Understanding Amorphous and Crystalline Molding

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

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
- Polyoxyethylene (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
  \[ \text{Density} = \frac{1}{\text{Specific Volume}} \]
  \[ \text{Specific Volume} = \frac{1}{\text{Density}} \]
- Density important to part weight
- Specific volume important to molding conditions

Density vs. Temperature at Atmospheric Pressure

![Graph showing density vs. temperature for amorphous and crystalline materials at different temperatures.](image)
Modulus vs. Temperature
Crystalline and Amorphous Polymers

![Diagram showing modulus vs. temperature for different crystallinities.]

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

Specific Volume, cc/g

Temperature, °F

Nylon 6,6

Tm

Tg

PC

P = 0

P = 15,000

P = 0

P = 15,000

Nylon 6,6

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

- No movement through gate
- Injection pressure led by cavity pressure (via transducer)
Amorphous Polymer
Post-Molding Deformation

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**

- 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

Room

Door

Corridor
Crystallization PVT Diagram

Allegory

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

Filling
Crystalline Polymer
Post-Molding 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 conditions
  - 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!