Understanding
Amorphous and Crystalline Molding

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Molding Workshop
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Amorphous vs Crystalline

Similarities and Differences

Crystalline vs amorphous polymers

Similarities

- Broad range of commercial formulation
  - Amorphous: ABS, PC, PS, PMMA, etc
  - Crystalline: PA, PE, PP, PET, PBT, etc..
- Multiple Processing Techniques
  - Injection, blow molding, extrusion
- Environmental sensitivities
  - Upper and lower use temperatures.
  - Weathering, mechanical and electrical properties

Crystalline vs amorphous polymers

Differences

- Molecular Interaction of the molecular chain
  - Amorphous: low order in solid phase
  - Crystalline: High order in solid phase
- Response to temperature changes
  - Amorphous: Tg only
  - Crystalline: Tg and Tm
- Solvent resistance
  - Crystalline polymers are generally better

Plastic Processing

Why are different processing conditions needed to mold crystalline and amorphous polymers?

Plastic Processing

- The density (volume) of amorphous and crystalline polymers change at a different rate under the influence of changing temperatures and pressures.

  Mold Fill and Pack Parameters

- Resin viscosity at processing temperatures and pressures

  Mold Fill

- The effect of resin modulus vs. temperature are different

  Ejectability

Thermoplastic Polymer Types

- Amorphous Structure

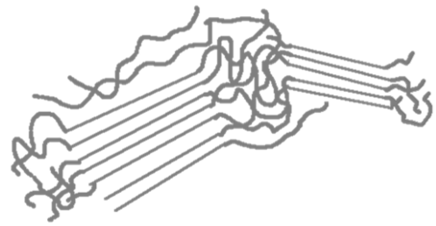
A polymer characterized by random entanglement of the individual polymer chains

Amorphous Thermoplastics

- Polycarbonate (PC)
- Polyphenylene Oxide (PPO)
- Acrylonitrile Butadiene Styrene (ABS)
- Polysulfone (PSU)
- Polyetherimide (PEI)
- Polystyrene (PS)
- Polymethyl Methacrylate (PMMA)
- Polyvinyl Chloride (PVC)

Thermoplastic Polymer Types

- Semi-
  Crystalline



A polymer structure characterized by the combination of amorphous & crystalline arrangements

Semi-Crystalline Thermoplastics

- Polyester (PET or PBT)
- Polyamide (PA), nylon
- Polyoxymethylene (POM), acetal
- Polyphenylene Sulfide (PPS)
- Polyethylene (PE)
- Polypropylene (PP)
- Polytetrafluoroethylene (PTFE), Teflon

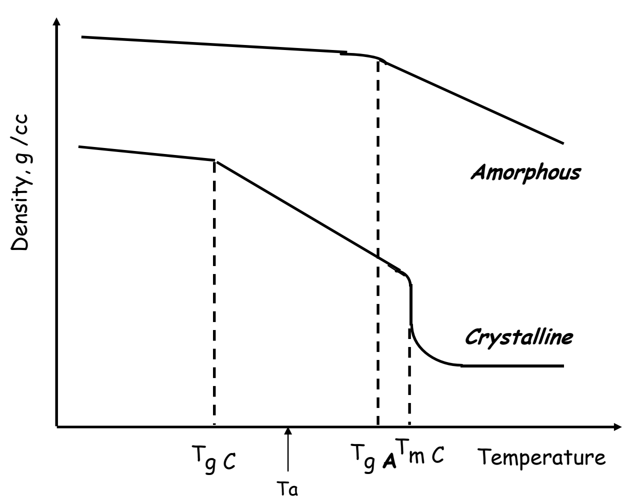
Density vs. Specific Volume

- Density = Mass/Volume (g/cc, oz/cu.ft….)
- Inverse Relationship

  Density = 1 / Specific Volume

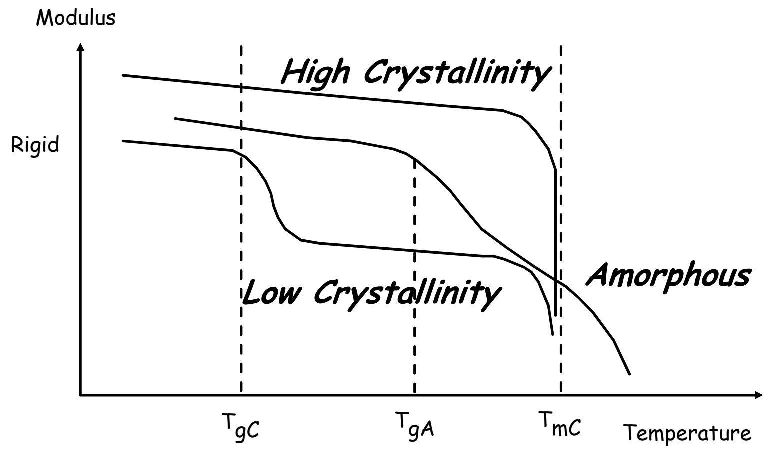
  Specific Volume = 1 / Density
- Density important to part weight
- Specific volume important to molding conditions

Density vs. Temperature at Atmospheric Pressure



Modulus vs. Temperature

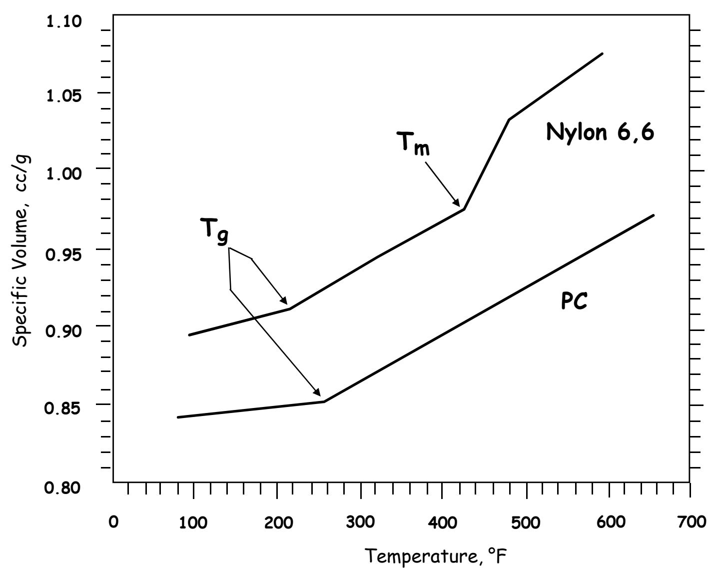
Crystalline and Amorphous Polymers



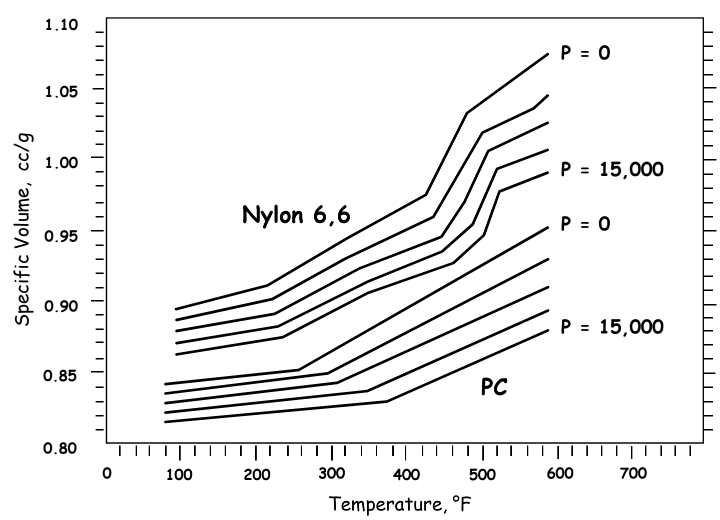
PVT Diagrams

- Plot of specific volume vs. temperature at different pressures
- Easy to find
  - T_g – Glass transition temperature
  - T_m – Melting point

PVT Data on Nylon 6,6 and PC



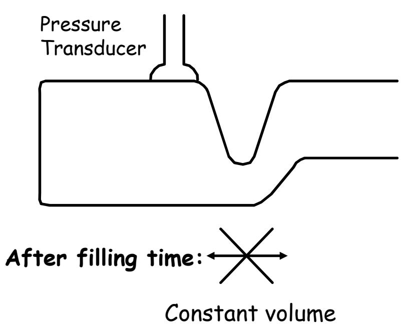
PVT Data on Nylon 6,6 and PC

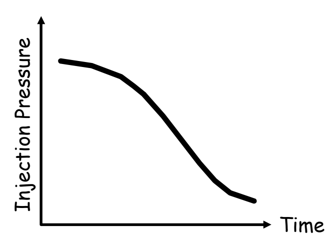


PVT Diagrams

- Plot of specific volume vs. temperature at different pressures
- Easy to find
  - T_g – Glass transition temperature
  - T_m – Melting point
- Easy to see how
  - Volume increases with increasing temperature
  - Volume decreases with increasing pressure
  - Crystalline polymers undergo a rapid volume change at T_m which is missing in amorphous polymers
  - Volume changes between RT and processing temperatures are:
    10 – 15% amorphous polymers
    20 – 25% crystalline polymers

Amorphous PVT Diagram
Effects on Molding Rules

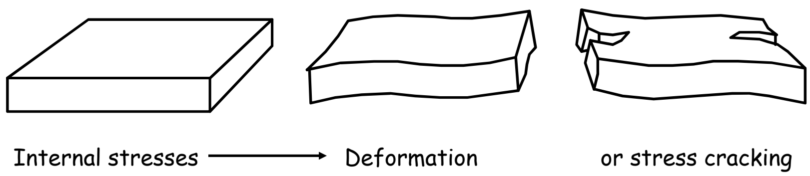




Means:

- No movement through gate
- Injection pressure led by cavity pressure (via transducer)

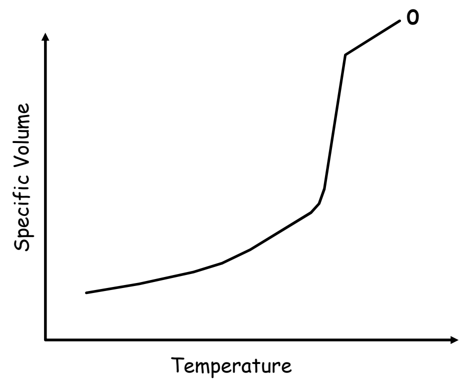
Amorphous Polymer
Post-Molding Deformation



Molding Amorphous Polymers

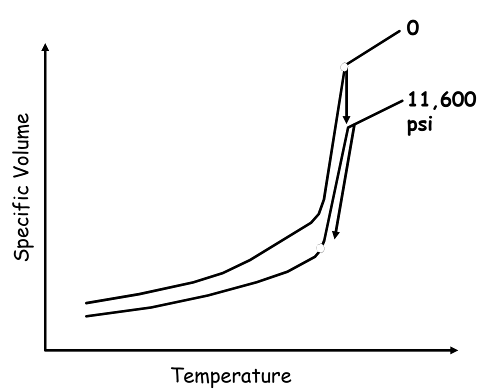
- Overpacking is a major concern
  - Parts stick in mold
  - Parts crack during ejection
  - Residual internal stress
- Optimum molding conditions
  - Inject using high pressure
  - Pack pressure should decrease with time – constant volume
  - High mold temperatures reduce internal stress

Crystalline PVT Diagram
Melting



- During melting process (solid to liquid) volume x 16%

Crystalline PVT Diagram
Injection – Crystallization



Crystallization

- Shrinkage by ~14%; Voids created have to be filled with liquid polymer
- Crystallization under constant pressure

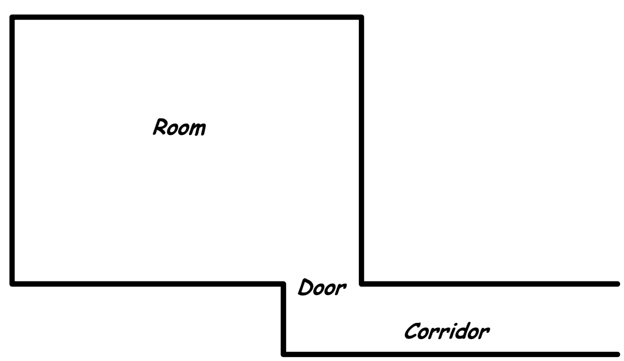
Important Implications

During the solidification process after dynamic filling

- The hold pressure is decreased with time for amorphous but is maintained constant for crystalline polymers.
- The flow through the gate is stopped for amorphous but it continues until the end of the crystallization for crystalline polymers.

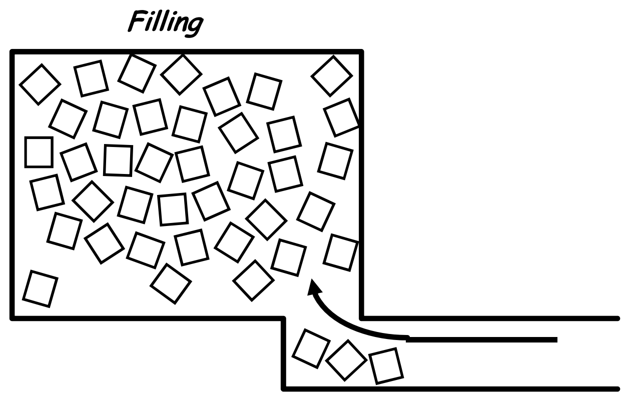
Crystallization PVT Diagram

Allegory



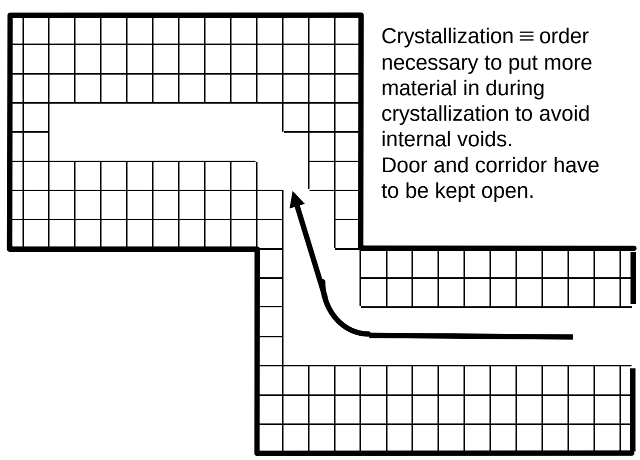
Crystallization PVT Diagram

Allegory



Crystallization PVT Diagram

Allegory



Crystallization ≡ order necessary to put more material in during crystallization to avoid internal voids.
Door and corridor have to be kept open.

Crystalline Polymer

Post-Molding Deformation

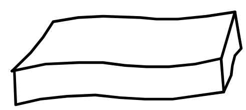
Cold mold → Bad crystallization

↓

Post shrinkage recrystallization with time and temperature

↓

Deformation



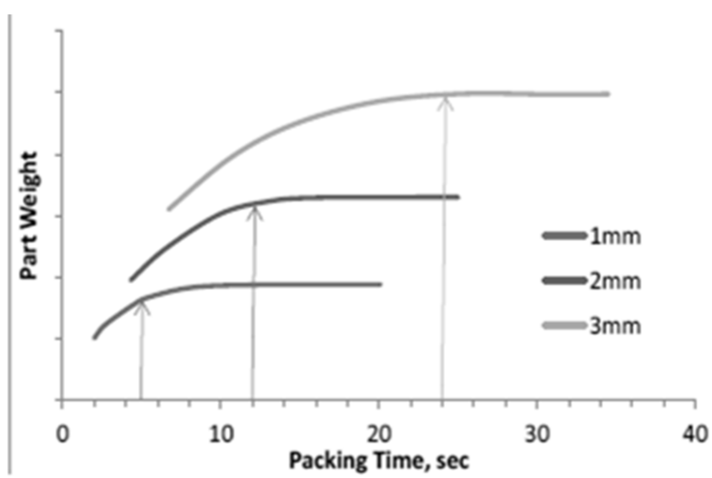
Controlling Crystallization During Molding

- Mold Temperature
  - The higher the mold temperature, the higher the crystallinity
- Pressure
  - Increases rate of crystallinity
- Stress During Crystallization
  - Can produce orientation

Molding Crystalline Polymers

- Underpacking is a major concern
  - Sinks and voids
  - Low part weight
- Incomplete crystallization is a major concern
  - Warpage
  - Consistent shrinkage
- Optimum molding conditons
  - Inject using moderate pressure
  - Pack with same pressure
  - High mold temperatures – aid crystallization

Part Weight vs Packing Time



Conclusions

- Properties depend on structure
  - Amorphous
  - Crystalline
- Processing depends on structure
  - Amorphous – small volume change with temperature: use constant volume rule
  - Crystalline – large volume change with temperature: use constant pressure rule

Thank You !