



Low Cost Manufacturing Process of Carbon Fiber and Composites



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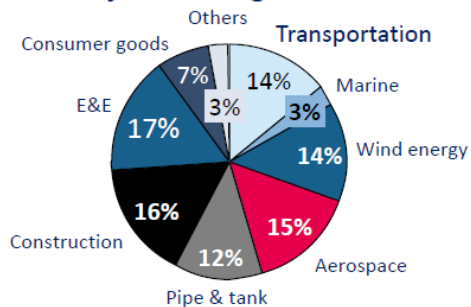
Global Carbon Fiber & Composites

Background

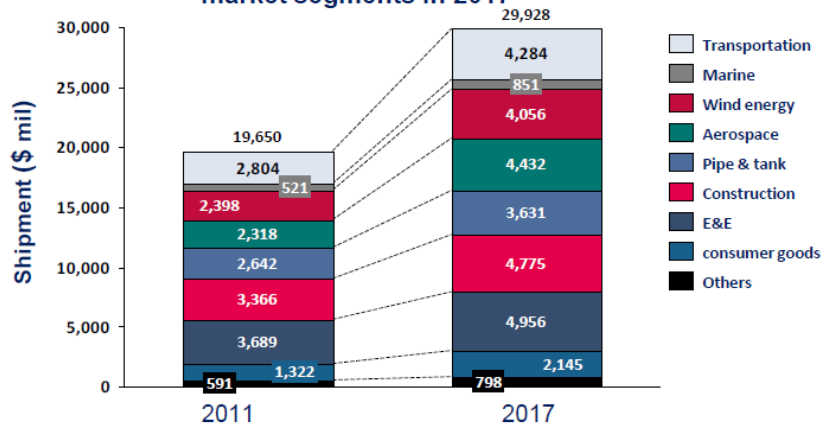
Carbon Fiber World Market

- Carbon fiber application move from aerospace sector to general industry

Global composite materials distribution (\$ mil)
by market segments in 2017



Global composite materials shipment (\$ mil) by
market segments in 2017



Key Insights

- Lucintel forecasts global composite materials market to grow by 8.2% in 2012
- Global composites end product market is expected to grow at 7.4% CAGR to 2017
 - Improved financing and availability of credit
 - Positive sign of healthy growth with gradual bounce back of automotive, construction, electronics and consumer goods markets
- Asia will drive future growth of composite materials to 2017. Europe to see moderate growth.

Limitation of application

- High price of carbon fiber, unreliable carbon fiber supply situation

※ Source: Lucintel, ACMA Composites 2012

Carbon Fiber Global Outputs

	Nameplate capacities, small tow[metric tons]	Brand	2013	2014	2015	2016	2017	2018
JAPAN	Toray, Ehime Plant	Torayca	8,000	9,000	9,000	10,000	10,000	10,000
	Toray , Japan – Large Tow	Torayca	300	300	300	300	300	300
	Toho Tenax Japan	Tenax	6,400	6,400	6,400	6,400	6,400	6,400
	Mitsubishi Rayon, Japan	Pyrofil	5,400	8,800	8,800	8,800	8,800	10,000
	Mitsubishi Rayon, Japan – Large Tow	Pyrofil	2,700	2,700	2,700	2,700	2,700	2,700
	Total(MT)		22,800	27,200	27,200	28,200	28,200	29,400
USA	Toray Carbon Fiber America [CFA], USA	Torayca	5,400	7,900	7,900	7,900	7,900	9,900
	Dow-Aksa, USA	Aksaca	-	-	-	-	-	3,500
	Mitsubishi Rayon, USA	Grafil	2,000	2,000	2,000	4,000	4,000	4,000
	Hexcel, USA	HexTow	6,650	6,650	9,150	10,550	10,550	10,550
	Cytec, USA	Thornel	2,500	2,500	2,500	5,000	5,000	5,000
	Ex-Zoltek, USA & Mexico– Large Tow	Panex	6,000	8,000	10,000	10,000	10,000	12,000
	SGL, Evanston, USA– Large Tow	Sigrafil	2,000	2,000	2,000	2,000	2,000	2,000
	SGL, Moses Lake, USA– Large Tow	Sigrafil	3,000	6,000	9,000	9,000	9,000	9,000
	Total(MT)		27,550	35,050	42,550	48,450	48,450	55,950
EUROPE	Toray Carbon Fiber Europe [CFE], France	Torayca	5,200	5,200	5,200	5,200	5,200	5,200
	Toho Tenax Europe, Germany	Tenax	5,100	5,100	5,100	5,100	5,100	5,100
	Hexcel, Spain	HexTow	650	650	650	650	650	650
	Hexcel, France	HexTow	-	-	-	-	-	3,000
	Dow-AKSA, Turkey	Aksaca	3,500	3,500	3,500	3,500	3,500	3,500
	Ex-Zolteck, Hungary– Large Tow	Panex	9,000	9,000	10,000	10,000	10,000	10,000
	SGL, Muir of Ord, UK– Large Tow		4,000	4,000	4,000	4,000	4,000	7,000
	Total(MT)		27,450	27,450	28,450	28,450	28,450	34,450
KOREA	Toray Advanced Materails Korea [TAK]	Torayca	2,200	4,700	4,700	4,700	4,700	7,200
	Hyosung	Tansome	2,000	2,000	6,500	6,500	10,500	10,500
	Taekwang Industrial	Acepora	1,500	1,500	1,500	1,500	1,500	1,500
	Total(MT)		5,700	8,200	12,700	12,700	16,700	19,200
TAIWAN	Formosa Plastics	Tairylfil	8,750	8,750	8,750	8,750	8,750	8,750
	Total(MT)		8,750	8,750	8,750	8,750	8,750	8,750

(Source : JEC magazine, April 2015, No.96)

Carbon Fiber Global Outputs

Nameplate capacities, small tow[metric tons]		Brand	2013	2014	2015	2016	2017	2018
CHINA	Hengshen Fiber Material	Starafil	3,000	3,000	3,000	6,000	6,000	6,000
	Zhongfu-Shenyang [CNBM]		4,000	4,000	4,000	4,000	7,500	7,500
	Jilin Tangu Carbon Fiber [Jilin Chemical Fiber]		2,500	2,500	2,500	2,500	3,500	3,500
	Weihai Tuozehan Fiber [150T[3K] et 2000T[12k]]		1,200	1,200	1,200	1,200	2,000	2,000
	Sinosteel Jiangcheng Carbon Fiber		500	500	500	2,000	2,000	2,000
	Dalian Xingke Carbon Fiber		180	180	180	1,000	1,000	1,000
	Bluestar China		-	1,500	3,200	3,400	3,400	3,400
	Henan Yong Coal Fibre		600	600	600	600	600	2,000
	Shenyang Zhongheng New Material		500	500	500	500	500	500
	Zhejiang Juxin Carbon Fibre		300	300	300	300	300	300
	Gansu Haoshi Carbon Fibre		260	260	260	260	260	260
	PetroChina Jilin Petrochemical		120	120	120	120	120	120
	Others		-	-	130	130	130	130
Total (MT)			13,160	14,660	16,490	22,010	27,310	28,880
RUSSIA	Kemrock, India	Jaitec	2,500	2,500	2,500	2,500	2,500	2,500
	Kemrock, India – Large Tow	Jaitec	-	-	-	-	1,500	1,500
INDIA	Holding Company Composite		1,500	3,000	3,000	3,000	3,000	6,000
	Rostec, Russia		200	200	200	200	1,500	1,500
Total(MT)			4,200	5,700	5,700	5,700	8,500	11,500
Total [small tow]			80,460	91,360	101,890	114,310	124,910	143,630
Output [coefficient 0.7]			56,322	63,950	71,320	80,000	87,400	100,541
Total [large tow]			27,000	32,000	38,000	38,000	39,500	44,500
Output [coefficient 0.9]			24,300	28,800	34,200	34,200	35,550	40,050
Output			80,622	92,750	105,520	114,200	122,950	140,591

(Source : JEC magazine, April 2015, No.96)

KOREA Carbon Fiber & Composites

Carbon Fiber Manufacturers in Korea

Domestic PAN-based carbon fiber capital expenditures plans for 2012 and later



- Operation : Sep. 2012
- Capacity : 1,500 ton
- Location : Ulsan
- 3, 6, 12, 24 K

Strength : 4,410 MPa, Modulus : 245GPa



Toray Advanced Materials Korea Inc.

- Operation : Jan. 2013
- Capacity : 4,700 ton
- Location : Gumi
- T700 Grade

Strength : 4,900 MPa, Modulus : 230GPa



- Operation : May 2013
- Capacity : 2,000 ton
- Location : Jeonju
- 6K, 12K, 24K

Strength : 4,400 ~ 5,500 MPa, Modulus : 240~290GPa



“Supply growth in the domestic carbon fiber market is expected to bring down prices, helping create new demand.”

Composites in Korea

Major export goods

2011		2012		2013	
item	Mil. \$	item	Mil. \$	item	Mil. \$
1 ship	56,588	Petroleum products	56,098	semiconductor	57,143
2 petroleum products	51,600	semiconductor	50,430	Petroleum products	52,787
3 semiconductor	50,146	Automotive	47,201	automotive	48,635
4 automotive	45,312	ship	39,753	ship	37,168
5 display & sensor	28,733	display & sensor	31,291	display & sensor	28,613
6 automotive parts	27,325	automotive parts	24,610	wireless device	27,575
7 wireless device	23,088	wireless device	22,751	automotive parts	26,079



Carbon Valley Project ('11~'16, 200M USD)

*“total **31 projects** including build up infrastructure were launched ”*

1. Manufacturing technology **large tow carbon fiber**
2. **low-energy-cost carbon fiber** Manufacturing Process
3. **Coal tar pitch-based isotropic carbon fiber** and thermal insulators
4. Application technology **for carbon fiber using petroleum residue**
5. **Anode coating pitch** and its application technology using petroleum
6. **Carbon fiber intermediate goods** and car composite components
7. **Infrastructure** to support molding technology of carbon composite components
8. Infrastructure to support first class carbon materials



(source : www.hyosung.com)

Carbon Valley Project(Infrastructure)

Infrastructure to support molding technology of carbon composite components

Preform equipment

- hybrid braiding equipment
- spreading equipment & weaving equipment

Intermediate manufacturing equipment

- wet-laid equipment
- thermoplastic UD prepreg
- AFP(auto fiber placement) machine

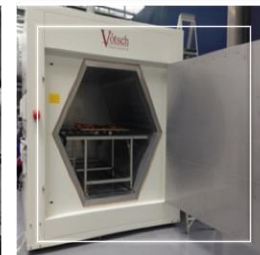
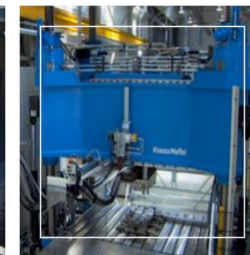
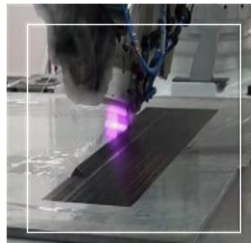
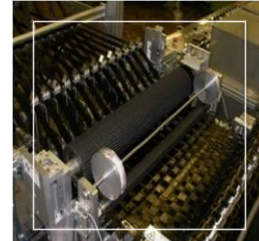
CFRP manufacturing equipment

- HP-RTM systems
- Pultrusion machine
- Filament winding machine
- 3D dynamic water jet
- high temperature furnace
- multi-axial carbon fabric machine
- ultrasonic machining center
- microwave oven



KC TECH

Korea Institute of Carbon Convergence Technology



Building a sustainable Low cost CF and CFRP

**Carbon
Precursor**

**Carbon
fiber**

CFRP

- High Cost Precursor

- High Cost of Conversion

- Low Productivity(Autoclave)

- Recycle Problem(Thermoset)

- Low cost Precursor

- Lignin

- Textile

- Polyolefin

- melt spinnable PAN



- advanced oxidation

- alternative LT & HT process

- MAP carbonization

- Advanced surface treatment

- preforming

- OoA process(microwave ...)

- high productivity

- manufacturing automation

- thermoplastic process

- recycle techniques

- application



Low Cost Carbon Fiber

Objectives

○ To develop **PAN precursor by melt spinning process**

① Synthesis of melt-processable copolymers

② Melt spinning process of copolymers

○ Finally,

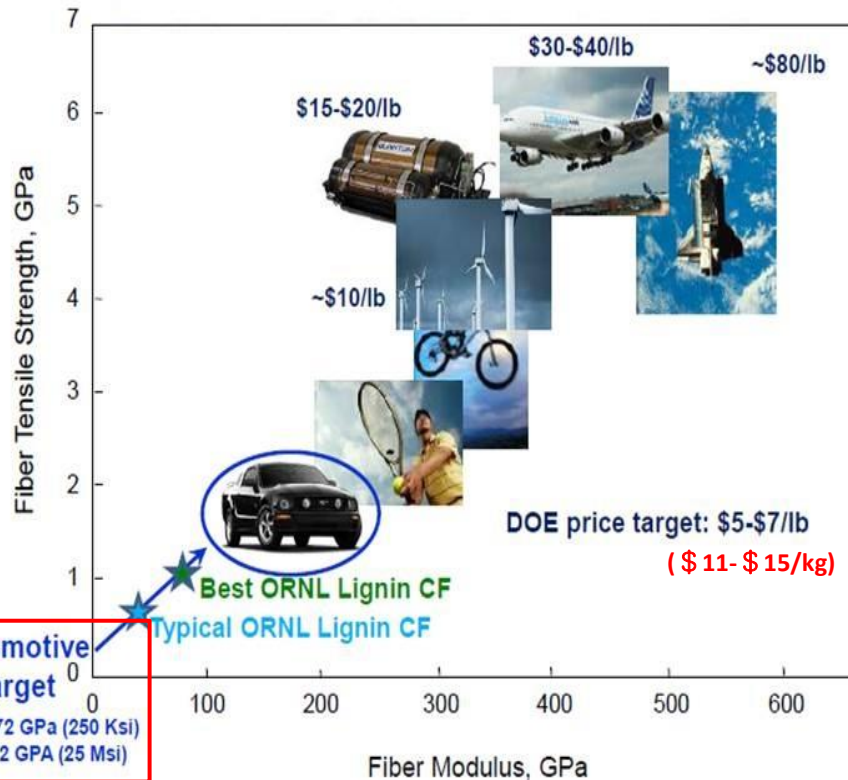
To develop low cost & general grade carbon fiber precursor

“ Commercial Grade & Low Cost Carbon Fiber Manufacturing Technology ”

Core Tech.	Precursor	Development of New PAN precursor for melt spinning	Goal	Strength	3.53 GPa
		PAN precursor melt spinning technology		Modulus	230 GPa
	Conversion to Carbon Fiber	Stabilization Technology		Elongation	1.5%
		Carbonization Technology		Fiber diameter	< 10μm

Overview

CF for Automotive Application



* Source : Ford, Carbon Fiber Workshop 2013, ORNL

Automotive Requirements

Strength : 1.72 GPa,
Modulus : 172 Gpa
Price : \$ 11- \$ 15/kg



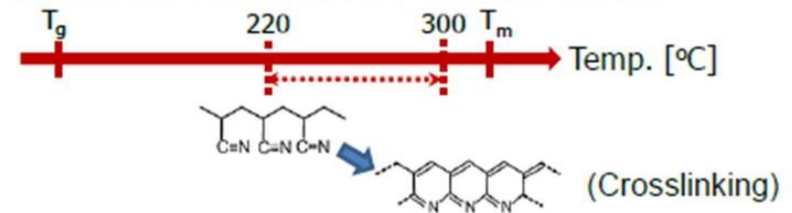
New Approach for low cost CF

New Approaches for Low Cost Carbon Fiber

New approach for low cost CF

1. Alternative - **raw materials**(low cost precursor)
 - Textile PAN, Olefin, Lignin, Melt PAN
2. Advanced process - **low cost manufacturing carbon fiber**
 - Spinning : Wet process → Melt Process
 - Heat treatment : Thermal → Microwave assisted plasma(MAP)

Why not for PAN-based precursor fiber...?



- Summary of Carbon Fiber Precursor -

PRECURSOR	GRADE	CHALLENGE	SPINNING	REMARK
PAN	Aerospace	Very Expensive	Wet	
PAN	Commercial	Expensive	Wet	
Textile PAN	Commercial	Fiber Properties	Wet	* ORNL(USA)
Melt PAN	Commercial	Processability, Fiber Properties	Melt	* KCTECH(KOREA)
Lignin	Commercial	Fiber Properties, Blending, Stretching	Melt	* ORNL(USA)
Polyolefin	Commercial	Material Properties	Melt	* NEWSPEC(ITALY)

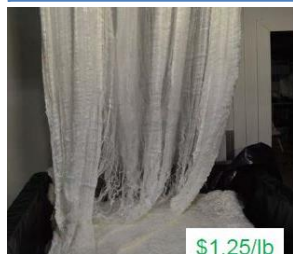
Development Trends

Textile acrylic fiber(T-PAN), ORNL(USA)

T-PAN : 610K Tow, Kaltex(Mexico)

- AN(~92%), MA(7%)
- Wet spinning, DMF solvent
- Filament Tenacity : 4.3g/d

	Target	Result
Tensile Strength	1.72 GPa (250ksi)	3.38GPa (490ksi)
Tensile Modulus	172 GPa (25Msi)	234 GPa (34Msi)



Unmodified Textile PAN Precursor
(Kaltex)



Commercial Carbon Fiber PAN Precursor

(Source : ORNL membership meeting 2014)



Carbon Fiber from Textile PAN Precursor



Commercial Carbon Fiber

Polyethylene(PE), NEWSPEC(ITALY)



- Budget : 10M EUR
- Consortium : 13
- Start/End : '13.11~'17.10(4yr)
- Target : PE- CF 10 EUR/Kg

	Target properties of the PE-CFs
Tensile strength	2 GPa
Tensile modulus	200-250 GPa
Elongation	> 1%
Fiber diameter	< 10 microns

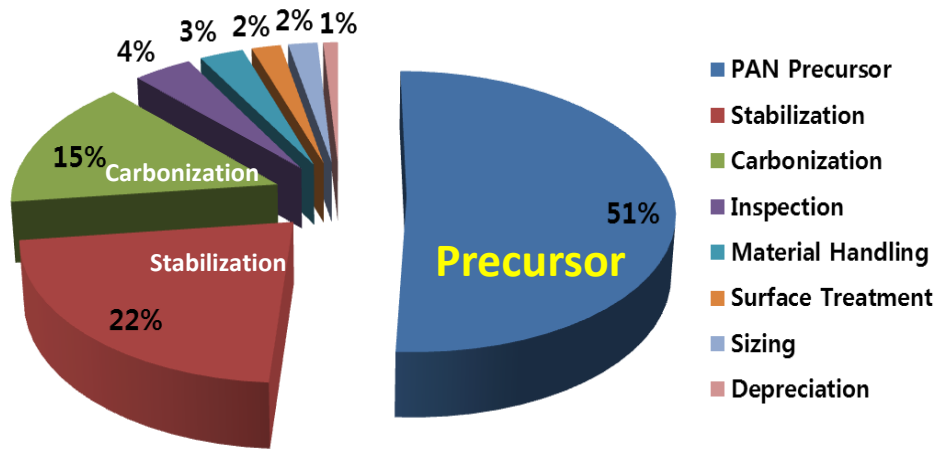


(Source : www.newspe.eu)

Overview

- Carbon fiber industry is one that is rapidly changing, in increasing end user demand
- Carbon fiber application move from aerospace sector to general industry
- Limitation of application
 - High price of carbon fiber from high processing costs

▪ Carbon fiber manufacturing costs



✓ With conventional processing using a carbon fiber grade PAN precursor is slightly over 50% of the carbon fiber manufacturing cost

✓ Thus, any reduction in precursor cost has the largest impact on CF manufacturing cost

* Source : THE CARBON FIBRE INDUSTRY WORLDWIDE 2011-2020

New Approach : Melt Spinning process

The replacement of wet spinning by a melt spinning process is one of the major approaches which can help in producing cost effective carbon fiber precursors

Current Technology : wet process

Acrylic precursor manufacturing processes

Manufacturer	CF Brand Name	Spinning
Toray	TorayTorayca	Wet Spinning(DMSO/H ₂ O) Air Gap Spinning(DMSO/H ₂ O)
Toho Tenax	Tenax	Wet Spinning(ZnCl ₂ /H ₂ O)
Mitsubishi Rayon	Pyrofil Grafil	Wet Spinning(DMAc/H ₂ O)
Hexcel	HexTow	Wet Spinning(NaSCN/H ₂ O)
Cytac	Thornel	Wet Spinning(DMSO/H ₂ O) Air Gap Spinning(DMSO/H ₂ O)
SGL	Sigrafil	
Formosa	Tairyfil	Wet Spinning(DMAc/H ₂ O)

- Main monomer : ≥95% Acrylonitrile(AN)
- Comonomer : 3-5%
Acrylic acid(AA), Methacrylic acid(MAA)
Methyl acrylate(MA), Acrylamide(AA), Itaconic acid(IA)

Ref. Potential CF Cost Matrix

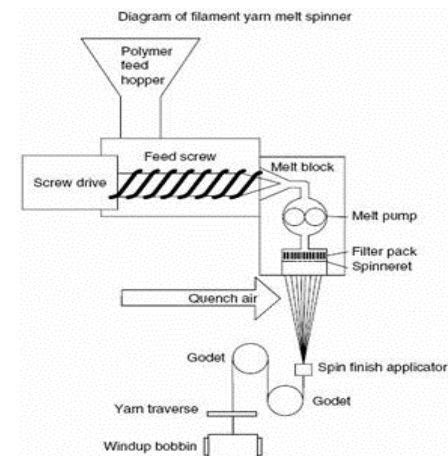
Precursor and Conversion	Cost \$/kg CF	Cost Savings,%
Wet spun PAN precursor conventionally converted	\$25.20	0%
Melt spun PAN precursor conventionally converted	\$17.44	~31%

-These cost estimates are derived primarily from the 2007 Kline reports and are based on petrochemical prices in CY2007Q1

New approach : melt process

- ✓ Low production cost
- ✓ High production rate
- ✓ Environment-friendly

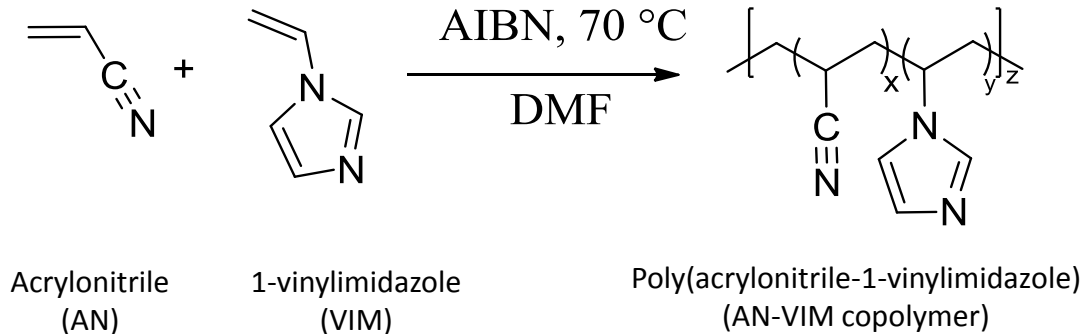
→ Solvent free



- Main monomer : ≥80% Acrylonitrile(AN)
- Comonomer : ~20% Vinylimidazole(VIM)

Development of low cost carbon fiber

Synthesis of melt-processable copolymers



VIM as comonomer

- ✓ disrupt PAN crystallinity
- ✓ thermally cross-linkable

Structure of AN/VIM copolymer by ^1H -NMR and FT-IR

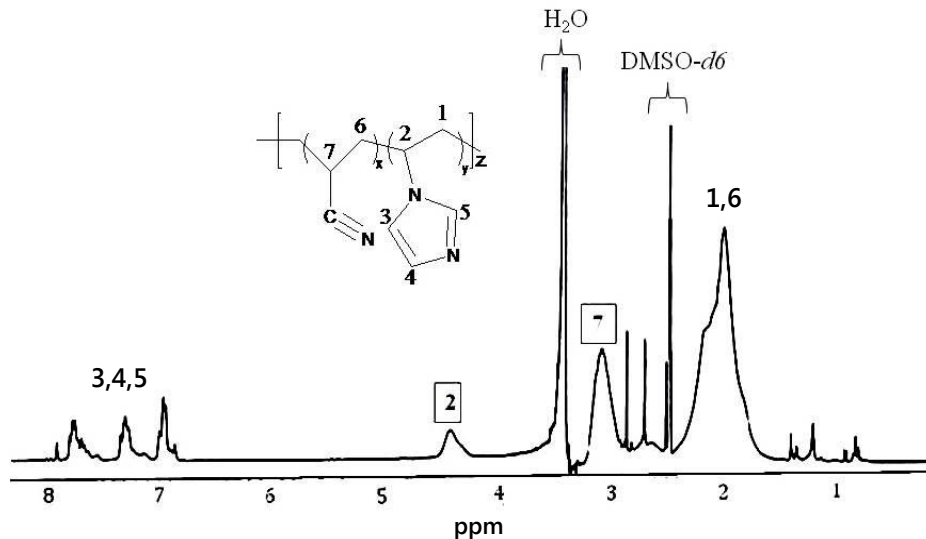


Figure 1. ^1H NMR of AN/VIM(82/18) copolymer in DMSO- d_6

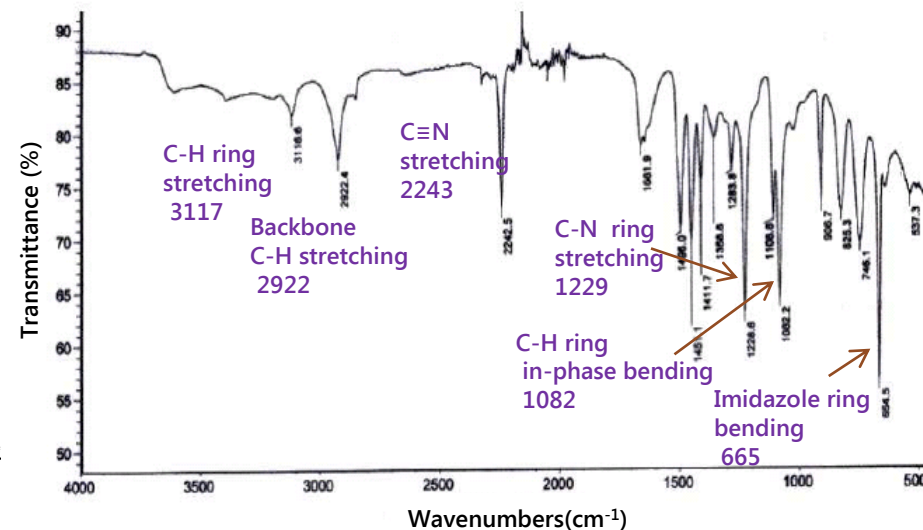
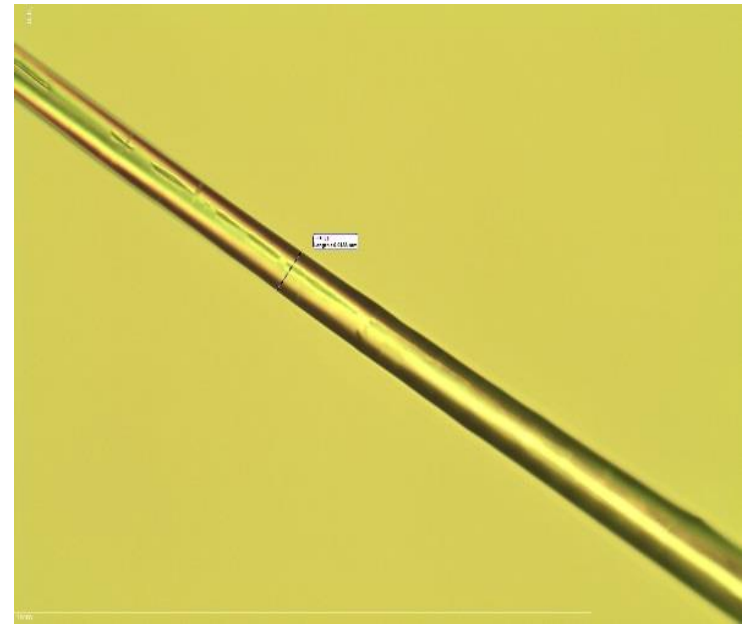


Figure 2. ATR-FTIR spectrum of 82/18 AN/VIM copolymer

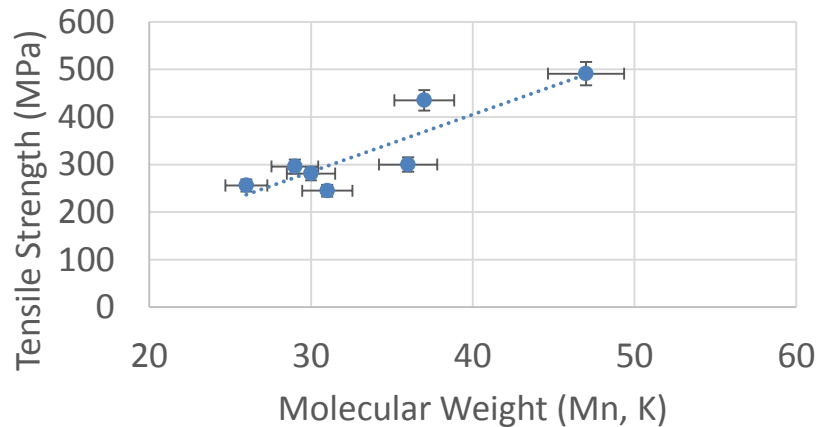
Development of low cost carbon fiber

Extruded PAN precursor fiber

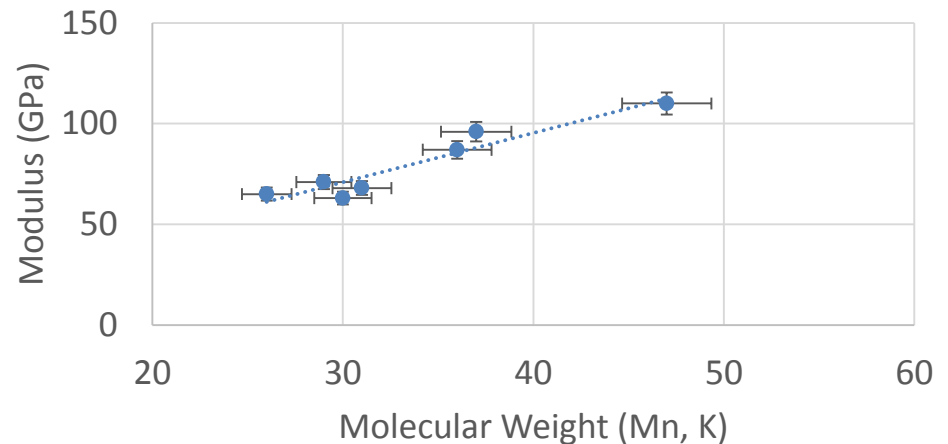
ID	Diameter (um)
a	43
b	39
c	28
Average	36



Tensile Strength vs Molecular Weight

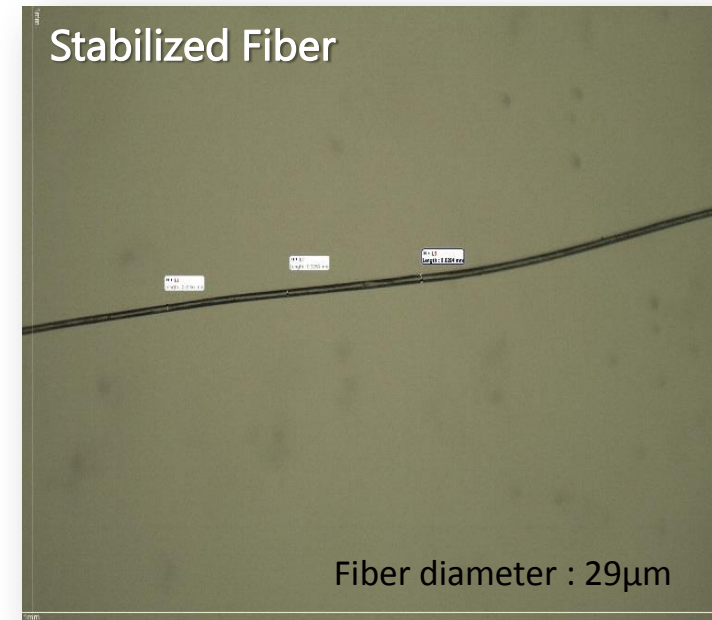
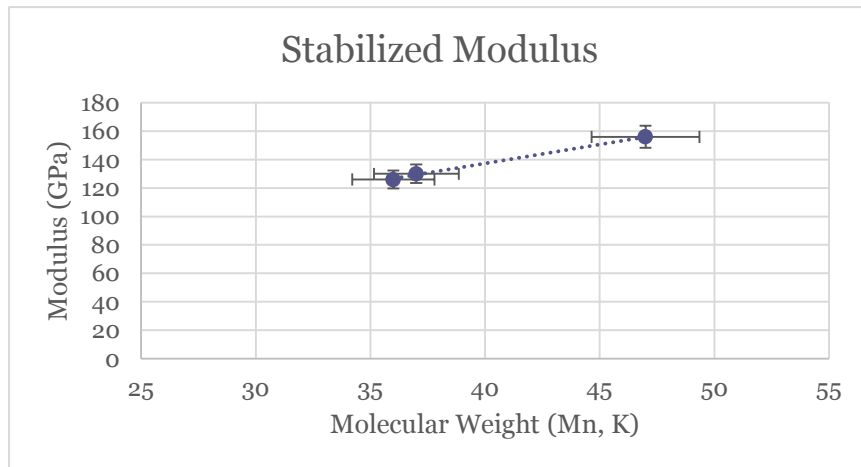
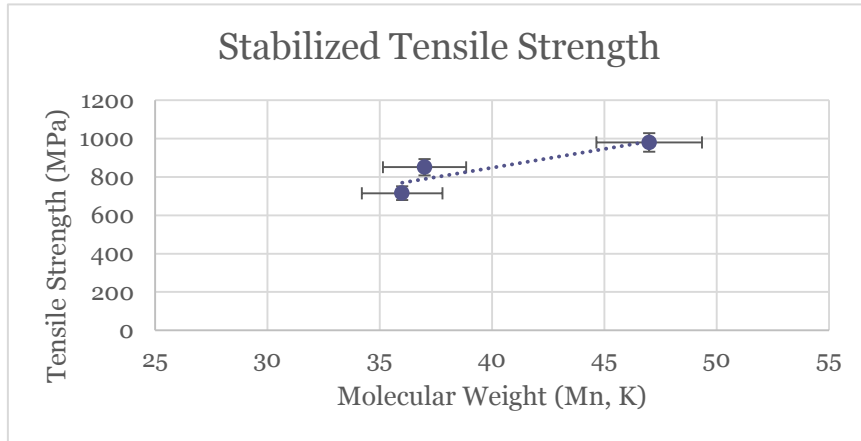


Modulus vs Molecular Weight

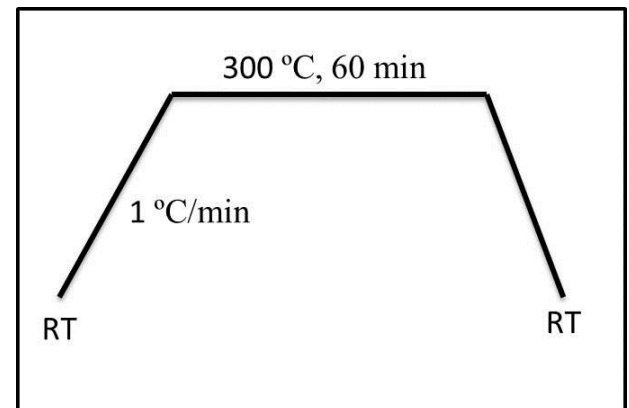


Development of low cost carbon fiber

Stabilization of PAN precursor fiber



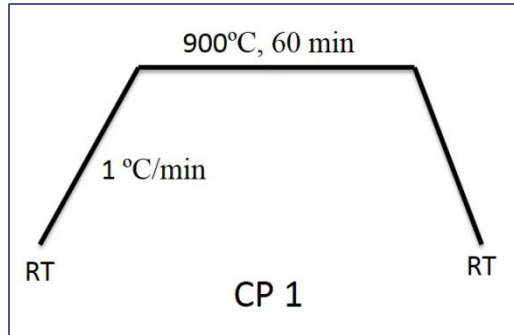
Temp. profile of Stabilization(under Air)



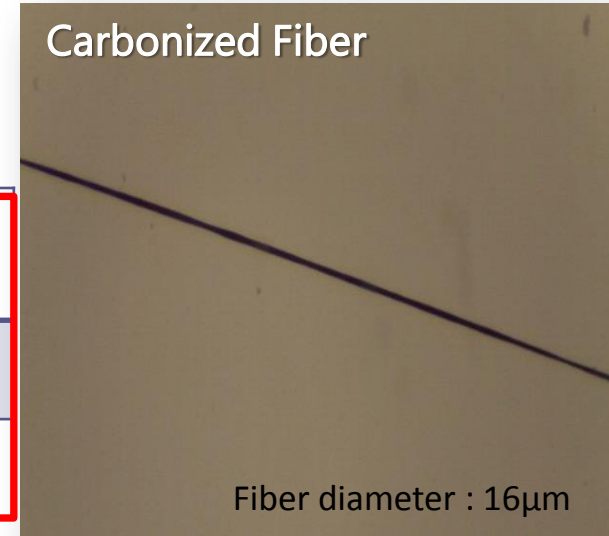
Development of low cost carbon fiber

Carbonization of PAN precursor fiber

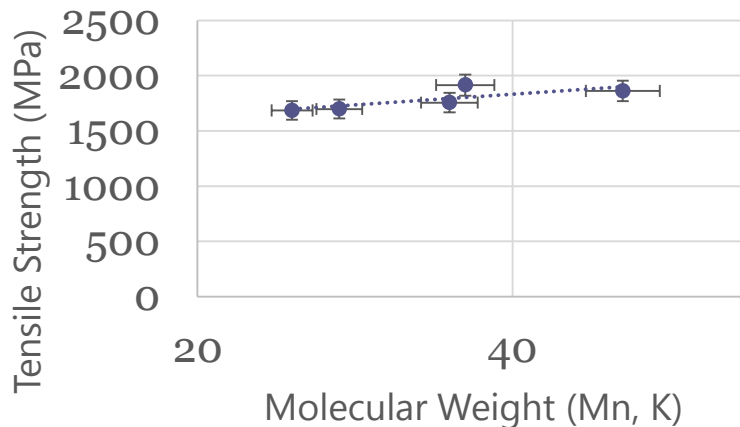
Temp. profile of Carbonization(under N₂)



	T-300 grade (Toray)	Automotive Requirements	Results (Lab.scale)
Strength	3.53 GPa	1.72 GPa	2.0 GPa
Modulus	230 GPa	172 GPa	180 GPa



Carbonized Tensile Strength



Carbonized Tensile Modulus

