Bridging the gap between Recycled and Virgin Nylon

Taehwan Kim
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Wellman Advanced Materials
01 Carpet Based PCR Nylon Nature

02. Wellman Wet Separation Process and Advantage
03. Advantage of 100% PCR Ecolon
04. Importance of Process Development
05. Ecolon for High Heat
06. Introduction to PRET/Wellman
Why is Ecolon differentiated from others?
Why is Ecolon differentiated from others?

What makes Ecolon superior and reliable?
Rheological, Thermal Behavior of Carpet Fiber

(1) Well ordered and oriented PA chains
- Lower viscosity
- Help nucleation $\Rightarrow$ Faster crystallization

(2) TiO$_2$ acts as heterogeneous nucleating agents to facilitate crystallization.

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Rheological, Thermal behavior of carpet fiber

Carpet fiber has inherently

Good flow !

Rapid cooling !

High Crystallinity

Crystallinity & Orientation vs Draw Ratio

Modulus & Elongation vs Draw Ratio

Carpet fiber has inherently Good flow !

Rapid cooling !

High Crystallinity

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Thermo-oxidation degradation: 20 yrs

Equivalent thermal aging at 150°C, after thermal history for 20 years

\[ k = Ae^{-\frac{E_a}{RT}} \]

\[ \tau_2 = \frac{\tau_1}{\frac{T_2-T_1}{2}} \alpha \]

\[ 2300 \text{ hrs} \atop 150\text{C} \]

\[ 500 \text{ hrs} \atop 150\text{C} \]
Thermo-oxidation degradation: 20 yrs

Equivalent thermal aging at 150°C, after thermal history for 20 years

\[ k = A e^{-\frac{E_a}{RT}} \]

\[ \tau_2 = \frac{\tau_1}{\frac{T_2-T_1}{2\alpha}} \]

PA66 + GF30% Long Term Heat Aging @ 150°C

Time [Hours]

Tensile Strength Retention [%]

0 Hrs 23°C 30°C 35°C

0°C 10°C 23°C 30°C 35°C

Temperature for 20 Years
Reused Auto Parts

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Thermo-oxidation degradation : 20 yrs

Equivalent thermal aging at 150°C, after thermal history for 20 years

\[ k = \frac{\tau_2}{t} \]
\[ \tau_2 = \frac{500}{500} \times 2300 \]

Equivalent Thermal aging of carpet for 20 years

<table>
<thead>
<tr>
<th>500 hours at 150°C</th>
<th>Minimum property loss</th>
</tr>
</thead>
</table>

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Wellman Wet Separation Process and Advantage

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Comparison of each recycling process

**Chemical Separation (DePolymerization)**

**Advantage**
- Purest Nylon
- No degradation in properties
- Perfect for fiber to fiber

**Disadvantage**
- Extreme CAPEX
- Only for PA6
- Limited capacity
- High cost than Virgin

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**Chemical Separation (Formic Acid)**

**Advantage**
- 2nd purity
- Capable to process both PA6 and PA66
- Moderate CAPEX
- Cost effective Nylon fiber

**Disadvantage**
- Color residue
- Other form of recycling for non-Nylon part

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**Dry Separation**

**Advantage**
- Low cost
- High volume
- Calcium fillers to be reclaimed
- Pre-processor for higher value recycling processes

**Disadvantage**
- Low value product
- Sensitive to cost
- High yield losses: 50 ~ 60%
- Can't separate carpet polymers
- High CAPEX for high volume op.

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**Wet & Dry Separation**

**Advantage**
- Relatively high purity
- Excellent $/performance
- Capable to be used for plastic compounding

**Disadvantage**
- Limited sources only available
- High CAPEX
- Quality of incoming carpet is important

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**Shearing or Skiving Separation**

**Advantage**
- Very high purity
- Relatively small CAPEX
- Capable of fiber to fiber
- Localization of processing facility at carpet collection location
- Low energy recycling

**Disadvantage**
- Low yield: 60 ~ 75%
- Backing plate disposition
- Out of 1MM PCR carpet sheared, 600K~750K is landfilled
We convert waste carpet into Car Parts

1. Polymer for carpet yarn
   - High molecular weight
   - Low viscosity

2. Spun fiber yarn
   - Highly ordered and oriented
   - Low viscosity
   - Faster Crystallization

3. Carpet

4. DRY Separation

5. WET Separation

6. PCR PA Feed Stock

7. Ecolon
   Compounded into Ecolon for Auto PA parts

Courtesy by BASF

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# Advantage of Dry/Wet Separation Process

## PA6+GF30

<table>
<thead>
<tr>
<th></th>
<th>Company E Virgin PA6</th>
<th>Company E Virgin PA6 Improved Flow</th>
<th>Recycled PA6 + GF30%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Wellman Ecolon GF3030</td>
<td>Comp. A (PIR)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Comp. A (Virgin + PIR)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Comp. B (Virgin + PIR)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Comp. D (PCR)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Comp. E (PCR)</td>
</tr>
<tr>
<td>Tensile Strength [MPa]</td>
<td>170</td>
<td>155</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>135</td>
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<td>160</td>
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<td>165</td>
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<td></td>
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<td>95</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>140</td>
</tr>
<tr>
<td>Tensile Modulus [MPa]</td>
<td>9,500</td>
<td>9,000</td>
<td>10,000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9,400</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>9,500</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>9,400</td>
</tr>
<tr>
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<td>6,500</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>9,000</td>
</tr>
<tr>
<td>Charpy Notched@23C</td>
<td>10.0</td>
<td>10.0</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10.0</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>6.0</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>6.0</td>
</tr>
</tbody>
</table>

### PA6+GF30% Comparison

DRY – WET separation process ensures the B.I.C mechanical properties

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03 Advantage of 100% PCR Ecolon

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Why does good flow matter?

Stress by thermal expansion

\[ \sigma_{\text{expansion-stress}} = E \cdot \varepsilon = E \cdot \frac{\Delta L}{L} = E \cdot \text{CLTE} \cdot (T_2 - T_1) \]

\[ \Delta L = \text{CLTE} \cdot \Delta T \]

Stress by thermal expansion

<table>
<thead>
<tr>
<th></th>
<th>Tensile strength</th>
<th>Tensile Modulus</th>
<th>CLTE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Dir</td>
<td>180</td>
<td>9,500</td>
<td>2.E-05</td>
</tr>
<tr>
<td>Transverse</td>
<td>90</td>
<td>4,000</td>
<td>1.E-04</td>
</tr>
</tbody>
</table>

\[ \Delta T_{(150 - 23^\circ C)} \]

<table>
<thead>
<tr>
<th></th>
<th>Thermal Stress</th>
<th>% [therm/tensile]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Dir</td>
<td>24.1</td>
<td>13%</td>
</tr>
<tr>
<td>Trans. Dir</td>
<td>50.8</td>
<td>56%</td>
</tr>
</tbody>
</table>

For plastic parts exposed to high thermal cycling environment like engine parts, thermal stress handling according to GF orientation is more critical than plastic material's tensile strength itself.
Why does good flow matter?

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<th>CLTE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA6, PA66 (CLTE Pl)</td>
<td>9,500</td>
<td>2.E-05</td>
<td></td>
</tr>
<tr>
<td>Steel (a1)</td>
<td>50.8</td>
<td>1.E-04</td>
<td></td>
</tr>
<tr>
<td>Aluminum (CLTE Al)</td>
<td>56%</td>
<td>13%</td>
<td></td>
</tr>
</tbody>
</table>

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<tr>
<td>Tensile</td>
<td>9,500</td>
<td>2.00E-05</td>
<td>1.00E-04</td>
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<tr>
<td>Modulus</td>
<td>4,000</td>
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<td></td>
</tr>
<tr>
<td>%</td>
<td>18.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>% (therm/tensile)</td>
<td>13%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>%</td>
<td>25.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For plastic parts exposed to high thermal cycling environment like engine parts, thermal stress handling according to GF orientation is more critical than plastic material's tensile strength itself.
Why does good flow matter?

Good flow worth more than 25MPa Tensile Strength for big plastic E/G parts!
# Engineering Challenge in Cam Cover

<table>
<thead>
<tr>
<th>Rating</th>
<th>Dimensional Control</th>
<th>Flatness Control</th>
<th>Thermal Stress Control</th>
<th>NVH (Related more to Cam cover shape)</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 : Excellent</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>3</td>
<td>3.6</td>
</tr>
<tr>
<td>3 : Fair</td>
<td>4</td>
<td>5</td>
<td>1</td>
<td>4</td>
<td>3.6</td>
</tr>
<tr>
<td>1 : Poor</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>2.4</td>
</tr>
</tbody>
</table>
PCR Ecolon Advantage for big part molding

PA66 + GF 35%

1. Best-In-Class flow performance
2. Shear thinning at mid-high speed
3. Excellent for big parts molding

PA66 + (MF+GF) 40%

1. Best-In-Class flow performance
2. Excellent shear thinning
3. Easy process setup: Max V
PCW Ecolon Advantage for productivity

Theoretic cooling time

\[ \tau_{\text{cooling}} = \frac{\rho \cdot c \cdot a \cdot t^2}{k} \ln \left( \frac{T_{\text{melt}} - T_{\text{mold}}}{T_{\text{eject}} - T_{\text{mold}}} \right) \]

- Material thermal properties dependent
- Part thickness, shape and design dependent
- Process & Tool design dependent

1. Well ordered and oriented molecular structures
2. TiO₂: Heterogeneous nucleating agents

Fast crystallization. ➔ Shorter cycle time

Thermal conductivity

Ecolon GF1960-BK2

Virgin PA66+GF35%

Specific Heat

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Carpet based PCR competitive rating

ECOLON Competitive Standing

- Tensile Strength
- Flowability
- Impact Strength
- Tensile Modulus
- Tensile Elongation

Best Fit
- Tensile Modulus
- Flowability
- Cam cover, E/G cover, F/Shroud, NVH, etc

Fair Fit
- Tensile strength
- Intake Manifold, Tanks & Reservoir, Mounts, Bracket, etc

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Importance of Process Development
Thermal transition point: PA vs PP

**PA66**
- **Ejection (380°F)**
- **Crystallization (410 – 430°F)**
- **Melting (500°F)**
- **Decomposition & Volatilization start (640°F)**

**Melt Range**

**PP**
- **Crystallization (255°F)**
- **Melting (320°F)**
- **Molecular Weight Reduction Begin (500-520°F)**
- **Decomposition & Volatilization start (575°F)**

**Melt Range**
Importance of process window

(1) Thermal History in molecules

500 hrs @150°C

(2) Small PP Contents

Sensitivity to Temperature

Thermal history in PCR molecules and small unseparated PP contents makes Ecolon PCR resin quite sensitive to high temperature. ✶✶✶ Special care when applying high melt temperature
Importance of process window

Shear Rate

Viscosity

Injection Molding: 1,000 ~ 10,000
Extrusion: 100 ~ 1,000
Compression Molding: 10 ~ 100

Pressure

Temperature

Thermal Degradation
Flash (Over packing)
Short Shot (Under packing)

Virgin material

Ecolon 100% PCR

Ecolon PCR 100 ~ 60,000

Shear Thinning

Temperature vs. Pressure Diagram

Viscosity vs. Shear Rate Diagram
Importance of gas handling

With gas present, high packing pressure can cause plastic material intact with compressed gas easily to degrade due to high compression heating. ➔ Poor weld line strength
1) Typical injection molding screw Compression Ratio
   2.5:1 ~ 4:1

2) Considering Propylene’s adiabatic gas compression process and volatilization at 300°C, max pressure allowed: 150 bar

3) Max back pressure range recommended: 40 ~ 50 bar (600 ~ 700 psi max)

Back Pressure Setting for Ecolon
- The lower, the better
- Maximum back pressure not to exceed 40-50 bar
1. **Flow directional Shrinkage**  
   - **Compatible** with most virgin GF grades

2. **Transverse directional Shrinkage**  
   - Slightly lower shrink rate than most virgin GF grades  
     ➔ Packing condition should be reduced to match with virgin dimension
Importance of CAE for dimensional control

Shrinkage [Flow-Dir]
Ecolon GF3030-BK1 vs Production

Shrinkage [Transverse-Dir]
Ecolon GF3030-BK1 vs Production

Mid Shell

<table>
<thead>
<tr>
<th>Material</th>
<th>Production</th>
<th>Ecolon GF3030-BK1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>273°C</td>
<td>279°C</td>
</tr>
<tr>
<td>Flow</td>
<td>0°C</td>
<td>0°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>0 MPa</td>
<td>0 MPa</td>
</tr>
</tbody>
</table>

Lower Shell

<table>
<thead>
<tr>
<th>Material</th>
<th>Production</th>
<th>Ecolon GF3030-BK1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>273°C</td>
<td>279°C</td>
</tr>
<tr>
<td>Flow</td>
<td>0°C</td>
<td>0°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>0 MPa</td>
<td>0 MPa</td>
</tr>
</tbody>
</table>

Upper Shell

<table>
<thead>
<tr>
<th>Material</th>
<th>Production</th>
<th>Ecolon GF3030-BK1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
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</tr>
<tr>
<td>Flow</td>
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<td>0°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>0 MPa</td>
<td>0 MPa</td>
</tr>
</tbody>
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Process control with valve gate

Valve gate nozzle tip freezing
Before valve gate closing

Virgin PA66+GF35
$\tau_{cool} = 148$ sec

Ecolon GF1960-BK
$\tau_{cool} = 118$ sec

How to prevent nozzle tip freezing?

Usual mistake

- Cause: Too cold nozzle tip temp.?
  - Fix: Raise valve gate temp.

  - Degradation & Gas
    - Clogging by Agglomeration
      - Weak weld line
        - Unstable process
          - Longer cycle time

Recommendation

- Cause: Fast PCR crystallization
  - Fix: Minimize SFT(Screw Forward T.)

  - Elimination of Hold Phase
    - Gate closure by valve gate
      - Smooth valve gate OP.
        - Good quality
          - Consistency
            - Shorter cycle time

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Usual mistake
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Recommendation
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Fix: Minimize SFT(Screw Forward T.)

Virgin PA66+GF35 $\tau_{out} = 148$ sec
Ecolon GF1960-BK $\tau_{out} = 118$ sec

Virgin PA66+GF35
Ecolon GF1960-BK

Valve gate nozzle tip freezing
Before valve gate closing

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Process optimization is the key to achieve 95% virgin PA performance.

Wellman CAE & Tech Service supports clients to achieve the best performance as available.
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Ecolon High heat PA66++

“PP” or “PA6” : Not “Contamination”, But “Natural Additives”
- Natural “Alloy” to value existing PA6 and PP contamination as “LTHA Additives”

PCR nature : High productivity
- Improved flow and fast crystallization

One formulation to serve broader temperature range
- BIC temperature range from 170C to 230C

BIC $Price/Performance
- Lowest formulation cost to offer BIC “$Price/Performance” value

Existing thermal history
- Prompt activation for high heat resistance

90% market
High heat PA66
- High volume
- Med Cost

BIC temperature range from 170 to 230C

230 C

170 C

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Ecolon High Heat PA66++

- Tensile Strength Retention: ~ 3000 Hrs
- Charpy Impact Retention: ~ 3000 Hrs
- Tensile Modulus Retention: ~ 3000 Hrs

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Ecolon High Heat PA66++

Ecolon High Heat++ Benchmarking

$/Performance

Sustainability

Neldability

Processibility

LTHA@170C

LTHA@190C

LTHA@210C

Tensile Strength Retention: ~ 3000 Hrs

Charpy Impact Retention: ~ 3000 Hrs

Tensile Modulus Retention: ~ 3000 Hrs

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Introduction to PRET/Wellman
Wellman History

1927 Wool Combing In Massachusetts
1965 Nylon Fiber from PIR Materials
1968 Engineering Resins Division Forms
1990 1st development of PCR Resins from carpet
1993 PRET Chemical R&D Institute Formed
1996 Jiaxing Plant
1998 Jinshan Plant
2003 Listed in the China Stock Exchange
2009 Shanghai Headquarters
2011 Initial Plant
2013 Win SAE & SPE Awards
2014 1st CAM Cover using 100% PCR Material.
2015 Wellman acquisition by PRET
2018 Opened European Office
2019 Win SAE & SPE Awards

PIONEERS IN SUSTAINABILITY

PRET WELLMAN

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40
Resin Choices Now Nearly Limitless

**Products Available**

- PPA
- PPS
- LCP
- PC/ASA
- PA6
- PC/PBT
- PA66
- PC/ABS
- LGF
- PA/ABS
- ABS
- ASA
- PP(TPO)
- PP
- PET

**Compounding**

- Glass Fiber
- BaSO\(_4\)
- Pre-Color
- Carbon Fiber
- EPDM
- LGF
- Mineral
- Talc

**PRET**

*High performance*

**EcoLon®**

*Green future*

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Conservative estimate of 315,000,000 lbs of EcoLon® used by Ford equates to...

- Over 85,000 US homes powered for 1 year
- Over 1.5 BILLION square feet of carpet out of landfills
- Equivalent of 2321 Times the MIS Speedway
- Over 21,000,000 Gallons of oil preserved