.7
4.5	186.5±4.7
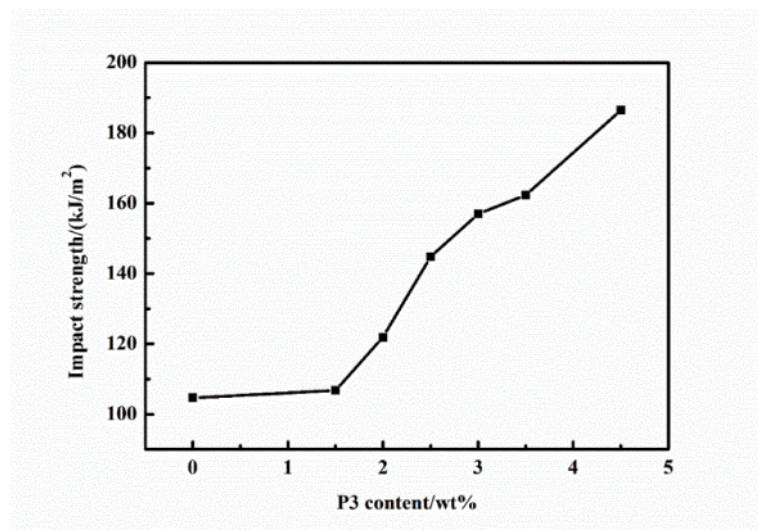
Figure 2. Influence of P3 concentration on Impact Strength of PSA/QF composites.

3.1.3. High-temperature mechanical properties

At 250 $^{\circ}$C, the ILSS and flexural strength of the 1.5 wt% composites reached 21.6 MPa and 242.9 MPa. The corresponding retention rates were 90.0% and 86.3%. On the other hand, the ILSS and flexural strength of the composites containing 3.5 wt% were 17.7 MPa and 273.5 MPa. The corresponding retention rates were 81.9% and 85.1%. At 500 $^{\circ}$C, the ILSS and flexural strengths of the 1.5 wt% composites reached 14.4 MPa and 170.3 MPa, with retention rate of 60.0%. The composites with 60.5% and 3.5 wt% showed interlaminar shear strength and flexural strength of 12.5 MPa and 190.6 MPa, with retention rates of 57.9% and 59.3%.The interfacial reinforcement effect, toughening and high-temperature mechanical properties appeared all improved. Compared to added common coupling agent, the copolymerization of P3 and PSA enhanced the high-temperature performance retention of the composites at 250 $^{\circ}$C and 500 $^{\circ}$C. This was related to heat-resistant structures, such as imide ring and benzene ring in P3 molecular chain[5].The siloxane segments in the block polymer also underwent self-aggregation, significantly improving high-temperature mechanical properties of the composites[18].

Table 3. Effect of P3 on the mechanical property retention rates of composites at 250 and 500 ^{o}C.

| Temperature/^{o}C	ILSS/MPa			Flexural Strength/MPa		
	Untreated	1.5 wt%	3.5 wt%	Untreated	1.5 wt%	3.5 wt%
RT	16.1	24.0	21.6	196.3	281.4	321.3
250	14.1	21.6	17.7	181.6	242.9	273.5
500	8.6	14.1	12.5	121.7	170.3	190.6

3.2. Surface Morphology
The surface morphology plays an important role in fiber reinforced polymer composites. Thus, study of the mechanisms undergoing at the interfaces in composites becomes very useful for in depth improvement of the mechanical properties at the interface.

3.2.1.X-ray photoelectron spectroscopy(XPS)
Surface morphology can further be verified by XPS (Figure3 and Figure4). The elemental composition changed after modification with silane coupling agent. To further characterize the interaction between the macromolecular coupling agent and fiber surface, the surface elemental states of quartz fiber before and after treatment with coupling agent P3 were analyzed. All the curves in Figure 3 display O1s and Si2ppeaks, which exhibit the characteristics of QF; meanwhile, the intensity of the C1s peak is significantly lower in pure QF than in any other samples.

Figure 4 shows C1s, N1s, O1s and Si2pcore-level spectra of pure QF and QF-P3.The untreated fiber surface mainly contained -C-C- (284.6 eV), -C-N- (286.1 eV), -C-OH (286.8 eV), and -C=O (287.2 eV) in C1s core-level spectra. These groups were mainly issued from the epoxy sizing agent[19] on the fiber. After treatment of the coupling agent in the bonding state corresponding to C element on QF surface, -C-OH vanished due to coverage of the coupling agent. The -C-N- content slightly increased due to introduced imide ring. The main binding mode of N element on QF surface was nitrogen-containing heterocyclic structure (398.5 eV). The addition of P3 reinforced the presence of rend imide ring (398.5 eV) on QF surface, with 50.3% content. The main binding modes of O element on QF surface were -C=O (532.2 eV), -Si-O-(532.0 eV), -C-OH (533.6 eV), and SiO_2 (532.7 eV). The bonding types of SiF on QF surface were -Si-OH (102.3 eV) and SiO_2 (103.4 eV). After P3 treatment, the -C-OH content in the combined state of O and Si elements declined. In addition to decreasing in -Si-OH and SiO_2 contents, a new functional group -Si-O-Si- appeared at 101.5 eV, with 29.1% content. This was mainly due to dehydration condensation of silane on QF surface after hydrolysis of siloxane in P3 to form new chemical structure of -Si-O-Si-, where P3 covered part of SiO_2. Meanwhile, since the molecular chain contained both imide ring and siloxane chain structure, the treated QF surface should have more imide rings and -Si-O-Si- structures, both present on the surface. These elemental contents were much significantly. The above results showed that macromolecular silane coupling agent P3 can chemically bond and attach to the fiber surface.
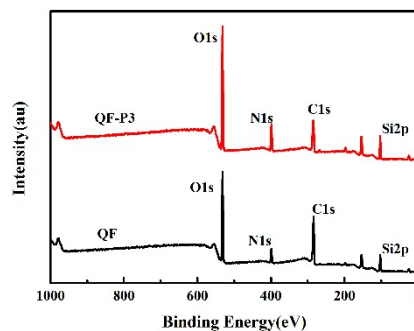
**Figure 3.** Wide-scan XPS spectra of QF and QF-P3.
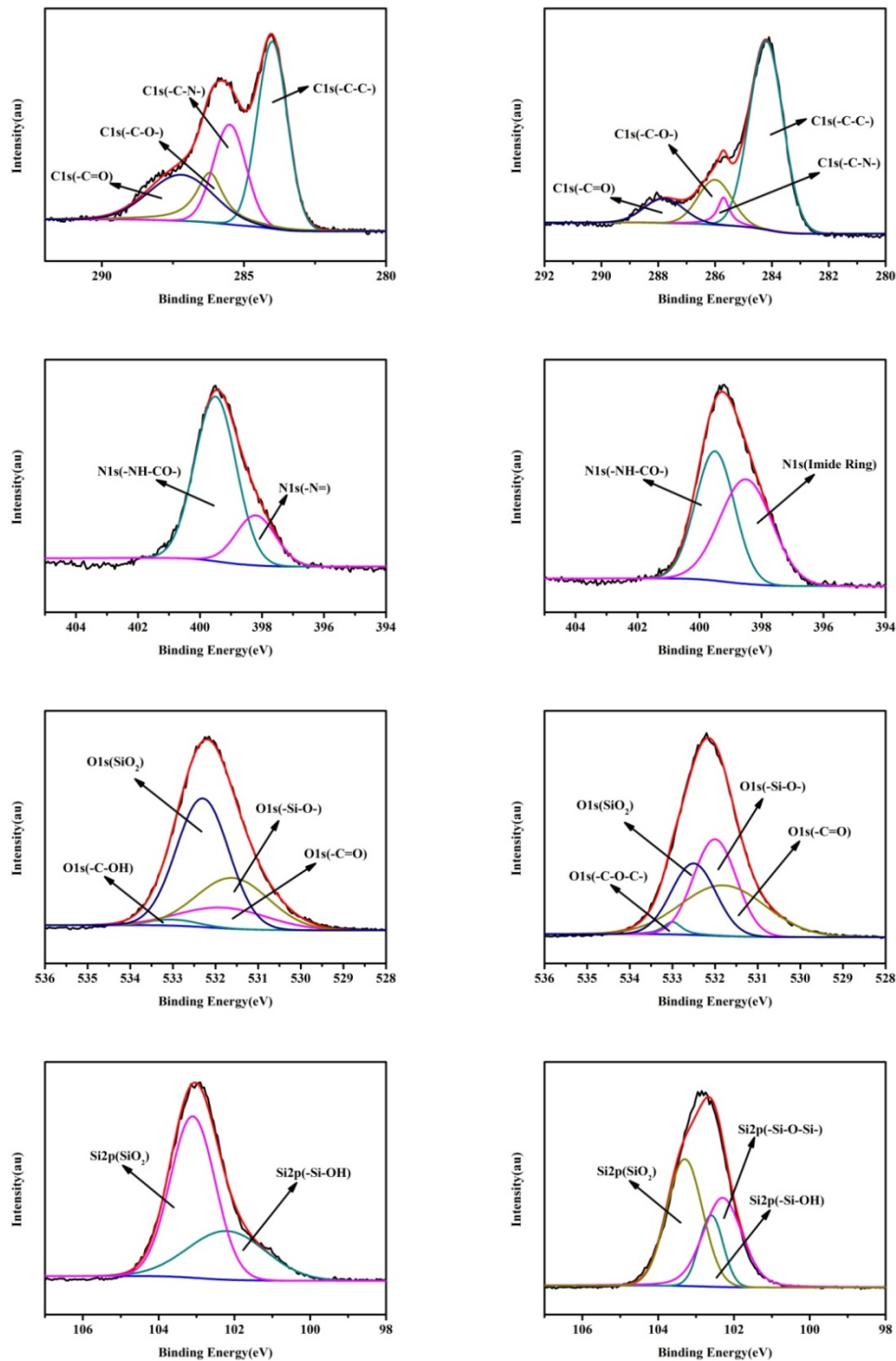
Figure 4. XPS spectra of (a,b)C1s spectra, (c,d)N1s spectra, (e,f)O1s spectraand (g,h)Si2p spectra.

3.3. Mechanism

The above data indicated that silane coupling agent(P3) played an important role in toughening and reinforcing PSA/QF composites. First, -Si-*O-CH₂-CH₃* in P3was hydrolyzed to hydroxyl(-Si-*OH*), as shown in Figure6. Next, both groups reacted with the hydroxyls present on the fibers surfaces and sizing agents to form hydrogen bonds[20]. When heated at high temperature, the hydroxyl groups

reacted with each other, and water molecules were removed to form -Si-O-Si- groups with temperature resistance properties. On matrix surface, several unreacted inner alkyne groups were present, which would form benzene rings with alkyne groups on P3 by ring trimerization and Diels-Alder resections[21]. After curing at high temperature, bothalkynyl cross linking and imidization reactions would take place on the surface to yield improved mechanical properties after addition of silane coupling agents. The overall mechanism is shown in Figure5. The diffused interface is very important, which would bring a "bridge" between the fibers and matrices. After treatment, the fibers interacted with matrix to generate a force due to chemical bindings between both sides(Figure5).
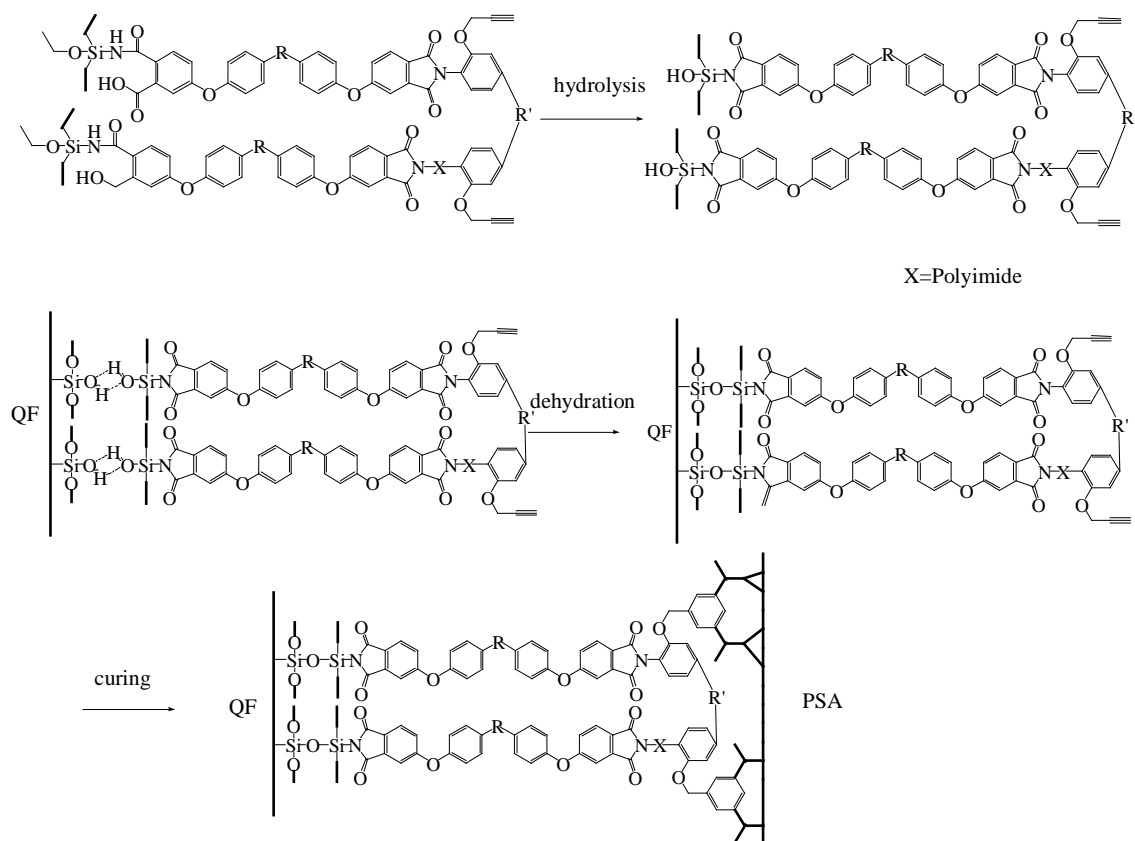
Figure 5. Mechanism of coupling agent(P3) bonding with QF and PSA.

4. Conclusions

A novel silane coupling agent P3 with PIS segments was synthesized by imidization process. The results showed that the interlaminar shear strength(ILSS), flexural strength and notched impact strength increased by 47.0%, 60.6% and 78.1%. At 250 °C, the retention rate of ILSS and flexural strength reached 81.9% and 85.1%. The retention rate of ILSS and flexural strength reached 57.9% and 59.3% at 500 °C, respectively. Addition of small amounts of P3significantly enhancedmechanical properties and heat resistance. XPS and SEM shown that outstanding performances were attributed to the particular structure of PIS-containing, including hard and soft block structures which were different from PSA/QF composites. Overall, these findings look promising for future in reinforcing PSA/QF composites and improving heat resistance property.

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