Overview of Maleic-Anhydride-Grafted Polyolefin Coupling Agents

A guide to understanding their uses, benefits, functions, selection, and developments

Louis W. Martin, Addcomp North America Inc.
The primary functions of coupling agents

- Connect olefinic polymers to dissimilar materials
- Connect (not compatibilize) olefinic polymers with dissimilar polymers
Fundamentals of polyolefin coupling agents

Connect polymers to dissimilar materials

- Inorganic materials:
  - Glass fiber
  - Carbon fiber
  - Metals

- Organic materials
  - Wood
  - Flax
  - Cotton
  - Hemp
Connect different polymers

• Join olefinic resin film with other film
• Not intended to compatibilize incompatible polymers within the same bulk
  − Polyolefins and polyamides
  − HDPE and PP
  − Others
Fundamentals of polyolefin coupling agents

Major uses for coupling agents

- Couple reinforcing fibers to polymer matrix
  - Glass, carbon, hemp, wood, flax, cotton
- Connect polymer with substrate
  - Coatings or linings for metal containers
  - Overmolded polymers on metal structures
- Tie layers between polymer films
- Adhesives
- Emulsions
Benefits of coupling agent use

- Reduction in fiber pullout
  - Increase impact strength
  - Increase tensile strength

- Reduction of water absorption
  - Prevent degradation in natural fibers
  - Prevent corrosion in metals

- Create tie layer between dissimilar materials
  - Provide strength for multilayer polymer films
Major classes of coupling agents

- Parts produced using melt compounding only
  - Polyolefins grafted with maleic anhydride
- Parts requiring reactive extrusion during production
  - Silanes
How coupling agents work

Polar group (B) grafted onto olefin group (A)

- A is polypropylene
- B is maleic anhydride
How coupling agents work

Two-part molecule

• Polar group
  – Creates chemical bond with substrate
    – Sizing on reinforcing glass fiber
    – Metal
    – Wood or other natural material
    – Polar resin

• Olefin section
  – Forms hair-like structure that becomes part of resin bulk
    – Mechanical entanglement with resin chains
How coupling agents work

Schematic of coupling

MAH  MAH  MAH  MAH

Substrate
Influences on selection of coupling agent

- Balance of polyolefin chain lengths
  - Longer chain length provides strength
    - Greater mechanical entanglement with resin
  - Shorter chain length provides mobility
    - Greater number of polar groups reach substrate
    - Increases melt flow

- Percentage of olefin molecules with grafted polar groups

- Amount of free MAH
Various combinations of molecular weight and percentage of grafted polar group are appropriate for different applications.
Inventory of reaction products

- Ungrafted PO
  - Unbroken chains, shortened chains
- PO-MAH
  - 1:1 grafted molecules
- MAH-PO-MAH
  - 2:1 grafted molecules
- Free MAH
Process influences on performance

- Typical level of free MAH in standard coupling agents
  - 0.2% to 0.25% (2000 to 2500 ppm)
  - This can be 50% of total MAH in coupling agent
- Process improvements currently in production can lower this to 0.005% or 0.6%
Process influences on performance

Higher concentrations of free MAH
  • Outgassing from materials and finished parts
    – Unacceptable odor
    – Fogging of proximate surfaces
    – Potential impact on color
    – Potential reduction of UV resistance
Optimum constituent levels

- 1:1 grafted MAH-PO molecules
  - No ungrafted PO molecules
  - No multi-grafted PO molecules
- Minimal free MAH
  - 20-50 ppm (0.002 - 0.005%) free MAH possible
Influence on tensile strength in fiber-reinforced polymers

• [Need to insert graph from 2009 short-fiber study here]
Process influences on performance

Influence on application suitability

Diagram showing the relationship between average Mw and % grafted MAH, with positive influence on Coatings and Tie Layers, negative influence on Coupling Agents, and no influence on Other Applications.
Next generation PO-MAH coupling agents

• Higher Mw PO @ constant grafted MAH %
  – Stronger mechanical entanglement with polyolefin
    – Higher tensile strength materials

• Lower % free maleic anhydride
  – Lower emissions of volatile organic compounds (VOCs)
    – Less fogging from applications in use
  – Less pollution of possible sites for bonding with substrate
    – Higher tensile strength
Higher Mw polyolefins

% Grafted MAH

Avg. Mw PO

PRIEX® 26090

20098

26098

20093

Development trends
Development trends

Lower % free maleic anhydride
Development trends

Lower VOCs and fogging

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Development trends

Higher tensile strength

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Discussion and Questions