Ken-React® KPR®

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

www.4kenrich.com

customerservice@4kenrich.com

technicalsupport@4kenrich.com

KENRICH®
PETROCHEMICALS, INC.

Agenda: Friday, 30 October 11:05-11:20 am

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

Salvatore J. Monte, President

KENRICH PETROCHEMICALS, INC.

October 28-30, 2015 | Chicago, Illinois USA

GPS2015

THE GLOBAL PLASTICS SUMMIT

On the Brink of New Capacity

Presented by IHS spi

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

Salvatore J. Monte, President

KENRICH PETROCHEMICALS, INC.

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.

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

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.

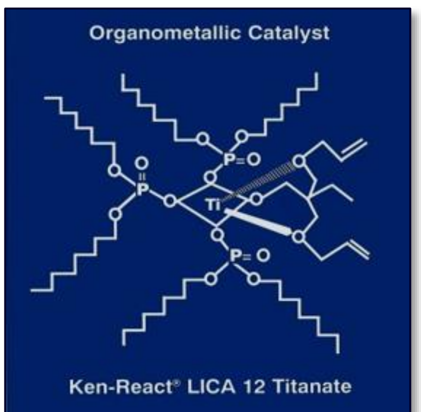
Works as a compatibilizer on addition polymers (HDPE, PP, etc.) and condensation polymers (Polyesters, Nylon, etc.), where MAH doesn't.

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

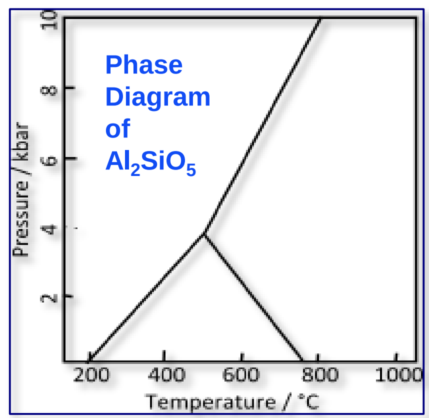
Ken-React® CAPOW® L® 12/HV

Ken-React® CAPS® L® 12/LV

This is The Titanium Catalyst Portion



+



This is The Mixed Metal Catalyst Portion

Metallocene-like

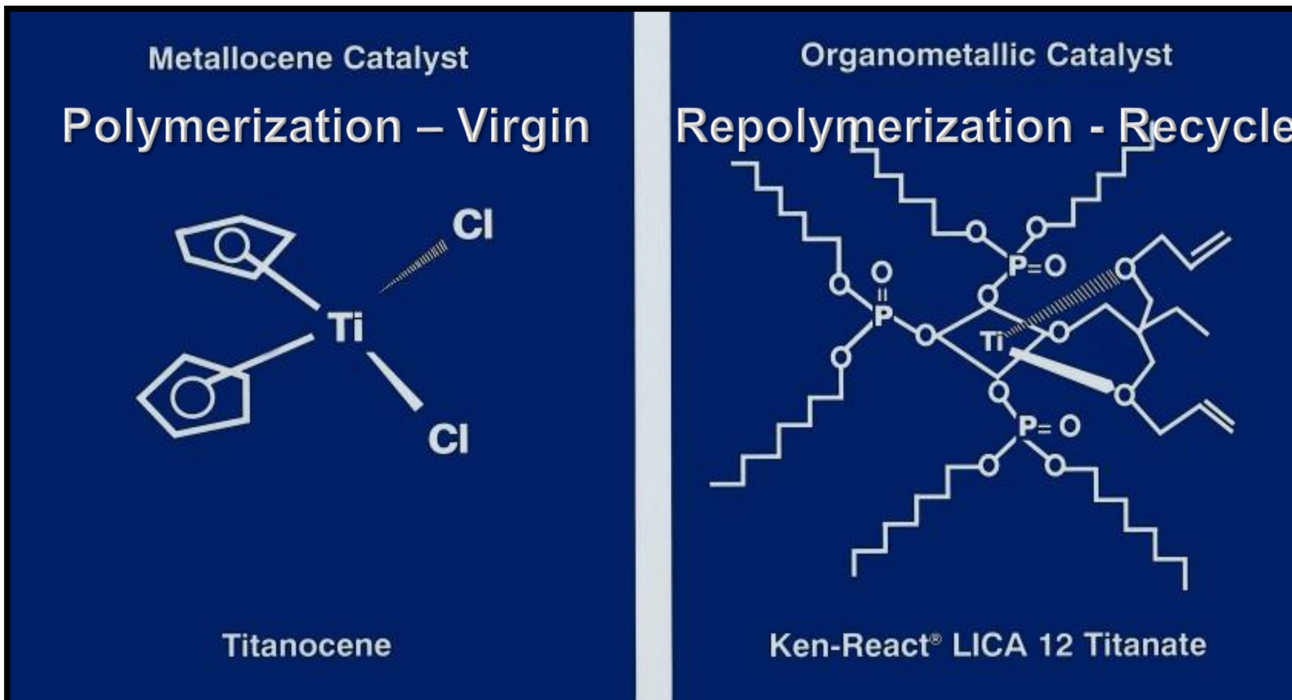
ZN-like

October 28-30, 2015 | Chicago, Illinois USA
GPS2015
THE GLOBAL PLASTICS SUMMIT
On the Brink of New Capacity

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



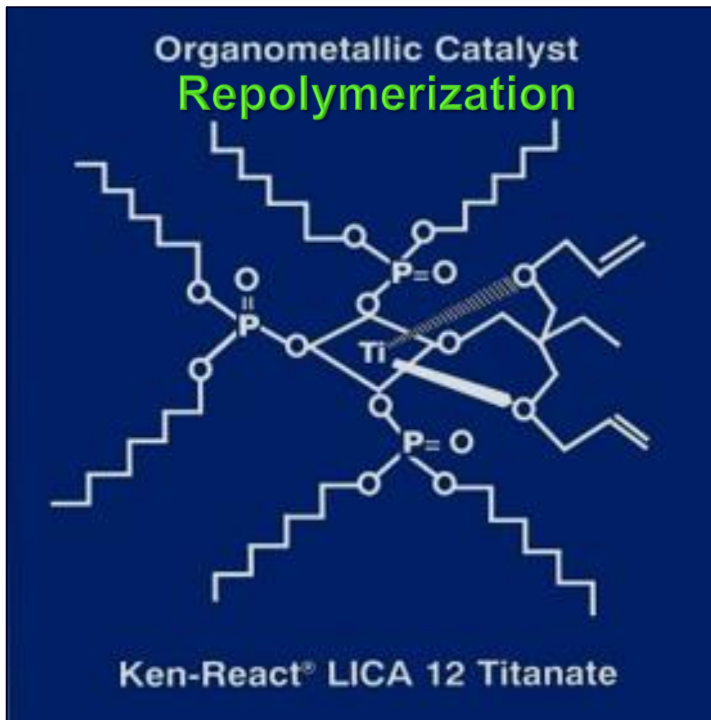
October 28-30, 2015 | Chicago, Illinois USA
GPS2015 THE GLOBAL PLASTICS SUMMIT
On the Brink of New Capacity

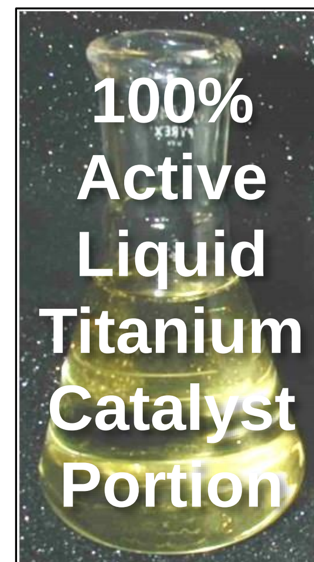
New Titanium-Mixed Metal Catalyst for Multi-Polymer Compatibilization and Post Consumer Recycle (PCR)

Ken-React® CAPOW® L® 12/HV

Ken-React® CAPS® L® 12/LV

This is The Titanium Catalyst Portion





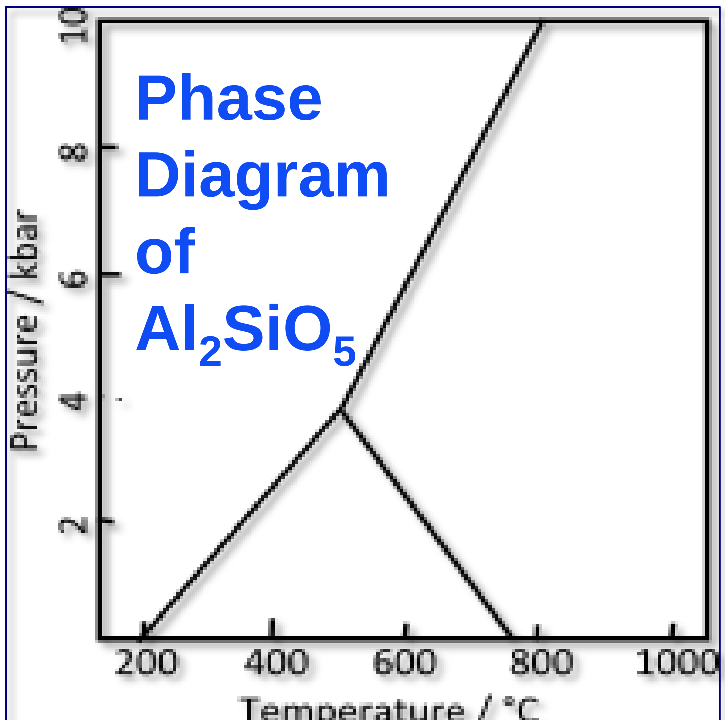
October 28-30, 2015 | Chicago, Illinois USA
GPS2015 THE GLOBAL PLASTICS SUMMIT
On the Brink of New Capacity

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

This is The Mixed Metal Catalyst Portion

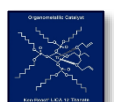


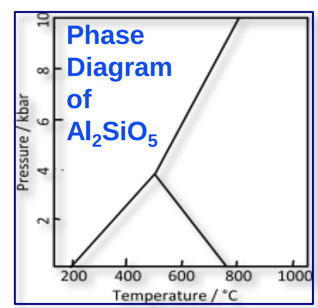
German Karl Ziegler, for his discovery of first titanium-based catalysts, and Italian Giulio Natta, for using them to prepare stereo regular polymers from propylene, were awarded the Nobel Prize in Chemistry in 1963.

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

Ziegler discovered that a combination of $TiCl_4$ and $Al(C_2H_5)_2Cl$ gave comparable activities for the production of polyethylene.

Natta used crystalline α-$TiCl_3$ in combination with $Al(C_2H_5)_3$ to produce the first isotactic polypropylene.

Monte uses Titanate  in combination with Al_2SIO_3 mixed metal catalyst in Powder & Pellet forms for In Situ Macromolecular Repolymerization and Copolymerization in the melt – i.e. Compatibilization.

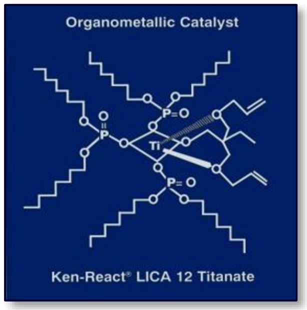


October 28-30, 2015 | Chicago, Illinois USA

GPS2015 THE GLOBAL PLASTICS SUMMIT

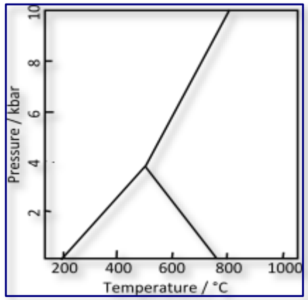
On the Brink of New Capacity

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



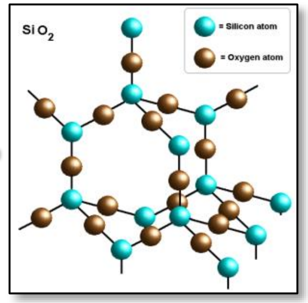
20%

+



19%

+



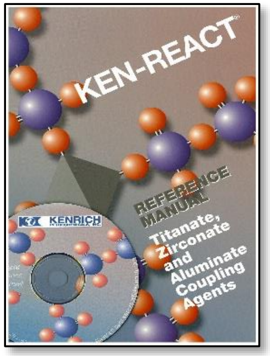
11%

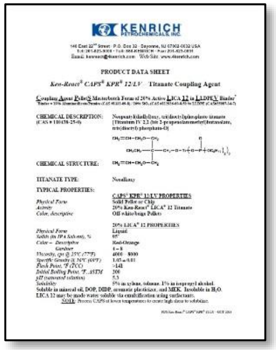
+

50%

=

Ken-React®
CAPS®
KPR® 12/LV





Ken-React® CAPS® KPR® 12/LV

Ken-React® = Titanate brand.

CAPS® = **C**oupling **A**gent **P**ellet**S**

KPR® = **K**enrich **P**olymer **R**ecycle

- 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

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.

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.

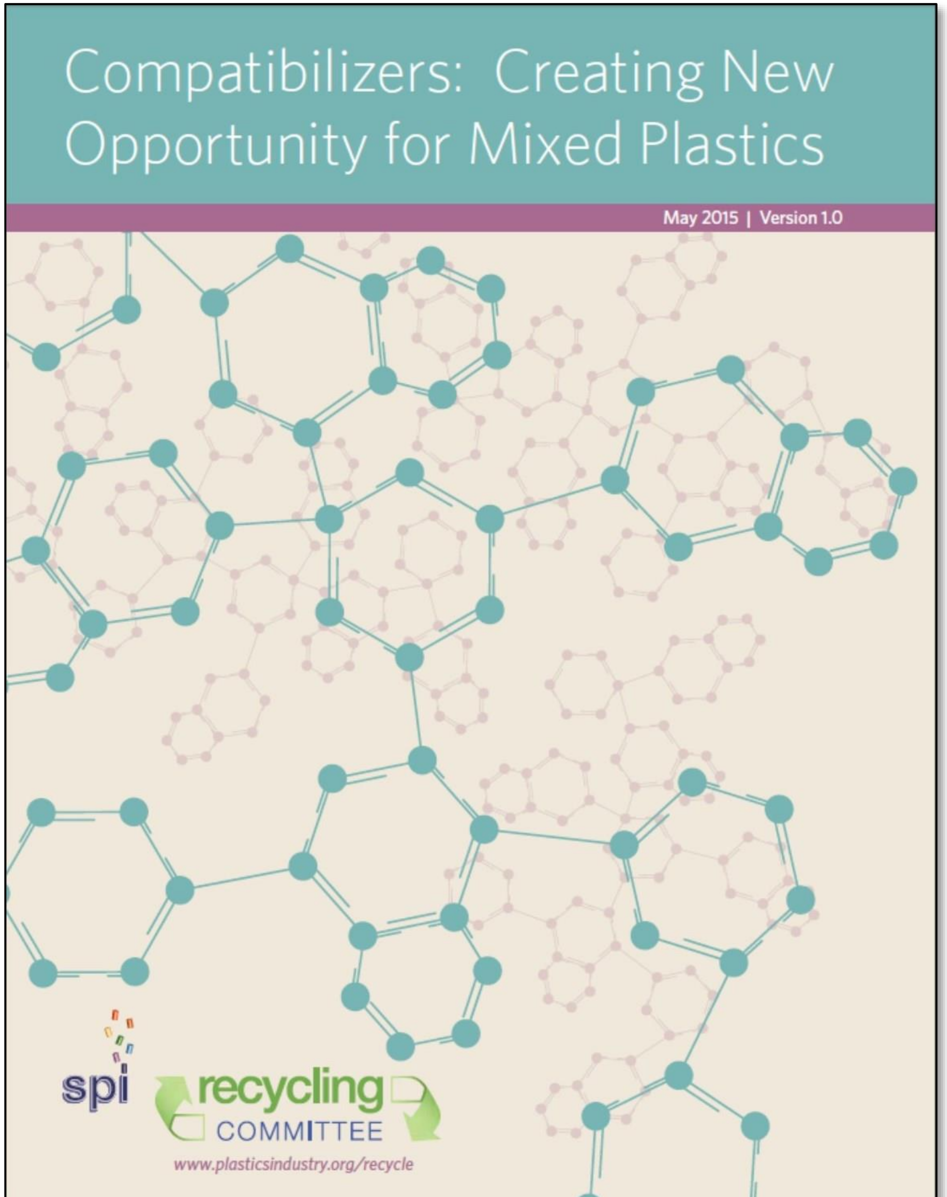
PETE and HDPE are incompatible.


LDPE is an olefin – an ADDITION Polymer.


PP is an olefin – an ADDITION Polymer.

LDPE is compatible with HDPE – Both are incompatible with PP.

Recycled Plastics to Reach Sustainability Goals Need Compatibilizers


Compatibilizers: Creating New Opportunity for Mixed Plastics

May 2015 | Version 1.0

spi recycling COMMITTEE

www.plasticsindustry.org/recycle

spi recycling COMMITTEE

www.plasticsindustry.org/recycle

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.

[download] http://www.plasticsindustry.org/Recycling/Content.cfm?ItemNumber=12140

Recycled Plastics to Reach Sustainability Goals Need Compatibilizers

Compatibilizers: Creating New Opportunity for Mixed Plastics

spi recy CON www.plastics

SPI: The Plastics Industry Trade Association

APPENDIX A: COMPATIBILIZER GUIDE

Material Supplier Company Name	Compatibilizer Brand Name	Target resins for blending (ie, PP and PE)	Website with product information
PolyGroup Inc.	Propoider® MPP2020 20 Micron Powder	PP, Copolymers, Others	www.polygroupinc.com
PolyGroup Inc.	Propoider® MPP2040 40 Micron Powder	PP, Copolymers, Others	www.polygroupinc.com
PolyGroup Inc.	Novacom® HFS2100 P 150 Micron Powder	PE, Copolymers, Others	www.polygroupinc.com
PolyGroup Inc.	Novacom® HFS2100 Pellet	PE, Copolymers, Others	www.polygroupinc.com
Kenrich Petrochemicals, Inc.	Ken-React® CAPS® L® 12/L (20% active pellet)	HDPE/PP Blends, Post-Consumer Recycle, Comm./Eng. Thermoplastics	www.4kenrich.com
Kenrich Petrochemicals, Inc.	Ken-React® CAPOW® L® 12/H (65% active powder)	HDPE/PP Blends, Post-Consumer Recycle, Comm./Eng. Thermoplastics	www.4kenrich.com
Kenrich Petrochemicals, Inc.	Ken-React® LICA® 12 (100% active liquid)	HDPE/PP Blends, Post-Consumer Recycle, Comm./Eng. Thermoplastics	www.4kenrich.com
Kenrich Petrochemicals, Inc.	Ken-React® CAPS® KPR® 12/LV (20% active pellet)	HDPE/PP Blends, Post-Consumer Recycle, Comm./Eng. Thermoplastics	www.4kenrich.com
Kenrich Petrochemicals, Inc.	Ken-React® CAPOW® KPR® 12/H (65% active powder)	HDPE/PP Blends, Post-Consumer Recycle, Comm./Eng. Thermoplastics	www.4kenrich.com
Kenrich Petrochemicals, Inc.	Ken-React® Titanates & Zirconates	HDPE/PP Blends, PCR, Blends of Two or More Polymers	www.4kenrich.com
Exxon	Vistamaxx® propylene-based elastomer	polyisobutylene (PIB), styrene isoprene styrene (SIS), polyvinyl chloride (PVC)	http://www.exxonmobilchemical.com/Chem-English/brands/vistamaxx-propylene-based-elastomers.aspx?ln=productsservices
Exxon	Santoprene® TPV		http://www.exxonmobilchemical.com/Chem-English/brands/santoprene-thermoplastic-vulcanizate-tpv.aspx?ln=productsservices
Exxon	Vistalon® EPDM Rubber		http://www.exxonmobilchemical.com/Chem-English/brands/vistalon-ethylene-propylene-diene-epdm-rubber.aspx?ln=productsservices
Exxon	Exact plastomers		
Exxon	Exxelor polymer resins	"most commonly used polar polymers and polyolefins"	www.exxonmobilchemical.com/Chem-English/brands/exxelor-polymer-resins.aspx?ln=productsservices

4

SPI: The Plastics Industry Trade Association

Material Supplier Company Name	Compatibilizer Brand Name	Target resins for blending (ie, PP and PE)	Website with product information
Dupont	Fusabond® M603	(Recycle Stream) PE/ PA, PE/ EVOH, PA/ EVOH/ PE	www2.dupont.com/Fusabond/en_US/assets/downloads/fusabond_m603.pdf www2.dupont.com/Polymer_Modifiers/en_US/functions/polymer-compatibilizer.html
Dupont	Fusabond® E226	(Recycle Stream) PE/PA, Surlyn EVOH or PA	www2.dupont.com/Fusabond/en_US/assets/downloads/fusabond_e226.pdf
Dupont	Bynel® 41E710	(Recycle Stream) PE/EVOH or PA/EVOH/PE	www2.dupont.com/Bynel/en_US/assets/downloads/bynel_41e710.pdf
Dupont	Surlyn® 1650	(Recycle Stream) Surlyn EVOH or PA	www2.dupont.com/Surlyn/en_US/assets/downloads/surlyn_1650.pdf
Dupont	Fusabond® P353	(Recycle Stream) PP/PA or PP/EVOH/PP	www2.dupont.com/Fusabond/en_US/assets/downloads/fusabond_p353.pdf
Dupont	Elvaloy® PTW	(Recycle Stream) Polysters/ PE	www2.dupont.com/Elvaloy/en_US/assets/downloads/elvaloy_ptw.pdf
Dupont	Elvaloy® 3427AC	(Recycle Stream) Polysters/ PE	www2.dupont.com/Elvaloy/en_US/assets/downloads/elvaloy_ac_3427.pdf
Arkema	Lotader® AX8840	PET, PBT, PPS, Metal, Paper, Glass	www.arkema.com/export/shared/.content/media/downloads/products-documentations/csca/pol/lotader/tds-lotader-ax8840.pdf
Arkema	Lotader® 3210	Polyamide/polyolefin	www.arkema.com/export/shared/.content/media/downloads/products-documentations/csca/pol/lotader/tds-lotader-3210.pdf
Arkema	Lotader® 3410	Polyamide/polyolefin	www.arkema.com/export/shared/.content/media/downloads/products-documentations/csca/pol/lotader/tds-lotader-3410.pdf
Arkema	Lotader® 3430	Polyamide/polyolefin	www.arkema.com/export/shared/.content/media/downloads/products-documentations/csca/pol/lotader/tds-lotader-3430.pdf
Arkema	Lotader® 4700	Polyamide/polyolefin	www.arkema.com/export/shared/.content/media/downloads/products-documentations/csca/pol/lotader/tds-lotader-4700.pdf

5

[download] http://www.plasticsindustry.org/Recycling/Content.cfm?ItemNumber=12140

spi recycling COMMITTEE

www.plasticsindustry.org/recycle

Compatibilizers fall into three general classes:

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

Recycled Plastics to Reach Sustainability Goals Need Compatibilizers

Compatibilizers fall into three classes:

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

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.*

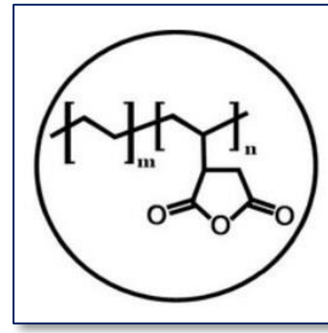
This approach works well with known segregated streams — such as a non-polar polyolefin with a polar polymer such as Nylon (PA) — ***but is of limited value in post-consumer recycle streams containing a multiplicity of polymers that vary from batch to batch and within a given batch.***

Recycled Plastics to Reach Sustainability Goals Need Compatibilizers

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.

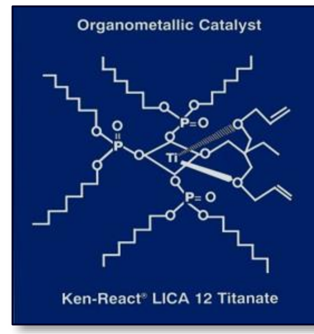
Recycled Plastics to Reach Sustainability Goals Need Compatibilizers

spi recycling COMMITTEE
www.plasticsindustry.org/recycle

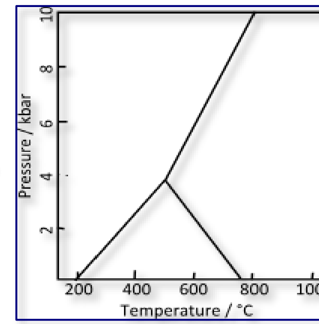
Compatibilizers fall into three classes:

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

3. In Situ Macromolecule Catalysts:



+



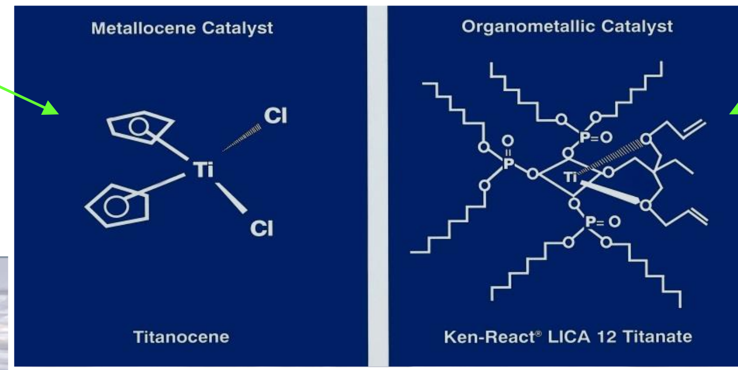
Since monomers become polymers (macromolecules) in the presence of catalysts — and all polymers are catalyzed — in situ macromolecular copolymerization of two or more dissimilar polymers in the melt via in situ catalysis using thermally stable organometallics/mixed metal catalysts holds the possibility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

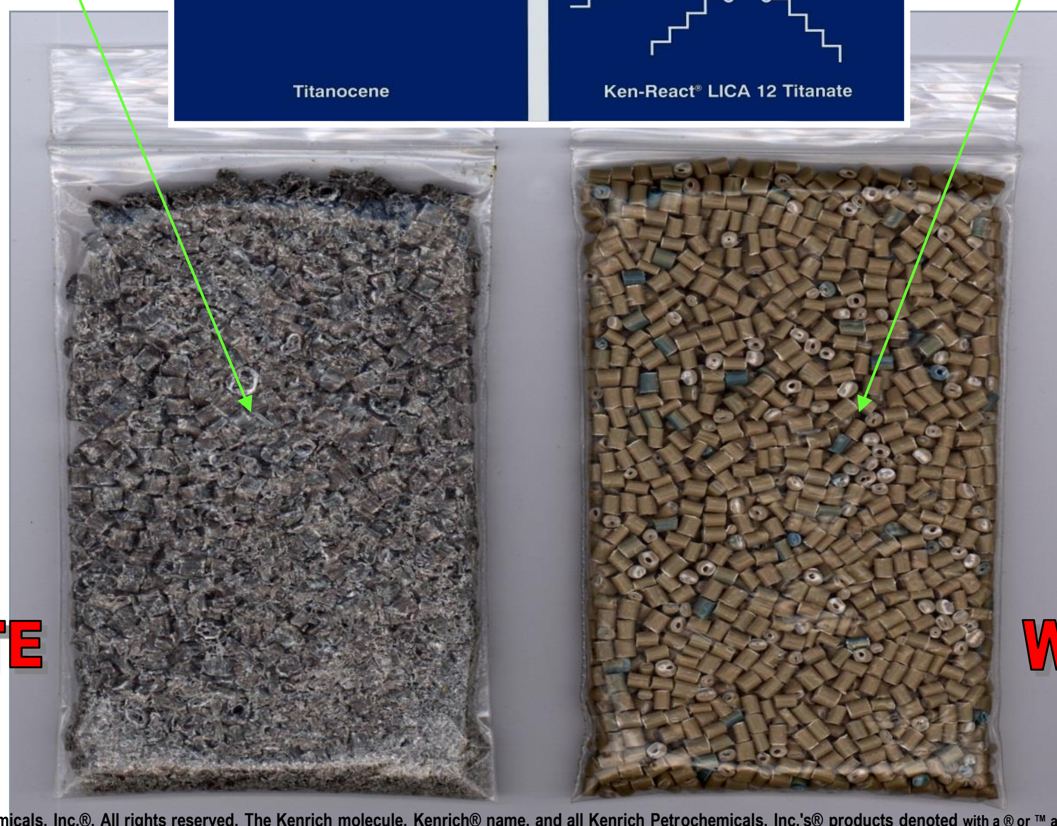
Let's show you why:

Compatibilization of LDPE/PP – 80/20 Regrind Using 1% Titanate Catalyst

Reactor
Titanocene Polymerization -
Ethylene Monomer

Extruder
Titanate Repolymerization -
Ethylene Polymers

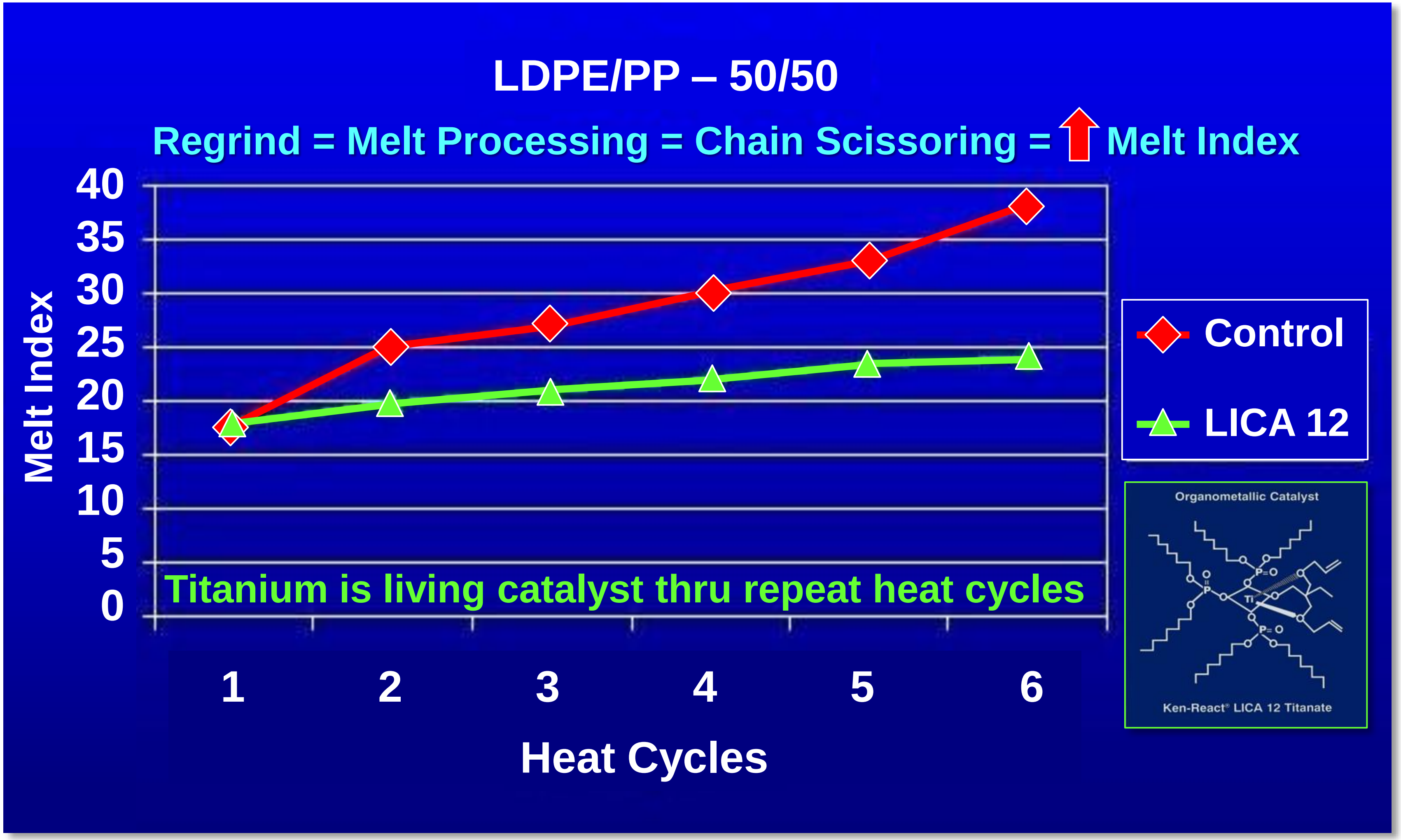




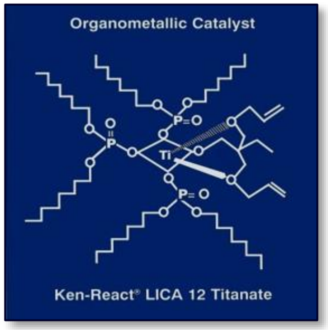
NO TITANATE

W. TITANATE

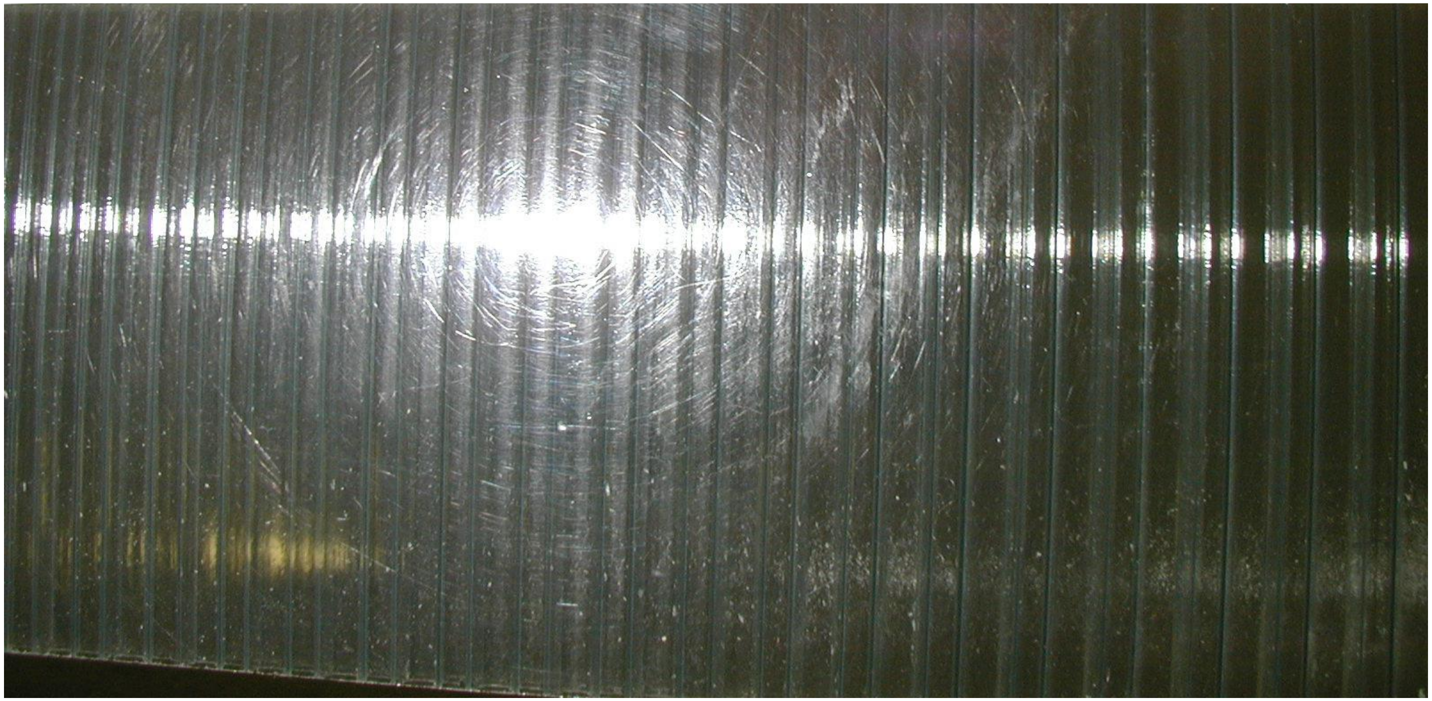
REPOLYMERIZATION of LDPE/PP – 50/50 Regrind
Using 1% Titanate Catalyst Pellet – 2 parts per thousand



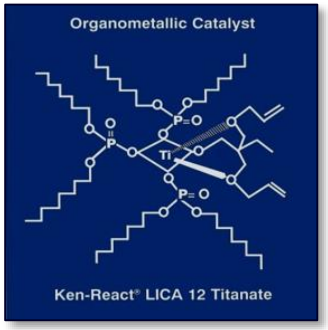
Recycled PET/Polycarbonate – 80/20 Blend Using 1% Titanate Catalyst



Extruded@ 180ºC using
0.3% CAPOW L12/H Titanate Catalyst
vs. 280ºC without the Additive



HDPE Regrind Using 1% Zirconate Catalyst

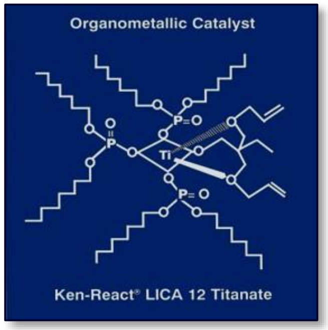


HDPE

1% Ken-React® CAPS® NZ® 12/L:

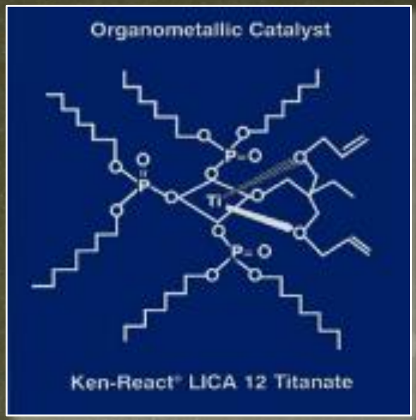
- **Reduced Part Wt. from 1745g to 1500g to equivalent drop weight impact strength.**
- **Reduced Cycle Time 156 to 116 seconds.**

Regrind: HDPE / Nylon Film Using 0.2% Titanate Catalyst



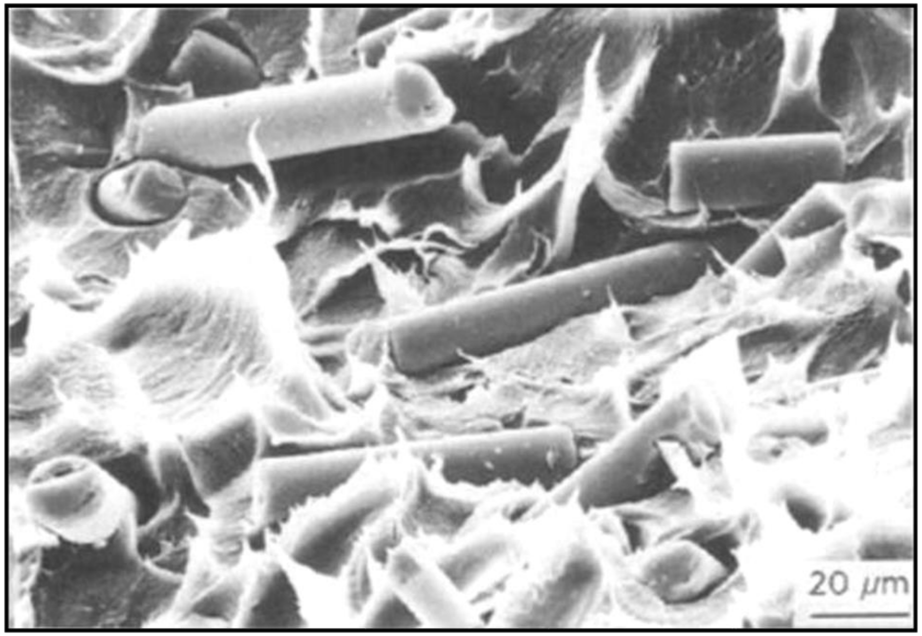
Ethylene Propylene Rubber Catalyst Effect of 0.2% Titanate

1000g EPR Rubber Sheeted off 2-roll Mill – Super Plasticizer

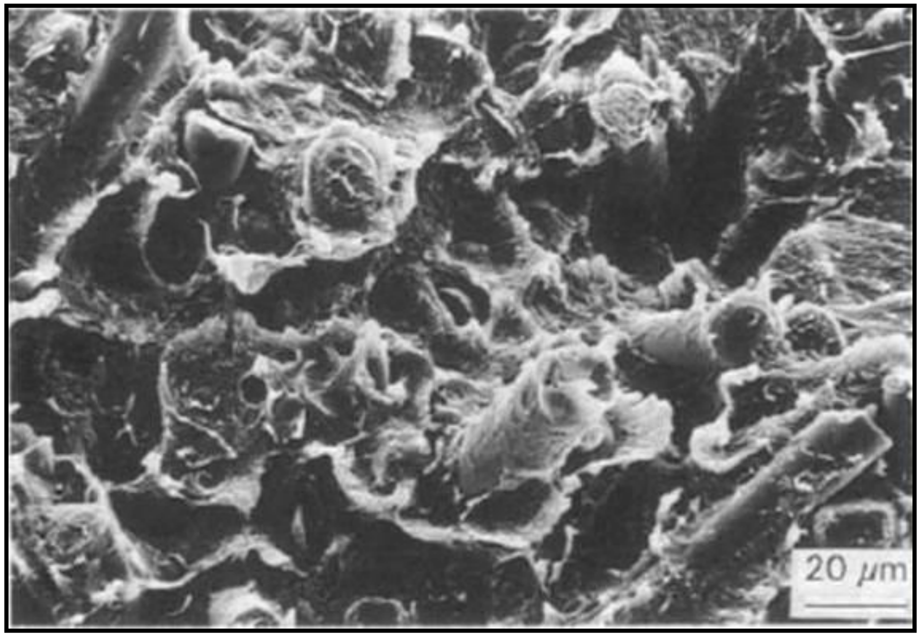


Effect of 0.2% Zirconate on Compatibility of the E-Glass/ Ethylene TetraFluoroEthylene Interface

E-Glass Fiber/ETFE (Ethylene TetraFluoroEthylene) Interface
ETFE (think Teflon®) is extremely non-polar

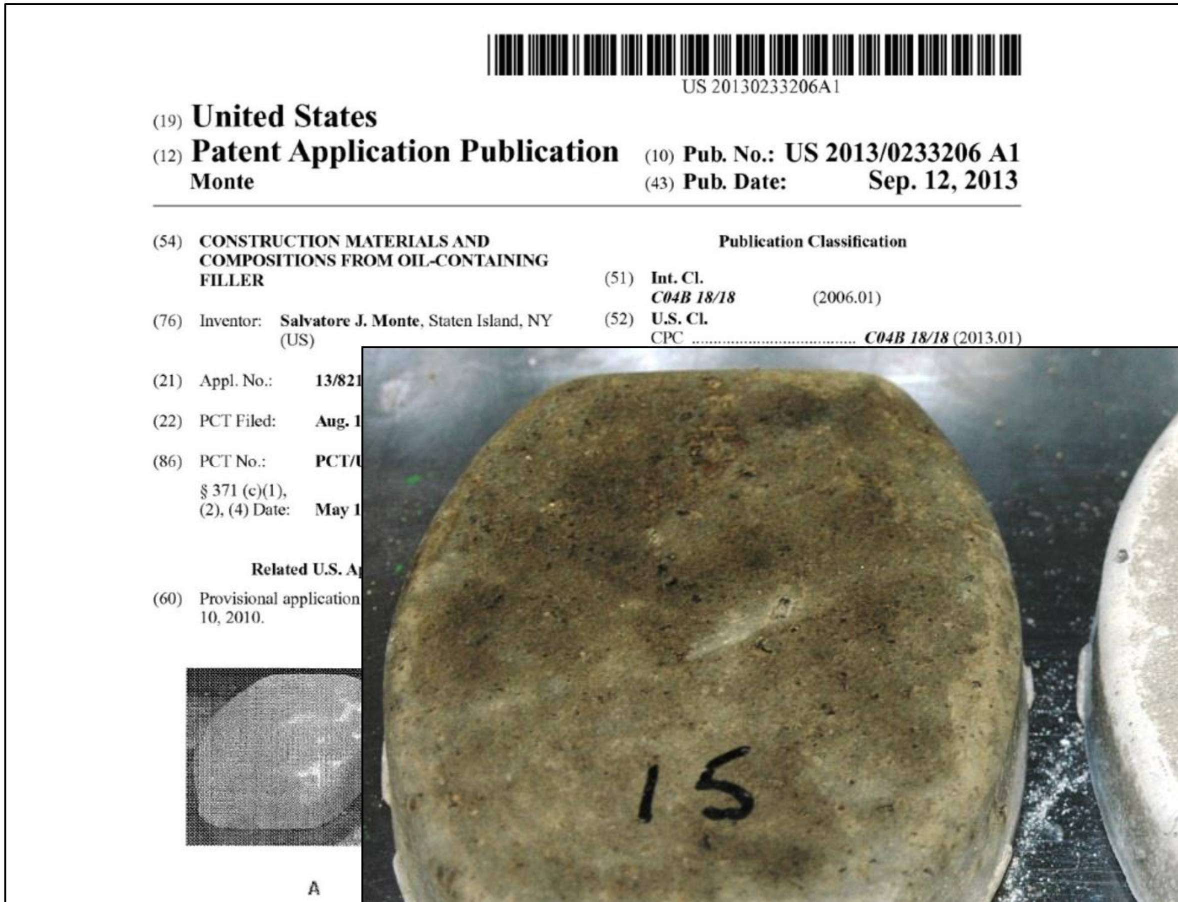


No Zirconate:
Silane Sized E-Glass Fiber/ETFE



With Zirconate:
Silane Sized E-Glass Fiber/ETFE

Effect of Titanate on Compatibility of the Interface of: Oil Soaked/Salt Water/Beach Sand and Portland Cement


US 20130233206A1

(19) United States
(12) Patent Application Publication (10) Pub. No.: US 2013/0233206 A1
Monte (43) Pub. Date: Sep. 12, 2013

(54) CONSTRUCTION MATERIALS AND COMPOSITIONS FROM OIL-CONTAINING FILLER

(76) Inventor: Salvatore J. Monte, Staten Island, NY (US)

(21) Appl. No.: 13/821

(22) PCT Filed: Aug. 1

(86) PCT No.: PCT/U

§ 371 (c)(1), (2), (4) Date: May 1

Related U.S. A

(60) Provisional application 10, 2010.

Publication Classification

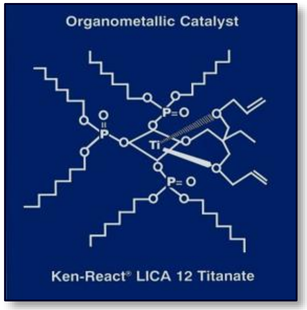
(51) Int. Cl. C04B 18/18 (2006.01)

(52) U.S. Cl. CPC C04B 18/18 (2013.01)

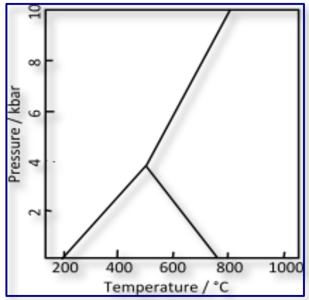
A

No Titanate **With Titanate**

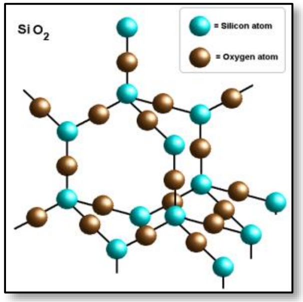
Compatibilization of Addition & Condensation Polymers



+



+



+

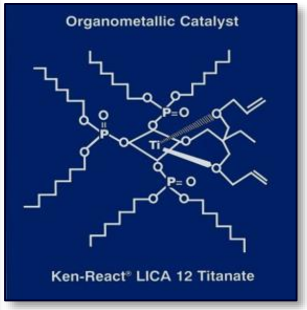
=

Ken-React®
CAPS®
KPR® 12/LV

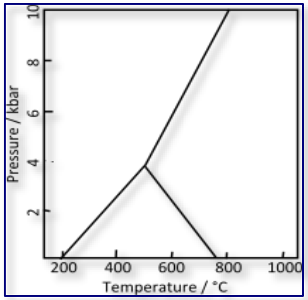
Incompatibility PET & PE

Incompatibility PE & PP

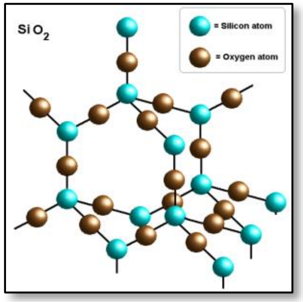
Compatibilization of Addition & Condensation Polymers



+



+



+

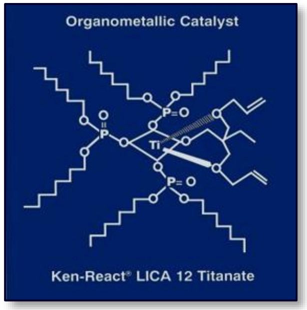
=

Ken-React® CAPS® KPR® 12/LV

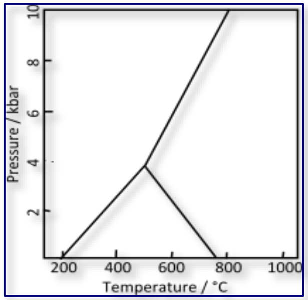
Incompatibility PP & PET & PE

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.

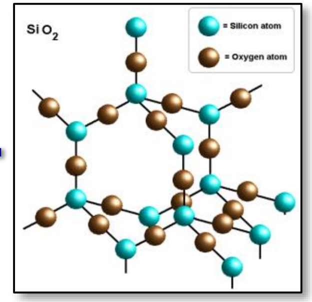
Compatibiization of Addition & Condensation Polymers – PP/PET/PE



+



+



+

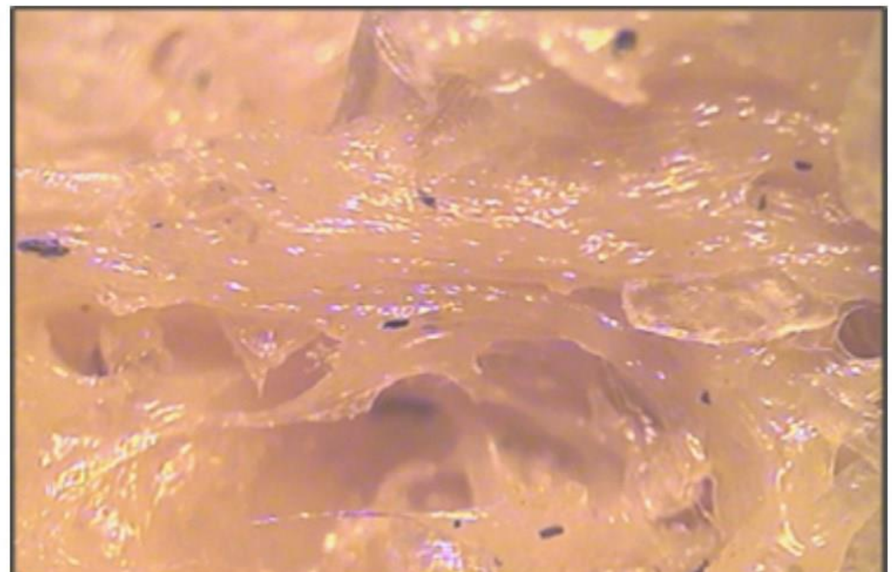
=

Ken-React® CAPS® KPR® 12/LV

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

Incompatible PP/PET/PE—

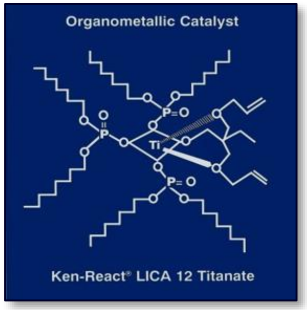
No Additive



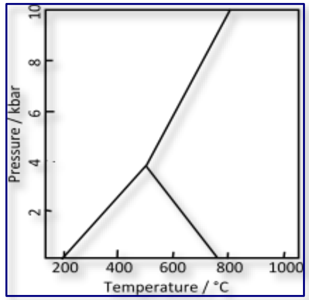
Compatibilized PP/PET/PE—

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

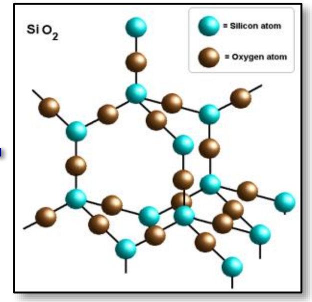
Compatibilization of Addition & Condensation Polymers



+



+



+

=

Ken-React® CAPS® KPR® 12/LV

Incompatibility PP & PET & PE

Polymer Specialties International Ltd.
175 Deerfield Road,
Newmarket, Ontario, L3Y 2L8
Cell: (905) 717-3723
E-mail: bryon.wolff@psi-cda.com

University of Waterloo Chemical Engineering department.

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.

Compatibilization of Addition & Condensation Polymers

LOWERING THE PROCESS TEMPERATURE FOR REACTIVE COMPOUNDING SHEAR IS CRITICAL

October 08, 2015 2:23 PM

From: Bryon Wolff [mailto:bryon.wolff@psi-cda.com]
Sent: Thursday, October 08, 2015 2:23 PM
To: Salvatore J. Monte <sjmonte@4kenrich.com>
Subject: Re: 2015 Global Plastics Summit

University of Waterloo
Chemical Engineering Dept.

Good afternoon Sal
Below I've written a response to each of your questions. Should you require additional information etc. please don't hesitate to come back to me.
Best Regards

Bryon Wolff
Chief Technology Officer

Polymer Specialties International Ltd.
175 Deerfield Road,
Newmarket, Ontario, L3Y 2L8
Cell: (905) 717-3723
E-mail: bryon.wolff@psi-cda.com

KENRICH PETROCHEMICALS, INC.

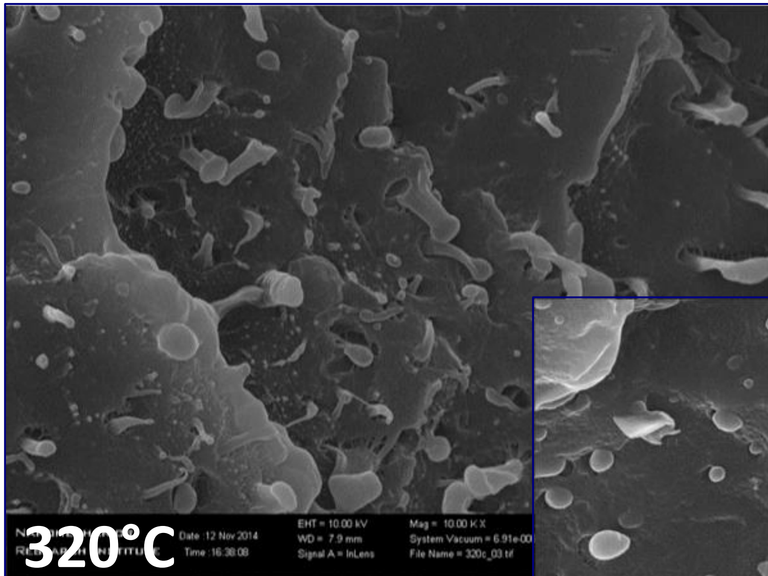
In your opinion, does the 10% drop in temperature from 320°F to 290°F indicate clearly the importance of reactive compounding shear? PSI **The surface of the extrudate exiting the die became significantly smoother. Upon further analysis with SEM and Izod, it was clear that the increasing the shear dramatically improved the dispersion and physical properties of the compound.**

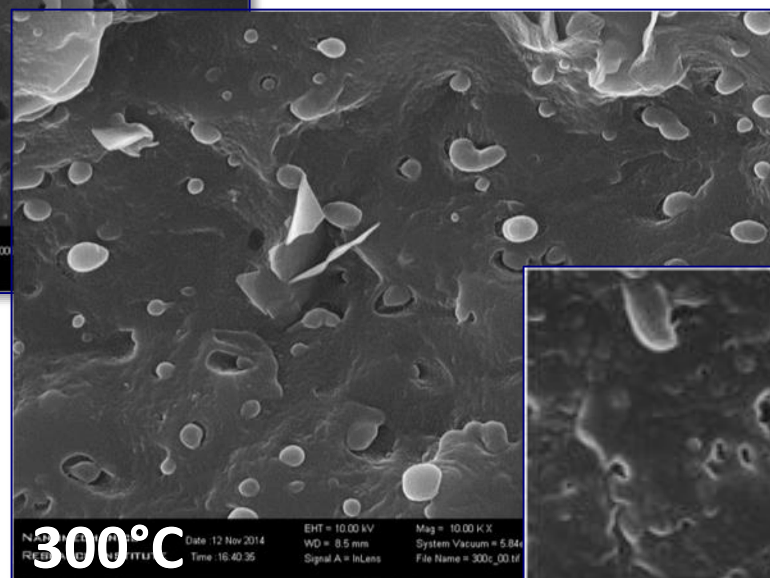
KENRICH PETROCHEMICALS, INC.

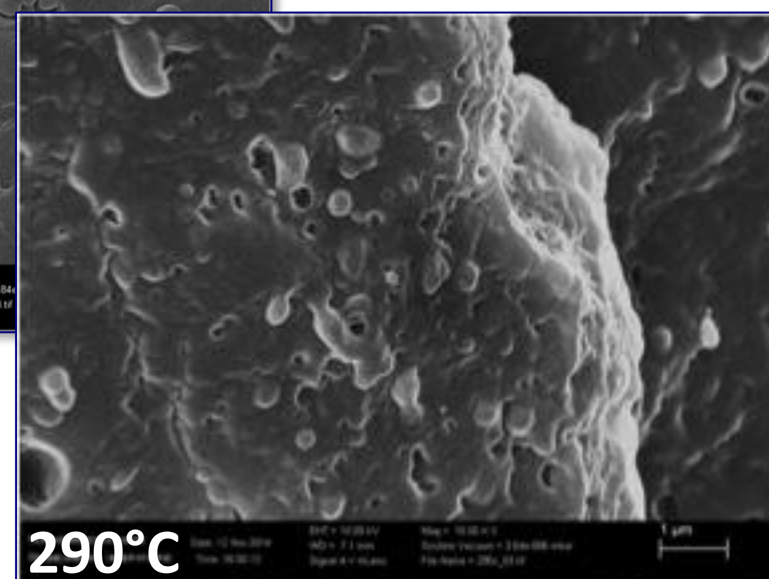
What is your next step? PSI **We're working on obtaining two industrial applications that generate over 10 million pounds of polyester and olefins waste to land fill every year. The goal behind this work is develop a compound or compounds which repurposes these materials into other applications which 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







SEM
Extruded Pellets

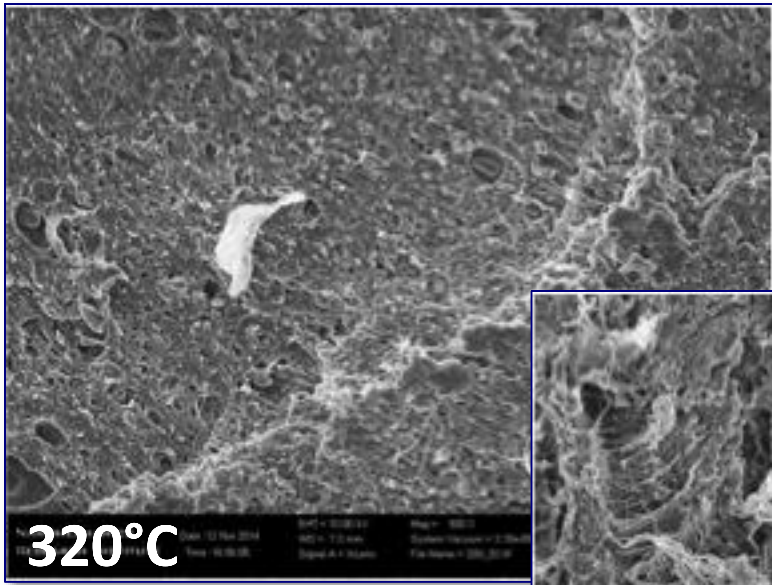
<u>Materials obtained from post-industrial waste streams</u>:

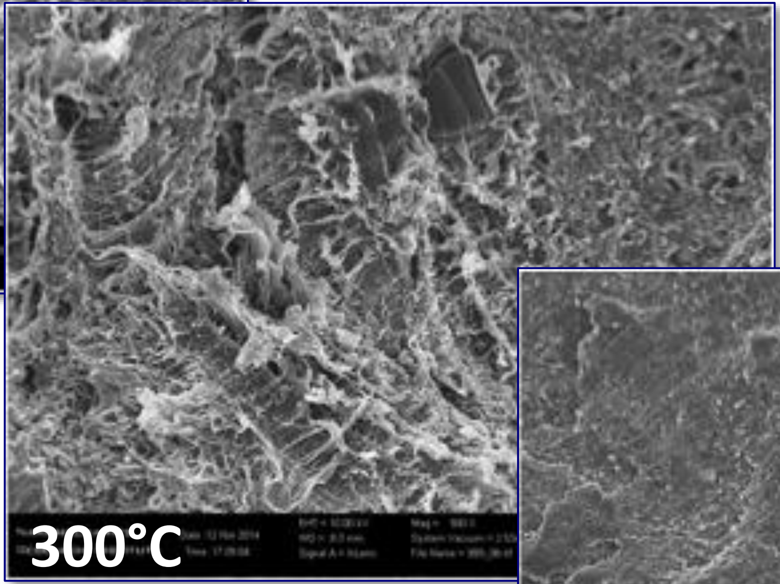
1. LLDPE from a fractional melt film,
2. PP Copolymer from mixed 20-35 MFI injection molded caps,
3. PET from thermoformed clamshell food packaging.

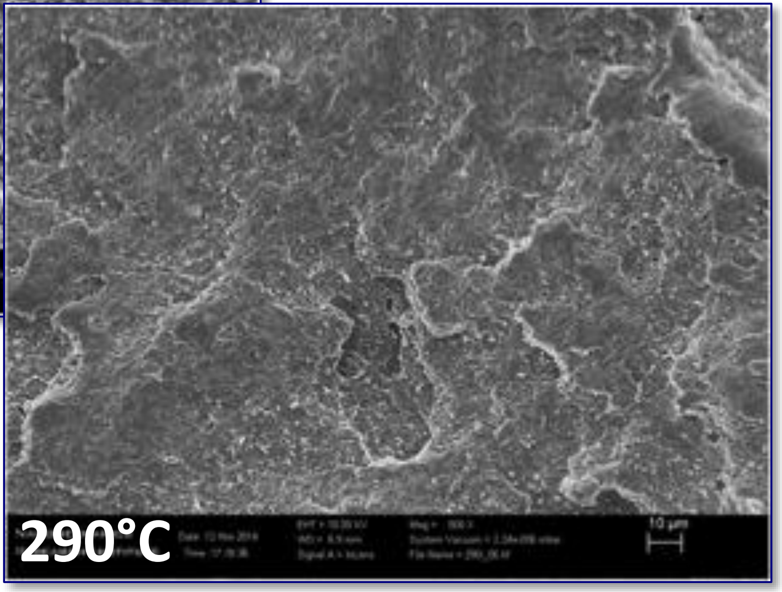
Compatibilization of Addition & Condensation Polymers

LOWERING THE PROCESS TEMPERATURE FOR REACTIVE COMPOUNDING SHEAR IS CRITICAL

SEM
Injection Molded





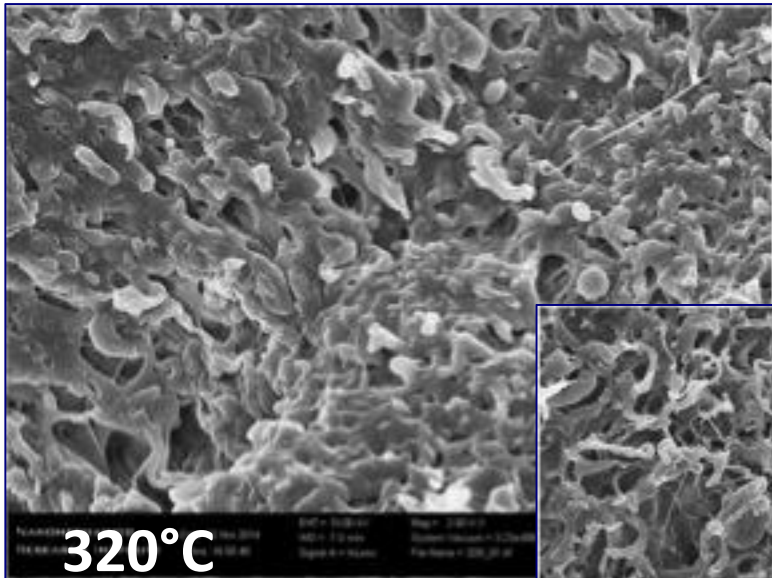


<u>Materials obtained from post-industrial waste streams</u>:

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.

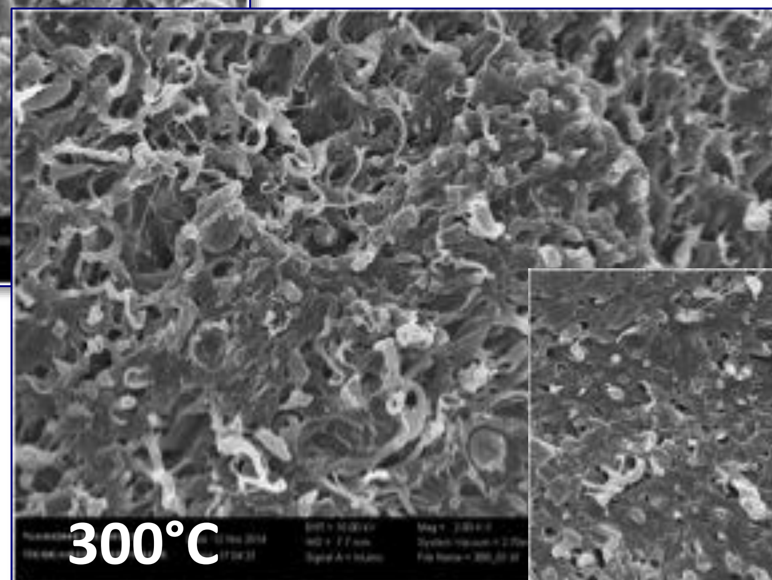
Compatibilization of Addition & Condensation Polymers

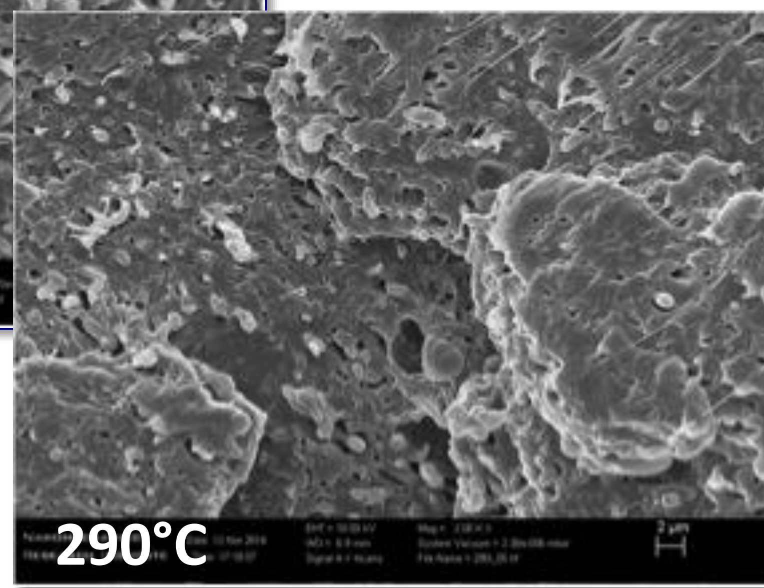
LOWERING THE PROCESS TEMPERATURE FOR REACTIVE COMPOUNDING SHEAR IS CRITICAL



SEM

Izod Impact





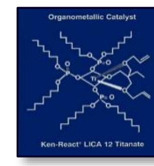
<u>Materials obtained from post-industrial waste streams</u>:

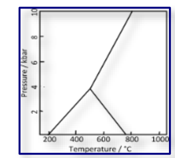
1. LLDPE from a fractional melt film,
2. PP Copolymer from mixed 20-35 MFI injection molded caps,
3. PET from thermoformed clamshell food packaging.

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

CONCLUSION

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





Ad appearing in Plastics Technology Magazine