



# Methods of the Sample Preparation and Interfacial Characterization and for Carbon Fiber Reinforced Plastics (CFRP)

22<sup>nd</sup> , April, 2019



1

**Research Background**

2

**Research Contents**

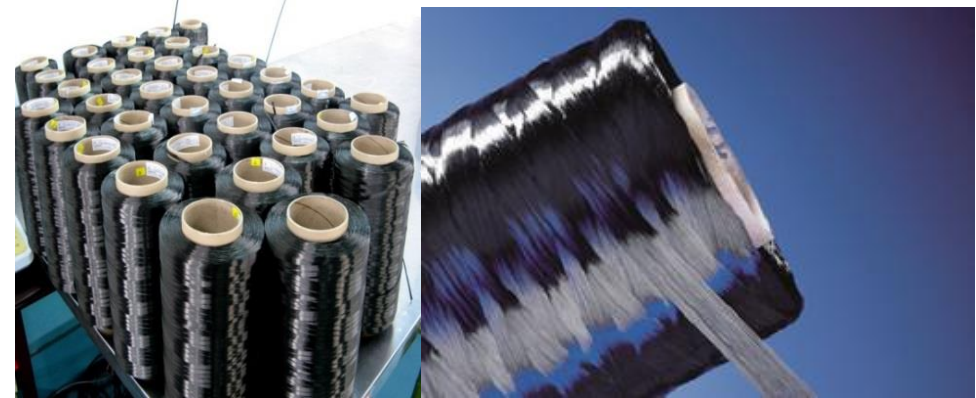
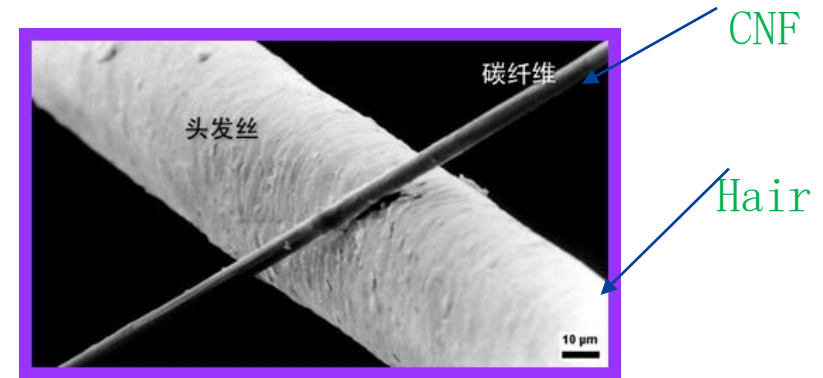
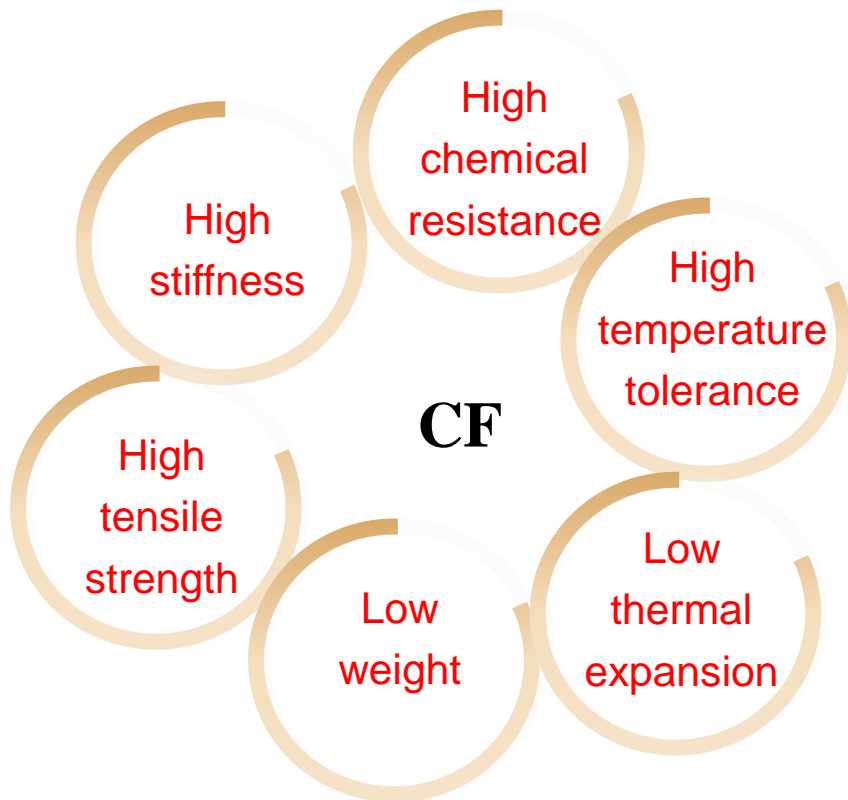
3

**Our research results**

# Background—Introduction of CF



**Carbon fibers** (alternatively CF, graphite fiber or graphite fibre) are fibers about 5–10 micrometres in diameter and composed mostly of carbon atoms.



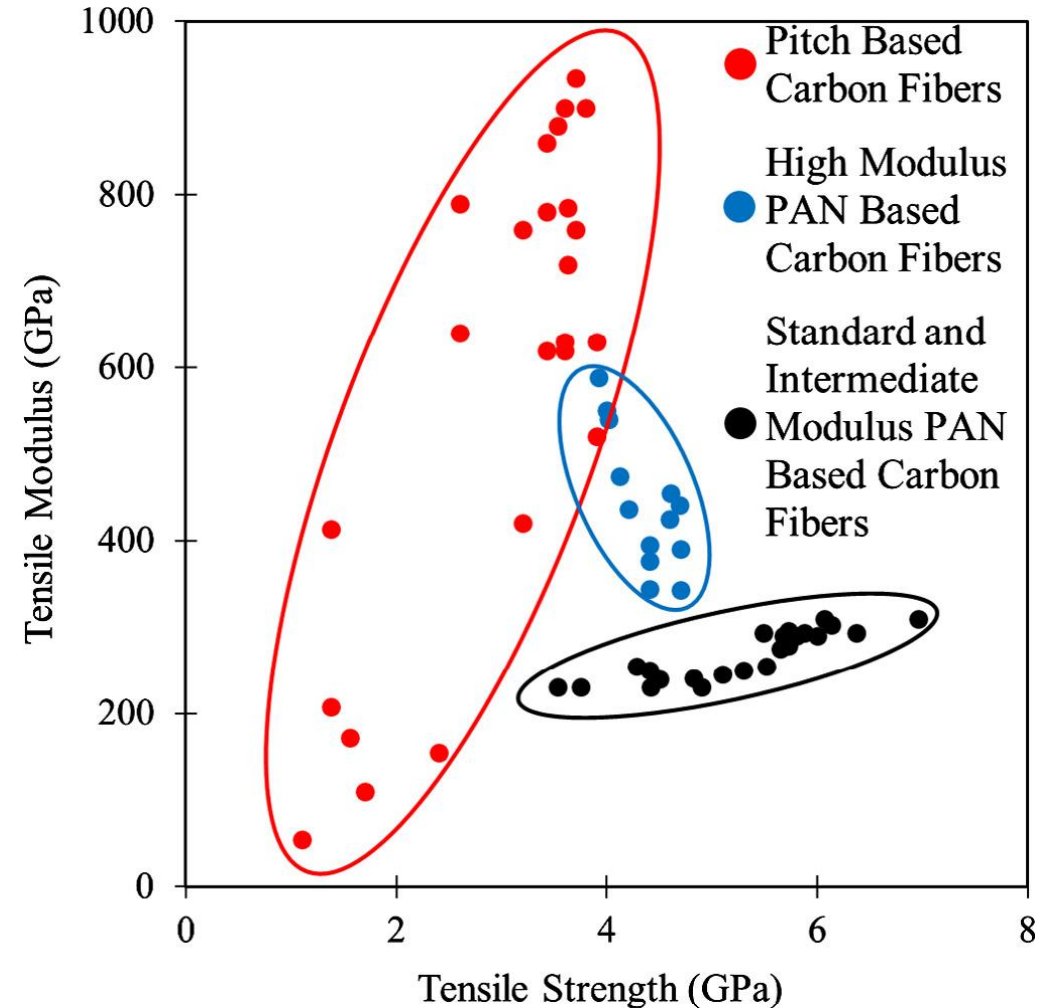
# Introduction of CF



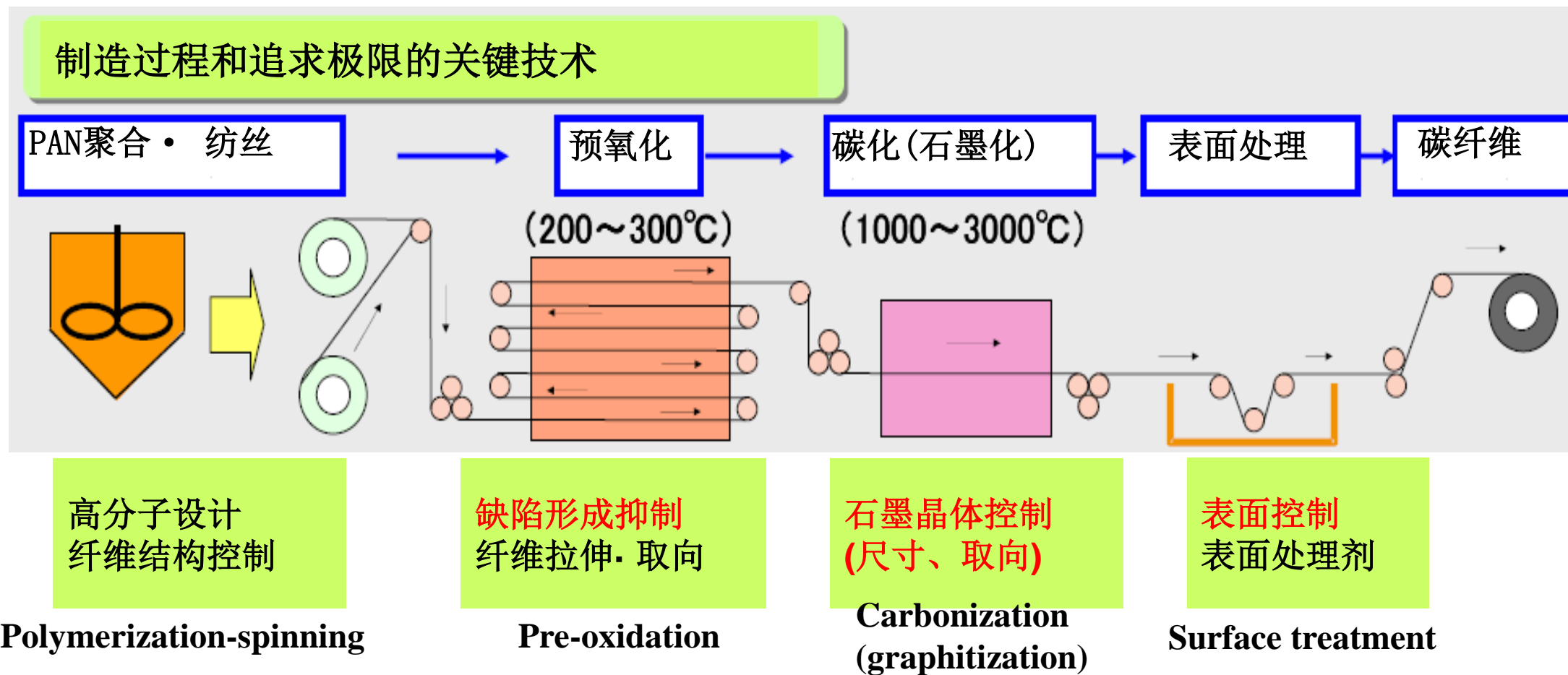
## Classification:

PAN (**Poly acrylonitrile**) -based Carbon Fiber  
Pitch-based Carbon Fiber  
Rayon-based Carbon Fiber

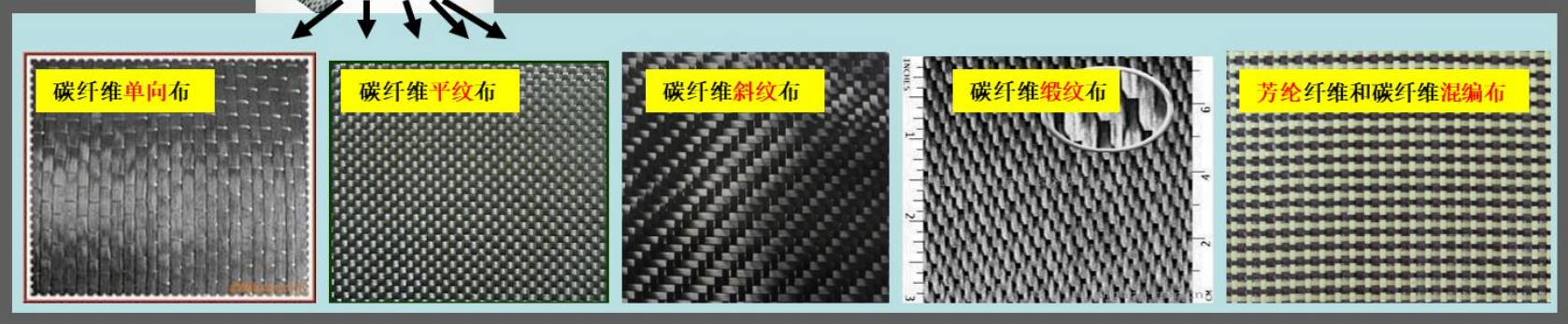
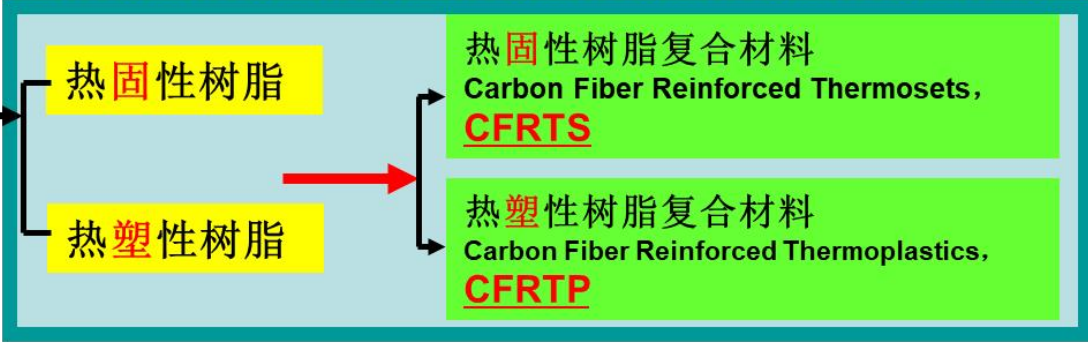
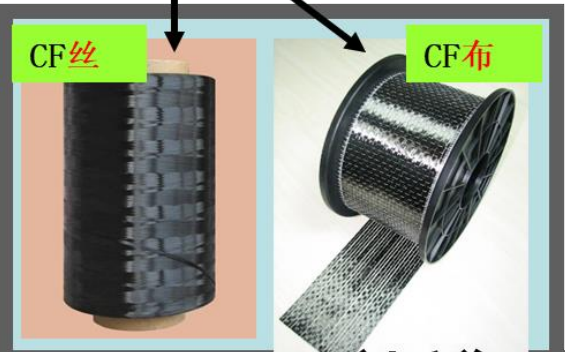
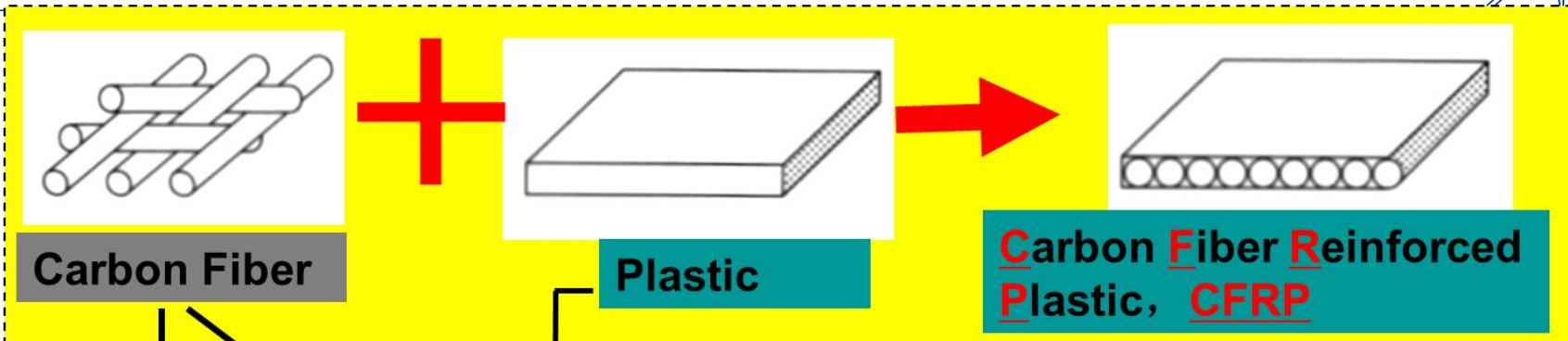
Density	1.5-2.0 g/cm <sup>3</sup>
Diameter	5-10 μm
Tensile strength	>300 GPa



# Production of CF



# Carbon fiber reinforced polymeric composites (CFRP)



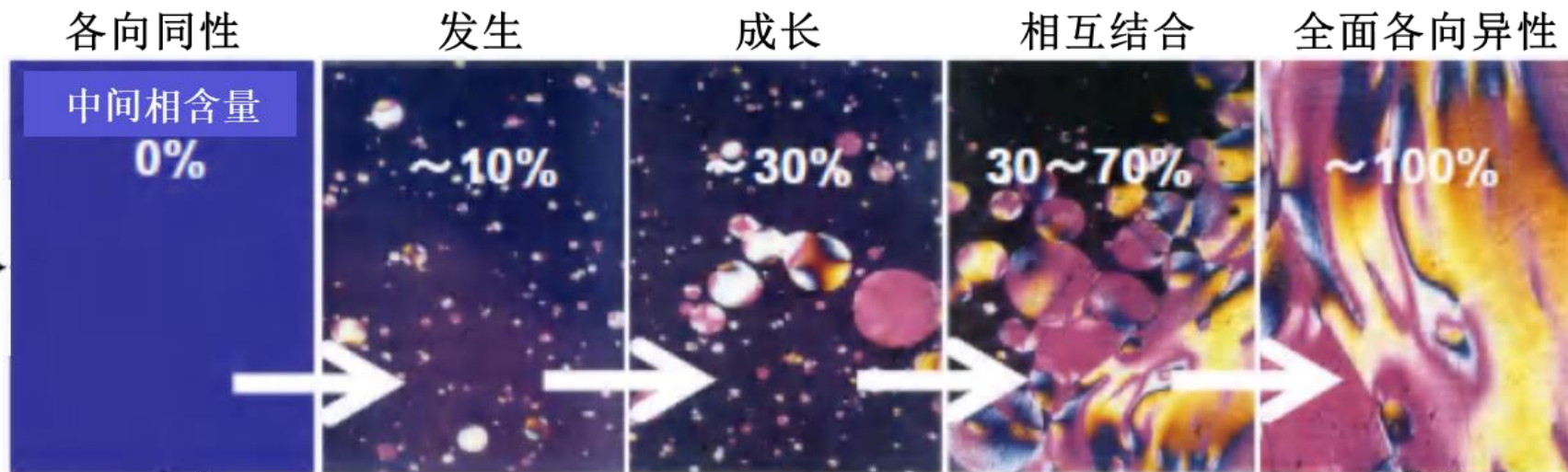
# Production of Pitch-based Carbon Fiber



制造过程和追求极限的关键技术——**液晶化反应**

**Liquid Crystallization**

精制后的  
◆煤焦油  
◆石油焦油



**通用CF**

各向同性沥青纤维

**高性能CF**

中介相沥青纤维

Mesophase pitch

**SPINNING**

Pitch-based CF

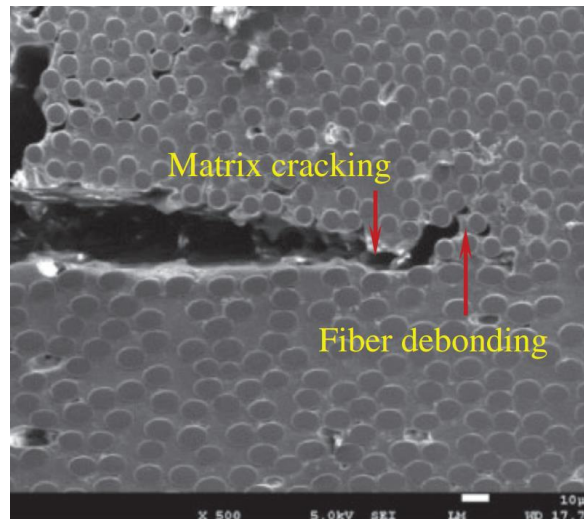
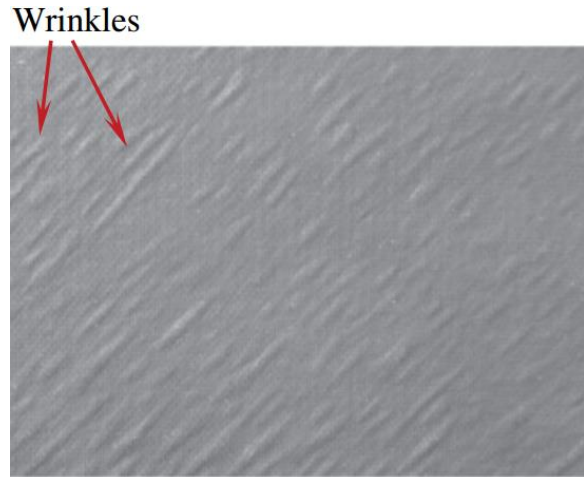
↓ 纺丝

↓ 纺丝

↓

# Interfacial Characterizations

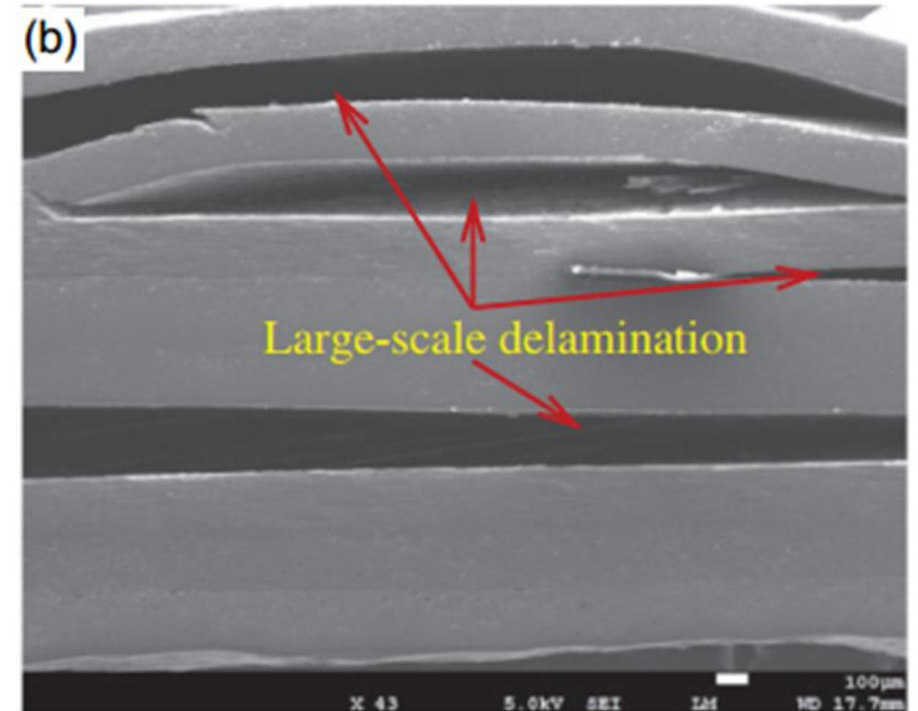
Interfacial chemical structure  
Interfacial physical structure  
Thickness  
Morphology  
Adhesion strength  
Residual stress



Interfacial structure

affect

Overall performance of CFRP





# Research Contents



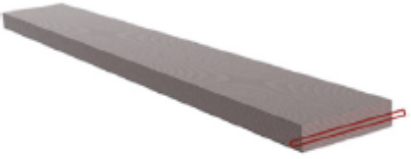



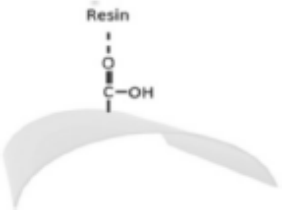
## Our Targets

- To built the quantitative interface characterization methods.
- To find the control or modification methods.
- To make clear the relationship between the composite properties and interface, or the mechanism of action in the interface change.
- To develop effective CFRP sample preparing processes.

# Research Contents——Interfacial adhesion characterization



**Table 1**  
Schematic diagram of interface adhesion characterization.

<p>Macroscopic test methods</p> 		<p>90° tensile Off-axis tensile Notched impact NOL ILSS SEM</p> <p><b>Noel ring Interfacial shear strength</b></p>
<p>Mesoscopic interface test methods</p> 		<p>IFSS SEM AFM Wetting characterization</p> <p>IFSS SEM AFM XPS Wetting characterization</p>
<p>Microscopic experimental methods</p> 		<p>SEM AFM XPS</p>

# Interfacial adhesion characterization



## Microscopic Experimental Methods

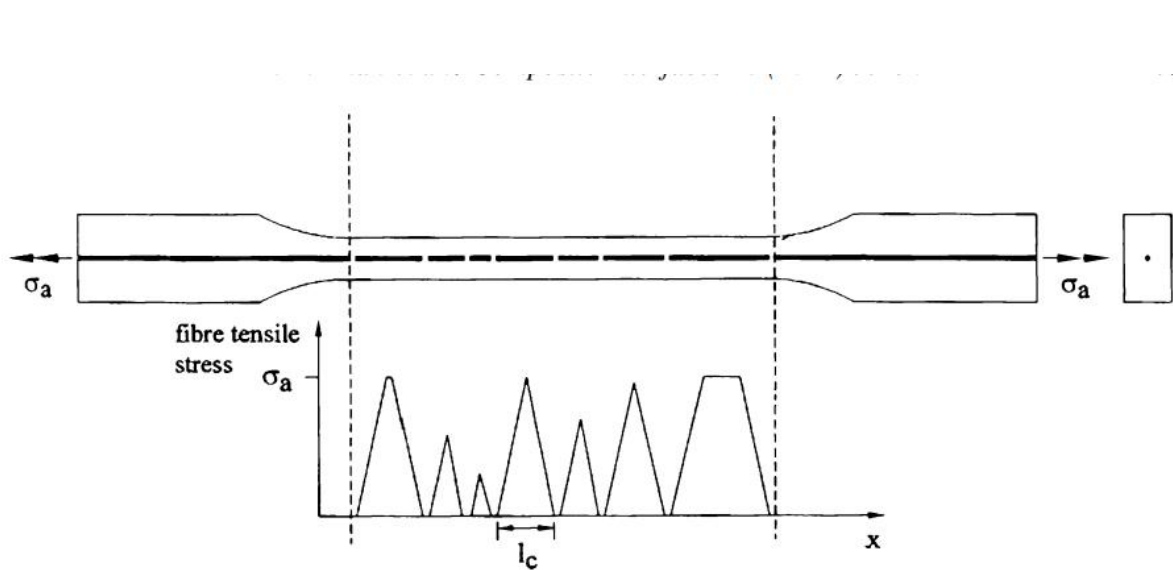
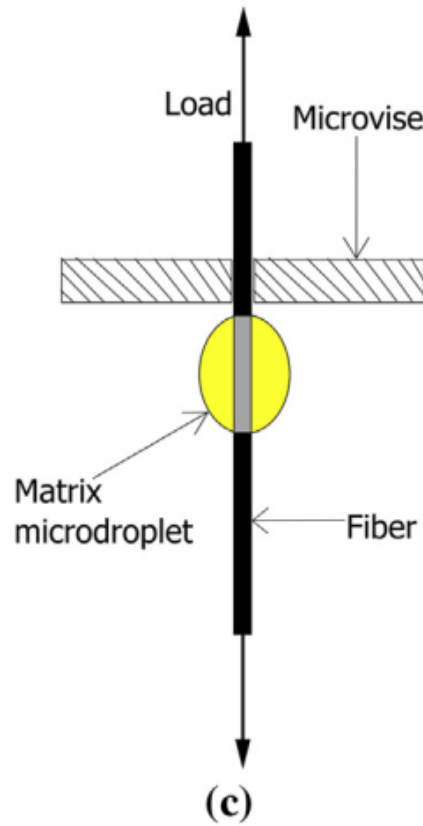
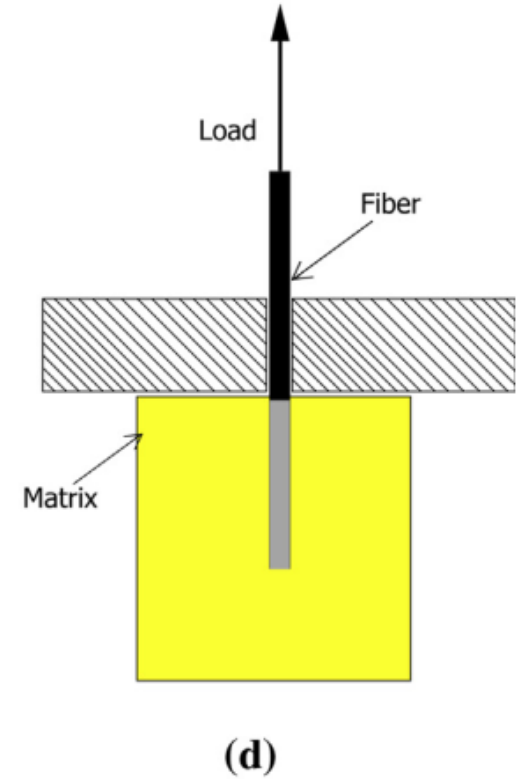


Figure 1. Fragmentation specimen geometry and associated axial fibre tensile stress distribution of fragments [11].

Fragmentation Method



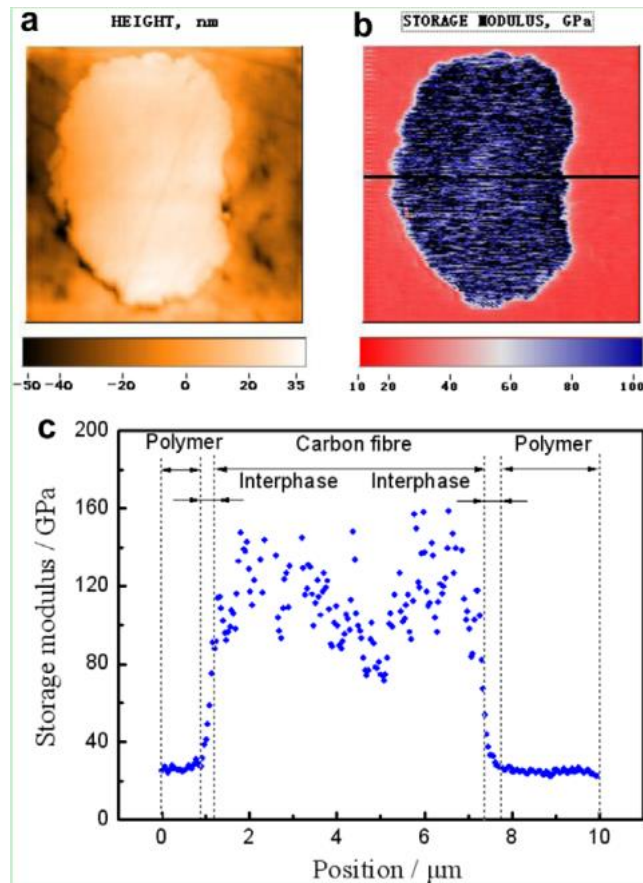
Micro-debonding Method



Single-fiber Pull-out Method

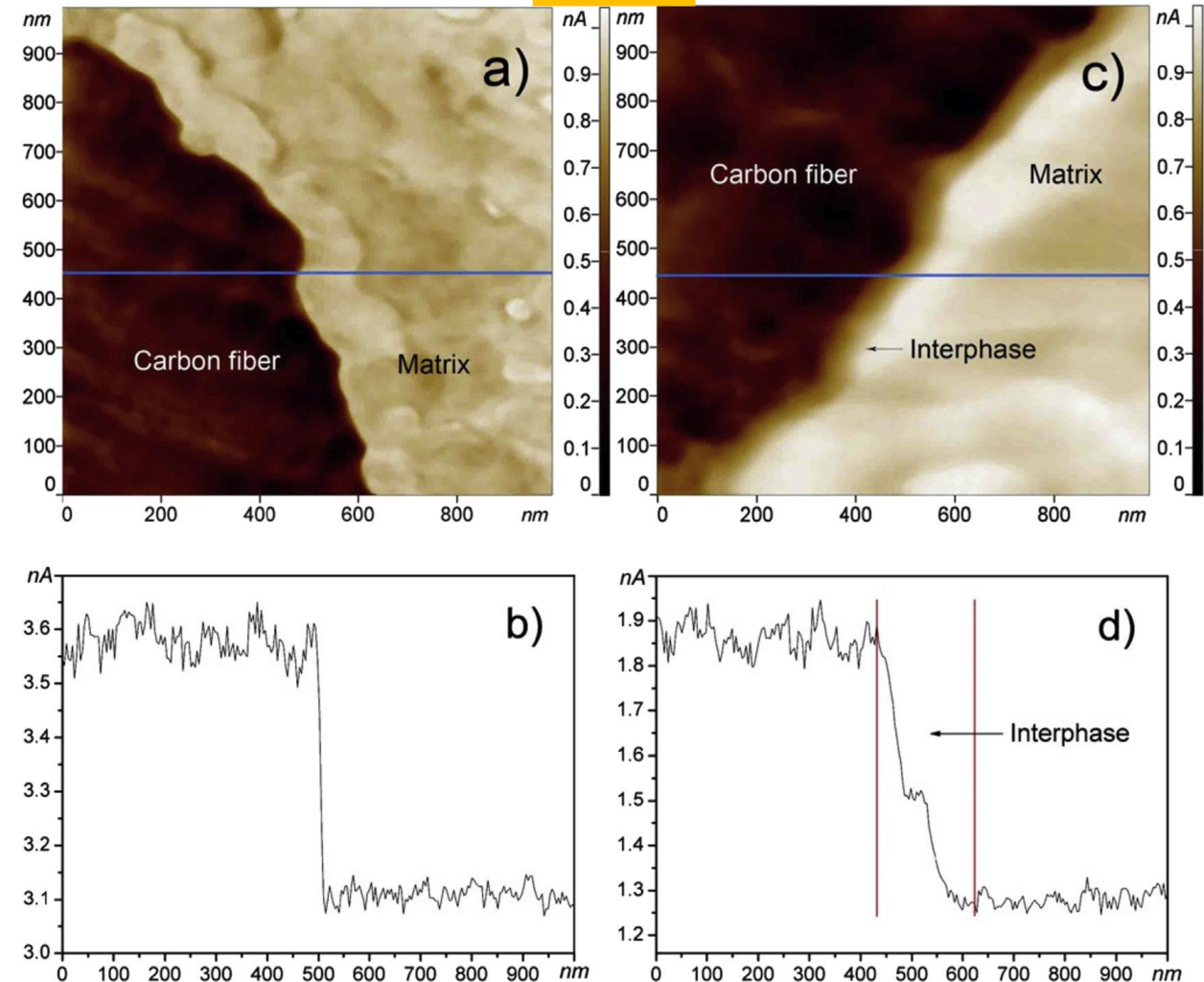
# Modulus Distribution Characterization

## Nanoscale Dynamic Mechanical Imaging

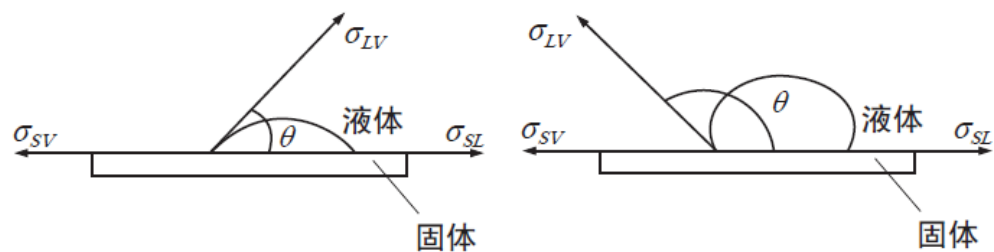


Carbon, 2010, 48(11):3229-3235

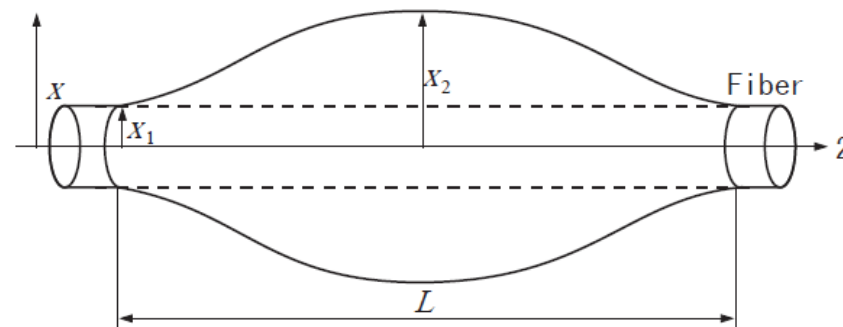
AFM



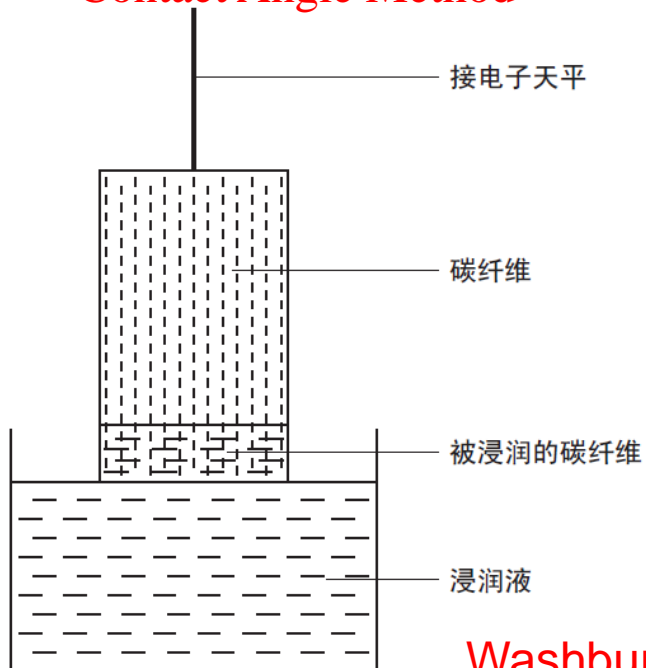
# Wetting Characterization



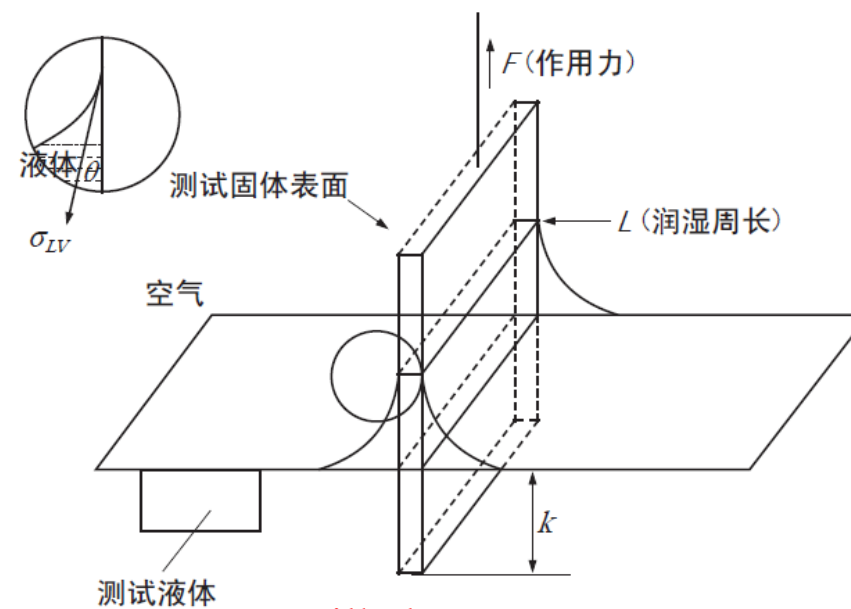
Contact Angle Method



Sessile Drop Method



Washburn Method

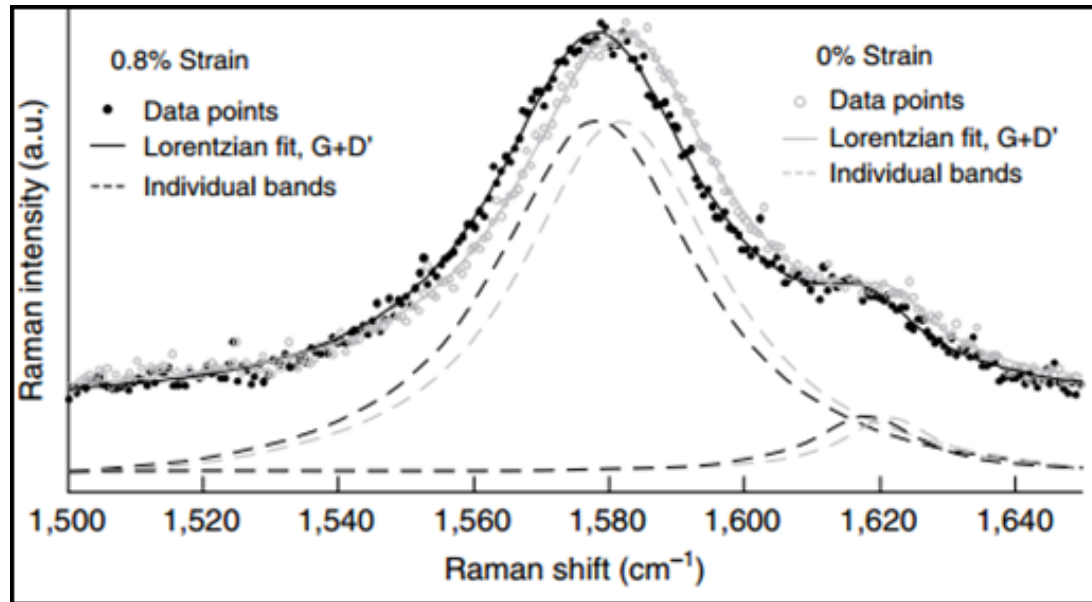


Wilhelmy Type

# Interfacial Stress Characterization

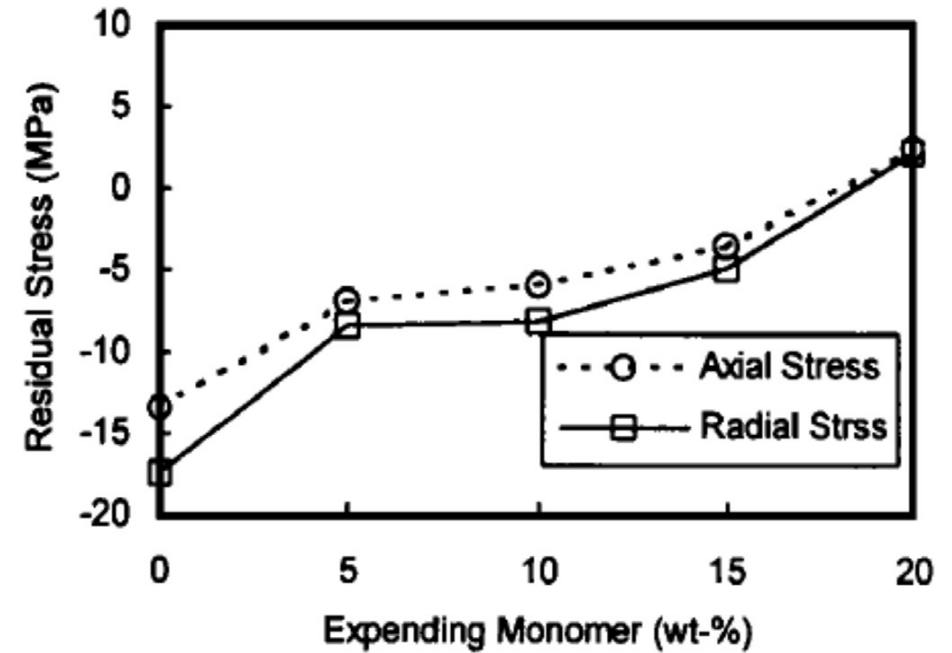


## Raman Spectra



Nature Communications, 2011, 2(1):255

## XRD



Technol. Lett. 2000, 72-74

# Surface Properties Characterization of CF



Surface Properties	Evaluation Method
Surface morphology	SEM, AFM, TEM, EDX
Chemical properties	XPS, FTIR, EDX, AES
Aggregation state	XRD, Raman
Surface absorption	BET

# Research Contents——CFRP sample preparing



## Problems

1. Pitch-based carbon fibers are too fragile and easily broken during sample preparation .
2. In the micro-debonding method, it's difficult to control the size of resin droplets.
3. In the modulus distribution tests, the residual powder of carbon fiber and resin caused by polishing will interfere the measurements of AFM.
4. The in-situ Raman test is difficult for CFRP to conduct.
5. Analysis of functional groups on the surface of CF through FTIR is a challenge.
6. The sample preparation skills are not so mature in micro-debonding test techniques in our research group, especially for pitch-based CF.



# Research Contents——CFRP sample preparing



## Challenges

- The small scale of the interface region.
- How to control or modify the CF surface.
- How to decrease or remove the effect of both CF and resin.
- How to prepare the suitable samples for characterizatin.

# Our Research Results

1

研究背景和研究内容

2

电热效应对CFRPs界面内应力的影响研究

3

湿热环境对CFRPs界面结合能力的影响研究

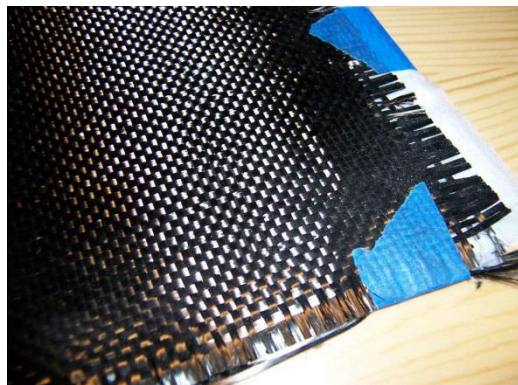
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有机溶剂对CFRPs热响应的影响研究

5

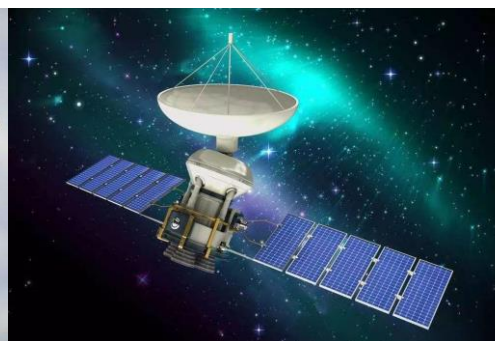
全文总结

# 碳纤维复合材料 (CFRPs)



➤ 碳纤维

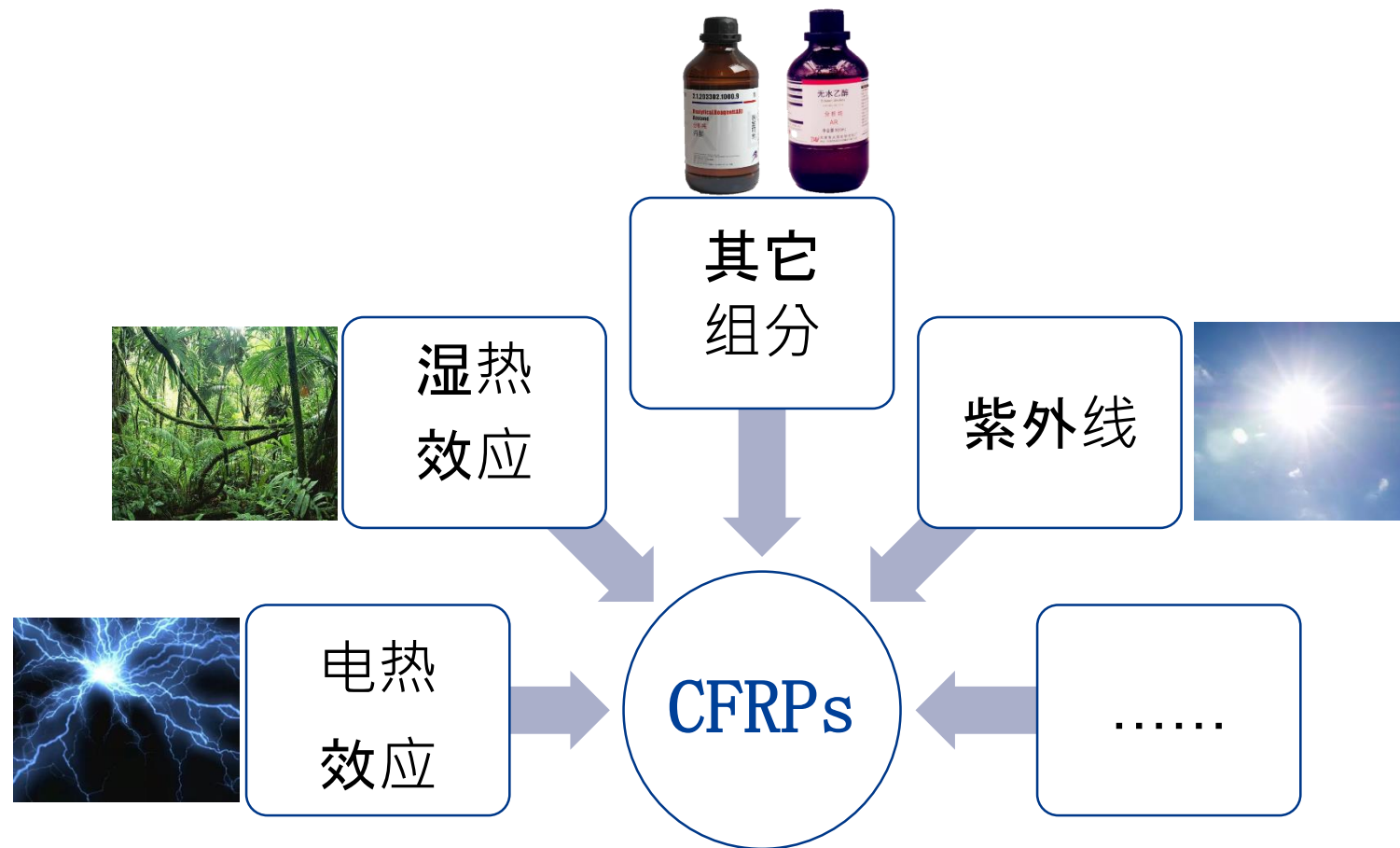
➤ 树脂



➤ 应用

<https://en.wikipedia.org/wiki/>  
<https://image.baidu.com/>

# CFRPs在实际使用中的威胁



# 电热效应-高电流

➤ 高电流对样品表面的破坏

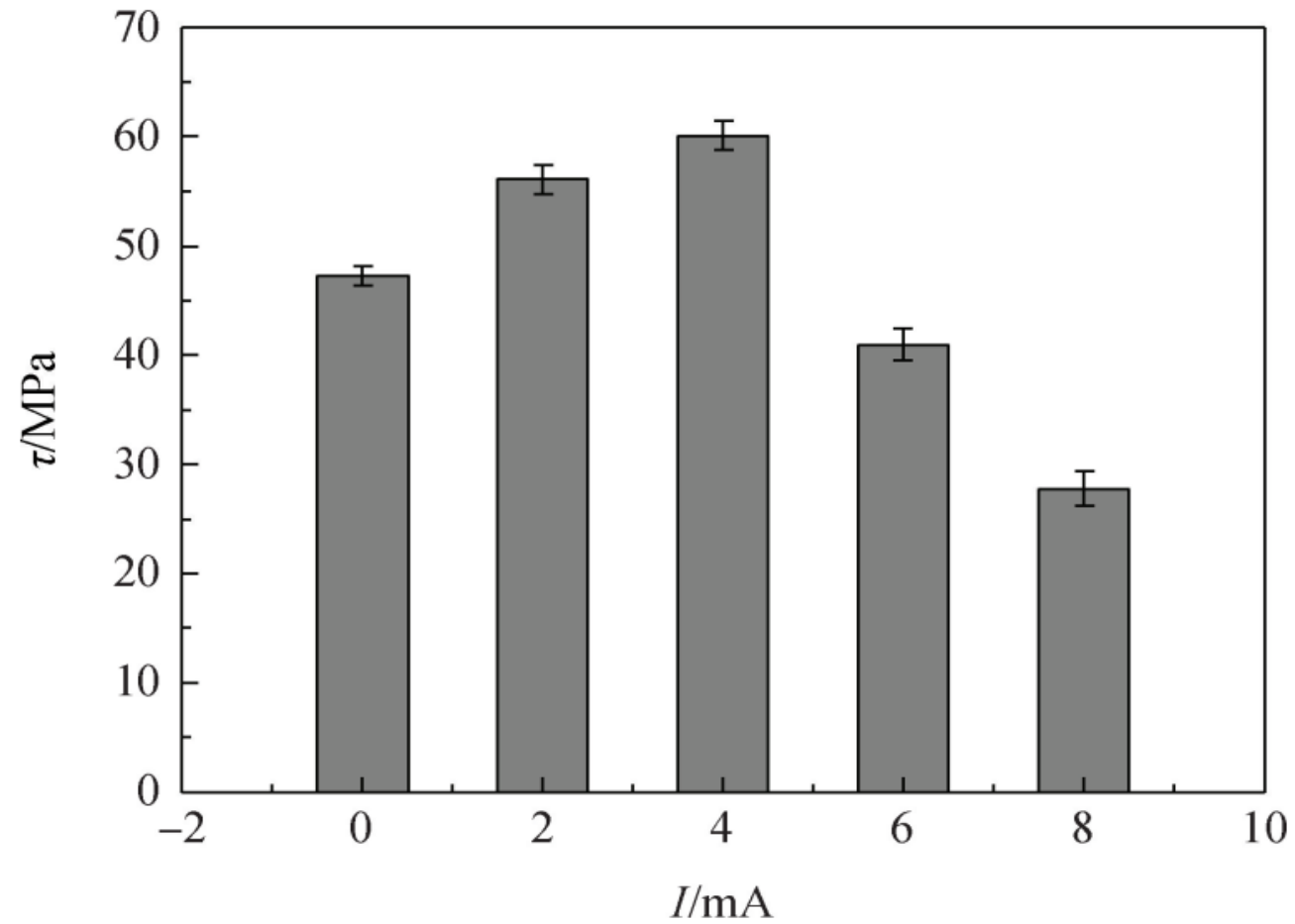


➤ 印尼飞机事故



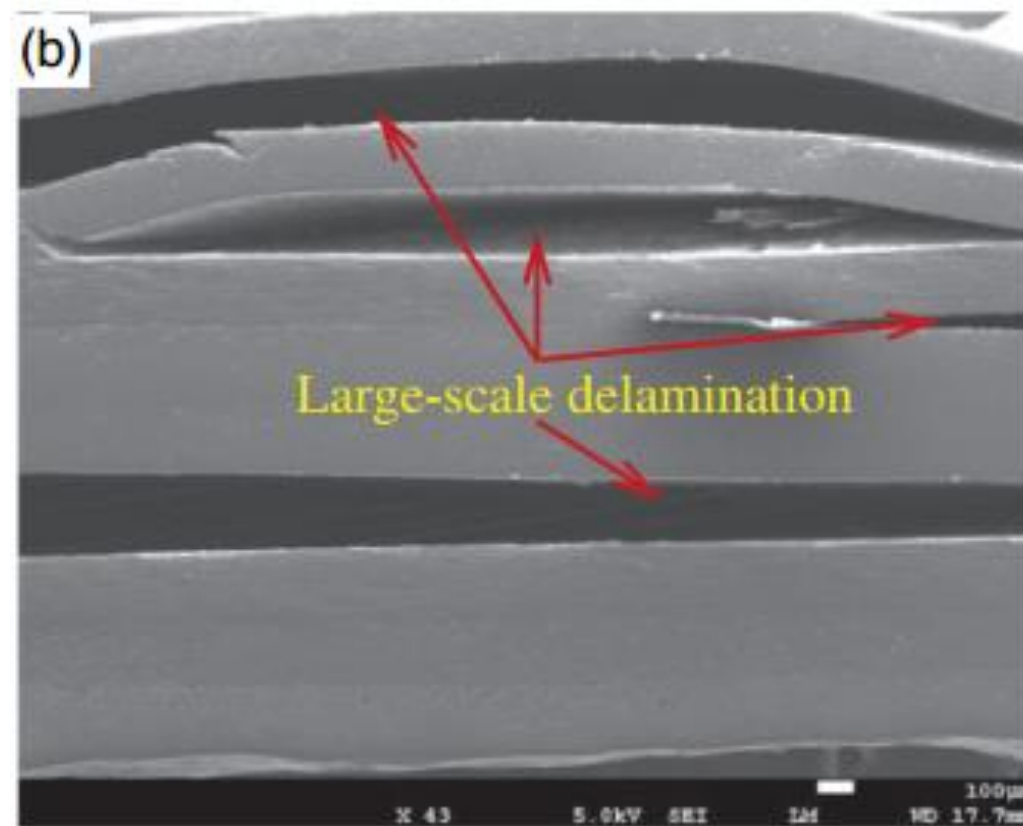
## 电热效应-低电流

➤ 不同电流下CFRPs拉伸强度



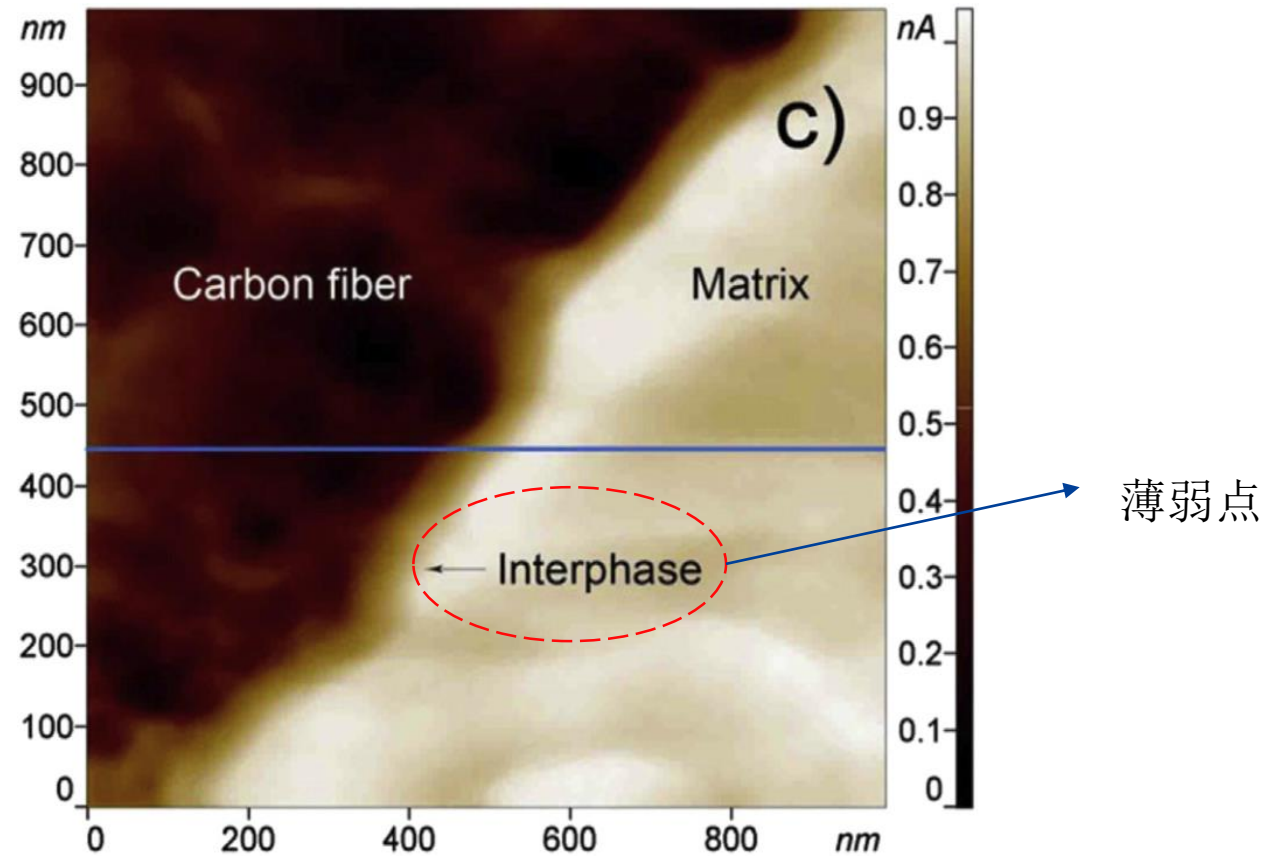
## 湿热效应对复合材料的影响

- 湿热环境引起的CFRPs脱层



# CFRP<sub>s</sub>界面研究的必要性

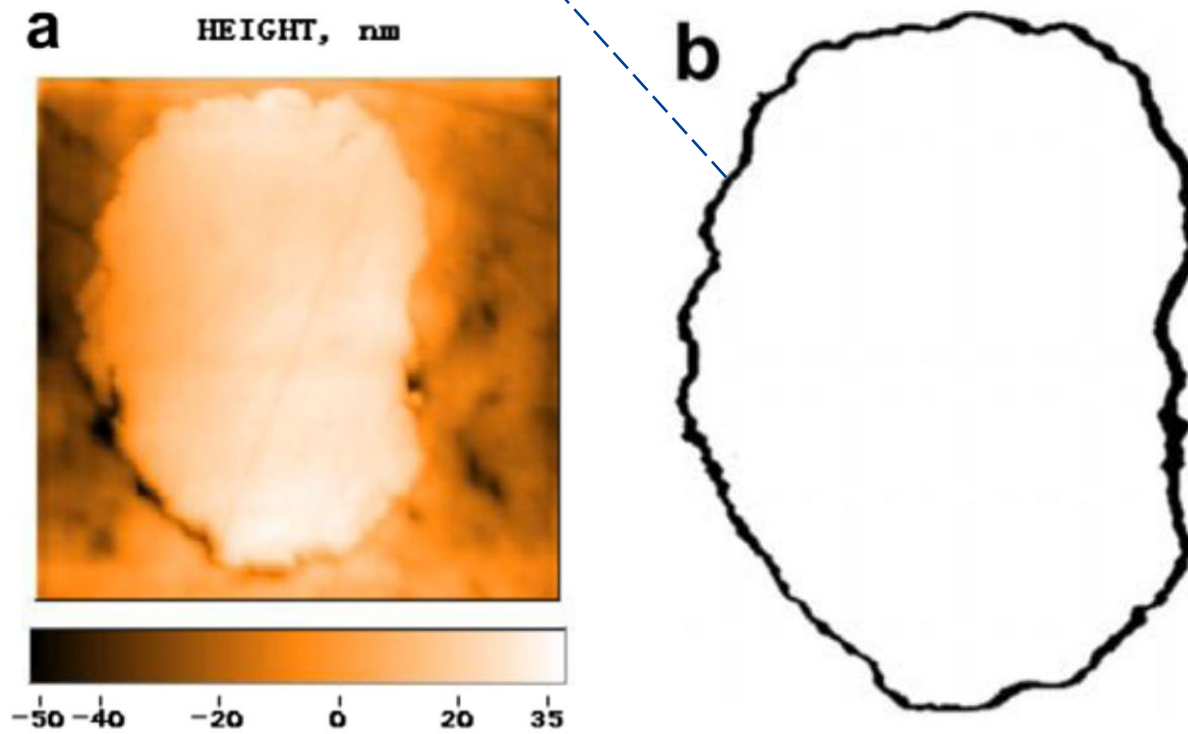
➤ 界面的AFM图像





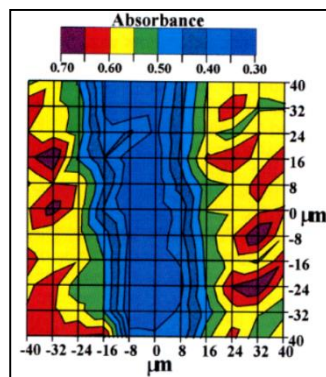
## CFRPs界面研究的必要性

➤ 界面尺度小：100-200nm厚



# CFRPs的界面表征现状

Applied Spectroscopy, 1996, 50(1):1-10

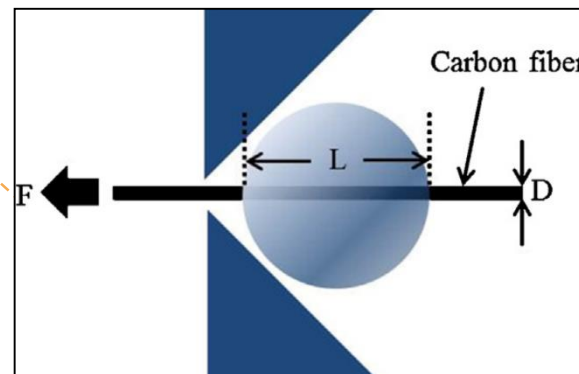


FTIR microscope

化学结构

结合强度

Applied Surface Science, 2015, 328:241-246.



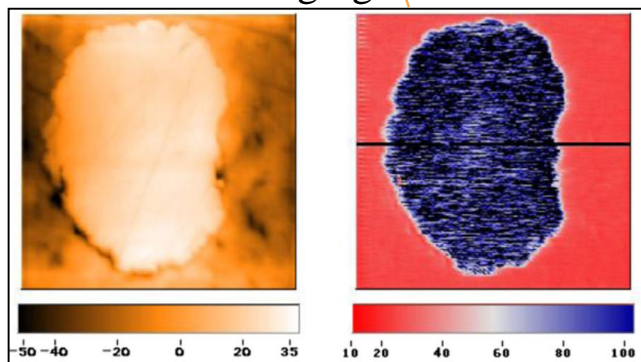
Micro droplet test

Nanoscale dynamic mechanical imaging

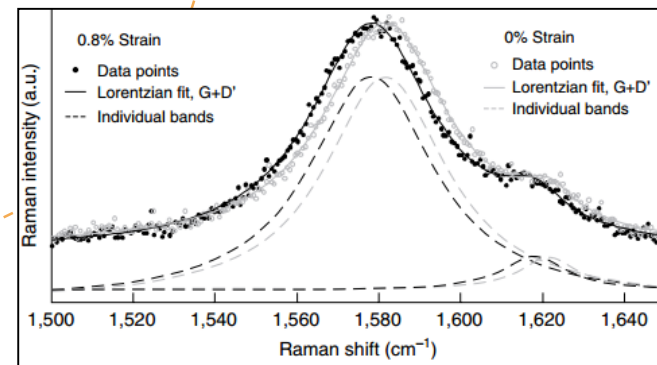
模量分布

残余应力

Raman spectra

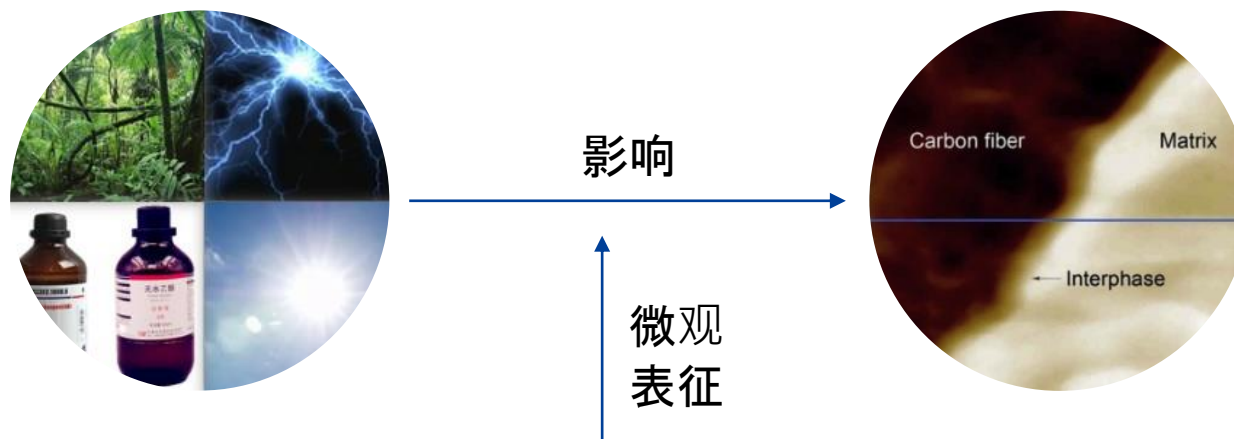


Carbon, 2010, 48(11):3229-3235



Nature Communications, 2011, 2(1):255

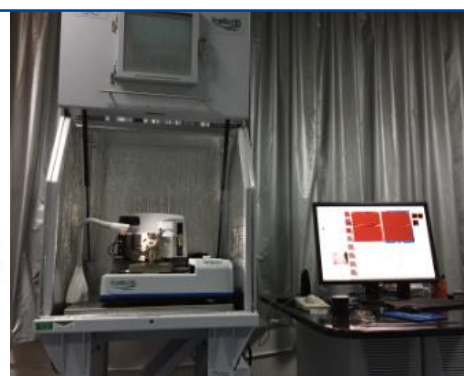
# 研究内容



➤ 拉曼光谱



➤ 显微红外光谱



➤ 原子力显微镜

**1** 研究背景和研究内容

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**2** 电热效应对CFRPs界面内应力的影响研究

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**3** 湿热环境对CFRPs界面结合能力的影响研究

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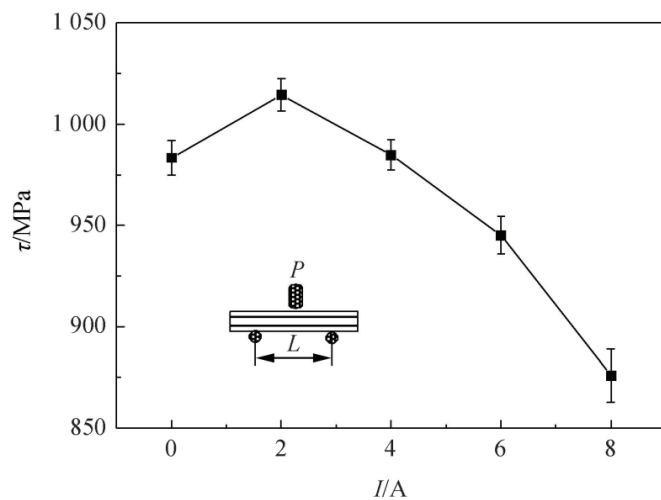
**4** 有机溶剂对CFRPs热响应的影响研究

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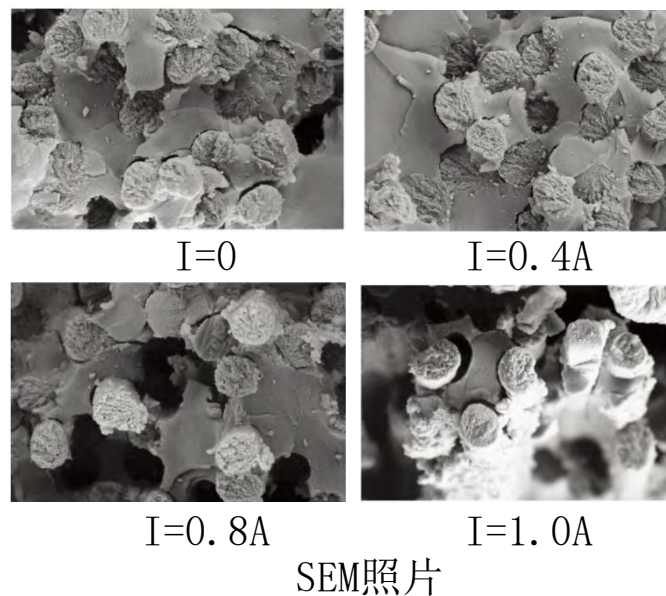
**5** 全文总结

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## 电热效应对CFRPs影响的研究现状



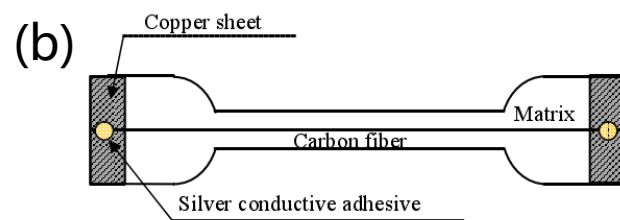
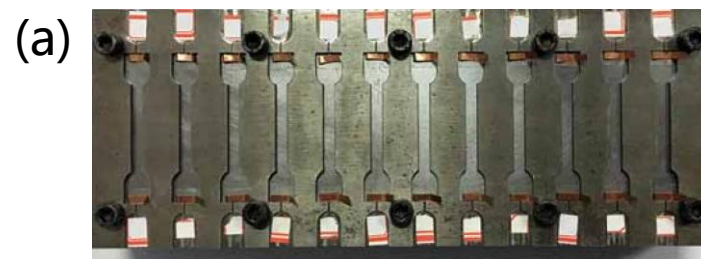
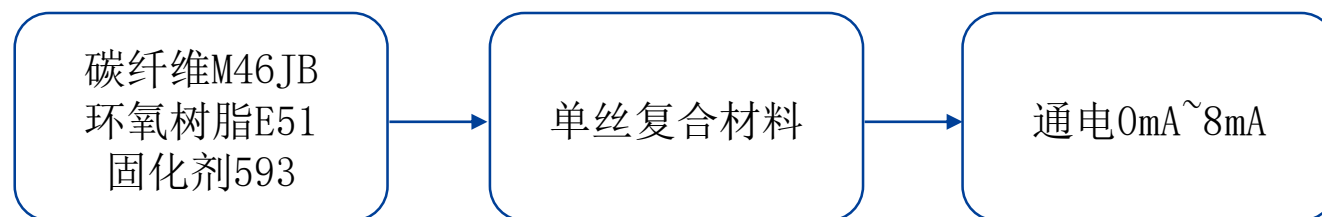
层间剪切



外观

界面内应力是否变化？

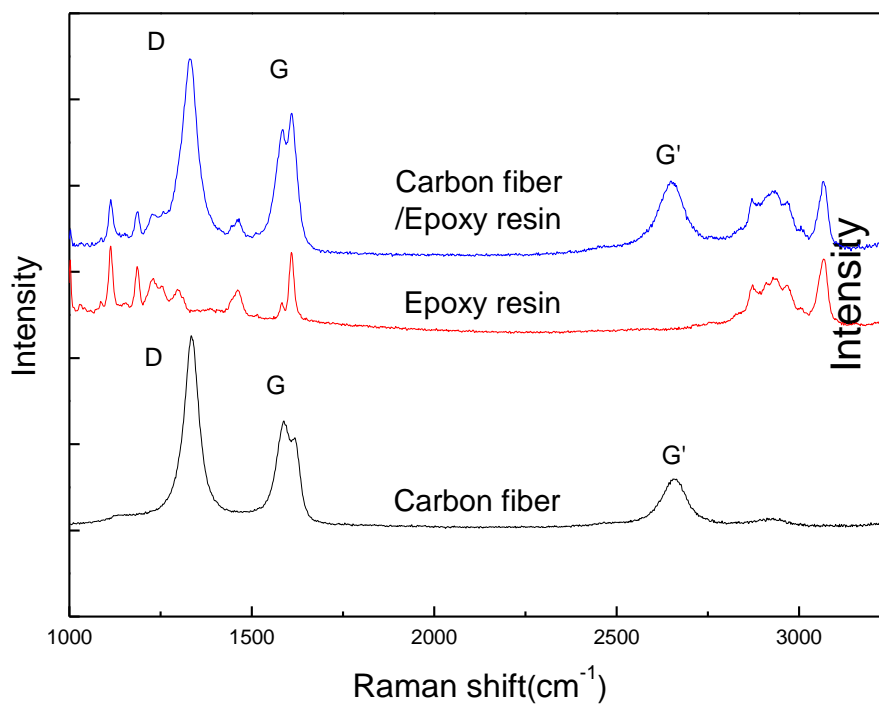
## 试样制备和电热处理



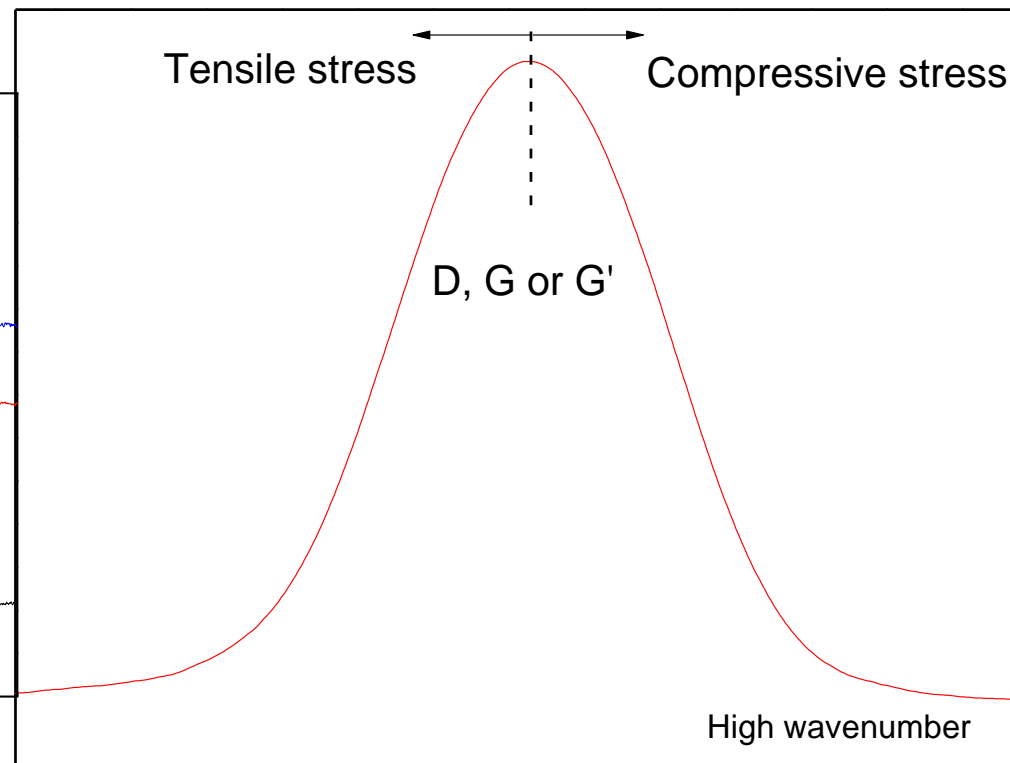
(a) 单丝模具 (b) 单丝样品示意图 (c) 单丝样品实物图

# 拉曼光谱研究微电流对界面内应力影响

## ■ 碳纤维拉曼光谱和内应力关系



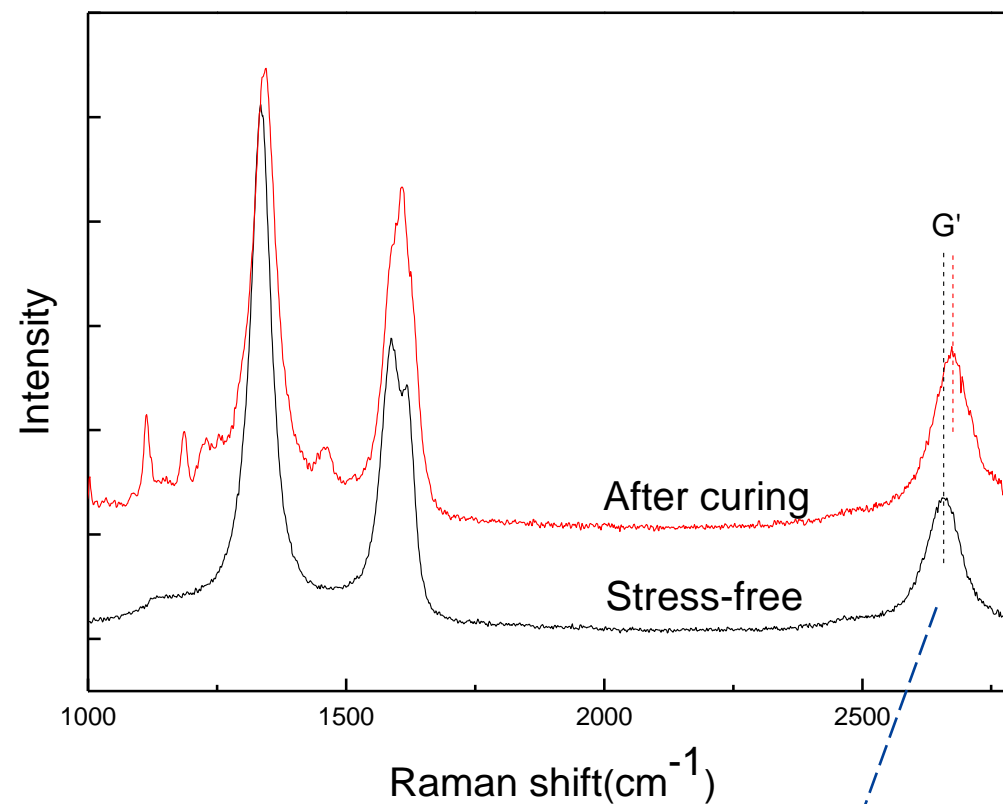
碳纤维、环氧树脂的拉曼光谱



应力作用下特征带的位移

## 拉曼光谱研究微电流对界面内应力影响

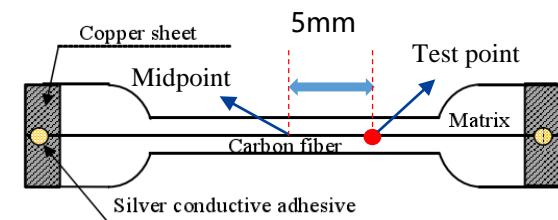
- 试样初始内应力情况



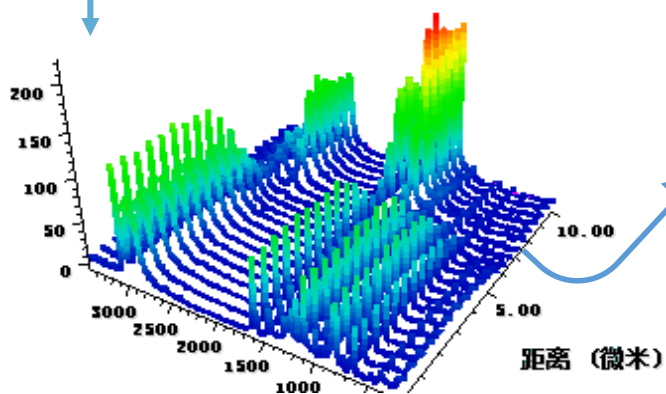
固化之后界面处产生压应力



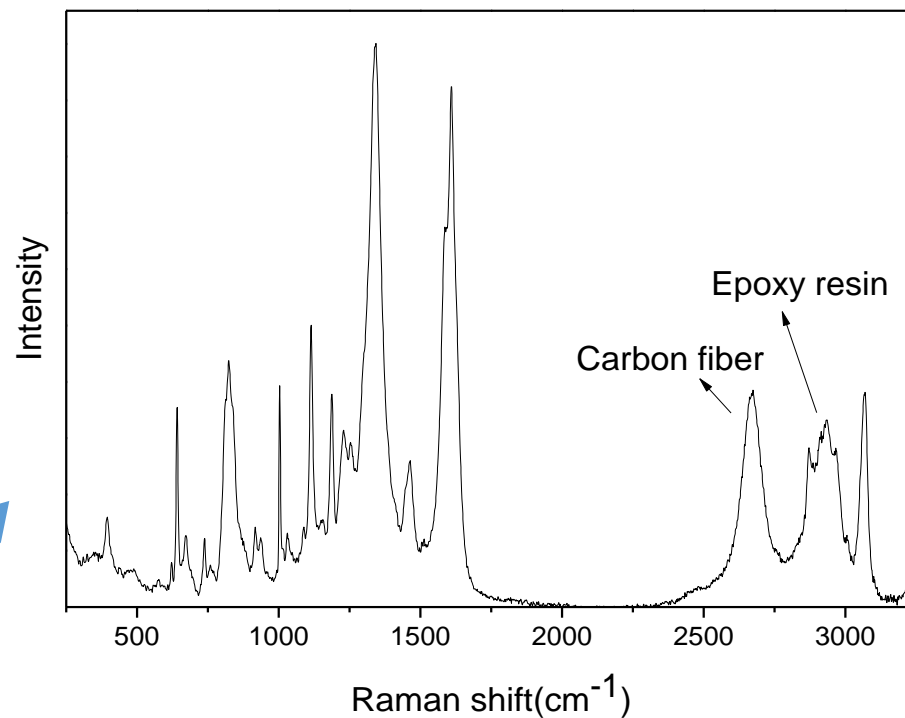
## ■ 试样测试位置的确定



测试点位置



测试点不同深度的拉曼光谱

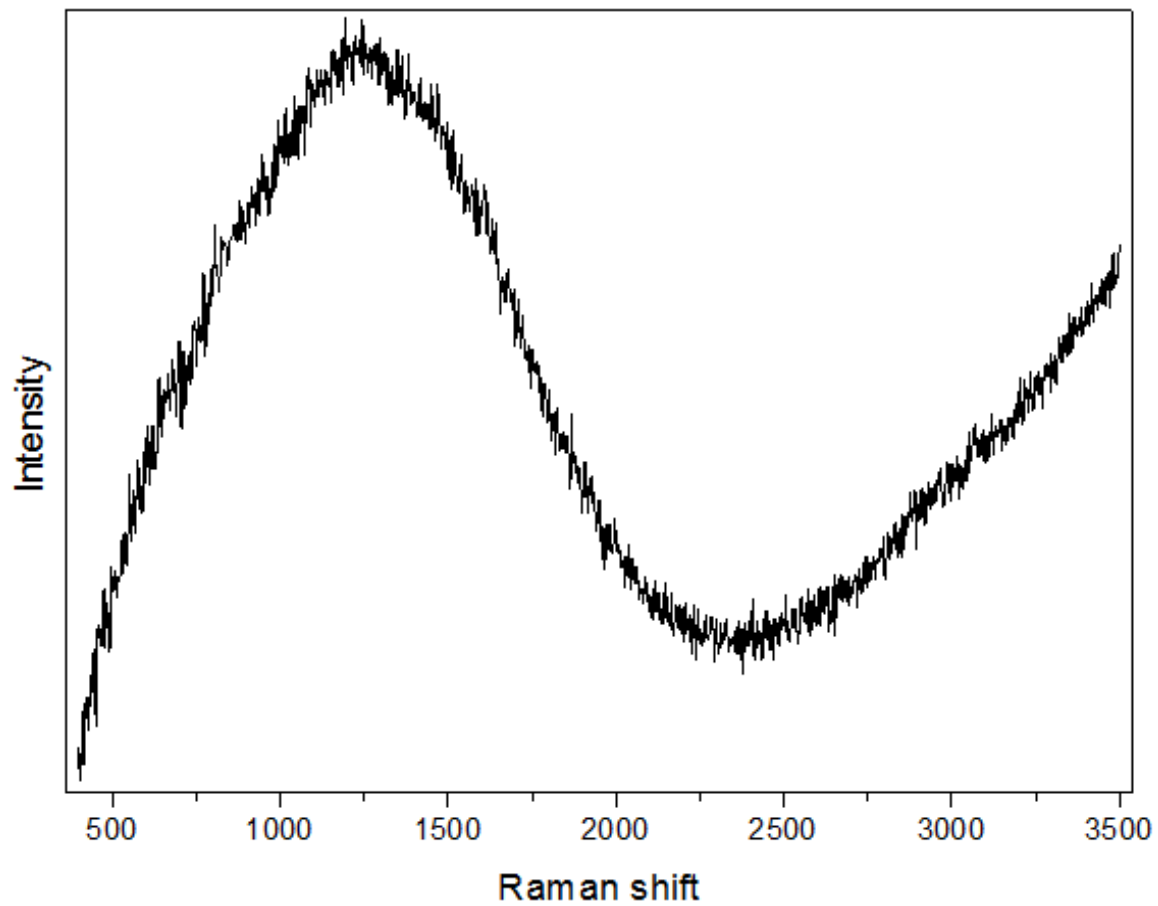


测试深度的界面拉曼光谱

测试位置不同,  
G' 带位移不同

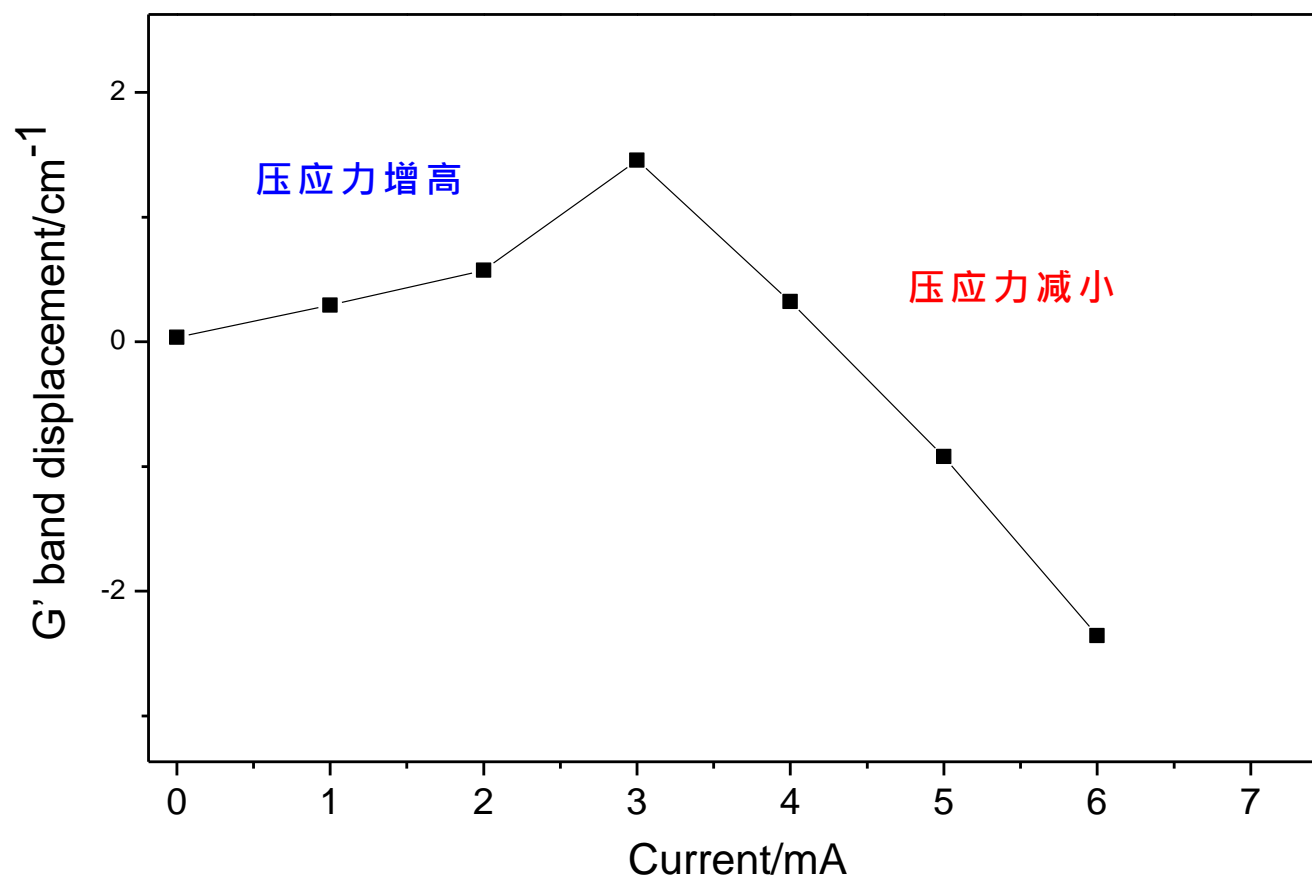
采取原位测试  
比较内应力变化

- 较高电流（7mA及8mA）处理后界面的拉曼光谱



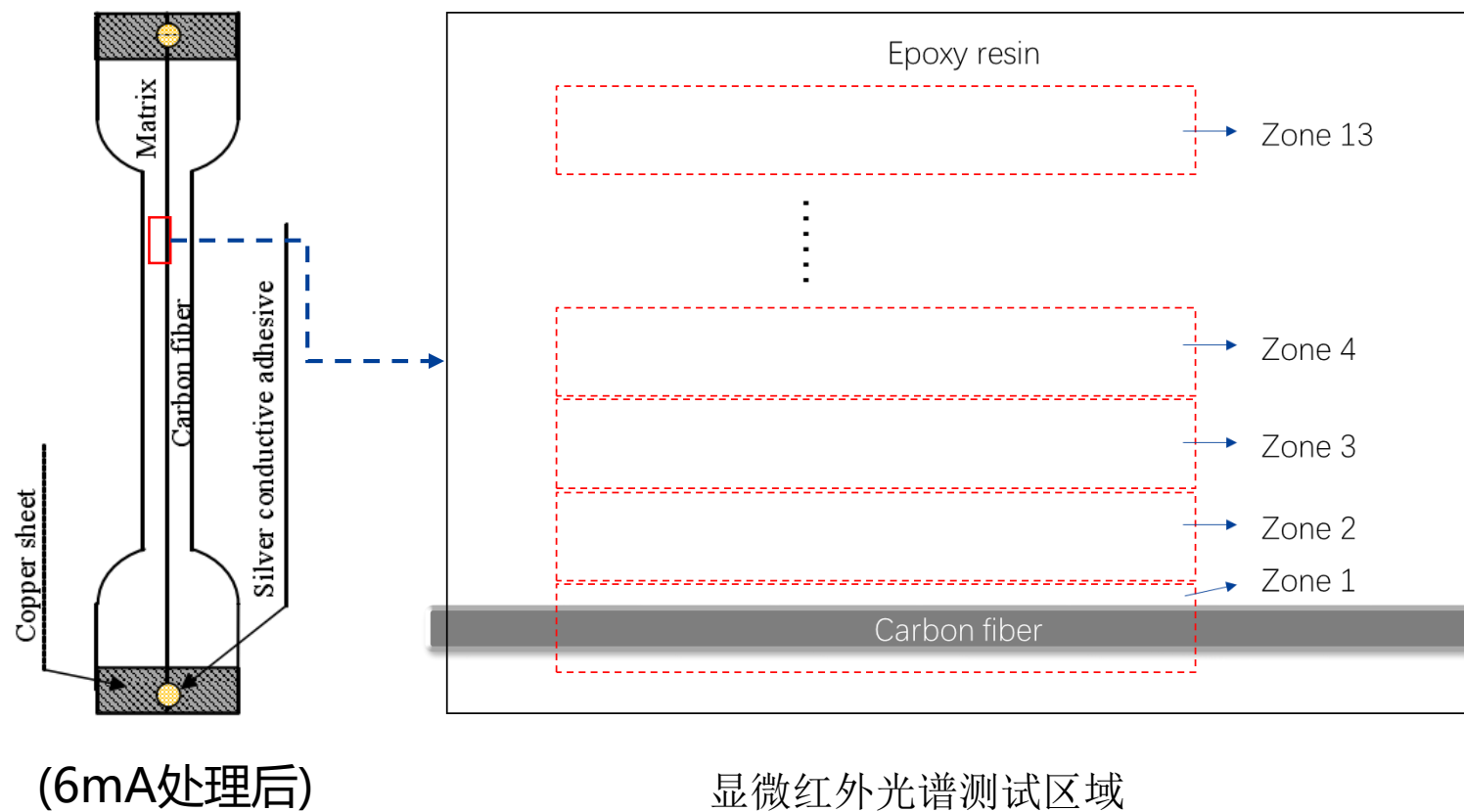
7mA电流处理后的单丝复合材料界面拉曼光谱

## CFRPs界面应力的变化规律 (0-6mA)

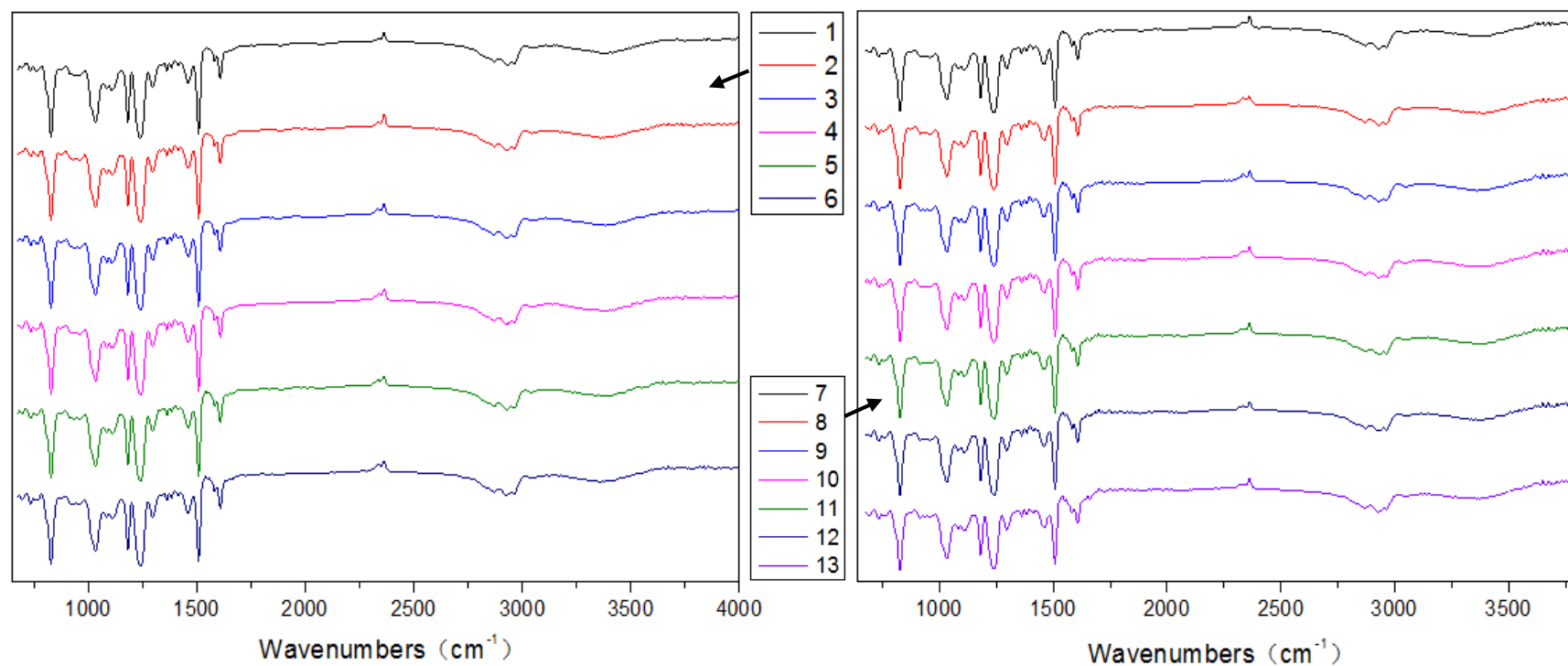


0-6mA电流作用后样品测试位置G' 带的位移量

## CFRPs界面附近区域的显微红外光谱表征

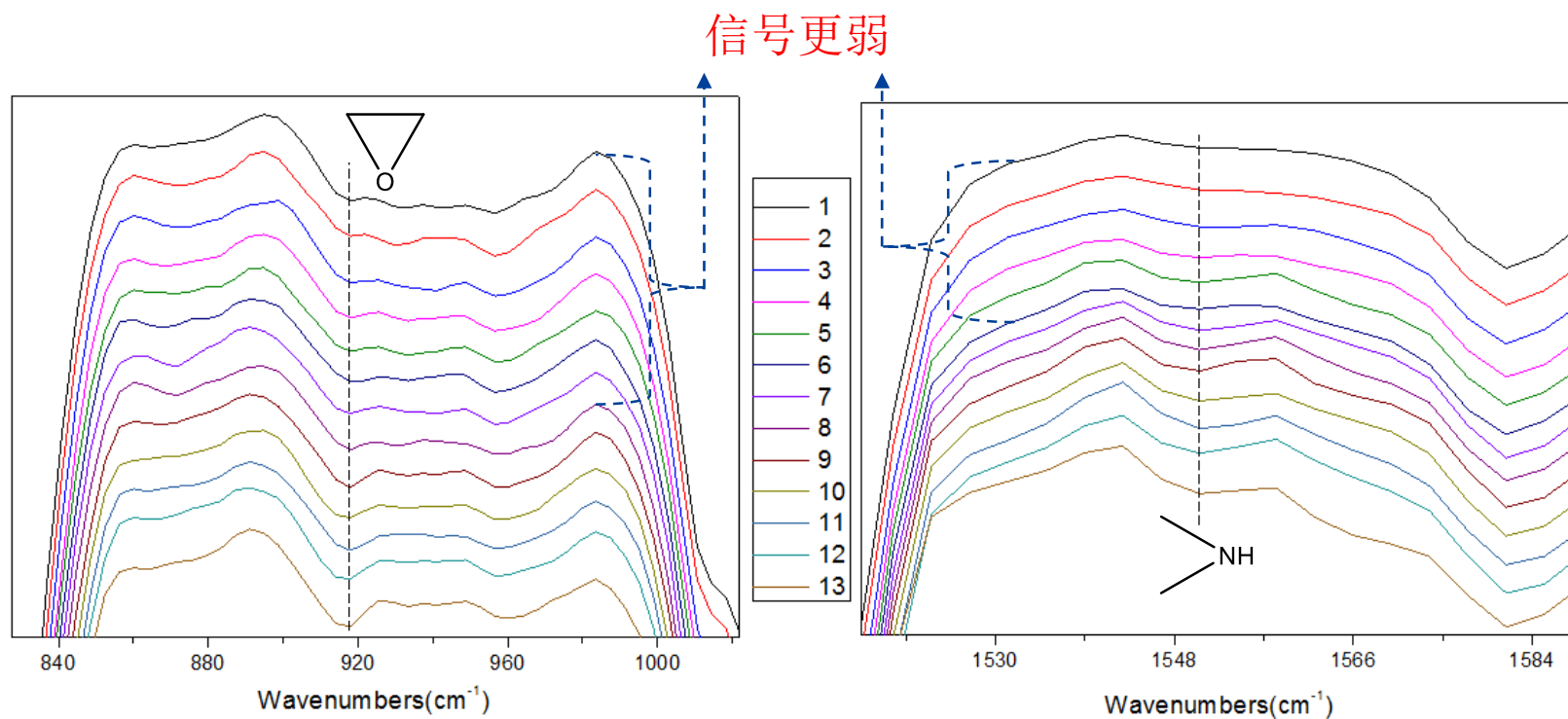


## CFRP<sub>s</sub>界面附近区域的显微红外光谱表征



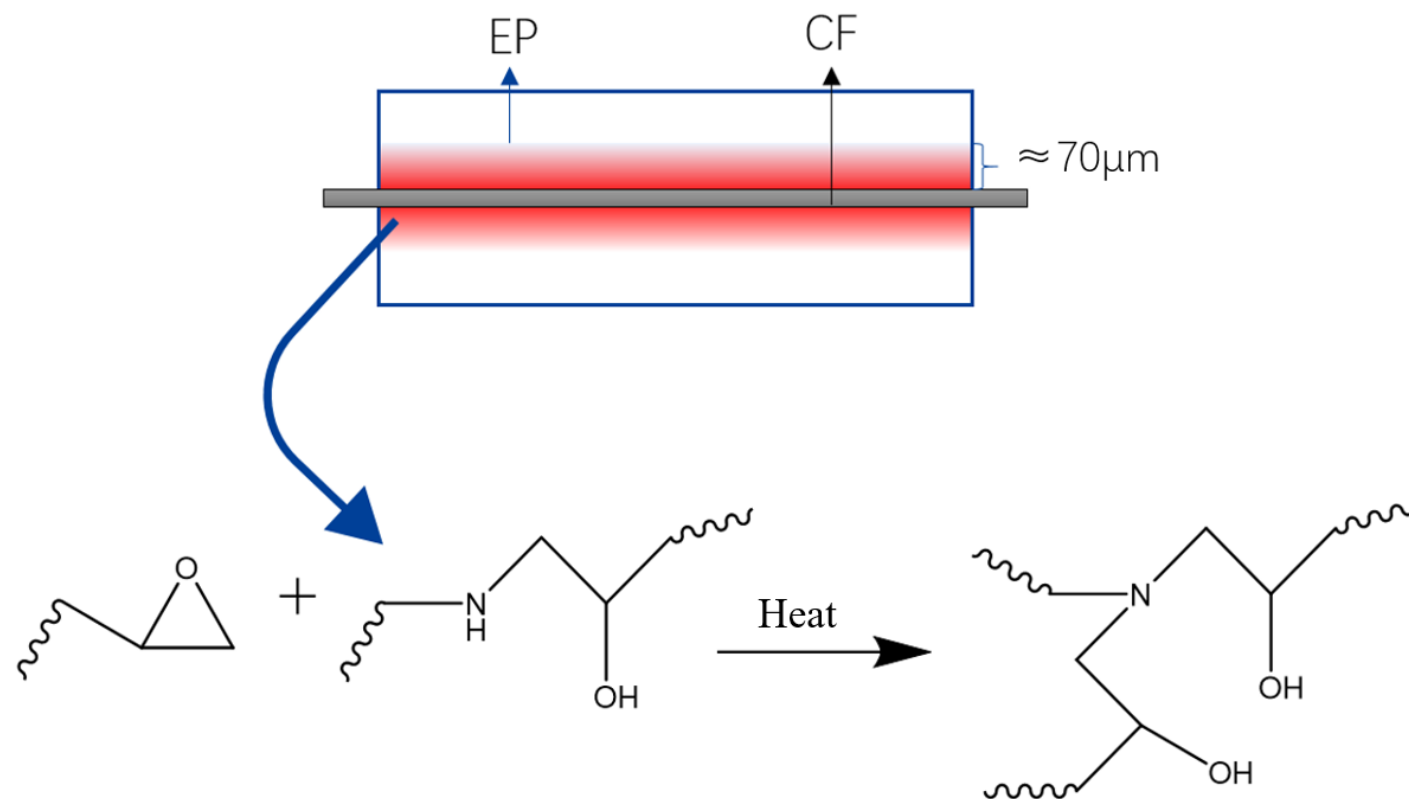
测试区域1-13的显微红外光谱

## CFRPs界面附近区域的显微红外光谱表征

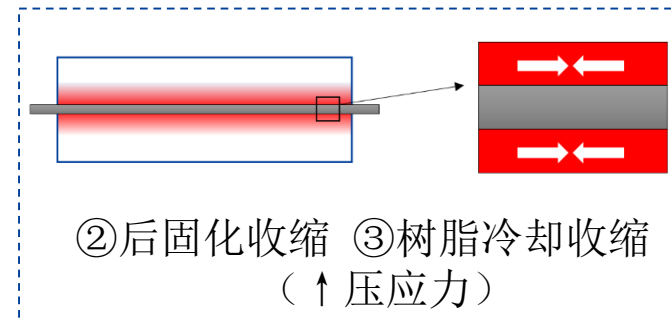
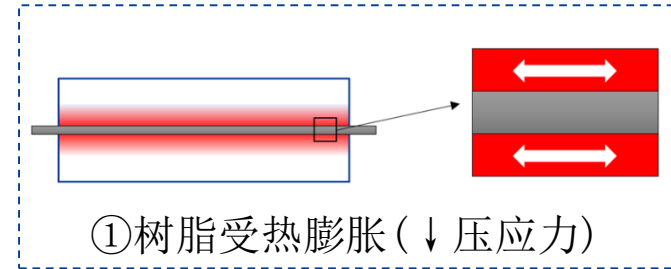
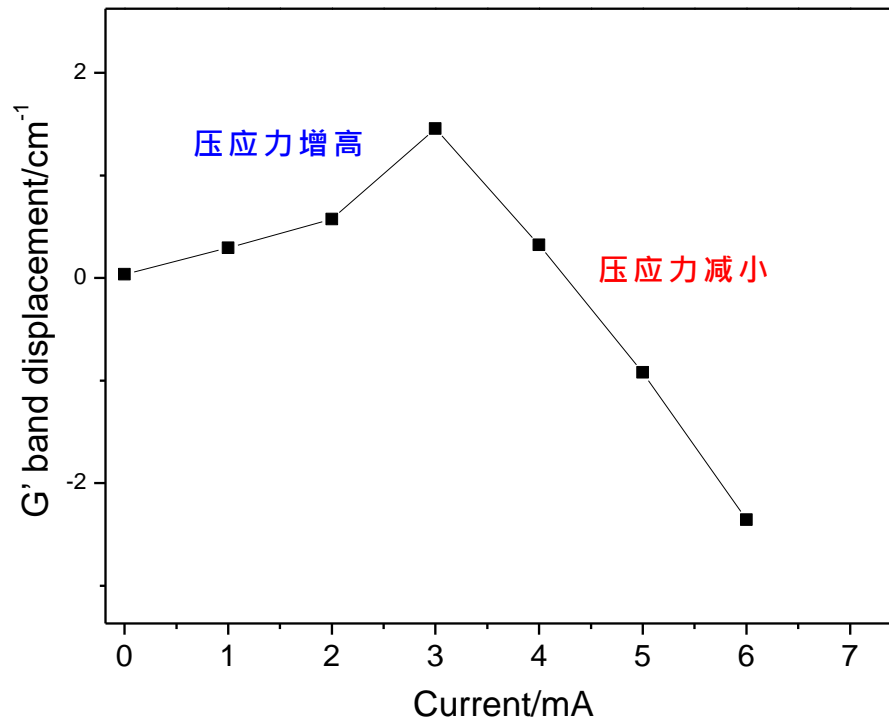


只有距纤维约70 $\mu\text{m}$ 范围内的树脂发生了进一步后固化

## CFRPs界面附近区域发生的进一步固化(后固化)



## 电热作用下内应力变化原因分析





## 2.4 本章小结

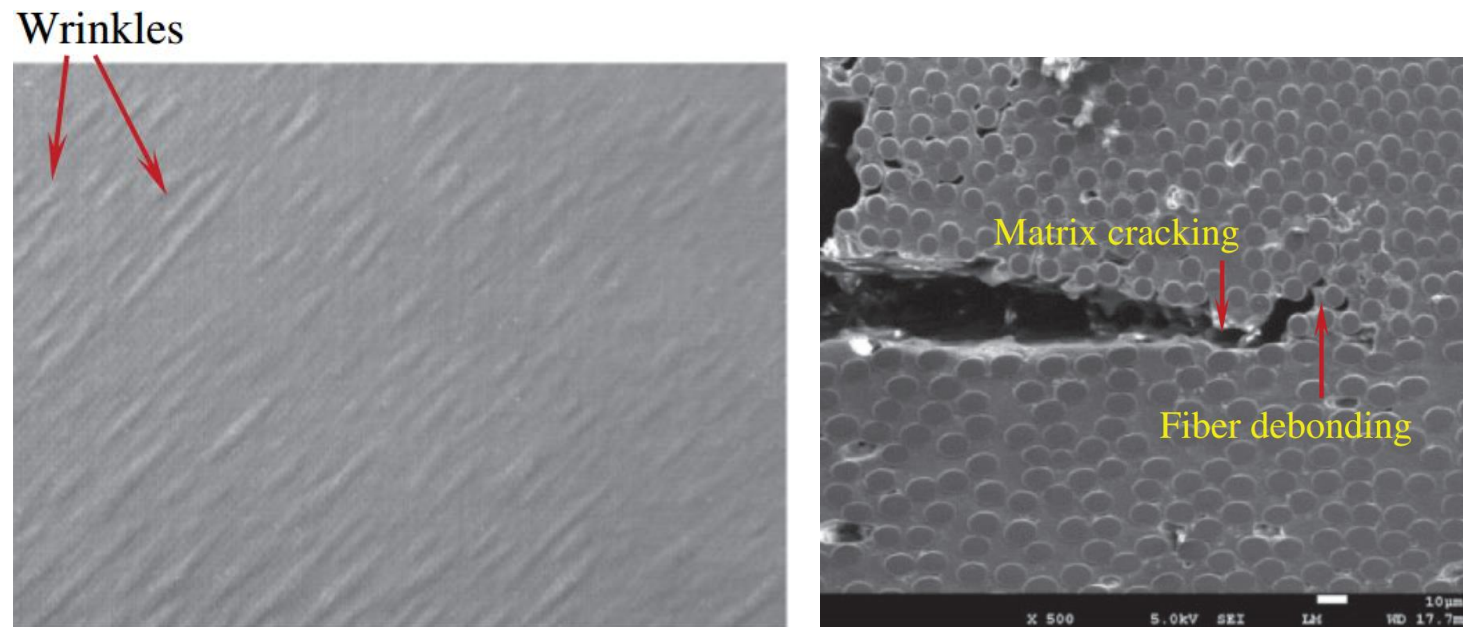
**1** 明确了试样初始界面应力为**压应力**。

**2** 电流使纤维附近约**70 $\mu\text{m}$** 范围的树脂发生后固化。

**3** 随处理电流增大(0-6mA), 界面压应力**先增后减**。

- 1 研究背景和研究内容
- 2 电热效应对CFRPs界面内应力的影响研究
- 3 湿热环境对CFRPs界面结合能力的影响研究
- 4 有机溶剂对CFRPs热响应的影响研究
- 5 全文总结

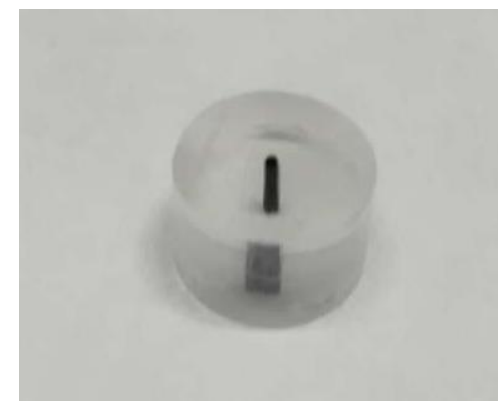
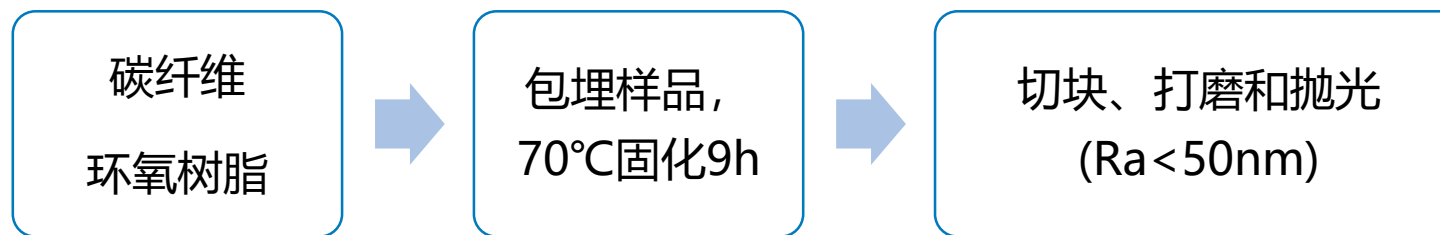
### 3.1 湿热环境对CFRPs界面结合能力的影响研究——研究背景



湿热处理造成的褶皱和结构破坏

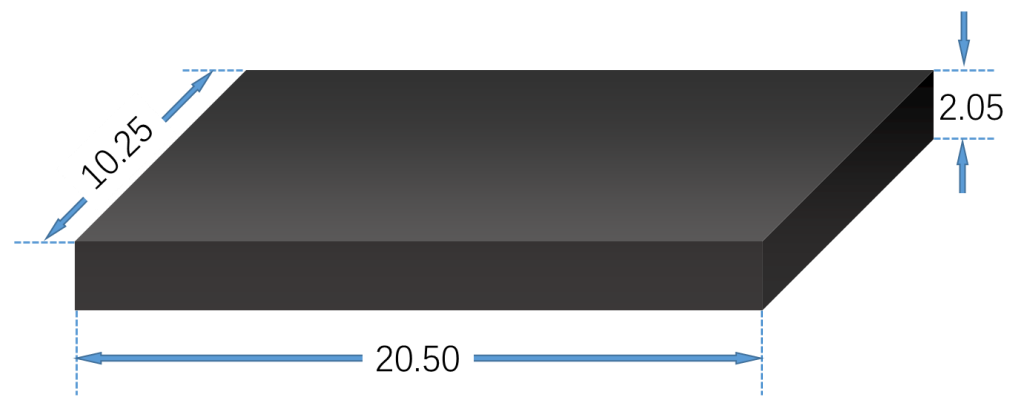
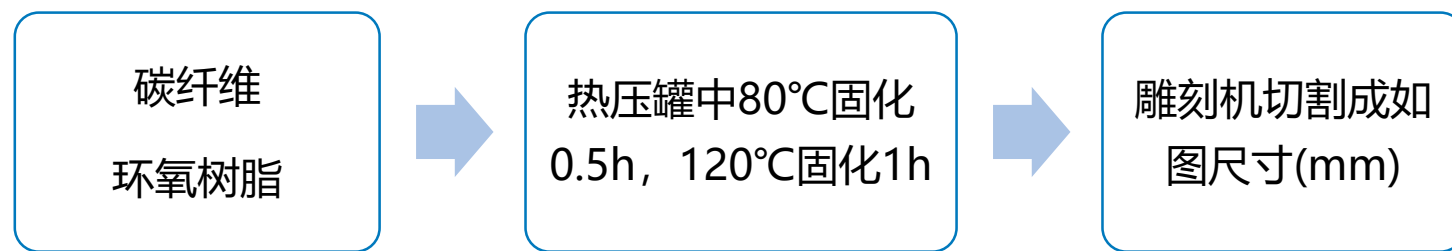
## 试样制备和处理方式

- **试样制备-截面复合材料(用作微观测试)**



## 试样制备和处理方式

- **试样制备-交叉层压板复合材料（用作宏观测试）**



## 试样制备和处理方式

- **试样处理方式(截面试样和层压板试样)**

---

1) **热处理**：100°C的烘箱中加热2小时；

---

2) **湿热处理**：100°C下水煮2小时；

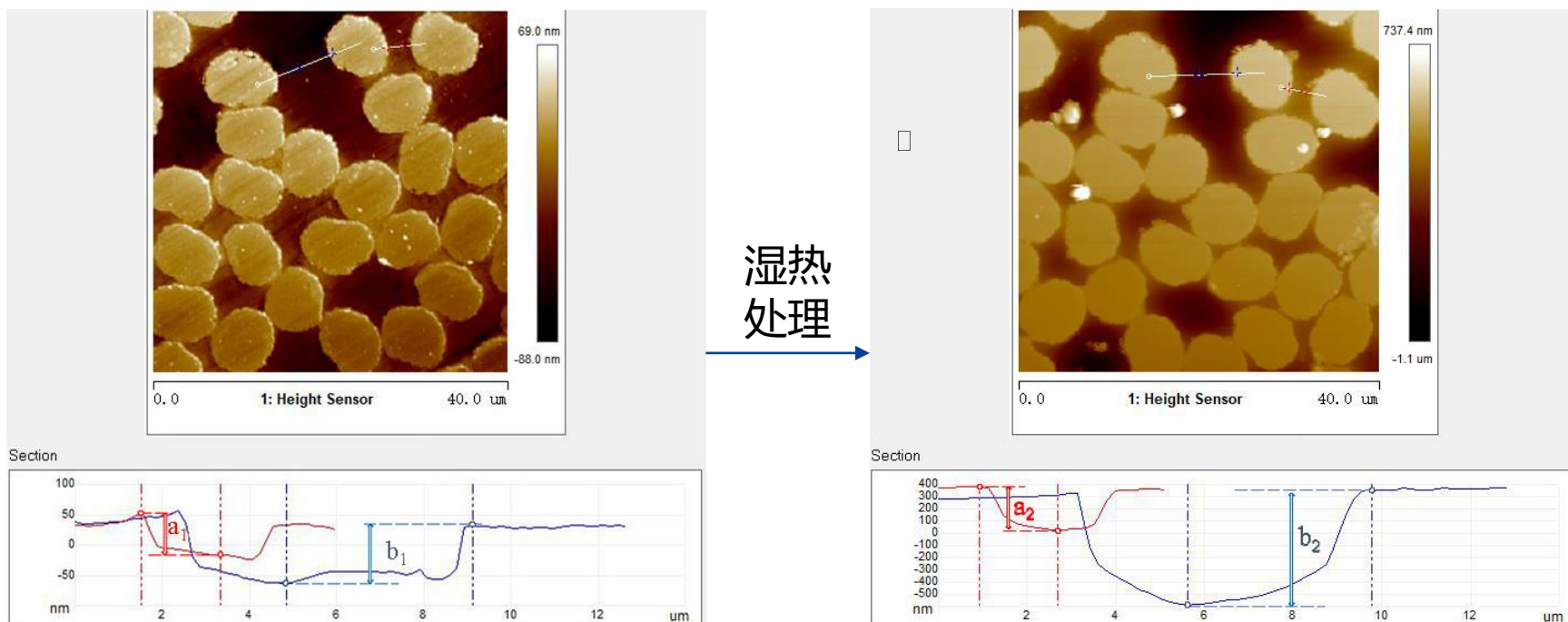
---

3) **对照组(未处理)**：始终存放于25°C干燥器。

---

## 热处理和湿热处理对树脂形貌的影响

### ■ 湿热处理对树脂形貌的影响

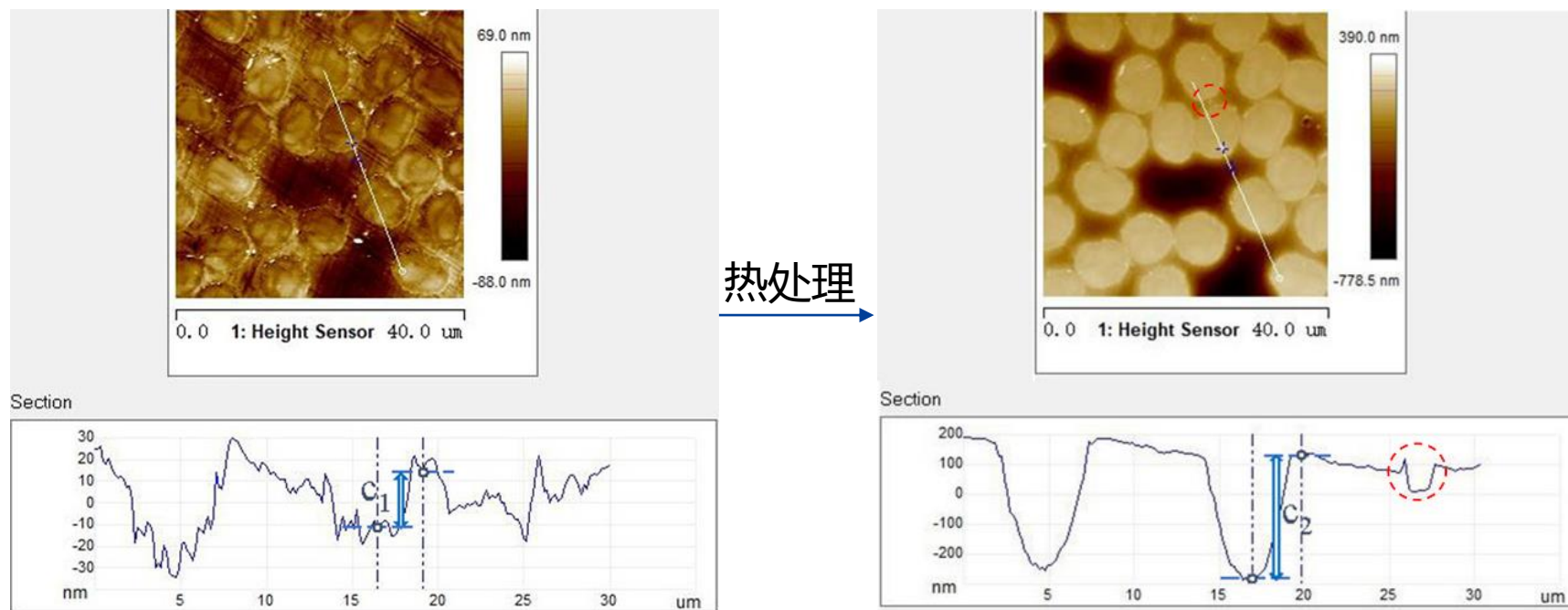


相同区域AFM形貌

收缩幅度:  $b_1 \rightarrow b_2 \gg a_1 \rightarrow a_2$

## 热处理和湿热处理对树脂形貌的影响

### ■ 热处理对树脂形貌的影响



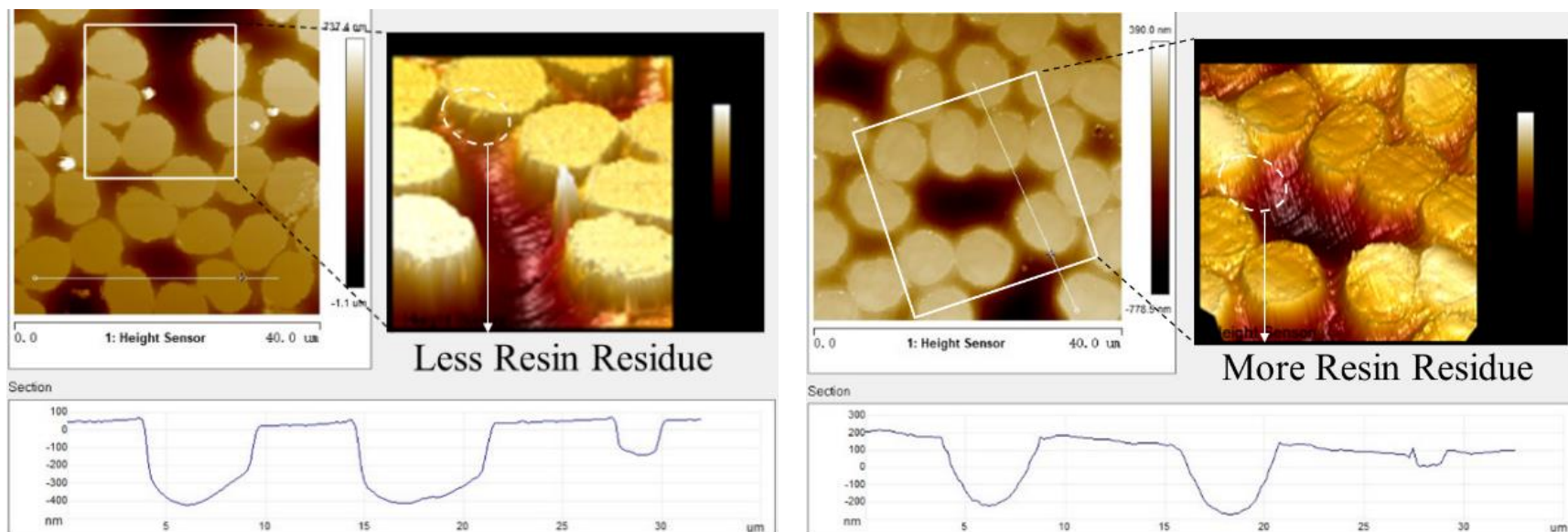
相同区域AFM形貌

树脂同样明显收缩



## 热处理和湿热处理对树脂形貌的影响

### ■ 湿热处理和热处理对树脂形貌影响的比较

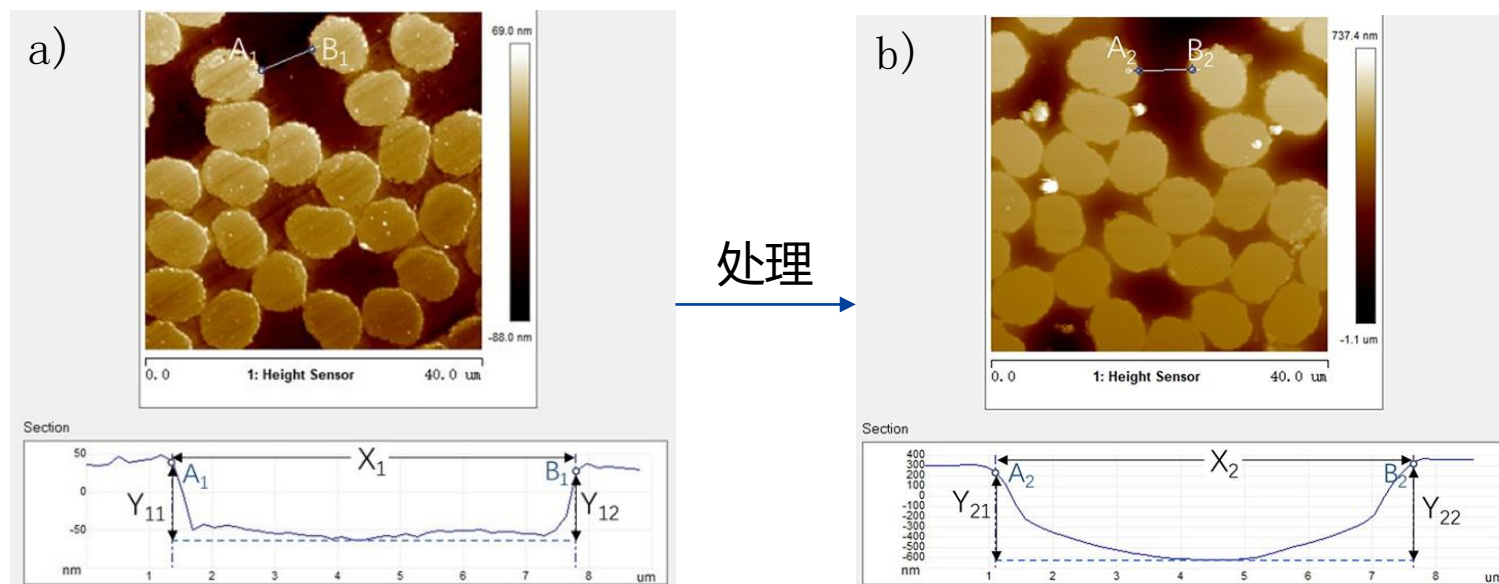


湿热处理之后  
U字形形貌

热处理之后  
V字形形貌

# 基于相邻纤维间树脂热响应的定量分析

## 参数设定



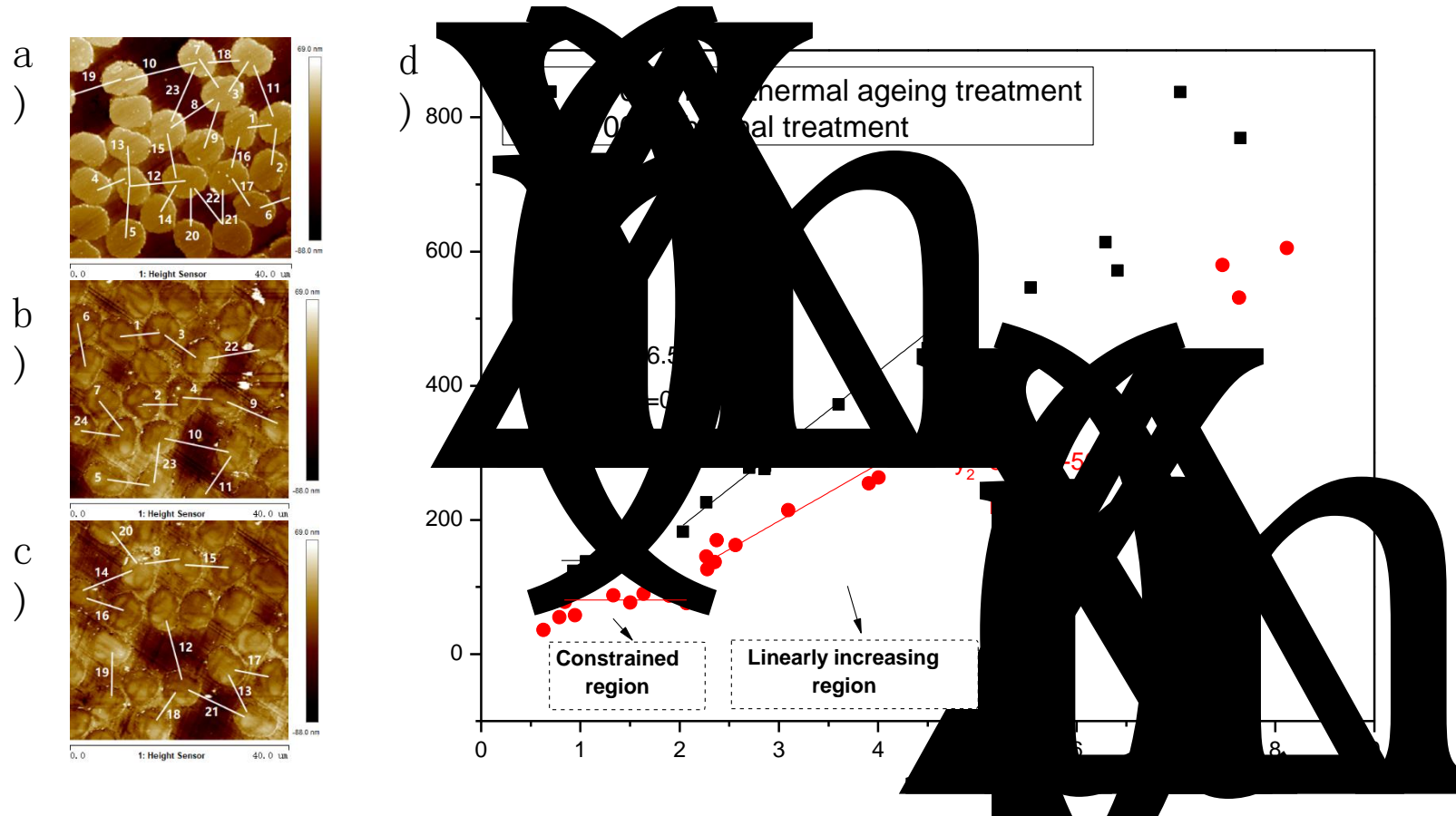
以白线位置A<sub>1</sub>B<sub>1</sub>（处理前）和A<sub>2</sub>B<sub>2</sub>（处理后）位置为例，定义：

- 两个相邻纤维之间的平均水平距离：
$$\Delta X = \frac{(X_1 + X_2)}{2}$$
- 纤维间树脂的收缩幅度：
$$\Delta Y = \frac{(Y_{21} + Y_{22})}{2} - \frac{(Y_{11} + Y_{12})}{2}$$

对 $\Delta X$ 和 $\Delta Y$ 关系进行研究 →

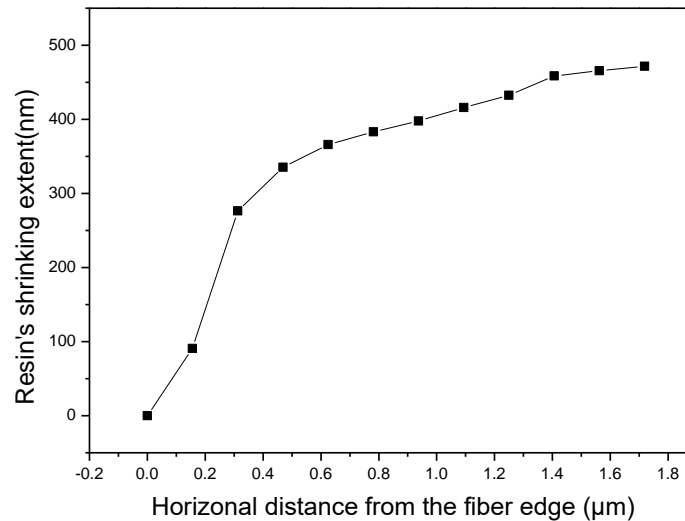
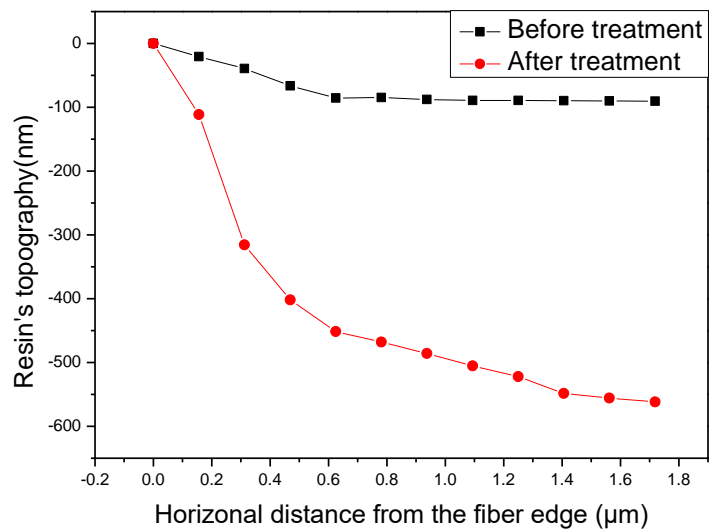
## ■ 热处理和湿热处理的树脂收缩规律差异

湿热处理: 更小束缚范围&能力; 更大收缩幅度增长率

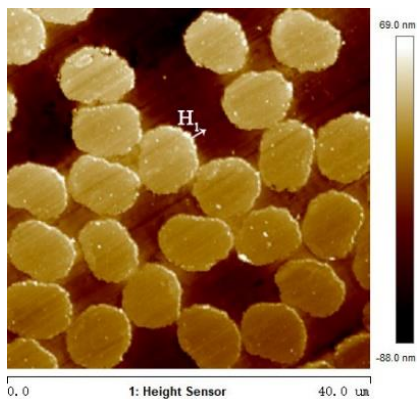


a) 湿热处理样品测试区域 b)、c) 热处理样品测试区域 d)  $\Delta X$ 和 $\Delta Y$ 之间关系

# 基于纤维外围树脂热响应的定量分析



树脂形貌



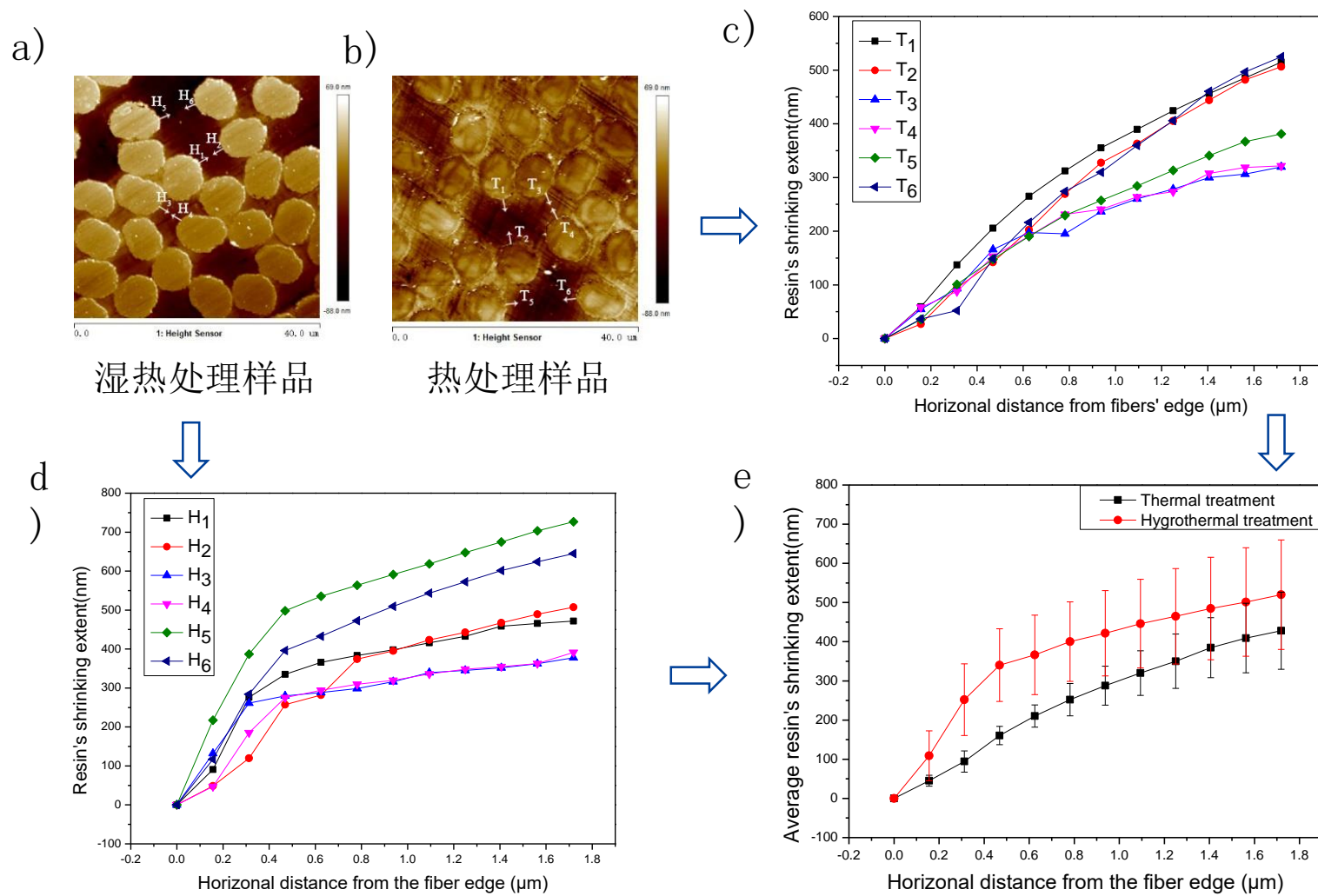
标记位置H1

树脂收缩幅度



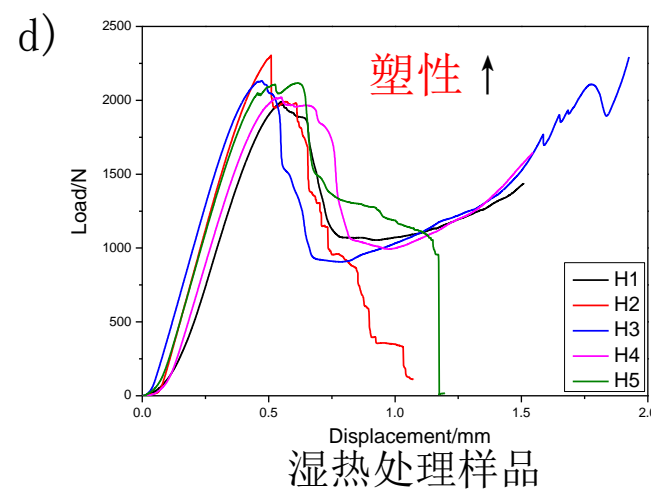
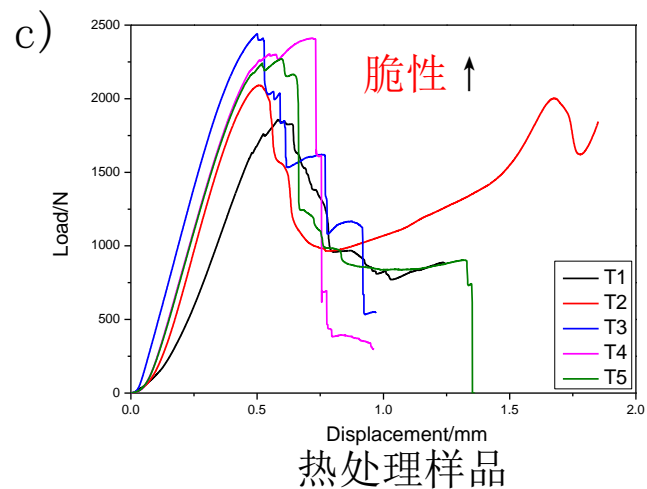
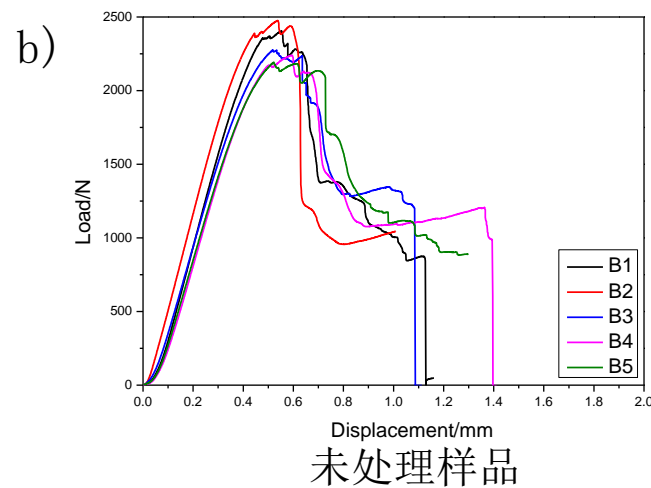
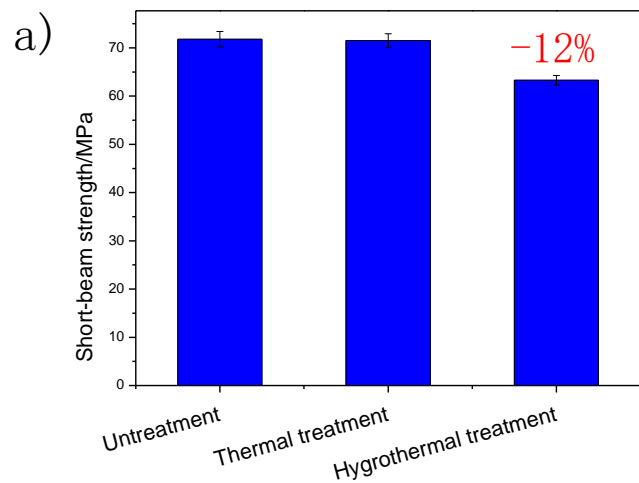
其它区域

## ■ 两种热处理条件对纤维外围树脂的影响比较



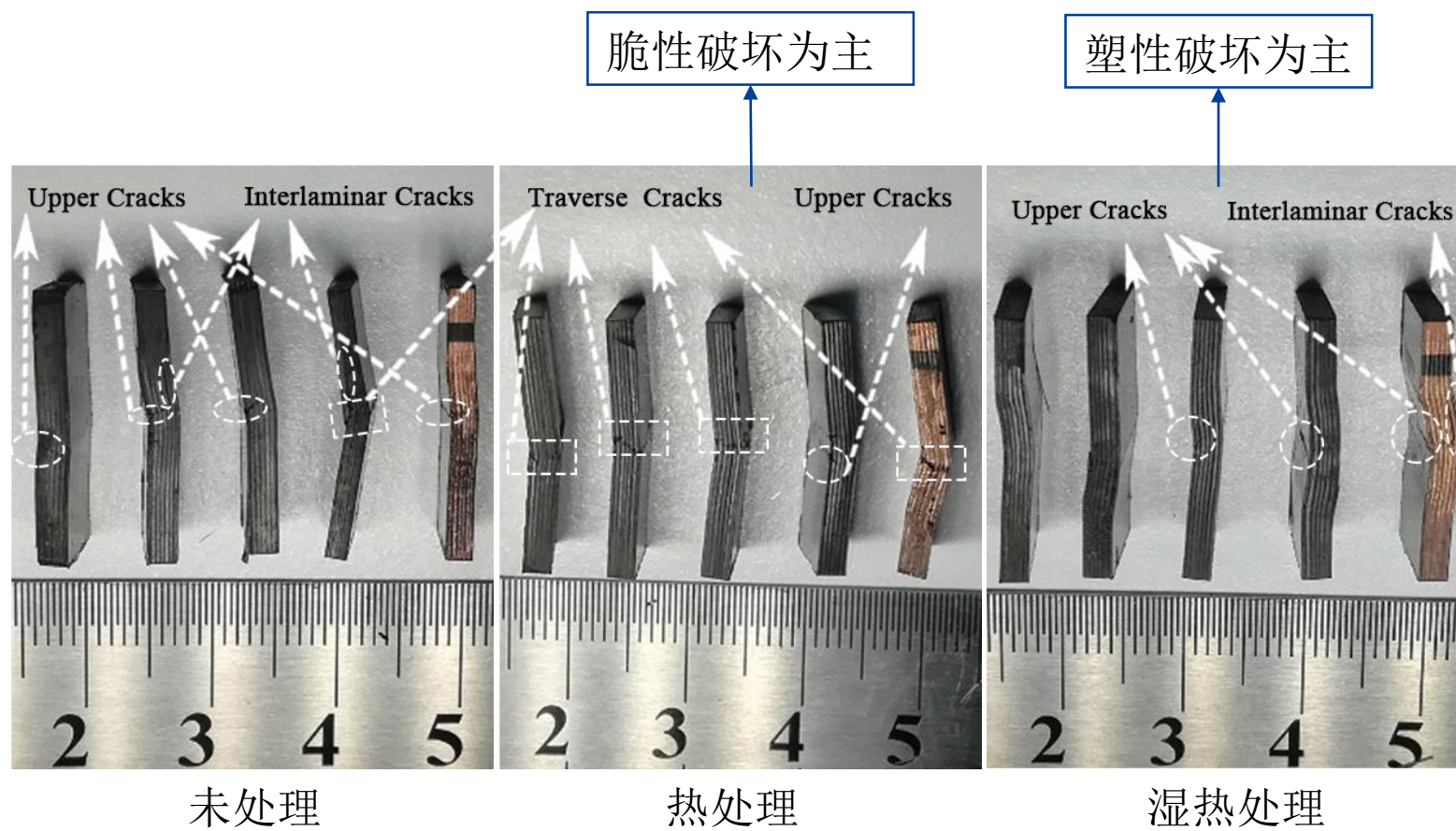
水分使距纤维 $0.5 \mu\text{m}$ 范围内的树脂急剧收缩

# 短梁剪切强度分析 Shear strength of short beams



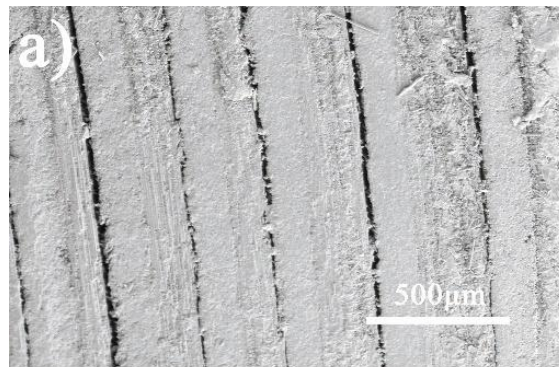
短梁强度试验

### 3.7 损伤形貌表征

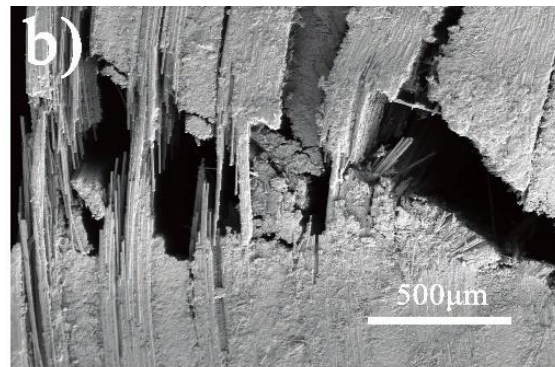


试样侧面破坏形貌

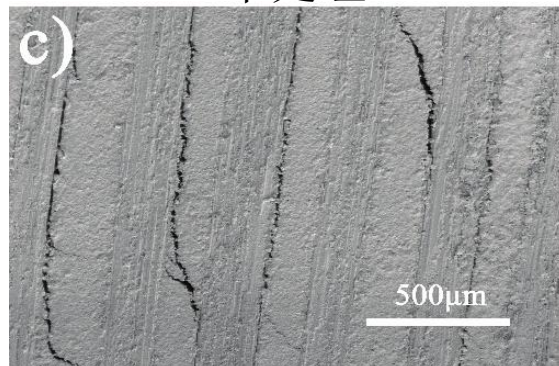
## 损伤形貌表征



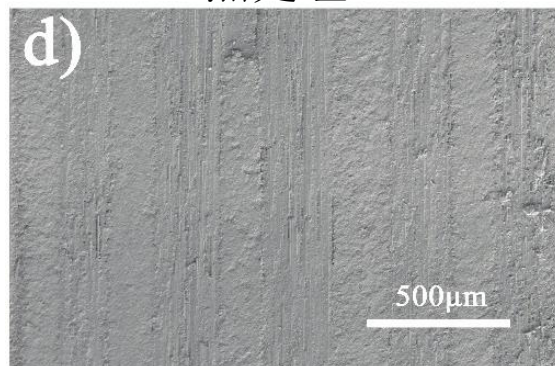
未处理



热处理



湿热处理

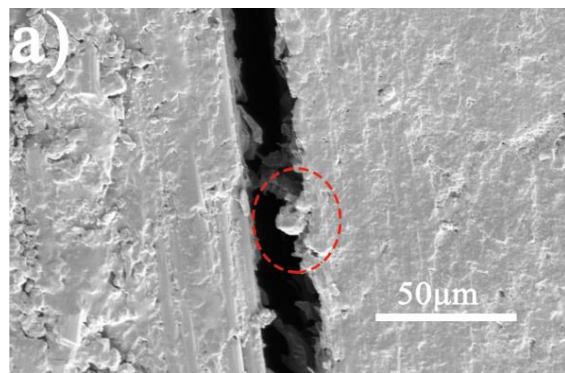


未破坏的对照组

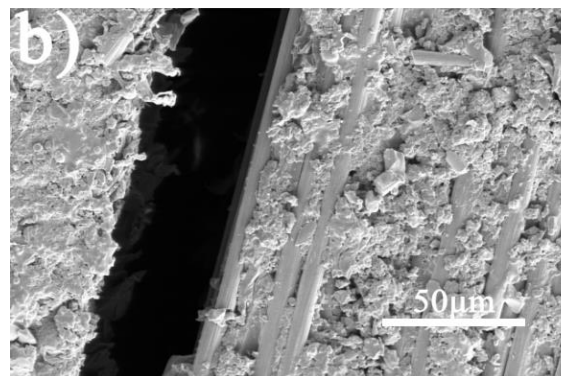
不同处理试样的侧面破坏形貌



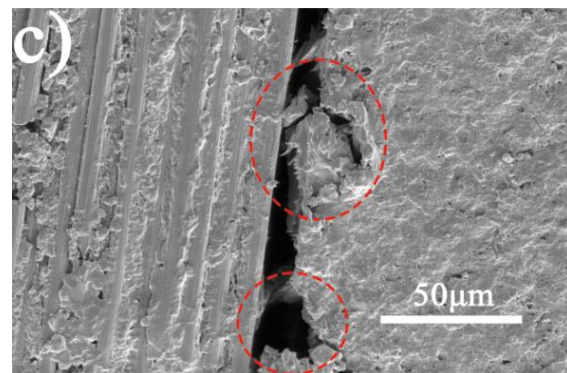
## 损伤形貌表征



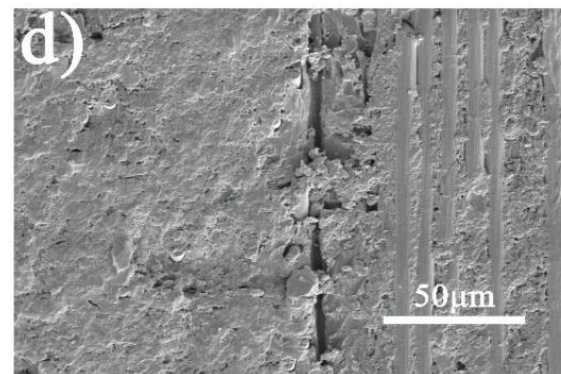
未处理



热处理



湿热处理



未破坏的对照组

不同处理试样层间破坏形貌

## 本章小结

1

建立一种**定量**表征CFRPs界面结合能力的方式。

2

100°C下，**湿热**处理试样中距纤维**0.5 $\mu$ m**范围内的树脂急剧收缩，说明水分破坏了CFRPs的**界面**结合能力。

3

宏观测试证实了**水分破坏了界面结合能力**：**湿热**处理试样短梁强度下降12%，而且出现更多纤维脱粘、微小裂纹。

1

研究背景和研究内容

2

电热效应对CFRPs界面内应力的影响研究

3

湿热环境对CFRPs界面结合能力的影响研究

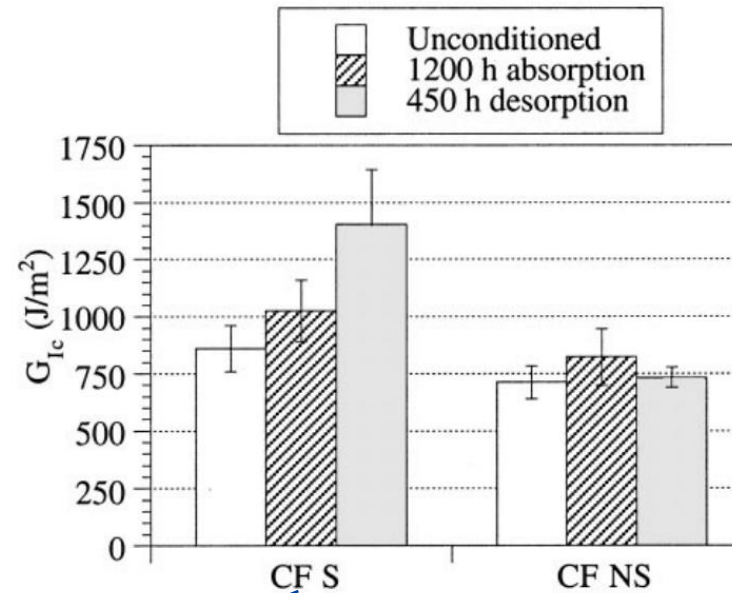
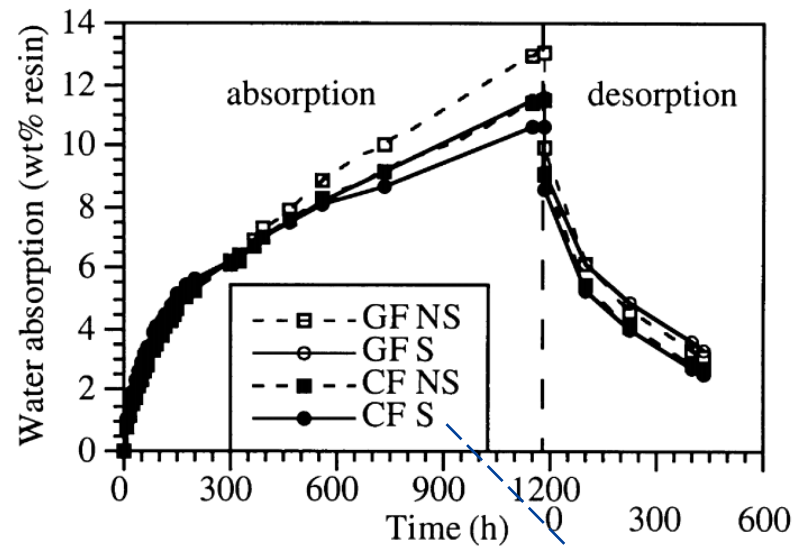
4

有机溶剂对CFRPs热响应的影响研究

5

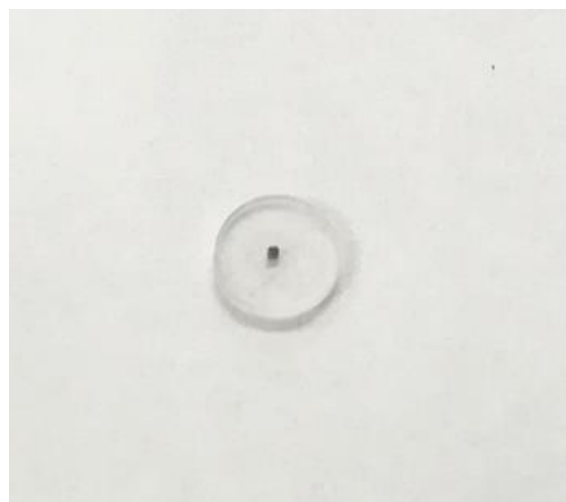
全文总结

## 有机溶剂对CFRPs热响应的影响研究——研究背景



溶剂的存在使CFRPs的吸水性降低，而层间断裂韧性提高

## 试样制备、处理和测试方式

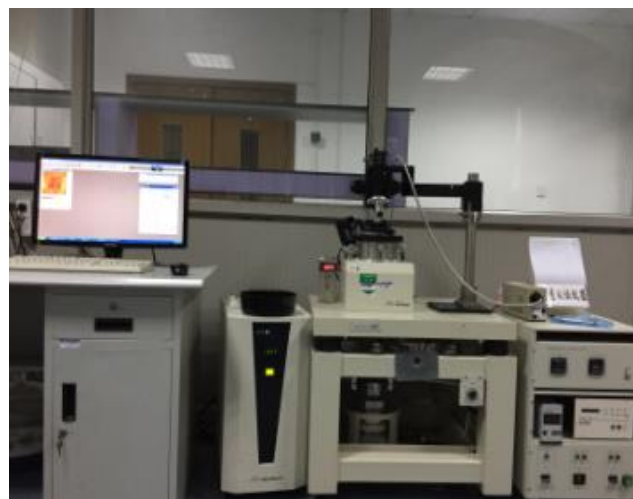


截面试样

乙醇处理

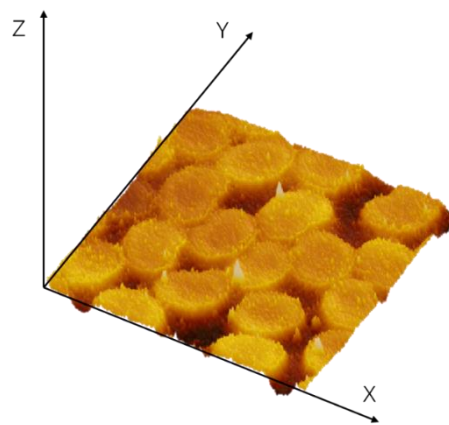
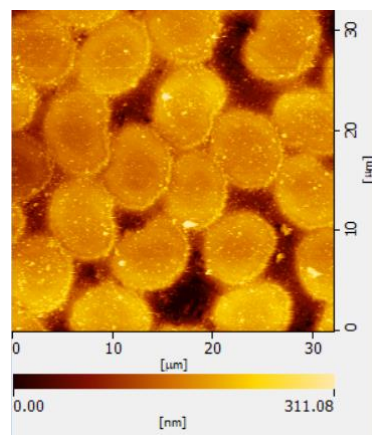


未处理

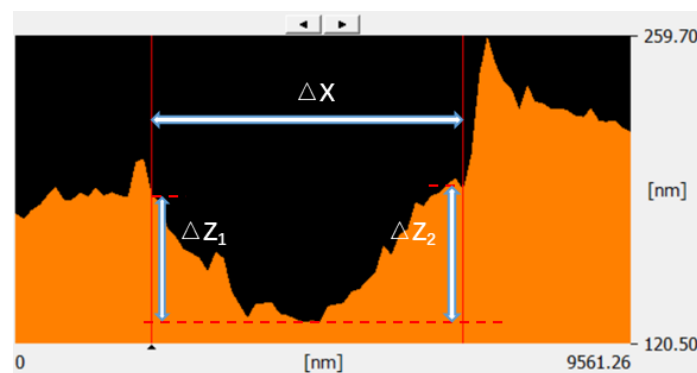
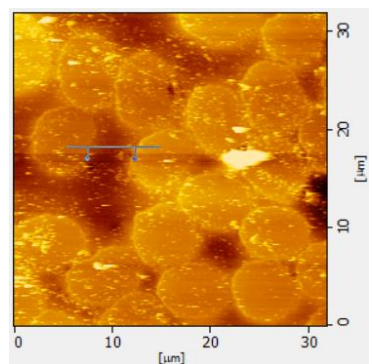


升温AFM测试

## 测试参数设定-树脂尺寸测试



样品X、Y、Z轴方向定义

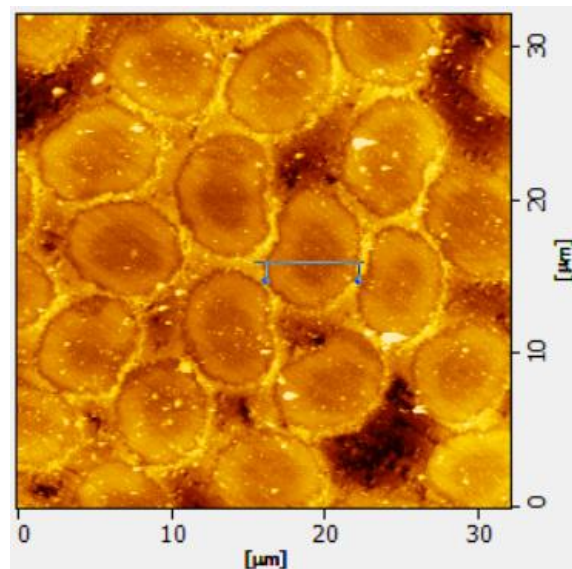


树脂X向宽度 $\Delta X$

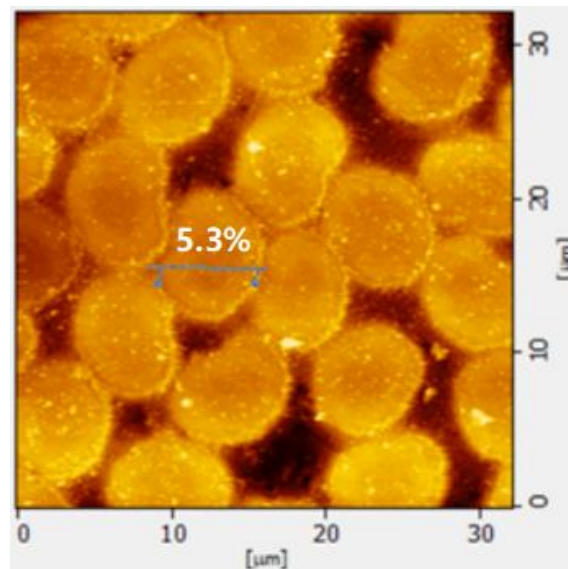
Z轴向高度差 $\Delta Z$ :

$$\Delta Z = \frac{\Delta Z_1 + \Delta Z_2}{2}$$

## 测试参数设定-纤维尺寸测试



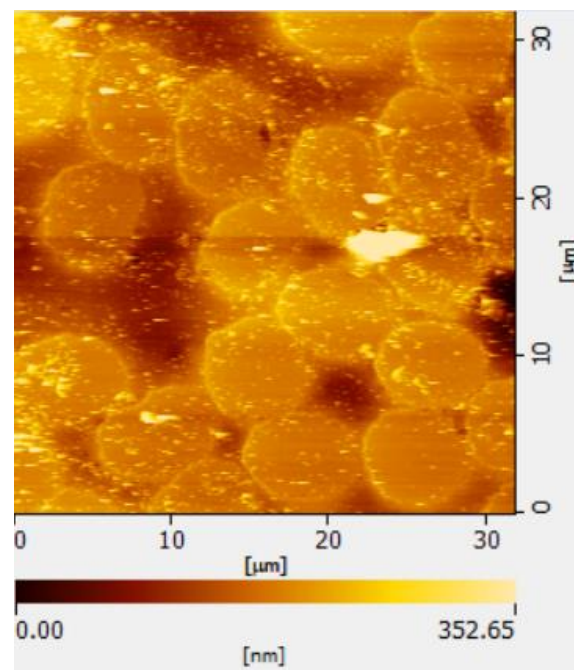
处理前(直径 $\phi_1$ )



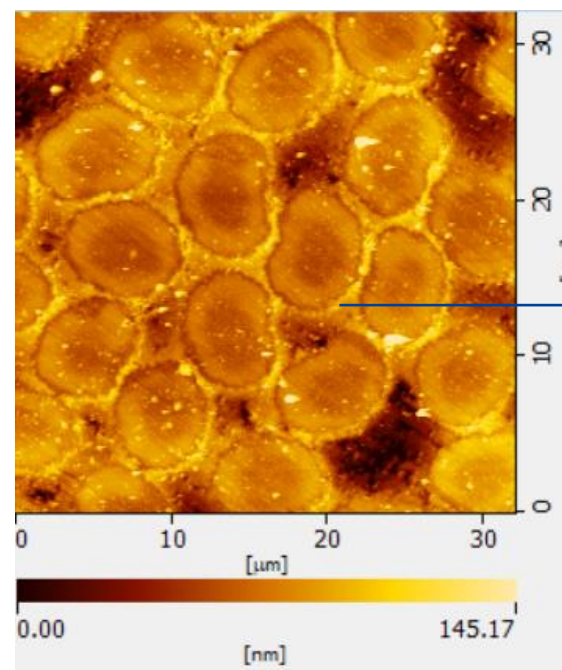
处理后(直径 $\phi_2$ )

X轴方向上纤维直径变化率: 
$$\alpha = \frac{\phi_2 - \phi_1}{\phi_1} \times 100\% = 5.3\%$$

## 乙醇处理对样品形貌的影响



未处理的样品

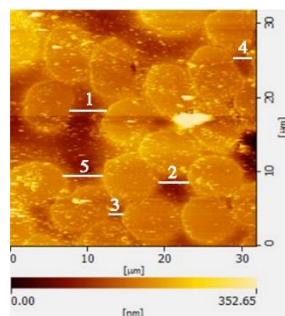


乙醇处理的样品

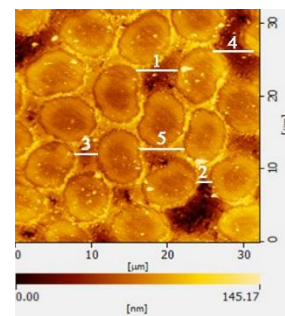
纤维外围  
树脂膨胀



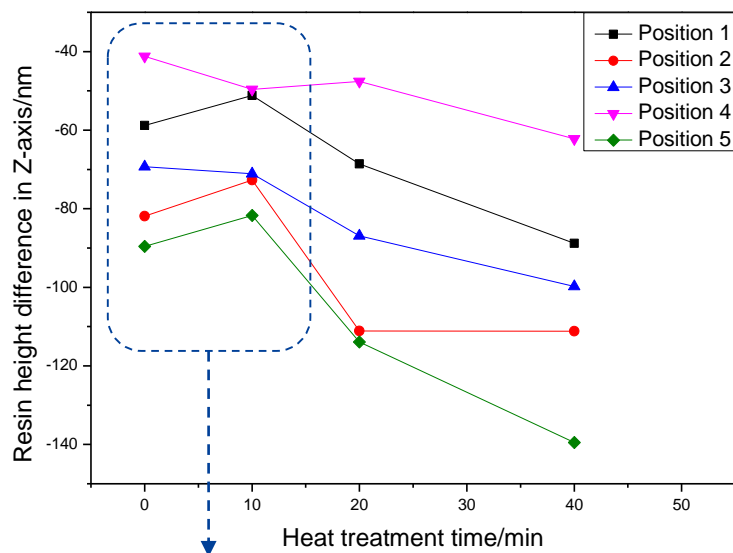
# 纤维间树脂的热响应



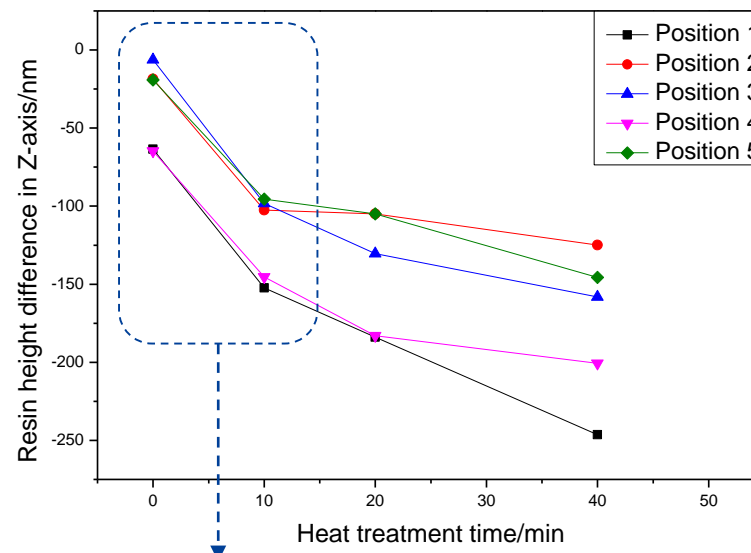
未处理



乙醇处理

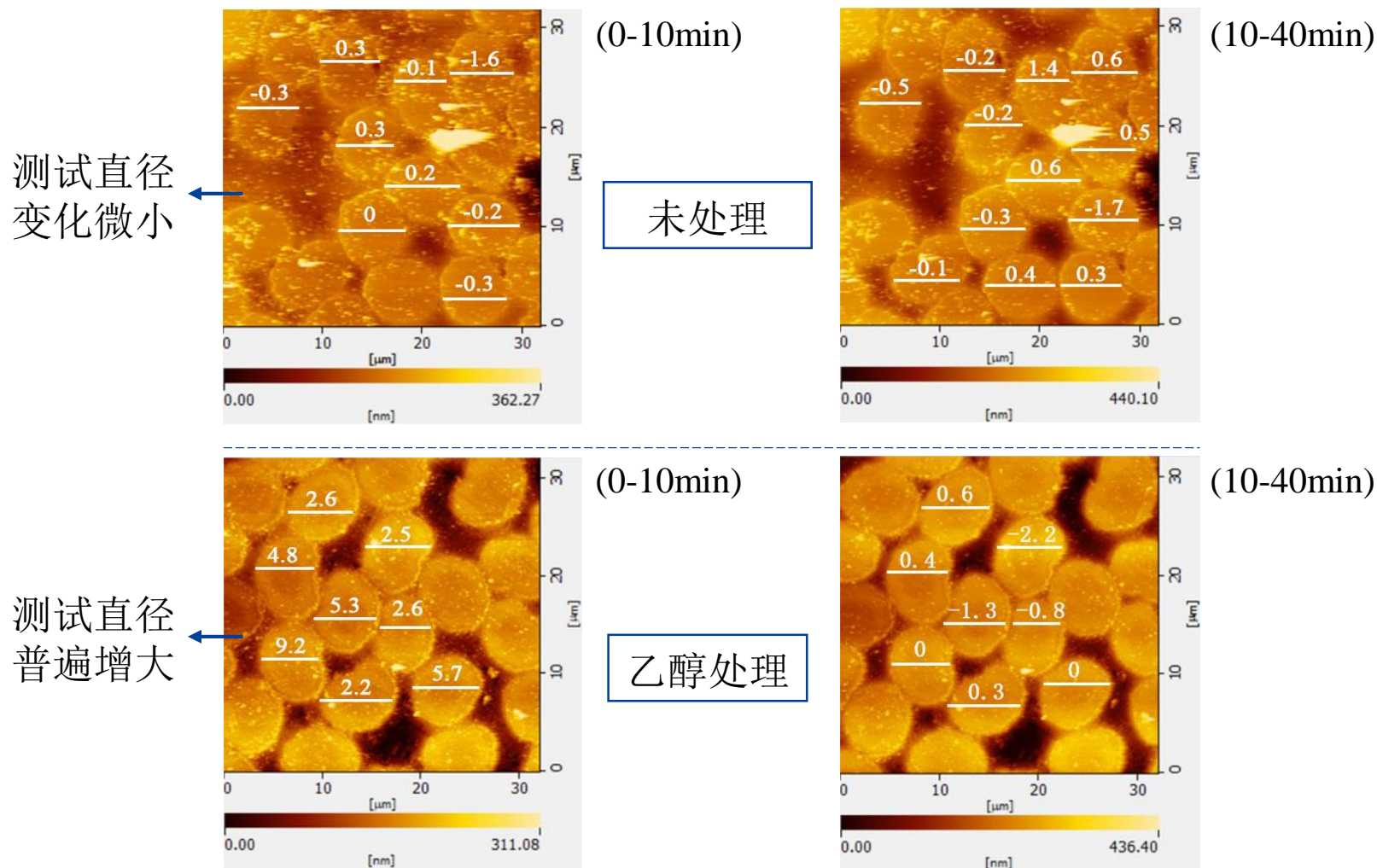


较稳定

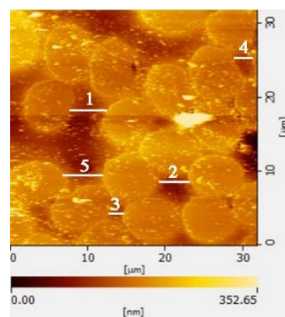


普遍降低

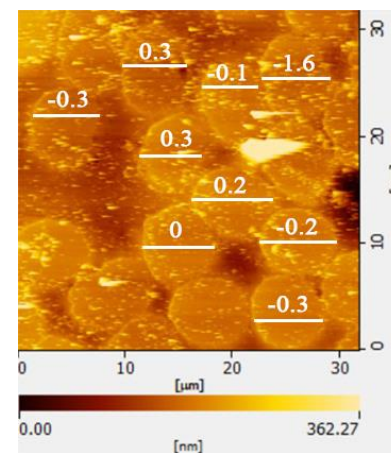
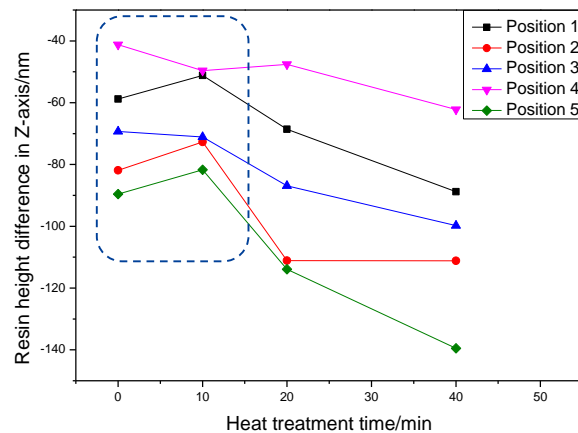
## 纤维在X轴轴向上的直径变化



# 树脂、纤维形貌变化的关系

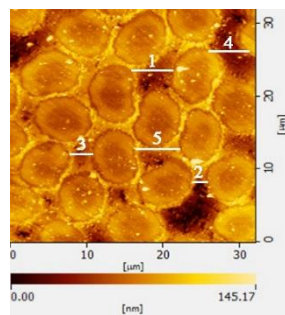


未处理样品

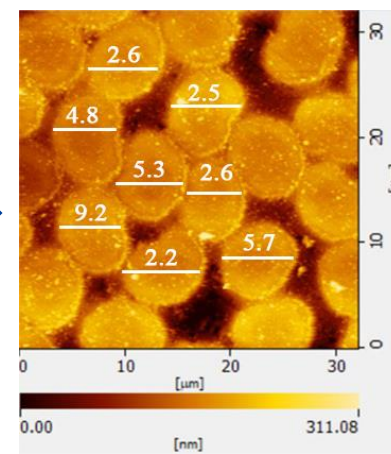
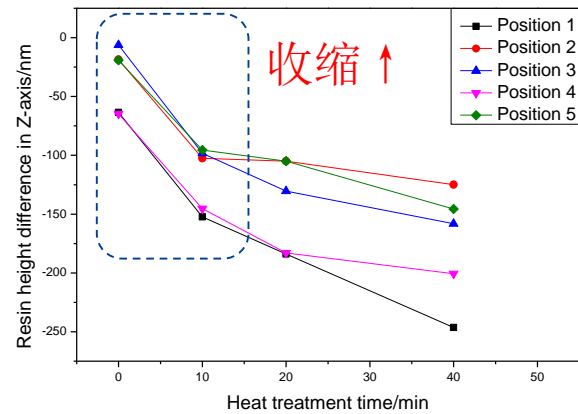


(0-10min)

膨胀



乙醇处理样品



(0-10min)

尺寸 ↑

## 本章小结

1

乙醇处理使得纤维外围树脂发生膨胀。

2

加热时，乙醇处理试样纤维外围树脂发生收缩，同时测试的纤维直径增大。

3

乙醇处理可能带来CFRPs表面结构的变化，从而影响其表面性能。

**Thank you!**

