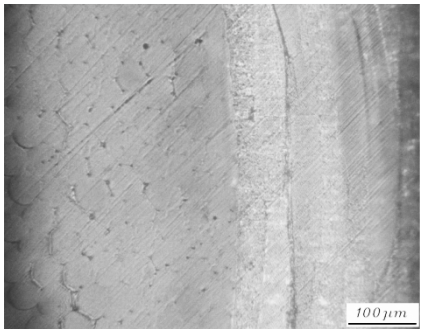

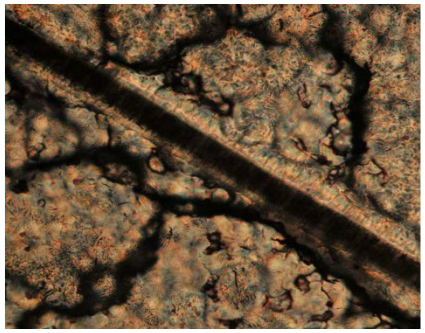
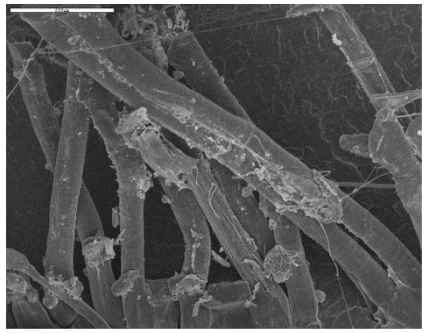
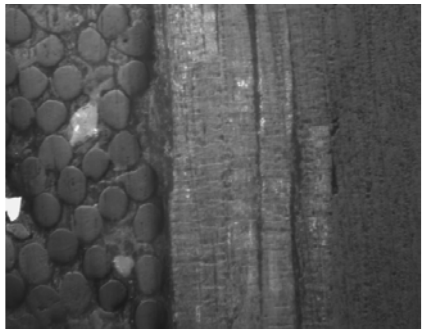

聚丙烯单聚合物复合材料（PP SPC）过冷膜层热压制备技术

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北京理工大学化工与环境学院
2014-03-20

Contents

- *前言（what, why, how)*
- *聚丙烯单聚合物复合材料*
- *过冷膜层热压技术*
- *结语*

引言

- 什么是单聚合物复合材料? *What?*
- **Single-polymer-composites (SPCs)**
  - **made by integrating h of the same polymer.**

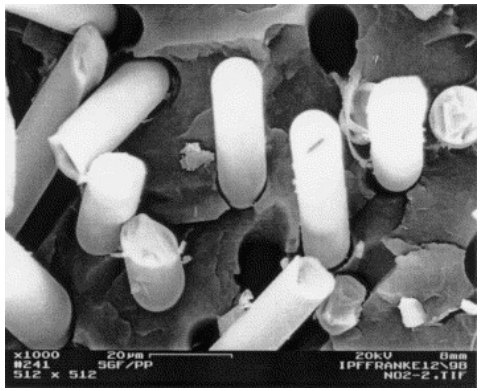
1975, Capiati and Porter introduced the first example of a SPC of PE





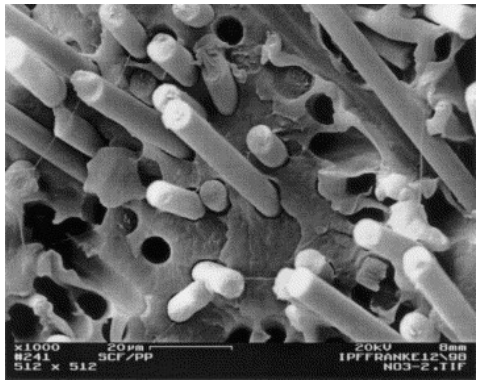
引言

- 为什么要用单聚合物复合材料? ***Why ?***
  - **Advantages:**
    - **Light weight**
    - **Good mechanical properties**
    - **Good interfacial properties**
    - **Good recyclable (no glass fibers..) and reusability**



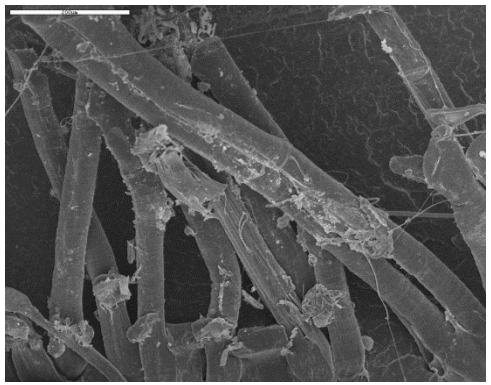
glass fibers

Density: 2.5-2.9 g/cm^3



carbon fibers

Density: 1.7-1.9 g/cm^3



polypropylene fibers

Density: 0.9 g/cm^3

(Compo A, 2000, 31, 1117)

引言

- 为什么要用单聚合物复合材料? ***Why ?***
  - SPC制品

引言

- 聚丙烯 (PP)
  - low density
  - high tensile strength
  - high compressive strength
- 聚丙烯复合材料
  - much academic and commercial interest in the past few decades

Recyclability
Interface adhesion

- 聚丙烯单聚合物复合材料PP SPCs

纤维增强PP复合材料具有设计灵活性高、可着色、强度高、弹性优良、耐化学腐蚀和耐候性好等特点，应用市场主要分为交通运输45%、电子电器35%、日用品10%和工业10%四部分。

引言

- 近年来，我国汽车工业得到了飞速发展，英国《金融时报》预测，我国今年将生产1960万辆汽车而超过欧洲。同时，废旧汽车数量也逐年递增。在汽车用塑料中，PP用量占汽车塑料总量的30%左右，而且还有替代其他材料或其他汽车塑料的趋势。这些应用于汽车里的PP通常需要通过玻纤增强，其力学性能能够同工程塑料相媲美，但是其再加工利用却很困难且造成了能源消耗。
- 欧盟在2000年对汽车的再利用、再恢复和再循环提出了ELVs（end-of-life vehicles）指令：截止到2015年，将汽车的再利用和再恢复率增加到至少95%，实现每年每辆汽车的平均质量的85%再循环。

因此，迫切需求开发力学和界面性能良好、回收利用率高的纤维增强PP复合材料。PP SPC成为替代传统的纤维增强PP复合材料的最好材料。研究掌握PP SPC制备关键技术以实现PP SPC产业化具有重要意义。

引言

- **Main challenge in the development of SPCs**
  - **Proximity in melting temperatures of matrix and reinforcement**

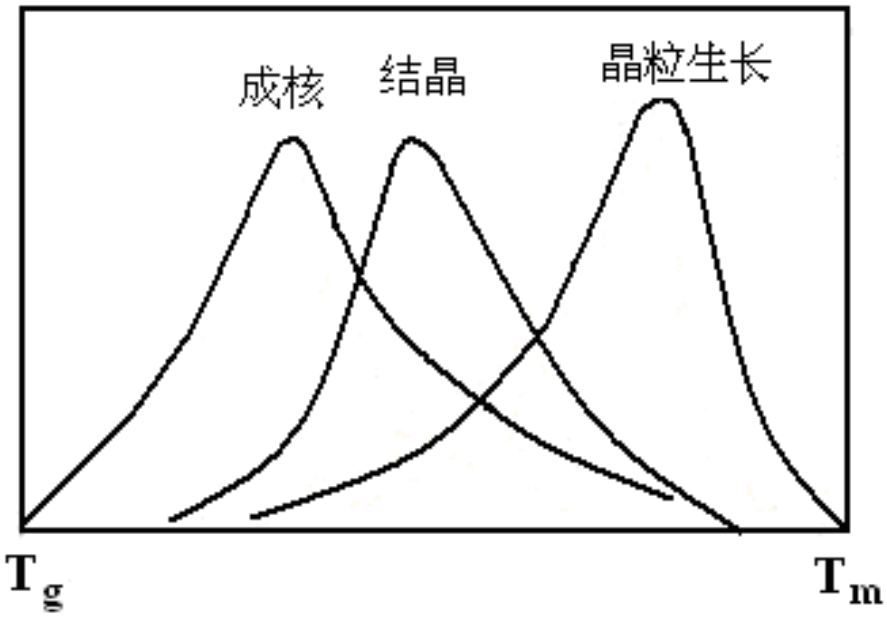
Processing temperature window

- **如何制备单聚合物复合材料？** ***How?***
  - **Hot compaction of fibers/tapes**
  - **Film-stacking**
  - **Combination of hot compaction and film stacking**
  - **Overheating**
  - **Co-extrusion**
  - **Undercooling**

过冷膜层热压技术

聚合物的过冷特性

- Undercooling or supercooling refers to cooling a substance below a phase-transition temperature without the transition occurring.
- Polymers can be easier to supercool because of their extremely high molecular weight and long molecular chains.

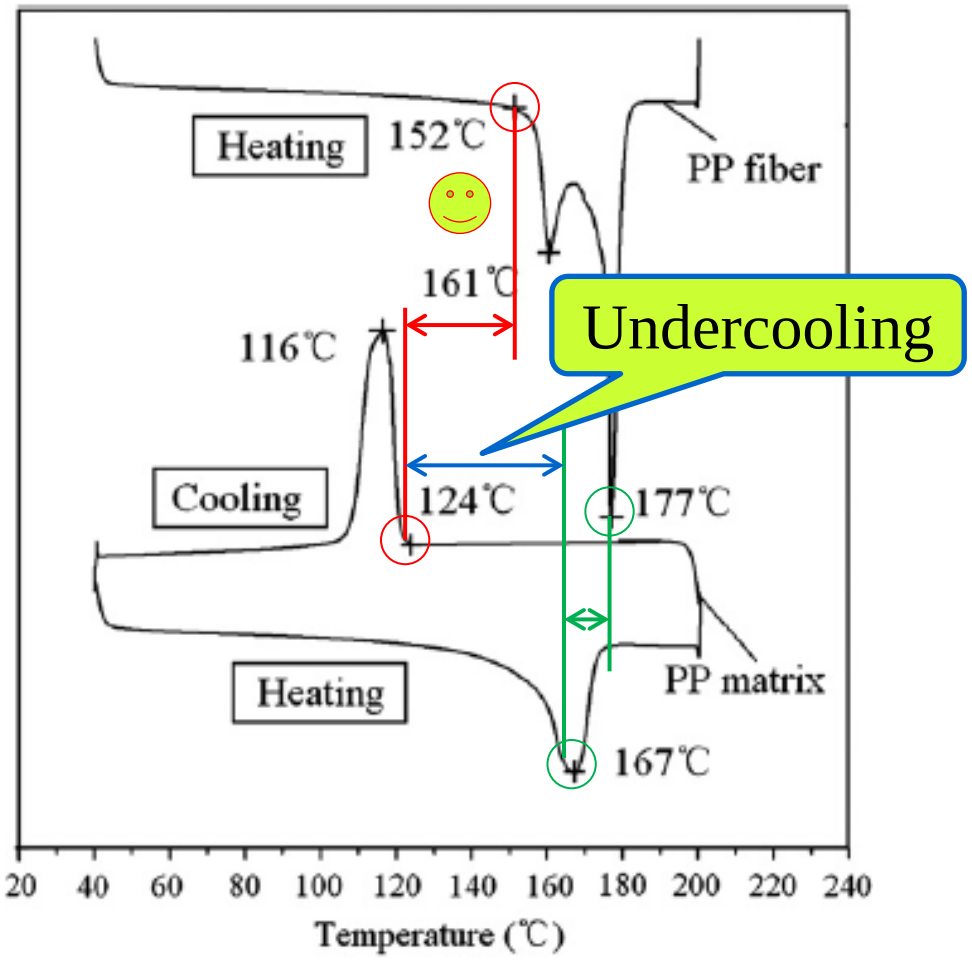


- Semi-crystalline polymers upon melting can be undercooled to a temperature well below the melting temperature while crystallization is largely absent.

过冷膜层热压技术

聚合物的过冷特性

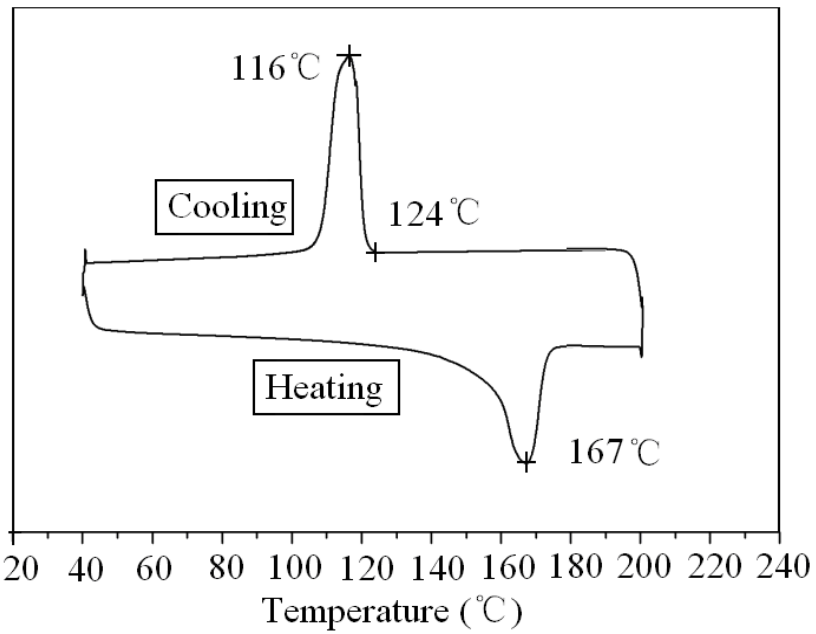
- The applicability of undercooled melt in SPCs processing is expected to be largely dependent on the supercooling degree that the polymer can undergo without solidification
- The larger the supercooling degree, the smaller the potential of heat damage to the strength of the polymer fiber.

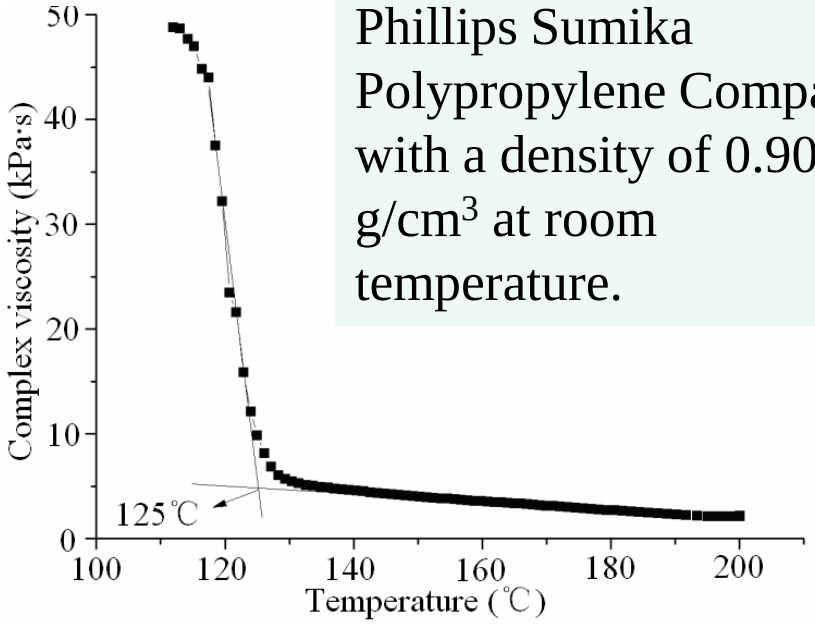


Processing temperature window: 125~150℃

过冷膜层热压技术

- 聚合物的过冷特性
  - **Development and characterization of undercooled PP used to prepare PP SPCs**





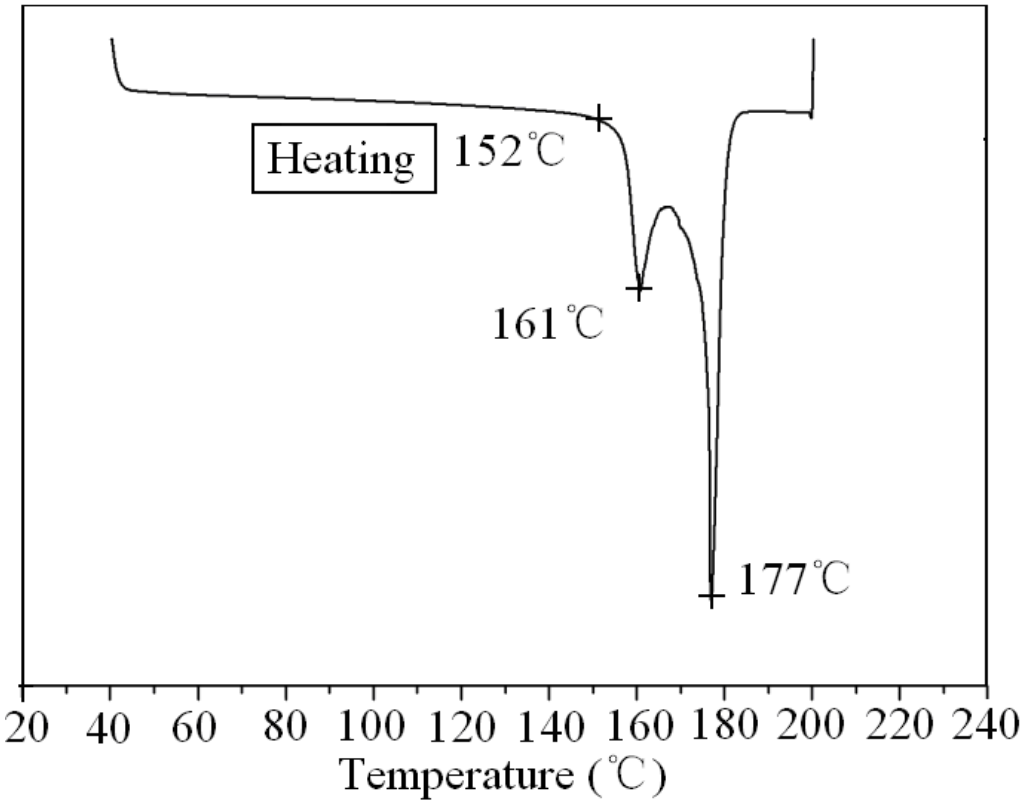
PP was supplied by Phillips Sumika Polypropylene Company, with a density of 0.905 g/cm^3 at room temperature.

supercooling degree could be up to 43 ℃ (T_m _ T_x).

过冷膜层热压技术

纤维增强体

High-strength woven polypropylene cloth was supplied by Innegrity LLC (Simpsonville,SC).



Processing temperature window: 125~150℃

过冷膜层热压技术

纤维增强体

High-strength woven polypropylene cloth was supplied by Innegrity LLC (Simpsonville,SC).

- Crystallite orientation 140 C and 150 C were hardly changed.
- A substantial change was observed when the heating temperature further increased to 160 C.
- Processing temperature should not exceed 150 C. Otherwise, a large reduction in tensile strength of fibers is expected.

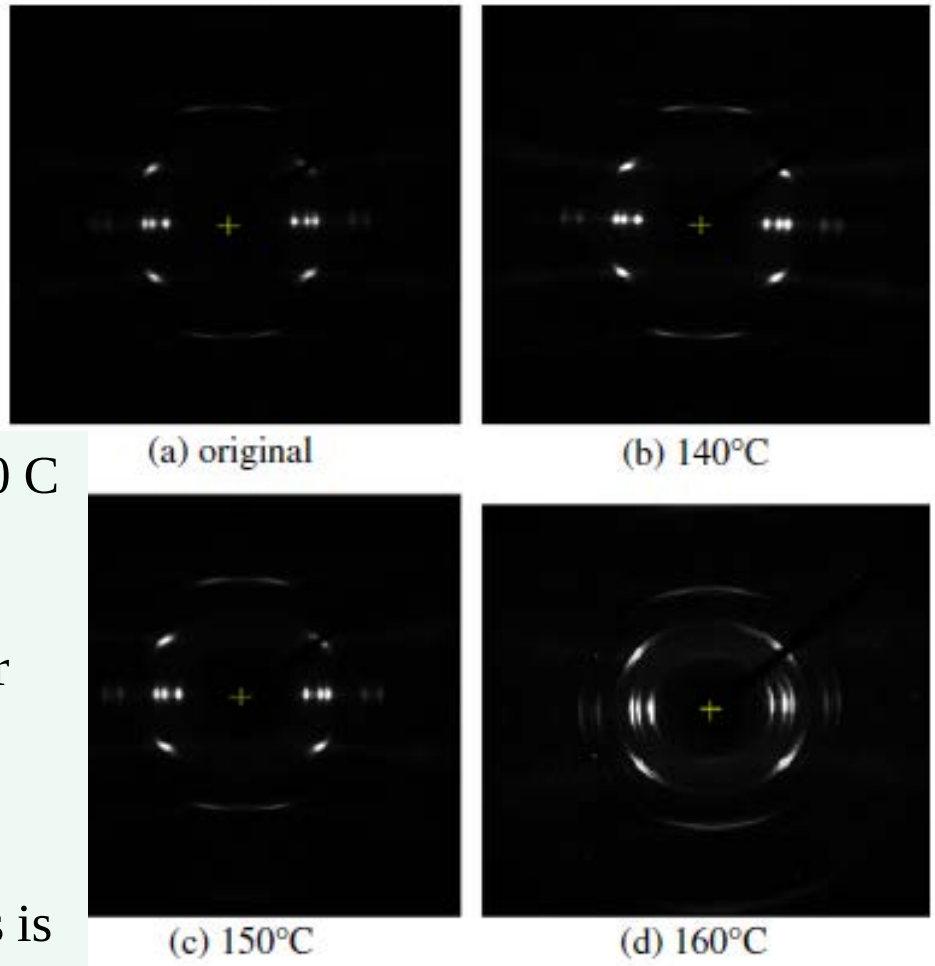
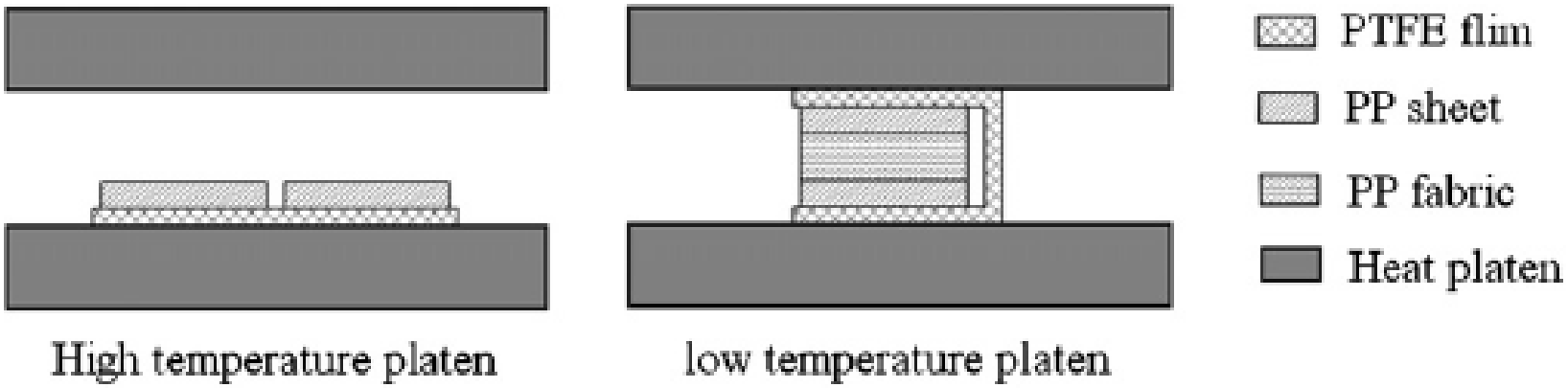


Fig. 5. X-ray fiber photographs of heat-treated PP fibers.

Processing temperature window: 125~150℃

过冷膜层热压技术

制备过程

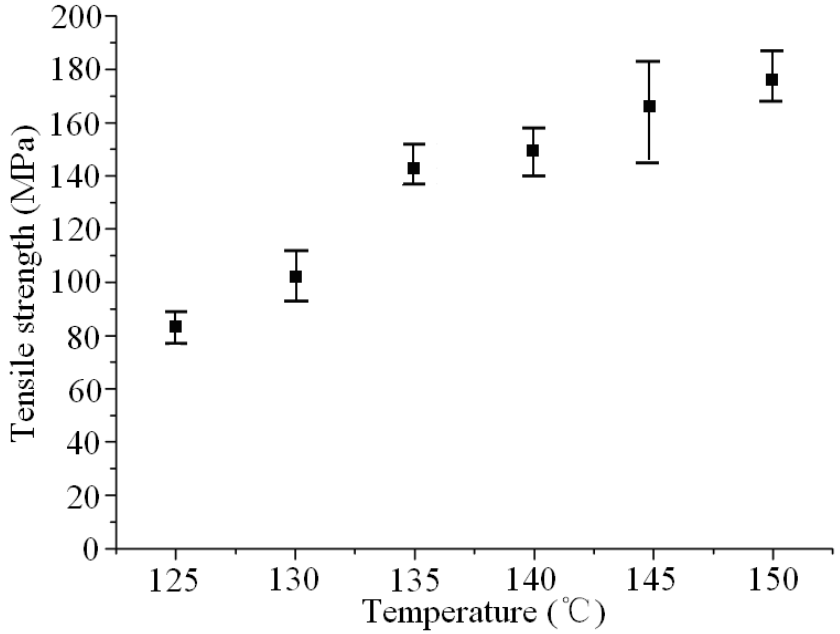


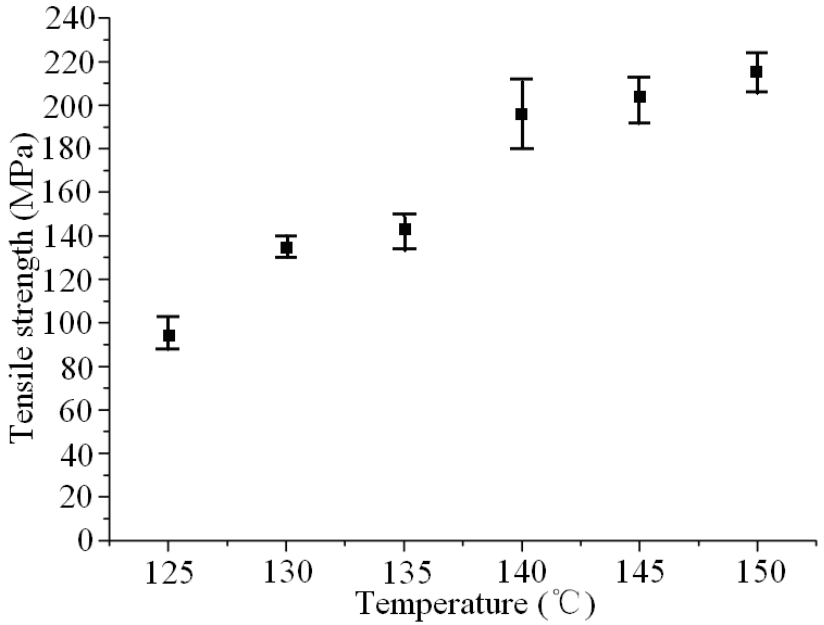
- PP sheets were first heated to 200 C for 10 min on the first station to obtain two layers of molten PP sheets.
- The molten PP sheets were then quickly transferred to the second station set at a lower temperature to be supercooled.
- Compressed under a pressure of 9 MPa for 10 min.

过冷膜层热压技术

拉伸性能

9 MPa for 10 min



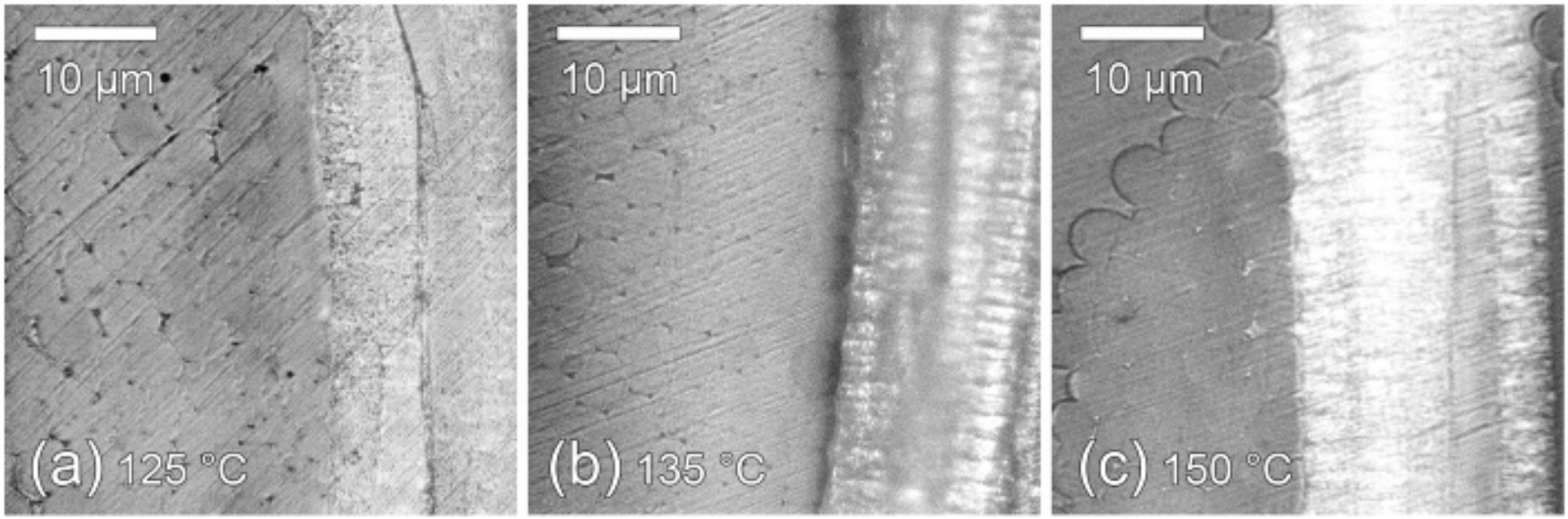


(a) Tested parallel to the warp direction

(b) Tested parallel to the weft direction

过冷膜层热压技术

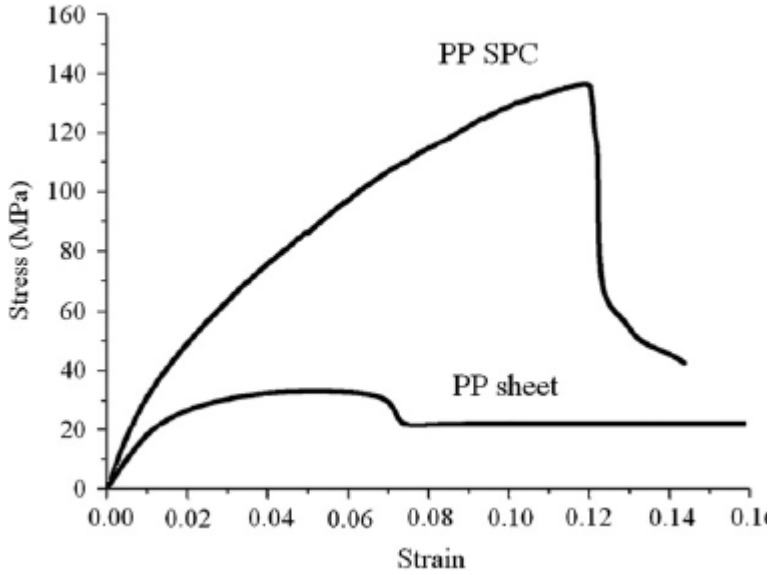
- 微观结构

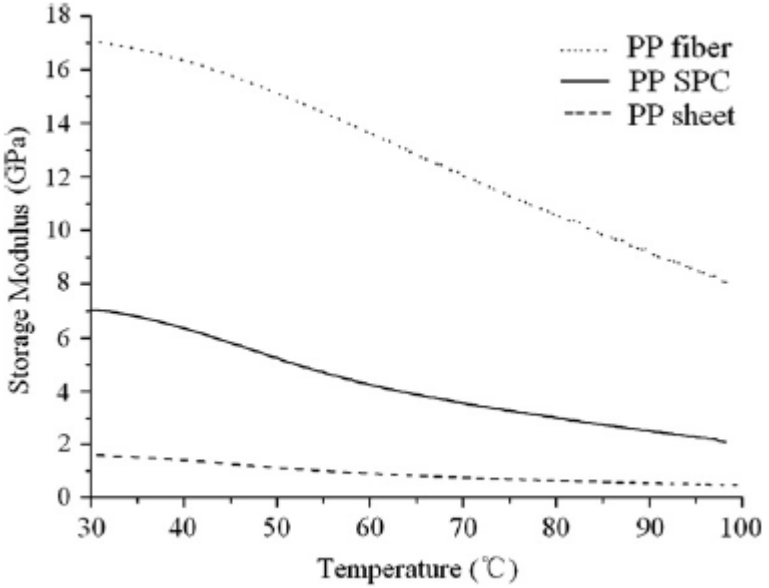


Metallographic observation

过冷膜层热压技术

拉伸性能比较





- Comparison of stress–strain curves for PP SPC sheets (weft direction) and non-reinforced PP sheets obtained by compression molding at 135 C.
- DMTA results for PP fibers, PP SPC sheets (weft direction) and non-reinforced PP sheets.

过冷膜层热压技术

拉伸性能

热压时间的影响

Exp.	Temperature (℃)	Time (min)	Warp tensile strength (MPa)	Warp tensile modulus (GPa)	Weft tensile strength (MPa)	Weft tensile modulus (GPa)
pressure: 9 MPa						
1	125	5	83±4	2.9±0.4	92±5	3.2±0.4
2	125	10	84±5	2.9±0.4	93±4	3.2±0.5
3	125	15	84±5	2.8±0.4	94±5	3.3±0.4
4	130	5	91±6	3.2±0.2	126±5	3.6±0.3
5	130	10	102±8	3.3±0.1	134±6	3.8±0.2
6	130	15	103±7	3.3±0.2	135±5	3.8±0.3
7	135	5	125±4	3.4±0.3	127±6	3.8±0.4
8	135	10	140±5	3.5±0.2	143±7	3.9±0.2
9	135	15	143±6	3.5±0.4	149±6	3.9±0.4
10	140	5	139±7	3.3±0.1	180±8	3.6±0.3
11	140	10	149±9	3.2±0.2	196±14	3.7±0.4
12	140	15	155±6	3.3±0.4	204±8	3.6±02

No variation

increased

increased

Strength increased, Modulus not changed

过冷膜层热压技术

拉伸性能

热压时间的影响

Exp.	Temperature (℃)	Time (min)	Warp tensile strength (MPa)	Warp tensile modulus (GPa)	Weft tensile strength (MPa)	Weft tensile modulus (GPa)
pressure: 9 MPa						
13	145	5	148±9	3.2±0.4	192±7	3.2±0.3
14	145	10	166±16	3.0±0.4	203±10	2.9±0.4
15	145	15	172±10	3.0±0.4	208±11	2.9±0.
16	145	20	169±8	3.1±0.3	204±9	2.9±0.
17	150	5	168±10	2.3±0.4	205±11	2.3±0.
18	150	10	176±11	2.3±0.5	215±9	2.2±0.2
19	150	15	175±8	2.2±0.4	213±8	2.2±0.4
20	150	20	169±7	2.2±0.4	210±9	2.2±0.3

Strength increased first then decreased, Modulus not changed

Strength increased first then decreased, Modulus not changed

过冷膜层热压技术

拉伸性能

热压压力的影响

Exp.	Temperature (℃)	Pressure (MPa)	Warp tensile strength (MPa)	Warp tensile modulus (GPa)	Weft tensile strength (MPa)	Weft tensile modulus (GPa)
1	125	6	83±3	2.9±0.3	93±5	3.2±0.3
2	125	9	84±5	2.9±0.4	93±4	3.2±0.5
3	125	12	84±4	2.8±0.4	94±5	3.1±0.5
4	130	6	100±6	3.3±0.3	134±3	3.8±0.2
5	130	9	102±8	3.3±0.1	134±6	3.8±0.2
6	130	12	104±9	3.3±0.4	136±7	3.8±0.4
7	135	6	120±5	3.4±0.3	128±8	3.7±0.3
8	135	9	140±5	3.5±0.2	143±7	3.9±0.2
9	135	12	148±6	3.6±0.1	152±8	3.9±0.1

No variation

increased

increased

过冷膜层热压技术

拉伸性能

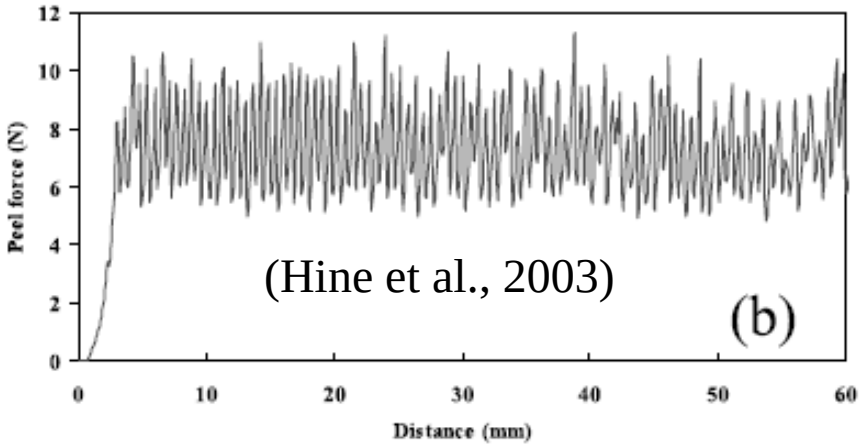
热压压力的影响

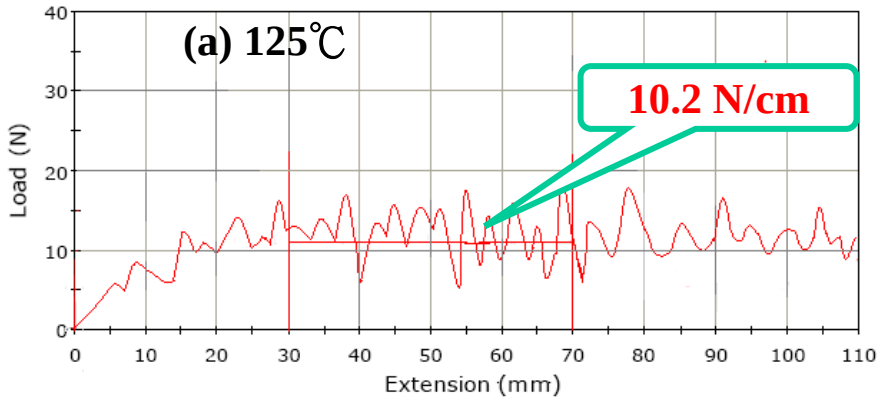
Exp.	Temperature (℃)	Pressure (MPa)	Warp tensile strength (MPa)	Warp tensile modulus (GPa)	Weft tensile strength (MPa)	Weft tensile modulus (GPa)
10	140	6	132±7	3.3±0.1	148±9	3.6±0.1
11	140	9	149±9	3.2±0.2	196±14	3.7±0.4
12	140	12	154±8	3.1±0.1	202±11	3.6±0.3
13	145	6	149±7	3.2±0.2	189±10	3.3±0.2
14	145	9	166±16	3.0±0.4	203±10	2.9±0.4
15	145	12	160±12	2.3±0.3	194±9	2.3±0.2
16	150	6	167±9	2.4±0.3	204±10	2.2±0.3
17	150	9	176±11	2.3±0.5	215±9	2.2±0.2
18	150	12	170±12	2.1±0.4	208±8	2.1±0.3

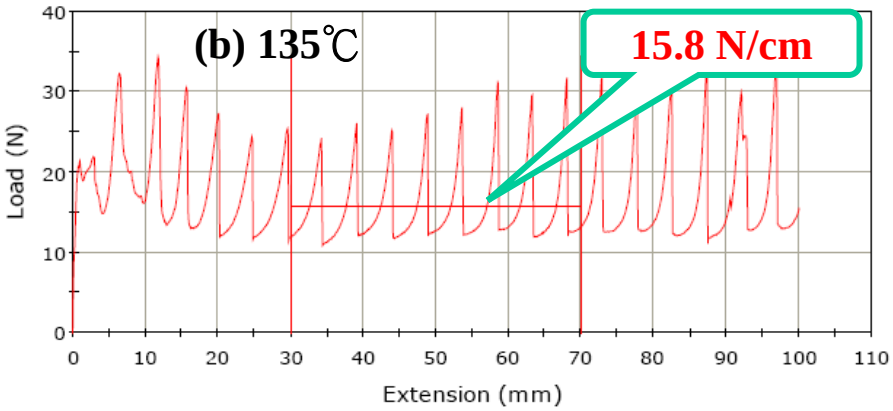
increased

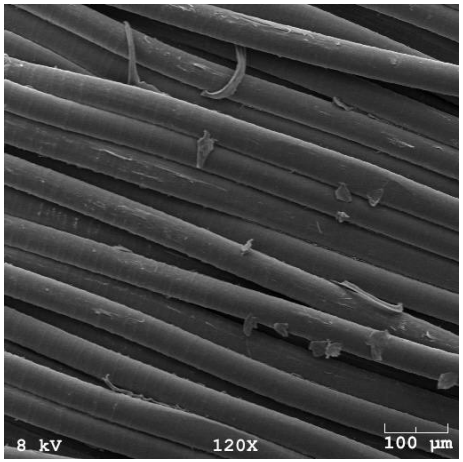
Strength increased first then decreased, Modulus not changed

Strength increased first then decreased, Modulus not changed

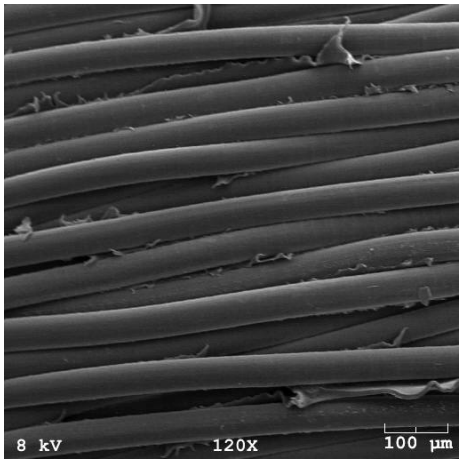

Peel force (N)
Distance (mm)
(Hine et al., 2003)
(b)


(a) 125℃
10.2 N/cm
Load (N)
Extension (mm)


(b) 135℃
15.8 N/cm
Load (N)
Extension (mm)


8 kV
120X
100 µm

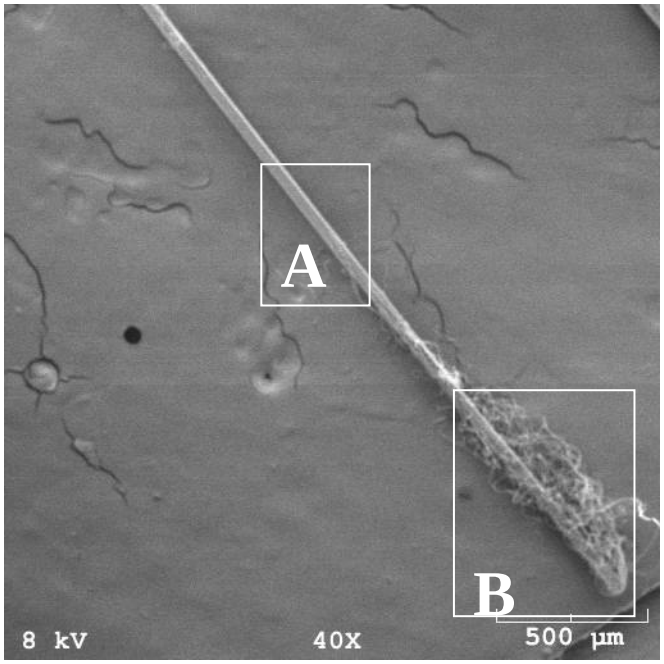
(a) 125℃


8 kV
120X
100 µm

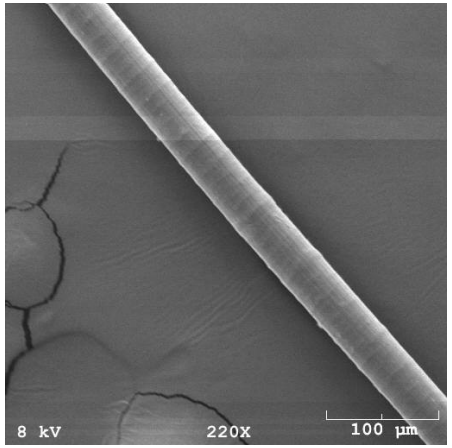
(b) 135℃

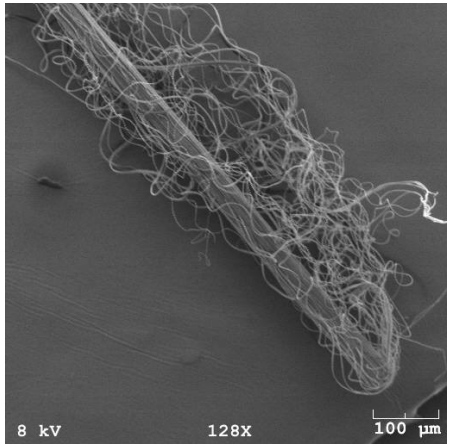
过冷膜层热压技术

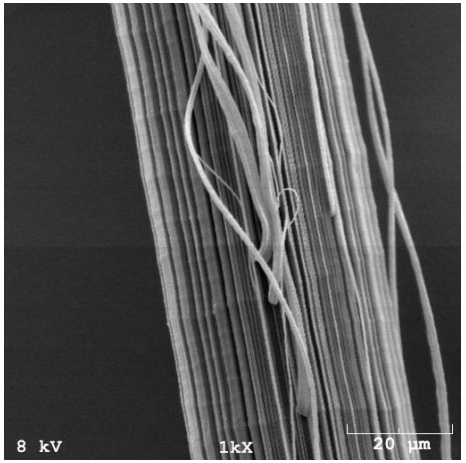
- 界面粘结性能



PP fiber pulled out from the matrix





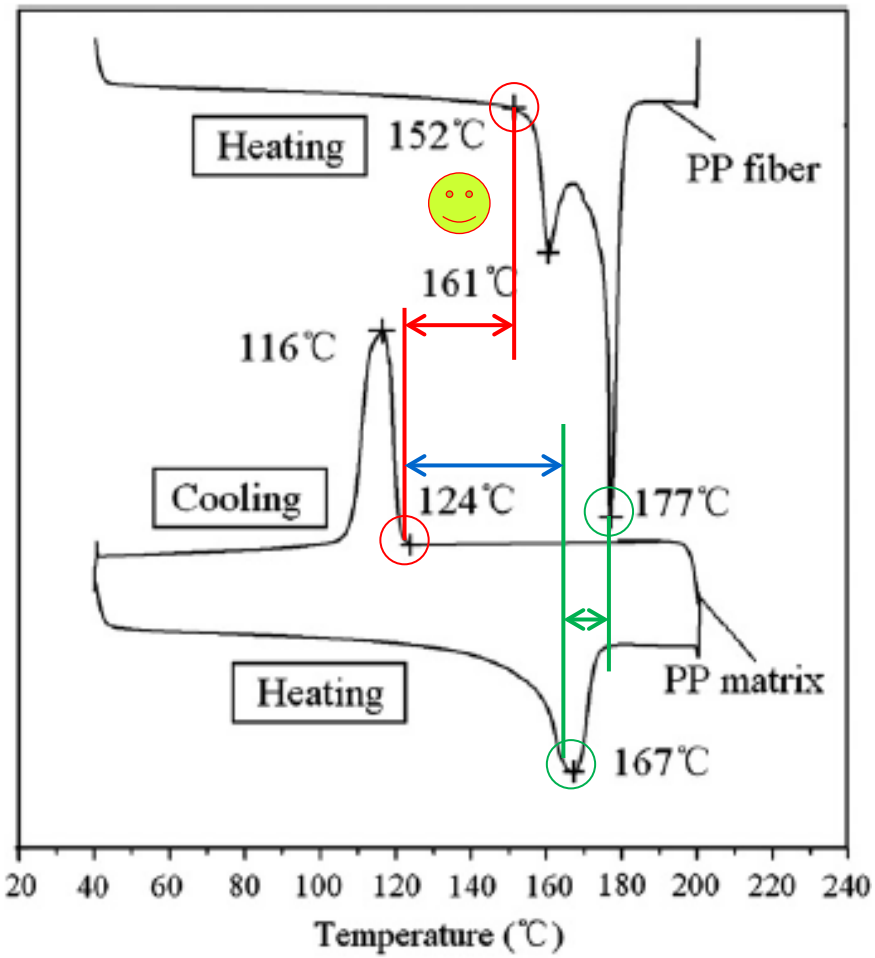


结语

Undercooling

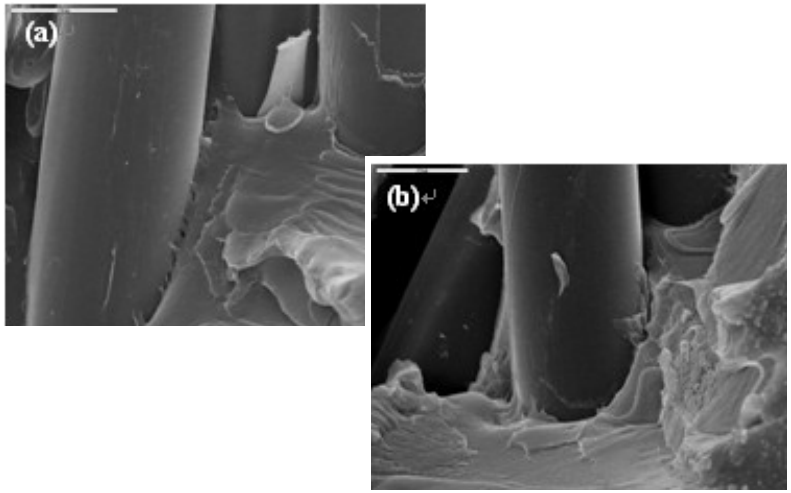
Pros and cons:

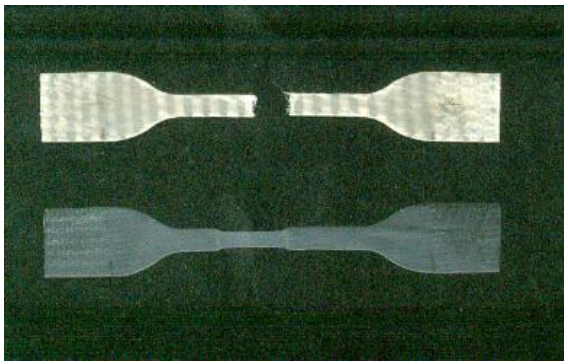
- Wide processing temperature window: below the matrix T_m, and the fiber T_m is even higher than the matrix T_m (due to orientated crystals).
- Good interfacial properties.
- But the temperature processing window is determined by different polymers and the processing parameters.

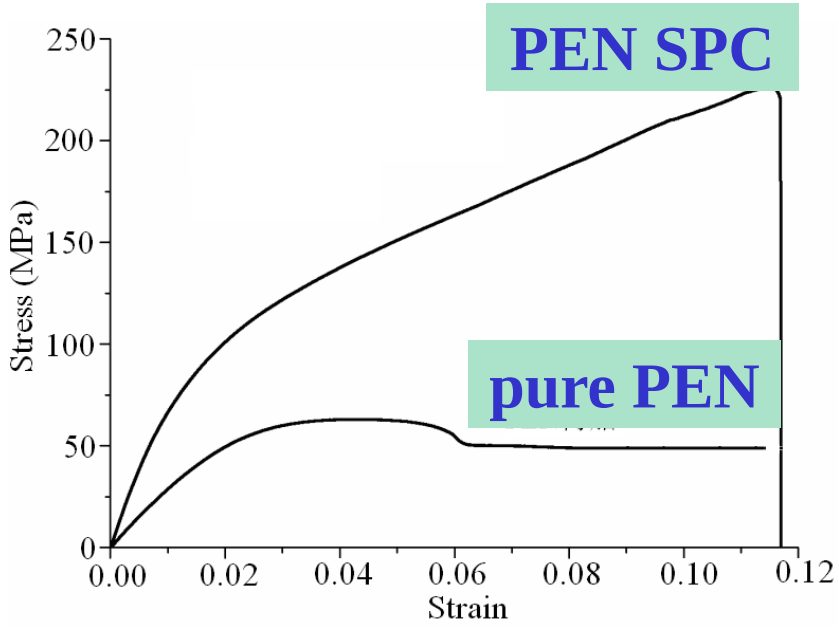


结语

- **Undercooling**
  - **PEN SPCs**







➢ Tensile strength is 3.6 times higher than that of pure PEN.

结语

- **Light weight**
- **Friendly recyclability**
- **Excellent fire/matrix adhesion**

- SPCs are developed to overcome the environmental problem of recycle and classical problem of poor interfacial bonding between the reinforcement and the matrix in traditional composites.
- PP is a thermoplastic with a wide range of applications. Over the past 30 years, the SPCs concept has been extensively investigated with PP.

结语

- **Hot compaction is still the principle method to produce SPCs**
- **Disadvantages:**
  - **long preparation cycle (several minutes)**
  - **products with simple shapes only**
  - **need post forming into appropriate shapes**

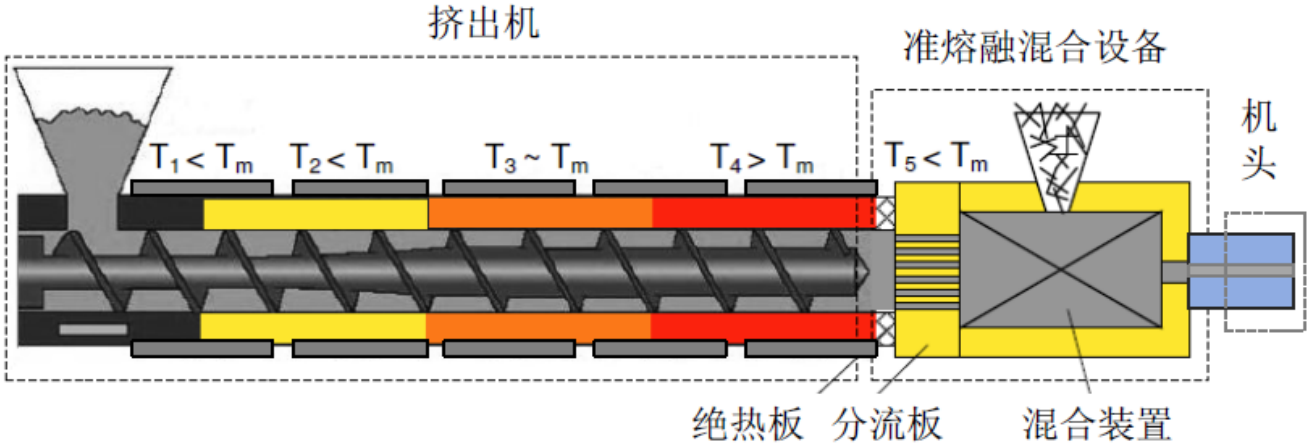
An intriguing challenge for SPCs is to develop processing techniques sufficiently versatile to be scaled up at an industrial level.

结语

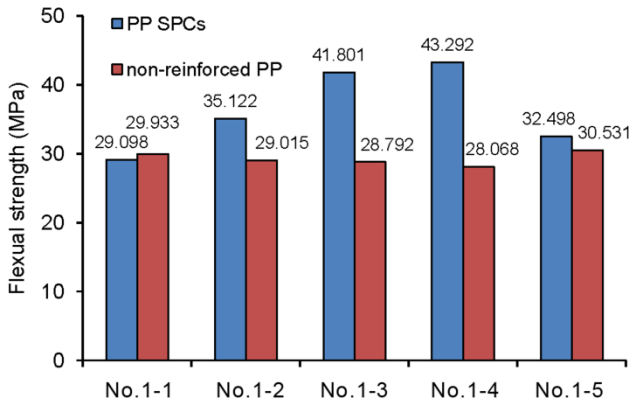
- Some widely used manufacturing processes such as extrusion and injection molding could be developed to realize SPCs production.
- Then the application area of SPCs will be enlarged.

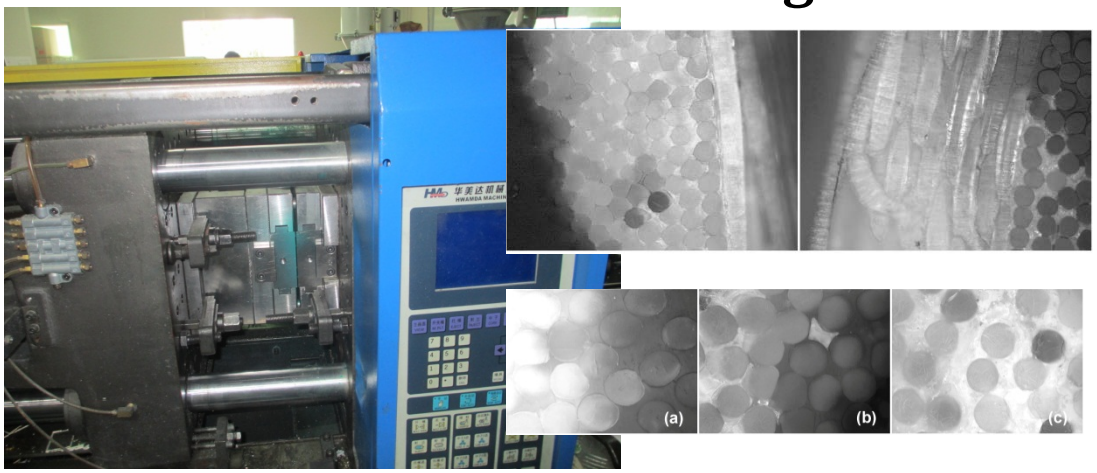
结语

Extrusion of PP SPCs with undercooling melt



Injection molding of PP SPCs with undercooling melt





THANK YOU FOR YOUR ATTENTION !

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