ENGINEERING THERMOPLASTIC ADDITIVES FOR BROAD PROPERTY ENHANCEMENT OF POLYURETHANES

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AGENDA

Overview of PPE or Poly(2,6-dimethyl-1,4-phenylene ether)
  • Micronized PPE and reactive PPE oligomer (PPE-M)

Use of (additive) micronized PPE and properties of:
  • Castings
  • Foam

Use of reactive PPE oligomer (PPE-M) and properties of:
  • Castings
POLY(2,6-DIMETHYL-1,4-PHENYLENE ETHER)

PPE

Poly(2,6-dimethyl-1,4-phenylene ether)

PPE FEATURES

- High temperature resistance ($T_g = 215^\circ C$)
- Hydrolytically stable
- Low moisture uptake
- Excellent electrical properties
  (over a wide temperature and frequency range)
- Inherent flame retardancy (non-halogen FR)
- Dimensionally stable
POLYPHENYLENE ETHER TRADITIONAL MARKET APPLICATIONS AND BENEFITS IN COMPOUNDED PLASTICS

PPE in blends and alloys of Engineering Thermoplastics

• With polystyrene
  • On average, increases in $T_g$ and HDT
  • Often easier to flame retard the total system

• With polyamide
  • Typically decreases moisture absorption
  • May increases many properties at elevated temperatures
  • Easier to integrate non-halogen FR chemistry
  • Generally improves toughness

• With polyolefins
  • Offers Non-halogen FR benefits
  • May increases heat resistance
Micronized PPE
- <10 micron particles size
- Thermoplastic and thermoset resins
- Used as an additive
- Do not melt or dissolve

PPE Macromonomer (referred to as PPE-M)
- Reactive PPE oligomer
  - Covalent bonds to TP and TS

For use in polyurethanes we studied:
Micronized PPE – additive
PPE-M (PPE Macromonomer) - reactant
MICRONIZED PPE IN CASTINGS
MICRONIZED PPE AS AN ADDITIVE

**PPE**

Engineering thermoplastic
Large particles – broad MWD
Melt compounded into blends and alloys

**Micronized PPE**

Additive for thermoplastics and thermosets
Very small particles – narrow MWD
Dispersed in resin without melting or dissolving
PHASE BEHAVIOR & MORPHOLOGY

PHASES
CONTINUOUS PHASE: Matrix - Controls main properties
DISPERSED PHASE: Specialized properties

DOMAIN SIZE
Attraction between phases increases with decreasing domain size

ATTRACTION
Urethane hydrogen bonds to PPE

Continuous phase - polyurethane
Dispersed phase - PPE

Interphase region between TPU and substrate: hydrogen bonding plays a key role
PREPARATION OF CASTINGS WITH MICRONIZED PPE

Micronized PPE – mean particle size ~ 6 microns

Micronized PPE slurried with:
- Polyester polyol
- Butane diol
- Catalyst

MDI – 4,4’-Methylenebis(phenyl isocyanate)

15wt% Micronized PPE in polyol
Stable suspension 30+ days

- Slurry was a “Drop in” for an existing PU formulation
- Formulations were not optimized
- 0, 10, 20, 30, and 40 wt% Micronized PPE were trialed
EFFECT OF MOISTURE

Water hydrogen bonds to hydrophilic moieties such as urethane & ether groups

Negative effects of absorbed moisture
- Alters thermo-mechanical properties
- Plasticize the resin
- Lower Tg
- Reduces interfacial adhesion
- Hygroscopic stress through differential swelling
- Induces corrosion
- Increases dielectric properties

Absorbed H₂O can cause integrity and reliability issues
Water absorption decreases with increasing micronized PPE.

Weight increase after 24 Hour immersion in water at 80°C.
VICAT SOFTENING TEMPERATURE

Vicat softening temperature - the temperature at which a flat-ended needle penetrates the specimen to the depth of 1 mm under a specific load (10N) following ASTM D1525 or ISO 306.

Vicat increases with increasing micronized PPE.
TENSILE MODULUS

As other performance is improved, modulus remains high.
TENSILE STRENGTH

Significant increase in strength as micronized PPE increases
Elongation % a break and yield remain high
DIELECTRIC PROPERTIES

Measured using parallel plate technique

Dielectric Constant, Relative Permittivity, $D_k$

![Bar chart showing the dielectric constant at 1 GHz for different PPE levels.](image)

Loss Tangent, Dissipation factor, $D_f$

![Bar chart showing the loss tangent at 1 GHz for different PPE levels.](image)

Lower dielectric properties with increasing micronized PPE levels
Shore D and A Hardness exhibit a slight increase with PPE
Slurried micronized PPE in polyols may offer a broad enhancement of properties of polyurethane castings

- Properties increase with increasing levels of PPE
- Lower moisture absorption
- Strength increases while maintaining high elongations
- Thermal properties increase
  - Higher VICAT
  - Higher modulus at elevated temperatures
- Lower density
- Lower dielectric properties
MICRONIZED PPE IN HIGH RESILIENT POLYURETHANE FOAM
PREPARATION OF PU FOAMS WITH MICRONIZED PPE

Micronized PPE – mean particle size ~ 6 microns

Micronized PPE slurried in EO-Capped oxypropylated polyether diol, chain extenders, surfactants, catalyst, etc.

15wt% Micronized PPE in polyol
Stable suspension
30+ days

2,4’ rich diphenylmethane diisocyanate

• “Drop in” to existing High Resilient polyurethane foams formulation
• Formulations are not optimized
• 0, 5.8, 10.9, 15.5, and 19.7 wt% Micronized PPE
• Faster Cream times and Gel times experienced with increasing micronized PPE
COMPRESSIVE FORCE DEFLECTION (CFD)

a.k.a. Indentation Load Deflection
The ability of material to resist a crushing load

- **CFD @ 25%** - the amount of force to deflect foam 25%
- **CFD @ 50%** - the amount of force to deflect foam 50%
- **CFD @ 65%** - the amount of force to deflect foam 65%

Sample Size:
2”x2”x1”
5.1cm x 5.1cm x 2.5 cm

Increased load bearing capability (higher CFD) with micronized PPE
WET AGED COMPRESSION FORCE DEFLECTION

Wet aged CFD @ 50% deflection

ASTM D 3574-08 Wet Aged CFD Change @ 50% Deflection (Test C after Wet Heat Aging)

Improved wet-aged CFD with small additions of micronized PPE
Improved resistance to compression set with micronized PPE
RESILIENCE

ASTM D 3574-08: Resilience via Ball Rebound (Test H)

High resilience over the range of PPE studied
TEAR STRENGTH

ASTM D 3574-08: Test F

Increasing tear strength with increasing levels of PPE
TENSILE STRENGTH AT BREAK

ASTM D 3574-08: Tensile Strength at Break (Test E)

Maintain good tensile strength over range of PPE studied
ASTM D 4986-98 - Horizontal Burning Characteristics of Cellular Polymeric Materials

Test part: 6” x 2” x 1” (15.24cm x 5.1cm x 2.54cm)
Profile of visible flame: 38 mm high (1.5 inches)
Remove the flame after 60 seconds
Measure burn rate

Burn rate decreases with addition of micronized PPE
SUMMARY - MICRONIZED PPE IN PU FOAM

Slurried micronized PPE as “drop-in” existing High Resilient polyol foams formulations may offer broad enhancement of PU products

• Properties increase with increasing levels of PPE
• Increased load bearing capability
• Improved wet aged load bearing capability
• Improved resistance to compression set
• Increased tear strength
• Good resilience and strength
• Reduced burning rate
PPE MACROMONOMER (PPE-M) IN POLYURETHANES
Micronized PPE - ADDITIVE
High molecular weight
Limited solubility in polyols

REACTIVE PPE Macromonomer
PPE-M
Very low molecular weight
Solubility in polyols

- **PPE features**
  - High temperature resistance
  - Hydrolytically stable
  - Low moisture uptake
  - Dimensionally stable
  - Excellent electrical properties

- **PPE-M FEATURES:** PPE features plus
  - Low MW, solubility in polyols
  - Increased functionality

PPE macromonomer was used to prepare PU castings
PPE-M dissolved in EO-Capped oxypropylated polyether diol, BD

4,4'-MDI

4,4'-Diphenylmethane diisocyanate

PPE-M reacts with isocyanates

FORMULATIONS:
• 0, 7.7, 15.3, and 23.0 wt% PPE-M
• Formulations were not optimized
• ~ 23% hard segment
Water absorption decreases with increasing PPE-M.
Higher elongations at elevated temperatures for PU systems reacted with PPE-M.
Increased thermo-oxidative resistance with increasing PPE-M
TEAR STRENGTH

Tear Strength improves with increasing PPE-M
SUMMARY - PPE MACROMONOMER IN PU CASTINGS

Dissolved PPE-M reacted with isocyanate in polyols may offer broad enhancement of polyurethane properties in ‘drop-in’ formulations

- Lower moisture absorption
- Higher elongations at elevated temperatures
- Increased thermo-oxidative resistance
- Increased tear strength
Additive and reactive PPE materials may offer valuable enhancements to various polyurethane systems.

Candidate performance improvements to well-known challenges in polyurethane systems while maintaining other critical parameters (i.e. modulus and elongation) over a wide range of formulations may include:

- Increased hydrophobicity
- Increased strength
- Increased thermal properties
- Decrease in burn rate
- Preliminary results suggest overall increased durability
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