

Processing and Molding Polymers with 1.5-Nanometer Titanates and Zirconates In Pellet Form

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PROCESSING AND MOLDING POLYMERS WITH 1.5-NANOMETER TITANATES AND ZIRCONATES IN PELLET FORM

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ABSTRACT

Added to the hopper just like a color concentrate, 2 to 3 parts of a phosphato titanate or zirconate in pellet masterbatch form per 1,000 parts of filled or unfilled compound provides a method (Function 1-Coupling) for in-situ interfacial nano-surface modification of most all inorganic and organic materials in a compound independent of the interface's hydroxyl content and absent the need for water to effect hydrolysis for coupling as with silanes while providing metallocene-like repolymerization catalysis (Function 2-Catalysis) and (Function 3) nano-intumescence for flame retardance resulting in: the use of larger amounts of regrind and recycle; copolymerization of blends of dissimilar addition and condensation polymers such as HDPE, PP and PET; prevention of delamination of PP/HDPE blends; faster production cycles at lower temperatures producing thermoplastic parts having less heat stress differentials, better finish, and increased stress-strain strength; and control of burn rate and burn rate exponent. Compounds having subject additives age better due to the removal of water at the polymer-reinforcement interface normally left when using a silane or no additives that cause loss of adhesion during water boil tests.

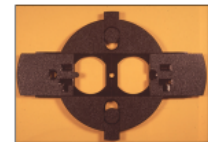
INTRODUCTION

OK. So you are up-to-date on Industry 4.0 and have the latest and greatest processing equipment, controls, sensors and software such as iMFLUX®. And you know your compound materials behavior such as “crystallinity” based on your data and pay attention to machine conditions to optimize their performance. But, the specific behavior of materials alone and in combination will always

remain a challenge as the Internet of Things – the basis of 4.0 – depends on data and the data depends on the accumulated experience inputted. Marcel Beraud, Director – Global Services AMT – The Association of Manufacturing Technology makes several key points in his article, *What Does it Take to Be 4.0 Ready?: “...As an avid floor manufacturing guy, to me it all starts with the basics. We need to have robustness in everything we do: our designs, our process instructions and controls, our material selection...”* – see link: https://issuu.com/amtonline/docs/amtnews_july_final_web/11. So, if your 40% fiberglass reinforced Polycarbonate part calls for an injection molding profile temperature setting input of 496-528°F while 1 to 2 parts per thousand parts of a titanate will allow a setting of 395-465°F, your 4.0 process with the higher temperature settings will have to overcome problems such as: shrinkage at the gate, sink marks, dimensional stability, uniform appearance and mechanical properties and not have the advantage of faster production cycle times. See IM PC Electrical Outlet Cover Table 1 data next:

		1% CAPS KR 134S/K						
		Control	#1	#2	#3	#4	#5	#6
Rear (°F)	496	456	445	445	435	425	420	395
Middle (°F)	516	495	490	480	470	460	455	440
Front (°F)	528	509	498	485	485	475	475	465
Injection Pressure	1500	1200	1200	1000	1000	1000	800	800
Injection Time (sec)	11	8	8	8	8	8	7	7
Injection Full Pressure (sec)	4.5	2.5	1.5	1.5	1.5	1.5	1.5	1.5
Cool (sec)	30	25	23	20	25	22	20	18
Total Cycle (sec)	47.5	37.5	34.5	31.5	36.5	33.5	30.5	28.5
Appearance	Good	Good	Good	Sinks	Better	←	No Sinks	→
Fit ^a	Tight	Tight	Loose	Loose	Looser	Looser	Very	Loose

Note^a: Tight fit caused by excessive shrinkage around gates.



Temperature is just one of the inputs. In a SPE Webinar entitled **Ductile to Brittle Transitions in Plastics - October 18, 2018** – see link:

<https://www.4spe.org/i4a/ams/meetings/?controller=meetings&action=loginOrGuest>, Jeffrey A.

Jansen, Senior Managing Engineer and a Partner at *The Madison Group* stated, “There are numerous factors that influence a ductile-to-brittle transition within plastic materials, such as:

- Temperature
- Stress Concentration
- Chemical Contact
- Molecular Weight
- Degradation
- Filler Content
- Contamination
- Poor Fusion
- Strain Rate
- Time Under Load
- Crystallinity
- Plasticizer Content

Within these variables such as Crystallinity listed above there are many subset phenomena that need to be understood and controlled.

According to Michael Sepe’s sequential chronological posts in **Plastics Technology Magazine** on Materials Processing: “There are several process-related issues that influence crystallinity besides cooling rate” – see links for detailed discussion:

Published: 10/1/2018

[Materials: A Processor's Most Important Job, Part 9](#)

How to establish molding conditions that minimize internal stress in a part.

Published: 8/28/2018

[Materials: A Processor's Most Important Job, Part 8](#)

How processing adjustments can control molded-in stress.

Published: 8/1/2018

[Materials: A Processor's Most Important Job, Part 7](#)

There are several process-related issues that influence crystallinity besides cooling rate. Let's examine a few.

Published: 6/1/2018

[Materials: A Processor's Most Important Job, Part 6](#)

The importance of mold temperature to the development of the desired polymer crystalline structure becomes absolutely crucial in the case of high-performance materials.

Published: 4/27/2018

[Materials: A Processor's Most Important Job, Part 5](#)

Using a mold temperature above a polymer's Tg ensures a degree of crystallinity high enough to provide for dimensional stability, even if the part must be used at elevated temperatures. But POM is an exception. Why?

Published: 3/29/2018

[Materials: A Processor's Most Important Job, Part 4](#)

Engineering polymers require higher mold temperatures to achieve their ideal structure. The temptation to turn down the mold temps can hurt part performance.

Published: 3/1/2018

[Materials: A Processor's Most Important Job, Part 3](#)

Processors are often expected to compensate for ill-advised decisions made earlier in the product-development process. In the case of shrinkage, one of the most common 'fixes' is to simply reduce the mold temperature.

Published: 1/23/2018

[Materials: A Processor's Most Important Job, Part 2](#)

Process conditions help determine the difference between the maximum degree of crystallinity that can be achieved in a polymer and the degree that is present in a molded part.

Published: 1/2/2018

[Materials: A Processor's Most Important Job, Part 1](#)

Many processors don't realize that preserving material characteristics is crucial to product success and failure. The focus here is on molecular weight.

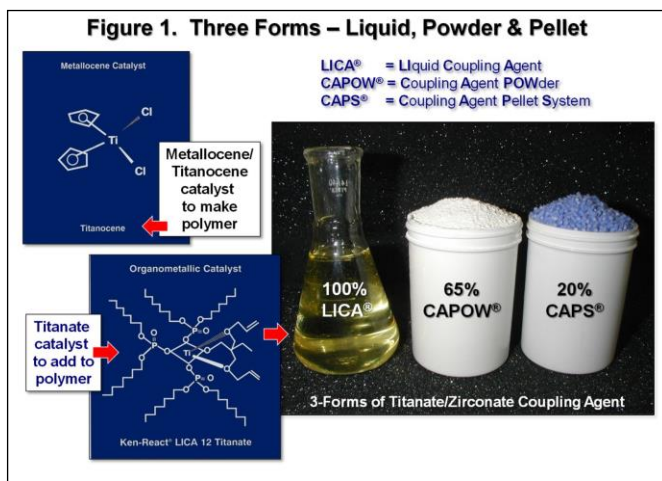
Published: 12/1/2017

Materials: Cycle Time—Science vs. Rules of Thumb, Part 6

This installment—on elastomers—completes a series, whose theme is to bring more science to the discipline of molding. The overall message: Ask a lot of questions whenever someone posits this or that ‘rule of thumb’ about processing...

So, what’s left in a processor’s arsenal to meet ever-increasing materials performance demands and resultant processing challenges intrinsic in the above variables in polymeric compositions?

How about ADDITIVES? Specifically, 1.5-nanometer Neoalkoxy Titanates and Zirconates in pellet form that provide a means to widen the window of material processing success via in situ organometallic Ti or Zr catalysis that improves flow and properties of unfilled and filled polymers. In effect, the materials in the polymer melt become the site of reactive titanium or zirconium interactions that provide for a more efficient use of raw materials.



This paper can be executive summarized (*like the doctor who says, “Take two aspirins and call me in the morning”*): “Tumble blend 1 part Ken-React® CAPS® L® 12/L (see Figure 1) additive with 100 parts of polymer compound material and then reduce processing temperature conditions by 10% for more for reactive compounding shear”.

DISCUSSION

There are over 450-ACS CAS Abstracts of “Works by S.J. Monte” starting with a December 1974

Modern Plastics magazine article entitled “New Coupling Agent for Filled Polyethylene” by S. J. Monte and P.F. Bruins, Professor of Chemical Engineering at Brooklyn Polytechnic Institute (now NYU Tandon School of Engineering) and my M.S. Polymeric Materials mentor in 1969. There are also several thousand ACS CAS Abstracted patents and technical papers issued to “others” based on my teachings.

In many of my past articles we taught the nano-technology of subject organometallics by discussing the chemistry of the SIX FUNCTIONS. I wrote a 340-page Ken-React® Reference Manual and distributed 80,000 copies over the period of 1985 to 1995 until the advent of the electronic era where people wanted CD’s and now Memory Sticks. Provided next are some links that are instructive beyond the scope of this article:

- *Plastics Recycling World – May/June 2018*
HELPING PLASTICS COME TOGETHER - Catalysis Approach to Compatibilization:

<https://content.yudu.com/web/1rl19/0A42x3p/PRWMayJun18/html/index.html?page=52&origin=reader>.

- *Rubber World Magazine – February 2918*
“Why Titanates and Zirconates May Be Better Adhesion Promoters Than Silanes for Silica & Carbon Reinforced Polymeric Compositions”:

http://digital.ipcprintservices.com/publication/?m=9911&l=1#{%22issue_id%22:476701,%22page%22:34}

- TITANIUM CATALYST PELLET ADDITIVE COPOLYMERIZES PCR (POST-CONSUMER RECYCLE) IN THE MELT: <https://4kenrich.com/wp-content/uploads/2018/02/Ken-React-KPR-Global-Plastics-Summit-2015-Chicago-Multi-SlidesTitanate-Catalyst-for-PC.pdf> .
- Paint & Coatings Industry Magazine – October 2017 – TITANATES & ZIRCONATES VS. SILANES: <https://4kenrich.com/wp-content/uploads/2017/10/pci1017p48->

[Kenrich-FT-PCI-Oct-2017-Issue-PCI-Approved-for-Publication.pdf](#) .

- TITANATES AND ZIRCONATES IN THERMOPLASTIC AND ELASTOMER COMPOUNDS:
<https://4kenrich.com/technical-information/titanates-and-zirconates-in-thermoplastic-and-elastomer-compounds/> .
- PIA White Paper: *Compatibilizers: Creating New Opportunity for Mixed Plastics*:
[https://www.plasticsindustry.org/sites/plastics.dev/files/Compatibilizers%20Whitepaper%20\(Versio%201.0\)_0.pdf](https://www.plasticsindustry.org/sites/plastics.dev/files/Compatibilizers%20Whitepaper%20(Versio%201.0)_0.pdf)
- Dental Materials Journal 2017; 36(5): 539–552: *Review of titanate coupling agents and their application for dental composite fabrication*: <https://4kenrich.com/wp-content/uploads/2018/09/Review-of-titanate-coupling-agents-and-their-application-for-dental-composite-fabrication-Dental-Materials-Journal-2017-365-539-552.pdf>

The SIX FUNCTIONS of the physical organic chemistry of tetravalent organometallic Titanium and Zirconium may explain why they work – but, many polymer processors are not chemists and are more schooled in mechanical engineering, IT – or come from sales, marketing and business management. So, I decided to approach this paper from Jeffrey A. Jansen and Michael Sepe’s processor viewpoints – and not the chemistry of the additive.

Let’s take the aforementioned Jansen’s *Ductile to Brittle Transitions in Plastics* factors starting with **Temperature** and comment on how titanate and zirconate additives will influence those factors in a positive way to give you – the polymer processor – a wider window of success for processors and then make our case with illustrations and data.

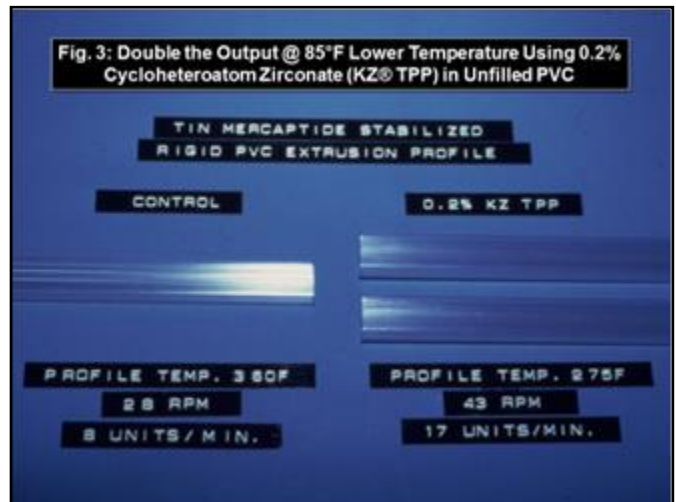
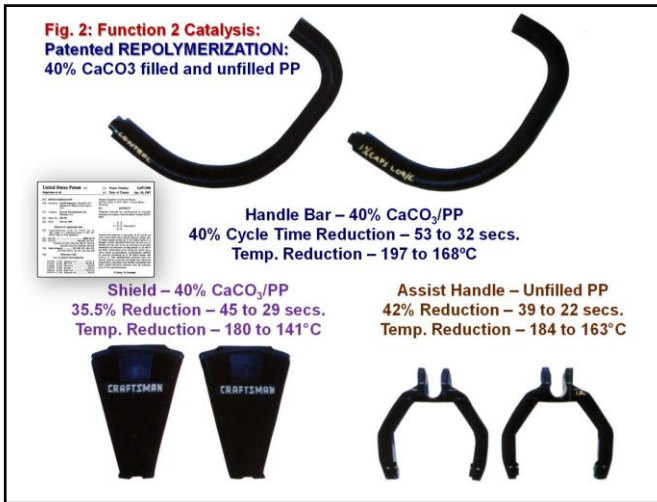
- **Temperature** – 2-parts additive per 1,000-parts polymer will allow the average process temperature to be lowered 10% and decrease cycle time by up to 40% and double extrusion rates. See Table 2 for parts produced.

TABLE 2 – A SUMMARY OF THE PRODUCTIVITY EFFECT (WHEN COMPARED TO A CONTROL) OF VARIOUS COUPLING AGENTS IN VARIOUS THERMOPLASTIC PLANT TRIALS

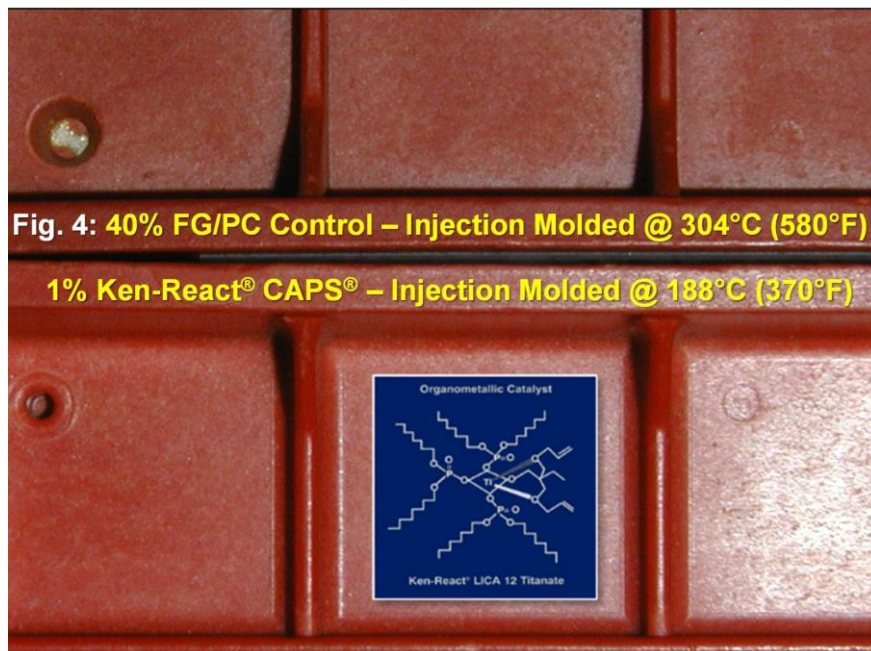
Plant Trial	Polymer	Molding Process	Part Produced	Coupling Agent	% Reduction	
					Temp.	Cycle Time
1*	HDPE (Phillips 5202)	Blow	Automotive	CAPS NZ 12/L	8.6	32.4
2	HDPE (Regrind 25053P)	Blow	Drum	NZ 12	9.2	18.9
3	HDPE (0.96M.I.)	Blow	Container	CAPS LZ 12/L	12.2	9.2
4	HDPE (Regrind 25053P)	Blow	Ski Board	CAPS L 12/E	16.1	18.4
6	HDPE (Undisclosed)	Inj.	Milk Crate	CAPS NZ 12/L	10.2	8.2
8	HDPE (Dow 08054)	Inj.	Drum.	LICA 12	6.6	15.8
10	HDPE (Dow 4052N)	Inj.	Drum Rim	CAPOW NZ 12/H	15.8	16.0
12	MDPE (100% Regrind)	Ext.	Profile	CAPS C.A./B.A.	12.3	14.1
13	LDPE (Undisclosed)	Inj.	Bumper	CAPS NZ 12/L	4.5	17.3
14*	PP	Inj.	Carry Box	CAPS L 12/E	8.3	8.7
15	PP	Inj.	Proprietary	LICA 12	12.0	28.5
16	PP (8310KO)	Inj.	Crock Pot	CAPS NZ 12/L	14.7	15.0
20*	HIPS	Inj.	Vac Nozzle	CAPS L 12/K	9.8	16.7
21	GPPS	Inj.	Closure	CAPS L 12/E	7.0	21.0
23*	ABS (BW KJC 34187)	Inj.	Computer	CAPS L09/K	11.9	22.1
24*	ABS (33838 Regrind)	Inj.	Carrier Box	CAPS L12/E	3.4	12.8
25	ABS (Undisclosed)	Inj.	Printer	CAPS L 09/K	7.9	16.4
27	ABS (Regrind)	Ext.	Frames	CAPS L 09/K	5.0	13.7
31	PBT	Inj.	Proprietary	CAPOW KZ TPP/H	3.4	31.2
32	PBT	Inj.	Proprietary	CAPOW L 2/H	1.1	30.5

Figure 2 shows that the temperature/cycle time reduction effect on filled and unfilled PP is the result of filler coupling and polymer catalysis.

Figure 3 shows a doubling of unfilled Rigid PVC extrudate output at 85°F lower temperature with no sacrifice in appearance or dimensional stability.



- Stress Concentration** – According to Sepe: *“Mechanical properties and dimensional stability of a part are greatly affected by the levels and uniformity of molded-in stresses. Mold-filling velocity and switchover point, as well as cooling rate and flow-channel dimensions are molders’ tools for controlling stresses in molded parts.”* Figure 4 shows the reduced stress and improved dimensional stability, better weld line formation, brighter color of a pre-compounded 40% fiberglass reinforced, red iron oxide pigmented PC injection molded part by the addition at the IM Press of 1% Ken-React® CAPS® L® 12/L by Stanley A. Watson of Diamond Machining Technology, Inc. enabling a temperature reduction of 210°F.



<https://www.youtube.com/watch?v=V6CHET-Mcpo>

Table 2 shows a 25% cycle time reduction and 20% temperature reduction for an IM PC part.

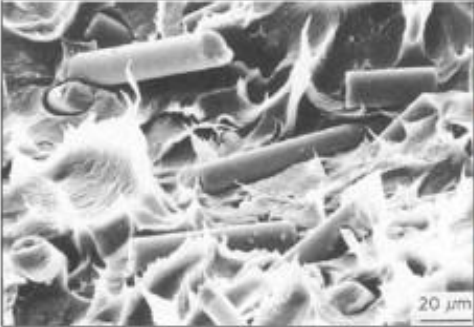
TABLE 2 – EFFECT OF 1% CAPS® L® 12/L ON CYCLE TIME & PROCESS TEMPERATURES OF AN INJECTION MOLDED FG/PC AUTOMOTIVE FUSE BOX COVER

Conditions	Control	1% CAPS® L® 12/L				
		I	II	III	IV	V
Temps., °F						
Rear	570	525	490	425	440	410
Center	560	550	519	450	460	450
Front	568	550	517	450	460	470
Valve	550	520	495	425	440	460
Cycle time, sec.	60	-	-	-	50	45
Observation	No Splay	Splay	Splay	Splay	Splay	No Splay
Injection Pressure, psi						
High	1100	-	-	-	-	-
Low	1250	-	-	-	1600	1550

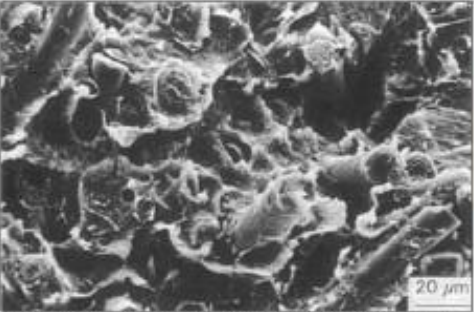
• **Chemical Contact** – The most chemical resistant plastics are PTFE, ETFE, PPS, etc. – see: <https://www.curbellplastics.com/Research-Solutions/Chemical-Resistance-of-Plastics>. Water is a polymer’s Achilles heel. When a filler or reinforcement or pigment is added to the plastic,

water on the filler is also introduced via: water bearing-agglomerates; or water at the nano-filler/polymer interface; or water of hydrolysis is left on the fiberglass during silane sizing – see Edwin P. Plueddemann quote from his book “Silane Coupling Agents” in Fig. 5:

Figure 5: FG/ETFE Without & With Zirconate




10% Silane Sized E-Glass in ETFE – No Zirconate



10% Silane Sized E-Glass in ETFE – With Ken-React® NZ® 44 Zirconate

PASS 10% SALT WATER BOIL TESTS




Unlike Silanes, Ken-React® Titanates and Zirconates do not need water for **hydrolysis**, surface hydroxyls, or pH control.

Promote adhesion via **in situ** proton coordination with all inorganics (i.e. CaCO₃) & organics (i.e. carbon) directly in the polymer/solvent phase.

No water added or condensation by-product formed.

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Edwin P. Plueddemann: “... Surfaces that showed little or no apparent response to silane coupling agents include calcium carbonate, graphite and boron. ... it must be concluded that water cannot be excluded from the interface between resin and a hydrophobic mineral reinforcement and the effect of water will vary with the nature of the mineral surface. Silane coupling agents do not exclude water from the interface, but somehow function to retain adhesion in the presence of water.”

Fig. 6 shows the added resistance to chemical contact by a titanate in a 49% FG/Vinyl Ester part having 2-month exposure to 5% caustic (NaOH):



• **Molecular Weight** – Generally, the strength of a polymer increases with its molecular weight at the expense of processability as measured by its melt flow index (MFI). In addition, melt processing of a polymer causes chain scissoring resulting in lesser mechanical properties of regrind or recycle. Subject heteroatom titanates/zirconates improve the processability of the polymer allowing the use of HMW polymer while maintaining or building MW in situ via Ti or Zr catalysis in the polymer melt. For example, Brabender readings using 0.16 phr of a 20% active zirconate pellet masterbatch (CAPS® NZ® 12/L) in unfilled PP show at 180°C a lower torque and higher mechanicals using a stronger (HMW) MFI 30 PP than a control using a weaker (LMW) MFI 120 PP – see Table 3 provided by a Swiss film processor:

Item	Torque, Nm	Tens. Str.	Elongation	Mix Amps
PP – MFI 120	160°			
Control	10.2	–	–	305
0.8% CAPS NZ 12/L	7.2	+10%	+15%	240
PP – MFI 120	180°			
Control	2.9	–	–	–
0.8% CAPS NZ 12/L	2.7	–	–	–
PP – MFI 30	180°			
Control	6.1	–	–	305
0.8% CAPS NZ 12/L	2.3	+10%	+15%	240

Polymer	Properties		
PE (Asahi)	Melt Index	Mol. Wt. Dist.	Low Mol. Wt. (5000) cont. %
Ziegler Natta	3.2	4.8	10.0
Z.N.+ KR TTS	2.1	3.4	2.5
PE (Asahi)	Output g/g	Mol. Wt. Dist.	Low mol. Wt. (5000) cont. %
Ziegler Natta	16,000	4.8	10.0
Z.N.+ KR 9S	21,000	3.3	2.4
PET (Teijin)	Melt pt., °C		(o-C ₆ H ₄ OH, 35°C)
Ti(OBu) ₄	258.3		0.600
KR 41B	262.8		0.662

Table 4 summarizes some of the early catalyst work done in Japan with monoalkoxy and coordinate titanates (invented by the author) on Z.N. catalyzed PE Addition Polymers and a PET Condensation polymer.

U.S. Patent 5,237,042 issued to the Korea Institute of Science and Technology (KIST) entitled, “*Process for the Preparation of Polybutylene Terephthalate Based Polymer*” disclosed the use of a complex catalyst consisting of antimony and titanium (KR® 41B) compounds to produce a PBT polymer “*having excellent color, a small amount of side-product and a high degree of polymerization within a short time*”. The KIST study sponsored by 7 S. Korean PET fiber producers cost \$3MM and spanned five years, confirmed KR® 41B (tetraisopropyl di(dioctyl) phosphito coordinate titanate) to be the most efficient polymerization catalyst for PET.

Fig. 7 illustrates two *catalysis/mol. wt.* points:

1. LDPE/PP – 50/50 blends of Addition polymers LDPE and PP are normally a compatibility issue prone to delamination during molding.
2. The Neoalkoxy phosphato titanate (LICA® 12) is a living catalyst constantly annealing molecular chains to maintain MFI integrity through several thermal cycles. (next page)

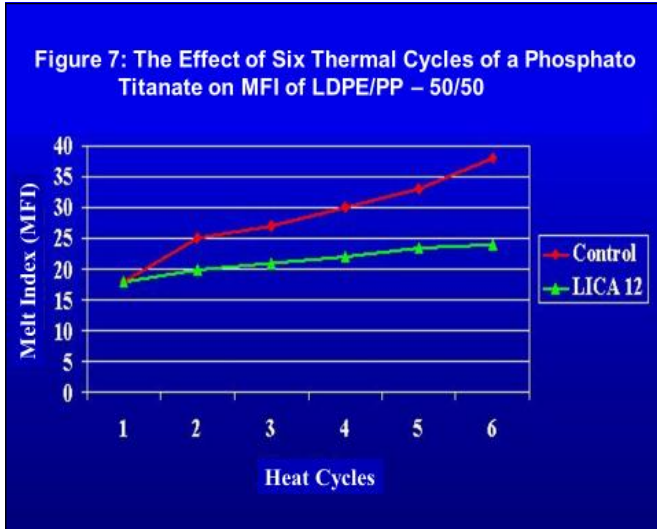


Fig. 9: Recycled Plastics to Reach Sustainability Goals Need Compatibilizers

The Nobel Prize in Chemistry 1963

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 showed a combination of $TiCl_4$ and $Al(C_2H_5)_2Cl$ gave comparable activities for the production of polyethylene.
- Natta used crystalline $\alpha-TiCl_3$ in combination with $Al(C_2H_5)_3$ to produce the first isotactic polypropylene.
- Kaminsky discovered that titanocene and related complexes emulated some aspects of these **Ziegler-Natta catalysts** but with low activity. He subsequently found that high activity could be achieved upon activation of these metallocenes with **methylaluminoxane (MAO)**. The MAO serves two roles: (i) alkylation of the metallocene halide and (ii) abstraction of an anionic ligand (chloride or methyl) to give an electrophilic catalyst with a labile coordination site.
- Monte uses **Neoalkoxy Titanate** in combination with Al_2SiO_5 mixed metal catalyst in Powder & Pellet forms for In Situ Macromolecular Repolymerization and Copolymerization in the melt – i.e. Polymer Compatibilization... AND ... The **Neoalkoxy Titanate** proton coordinates with inorganic fillers and organic particulates to couple/compatibilize the dissimilar interfaces at the nano-atomic level reducing the need for sorting.

Fig. 8: Addition & Condensation Polymers – PP/PET/PE Compatibilized

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

Fig. 10: Compatibilization of LDPE/PP – 80/20 Regrind

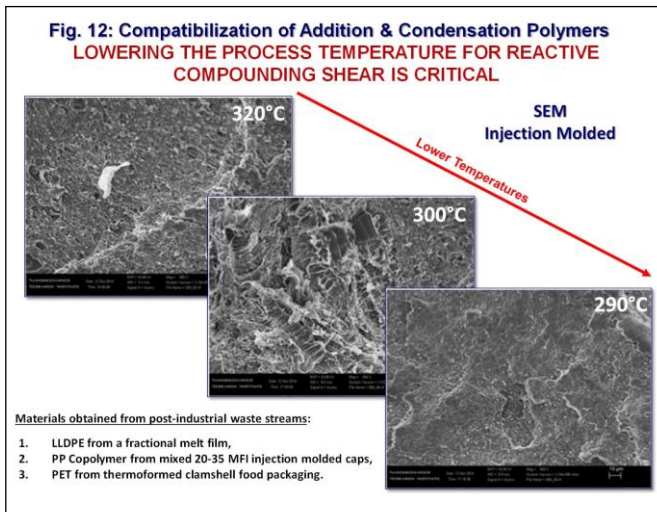
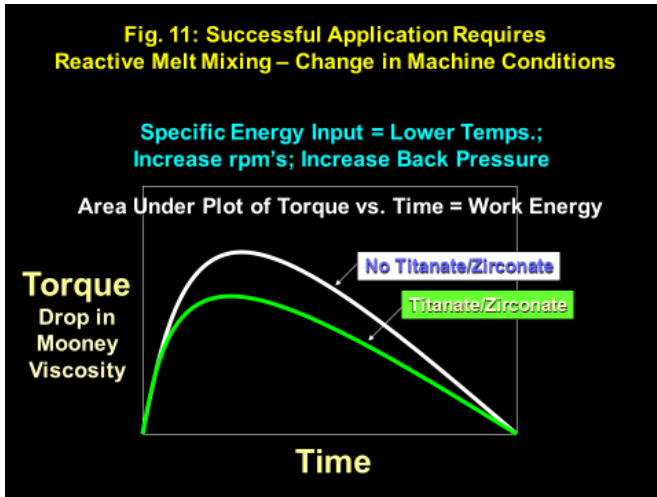
Prevents Delamination of PP/PE Blends

Fig. 8 shows the copolymerization effect of proprietary Ken-React® CAPS® KPR® 12/LV technology on a blend of dissimilar post-consumer (PE/PP/PET) recycle consisting of: LLDPE from a fractional melt film; PP Copolymer from mixed 20-35 MFI injection molded caps; PET from thermoformed clamshell food packaging.

Figure 9 provides some of the history of the evolution of Z-N, Metallocene, and subject titanate catalysts, which are unique because of their ability to copolymerize Addition (PE, PP) / Condensation (PET, PA) Polymers. Note: MAH compatibilizers depolymerize Condensation polymers. Figure 10 shows the compatibilization effect on a LDPE/PP regrind blend and illustrates a titanocene designed for polymerization and a titanate (LICA® 12) for repolymerization catalysis.

In melt processing of the titanate catalysts it is important to maintain reactive compounding shear as the titanate will reduce compound viscosity. The subsequent loss of shear at the interface must be regained by controlling temperature, pressure and rpms to optimize the nano-reactions that cause total titanium organometallic filler coupling and polymer catalysis. Figure 11 (next page) is the general processing principle of maintaining the interfacial Work Energy (defined as the Area under the plot of Torque vs. Time) and Figure 12 shows the positive effect of lowering temperatures for reactive compounding shear and subsequent compatibilization of the materials in Figure 8.

The use of heteroatom titanates and zirconates in polymer melt processing changes significantly the data reference points for Industry 4.0.



• **Degradation** – Degradation of a thermoplastic polymer composition can occur within the polymer itself or at the interface where the polymer and fillers, pigments, or fibers such as fiberglass, graphite, aramids and cellulose come together. The degree of dispersion of the filler in the polymer is a major degradation factor. Dispersion being defined as the complete deagglomeration of the filler particulates with its entrained air and moisture being displaced by the titanate/polymer phase to create a void-free and moisture-free composition. Thermosets may also experience breakdown of x-links.

Another source of degradation is water left on the surface of fiberglass after the silane hydrolysis adhesion mechanism (see Figure 5). The article entitled, “Review of titanate coupling agents and their application for dental composite fabrication”

(see link in the introduction) states in its abstract: “Silane is a dominant coupler that is widely used in dentistry to promote adhesion among the components of dental composites. Silica-based fillers can be easily silanized because of their similarly ordered structure. However, silane is hydrolytically degraded in the aqueous oral environment and inefficiently bonds to non-silica fillers. Thus, the development of hydrolytically stable dental composites is an important objective in the research on dental materials. Titanate coupling agents (TCAs) exhibit satisfactory interfacial bonding, enhanced homogeneous filler dispersion, and improved mechanical properties of the composites. Titanates also provide superior hydrolytic stability in wet environments, which should be considered in fabricating dental composites. The addition of a small amount of titanates can improve the resistance of the composites to moisture ...”

Another example prevention of polymer degradation is shown in Figure 13 wherein the titanate catalytic effect doubles the elongation of the silicone rubber jewelry mold compound and allows hot metal castings to increase from 11 to 250 cycles @ 460°C before degradation failure.

• **Filler Content** – Many of the negative factors of filler effects on polymer processing and mechanical properties are obviated when subject additives are used. There is a fundamental shift in the Critical Pigment Volume Concentration (CPVC) point of the filler/polymer ratio.



For example, the addition of CaCO₃ filler will result in a loss in Elongation in direct proportion to the amount of filler added. Polymer Toughness is

defined as the Area under the Plot of Stress vs. Strain. Strain is defined as the Elongation per Unit Length. Figure 14 shows that a titanate treated CaCO_3 will exhibit Elongations higher than unfilled polymer when loaded below the CPVC of the filled polymer composition.

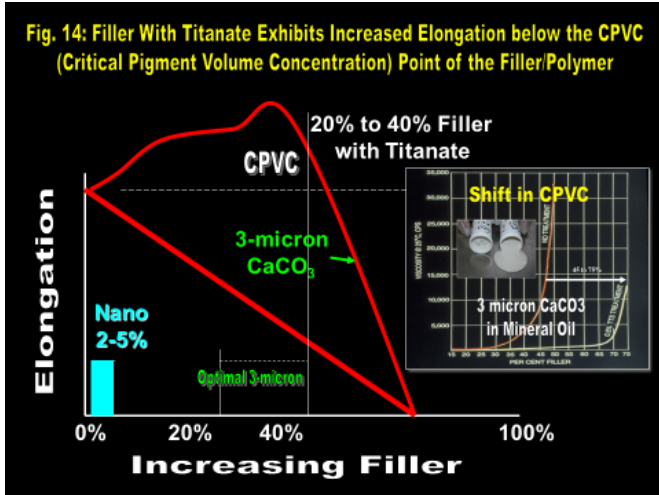
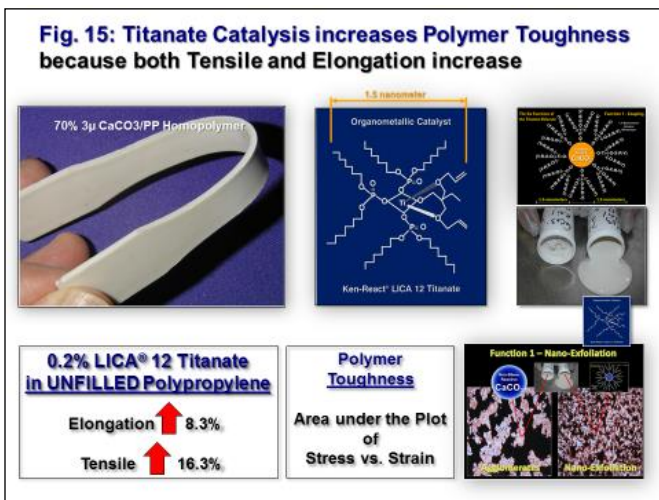
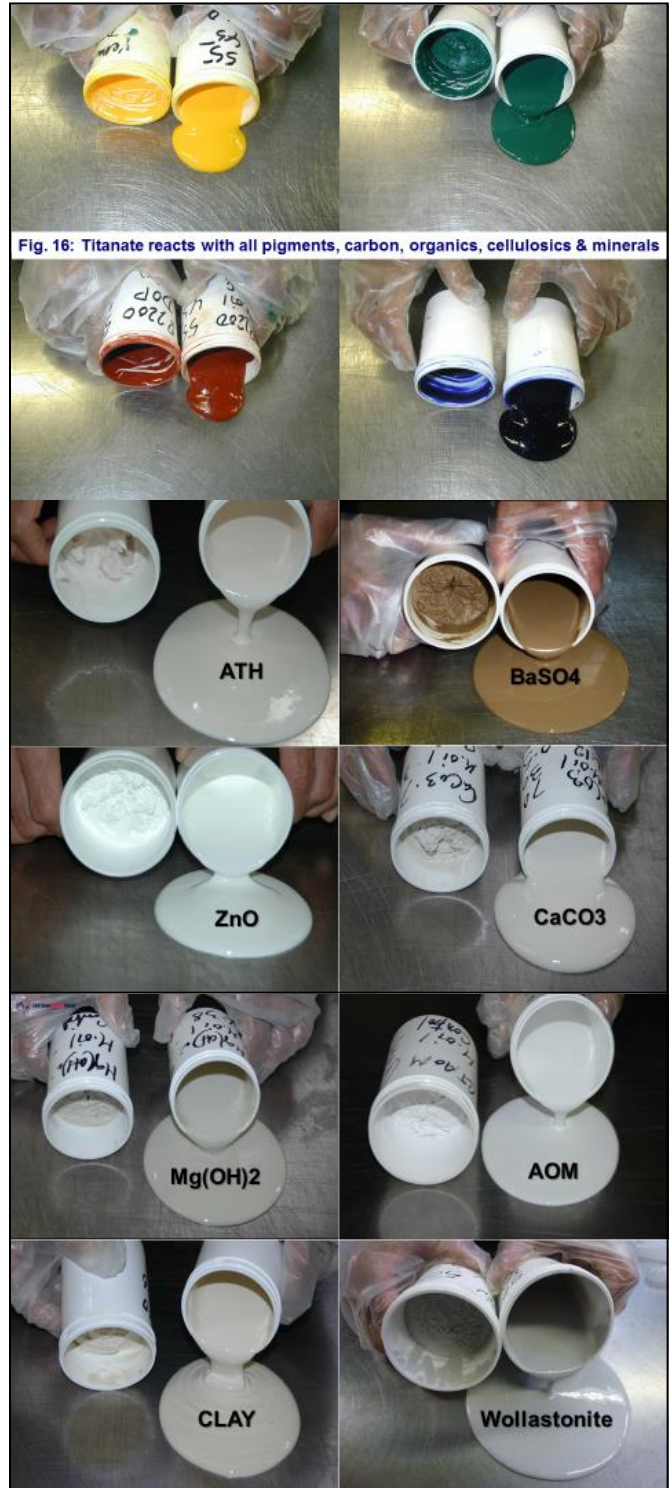


Figure 15 shows that the titanate deagglomerated filler – now devoid of mechanical property decreasing air and water voids – becomes a catalyst support bed for Titanium or Zirconium “Repolymerization” of the polymer phase producing unfilled to filled compositions that flow more readily and have greater flexibility.



The proton coordination coupling mechanism of titanates allows for reaction with any inorganic or

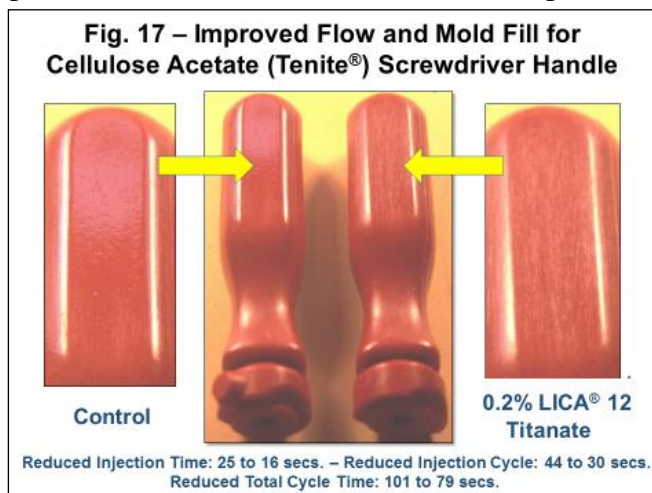
organic substrate (see Fig. 16) and does not have silane hydrolysis-hydroxyl requirements.



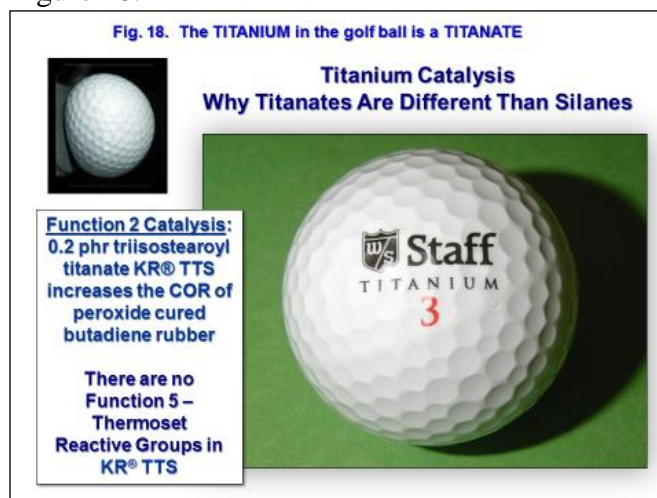
- **Contamination** – Besides the intrinsic incompatibility of many polymers, filler contamination without a coupling agent can

diminish properties such as impact strength – see Figure 14.

- **Poor Fusion** – Fusion of plastics depends on many factors related to polymer flow and surface compatibility. Fig. 17 shows the improved flow and part definition of a Cellulose Acetate compound:



- **Strain Rate - Time Under Load** – These properties are a function of elongation and tensile strength and are measured in many different ways such as the COR (Coefficient Of Restitution). The COR is related to the square root of the Yield Strength divided by the Elastic Modulus – see Figure 18.



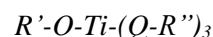
- **Crystallinity** – U.S. Patent 5,340,861 entitled “Polyphenylene Sulfide Composition with improved Crystallizing Characteristic” was issued to the Industrial Technology Research Institute, Hsinchu, Taiwan. Typically, the isothermal

crystallization time at 250°C was reported substantially decreased from 175.2 to 105.8 seconds and the crystallization temperature was increased by 8.09°C using LICA® 09.

Excerpts from “Detailed Description of the Preferred Embodiments” of the patent are provided here:

EXAMPLE 1

A modified polyphenylene sulfide resin containing 3 wt. % titanium organometallic compound and 97 wt. % of molten polyphenylene sulfide resin was prepared. The titanium organometallic compound, which is designated as Organometallic Compound (1), has the following structure:



Wherein:

R' is an alkyl group having three carbons,

Q is a SO₃ group.

R'' is represented by the following formula:

Wherein *R* is an alkyl group, $C_nH_{2n'+1}, n'=12'$.

The molten polyphenylene sulfide resin had a viscosity of 1,800 poise (measured at a temperature of 310°C, and a shear rate of 100 sec⁻¹). The modified polyphenylene sulfide was compounded with a Werner & Pfleider twin-screw extruder (Model ZSK-30). The temperature of the screw die was maintained at 315°C. After the modified polyphenylene sulfide composition was evenly compounded, it was palletized, dried, cooled, and monitored with a Perkin-Elmer differential scanning calorimeter (Model DSC-7) to study the crystallization rate by measuring the isothermal crystallization time and crystallization temperature.

Isothermal crystallization time is defined as the time required for the polyphenylene sulfide sample to crystallize at a given temperature, after the sample was quickly cooled to that given temperature. During the differential scanning calorimetry study, the polyphenylene sulfide sample was heated to a temperature of 310°C, remained there for 3 minutes. Then the sample was quickly cooled at a rate of 200°C/min to a pre-determined temperature of 250°C and maintained at 250°C for 10 minutes. The isothermal crystallization time was determined from the differential scanning calorimetry curve. A lower value of isothermal crystallization time indicates a more rapid crystallizing rate. Crystallization temperature is defined as the temperature at which an exothermic peak was observed in the differential scanning calorimetry study under an isothermal cooling condition. The temperature of the polyphenylene sulfide sample was

first raised to 310°C, and remained there for 3 minutes. The sample was cooled at a rate of 10°C/min to 50°C, and monitored with a differential scanning calorimeter. A higher value of crystallization temperature indicates a more rapid crystallizing rate, which is a desirable characteristic in the fabrication of the polyphenylene sulfide resin.

Results of the isothermal crystallization time and the crystallization temperature are summarized in Table 1.

Comparative Example 1

A polyphenylene sulfide sample was prepared and tested using the same procedure as described in Example 1, except that the test sample did not contain the titanium organometallic compound. Results of the isothermal crystallization time and the crystallization temperature for this comparative sample are also summarized in Table 1.

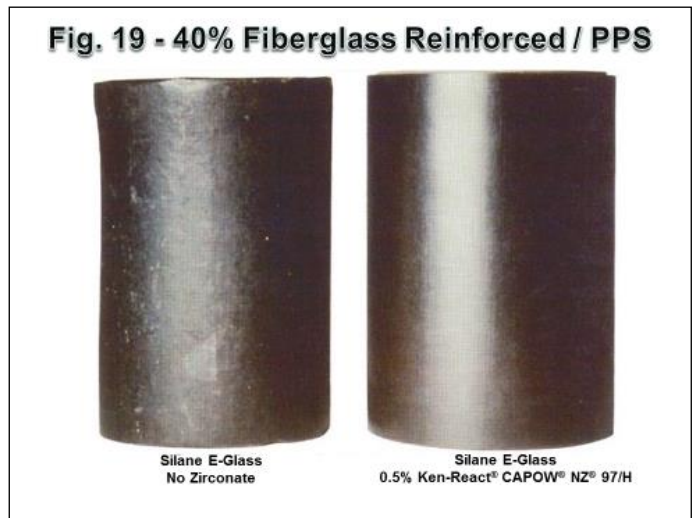
From Table 1, it is evident that the addition of the titanium organometallic compound significantly improves both the isothermal crystallization time and the crystallization temperature of the polyphenylene sulfide resin. The isothermal crystallization time (at 250°C.) was substantially decreased from 175.2 seconds to 105.8 seconds and the crystallization temperature was increased by 8.09°C, with the addition of titanium organometallic compound.

TABLE 1

Item	Example 1	Comparative Example 1
Wt % of PPS Resin	97.0	100.0
Wt % of Organometallic Compound	3.0	0.0
Crystallization Temp. (°C)	246.81	238.72
Crystallization Time (sec.)	105.8	175.2

Our experience has shown levels of titanate at less than 0.1% and typically in the range of 0.2 to 0.4% by weight of polymer produce good results.

For example, An extruded part using 0.5% Ken-React® CAPOW® NZ® 97/H (65% active aromatic amino zirconate on silica powder) Henschel mixed with PPS powder and next extruded is shown in Fig. 19 exhibited increased flow; eliminated necking; doubled Elongation; eliminated embrittlement and cracking; and produced a smooth finished part.



• **Plasticizer Content** – The plasticizer effect of subject titanates and zirconates are largely misunderstood because of prior art thinking as to how process aids, wetting agents, surfactants and plasticizers work in polymers. In its simplest terms, a plasticizer works by being polymer compatible to increase flow and elongation while decreasing tensile strength. In contradistinction, subject titanates are thermally stable catalysts that change the morphology of the polymer to obtain the effect of a plasticizer. At 0.3 phr dosage levels – not only flow and elongation are improved – but also tensile strength – thus allowing significant reductions in plasticizer content or the use of higher molecular weight polymers for added strength.

For example, Fig. 20 shows the denerving of unfilled EPR (Vistalon® 404) rubber with just 0.3 phr of a monoalkoxy phosphato titanate in powder form called Ken-React® CAPOW® KR® 12/H.



Evidence of Ken-React[®] LICA[®] 12 (Neoalkoxy trioctylphosphato titanate) catalytic effects on the morphological behavior of FR PBT was observed by Ping Yuan Liu in EP 547809; Page 7 lines 29 to 51: *“The Neoalkoxy titanate compounds are described in the chapter entitled “Neoalkoxy Titanates” in Bulletin No. KR 1084L-4, “Titanate, Zirconate and Aluminate Coupling Agents” Revised 1987, published by (Kenrich Petrochemicals, Inc.) are the neopentyl (diallyl) oxy titanates. Most preferred is neopentyl (diallyl) oxy,tri (dioctyl) phosphate titanate which is manufactured by Kenrich Petrochemicals, Inc. under the trade name LICA 12. The neoalkoxy titanate processing aid is preferably compounded in a carrier to aid in its distribution throughout the polymer system of the present invention. A compatible carrier can be employed for this purpose, although the preferred carriers are ethylene vinyl acetate or ethylene ethyl acetate. The preferred ratio of the neoalkoxy titanate to the carrier is from 10 to 30 parts of neoalkoxy titanate for 100 parts of neoalkoxy titanate and carrier, with a preferred range of from about 15 to 25 parts neoalkoxy titanate for 100 parts of neoalkoxy titanate and carrier. Any amount of neoalkoxy titanate that will serve to improve the physical properties of the final composition is suitable for use herein. However, the preferred range of the neoalkoxy titanate utilized in the present invention will be from 0.02 weight percent to 1.5 weight percent of the total composition, and preferably from 0.1 weight percent to 1.0 weight percent, and most preferably from 0.2 weight percent to 0.8 percent of the total composition. It has been discovered, surprisingly, that a weight parts above four weight percent of the neoalkoxy titanate, the melt viscosity of the composition is equivalent to what to what it was at when no neoalkoxy titanate was utilized therein. It has also been surprisingly discovered that when the melt viscosity of the resulting composition was decreased through the use of the neoalkoxy titanate the strand integrity, contrary to general experience, is increased to improve the processability of the final composition. This is very surprising because strand integrity, which is directed to the integrity of the strand of the entire composition, is a function of melt strength. It is known that melt strength is a component of melt viscosity, therefore, typically it would be expected that when melt viscosity is decreased the melt strength will also be decreased. In the present invention, the opposite occurs, in that a decrease in melt viscosity does not bring about a corresponding decrease*

in strand integrity. This combination of properties is unexpected”.

Table 5 (next page) summarizes the effect of 0.3% of the 65% active powder form of the neoalkoxy trioctyl phosphato titanate and zirconate on eleven unfilled thermoplastics showing consistently a significant increase in elongation and an increase in tensile strength.

Typically, plasticizer content can be reduced up to 18% in a compound without sacrificing elongation or flexibility.

Examples: In flexible PVC compound, 3-micron CaCO₃ amount can be increased from 45 to 65 phr for Wire and Cable Sheathing applications or from 80 to 150 phr for PVC Window Sills while providing processing and mechanical properties equivalent to conventional plasticizer art.

- **Foamed Parts** – Chemical blowing agents such as Azodicarbonamide are used to offset the increase in compound weight caused by addition of mineral fillers. Since subject organometallics proton coordinate with organics they can be used not only to disperse the AZO but also increase the foamability of the polymer due to the catalytic effect of increasing elongation and tensile, thus reducing open cell formation– see Fig. 21.

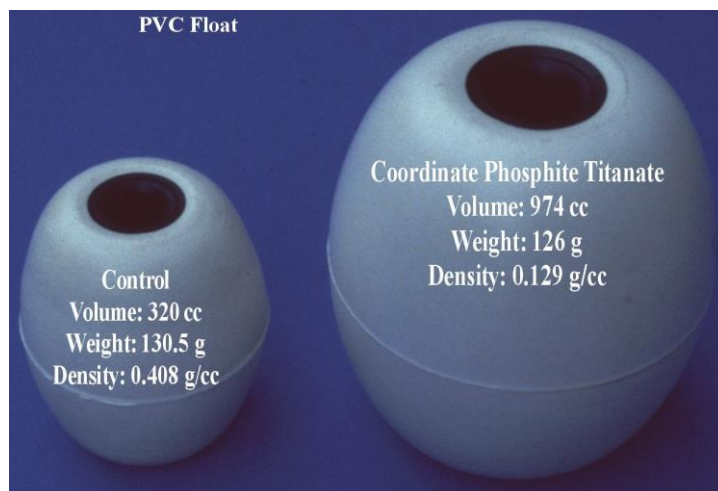


Figure 21 – Exothermic AZO foamed PVC float-130.5g weight (left) with no titanate and a similar PVC float-126.0g (right) using KR[®] 55 to create finer cell structure and triple the volume by virtue of AZO dispersion and polymer catalysis.

TABLE 5 – EFFECT OF NEOALKOXY TITANATE (LICA® 12) AND NEOALKOXY ZIRCONATE (NZ® 12) ON THE PROPERTIES OF INJECTION MOLDED UNFILLED POLYMERS

Coupling Agent Additive	Polymer Type Resin	CAPOW®	Tensile Yield K psi	% Elongation @ Break	Flexural Strength K psi	Flexural Modulus psi x 10 ⁴	Notched Izod @ R.T. ft.lb./in.	% Water Absorption @ R.T. 24 Hr. Imm.
		Form Weight % of Resin						
None	ABS	-	7.1	18	12	41	3.0	0.30
LICA 12	ABS	0.3	8.4	39	26	62	4.4	0.19
NZ 12	ABS	0.3	8.2	34	30	70	4.1	0.20
None	Acetal	-	8.8	40	13	38	1.0	0.22
LICA 12	Acetal	0.3	9.9	64	20	47	2.7	0.17
NZ 12	Acetal	0.3	9.7	61	21	53	2.1	0.14
None	Acrylic	-	1.2	5	15	26	0.3	0.27
LICA 12	Acrylic	0.3	1.7	31	23	29	0.7	0.15
NZ 12	Acrylic	0.3	1.7	23	24	35	0.7	0.17
None	CAB	-	5.8	42	8.3	25	1.7	1.8
LICA 12	CAB	0.3	6.5	72	9.4	33	2.6	0.9
NZ 12	CAB	0.3	6.4	67	9.3	32	1.9	1.5
None	Nylon 6	-	18	60	16	41	1.0	1.6
LICA 12	Nylon 6	0.3	24	81	25	52	1.8	0.9
NZ 12	Nylon 6	0.3	19	78	22	49	1.7	1.0
None	PC	-	9.7	65	13	33	6.0	0.20
LICA 12	PC	0.3	10.5	89	27	41	6.9	0.14
NZ 12	PC	0.3	10.4	69	19	42	7.4	0.16
None	PP	-	4.9	120	-	21	0.7	-
LICA 12	PP	0.3	5.7	142	-	26	1.1	-
NZ 12	PP	0.3	5.9	157	-	26	1.4	-
None	HDPE	-	4.5	820	-	19	6.0	-
LICA 12	HDPE	0.3	5.4	1000	-	24	6.7	-
NZ 12	HDPE	0.3	4.9	870	-	20	6.9	-
None	PBT	-	8.7	200	12	34	1.0	0.08
LICA 12	PBT	0.3	9.6	250	17	49	1.7	0.03
None	PPO	-	11	48	35	35	10	0.10
LICA 12	PPO	0.3	12	50	38	39	13	0.07
NZ 12	PPO	0.3	14	57	43	35	14	0.06
None	PS	-	5.1	10	9.5	37	2.5	-
LICA 12	PS	0.3	5.9	51	9.9	37	3.7	-
NZ 12	PS	0.3	5.8	17	10.3	41	2.9	-

Using Optical Expandometry Javier Escudero Arconada jabo@fmc.uva.es and Professor Miguel Ángel Rodríguez Pérez marrod@fmc.uva.es reported data on AZO foamed PP in their work entitled, “*Study of the products CAPS® KR® 12/L and CAPOW® KR® 12/H from Kenrich Petrochemicals*”, as shown in Figures 22 to 27

Conclusion – Many of the sustainability challenges facing the molding and processing of polymer compositions of dissimilar organic and inorganic materials can be facilitated using subject 1.5-nanometer heteroatom organometallic titanates and zirconates to make their use more efficient and move the bar on Industry 4.0 parameters.

Work performed by:
 Javier Escudero Arconada jabo@fmc.uva.es
 Miguel Ángel Rodríguez Pérez marrod@fmc.uva.es

Study of the products CAPS KR/12L and CAPOW KR/12H from Kenrich Petrochemicals

CellMat Laboratory

CellMat Group, Condensed Matter Physics Department
 Faculty of Sciences, University of Valladolid, Spain

Figure 24

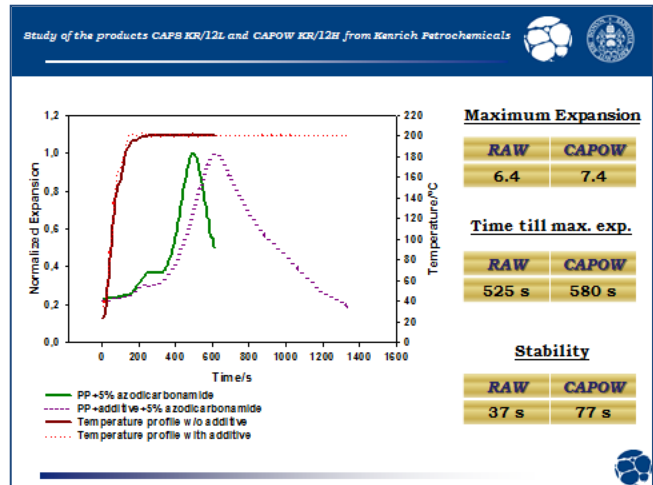


Figure 27

Study of the products CAPS KR/12L and CAPOW KR/12H from Kenrich Petrochemicals

Optical Expandometry

PP + 5% azodicarbonamide PP + CAPOW + 5% azodicarbonamide

Using image processing procedures quantitative data has been obtained

Figure 25

Study of the products CAPS KR/12L and CAPOW KR/12H from Kenrich Petrochemicals

Mechanical Properties for PP

Expansion Ratio 5 (No CAPOW) Expansion Ratio 5 (CAPOW)

Expansion Ratio 6 (No CAPOW) Expansion Ratio 6 (CAPOW)

Figure 28

Study of the products CAPS KR/12L and CAPOW KR/12H from Kenrich Petrochemicals

Optical Expandometry

PP + 5% azodicarbonamide

PP + Ken-React® CAPOW® KR® 12/H + 5% azodicarbonamide

Using image processing procedures quantitative data has been obtained

Figure 26

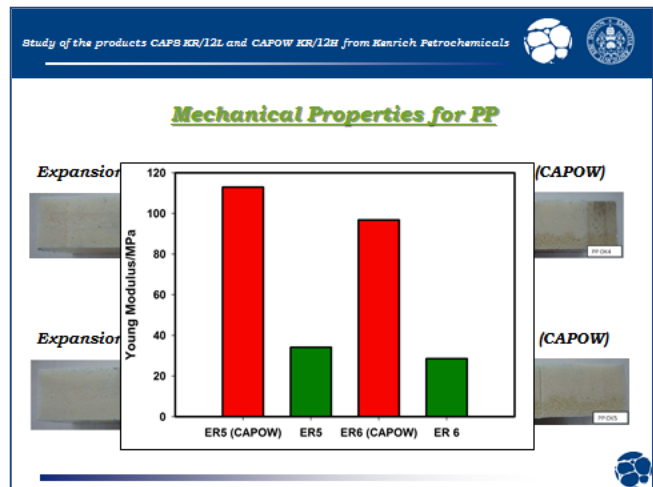


Figure 29