Synthesis and application of a novel dicyanide-containing silane coupling agent

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Abstract. Silicon-containing arylacetylene (PSA) is a novel resin with excellent heat resistant properties and it has potential application in the field of aerospace. However, Quartz fiber(QF)/PSA composites has poor interfacial adhesion, and commonly used silane coupling agents decompose at high temperatures. In this paper, a novel silane coupling agent DCA was synthesized through the reaction of 2,3-diamino-2-butenedioleonitrile, 2-keto-glutaric acid, 3-aminophenylacetylene and propyltriethoxysilane. In QF/PSA composites, the surface roughness and surface energy of QF had improved after modified by DCA. Spectral and thermal studies gave evidence for both homopolymerization of propargylic groups and nitrile groups during thermal curing, which indicated that DCA could co-cure with propargylic groups of PSA. After the cyclization reactions of nitrile groups, a strong interfacial layer had been formed which could remarkably improve the thermal stability of composites. After modification, ILSS can reach 27.6MPa at room temperature, the retention rate was 54.7% at 500°C.

1. Introduction
Among the class of high performance thermosets, PSA[1,2] is of much interest owing to its excellent mechanical properties, chemical resistance and exceptional thermal stability. After curing, the polymer forms highly cross-linked structure and possesses rather high decomposition temperature(>500°C) and high char yield(>90%) at 900°C. As a result, PSA has widely used in aerospace applications. In QF/PSA composites, however, there is less adhesion between matrix and fiber because of the non-polar structure and the relatively low surface energy of the matrix resin[3]. Silane coupling agents[4,5] are usually used to modify the interfacial properties of composites, but commonly used silane coupling agents,such as KH550, tend to decompose at high temperature and become defects in the composite system which will severely reduce the mechanical properties of composite materials. Novel silane coupling agents[6,7] with high temperature performance are highly demanding for advanced composites used in the field of aeronautics and astronautics.

Phthalonitrile[8-10](PN) resins have been studied over the past 30 years as novel heat resistant polymers. Phthalonitrile units can form different heterocyclic aromatic structures, including phthalocyanine, isindoline and triazine according to different reaction conditions, which result in many excellent properties such as high thermal and oxidative stability, low water absorption, flame retardance, and the absence of Tg before thermal decomposition temperature. The curing procedure of neat PN compounds is slow at temperature above 300°C, which limited their further applications. Furthermore, the curing reactions was found to be remarkably promoted in the presence of a small amount of curing catalysts such as phenols and organic amines. And self-promoted phthalonitrile derivatives with phenol or amine groups were also been designed and synthesized.
In this paper, we designed and synthesized a novel coupling agent DCA, introducing dicyanide groups into molecules. The structure was confirmed by Fourier Transform Infrared Spectroscopy (FTIR), $^1$H-NMR and $^{13}$C-NMR. The thermal behaviors of DCA were investigated by differential scanning calorimetry (DSC) and FTIR. The interfacial properties were characterized by XPS and contact angle. The surface roughness was investigated by Atomic Force Microscope (AFM). The mechanical properties were investigated by tensile test at room temperature and 500°C.

2. Experimental

2.1. Materials

2,3-Diaminomaleonitrile (DAMN) was bought from Xianding Co., Ltd, while 3-Aminophenylacetylene was bought from Meryer. Triethoxy (3-isocyanatopropyl)silane was bought from Alfa Aesar. 2-Keto-glutaric acid (99%), Hydrochloric Acid (AR), Ethanol (AR), Tetrahydrofuran (AR), Dibutyltin Dilauroate (95%), Acetone (AR) and N,N-Dimethylformamide (AR), N'- (Ethyliminomethylene) -N, N-Dimethyl-1,3-Propanediamine Monohydrochloride (97%) and N, N-Dimethyl-4-Pyridinamine (99%) were bought from Tansoole Co., Ltd. Quartz Fiber (B type) was purchased from Feilihua Quartz Fiber Co., Ltd. PSA was synthesized by Key Laboratory for Special Polymer Materials and Related Technology in East China University of Science and Technology.

2.2. Synthesis Routes

![Synthesis routes of DCA.](image)

3-(5,6-dicyano-3-hydroxypyrazin-2-yl)propanoic acid (DC-1)

The mixture of 2, 3-diamino-2-butenedioleonitrile (10 mmol, 1.08 g) and 2-keto-glutaric acid (10 mmol, 1.46 g) was dissolved in 30ml anhydrous ethanol and then added into a 100ml three-necked flask. After stirring for 30 minutes, then poured the solution into 300ml deionized water, put the beaker in fridge at 2-8°C overnight, filtered and washed by deionized water three times and dried, colorless acicular crystal was obtained (71%). FTIR (KBr, $\nu$): 2237 cm$^{-1}$ (-C≡N), 1698.3 cm$^{-1}$ (-C=O), 1598 cm$^{-1}$, 1208 cm$^{-1}$ (pyrazine); $^1$H-NMR (DMSO, TMS)δ (ppm): 2.66 (t, 2H, Hb), 2.98 (t, 2H, Hb), 1.10 (s, 6H, CH$_3$); $^{13}$C-NMR (DMSO), 173.69, 159.23, 155.84, 127.90, 120.37, 115.03, 113.70, 29.64, 27.47. 3-(5,6-dicyano-3-hydroxypyrazin-2-yl)-N-(3-ethynylphenyl)propanamide (DC-2)
DC-1 (5 mmol, 1.09 g) was dissolved in DMF (50 ml), and N′-(Ethyliminomethylene)-N, N-Dimethyl-1,3-Propanediamine Monohydrochloride (5 mmol, 0.96 g) and N, N-Dimethyl-4-Pyridinamine (5 mmol, 0.61 g) were added as catalyst at 0 °C. After stirring for 1 h, 3-aminophenylacetylene was added and warmed up to room temperature, then stirred for 24 h. Brown solution turned into black, and added into 500 ml hydrochloric acid (15%) dropwise, brown powder precipitated in the bottom of the beaker. After filtering, washed the product with deionized water three times and dried, brown powder was obtained (89%). FT-IR (KBr, ν): 3342.9 cm⁻¹ (-NH-), 3261.6 cm⁻¹ (-C≡CH), 2240 cm⁻¹ (-C≡N), 2105.3 cm⁻¹ (-C≡C-), 1678.7 cm⁻¹ (-C=O). ¹H-NMR (DMSO, TMS) δ (ppm): 2.84 (t, 2H, Hb), 3.07 (t, 2H, Ha), 4.16 (s, 1H, Hh), 7.15 - 7.77 (m, 4H, Hdefg), 10.20 (s, 1H, Hc). ¹³C-NMR (DMSO), 170.82, 159.22, 156.15, 140.09, 129.42, 127.57, 126.73, 122.41, 122.27, 120.26, 120.04, 115.29, 113.74, 83.86, 80.91, 32.02, 27.87. 5,6-dicyano-3-(3-((3-ethynylphenyl)amino)-3-oxopropyl)pyrazin-2-yl(3-(triethoxysilyl)propyl)carbamate (DCA)

DC-2 (2.5 mmol, 0.79 g), Triethoxy(3-isocyanatopropyl)silane (5 mmol, 1.24 g), 2 drops of DibutyltinDilaurate and 30 ml Tetrahydrofuran were mixed in a 100 ml three-necked flask under a nitrogen atmosphere and refluxed at 70 °C. After stirring for 24 h, the solvent was removed under reduced pressure. The mixture was extracted with anhydrous ethyl aether and filtered. The solution was evaporated under reduced pressure, yellow solid was obtained (54%). FT-IR (KBr, ν): 3342.9 cm⁻¹ (-NH-), 3261.6 cm⁻¹ (-C≡CH), 2931.2 cm⁻¹ (-CH₂-), 2886.6 cm⁻¹ (-CH₃), 2240.1 cm⁻¹ (-C≡N), 2105.3 cm⁻¹ (-C≡C-), 1699.7 cm⁻¹ (-C=O), 1258.5 cm⁻¹ (-Si-C-), 1073 cm⁻¹ (-Si-O-). ¹H-NMR (DMSO, TMS) δ (ppm): 0.56 (t, 2H, Hl), 1.15 (t, 9H, Hn), 1.45 (t, 2H, Hk), 2.84 (t, 2H, Ha), 2.95 (s, 1H, Hj), 3.07 (t, 2H, Hb), 4.16 (s, 1H, Hh), 7.15 - 7.77 (m, 4H, Hdefg), 7.05 (s, 1H, Hi), 10.20 (s, 1H, Hc). ¹³C-NMR (DMSO), 170.52, 159.16, 156.69, 156.10, 139.84, 129.54, 127.66, 126.69, 122.43, 22.27, 120.15, 120.0, 115.27, 113.73, 83.82, 80.64, 56.51, 43.36, 32.04, 27.89, 25.53, 19.06, 15.22.

Figure 3. FTIR, ¹H-NMR and ¹³C-NMR spectra of DC-2

Figure 4. FTIR, ¹H-NMR and ¹³C-NMR spectra of DCA
2.3. Preparation of QF/PSA Composites
Different content(0%, 1%, 1.5%, 2%, 2.5%, 3%) of DCA was resolved in 30ml THF, and then coated on QF, volatilize for at least 1h. After that, PSA was resolved in THF, immersed on QF and stayed for 6h. Then THF was evaporated at 65°C in vacuum oven for 2h. The composite was put in a preheated mold, and cured in the procedure: 170 °C for 2 hours, 210°C for 2 hours and 250°C for 4 hours and the QF/PSA composites was obtained.

3. Results and Discussion
3.1. Interlaminar Shear Strength of QF/PSA composites
Table 1 showed the effect of DCA on the interlaminar shear strength(ILSS) of QF/PSA composites at room temperature and 500°C. ILSS increased from 16.9 MPa to 27.6 MPa when the additive amount is 2.0wt%, which increased by 63.3%. Retention rate of ILSS is 54.7%, it indicated the heat resistant property of DCA. If excessive DCA was added, ILSS begins to decrease. Because excessive DCA will form multi-layers between QF and PSA and alkyne groups on the surface of QF cannot co-cure with PSA, which resulted in interfacial defects. Therefore, DCA should be added in an appropriate amount to exert the best performance of it.

| DCA Content/% | ILSS-RT/MPa | ILSS-500°C/MPa |
|---------------|-------------|---------------|
| 0             | 16.9±0.4    | 8.7±0.2       |
| 1.0           | 22.6±0.4    | 12.3±0.1      |
| 1.5           | 24.5±0.3    | 13.4±0.4      |
| 2.0           | 27.6±0.9    | 15.1±0.7      |
| 2.5           | 25.7±0.8    | 12.4±0.3      |
| 3.0           | 22.0±0.7    | 11.7±0.5      |

3.2. Surface Morphology
3.2.1. Contact Angle
Figure 5and Table 2 showed the change of contact angle of PSA solution on quartz fiber and quartz fiber modified by coupling agent DCA. As shown in the chart, the PSA solution was dropped on the quartz fiber and the contact angle was 39.19°. After modified by DCA, the contact angle reduce by 37%, which was 28.59°. DCA changed the original organic/inorganic interface into an organic/organic interface, enhancing the interfacial compatibility and made it easier for the PSA resin to adsorb, infiltrate and spread on the surface of the quartz fiber, which significantly increased the interfacial adhesion and mechanical properties of QF/PSA composites.

| Detection reagent | Contact angle on the QF/° |
|-------------------|---------------------------|
|                   | Untreated | Treated by DCA |
| PSA resin solution| 39.19     | 28.59          |
3.2.2. Atomic Force Microscope (AFM)

Figure 6. AFM images of QF (a) unmodified, (b) modified by DCA

Figure 5. Contact angle of QF with PSA: (a) before modified; (b) after modified by DCA

3.2.2. Atomic Force Microscope (AFM)

Figure 6 and Table 3 showed the change of the surface roughness of the QF after modified by the coupling agent DCA. The root mean square roughness (Rq) and the arithmetic average roughness (Ra) of the surface were observed and calculated. Rq and Ra of the QF were 80.34 nm and 69.12 nm respectively. After immersed by DCA, Rq and the Ra became 127.81 nm and 109.35 nm. It can be explained that the coupling agent DCA can etch QF, causing pits, bulges and wrinkles on the surface of it, increasing the roughness. The increase of the surface roughness of the quartz fiber and the increase of the surface area and the specific surface area, can form a stronger mechanical lock with the PSA resin when composite material formatted, and can fully exert its effect when the longitudinal shear force is applied. Combined with the mechanical properties of the composites modified by DCA, it can be proved that the coupling agent DCA does interact with QF.

Table 3. Changes of QF surface roughness before and after modification

| Sample          | Rq/nm | Ra/nm |
|-----------------|-------|-------|
| Unmodified      | 80.34 | 69.12 |
| Modified by DCA | 127.81| 109.35|

3.3. Thermal Behavior

3.3.1. FTIR of curing DCA

Figure 7 shows the FTIR spectrum of the curing DCA at different steps. It may produce three different heterocyclic aromatic structures, including phthalocyanine, isoindoline and triazine. Furthermore, it
can be seen that the absorption peak of nitrile groups at 2230 cm\(^{-1}\) did not change obviously before 210\(^\circ\)C, and the peak decreased between 210\(^\circ\)C and 250\(^\circ\)C, indicating that the nitrile groups polymerized between 210\(^\circ\)C and 250\(^\circ\)C, while the curing temperature of pure phthalonitrile(PN) is above 300\(^\circ\)C. It is the self-promoted effect of -Si-OH hydrolyzed from -Si-O-CH\(_2\)-CH\(_3\) that made the curing temperature lower than 250\(^\circ\)C. After DCA was cured, the nitrile peak did not disappear completely, because it produced triazine structure, and there were still half of nitrile groups left. The disappearance of alkyne absorption peaks at 3266cm\(^{-1}\) and 2105cm\(^{-1}\) indicated that DCA can co-cure with PSA. In summary, DCA can co-cure with PSA to establish chemical bonds between PSA and QF, and nitrile groups can homopolymerize to form a strong interfacial layer and improve the thermal stability of the QF/PSA composites.

![Figure 7. FTIR spectrum of curing DCA and cured structure](image)

3.3.2. **Differential Scanning calorimeter (DSC) analysis**

Figure 8 showed the DSC Curves of DC-1, DC-2, and DCA. Under catalytic conditions, the thermal curing temperature of -CN can be reduced to around 220\(^\circ\)C, and the curing exothermal peak is sharp. As shown in the figure, the curing exothermal peak of DC-1 is concentrated at 227.5\(^\circ\)C, while that of DC-2 is 223.7\(^\circ\)C, DCA is 229.1\(^\circ\)C. It can be proved that the coupling agent will cure at high temperature and form molecular interconnect, enhancing the interface adhesion. The curing peak of alkyne of DC-2 is at 243.5\(^\circ\)C, and that of DCA is at 258.0\(^\circ\)C, which can form a chemical bond with the coupling agent molecules, enhancing the interfacial bonding, thus provide the structural basis for curing with PSA, playing a bridging role between resin and fiber.

![Figure 8. DSC tracing at different stages a: DC-1, b:DC-2 c:DCA](image)
3.4. Mechanism of DCA

The mechanism of the coupling agent DCA can be naturally inferred from the evidence and analysis above. After hydrolysis, the ethoxy groups of DCA changed to -Si-OH which can form hydrogen bonds with the -Si-OH on the surface of QF, and then they can form -Si-O-Si- bonds after dehydration. The Alkynyl groups of DCA are able to co-cure with that of PSA and form benzene structure after cyclization reaction. So DCA can form chemical bonds as bridges between fibers and matrix. In addition, nitrile groups of DCA can also homopolymerize at 229.1°C, and form triazine structure which will enhance the interactions between DCA molecules and improve the high temperature performance. Besides these, DCA can etch the surface of QF and improve the roughness and surface energy, made it easier for QF and PSA to combine closely with each other. Because of the chemical and physical effects, DCA will remarkably improve the mechanical properties and heat resistance of QF/PSA composites.

3. Conclusion

In this paper, a novel silane coupling agent DCA was synthesized and characterized. It exerted excellent performance in QF/PSA composites because of the chemical bonds formed between fiber and matrix. After adding 2.0wt% DCA, the interlaminar shear strength(ILSS) increased by 63.3%. Due to the cyclization of nitrile groups and the formation of triazine, DCA showed outstanding heat resistance, and ILSS retention rate of composites was 54.7% at 500°C. All the brilliant characteristics indicated that DCA had potential application in the field of aerospace.

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