Advanced Composite Polymer for the Automotive Market

Long Fiber Reinforced Linear Polyphenylene Sulfide (PPS)

SPE ACCE Conference
September 11 - 13, 2007

Presented by:
Walt Maruszczak, HEV Global Platform Leader
Ticona Engineering Polymers
Long Fiber Reinforced Linear Polyphenylene Sulfide (PPS)

- Introduction
- Properties & Requirements
- Processing
- Applications
Ticona: Polymers and Solutions

- Global Supplier - Production facilities in Americas, Europe and Asia
- Global Presence - Leading market position in most products / regions
- Significant Sales - $915 million in 2006
- Diverse Portfolio - High quality engineering plastics
- Added Value - Solutions provider and technology enabler
Broad Portfolio of Engineering and High Performance Polymers

High Performance Polymers (HPPs) are:
- PPS: Polyphenylenesulfide
- LCP: Liquid Crystal Polymers
- PES: Polyyarylether Sulfones
- PEI: Polyetherimides
- PSU: Polysulfones

Engineering Polymers (ETPs) are:
- POM: Polyacetals
- PC: Polycarbonate
- PA: Polyamide
- PBT: Polybutyleneterephthalate
- PET: Polyethylene
- Ultra High Molecular Weight Polyethylene
- PEEK: Polyetherketone
- PI: Polyimide
- FP: Fluoropolymers
- PAI: Polyamide Imide
- PAR: Polyarylate
- PPA: Polyphthalamide
- PPO: Polyphenylene Oxide
- LFT: Long Fiber Thermoplastics

Source: Market Information, Celanese
Composition of Typical Composites

- **Short-glass-fiber-reinforced compounds**
  - e.g., Fortron® PPS 40% glass fiber (d50 = 200 µm)
    - Typical injection molding material

- **Long-glass-fiber-reinforced compounds**
  - e.g., Fortron® PPS 40% glass fiber (d50 = 400 µm)
    - For high-strength components

- **Carbon fabric (CF) plus polymer matrix**
  - e.g., Cetex® (d50 = component size)
    - Suitable for extremely high stresses

Cetex is a registered trademark of Ten Cate Advanced Composites BV.
What are Composites?

Composites are construction materials composed of:

**Fibers** to carry the load embedded in a **Matrix** to protect the fibers and distribute the load.
Reinforcing Fibers – Main Categories

A wide variety of fibers can be used:

Most common Glass and Carbon

- Glass
  - E-Glass
  - S-Glass
- Metal
- Carbon
  - HT-Fiber
  - HM-Fiber
- Aramid
  - Twaron
  - Kevlar®

Other Fibers used: Ceramic, Boron, Basalt, Silicon-Carbide, Alumina.

Kevlar is a registered trademark of E.I. du Pont de Nemours and Company.
Matrix Materials – Main Categories

Matrix

Inorganic
Concrete

Organic

Thermoplastic

Fortron® PPS
Polyphenylenesulfide

PEI
Polyetherimide

PEEK
Polyetherketone

PSU
Polysulfone

Thermoset

Epoxies

Vinyl-Ester

Phenolics

unsat. Polyesters
Long Fiber Reinforced Linear Polyphenylene Sulfide (PPS)

- Introduction
- Properties & Requirements
- Processing
- Applications
From Monomer to Polymer (The Chemistry)

\[ \text{Cl-} \text{C} \equiv \text{Cl} + \text{Na}_2\text{S} \rightarrow \text{[Polyphenylene Sulfide]} + 2 \text{NaCl} \]

- Dichloro Benzene
- Sodium Sulfide
- Polyphenylene Sulfide
- Sodium Chloride
Linear PPS
Summary – Structure and Properties

- **Semicrystalline**
  - $T_g$ 85°C, $T_M$ 285°C
  - Density 1.35 g/cm$^3$
- **Inherently Flame Retardant:**
  - UL94-V0, LOI > 45
- **Chemical Resistance – Dimensional Stability**
  - Fuels, oils, solvents
  - Water-glycol
- **Easy to Process**
  - Injection molding
  - Extrusion

Polyphenylenesulfide (PPS)
Poly(thio – 1,4 - phenylene)
Linear PPS

Semi-crystalline thermoplastic polymer, perfectly suited for parts that have to withstand the high mechanical and thermal requirements which require…

- A high melting point range between 280 and 290°C
- Inherently flame retardant
- Excellent resistance to chemicals, oils and fluids
- An ideal alternative to conventional materials such as thermosetting polymers and metals
- High hardness and stiffness and superb long-term creep under load properties
- Ease to injection mold, blow mold and machine
- Weight reduction combined with high dimensional stability
Linear PPS Characterization – Crystallinity
Semi-Crystalline Material

Crystalline Phase
- 1.430 g/cm³
- 28 vol. %

Amorphous Phase
- 1.3195 g/cm³
- 72 vol. %

Solid
- 1.35 g/cm³
# Linear PPS – Crystallization Properties

## Phase Transitions

<table>
<thead>
<tr>
<th>Transitions</th>
<th>Temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>( T_g )</td>
</tr>
<tr>
<td>Crystallization on Heating</td>
<td>( T_{ch} )</td>
</tr>
<tr>
<td>Melting Point Range</td>
<td>( T_M )</td>
</tr>
<tr>
<td>Recrystallization on Cooling</td>
<td>( T_{cc} )</td>
</tr>
</tbody>
</table>

- **Glass**: \( T_g \) = 85 – 95
- **Crystallization on Heating**: \( T_{ch} \) = 120 – 140
- **Melting Point Range**: \( T_M \) = 280 – 288
- **Recrystallization on Cooling**: \( T_{cc} \) = 255 – 220

---

*Image: DSC Measurements for Linear PPS showing transitions.*

---

*Image: Graphs showing heating and cooling transitions.*
## Linear PPS – Chemical Properties

<table>
<thead>
<tr>
<th>Flammability</th>
<th>Chemical Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loss On Ignition (LOI): &gt; 45</td>
<td>Excellent:</td>
</tr>
<tr>
<td>UL94: V0 or V5A</td>
<td>- Fuels, synthetic oils, water, solvents, salts, kerosene</td>
</tr>
<tr>
<td>ABD0031: passed</td>
<td>Limited:</td>
</tr>
<tr>
<td>FAR/JAR 25.853: passed</td>
<td>- Hydrochloric acid, strong oxidizing agents</td>
</tr>
</tbody>
</table>

- Strong oxidizing agents
Reasons to Use Linear PPS as Base Polymer for High Performance Composites

- **Excellent Chemical Resistance**
  - Resistant to acids & alkali
  - Resistant to lubricants
  - Resistant to anti-freeze agents

- **Lower Density than Aluminum**
  - Parts are lighter and have improved properties

- **New Process Techniques**
  - Components may be induction-welded, linear vibrationally welded

- **Reduce Time for Installation**

- **Excellent Property Profile**
  - High stiffness and flexibility
  - Improved ductility
Matrix Materials
Thermosets vs. Thermoplastics

**Thermoset**
- Chemical crosslinking reaction for part manufacture
- Irreversible
- Limited shelf time
- Part assembly
  - Conventional
    - Nuts – Bolts – Screws

**Thermoplastic**
- Part manufacture by physical phase transition
  - Solid – Liquid – Solid
- Repeatable
- Unlimited storage @ room temperatures
- Part assembly
  - Conventional
    - Nuts – Bolts – Screws
  - Welding
PPS-GF40-01 (40% Long Glass Fiber)

Composition

- High temperature polyphenylene sulfide matrix
- 40 wt% glass fibers; other wt% available

Standard Availability

- Dust-free pellets ca. 3 x 11 mm
- 55 to 40,000 lbs. shipments (25 to 20,000 kg)
PPS-GF40-01 (40% Long Glass Fiber)

Chemical & Thermal Resistance

- Outstanding thermal resistance
- Good moisture and chemical resistance
- Does not corrode
- Inherent flame resistance
PPS-GF40-01 (40% Long Glass Fiber)

Wear Resistance, Strength & Rigidity
- Excellent wear resistance; passed automotive “gravelometer” test
- Superior impact strength

Regulatory Listings
- Underwriters Labs. V0 rating; file E113269

Cost Savings
- Eliminates metal fabrication, painting and later corrosion costs
PPS-GF40-01 (40% Long Glass Fiber)

- **Thermoset Composites**
- **GMT**
- **Short Fiber Reinforced Thermoplastics**
- **Celstran® Long fiber reinforced thermoplastics**
- **Advanced Composites**
- **Structural Metals**

The diagram illustrates the performance and cost of various composite materials.
PPS-GF40-01 (40% Long Glass Fiber)

Applications

- Electrical connectors & switches
- Pump housings & water fittings
- Parts exposed to high temperature & corrosive environments
# PPS-GF40-01 (40% Long Glass Fiber)

<table>
<thead>
<tr>
<th>Typical Properties</th>
<th>ASTM Method</th>
<th>English System</th>
<th>International System</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Units</td>
<td>°F</td>
</tr>
<tr>
<td>Density</td>
<td>D-792</td>
<td>g/cm³</td>
<td>72°</td>
</tr>
<tr>
<td>Tensile Strength at Break</td>
<td>D-638</td>
<td>psi x 10³</td>
<td>-40°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>72°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>300°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>400°</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>D-638</td>
<td>psi x 10³</td>
<td>-40°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>72°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>300°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>400°</td>
</tr>
<tr>
<td>Elongation at Break</td>
<td>D-638</td>
<td>%</td>
<td>-40°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>72°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>300°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>400°</td>
</tr>
<tr>
<td>Flexural Strength at Break</td>
<td>D-790</td>
<td>psi x 10³</td>
<td>-40°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>72°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>300°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>400°</td>
</tr>
<tr>
<td>Flexural Modulus</td>
<td>D-790</td>
<td>psi x 10³</td>
<td>-40°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>72°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>300°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>400°</td>
</tr>
<tr>
<td>Notched Impact, Izod</td>
<td>D-256</td>
<td>ft-lb/inch</td>
<td>-40°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>72°</td>
</tr>
<tr>
<td>Deflection Temperature @ 264 psi (1.8 MPa)</td>
<td>D-648</td>
<td>°F</td>
<td>n.a.</td>
</tr>
<tr>
<td>Poisson’s Ratio (+/- 0.05)</td>
<td>D-638</td>
<td>Inch/inch</td>
<td>72°</td>
</tr>
<tr>
<td>Shrinkage, flow direction</td>
<td>D-955</td>
<td>Inch/inch</td>
<td>72°</td>
</tr>
<tr>
<td>Shrinkage, cross-flow</td>
<td></td>
<td></td>
<td>72°</td>
</tr>
</tbody>
</table>
PPS-GF40-01 (40% Long Glass Fiber)

- **Stiff and Tough**
- Dynamic mechanical analysis (DMA) measures the flexural modulus (stiffness) of samples molded from Celstran® LFRT materials vs. temperature.
- Long fiber reinforcements provide stiffness over a wide temperature range.
- Increased fiber loadings increase stiffness.
- Stiffness with good impact, tensile and flexural strengths – stiff and tough, *the long fiber advantage*. 
PPS-GF40-01 (40% Long Glass Fiber)

Celstran® Long Fiber PPS-GF Flexural Modulus vs. Temperature via DMA
PPS-GF40-01 (40% Long Glass Fiber)

Flexural Creep at Room Temperature

- Long Fiber-Reinforced PP – 4,000 psi
- Long Fiber-Reinforced PP – 10,000 psi
- Long Fiber-Reinforced PPS – 5,000 psi
- Long Fiber-Reinforced PPS – 10,000 psi
## PPS-GF50-01 (50% Long Glass Fiber)

<table>
<thead>
<tr>
<th>Typical Properties&lt;sup&gt;a&lt;/sup&gt;</th>
<th>ASTM Method</th>
<th>English System</th>
<th>International System</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Units</td>
<td>°F</td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>D-792</td>
<td>g/cm³</td>
<td>72°</td>
</tr>
<tr>
<td><strong>Tensile Strength at Break</strong></td>
<td>D-638</td>
<td>psi x 10³</td>
<td>-40°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>72°</td>
</tr>
<tr>
<td><strong>Tensile Modulus</strong></td>
<td>D-638</td>
<td>psi x 10³</td>
<td>-40°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>72°</td>
</tr>
<tr>
<td><strong>Elongation at Break</strong></td>
<td>D-638</td>
<td>%</td>
<td>-40°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>72°</td>
</tr>
<tr>
<td><strong>Flexural Strength at Break</strong></td>
<td>D-790</td>
<td>psi x 10³</td>
<td>-40°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>72°</td>
</tr>
<tr>
<td><strong>Flexural Modulus</strong></td>
<td>D-790</td>
<td>psi x 10³</td>
<td>-40°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>72°</td>
</tr>
<tr>
<td><strong>Notched Impact, Izod</strong></td>
<td>D-256</td>
<td>ft-lb/inch</td>
<td>-40°</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>72°</td>
</tr>
<tr>
<td><strong>Deflection Temperature @ 264 psi (1.8 MPa)</strong></td>
<td>D-648</td>
<td>°F</td>
<td>n.a.</td>
</tr>
<tr>
<td><strong>Poisson’s Ratio&lt;sup&gt;b&lt;/sup&gt;</strong></td>
<td>D-638&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Inch/inch</td>
<td>72°</td>
</tr>
<tr>
<td><strong>Shrinkage, flow direction</strong></td>
<td>D-955</td>
<td>%</td>
<td>72°</td>
</tr>
<tr>
<td><strong>Shrinkage, cross-flow</strong></td>
<td></td>
<td></td>
<td>72°</td>
</tr>
</tbody>
</table>

<sup>a</sup> Unless otherwise noted, samples were molded from natural colored Celstran® materials and tested per ASTM methods. The data, while believed to be accurate, are for information purposes only. The values shown fall within the normal ranges of properties for these materials. The suitability of these materials for any use is the user's responsibility, who must assure himself/herself the material as subsequently processed meets the requirements of that use. Sales of these products are governed by the terms of the agreement under which they are sold.

<sup>b</sup> Poisson’s ratio (±0.05) calculated from tensile bar elongation vs. width change.
Long Fiber Reinforced Linear Polyphenylene Sulfide (PPS)

- Introduction
- Properties & Requirements
- Processing
- Applications
Manufacturing Supply Chain

- Plastic Pellets
- Film Producer
- Producer of Composites
- Thermo-Forming Process
- Assembly
- Automotive
Station 1: Film Production

Starting product:

Linear PPS pellets
- Temperature stability
- High level of hardness and impact strength
- Excellent resistance to chemicals
- Broad temperature range
- Inherent flame resistance

Film production

Station 1 – Lipp-Terler GmbH in Gaflenz near Linz, Austria. The pellets are converted into films with a thickness of 50 to 200 µm. The film leaves the special plant in rolls of 100 kg in a flawless state, crystal clear and with the required characteristics with regard to strength and dimensional stability.
Station 2: Composite Production

Starting product:
Basic Matrix of Linear PPS / Carbon Fiber Fabric

Laminate production
Station 2 – Ten Cate Advanced Composites BV, Nijverdal, Netherlands. The carbon fiber fabric and linear PPS film are bonded together in a press, under high pressure and high temperature, into high-strength, dimensionally stable and resistant composites in the desired layer thickness.
Station 3: Thermoforming

Starting product:
Composite plates in the required size

Shaping
Station 3 – Fokker Special Products, Hoogeveen, Netherlands. The composite plates are pre-heated and subsequently shaped into the desired form under pressure and high temperature.
Station 4: Assembly

Starting product:
Front wing portion
(Weight of the parts is 20 percent less than aluminum)

Assembly
Station 4 – Airbus.
The completed construction element is mounted at the intended location.
Processing of Pre-pregs

- Production of composite components (pre-pregs)
- Cutting
- Laser projection
- Large thermoplastics press
- High temperature autoclaves
- Ultrasonic and resistance welding
- Controlled 5-axis machining
Fortron® PPS – Success in the Aviation Industry

- Safe, efficient, environmentally friendly
- Modern design
- Licensed for aircraft construction
Why Use Thermoplastics?

**Answer:** Low-cost manufacturing

1. Press-forming of ribs
2. Folding of trailing edges
3. Resistance welding of assemblies
Long Fiber Reinforced Linear Polyphenylene Sulfide (PPS)

- Introduction
- Properties & Requirements
- Processing
- Applications
Technology Penetration in Aircraft Industry
Mid ‘90’s:
Need for Chemically Resistant Material

Linear PPS Chosen for:

- Excellent chemical resistance
- Ease of processing
- Permits complex component geometry
Technology Validation Carbon Fiber/PPS: Fokker 50 Undercarriage Door

- Final step in 10-year program
- Press-formed ribs and spars
- Welded assembly
- Qualified carbon fiber / PPS Material
- Flown on a KLM aircraft for 3.5 Years
Technology Breakthrough: Fixed Wing Leading-Edge Airbus A340-500/600

- Welded structure
- Low weight and low cost monolithic design
- Strong partnering with Airbus UK and Ten Cate
- Technology now state-of-the-art: newest application Airbus A380
Metal Substitution with Linear PPS Composite Resulted in 20–50% Lighter Components

Keel Beam Application

Multi-Technology Concept:
- Panels and Spars: Thermoset Prepreg Lay-Up.
- TP Ribs and Angles
- Alu. and Titanium Brackets
Airbus A340 500/600 Aileron
Thermoplastic Composite Components

- Edge Ribs
- Main Ribs
- Edge Rib
- Leading-Edge Ribs, Angles & Panels
Airbus A340 500/600
Thermoplastic Composite Components

**Part Description:** Panel of the Pylon Forward Second Structure - 22 per Aircraft

**Dimensions:**
- L = 700 – 1400 mm
- W = 200 – 400 mm
- Thickness 2.8 mm
- Double-Curvature Shape

**Material:**
- Linear PPS / Carbon Fiber
- Bronze Mesh Top-layer for EMI Shielding
Cetex is a registered trademark of Ten Cate Advanced Composites BV.
ABS Brake Sensor Housing

**Material:** PPS-GF50-01  
**Company:** Delphi Chassis  
**Benefits:**  
- Impact strength (6.9 ft-lb/in)  
- Compressive strength (33.6 psi x 103)  
- Dimensional stability  
- Chemical resistance  
- Dimensional tolerance for outside diameter (59.71mm): 0.2mm  
- The molded housing has to withstand tight press-fitting (0.38mm) into the bearing housing (shear force 600 pound-force)  
- No leakages at a pressure of 15 psi (before alternating temperature stress test). 3 x alternating temperature test between -40°F and 250°F, in which the mounted unit must withstand a shear force of 100 psi.  
- Impact strength test with gravelometer  
- Road salt resistance (standard requirement of General Motors)
Connector Body and Sleeve

**Material:** PPS-GF40-01  
**Company:** Titeflex Corporation  
**Benefits:**
- Tensile strength (25.5 psi x 103)
- Excellent dimensional stability
- High rigidity and low creep
- Withstands corrosion and attack by petroleum fluids
- Low warpage and shrinkage to provide fittings to specification
- Excellent impact strength
Leading Edge Airbus A380

- 8 assemblies / wing
- Wing length: 26 meters
- 16 segments, 52 meter length
- 400 kg total weight
First Wing Airbus A380
Advanced Composite Polymer for the Automotive Market

Long Fiber Reinforced Linear Polyphenylene Sulfide (PPS)

Thank you.

For more information, please contact:
Walt Maruszczak
HEV Global Platform Leader
(248) 656-4848
W.Maruszczak@ticona.com
Information is current as of August 3, 2007 and is subject to change without notice.
The information contained in this publication should not be construed as a promise or guarantee of specific properties of our products. Any determination of the suitability of a particular material and part design for any use contemplated by the user is the sole responsibility of the user. We strongly recommend that users seek and adhere to the manufacturer’s current instructions for handling each material they use. Any existing intellectual property rights must be observed.

© 2007 Ticona. Except as otherwise noted, trademarks are owned by Ticona or its affiliates. Fortron is a registered trademark of Fortron Industries LLC.