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ARTICLE TYPE

Simultaneously Improving the Tensile Strength and Modulus of Aramid Fiber by Enhancing Amorphous Phase in Supercritical Carbon Dioxide

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The aramid fiber made from poly (p-phenyleneterephthalamide) PPTA has high strength and high modulus, due to its high orientation of macromolecular rigid chain. Many attempts to improve the mechanical performance of aramid fiber is proposed during last decade, however simultaneously improving the strength and modulus of aramid fiber is still a great challenge as most methods can only improve the modulus at the expense of reducing the tensile strength. The mechanism for broken of Kevlar fiber shows that the weak point of aramid fiber is at amorphous phase among the orientation fibrous. Therefore, if the amorphous phase can be enhanced, the mechanical performance of PPTA fibers would be improved. Here a novel method is reported to enhance the amorphous phase of PPTA fibers by treating the aramid fiber in supercritical carbon dioxide (ScCO$_2$) with or without using hexmethylene diisocyanate (HDI). In this new process, the ScCO$_2$, with or without the crosslinker HDI in ScCO$_2$, is diffused into amorphous phase of PPTA fibers and the amorphous phase was enhanced by re-arrangment of molecular segment or HDI reacting with the groups (-NH$_2$, -COOH, and -NHCO-) of PPTA fibers, without breaking the crystalline and orientation by carefully controlling the reaction temperature, pressure and time. The results showed that the tensile strength and modulus were simultaneously increased. The molecular weight could be increased under the appropriate treatment, while the crystalline structures of PPTA fibers were almost unchanged. Dynamic mechanical analysis (DMA) and Thermomechanical analysis (TMA) tests showed that the glass-transition temperature increased. All the results implied the chain crosslinking mainly took place in amorphous phase of the PPTA fibers and the performance improvement was contributed to the amorphous enhancement.

Keywords: Supercritical carbon dioxide (ScCO$_2$); crosslinking reaction; amorphous phase

1. Introduction

Poly(p-phenylene terephthalamide) (PPTA) fibers are organic fibers that can be used as reinforcement for advanced composites, which have a great potential application in fields of aeronautical and astronautical, military, industry and other advanced domains due to their excellent high tensile strength, modulus, great thermal stability and good solvent resistivity.[1] The exceptional strength of the fibers is a direct result of its chemical structural characteristics including its stiff, extended chain conformation and nearly perfect uniaxial orientation.[2] Also in PPTA, the presence of amide groups at regular intervals along the linear macromolecular backbone facilitates extensive hydrogen bonding in a lateral direction between adjacent chains. This, in turn, leads to efficient chain packing and high crystallinity.[1]

Aramid fibers are known to be composed of fibrils or microfibers in their microstructure. The bonding between these fibrils is rather weak, which enables the fibers to be easily damaged, due to external abrasion as well as low compression strength. This is important in composites. Weak inter-fibril bonds also limit the degree of improvement in aramid/matrix interfacial bond strength since the fibrils on the surface of the fibers can be peeled away before the fiber/matrix interface fails.[3,4] Many attentions have been paid to improve the performance of fibers made from the rigid-rod polymers by increasing the transverse interactions or by increasing the crystallity at the polymer chain level. For example, the method of heat treatment is a modification process used previously on polyethylene terephthalate fibers by Peszkin et al.[5] The high modulus fibers Kevlar 49 were produced by the heat treatment of Kevlar fiber under tension by DuPont, and after the treatment the Young's modulus could be improved, while tension strength reduced in some extent as the heat treatment causes the products degradation.[4, 6, 7, 8, 9] The compressive strength is important in composites, many researchers studied the crosslinking at the molecular level and incorporation of bulky groups in the backbone of the polymer to disrupt their nematic packing order.[8, 10, 11, 12 13] To improve inter-fibrillar bond strength, Mathur and Netravali et al[14] reported that both the fibers tensile and compression strengths increased because the plasma treatments could potentially improve the inter-fibrillar adhesion or cohesion and thus improve the fiber tensile strength as well as the IFSS.

The ScCO$_2$ has frequently been employed as an extraction medium due to its combination of low viscosity and negligible surface tension.[15] Zhao et al[16] designed a new pretreatment process, in which the organ metallic complex was impregnated into Kevlar® fabrics/fibers by using ScCO$_2$ to electro conductive composite fabrics/fibers. Lesser et al. investigated the use of supercritical carbon dioxide (ScCO$_2$) to directly wash the residual phosphoric acid out of the poly-p-phenylene-benzobisoxazole fibers. [17]

In order to improve the properties, we develop a new pretreatment process, to enhance the amorphous phase of PPTA fibers by treating the aramid fiber in ScCO$_2$ with or without HDI as crosslinker. In this new process, the $ScCO_2$, with or without crosslinker HDI ,is diffused into amorphous phase of PPTA fibers, and the amourphous phase was enhanced by re-arranging of molecular segment or HDI reacting with the groups (-NH_2,-COOH and –NHCO-) of PPTA fibers.

2. Materials and methods

2.1 Materials

PPTA fibers were supplied by Hebei Silicon Valley Chemical Co., Ltd. China. The yarn is made of 1000 filaments with the diameter of 12.7 μm and the specific linear density of 1111 dtex. Carbon dioxide (CO_2) (purity: +99.99%) was purchased from Shanghai Chenggong Gases Co., Ltd., China and used as received. Hexa-methylenediisocyanate (HDI) (purity: 99%) was purchased from J&k chemical Ltd (Shanghai, China) and used without further purification. Acetone (chemically pure grade) was brought from the Shanghai Ling Feng Chemical Reagent Co., Ltd. (China).

2.2 Treated aramid fiber in $ScCO_2$

PPTA fibers were washed in the Soxhlet extractor with acetone at the temperature of 75 °C (20 h), and dried in an air oven at 110 °C for 3 h to remove acetone thoroughly prior to preceding the $ScCO_2$ pretreatment. Details of the experimental procedure and the apparatus employed are given elsewhere.[16] The reactions were carried out in high-pressure stainless steel vessels. All parts of the vessels were washed in clean acetone, acid bathed (2.0 M aqueous sulfuric acid), then thoroughly rinsed in clean water, and finally dried at 120 °C. The $ScCO_2$ impregnation process was carried out in a 50 cm^3 cartridge. Samples were rolled, tied on a stainless steel formwork. The concentration of HDI in $ScCO_2$ was 10 wt%. When the vessel reached the set temperature, the cartridge was introduced. Then, CO_2 gas was supplied via a high-pressure syringe pump and maintained at a preset pressure. Subsequently, the system was kept stable during a certain period of time to allow the HDI to dissolve into $ScCO_2$ and to react with the aramid fibers. Finally, decompression was slowly conducted. The impregnation processes were carried out under static conditions.[18]

2.3 Characterization

2.3.1 Intrinsic viscosity [η]

The intrinsic viscosity of the fibers was determined at 30 °C by a solution containing 0.5 g of polymer per 100 mL of concentrated sulfuric acid (H_2SO_4) using an Ubbelohde viscometer.

2.3.2 Tensile experiment

Tensile tests were carried out by using a tensile strength tester 0-100 CN (XQ-1A) with a head speed of 10 mm/min at gauge length 10 mm. The average values were calculated from at least 20 samples.

2.3.3 Fourier transform infrared (FTIR)

Spectrophotometer (Nicolet 8700) was used to obtain the spectra of untreated and treated fibers at room temperature ranging from 4000 to 400 cm^{-1}.

2.3.4 X-Ray Diffraction (XRD).

The crystallites of the fibers were tested by using a Rigaku D/Max-2550 PC X-ray diffractometer (Rigaku Co., Janpan) with CuKα radiation as the source.

2.3.5 Thermomechanical analysis (TMA)

TMA experiments were performed on a Thermal Mechanical Analyzer (TMA) (TA Instruments, Model 400EM) in nitrogen with a constant applied load of 20 mN at a heating rate of 5°C min^{-1} by tension mode from 30 to 400 °C.

2.3.6 Dynamic mechanical analysis (DMA).

DMA measurements for PPTA fibers were conducted using a dynamic mechanical analyzer (DMA Q800, TA Instruments, USA). DMA test was performed in fiber fixture mode and the testing temperature ranging from 30 to 450 °C at a heating rate of 10 °C min^{-1} at a frequency of 1 Hz.

3. Results and Discussions

3.1 Simultaneously improving tensile strength and modulus of aramid fiber

The results of mechanical properties testing with temperature, pressure, time for as-received and HDI treated PPTA fibers in $ScCO_2$ with or without HDI are summarized in Table 1- 3. Compared with that of as-received fibers, the mechanical properties (the average tensile strength and the Young's modulus) of the treated fibers with or without HDI in $ScCO_2$ tend to increase with the increase of the heating temperature as used. However, the mechanical properties of the fibers treated without HDI were improved less than that of fibers treated with HDI, For the fiber treated in pure $ScCO_2$, the improvement of mechanical properties was due to the compact microstructure and the reduced defects with the aid of the plasticizing ability of $ScCO_2$.When the fibers in the $ScCO_2$ at the hydrostatic pressure, the structural reorganization has occurred as the chain-chain interaction decreased, while the segment and chain mobility increased.

When the HDI was brought into, most of the properties were improved larger than these treated at the same condition without HDI as shown in Table 1- Table 3, that's because except for the effect mentioned above caused by the $ScCO_2$, the functional group NCO- reacted with the group having the H-bonding formed the crosslinking in the fibril, for example, the NH_2-, -NH-CO- and COOH. However too higher temperature will bring the deposition of the fibers and decrease the tensile strength. And high pressure, more treatment time alike. When PPTA fibers were treated for 90 min as shown in Table 3, the tensile strength and modulus were improved apparently which might be resulting from more crosslinking reaction happened, but actually the fibers treated at this condition were too stiff to make further use of them. Compared with different treating conditions, seen from the Table 1-3, treating time plays an important role than treating pressure and temperature, and the fibers exhibit a good property at the condition of pressure of 13 MPa at the 90 °C, treating time 40 min, the tensile strength increased by 8.7%, modulus increased by 14.5%, which is likely due to an improved interfibril bond strength.

3.2 Structure characterization

In order to investigate the mechanism of the effect of the $ScCO_2$ and HDI on the fibers, surface chemical structure of fibers (fibers treated in $ScCO_2$ / 90 °C /40 min / 13 Mpa HDI), fibers treated in $ScCO_2$ / 90 °C / 40 min /13 MPa, as received) were characterized. As can be seen from Figure 1, these FTIR spectrums are very similar to each other. The spectrum of treated fibers with HDI has an extra peak located at 2940 and 2852 cm^{-1}, which is attributed to stretching vibrations of CH_2 groups involved in the HDI. The amide Ⅱ band is a mixed mode containing contributions from the N-H in-plane bending, the C-N stretching, and the C-C stretching vibrations.[19] After treated by the HDI in $ScCO_2$, the peak intensity at 1514cm^{-1} is stronger than others, which are assigned to -CO-NHR. The results indicated new groups were formed after treated with HDI. Possibly, −NCO groups in HDI reacted with $-NH_2$, −NHCO− and -COOH groups in PPTA fibers to form a certain degree of grafting and cross-linking.

The viscosities of the fibers in concentrated sulfuric acid were measured to evaluate the molecular weight of the fibers. The results were summarized in the Table 4.The viscosity of the fibers treated in $ScCO_2$ was higher than that of untreated fibers, which might be caused by the extraction effect of $ScCO_2$ to remove the small molecule. And when treated with HDI in $ScCO_2$, the viscosity was the highest and was significantly improved compared to others . This is due to these fibers consisting of polymer chains with slipping for terminal segment,[20] some ends groups of molecular chains can reacted with the NCO groups of HDI, the number of chains will be reduced and length of the molecular chains would be increased, so the molecular weight of the polymer will increase.

In order to gain insight into the influence of $ScCO_2$ and the HDI on the crystalline structure of PPTA fibers, XRD studies were performed on specimens treated in $ScCO_2$. From the Figure 2, there is a little difference of the XRD results among these samples. Two strong equatorial diffraction peaks can be due to the 110 and 200 planes at 20.7^{o} and 23.1^{o}, respectively. As it can be seen from Table 5, the crystallinity increased slightly, indicating the recystallize of molecule at the surface of lamellae.[21] The peak's intensity 200 plane was enhanced and the crystallites was improved after the fibers treated in $ScCO_2$ without HDI, and their microstructures in amorphous region was recognized and the chain compacted and defects were reduced as the result of the plasticizing ability of $ScCO_2$.[15] Panar et al[22] postulated that surface fibrils are uniform, axially oriented, while fibrils in the fiber core are imperfectly packed and ordered. This suggests that core may be more readily to effect. As shown in Table 5, the treatment conditions shows no difference with respect to the crystallites sizes, moreover these results imply that the perfection of crystallites increased. However, for the treated with HDI, there was little effect on the intensity of the diffraction peak, indicating that the crosslinking and the molecular weight improvement might happen in the amorphous regions of the fibers.

The glass transition temperature (Tg) can generally be measured by differential scanning calorimetry (DSC), thermo mechanical analysis (TMA), and dynamic mechanical analysis (DMA), however the DSC is too low sensitive to characterize the difference among our samples , whose main chains are difficult to move over a wide range due to the rigidity of the molecular chains. As TMA and DMA can clearly show the Tg, we use TMA and DMA measurements to determine the Tg of PPTA fibers. There were a few documented literatures about the TMA and DMA study on para-aramid fibers, [23,24,25] TMA measures the dimensional change of a sample as a function of temperature, when it is being compressed or stretched. The TMA curves are shown in the Figure 3 for the PPTA fibers. The inflection point of thermal expansion curve is defined as TMA Tg. The TMA curves showed a change of slope at about 100°C due to dehydration of the fibers , and an inflection near 250°C for PPTA fibers which was attributed to the glass transition. Tg of PPTA fibers treated in $ScCO_2$ with HDI (about 275 ^{o}C) is higer than the fibers not treated and treated in $ScCO_2$ without HDI (250^{o}C), implying some crosslink reactions happened in amorphous region of the fibers to make more difficult for the mobility of molecule chains.

The glass transition temperature also can be obtained by dynamic mechanical analysis (DMA Tg). The changes in loss modulus and loss factor as functions of temperature are shown in Figure 4. Dynamic mechanical loss tangent (tanδ), also called dissipation factor, is the ratio of the loss modulus to the storage modulus and the most important parameter to investigate the properties of materials. And as the loss modulus peak temperature is very close to Tg of the polymeric system and in this paper we focous on discussing the glass temperature, here in Figure 4 we only choosed the curve tanδ and loss modulus to characterize Tg. The glass transition temperature of 205^{o}C has been reported for Twaron2000 (also a PPTA fiber) by Liang.et.al using DMA testing.[25] The loss modulus of the fibers treated in $ScCO_2$ without HDI leveled off 250 ^{o}C, this phenomenon was not observed in the untreated fibers, this may have been a result of crosslinking in the chain. When not adding HDI, the glass transition temperature was reduced slightly, because of plasticizing effect of the supercritical carbon dioxide on fibers and the β relaxation in the crystalline region, the mobility of the amorphous phase was enhanced by relaxation.[22] When HDI added, the glass transition temperature increased slightly, this may be due to some crosslinking interactions happened between molecular chains, the intermolecular forces increased, the flexibility of chain segment was reduced, leading to the decrease of activity of chains. The competition, the plasticizing effect of supercritical carbon dioxide on fibers and the crosslinking of HDI, makes the glass transition temperature changed slightly the curve peak appears at 250℃, which was in good agreement with the TMA results. As the XRD shows the crystallinity did not changed, the cross-linking reaction happened only in the amorphous phase.

3.3 Mechanism of enhancement of properties

The property improvement of aramid fiber is contribute to the enhancement of amorphous phase by re-arranging of the PPTA macromolecular segment or HDI reacting with the PPTA macromolecular groups ($-NH_2$, -COOH, and -NHCO-) of PPTA fibers.

Possible chemical interactions could occur at four positions as shown in Figure 5, [26] according to the PPTA molecular structure and the results shown in FTIR, the reaction may be taken place in the position 3. Possible chain interactions are as shown in scheme 1, 2 and 3, 4, 5, 6. Scheme 1, 2, 3, 4, 5, 6 show possible interactions for groups –NH-CO- in PPTA molecules, end groups $-NH_2$, COOH with groups –NCO in HDI can react with groups –NCO in HDI and form new molecular chains, the chains will become longer as shown in Figure 6 (a). Owing to the $ScCO_2$ plasticsing effect, the new formed chains will be moved and rearranged regularly. As we known, most of the end groups of macromolecular chain existed in the amorphous regions, these reactions may be happened in the amorphous region as shown in the figure 6 (b). These mechanisms are considered to be responsible for the chemical composition changes revealed. The tensile strength and modulus increased when treated in $ScCO_2$ with HDI, which may have been due to the presence of new chemical bonding formed, making the intermolecular forces increased and their microstructures in amorphous region recognized, and the chain compacted and defects was reduced.[15] So after treated in $ScCO_2$ with or not with HDI, fibers show good performance than not treated fibers.

4. Conclusions

The tensile strength and modulus of PPTA fibers can be simultaneously improved by treated solid aramid fiber in ScCO2 with or without HDI. The structure analysis by FTIR, XRD, TMA, DMA and molecular weight measurement imply that the improvement of mechanical performance was due to the enhancement of amorphous phase among fibrils in aramid fiber by segment movement of chain with $ScCO_2$ as plasticizer when without HDI, and by the cross-linking reaction of HDI with active hydrogen group in CONH, NH_2 or COOH in amorphous phase among fibril of PPTA fiber when with HDI as crosslinker,

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Notes and references

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Table 1 The mechanical properties of aramid fiber treated at various temperature in $ScCO_2$
(Pressure 13 MPa, treated time 40 min)

Temperature (^oC)	Tensile strength (cN/dtex)	Young's modulus (cN / dtex)	Tensile strain (%)
As-received	21.7	480.7	2.4
Treated in $ScCO_2$ without HDI			
40	22.0	490.4	2.3
60	22.3	510.6	2.6
90	22.6	541.9	2.5
120	22.1	522.3	2.4
Treated in $ScCO_2$ with HDI			
40	22.8	515.4	2.6
60	23.1	531.6	2.7
90	23.6	550.6	2.8
120	22.5	464.3	2.5

Table 2 The mechanical properties of aramid fiber treated at various pressure in $ScCO_2$
(treated time 40 min, temperature 90 ^oC)

Pressure (MPa)	Tensile strength (cN / dtex)	Young's modulus (cN / dtex)	Tensile strain (%)
As received	21.7	480.7	2.4
Treated in $ScCO_2$ without HDI			
10	21.9	498.2	2.6
13	22.6	541.9	2.5
15	22.1	502.3	2.4
18	22.4	513.5	2.3
Treated in $ScCO_2$ with HDI			
10	22.2	515.9	2.6
13	23.6	550.6	2.8
15	23.2	520.7	2.5
18	22.7	476.8	2.7

Table 3 The mechanical properties of aramid fiber treated at various time in $ScCO_2$
(treated pressure 13 MPa, temperature 90 ^oC)

Time(min)	Tensile strength (cN /dtex)	Young's modulus (cN / dtex)	Tensile strain (%)
As received	21.7	480.7	2.4
Treated in $ScCO_2$ without HDI			
40	22.6	541.9	2.6
90	22.4	520.2	2.5
120	22.3	510.1	2.4
180	20.2	494.3	2.8
Treated in $ScCO_2$ with HDI			
40	23.6	550.6	2.8
90	25.4	570.8	2.4
120	23.1	530.4	2.6
180	21.0	462.8	3.0

Table 4 The viscosities of PPTA in the fibers

Sample	η(dl/g)
As-received	6.96
$ScCO_2$ without HDI	7.02
$ScCO_2$ treated with HDI	7.23

5

Figure Captions:

Figure 1 FTIR spectrum of PPTA fibers before and treated in $ScCO_2$ (with HDI)

Figure 2 The wide-angle X-ray diffraction of the PPTA fibers

Figure 3 TMA curves of the PPTA fibers

Figure 4 Dynamic loss tangent (tanδ) and the loss modulus (E'')as a function of temperature for PPTA fibers (a) as-received PPTA fibers, (b) ScCO2 treated fibers without HDI, and (c)ScCO2 treated fiberswith HDI

Figure 5 Four potential reaction sites of PPTA

Figure 6 The mechanisms of the new chemical reaction in ScCO2 (a) some reaction of the end agent (b) the amorphous region reaction

Scheme Captions:

Scheme 1 $-NH_2$ reacted with NCO-

Scheme 2-NH_2-CO-NH reacted with NCO-

Scheme 3 -CO-NH reacted with NCO-

Scheme 4–COOH reacted with NCO-

Scheme 5 -NHCO-/-COOH reacted with NCO-

Scheme 1 NH_2-/-COOH reacted with the NCO-

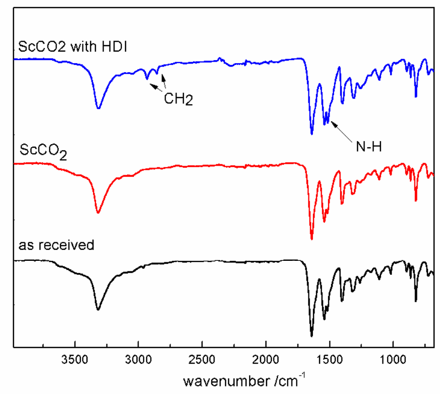

ScCO2 with HDI
CH2
N-H
ScCO$_2$
as received
3500
3000
2500
2000
1500
1000
wavenumber /cm^{-1}

Figure 1

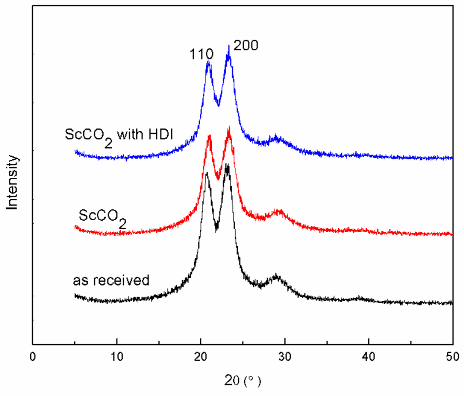

110
200
ScCO2 with HDI
ScCO2
as received
Intensity
0
10
20
30
40
50
2θ (°)

Figure 2

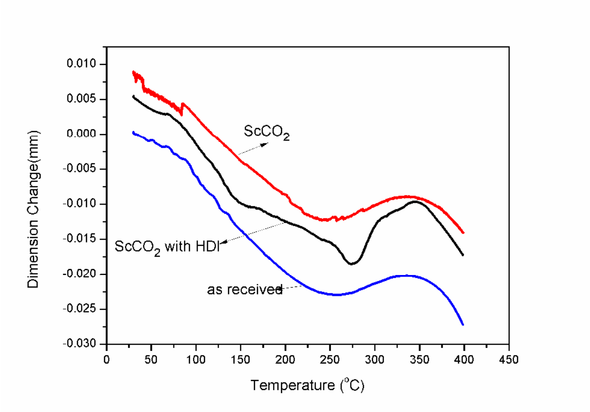

0.010
0.005
0.000
-0.005
-0.010
-0.015
-0.020
-0.025
-0.030
Dimension Change(mm)
0
50
100
150
200
250
300
350
400
450
Temperature (°C)
$ScCO_2$
$ScCO_2$ with HDI
as received

Figure 3

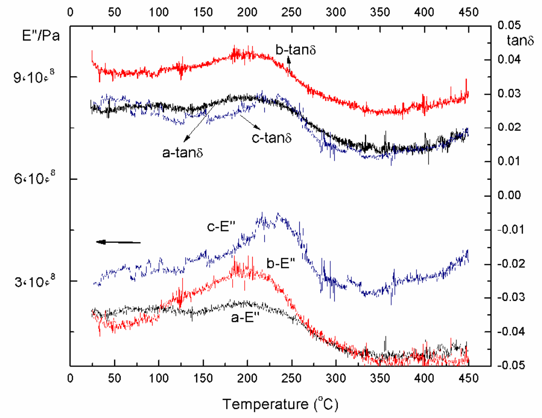

0
50
100
150
200
250
300
350
400
450
E"/Pa
9‹10ε8
6‹10ε8
3‹10ε8
0.05
tanδ
0.04
0.03
0.02
0.01
0.00
-0.01
-0.02
-0.03
-0.04
-0.05
b-tanδ
a-tanδ
c-tanδ
c-E"
b-E"
a-E"
Temperature (°C)

Figure 4

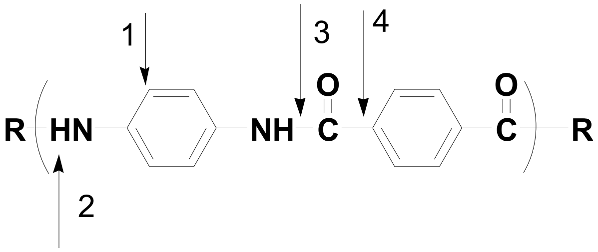


Figure 5

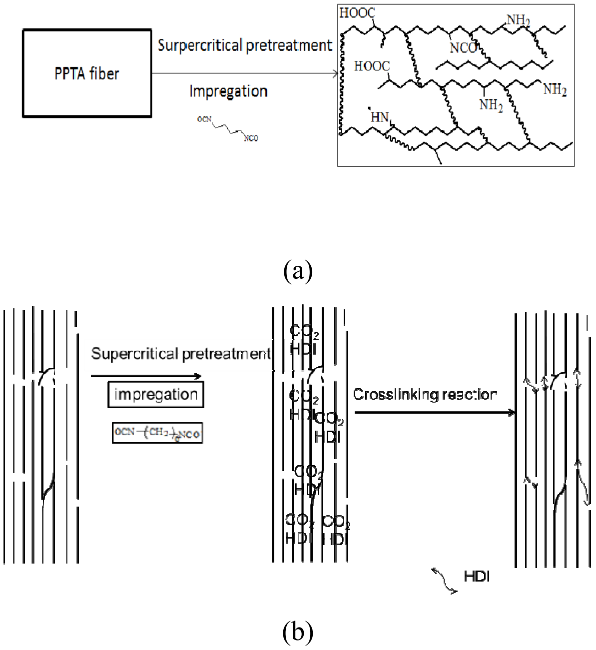
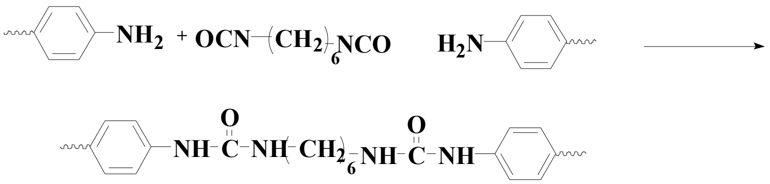
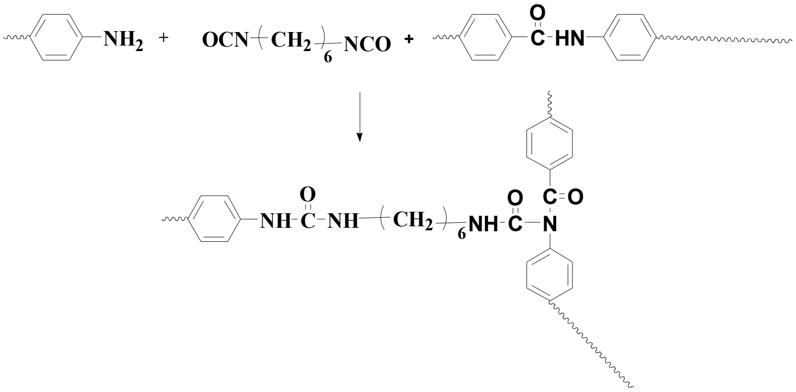

PPTA fiber
Supercritical pretreatment
Impregnation
OCN
NCO
HOOC
NH2
NCO
HOOC
NH2
NH2
HN
(a)
Supercritical pretreatment
impregnation
OCN—(CH2)6—NCO
CO2
HDI
Crosslinking reaction
HDI
(b)

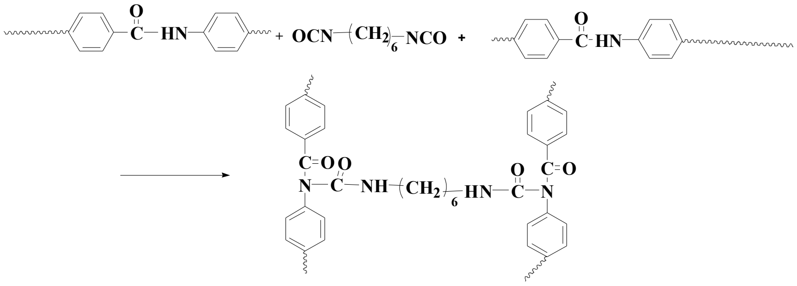
Figure 6



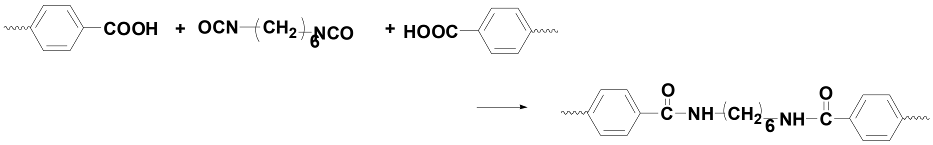
Scheme 1



Scheme 2



Scheme 3



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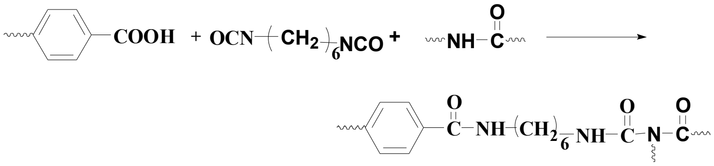
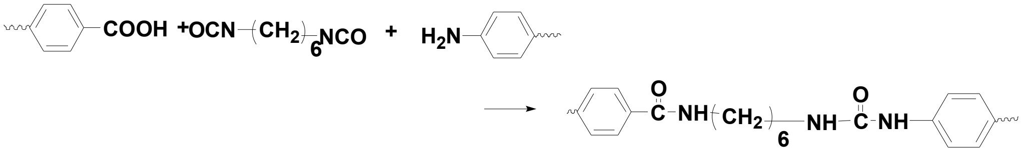
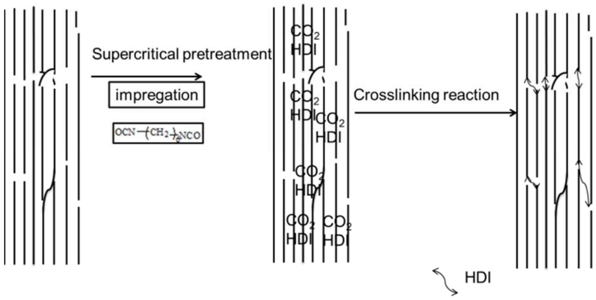


Scheme 5



Scheme 6



Textual abstract: Improving the tensile strength and modulus of aramid Fiber by enhancing amorphous phase in supercritical carbon Dioxide simultaneously