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Effect of Calcium Chloride on the Surface Properties of Kevlar Fiber

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ABSTRACT: In this study, we present a new approach to modify the surface of Kevlar-29 fiber by the complexation. The surface of Kevlar-29 fiber was treated by calcium chloride ($CaCl_2$) ethanol solution. The structure and morphology of the modified Kevlar-29 fiber were characterized by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction instrument, atomic force microscopy, and scanning electron microscopy. The results showed that $CaCl_2$ treatment's method can cause changes of the chemical groups of Kevlar-29 fiber. The amino-groups of Kevlar-29 fiber were freed and the contents of -C-N- increased. The changes can improve the surface roughness of Kevlar-29 fibers. This can increase the adhesive of Kevlar fiber/epoxy composites. From the ILSS and mechanical properties values, it can be concluded that treatment with 5 wt % $CaCl_2$ for 5 h is the optimum complexation condition. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41358.

KEYWORDS: composites; fibers; morphology

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INTRODUCTION

Kevlar fiber exhibits an excellent thermal stability, lightweight, lower dielectric, as well as superior tensile strength and modulus and chemical inertness. Science it came to market in 1972, they are widely used as an excellent reinforcement material for the advanced polymer composites such as fiber-reinforced composites, rubber goods, ropes and cables, ballistic, gaskets, and so forth.[1–3]

However, the Kevlar fiber-reinorced composites show poor interfacial adhesion between the Kevlar fiber and matrix resin, due to the low surface energy and chemically inert surface of the fiber.[4] So the interfacial adhesion between the fiber and the matrix has been known as a key factor that determines the mechanical interfacial strength of fiber-reinforced polymer matrix composites. Therefore, surface modification or functionalization of Kevlar fiber is considerably urgent and necessary to obtain high performance Kevlar fiber/epoxy composites from effective interfacial interaction.

Various methods of fiber surface modification or functionalization such as plasma treatment,[5–11] heat treatment,[1] chlorosulfonation,[9] aceticanhydride treatment,[4] and graft polymerization[12,13] have been developed. However, there were few reports on using complexation method on Kevlar fiber surface modification. Roberts and Jenekhe have demonstrated that polyamides can undergo complex formation with strong Lewis acids such as $GaCl_3$, and $AlCl_3$, by reacting with the Lewis base sites, CONH, in the polymer chain.[14–16] This knowledge opens up the possibility to deform the polymer and manipulate the molecular arrangements in the absence of crystallinity and hydrogen bonding. Vasanthan,[17] Yang et al.,[18] and Zhang et al.[19] have used $GaCl_3$ and $CaCl_2$ complexing with carbonyl groups to disrupt hydrogen bonding in polyamide. Kevlar fiber has the same structure aramid group as polyamide. So we can use the same method to modify Kevlar fiber.

In this article, we have investigated the possibility of calcium chloride modifying Kevlar fiber. The surface of Kevlar fibers were modified using calcium chloride ethanol solution in order to increase the interfacial properties between Kevlar fiber and epoxy. After the modification, the interfacial adhesion of Kevlar fiber reinforced epoxy resin composites was evaluated by interlaminar shear strength (ILSS). The crystalline state of Kevlar fibers was determined by X-ray diffraction instrument (XRD). The surface elements of Kevlar fibers were determined by X-ray photoelectron spectroscopy (XPS). The possible changes of the chemical structure of Kevlar fibers were investigated by Fourier transform infrared spectrum (FTIR). The surface morphology and roughness of Kevlar fibers were analyzed by Scanning electron microscope (SEM) and Atomic force microscopy (AFM).

EXPERIMENTAL

Materials

The Kevlar fibers used in this study were Kevlar 29 (Type 956, 1670 Dtex, 1500D, manufactured by Du Pont, USA). Calcium

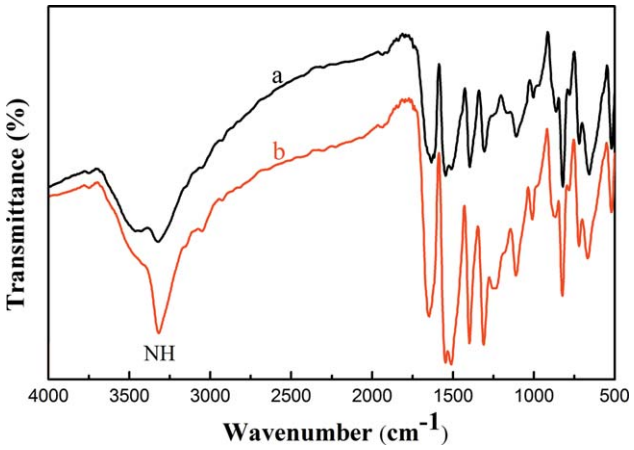
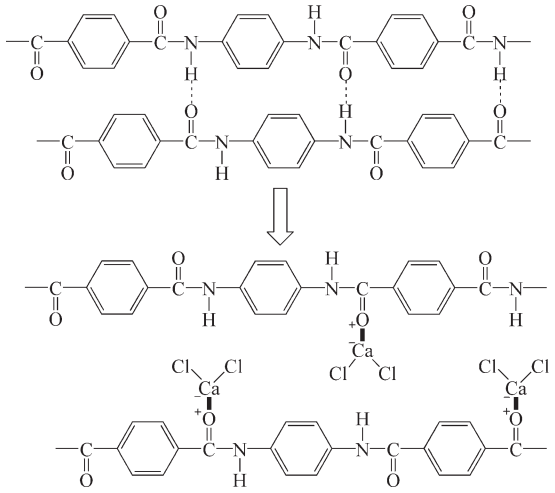


Figure 1. FTIR spectra of Kevlar fiber (a) untreated; (b) treated with 5 wt % $CaCl_2$ for 5 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 1. Schematic illustration of hydrogen-bonded sheet structure of Kevlar fiber and $CaCl_2$-Kevlar complex.

chloride (AR), Acetone (AR), and Anhydrous ethanol were obtained from Chongqing Chuandong Chemical (Group). Deionized water obtained from a Millipore Milli-Q water purification system. Epoxy resins were diglycidylether of bisphenol-A (DGEBA, 618), which had an epoxide equivalent weight of 185∼210 g/eq, hardener was methyl tetrahydrophthalic anhydride (MeTHPA) both supplied by Shanghai Resin, China.

Samples Preparation

Before the surface modification, the Kevlar-29 fiber was pretreated with acetone to eliminate the surface's contamination. After being dried in the oven for 3 h at 100°C, the fiber was cooled to room temperature and put in a desiccator for storage.

Surface Treatment

Firstly, the calcium chloride ethanol solution was prepared containing 95 mL ethanol, 5 g $CaCl_2$, then transferred them into a 3-mouth flask and then the flask was warmed to 79°C (the boiling point of ethanol) in the water bath. Subsequently, the fibers were added and the modification reaction carried out for different treatment time (0 h, 2 h, 3 h, 5 h, 9 h), and different concentration (1, 3, 5, 7, 10 wt %). Moreover, the reasons, why the reaction temperature was set to such a high level, are that: (1) a stronger reaction condition is needed to destroy the hydrogen bond between the chains of fiber; (2) the ebullition of the whole reaction system at the boiling point of ethanol can produce an ideal vibration to replace the mechanical agitation which will make Kevlar-29 fibers entwine the stirrer and contact with the treatment reagent insufficiently.[20] At the same time, a condensate reflux device is needed by the flask to avoid ethanol vaporizing too fast to receive a satisfied modification result. After modification the aramid fibers were taken out from the flask and washed several times in acetone to remove any unreacted reagent, and rinsed in deionized water. Finally, the fibers were placed in a soxhlet apparatus to extract for 2 h with deionized water, and then dried at room temperature in vacuum oven for 24 h.

Composites Samples Preparation

Kevlar fiber/epoxy composites were fabricated using the untreated and treated fibers as reinforcements according to the previous literature.[12] Unidirectional composite laminates were prepared by continuous impregnation of the fibers using a drum winding technique for manufacturing prepregs with subsequent hot pressing. Laminates were made with 20 plies of prepregs. The unidirectional samples were cured under ambient condition at 80°C for 2 h, followed by 3 h at 150°C at a pressure of 2 Mpa. The mold was cooled to room temperature before the presure was released. Then cut into 20 mm × 10 mm × 2 mm. The Kevlar fiber/epoxy composites were controlled to contain 55% weight fraction of Kevlar fiber.

MEASUREMENTS

FTIR Analysis

To analyze the functional groups on the surface of the untreated and treated Kevlar fibers, FTIR spectroscopy measurements (NEXUS670, Thermo Instrument, USA) in the mid infrared (4000–500 cm^{-1}) were performed. The specimens must be dried sufficiently to avoid the disturbance of water. FTIR spectra were recorded on powder samples, which were obtained from the cut Kevlar fibers, dispersed in dry KBr using Bruker IFS/66v. Moreover, the fibers must be finely cut into segments (length is <1 mm) via a special cutting machine before being mixed with potassium bromide, because it is so easy for Infrared light wave to be reflected by long fibers that the analysis sensitivity and precision will be decreased enormously. After the preparation, the FTIR spectra of original and treated Kevlar fibers were recorded on a Nicolet 5700 spectrometer using potassium bromide pellet technique and the scanning was carried out from 500 cm^{-1} to 4000 cm^{-1}.

XPS Analysis

The surface elements and functional groups analysis of Kevlar fibers were performed by XPS (Axis Ultra DLD, Kratos, England) equipped with an Al-Kα X-ray source. The base pressure in the sample chamber was controlled in the range of 10^{-8} to 10^{-9} Torr.

SEM Analysis

The surface conditions of the Kevlar fibers with $CaCl_2$ treatment and unidirectional Kevlar fiber composites were observed by

Table I. Chemical Compositions on the Surfaces of Untreated and $CaCl_2$-Treated Kevlar Fibers (for 5 h, 5 wt %)

	Chemical composition (at %)					Atom ratio (%)	
Sample	C	N	O	Ca	Cl	O/C	N/C
Untreated	79.97	4.56	15.47	0	0	0.19	0.057
Treated	77.12	5.49	15.64	0.73	1.02	0.20	0.071

SEM (Model JSM-7500F, JEOL. Japan), with magnifications setting at 5000X. The surfaces of the specimens were fixed to a copper stub by a conductive adhesive, then, sputtered coated with a thin layer of platinum prior to SEM examination.

AFM Analysis

Surface roughness and morphologies of Kevlar fibers were analyzed by AFM (Dimension Icon, Bruker, Germany). The images with a $4 \times 4\ \mu m^2$ scan area were obtained under the tapping mode. The roughness of fiber surface was characterized by mean square roughness (Rq) and arithmetic mean roughness (Ra) calculated automatically by the software.

Mechanical Properties Analysis

Fiber mechanical properties were obtained using a fiber tensile machine (XQ-1C, Shanghai New Fiber Instrument, China). All tests were performed on single filaments using a gauge length of 20mm and crosshead speed of 10 mm/min at room temperature according to GB/T 14337-2008. The average of 50 fibers was presented for each sample.

XRD Analysis

The crystal structure of Kevlar fibers with and without the treatment was determined by XRD instrument (X'Pert Pro MPD, PANalytical, Holland). The preparation process of the specimens used for XRD test was as follows: the adequate length fibers were homogeneously laid on the special slide, and then the two ends of fibers were fixed on the edge of the slide with double-faced adhesive tape. The test conditions were Cu K_α-radiation ($\lambda = 1.54 \times 10^{-10}$ m), tube voltage 40 kV, current 40 mA, sequential scanning counting mode and diffraction angle (2θ) range 0°–45°. The scanning speed was 4°/min, scanning step was 0.02°. The crystallinity degree (X_{CR}) was calculated as the ratio of deconvoluted diffraction peaks areas to the total scatter under the normalized intensity scan by the equation

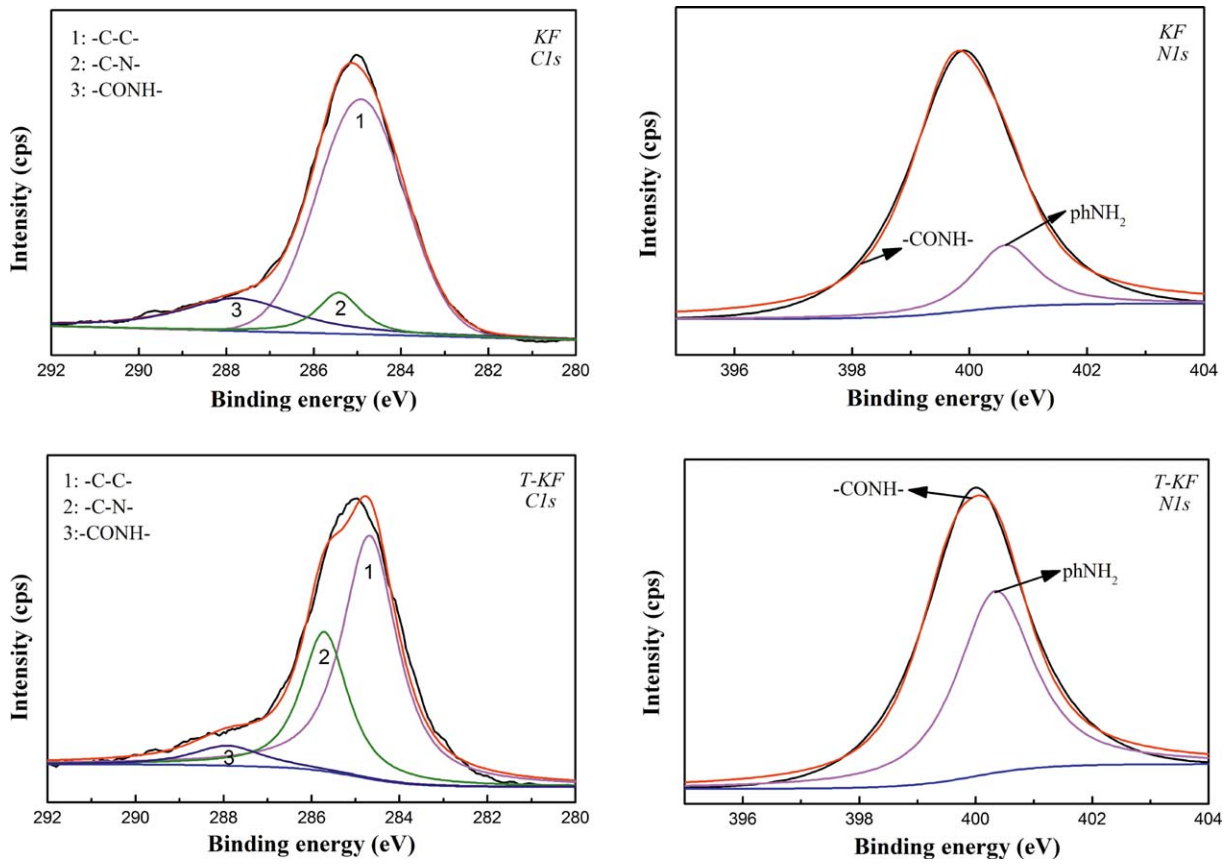


Figure 2. XPS spectra of C1s and N1s for untreated Kevlar fiber (KF) and $CaCl_2$-treated Kevlar fibers for 5 h, 5 wt % (T-KF). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Deconvolution Analysis of C1s Peaks of Untreated and $CaCl_2$-Treated Kevlar Fibers (for 5 h, 5 wt %)

	Content of functional group (at %)		
Sample	—C—C—	—C—N—	—CONH—
Untreated	72.84	18.32	8.84
Treated	62.73	30.65	6.62

$$X_{CR}=\frac{\sum_{i=1}^{B}\int_{2\theta_1}^{2\theta_2} I_i(2\theta)d(2\theta)}{\int_{2\theta_1}^{2\theta_2} I_T(2\theta)d(2\theta)} \quad (1)$$

where B is the number of deconvoluted peaks.

Interlaminar Shear Strength

The ILSS was used to estimate the interfacial adhesion strength of the composites according to a previous report,[12] using the short-beam method by ASTM-D-2344. Specimen demensions were norminally 20 mm × 10 mm × 2 mm, with a span to thickness ratio of 5 : 1. The specimen was tested at a rate of cross-head movement 1 mm/min. The condition of the test specimen and the test in an enclosed space was maintained at 23°C and 50% relative humidity. The ILSS, τ, for the short-beam test is calculated by the equation:

$$\tau=\frac{3P}{4Bh} \quad (2)$$

where P is the maximum load in Newtons, B is the width of specimen in m, and h is the thickness of specimen in m. Each reported ILSS value is the average of more than 10 successful measurements.

RESULTS AND DISCUSSION

Effects of $CaCl_2$ Treatment on the Chemistry of Kevlar Fibers

FTIR spectra of untreated and treated fiber are shown in Figure 1. The appearance of three peaks, attributed to the absorption bands of para-aromatic ring (818 cm^{-1}), N—H (3400 cm^{-1}) and —C═O (1645 cm^{-1}) groups, respectively, represents the ontology structure of Kevlar fibers.[8] Compared with the spectrum of untreated fiber, the treated fiber shows a higher intensity at 3400 cm^{-1}, while the stretching vibration peak at 1650 cm^{-1} almost has no increase. These changes suggest that $CaCl_2$ and —C═O group formed a complex after the treatment, and the complexation destroyed the hydrogen bond and made the N—H free.

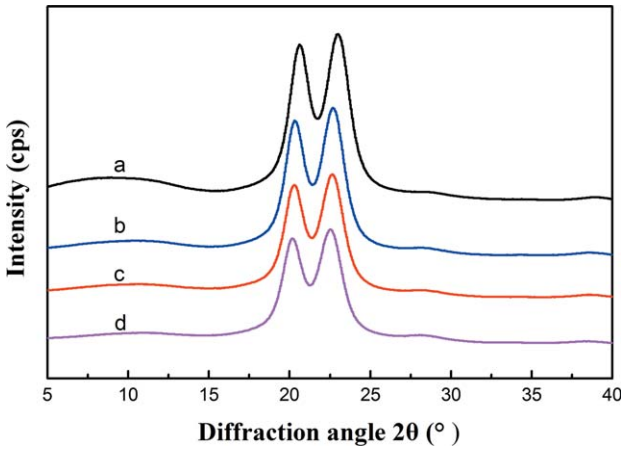


Figure 4. X-ray diffraction of Kevlar fibers treated with $CaCl_2$ for different time: (a) 0 h, (b) 2 h, (c) 5 h, (d) 9 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The amide group is potentially a bi-functional electron donor with $2sp^2$ "lone pairs" at the oxygen atom and a $2p_z^2$ "lone pair" at the nitrogen atom, and therefore it has two possible electron-donating sites to coordinate with the Ca^{2+} cation.[18] Overlap of $2p_z$ orbital of the benzene ring, carbon, and oxygen atoms in the planar amide group would reduce the electron density on the nitrogen atom, and favor the coordination of the metal ion with the carbonyl oxygen atom. This can prove that the Ca^{2+} cation indeed coordinated with carbonyl oxygen atom of the modified fibers. Scheme 1 shows the possible complexation reactions of $CaCl_2$ and Kevlar fiber.

XPS is a very useful technique in the determination of the chemical composition and functional groups of the fiber surface and the testing depth is about 5 nm. The surface of the fiber can be understood easily by XPS. Table I shows the relative chemical compositions on the surface of untreated and treated

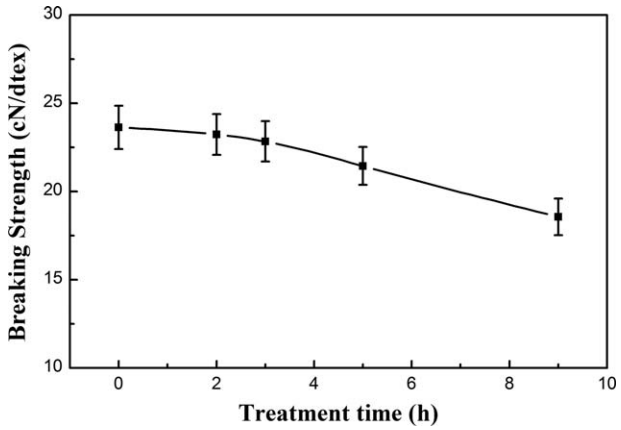


Figure 3. Mechanical properties of Kevlar fiber with different treatment time.

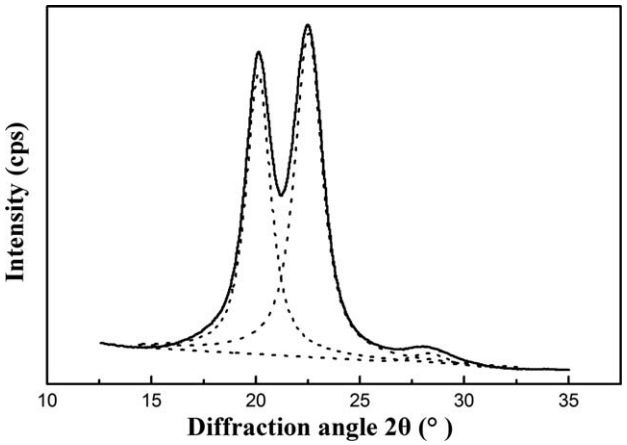


Figure 5. The fitting curves of XRD patterns.

Table III. Crystallinity of the Fibers with Different Treatment Time

Treatment time (h)	Crystallinity (%)
0	80.68
2	78.67
5	65.32
9	58.76

Kevlar fibers (for 5 h, 5 wt %). It was found that the carbon concentration on the surface of treated fiber was smaller than that of untreated fiber, while the nitrogen concentration of treated fiber was larger than that of untreated fiber. Specifically, the ratio of N/C increased from 0.057% to 0.071%, while the ratio of O/C changed very little during the process of $CaCl_2$ treatment, indicating that $CaCl_2$ treatment can change the amount of nitrogen on the surface of Kevlar fibers. Meanwhile. The treated Kevlar fiber contained 0.73% calcium and 1.02% chloride on the surface, which indicated that Kevlar fiber was complexing with $CaCl_2$. The content of $CaCl_2$ was low, which may due to the decomplexed during the washing process.[20]

To further compare the chemistries changes between untreated Kevlar fiber (KF) and treated Kevlar fiber (T-KF), the deconvolution analysis of C1s and N1s peaks in XPS spectra were performed to study the concentration of various functional groups.[7] Figure 2 shows the C1s spectra of KF and T-KF. The C1s spectra can only be fitted to three separate peaks with a binding energy near about 284.8, 285.3 and 287.7 eV, attributed to —C—C—, —C—N—, and —C═O, respectively. The content of functional groups can be caculated from the related peak areas in XPS C1s spectra, as shown in Table II . The most significant difference between the spectra of KF and T-KF was the content changes of —C—N—, which increased sharply from 18.32% to 30.65% during the process of $CaCl_2$ treatment. The content's increasing of $phNH_2$ can be obviously observed from the deconvolution analysis of N1s. The results illustrated that $CaCl_2$ and —C═O group formed a complex after the treatment, which made the —N—H bond free. These conform to the results of FTIR.

Effects of $CaCl_2$ Treatment on the Mechanical Properties and Structure

The mechanical properties of Kevlar fiber treated with 5 wt % $CaCl_2$ with different time were investigated to study the effect of complexation on fiber breaking strength.[21,22] The results are shown in Figure 3. It can be found that with the increase of treatment time the breaking strength decreased obviously. The breaking strength of the untreated fiber was 23.63 cN/dtex, after treated with 9 h it decreased to 18.56 cN/dtex. This was because

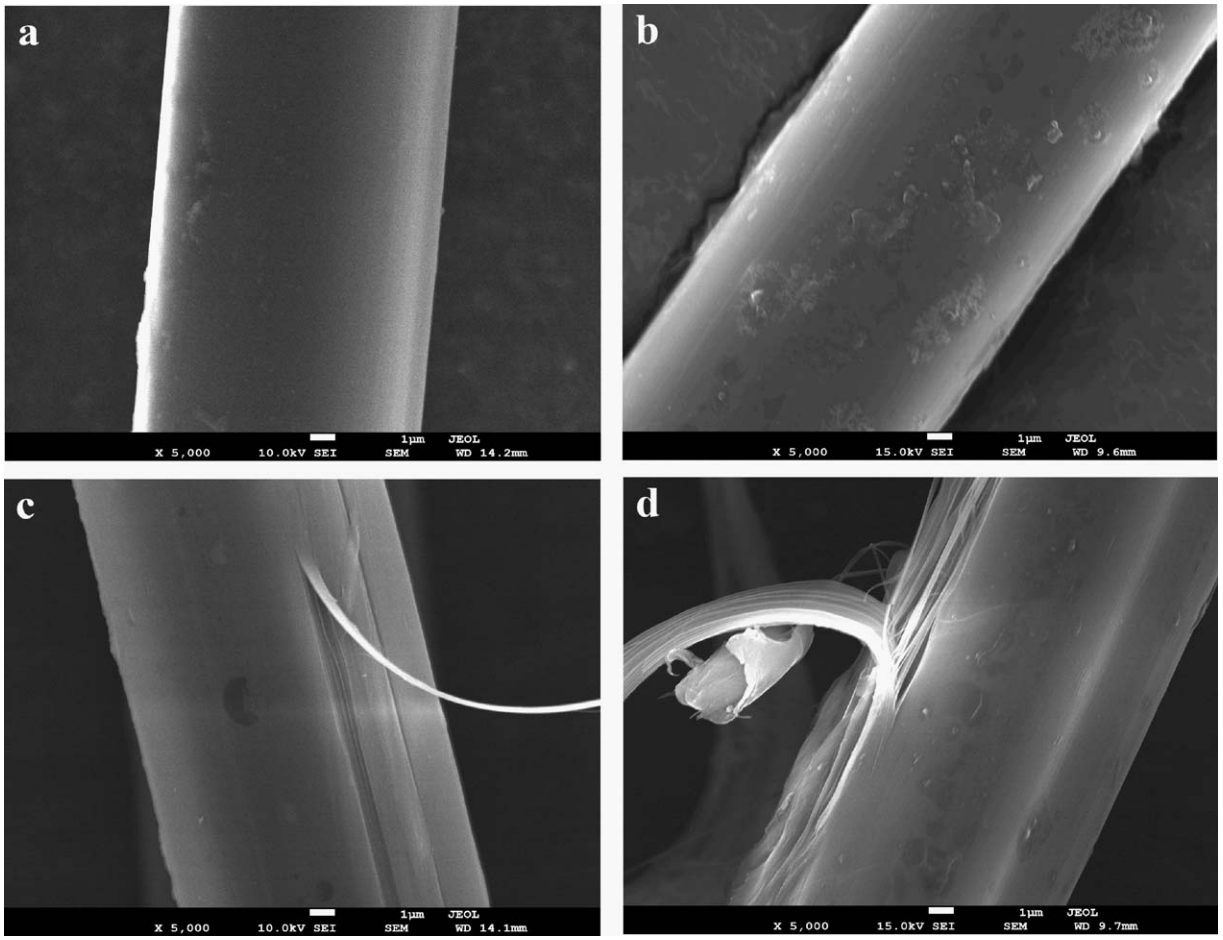


Figure 6. SEM images of Kevlar fiber treated with $CaCl_2$ for different time: (a) untreated fibers, (b) 2 h, (c) 5 h (d) 9 h.

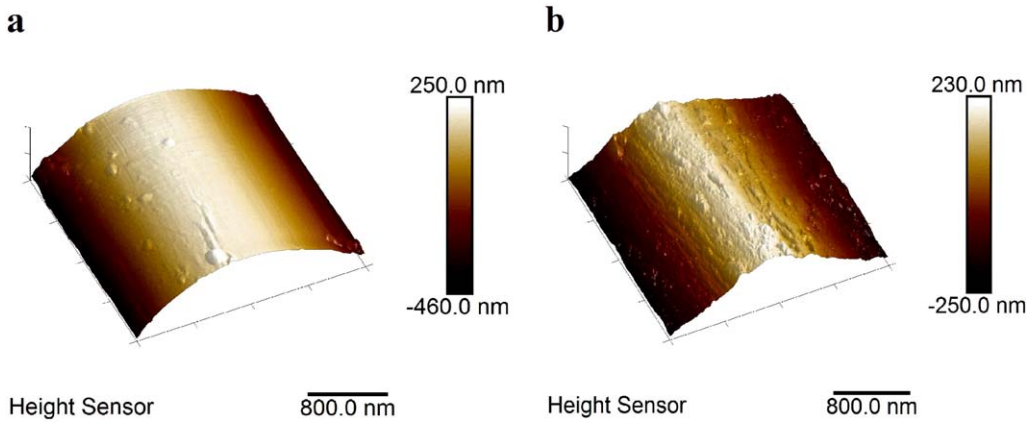


Figure 7. AFM images of Kevlar fibers: (a) untreated; (b) treated with5 wt % $CaCl_2$ for 5 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the complexation destroyed the fiber and it verifies the SEM results. So $CaCl_2$ treatment not only can increase the roughness but also decrease the strength of fiber.

Kevlar fiber is a compound linear chain macromolecule material which has high crystallization and high orientation.[23,24] The crystal structure of Kevlar fiber has been often investigated by means of wide-angle X-ray diffraction.[25,26] The fibers treated with different time (0 h, 2 h, 5 h, 9 h) were chosen to analyze the effect of treatment time on crystal properties. The results are shown in Figure 4. Peak fitting was determined using a regression analysis according to the previous studies.[27,28] Gaussian function was found to give a better fit shown in Figure 5. The X-ray diffractogram of the studied Kevlar fiber sample contains three peaks at $2\theta \approx 20.8°$, 23°, and 29° corresponding, respectively, to the (110), (200), (211) reflections.[29] It was shown that there was no distinct variety from among the XRD spectra, and no additional diffraction peak appeared, which indicated the fact that the new method did not change the crystal type. However the spectra intensity of the treated specimen decreased obviously, this indicated the decrease of crystallinity of the fiber. As we can see from Table III, the crystallinity decreased from 80.68% to 58.76%, decreased by about 27.17%. This fact was due to the reduced number of hydrogen between —NH and —C═O groups and destroyed the order of Kevlar molecular chain.

Effects of the $CaCl_2$ Treatment on the Morphologies

The fiber surface physical features can remarkably influence the interfacial adhesion property of composites, which is closely related to the fracture mechanisms between fiber and resin matrix. The surface morphologies of untreated and treated Kevlar fibers were analyzed by SEM. Figure 6 shows the surface of fibers with different treatment time. Compared with the smooth surface of untreated Kevlar fiber in Figure 6(a), there are some small globular-like microstructures and obvious grooves on the surface of each treated fiber this is attractive for reinforcing composites. Figure 6(b) shows the fiber treated with $CaCl_2$ for 2 h. We can see some tiny uneven parts appeared on the fiber surface. When the treatment time increased to 5 h some long grooves come into being on the surface of fiber and we can see that the "skin" of the fiber has been removed in Figure 6(c). But when the treatment time increased to 9 hours the body of the fiber can be hardly destroyed as we can see from Figure 6(d). This illustrated that with long treatment time the erosion of the fiber was more serious. This was due to the complexation reaction between $CaCl_2$ and the carbonyl that destroyed the hydrogen bond between the fiber molecular chains as we supposed the reaction mechanism in scheme 1.

The AFM was used to investigate the surface roughness of untreated and treated Kevlar fibers. In Figure 7, remarkable difference can be observed in the micrographs, which could prove that $CaCl_2$ treatment indeed changed the morphology of the fiber surface. Table IV summarized the root mean aquare roughness (Rq) and arithmetic mean roughness (Ra). It shows that the $CaCl_2$ treatment remarkably increases the surface roughness of Kevlar fiber. The Rq and Ra of untreated fibers was 143.76 nm and 128.79 nm, respectively, while the Rq and Ra increased to 201.32 nm and 198.84 nm after $CaCl_2$ treatment, revealing that the surface roughness increased owing to the $CaCl_2$ treatment. These results are in good consistence with above SEM pictures. The increased surface roughness of treated fiber is attractive for reinforcing polymers, because the rougher surfaces bring stronger mechanical interlocking (or anchoring) between the fibers and the matrix, and thus lead to improved composites interfacial properties.[30]

Effects of $CaCl_2$ Treatment on the Interlaminar Shear Strength of Kevlar Fiber/Epoxy Composites

The surface properties of Kevlar fiber play an important role in the enhancement of interfacial adhesion in fiber reinforced matrix composites. ILSS measurement is applied to evaluate the interfacial strength in Kevlar fiber reinforced epoxy resin composites. After fixing the treatment tempeture, the concentration

Table IV. Root Mean Square Roughness (Rq) and Arithmetic Mean Roughness (Ra) of Kevlar Fibers

Fiber sample	Rq (nm)	Ra (nm)
(a) Untreated	143.76	128.79
(b) Treated for 5 h, 5 wt %	201.32	198.84

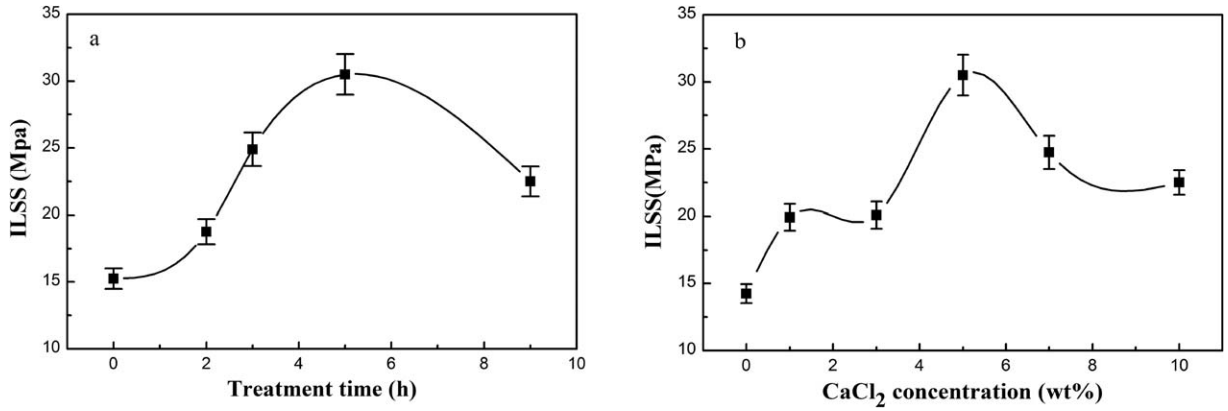


Figure 8. ILSS for untreated and treated Kevlar fibers/epoxy composites with different (a) treatment time and (b) concentration.

of $CaCl_2$ and treatment time were two important parameters that affected the adhesive properties between fibers and resin. Figure 8(a,b) show the ILSS values of composites based on treated fiber with different treatment time and concentration. All ILSS values of treated Kevlar fiber/epoxy resin composites are higher than that of untreated fiber/epoxy resin composites. Figure 8(a) shows the relationship between ILSS and $CaCl_2$ concentration. When the treatment time was 5 h, the best ILSS was acquired with a 53.3% improvement. With increasing the treatment time to 9 h the ILSS decreased, because the body of Kevlar fiber had been destroyed as we can see in Figure 6(d), this reduced the strength of Kevlar fiber. Under the most suitable treatment time 5 h and fixed the tempeture, the ILSS changing with $CaCl_2$ concentration was shown in Figure 8(b). The results showed that the optimum concentration was 5 wt %. In comparision with the two graphs and on the basis of mechanical properties results, the optimum processing condition is 5 wt % for 5 h.

The fracture surface of the ILSS specimens were examined by SEM and illustrated in Figure 9. We can see that the ruptures of composites with and without treatment are obviously different. As shown in Figure 9(a), smooth surface with a small amount of adhered resin can be seen in the untreated fiber surface. This means that the interfacial bonding is poor and the interface structure might not transfer stress at satisfactory effect. On the rupture of treated fiber composites in Figure 9(b), the surface adhered more resin, considerable matrix deformation together with fibers were tightly held by the matrix. As can be seen, after $CaCl_2$ treatment composite interfacial adhesion was improved significantly and the SEM micrographs of the fracture surface well corresponded to the results of ILSS testing.

CONCLUSIONS

In this article, we investigated the effects of calcium chloride on the surface of Kevlar-29 fiber and presented a new approach to modify Kevlar fiber. The structure and morphology of the treated Kevlar-29 fiber were characterized by FTIR, XPS, XRD, SEM. The results showed that the complexation was happened between $CaCl_2$ and Kevlar-29 fiber. It was proved that $CaCl_2$ treatment had great influence on the structure and properties of Kevlar-29 fibers. The amino-groups of Kevlar-29 fiber were freed and the contents of —C—N— increased from 18.32% to

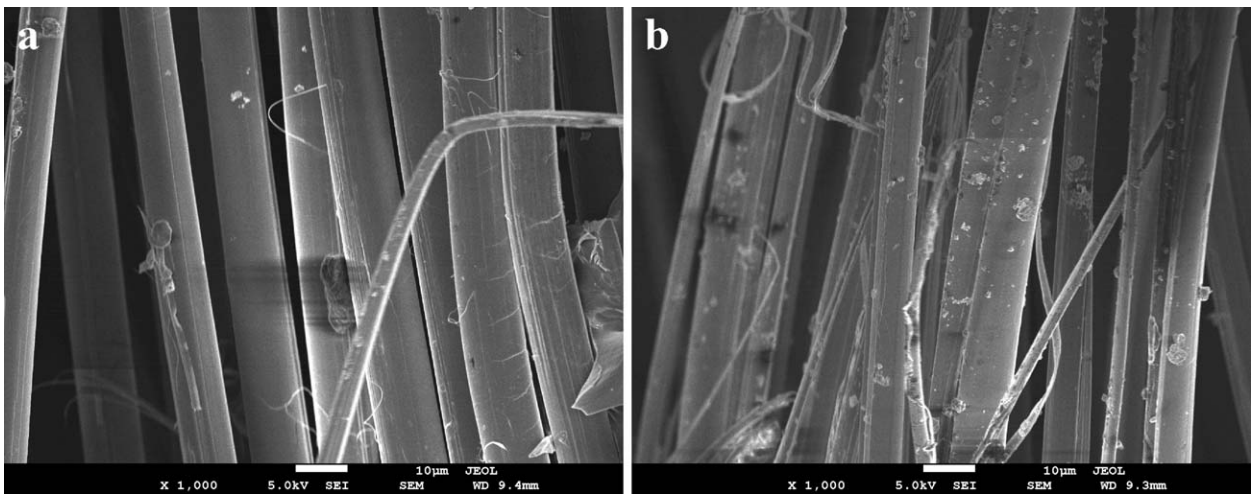


Figure 9. SEM images of interlaminar shear ruptures of untreated Kevlar fiber/epoxy resins and $CaCl_2$ treated Kevlar fiber/epoxy resins composites.

30.65% after $CaCl_2$ treatment. The obvious grooves presented on the surface of Kevlar fibers and the roughness increased consequently. The contents of —NH functional group on the surface of fibers also increased. These were due to the complexation destroyed the surface structure of the fiber and decreased it's crystallinity. From the ILSS and mechanical properties values, it can be concluded that treatment with 5 wt % $CaCl_2$ for 5 h is the optimum modification condition.

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