Improved adhesion performances of aramid fibers with vinyl epoxy via supercritical carbon dioxide modification

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Abstract. In this paper, aramid fibers were treated under supercritical carbon dioxide (SCCO₂) with isocyanate terminated liquid nitrile rubber to improve the adhesion performances of vinyl epoxy composites. The interfacial shear strength (IFSS) of vinyl epoxy composites was investigated by micro-bond test. The results indicate that the surface modification of aramid fibers in SCCO₂ was an efficient method to increase the adhesion performances between fibers and vinyl epoxy. Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) were adopted to investigate the surface structure and composition of aramid fibers. The flexural strength and interlaminar shear strength (ILSS) of treated aramid fibers/vinyl epoxy composites was improved by 18.1% and 28.9% compared with untreated aramid fibers, respectively. Furthermore, the fractured surfaces of the composites were observed by SEM, which showed that the interfacial adhesion of composites has been remarkably changed.

1. Introduction
Aramid fiber (AF) has triggered tremendous attention due to its unique characteristics, such as high tensile and modulus strength, low density and high thermal resistance[1-3], and it can be used as reinforced materials of advanced composites in a wide range of industrial fields such as aerospace, sports, automobiles and aviation [4-8]. However, due to the poor adhesion performances between aramid fibers and matrix, the application of the composites materials was limited[9]. Numerous efforts have been devoted to improve the interfacial characteristics of the aramid fiber/matrix composites, such as chemical etching and grafting[10-14], plasma treatment[15-17], ultrasound[18] and polymer coating[19-22]. However, these methods require harsh reaction conditions and may destroy the tensile strength of the aramid fibers.

Supercritical carbon dioxide (SCCO₂) has been widely used in many fields arising from its low viscosity and negligible surface tension. In this context, examples include polymer processing, food, cosmetics and pharmaceuticals industries[23-26]. SCCO₂ is an effective method for surface modification of fibers, owing to its liquid and gas properties and liquid-like density[27]. For example, Zhao et al. employed the mixture of SCCO₂ and organometallic complex for impregnation of the aramid fibers to prepare electro conductive composite fabricies[28]. Zheng and co-workers systematically investigated the effects of the SCCO₂ fluid on the structures and properties of the PMIA
fiber [29-30]. Our previous work also demonstrated the improved interfacial shear strength of the PPTA fiber-based epoxy composites by modification of the fibers in SCCO$_2$ with Hexamethylene Diisocyanate [7]. However, this method can only improve the interfacial adhesion toward epoxy. In order to extend the scope of this strategy to aramid fiber for other resins composites, it requires one to introduce a new type of isocyanate in SCCO$_2$ condition, which can enhance the interfacial adhesion of composites based on various resins such as epoxy, rubber and vinyl epoxy resin.

In this study, we introduced a long flexible chain segment with isocyanate terminated liquid nitrile rubber in SCCO$_2$, which can improve interfacial adhesion of the vinyl epoxy resin. Isocyanate terminated liquid nitrile rubber, on the one hand, contains CH=CH group that can react with the vinyl group of the vinyl epoxy resin under curing agents to improve interfacial adhesion of vinyl epoxy composites, on the other hand, can improve interfacial adhesion of the epoxy composites in SCCO$_2$. Based on these points, isocyanate terminated liquid nitrile rubber was firstly adopted to treat the surface of aramid fibers in SCCO$_2$ for improving the interfacial adhesion of the vinyl epoxy resin. The micro-debond tests was utilized to characterize the IFSS of the aramid fibers with vinyl epoxy. The effects of treatment pressure, time, temperature and concentration on the IFSS in SCCO$_2$ with isocyanate terminated liquid nitrile rubber was discussed, and the results indicated that the IFSS was improved by 44.4% under the optimum treatment conditions. The chemical microstructures and compositions of the aramid fiber were investigated by FT-IR and XPS. The morphology of the aramid fibers was investigated by scanning electron microscopy (SEM). To illustrate the effect of the mechanical properties of composites, the ILSS were also discussed. In additional, SEM was carried out to illustrate the tensile fractured surfaces of composites.

2. Experiment

2.1. Materials
Isocyanate terminated liquid nitrile rubber was synthesized in our lab, carbon dioxide (CO$_2$) gas (99.99% pure) was supplied by Shanghai Chenggong Gases Co., Ltd. Acetone with analytical regent grade was purchased from Sinopharm Chemicl Reagent Co., Ltd. The aramid fibers (K49) with a diameter of 15 um were supplied by DuPont Co., Ltd. The fibers were extracted with acetone overnight and dried at 60 °C for 6 h before use. Vinyl epoxy resin (MFE-2) was purchased from Sino Polymer Co., Ltd, China. Cobalt (II) naphthenate was bought from Sinopharm Chemicl Reagent Co., Ltd. 2-Butanone peroxide was purchased from Shanghai Aladdin biological Co., Ltd. The ratio of the vinyl epoxy resin and curing agent is100:1.5:1 (resin: 2-Butanone: cobalt (II) naphthenate).

2.2. Treatment of aramid fibers in SCCO$_2$
The treatment of aramid fibers in SCCO$_2$ was demonstrated in previous studies [7]. Briefly, the aramid fibers were purified with acetone and washed with distilled water at room temperature, and then dried in a vacuum oven at 100 °C for 12 h to remove residues. The pretreated aramid fibers were added in isocyanate terminated liquid nitrile rubber-acetone solution by a stainless steel filter. Then CO$_2$ was pressurized through a high-pressure pump at a desired temperature for several hours. Finally, the treated aramid fibers were obtained after washing by acetone for several times and dried at 80 °C in a vacuum oven for overnight.

2.3. Preparation of epoxy resin composites
The vinyl epoxy resin and curing agent were added prior to hand mixing for approximately 20 min. The vinyl epoxy resin and curing agent were mixed and degassed by a vacuum pump. Then, the resin mixture was poured into the mold, followed by adding pretreated aramid fibers. Then aramid fabric was stacked in the mold cavity. The samples were precured at 80 °C for 2 h and then postcured at 130 °C for 3 h under a certain pressure. Then the cured specimens were slowly cooled to room temperature.
2.4. Characterization
An Infrared spectrometer (Nicolet 8700) was used to measure the change of the surface structure of the aramid fibers at room temperature ranging from 4000 to 500 cm\(^{-1}\). The surface morphology of the aramid fibers and tensile fractured surfaces of the composites were analyzed by scanning electron microscopy (FE-SEM, Su8010, Hitachi, Japan). The surface chemical composition of the aramid fibers was performed by X-ray photoelectron spectroscopy (XPS) on a RBD upgrade PHI-5000C ESCA system (USA). The XPS spectra was provided by Mg K\(_\alpha\) radiation (h=1253.6 eV) source with power of 250 w, high voltage of 14.0 kV at a detection angle of 54\(^{\circ}\). The IFSS of the fiber/epoxy composites was evaluated by micro-bond technique, the epoxy resin mixture was dropped on the aramid fibers, and the microdroplet resin were formed on the monofilament fiber then the specimens were cured at 120 °C in a vacuum oven for 6 h. The micro-bond tests were measured on an XQ-1 fiber tensile testing machine with an upper clamp displacement rate of 0.1 mm/min. The IFSS was calculated by the following equation:

\[
\text{IFSS} = \frac{F}{\Pi dL}
\]

where F is the maximum pullout force, d is the fiber diameter, and L is the microdroplet embedded length of the aramid fibers in vinyl epoxy resin. The average value of the sample showed was an average of 30 tests. The flexural strength and ILSS of the aramid fiber/vinyl epoxy composites were measured at room temperature using a LD24 microcomputer control electronic testing machine (Shenzhen, China). The flexural test was performed on a three point bending using ASTM D790 system, while ILSS was measured using ASTM D2344 system. More than five parallel samples were measured for each test.

3. Result and discussion
3.1. Interfacial adhesion of vinyl epoxy resin to aramid fiber
Figure 1 shows the IFSS of vinyl epoxy resin to aramid fibers under different treatment conditions. Figure 1a demonstrates that the IFSS increases firstly and then decreases with the increase of treatment concentration under the treatment conditions at 100 °C, 13 MPa and 60 min. It can be observed that the optimum concentration was 0.15%. The best value of the IFSS was acquired when the treatment time was 60 min when the treatment temperature was 100 °C, pressure was 13 MPa and concentration was 0.15% (Figure 1b). As shown in Figure 1c, the IFSS of the epoxy resin to aramid fiber increases to maximum at 100 °C, and then decreases when temperature higher than 100 °C. Meanwhile, it can be seen from Figure 1d that the IFSS displays the same tendency with Figure 1c. From the above results, one can conclude that the optimum processing conditions were achieved with treatment temperature of 100 °C, treatment time of 60 min, pressure of 13 MPa and concentration of 0.15%. The IFSS was improved by 44.4% under the optimum treatment conditions. In brief, the adhesion properties of vinyl epoxy resin to aramid fibers were obviously improved after SCCO\(_2\) treatment with isocyanate terminated liquid nitrile rubber. This reveals that SCCO\(_2\) treatment with isocyanate terminated liquid nitrile rubber was an effective approach to improve the interfacial properties. To further illustrate this reason, we propose a possible reaction mechanism, as shown in Figure 2. The reason was that CH=CH group would undergo a cross-linking reaction with CH=CH of vinyl epoxy resin in the presence of curing agents. In addition, the as-generated –NH\(_2\) groups can react with epoxy to improve the interfacial adhesion of the epoxy resin. The related results were reported in our previous work[7].
Figure 1. IFSS of aramid fibers/vinyl epoxy composites at different treatment conditions: concentration (a), time (b), temperature (c) and pressure (d).

Figure 2. The proposed mechanism of the reaction between aramid fibers and vinyl epoxy resin.

3.2. Surface chemical structure of the modified aramid fibers

FTIR was employed to investigate the chemical structures of the aramid fibers before and after treatment in SCCO₂ condition with isocyanate terminated liquid nitrile rubber. As shown in Figure 3a, the characteristic absorption bands at 3320 cm⁻¹ were assigned to hydrogen bonded N-H band, 1645 cm⁻¹ was originated from amide I, and 1542 cm⁻¹ was assigned to amide II, respectively. Compared to those of untreated aramid fiber, new absorption bands at 2919, 2847 and 1450 cm⁻¹ were attributed to CH₂ asymmetric stretch vibration, CH₂ symmetric stretch vibration and CH stretching vibration plane, respectively. Furthermore, the absorption bands at 2284, 2238 and 967 cm⁻¹ can be assigned to CNO, CN and CH=CH stretch vibration. After treatment with isocyanate terminated liquid nitrile rubber in
SCCO$_2$, the intensity of the characteristic bands at 1511 cm$^{-1}$ became stronger (Figure 3b), this shift may be attributed to the combination of CO-NHR. The results showed that new groups (NH$_2$) were formed during this treatment, which is favorable to produce reaction with epoxy resin. It is possibly that –CNO groups can react with –NH$_2$, –NHCO and –COOH groups in aramid fibers to form a certain degree of grafting and cross-linking[31].

![Figure 3](image-url)  
**Figure 3.** FTIR spectrum of aramid fibers before and after treatment in SCCO$_2$ with isocyanate terminated liquid nitrile rubber with wavenumber ranging from 600-4000 cm$^{-1}$ (a) and 1400-1600 cm$^{-1}$ (b).

3.3. Surface chemical composition of the treated aramid fibers

The surface chemical composition of the aramid fibers was observed by XPS measurements. It can be seen from Table 1 that after treated in SCCO$_2$, the atomic concentration of oxygen (O) and the ratio of oxygen to carbon (O/C) were slightly increased from 20.4 to 20.6 and 0.26 to 0.27, respectively. It is worth noting that the atomic concentration of nitrogen (N) increased from 1.2% to 2.1% and the ratio of nitrogen to carbon (N/C) increased from 0.015 to 0.023. To investigate the change of the chemical interactions, as shown in Figure 4, the C 1s spectrum was deconvolved in four components, i.e., C-C (284.2 eV), C-N/C=O (285.5 eV), C=O (287.3 eV) and O-C=O (288.5 eV) groups. As a comparison, the same components in the original sample after the SCCO$_2$ treatment were also observed, with some slight changes on the fiber surface. As shown in Table 2, the content of C-C group decreased from 89.8% to 89.1%, while the C-O/C-N and C=O groups respectively increased from 1.4% to 2.1, and 3.3% to 4.4%. In addition, the O=C=O group decreased slightly after SCCO$_2$ treatment. These results revealed the presence of some functional groups formed on aramid fiber surface. The reason was that there were some polar groups could be introduced through reactions between CNO and the fiber surface after SCCO$_2$ treatment. It also can well explain the improved adhesive properties between aramid fiber and epoxy resin matrix.

Table 1. Surface elements of aramid fibers before and after treatment in SCCO$_2$ with isocyanate terminated liquid nitrile rubber.

| Samples          | Atomic concentration (%) | Atomic ratio |
|------------------|---------------------------|--------------|
|                  | C     | N    | O    | O/C  | N/C  |
| Untreated AF     | 78.4  | 1.2  | 20.4 | 0.26 | 0.015|
| Untreated AF     | 77.3  | 2.1  | 20.6 | 0.27 | 0.027|
Figure 4. C 1s spectra of the untreated aramid fibers (a) and treated ones in SCCO$_2$ with isocyanate terminated liquid nitrile rubber (b).

Table 2. Deconvolution analysis of C 1s peaks of the untreated and treated aramid fibers in SCCO$_2$ with isocyanate terminated liquid nitrile rubber.

| Sample    | C-C   | C-N/C-O | C=O   | O-C=O |
|-----------|-------|---------|-------|-------|
| Untreated | 89.8  | 1.4     | 3.3   | 4.8   |
| Treated   | 89.1  | 2.1     | 4.4   | 4.4   |

3.4. Surface morphology of the aramid fibers

The surface morphology of the aramid fibers before and after SCCO$_2$ treatment with isocyanate terminated liquid nitrile rubber was estimated by SEM. As shown in Figure 5a, the surface of the pristine fibers is extremely smooth and clean, which is similar to our previous report[7]. Compared to Figure 5a, the aramid fiber after treated in SCCO$_2$ with isocyanate terminated liquid nitrile rubber, a much rough surface was observed due to the formation of a thin layer of the polymer coating (Figure 5b). The structure transformation enables the compatibility of the aramid fibers and the vinyl epoxy resin, thus, can enhance the adhesion properties of the aramid fibers/vinyl epoxy composites.

Figure 5. Surface morphology of the untreated aramid fibers (a) and those treated in SCCO$_2$ with isocyanate terminated liquid nitrile rubber (b).

3.5. Mechanical properties of the aramid fibers reinforced vinyl epoxy resin composites

The flexural properties of the aramid fibers/vinyl epoxy resin composites were initially measured by three-point flexural method. As shown in Figure 6a, it is apparent that the flexural strength of the aramid fibers treated by SCCO$_2$ of vinyl epoxy composites was 18.1% higher than that of the untreated
aramid fibers. This indicates that SCCO$_2$ could improve interfacial adhesion between the fibers and the matrix. The ILSS was used to further investigate the interfacial adhesion between fibers and matrix. It can be seen from figure 6b that after treated in SCCO$_2$ with isocyanate terminated liquid nitrile rubber, the ILSS was increased from 42.5 MPa to 54.8 MPa. The improvement of flexural strength and ILSS of the aramid fibers/vinyl epoxy composites was given rise to the cross-linking reaction between CH=CH bonds and vinyl groups of vinyl epoxy resin.

Figure 6. The mechanical properties of the aramid fibers reinforced vinyl epoxy composites.

3.6. Fracture morphology of the composites
To directly investigate the interfacial adhesion in aramid fibers/vinyl epoxy composites, the fractured surfaces of the composites was measured by SEM. The fracture surface morphologies of the aramid fibers/vinyl epoxy composites are shown in Figure 7. It can be seen from Figure 7a that the pull-out of the aramid fibers was relatively smooth with a small amount of resin. However, it is obvious that the entire fiber surface were wrapped with a thin layer of resin after SCCO$_2$ treatment (Figure 7b). These results showed that the interfacial adhesion of the aramid fibers treatment in SCCO$_2$ has been remarkably changed. The results agreed well with the above interfacial and mechanical properties.

Figure 7. SEM images of the untreated (a) and SCCO$_2$ treated (b) fracture aramid fibers reinforced vinyl epoxy composites.

4. Conclusion
In summary, we developed an efficient method to improve the adhesion performances of the aramid fiber for composites. Isocyanate terminated liquid nitrile rubber was successfully introduced to the surface of the aramid fibers in SCCO$_2$. The adhesion properties of the aramid fibers were improved by 44.4% after SCCO$_2$ treatment with isocyanate terminated liquid nitrile rubber. Furthermore, SEM was
also measured the fractured surfaces of composites, the results showed the interfacial adhesion of the aramid fibers after SCCO₂ treatment with isocyanate terminated liquid nitrile rubber for vinyl epoxy resin composites was greatly changed. We believe the processes provide a new approach to prepare composites with enhanced adhesion properties, making it possible to be used in preparation of other composites.

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