Annealing of Stanyl®
Symmetry of chemical structure Stanyl® is the basis for its unique performance

Stanyl® PA 46 → symmetry ensures perfect fit in crystal structure

T melt = 295 °C
T glass = 75 °C
Degree of crystallinity = 70%
Water uptake = 13 %

➢ Higher crystallization rate
➢ Higher melting temperature
➢ Higher degree of crystallinity
➢ Higher water uptake due to C4 diamine and crystallization rate (creating open amorphous phase)

PA 66 → A-symmetry results in a misaligned crystal structure

T melt = 260 °C
T glass = 55 °C
Degree of crystallinity = 50%
Water uptake = 8.5 %
Stiffness versus Temperature comparison

➢ Tg of Stanyl® similar to other aliphatic polyamides
➢ Stiffness above Tg, highest for Stanyl®
Polyamides & Moisture Absorption

- PA's absorb water due to the presence of this amide group

- Water is “bound” by hydrogen bonding to this polar grouping

Moisture absorption

Absorption takes place in the amorphous phase and depends on:

- Polyamide type (based on ratio of CH₂ to amide groups)
- Polyamide content in a compound (versus fillers or other)
- Environmental conditions (temperature, relative humidity)
- Crystallinity level
- The density of the amorphous phase
Polyamides and Moisture Absorption

Fast crystallization of Stanyl® allows short cycle times, it also allows a low dense amorphous phase

Stanyl® high water uptake due to:
- High polarity
- Low dense amorphous phase (caused by the fast crystallization)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>50% RH</th>
<th>75% RH</th>
<th>100% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA6</td>
<td>3.5%</td>
<td>5.5%</td>
<td>11%</td>
</tr>
<tr>
<td>PA66</td>
<td>3%</td>
<td>5%</td>
<td>9%</td>
</tr>
<tr>
<td>PA46</td>
<td>3,7%</td>
<td>7%</td>
<td>13%</td>
</tr>
<tr>
<td>PPA</td>
<td>2.5%</td>
<td>4.2%</td>
<td>6%</td>
</tr>
</tbody>
</table>
Can Annealing help?

Annealing . . .

- Is **heat treatment** of a molded article (time, temp.)
- Accompanied by **property changes**
- Is **irreversible**
- Has been studied and modeled in a wide T, t area
- Often **happens ‘in service’** of a part (at elevated T)
How does Stanyl® change after Annealing?

- Stiffness and yield strength increase, especially above $T_g$
- Annealing reduces variability of parts over time. Parts not annealed, shrink more during operation
- Moisture uptake of the material decreases
- Shrinkage upon annealing
- ..... 

**NOTE:** The speed at which these changes occur varies with annealing time
Details of annealing Stanyl®

1. Recommended annealing conditions
2. Moisture uptake
3. Mechanical properties
4. Dimensional stability
5. Fatigue behavior
6. Annealing Challenges
7. Additional advantages
1. Annealing conditions

Recommended annealing conditions are:
2 hours at 230°C under Nitrogen (preferred) or air

- In general, properties after bake in air and nitrogen are similar, including resulting moisture uptake and bulk mechanical properties
- Annealing results in an increase in the density of the amorphous phase (which is 30% amorphous in highly crystalline Stanyl®)

This condition can vary depending on the needs of the application. Applications may need 4hrs or 16hrs annealing at 260°C, and there are also examples of 2hrs at 230°C
Annealing and moisture uptake of Stanyl® TW341 annealed at $T = 260^\circ C$

The moisture uptake of Stanyl® can be reduced depending on annealing conditions. Even relatively short annealing give significant improvements.

R.Janssen 2002
1. Annealing conditions

The Major cause for the high moisture absorption in Stanyl® is the low dense Amorphous phase.

Annealing does not increase crystallinity much, it mainly densifies the amorphous phase ➔ reducing the moisture uptake.

Annealing 16 hrs at 230 °C (Nitrogen <10ppm Oxygen)

The diagram shows the volume of Crystalline and Amorphous phases before and after annealing for PA46 and PA66. Annealing increases the crystalline phase while densifying the amorphous phase, reducing moisture uptake.
2. Moisture uptake

Reduction of moisture uptake at different annealing conditions at 230ºC

Moisture uptake was done at 30ºC and 100%RH
3. Mechanical properties at 23°C

E-Modulus after annealing at 230°C

Increase in stiffness / modulus upon annealing
3. Mechanical properties at 23°C

Tensile strength at 23°C nearly unchanged after annealing.

- Tensile strength after annealing at 230°C
- Tensile strength at 23°C nearly unchanged after annealing
3. Annealing and properties above $T_g$

Properties above Glass transition temperature of Unfilled Stanyl® increase significantly after annealing.
3. Mechanical properties

Significant decrease in elongation after annealing in Unfilled Stanyl® though still at >5% EaB even after 16hrs 230°C

Elongation at break after annealing in Glass filled compounds is similar
4. Dimensional stability & Shrinkage

**Shrinkage upon annealing of gears**

<table>
<thead>
<tr>
<th>Shrinkage upon annealing</th>
<th>Size 1 change</th>
<th>Thickness change</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.40%</td>
<td>-0.70%</td>
<td></td>
</tr>
</tbody>
</table>

**Material:** Unfilled Stanyl® TW341

**Annealing conditions:** 16 hours at 235°C

Water uptake and dimensional change measured before and after equilibrium 90°C in water

**Significant reduction in dimensional change after annealing**

**Dim. Change upon annealing of gears**

<table>
<thead>
<tr>
<th></th>
<th>Size 1 change</th>
<th>Thickness change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expansion upon water uptake</td>
<td>+2.8%</td>
<td>+4.2%</td>
</tr>
<tr>
<td>before annealing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Expansion upon water uptake</td>
<td>+1.2%</td>
<td>+2.1%</td>
</tr>
<tr>
<td>after annealing</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5. Fatigue of unfilled Stanyl®
(Tests at 100°C, 4Hz)

Annealed Stanyl® has improved performance on low cycle fatigue, and similar performance for high cycle fatigue.
5. Fatigue of 30% glass filled Stanyl® (tested at 140°C, 8Hz)

For 30% GF Stanyl®:
Annealed Stanyl® show a slightly better fatigue behaving to the non-annealed. This is especially evident for the higher stress levels / low cycle fatigue. A similar fatigue behavior is found at higher cycle fatigue.

Annealed Stanyl® has less temperature rise during the 8Hz cycling.
6. Annealing Challenges

Elongation / Impact decrease

Shrinkage during the annealing process (change of dimensions) ➔ Needs to be taken in account during Design!

Annealing in Air vs. Nitrogen (Inert environment):
• Short annealing (2 hours 230°C) can be done either in Air or in Nitrogen
• For long annealing & wear intensive applications it is advised to use nitrogen.

Be aware of discoloration especially when annealing in air
7. Additional advantages of Annealing

Additional advantages of annealing Stanyl®:

- Annealing improves significantly the **salt spray resistance**, also known as the Denso CaCl2 test.

- Internal experiments of annealing unfilled Stanyl® at 32hrs @ 230C (under Nitrogen) found the **wear resistance** better or at least equal to untreated Stanyl®. These properties can be better in annealing under nitrogen compared to air.
Annealing in applications

Applications using annealing like Gears

Major reasons:
• Improve dimensional stability
• Reduce influence of moisture
• Improve mechanical performance
Summary

Pros of annealing:
✓ Reduce moisture uptake
✓ Increase Modulus and Strength especially at temps > Tg
✓ Increased dimensional stability (Temp. and moisture)
✓ Better or equal fatigue behavior
✓ Improved CaCl2 resistance
✓ Better or equal wear resistance (Nitrogen annealing)

Point of attention:
▪ Reduced Elongation and impact behavior (Mainly for unfilled)
▪ Dimensional change upon annealing (Shrinkage)

Balance properties well-suited for the application