Future Lower Cost Carbon Fiber for Autos: International Scale-up & What is Needed



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- DOE's largest multiprogram science laboratory
- Nation's largest energy R&D laboratory
- Nation's largest concentration of open source materials research
- World-class computing facilities
- Built the \$1.2 billion Spallation Neutron Source
- \$300 million modernization program in progress
- \$1 billion budget
- 4200 employees
- 3000 research guests annually

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Light-Duty Vehicle Trends

Weight and Performance by Model Year

(Three Year Moving Average)

Adjusted Fuel Economy by Model Year (Three-Year Moving Average)



Source: Light Duty Automotive Technology and Fuel Economy Trends: 1975 through 2004, U.S. Environmental Protection Agency, April 2004.

Key Drivers and Technology Enablers



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USA Transportation Petroleum Use by Mode (1970-2025)



Note: Domestic production includes crude oil, natural gas plant liquids, refinery gain, and other inputs. This is consistent with EIA, MER, Table 3.2. Previous versions of this chart included crude oil and natural gas plant liquids only. Source: <u>Transportation Energy Data Book: Edition 24</u>, ORNL-6973, and <u>EIA Annual Energy Outlook 2005</u>, Preliminary release, December 2004.





China, with 13 vehicles per 1000 people, is where the U.S. was in 1913

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Materials in a Typical NA Vehicle



A 10% mass reduction translates to a 6-7% increase in fuel economy or may be used to offset the increased weight and cost per unit of power of alternative powertrains

		Critical Challenges				
	Carbon-fiber Composites	Low-cost fibers	High-volume Mfg.	Recycling	Joining	Predictive Modeling
	Aluminum	Feedstock Cost	Manufac-ing	Improved Alloys	Recycling	
SU	Magnesium	Feedstock Cost	Improved Alloys	Corrosion Protection	Manufac-ing	Recycling
Optio	Advanced High- strength Steels	Manufacturability	Wt. Red. Concepts	Alloy Development		
rial (Titanium	Low-cost Extraction	Low-cost Production	Forming & Machining	Low-cost PM	Alloy Development
late	Metal-matrix Composites	Feedstock Cost	Compositing Methods	Powder Handling	Compaction	Machining & Forming
V	Glazings	Low-cost Lightweight Matls.	Noise, Tº struc. models simulations	Noise reduction techniques	UV and IR blockers	
	Emerging Materials and Manufacturing	Material Cost	Mfg-ability	Design Concepts	Performance Models	

Chart is provided courtesy of Robert McCune - Ford Motor Company



1978 Ford LTD



\$1M Demonstration Vehicle



Composites in the Automotive Industry





Carbon fiber composite rear deck lid and seat (4500 units total)

Carbon fiber fenders, wheel house, and floorpan (7000 units/year)

2006 Z06 Corvette





2006 Dodge Viper





Carbon fiber LH/RH fender/sill supports, LH/RH door inner reinforcements, windshield surround reinforcement (2000 units/year)

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Composites in the Automotive Industry

BMW M3 CSL





Carbon fiber roof (3000 units/year)

Carbon fiber intensive (500 units/year)

2005 Mercedes Benz SLR McLaren

McLaren



Aston Martin Vanquish





Carbon fiber composite transmission tunnel, braided A-pillar, front end crash structure (400-800 units/year)

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Carbon Fiber Supply and Demand



Source: Cliff Eberle, ORNL and Mohamed Abdullah, MGA Consultants



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2X World

North American Vehicle Production > 16 / year 12 pounds of Carbon Fiber per Vehicle: 192M lb/year



Source: U.S. Department of Defense, "Polyacrylonitrile (PAN) Carbon Fibers Industrial Capability Assessment", OUSD(AT&L) Industrial Policy, October 2005.

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Carbon Fiber Market History



Sources: High performance Composites Magazine Proceedings of the Global Outlook for Carbon Fiber 1998 to 2007 CEH Marketing Research Report: Carbon Fibers, SRI Consulting The Market Prespective for PAN-Based Carbon Fiber 1999 - 2005 Kline& Company



PAN Dependence on Oil Price



Current Carbon Fiber Raw Materials are Tied to Oil



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Projected Carbon Fiber Market Demand



The Growth and Challenges are Multi-Industry



Carbon fiber is a leading candidate for mass reduction.

- 10% Mass Savings = 6-7% Fuel Savings
- Mass reduction allows earlier introduction of alternative propulsion systems.

Price too high for medium to large volumes. Supplies are insufficient. Processing technologies undeveloped.









Longer blade design requires use of CF.

- Energy captured is greater with longer blades
- Blades must be both stiff and light.

Insufficient volume of CF at any price. Lower price needed for more efficient designs.

Needs: Higher volume at lower price. (Needed now for rapid deployment)









In deeper waters strength/weight and stiffness/weight becomes critical.

Pipes, drill shafts and other structures must support their own weight while being constructed.

Need stable, larger supply. Significant materials development. Materials processing development. Competitive pricing.









Carbon fiber could replace steel with Equivalent stiffness - similar "packing factor" of reinforcement

- Increased strength higher tension permissible
- Low (slightly negative) CTE less sag compensation needed for low temps
- Reduced weight (~94 lbs vs 344 lbs) more conductor for equivalent sag

Need ready supply of materials at volume pricing and development of materials and processing technologies.







Strength to weight demands CF for pressurized H2 storage. Could make more compact NG storage with higher pressures. Cost of fiber makes designs prohibitively expensive.

Cost of fiber makes Designs prohibitively expensive. Insufficient volume of CF available.



40 - 80% is carbon fiber cost



Carbon Fiber Glass Fiber Epoxy Curatives Liner Polymer Foam Dome Front Boss Aft Boss 1-1/8 Adapter Seals Valve PRD Miscellaneous





Retrofit and new construction in days rather than months. Large structures fabricated in plants rather than on site. High demand for rebar.

Need standard materials. Standard construction processes. Affordable materials. Steady supply of materials. Rapid Repair









Strong History in Aerospace Needed for lightweight portable ground and sea systems.

Affordable materials for rapid deployment of ground systems.

non-flying equipment.













- 1. Oil refinery profitability is in making fuel AND other products from input material.
- 2. Virtually all input Crude is turned into a valueadded product.
- 3. To be economically viable, a bio-refinery will have to operate in much the same manner.





Lignin Based Carbon Fiber may be one Value-Added Product to make Bio-Refineries economically Attractive

Millions of Barrels/Year US Refineries	2006	2007
Liquified Refinery Gases	209.0	229.0
Motor Gasoline	2225.4	1964.4
Aviation	570.4	546.7
Kerosene	23.9	17.3
Fuel Oil	1672.4	1706.6
Petrochemical Feedstocks	141.9	143.9
Lubricants	61.2	66.8
Waxes	5.8	5.4
Petroleum Coke	304.7	309.4
Asphalt and Road Oil	186.7	184.7
Still Gas	249.5	258.9
Miscellaneous	21.4	25.2

Source: Energy Information Administration



Common Issues and Needs

Storage

Civil Infrastructure Rapid Repair and Installation, Time and Cost Savings



Power Transmission Less Bulky Structures **Zero CLTE**



Bio-Mass Materials FUELING OUR FUTURE Alternative Revenue **BIOMAS** Waste Minimization



Fiber Cost Fiber Availability Design Methods Manufacturing Methods Product Forms

Oil and Gas **Offshore Structual** Components



Vehicle Technologies Necessary for 50+% **Mass Reduction**





Wind Energy **Needed for Longer Blade Designs**





If the Demand is so Great, Why Don't we see more applications in Automotive and other Industries?

#1 Reason \$\$\$\$\$

But there are other Reasons



Designers are not comfortable with composites, especially in Crash critical applications. Full system & subsystem demonstration needed.





Many composite processing methods are optimized for performance not production rate efficiency. Cost optimization of production methods needed.



Capital investment already sunk into metal forming equipment. Must be ready for the next generation.

Size of the carbon fiber industry cannot support large scale utilization. Must choose applications and ramp up capacity.

Boom or bust nature of the market. Automotive industry needs long term pricing and stable long term partners.

The secret art of sizing. Collaborative development efforts are needed.

The lack of resin targeted systems. Need sizings optimized for specific classes of resins that are of interest to the automotive companies.



Companies with US Facilities

Company	US Facilities	Non-US Facilities
Hexcel (US)	Decatur, AL; Salt Lake City	Spain
Cytec (US)	Greenville, SC; Rock Hill, SC	None
Toray (Japan)	Decatur, AL	Japan
SGL (Germany)	Evanston, WY	Scotland, Germany
Zoltek (US)	Abilene, TX; St. Louis, MO	Mexico, Hungary
Mistubishi (Japan)	Sacramento, CA	Japan
Toho Tenax (Japan)	Rockwood, TN	Japan, Germany

Source: Polyacrylonitrile (PAN) Carbon Fibers Industrial Capability Assessment, Department of Defense

Universities with significant research in Carbon Fiber production Clemson University University of Kentucky Virginia Tech

Note: Large efforts in carbon fiber composite development and many laboratories and universities.



- Aircraft orders straining Capacity Worldwide Boeing (787), Airbus (380)
- Current Carbon Fiber manufacturers replicating Capacity. Announcements from all manufacturers regarding expanded capacity.
- Japanese moving into automotive by vertically integrating into Tier I supply chain Announcements made by large teams from fiber supplier throught OEMs
- Attempts to entice development of capacity in Middle East in at least 2 different countries
- EU developing automotive, infrastructure & wind applications but only with existing business models for fiber production
- UB Koltrefjar ehf in Iceland investigating the development of a carbon fiber plant to be located there due to the reduced cost of energy and potential homeland applications.



•Chinese quietly developing a 40 Million lb/year plant for industrial grade fiber

- Claimed applications are wind, power transmission and automotive
- Russia, China and Japan have increase R&D efforts significantly
- United States Expanded interest on all fronts
 - Strong interest from end user communities
 - •. Growing interest from potential new carbon fiber producers
 - R&D for Carbon Fiber Production focused on high volume



To Rapidly Expand the Carbon Fiber Industry

Carbon Fiber Obstacles to High Volume, Affordable Supplies

Industry Age < 50 years

Limited Precursors – Pitch, PAN, Rayon

Aerospace Mind-Set – High Margin, Low Volume Limited Technical Advances Prohibition against process changes Bound to epoxy chemistry

Small Industry and Company Size – 100M lb/yr Limited resources Specialty material mentality

> Limited Research Community Few Scientists (handful worldwide)

What can be done?

Accelerate Learning Curve

Develop Lower Cost Precursors

Develop New Applications Investment by High Vol Industry Involve other R&D Organizations Develop New Processing Methods Develop Non-Epoxy Chemistry

Large Manufacturers Enter the Market Invest in high volume plants Develop commodity mat'l forms Industry Standards Bring together toward 1 Goal Sponsor graduate degrees in US



To Rapidly Expand the Carbon Fiber Industry

- 1. Develop a multiple End Use sector approach.
- 2. Large investment in NEW production methods required.
- 3. Development of Lower Cost Precursors.
- 4. Product forms amenable to High Volume industries needed.
- 5. Development of a larger EXPERT base required.
- 6. Industry Standards



Strength: \geq 250 Ksi (1.73 GPa)Modulus: \geq 25 Msi (173 GPa)Strain: \geq 1%

12/24k: \$12/lb 1993, \$18/lb 1997, \$9/lb 2000 [Walsh, Zoltek 8/2000] All time low \$5.25/lbs std grade (mid-grade) 2003



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Thermal reduction of a limited number of precursors by pyrolysis of all but the carbon followed by heat treatment of the carbon to obtain desired structure.

Are these the only materials and the only way?





Hístorícally: No cost dríver for lower cost. Only better Performance.

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Carbon Fiber Costs (Production Costs)





Carbon Fiber Costs (Production Costs)

<u>3 Precursor Options</u>

1. Textile Grade PAN (MA or VA formulations)

- 2. Lignin Based Precursor (Hardwood or Softwood)
- 3. Polyolefins (not shown on charts)

Other Important Precursor Technologies:

- 1. Melt-Spun PAN
- 2. Scaling to Pilot Plant
- 3. Cost Studies

Alternative Precursors and Conventional Processing



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Carbon Fiber Costs (Production Costs)

Alternative Processing

<u>3 Processing Options</u>

- 1. Advanced Stabilization
- 2. Plasma Oxidation
- 3. MAP Carbonization

Other Important Processing Technologies:

- 1. Tow Splittng
- 2. On-line Feedback
- 3. Scaling to Pilot Plant
- 4. Development of carbon fiber SMC
- 5. Plasma Modification of Surfaces
- 6. Cost Studies



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Program Integration





Future Biorefinery FCVT Low-cost Carbon Fiber R&D Washed Hardwood Kraft Lignin Low-cost Lingnin content (%) Lignin Carbon Fiber Target energy value: about \$60/ton = \$5-7/lb Thermo-chemical What is this cost? Melt Spinning, and enzymatic Lígnin) Thermal Processing, hydrolysis, etc. hybrid systems Other Cellulose and value-Hemi-cellulose added **ITP R&D** products **OBP R&D OFCVT R&D** Ethanol at \$1.07/gal PAN Oxidation Carbonization Graphitization ST \$3.53 (44.8%) \$1.34 (17.0%) \$1.00 (12.7%) \$1.19 (15.1%) \$0.82 (10%)



- Demonstrated that solvent-extracted, purified hardwood lignin (provided by MeadWestvaco) can be continuously melt-spun into fiber form
- Successfully Spun 12 filament tows with no additives and no problems using lignin from MeadWestvaco's "Organosolv" process
- Lignin fiber diameters were successfully varied under controlled conditions from 20 down to 10 microns.





Achieved Excellent Structural Characteristics in Melt Spun Lignin Fiber:







12-filament fiber spun from solvent-extracted hardwood lignin (HWL-SE1)







Processed carbon fibers from a Hardwood/Softwood lignin blend.

A Hardwood lignin was used as the plasticizer for the softwood lignin.



-				-
PAN \$3.53 (44.8%)	Oxidation \$1.34 (17.0%)	Carbonization	Graphitization	ST \$0.82 (10%)
φοιού (11.076)	φ1.01 (17.070)	φ1.00 (12.17)	φ1.10 (10.170)	Ψ0.02 (1070)



PAN

\$3.53 (44.8%)

- *Chemical Modification* of textile acrylic fibers reduces stabilization time and increases CF mechanical properties.
- Established recommended "recipes" to produce carbon fiber from chemically modified or radiated commodity textile acrylic tow
- Reduced Oxidation time from 85 min down to 50 minutes

			TEXTILE		CONVENTIONAL	
		Spool 1	Spool 2	Zoltek Panex 33	Fortafil F3(C)	Goals GPA
Production Line Speed	(in/min)			-	-	
Modulus	(GPA)	212	208	180	214	172
Ultimate Strength	(GPA)	2.75	2.71	2.81	3.35	1.72
Elongation at Break	(%)	1.30	1.30	1.56	1.57	1.0
			Project Im	pact	· · · · · · · · · · · · · · · · · · ·	

Oxidation

\$1.34 (17.0%)

Carbonization

\$1.00 (12.7%)

Graphitization

\$1.19 (15.1%)

ST

\$0.82 (10%)

Data from Hexcel Development Project



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Textile Precursors



Steepest part of slope determines speed of stabilization. Location of ramp up start & peak determine oxidative stabilization temp range.

Chemically treated textile could be undergo oxidative stabilization in less time but a slightly higher temperature.



Textile Precursors











Transforms PAN from a thermoplastic linear polymer structure to an infusible, highly condensed cyclized structure (thermoset) capable of further processing at high temperatures

•Conducted in an oxidizing medium (e.g., air) at ~ 200 - 250°C



Oxidative Stabilization



Left: Before stretching. Right: Entry end of 1st oxidation oven.

Oxidative Stabilization represents 75-80% of fiber residence time and 18-20% of cost.

PAN

\$3.53 (44.8%)

Project Impact

Oxidation

\$1.34 (17.0%)

 ✓ Oxygen needs to diffuse through the stabilized "skin"

Single Filament Cross-Section



Carbonization

\$1.00 (12.7%)

Stabilized and oxidized region

Mainly stabilized region



Graphitization

\$1.19 (15.1%)

ST

\$0.82 (10%)



Acid Digestion Removes Unstabilized Material



Poorly Stabilized but Typical for Many Lower Cost Fibers

Fully Stabilized Core





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Oxidative **Stabilization**





Two Early Generation Oxidation Modules

Proprietary Oxidation Process Developed based on Non-Thermal **Atmospheric Plasma**

Project Impact

Process able to replace later ³/₄ of conventional oxidation but requires the use of slightly pre-stabilized precursor.

> Effort began to develop a rapid Pre-Stabilization Technique

, ,				
PAN	Oxidation	Carbonization	Graphitization	ST
\$3.53 (44.8%)	\$1.34 (17.0%)	\$1.00 (12.7%)	\$1.19 (15.1%)	\$0.82 (10%)



- Objective is to stabilize (cross-link) the precursor sufficiently that it can subsequently be plasma oxidized
- Needs to be fast (high throughput) and Inexpensive (<\$0.05/lb)
- Three routes investigated

Stabilization	Time	Thermal Post	Plasma	Total
Method	ReQ'd	Treatment	Oxidation	
AE-Boom	Socs	20-26 min	20-21 min	40-50 min
Bultraviolet	6-7 min	None	20-24 min 20-24 min	26-31 min
^c Thermo-Chemical	5-10 min	None	20-24 min	25-34 min
Conventional				100-120 min

^APost Treatment believed to be due to over processing. Potentially may be eliminated. ^B6-7 minutes would require a huge amount of lamps at textile line speeds. ^CBy far the easiest to implement in existing plants

Down Select – Thermochemical (E-Beam)





Microwave Assisted PlasmaCarbonization

Generation A

- VFME was discarded as primary energy source for this process.
- Single frequency microwave energy became a major player.
- Hand processed samples



PAN

\$3.53 (44.8%)



Generation B

- Microwave direct heating of carbon fiber using a long, tunable, resonant cavity.
- Capability to monitor fiber temperature
- Pre-heating of fiber with nitrogen/air to enhance microwave coupling.
- Line speed 2-4 inches/minute

Oxidation \$1.34 (17.0%)

Carbonization \$1.00 (12.7%) Graphitization \$1.19 (15.1%)

ST

\$0.82 (10%)



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Microwave Assisted PlasmaCarbonization



Met Final Milestone

- Produced fibers for ACC testing
- Ran 3 large tows at 44in/min for > 1 hr in August 2006 with satisfactory mechanical properties

Project paused While other Technologies Catch-up





- Fiber surface chemistry, due mainly to treatment and sizing, is important to adhesion-sensitive mechanical properties
 - Oxygen concentration on fiber surface is very important
- Preliminary ORNL plasma surface treatment results far superior to conventional treatment results
 Condition
 O
 O/C



Effect of varying plasma gas composition

PAN \$3.53 (44.8%)

Oxygen content indicates density of available bonding sites

Condition	0	O/C	CV
Untreated commercial fiber	4.7%	0.051	0.21
O ₃ treated commercial fiber	6.2%	0.069	0.26
AP-A	24%	0.42	0.38
AP-B	30%	0.55	0.22
AP-C	29%	0.52	0.40
AP-D	21%	0.35	0.80
AP-E	28%	0.54	0.19

Data from XPS analysis

Project Impact

ST

\$0.82 (10%)

Oxidation \$1.34 (17.0%)

Carbonization \$1.00 (12.7%)

nizationGraphitization(12.7%)\$1.19 (15.1%)



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Pitch:

PE:





Thank You