Ken-React® KPR®
New Titanium-Mixed Metal Catalyst for Multi-Polymer Compatibilization and Post Consumer Recycle (PCR)
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New Titanium-Mixed Metal Catalyst for Multi-Polymer Compatibilization and Post Consumer Recycle (PCR)

Salvatore J. Monte, President
Abstract: Conventional polymer compatibilization and recycled plastic art centers around equipment that sorts, cleans, demagnetizes, washes, granulates, bales or melt processes recycle – or polymer compatibilizers based on maleic anhydride chemistry – or bipolar thermoplastics that have affinity for two select recycle polymer streams. … A new titanium-mixed metal catalyst methodology will be shown to create in the compounding melt not alloys, but new complex co-polymers having much higher mechanical properties, which portends the achievement of high loadings of PCR in virgin polymers to meet sustainability mandates in consumer plastics.
Kenrich Petrochemicals, Inc. – makers of titanates and zirconates – introduces to GPS 2015 a new “In Situ Macromolecule Titanium-Mixed Metal Catalyst” in pellet (CAPS®) and powder (CAPOW®) form that regenerates PCR in the melt to virgin-like properties.

Works as a compatibilizer on addition polymers (HDPE, PP, etc.) and condensation polymers (Polyesters, Nylon, etc.), where MAH doesn’t.
New Titanium-Mixed Metal Catalyst for Multi-Polymer Compatibilization and Post Consumer Recycle (PCR)

This is The Titanium Catalyst Portion

Metalloocene-like  ZN-like

This is The Mixed Metal Catalyst Portion
New Titanium-Mixed Metal Catalyst for Multi-Polymer Compatibilization and Post Consumer Recycle (PCR)

Ken-React®
CAPOW® L® 12/HV

Ken-React®
CAPS® L® 12/LV

Metalocene Catalyst
Polymerization – Virgin

Organometallic Catalyst
Repolymerization - Recycle

Titanocene

Ken-React® LICA 12 Titanate
New Titanium-Mixed Metal Catalyst for Multi-Polymer Compatibilization and Post Consumer Recycle (PCR)

Ken-React®
CAPOW® L® 12/HV

Ken-React®
CAPS® L® 12/LV

This is The Titanium Catalyst Portion

Organometallic Catalyst Repolymerization

Ken-React® LICA 12 Titanate

100% Active Liquid Titanium Catalyst Portion
New Titanium-Mixed Metal Catalyst for Multi-Polymer Compatibilization and Post Consumer Recycle (PCR)

Ken-React®
CAPOW® L® 12/HV
79% Active Catalyst

Ken-React®
CAPS® L® 12/LV
39% Active Catalyst

Phase Diagram of Al₂SiO₅

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German Karl Ziegler, for his discovery of first titanium-based catalysts, and Italian Giulio Natta, for using them to prepare stereo regular polymers from propylene, were awarded the Nobel Prize in Chemistry in 1963.

Ziegler–Natta catalysts have been used in the commercial manufacture of various polyolefins since 1956.

Ziegler discovered that a combination of TiCl$_4$ and Al(C$_2$H$_5$)$_2$Cl gave comparable activities for the production of polyethylene.

Natta used crystalline $\alpha$-TiCl$_3$ in combination with Al(C$_2$H$_5$)$_3$ to produce the first isotactic polypropylene.

Monte uses Titanate in combination with Al$_2$SiO$_3$ mixed metal catalyst in Powder & Pellet forms for In Situ Macromolecular Repolymerization and Copolymerization in the melt – i.e. Compatibilization.
New Titanium-Mixed Metal Catalyst for Multi-Polymer Compatibilization and Post Consumer Recycle (PCR)

Ken-React® CAPS® KPR® 12/LV

Ken-React® = Titanate brand.
CAPS® = Coupling Agent PelletS
KPR® = Kenrich Polymer Recycle

- 20% Active LICA® 12 Titanate (CAS # 110438-25-0)
- 19% Aluminosilicate (CAS #1332-09-8)
- 11% SiO2 (CAS #112926-00-8)
- 50% LLDPE(V) (CAS#25087-34-7)
Why is only 9 percent of plastic recycled from the municipal solid waste stream?

And why Walmart cannot reach 25% PCR content sustainability goals in blow molded HDPE soap bottles on their store shelves?

Because polymers do not add up – as most polymers are incompatible. >5% PCR in HDPE = More Waste. Why?

POLYMERS 101

Because PolyMers [(Poly = Many) + (Mers = Units)] are made using different Catalysts and processes during PolyMerization. For Example:

PETE is an ester – a CONDENSATION Polymer.

HDPE is an olefin – an ADDITION Polymer.

PETE and HDPE are incompatible.
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**HDPE is an olefin – an ADDITION Polymer.**

**PETE and HDPE are incompatible.**

**LDPE is an olefin – an ADDITION Polymer.**

**PP is an olefin – an ADDITION Polymer.**

**LDPE is compatible with HDPE – Both are incompatible with PP.**
This whitepaper outlines the roles of compatibilizer additives in plastics, the opportunities and challenges associated with their use, and provides a guide on commercially-available compatibilizers.
Compatibilizers fall into three general classes:

1. Bipolar Copolymers
2. Maleated Copolymers
3. In Situ Macromolecule Catalysts
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1. **Bipolar Copolymers:**

Polymers with dissimilar polarities can be made compatible by using bipolar copolymer compatibilizers that bridge the polarities. For example, Santoprene® TPV (see SPI data table) is a block copolymer of polar aromatic styrene monomer and non-polar aliphatic butadiene monomer.

This approach works well with known segregated streams — such as a non-polar polyolefin with a polar polymer such as Nylon (PA) — but is of limited value in post-consumer recycle streams containing a multiplicity of polymers that vary from batch to batch and within a given batch.
Compatibilizers fall into three classes:
1. Bipolar Copolymers
2. Maleated Copolymers
3. In Situ Macromolecule Catalysts

2. Maleated Copolymers:

Bond formation between maleic anhydride-g-polypropylene (PPg) and polyamide 6 (PA) by in situ block copolymer formation can be called Fusion Bonding. Maleated polymers can be prepared directly by polymerization or by modification during compounding via the reactive extrusion process. Their anhydride groups can react with amine, epoxy and alcohol groups.

The limitation of this class of additives is their specificity for the polymers to be compatibilized. In addition, maleic anhydride depolymerizes condensation polymers such as PET and PC, thus obviating their use in mixed streams such as PCR containing olefins, PET and assorted other polymers.
Compatibilizers fall into three classes:
1. Bipolar Copolymers
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3. In Situ Macromolecule Catalysts

3. In Situ Macromolecule Catalysts:

Since monomers become polymers (macromolecules) in the presence of catalysts — and all polymers are catalyzed — in situ macromolecular copolymerization of two or more dissimilar polymers in the melt via in situ catalysis using thermally stable organometallics/mixed metal catalysts holds the possibility of allowing the use of high levels of PCR in consumer goods.

Let’s show you why:
Compatibilization of LDPE/PP – 80/20 Regrind Using 1% Titanate Catalyst

Reactor
Titanocene Polymerization - Ethylene Monomer

Extruder
Titanate Repolymerization - Ethylene Polymers

NO TITANATE

W. TITANATE
REPOLYMERIZATION of LDPE/PP – 50/50 Regrind
Using 1% Titanate Catalyst Pellet – 2 parts per thousand

LDPE/PP – 50/50
Regrind = Melt Processing = Chain Scissoring = Melt Index

Melt Index

Titanium is living catalyst thru repeat heat cycles

Heat Cycles

Control
LICA 12

Organometallic Catalyst
Ken-React® LICA 12 Titanate
Recycled PET/Polycarbonate – 80/20 Blend Using 1% Titanate Catalyst

Extruded@ 180°C using 0.3% CAPOW L12/H Titanate Catalyst vs. 280°C without the Additive
HDPE Regrind Using 1% Zirconate Catalyst

1% Ken-React® CAPS® NZ® 12/L:

- Reduced Part Wt. from 1745g to 1500g to equivalent drop weight impact strength.
- Reduced Cycle Time 156 to 116 seconds.
Regrind: HDPE / Nylon Film Using 0.2% Titanate Catalyst

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Ethylene Propylene Rubber Catalyst Effect of 0.2% Titanate

1000g EPR Rubber Sheeted off 2-roll Mill – Super Plasticizer
Effect of 0.2% Zirconate on Compatibility of the E-Glass/ Ethylene TetraFluoroEthylene Interface

**E-Glass Fiber/ETF E (Ethylene TetraFluoroEthylene) Interface**

ETF E (think Teflon®) is extremely non-polar

No Zirconate:
Silane Sized E-Glass Fiber/ETF E

With Zirconate:
Silane Sized E-Glass Fiber/ETF E
Effect of Titanate on Compatibility of the Interface of:
Oil Soaked/Salt Water/Beach Sand and Portland Cement

No Titanate

With Titanate
Compatibilization of Addition & Condensation Polymers

Incompatibility PET & PE

Incompatibility PE & PP

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Compatibilization of Addition & Condensation Polymers

Incompatibility PP & PET & PE

Let’s look at the effect of 1.5% Ken-React® CAPS® KPR® 12/LV on Brabender melt compounded PP/PET/PE Recycle Plastics at 9% lower temperatures.
Compatibilization of Addition & Condensation Polymers – PP/PET/PE

Brabender Plasticorder Blends of Three Recycled Polymers: PP/PET/PE

Incompatible PP/PET/PE—

No Additive

Compatibilized PP/PET/PE—

1.5% Ken-React® CAPS® KPR® 12/LV Pellets

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Incompatibility PP & PET & PE

Let’s look at the effect of 1.0% Ken-React® CAPS® KPR® 12/LV on Single Screw melt compounded PP/PET/PE Recycle Plastics at 10% lower temperatures.

Materials obtained from post-industrial waste streams:
1. LLDPE from a fractional melt film,
2. PP Copolymer from mixed 20-35 MFI injection molded caps,
3. PET from thermoformed clamshell food packaging.

Material ground into 1/4 – 1/2” flakes and melt compounded into pellets for IM using a 30:1 L/D - 20 mm single screw extruder.
In your opinion, does the 10% drop in temperature from 320°F to 290°F indicate clearly the importance of reactive compounding shear? The surface of the extrudate exiting the die became significantly smoother. Upon further analysis with SEM and Izod, it was clear that the increasing the shear dramatically improved the dispersion and physical properties of the compound.

What is your next step? We’re working on obtaining two industrial applications that generate over 10 million pounds of polyester and olefins waste to landfill every year. The goal behind this work is develop a compound or compounds which repurposes these materials into other applications which would keep them from entering landfill. Initial feedback has been very positive.
Compatibilization of Addition & Condensation Polymers

LOWERING THE PROCESS TEMPERATURE FOR REACTIVE COMPOUNDING SHEAR IS CRITICAL

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SEM
Izod Impact

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CONCLUSION

3. In Situ Macromolecule Catalysts are a significant strategic approach to reach PCR sustainability goals.