Ti AND Zr CATALYSTS IN THE MACROMOLECULAR MELT REGENERATE UNFILLED AND FILLED VIRGIN, REGRIND AND RECYCLED PLASTICS

Salvatore J. Monte, Kenrich Petrochemicals, Inc. www.4kenrich.com

Abstract

A thermally stable neoalkoxy titanate coupling agent [neopentyl (diallyl) oxy, tri(dioctyl)phosphato titanate] and its zirconate analog are shown to act as a REPOLYMERIZATION catalyst in the unfilled or filled macromolecular melt to increase mechanical properties.

When two or more polymers are present, COPOLYMERIZATION occurs to create a compatibilzation effect of multi-dissimilar addition & condensation polymers.

For example, where delamination occurs in the injection molding of HDPE parts containing more than 5% PP, blends of PE/PP-50/50 are made compatible with titanate catalyst.

Since Ti and Zr are used as catalysts in the formation of addition (polyolefins) and condensation (polyesters) polymers, the catalytic compatibilization effect will be shown to occur in a mixture of macromolecules such as HDPE/PP/PET. Multi-polymer compatibility obviates the need for matching polarities such as needed with copolymer compatibilizers and depolymerization concerns when maleated copolymers come in contact with condensation polymers such as PET and Nylon.

When powder or pellet masterbatches of subject organometallics are made using Aluminum based inorganics as the carrier, a combination metallocene-ZN catalysis effect is obtained to optimize compatibilization.

In addition, the Neoalkoxy structure of the organometallic catalyst allows for proton coordination coupling with the interface of non-silane reactive inorganics and organics such as CaCO3, Portland cement, BaSO4, Carbon Black, and other organics such as pigments, dyes, and cellulosics. The titanate coupling mechanism does not require hydrolysis as with silanes wherein water of condensation remains at the interface to create subsequent delamination when subjected to water boil aging tests.

The combination of the SIX FUNCTION effects of subject organometallics will be shown to achieve many of the issues related to the sustainability goals of plastic recycling and the more efficient use of raw materials.

Introduction

The author invented the first heteroatom titanate in 1973 and has stayed true to his original mission statement to “teach the more efficient use of raw materials through titanium chemistry”. The results are shown in: 31-U.S. Patents; a 340-page Ken-React® Reference Manual (80,000 copies distributed); several book chapters; over 450-ACS CAS abstracted “Works by S.J. Monte”; several thousand patents and abstracted works by others employing his invention catalysts in applications as diverse as cosmetics, digital copier toner, proppants for fracking; OLED’s for brighter screens; LOVA gun propellant; and solid rocket fuel. The latter two author’s application patents were held under U.S. DOD Secrecy Orders for 14-years. See References.

This paper will be focused on catalysis and coupling to achieve compatibilization and regeneration of filled and unfilled plastics during melt processing.

Discussion

Figure 1 points to the SIX FUNCTIONS of a neopentyl (diallyl) oxy, tri(dioctyl)phosphato zirconate and why Function 1 COUPLING is different than silanes.

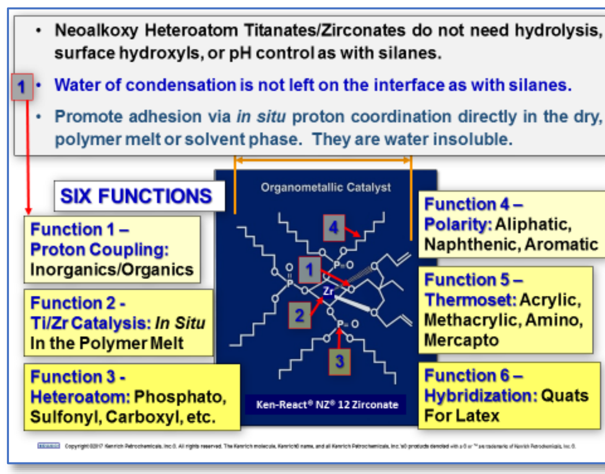


Figure 2 illustrates FUNCTION 1 coordination coupling of a neoalkoxy titanate to non-silane reactive 3-micron $CaCO_3$.

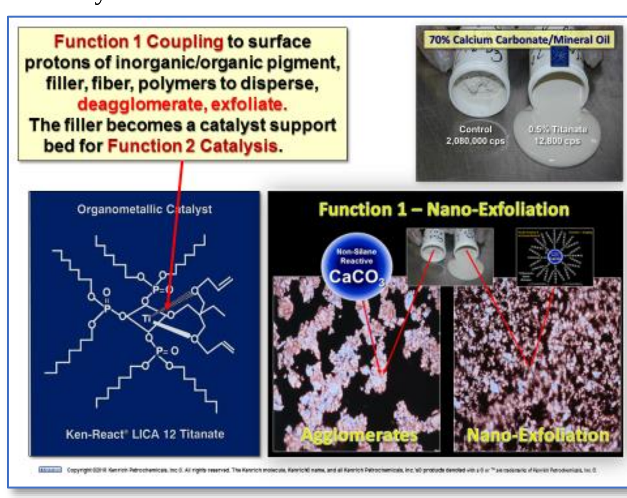


Figure 3: Filled and Unfilled PP mold faster and at lower temperatures similarly because of Function 2 Catalysis. Eureka! Flow is not due to Function 1 Filler Coupling alone.

Figure 4: The combination of Function 1 Coupling and Function 2 Catalysis creates flexible compositions.

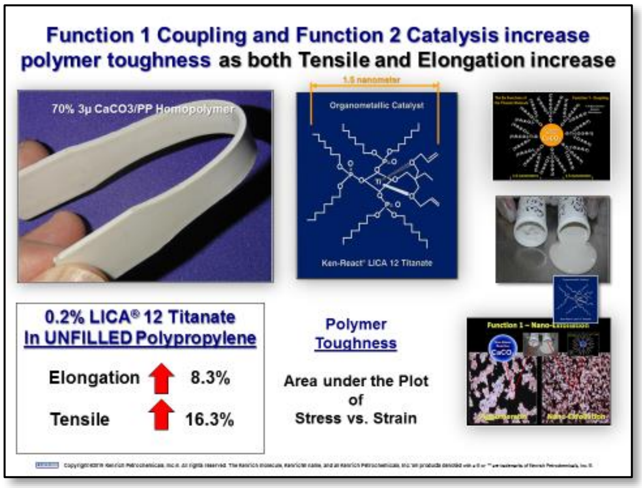


Table 1: Unfilled PP Mechanical Properties are improved due to Function 2 Catalysis increasing both elongation and tensile predicting higher impact strength and greater foamability.

TABLE 1 – REPOLYMERIZATION CATALYSIS EFFECT OF NEOALKOXY TITANATE CAPOW® L® 12/H ON THE PROPERTIES OF INJECTION MOLDED UNFILLED PP

CAPOW® Coupling Agent Additive	Weight % of Resin	Tensile Yield K psi	% Elong. @ Break	Flexural Modulus psi x 10^4	Notched Izod @ R.T. ft.lb./in.
Control	0.00	4.9	120	21	0.7
L 12/H	0.10	5.4	127	24	0.9
L 12/H	0.30	5.7	142	26	1.1
L 12/H	0.50	5.6	148	22	1.4
L 12/H	0.75	5.2	139	21	1.1

Table 2: Unfilled HDPE Mechanical Properties are also improved due to Function 2 Catalysis.

TABLE 2 – REPOLYMERIZATION CATALYSIS EFFECT OF NEOALKOXY TITANATE CAPOW® L® 12/H ON THE PROPERTIES OF INJECTION MOLDED UNFILLED HDPE

CAPOW® Coupling Agent Additive	Weight % of Resin	Tensile Yield K psi	% Elong. @ Break	Flexural Modulus psi x 10^4	Notched Izod @ R.T. ft.lb./in.
Control	0.00	4.5	820	19	6.0
L 12/H	0.10	4.9	910	27	6.2
L 12/H	0.30	5.4	1000	24	6.7
L 12/H	0.50	5.0	1000	21	7.0
No Run					

Table 3: Both Addition and Condensation polymers flow faster at lower temperatures during melt processing plant trials of molded/extruded parts due to Function 2 Catalysis.

TABLE 3 – A SUMMARY OF THE CATALYTIC EFFECT OF VARIOUS TITANATES AND ZIRCONATES ON THE % REDUCTION IN PROCESS TEMPERATURE AND CYCLE TIME OF MELT PROCESSED MOLDED AND EXTRUDED PLASTIC PARTS

					% Reduction	
Plant Trial	Polymer	Molding Process	Part Produced	Coupling Agent	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.	14,928 gms.	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 (Soltex)	Inj.	Carry Box	CAPS L 12/E	8.3	8.7
15	PP (Himont SB-787)	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 L 09/K	11.9	22.1
24*	ABS (33838 Regrind)	Inj.	Carrier Box	CAPS L 12/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 (Celanese #2012)	Inj.	Proprietary	CAPOW KZ TPP/H	3.4	31.2
32	PBT (Cel. 2002-2EK)	Inj.	Proprietary	CAPOW L 12/H	1.1	30.5

Figure 5 shows the super plasticizer catalytic effect of 0.2 phr of a phosphato titanate on 1000g of Vistalon® 404 EPR (Ethylene Propylene Rubber) sheeted off a 2-roll mill.

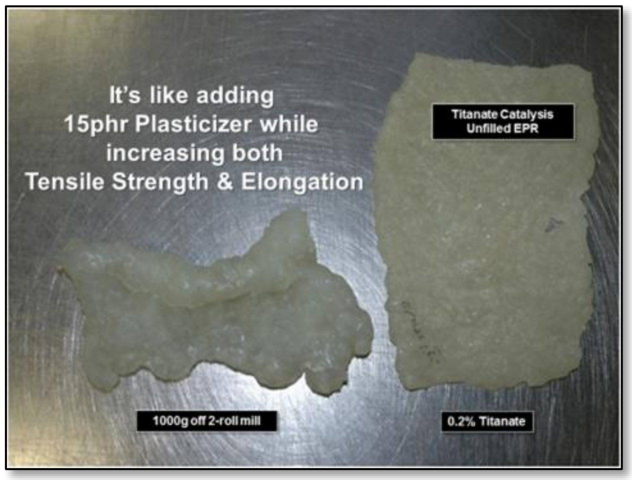


Figure 6: A phosphato titanate Function 1 couples organic AZO while Function 2 catalysis makes Unfilled PP stronger to accept N_2 gas without open cell structure formation.

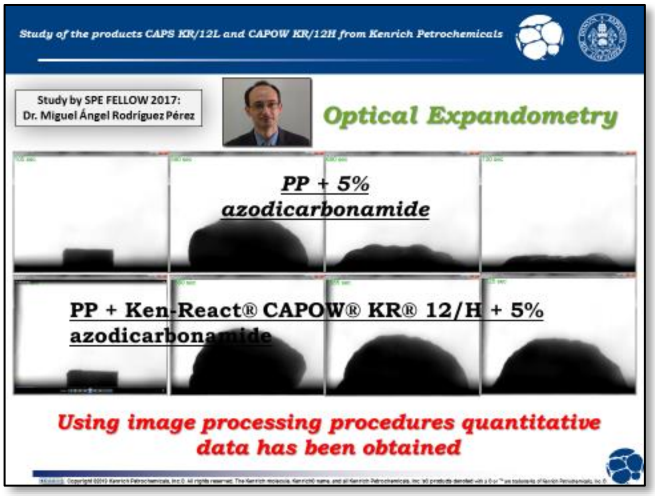


Figure 7: Polyolefin Foam Stability is doubled using titanate catalyst.

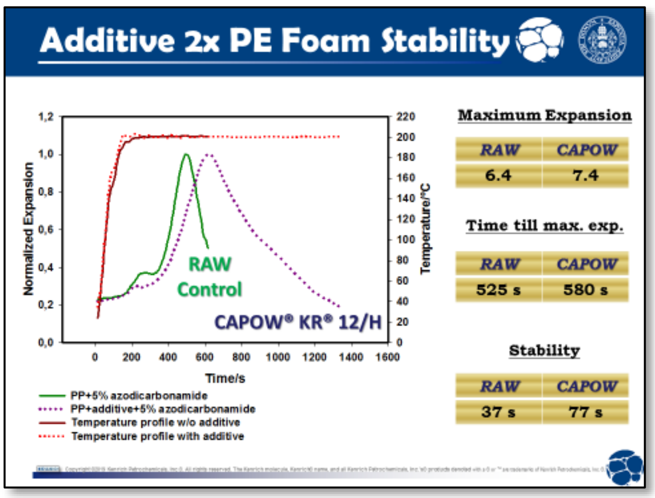
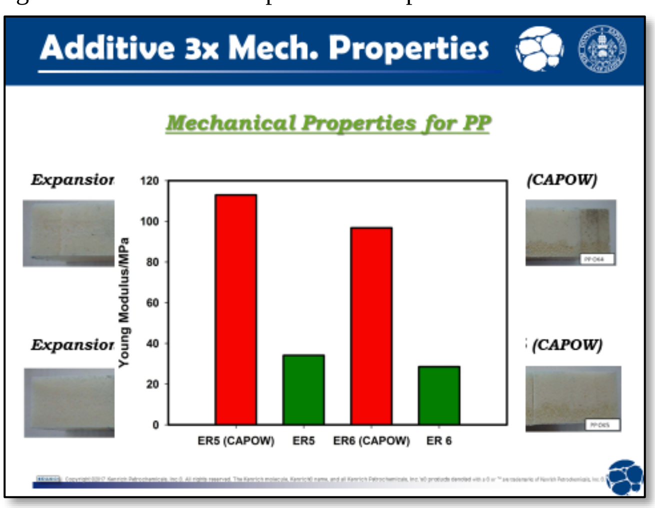


Figure 8: Mechanical Properties are tripled.



RDX/CAB propellants are made more powerful and safer.

Figure 9: 0.2% phosphato zirconate catalyzes 100% unfilled HDPE Regrind to make it stronger and blow mold faster.

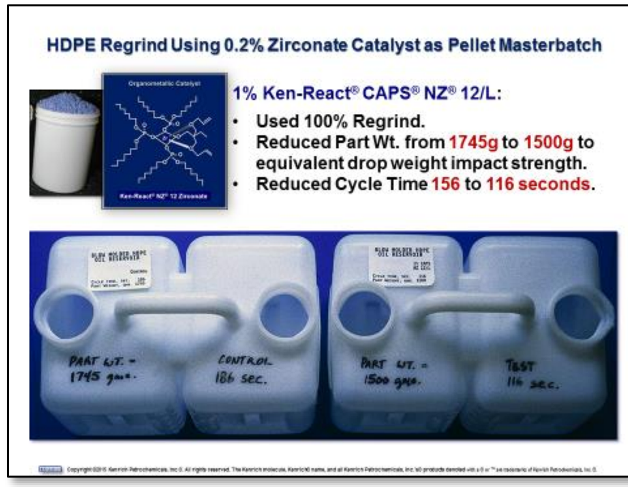


Figure 10: 0.2% phosphato zirconate added to blue liqui-color catalyzes pigmented HDPE Virgin/Regrind blend to make part stronger and blow mold faster at lower temperature.

Figure 11: 0.2 phr of a cycloheteroatom zirconate catalyst doubles the output at 85°F lower temperature of a clear recycled PVC extrudate while maintaining dimensions.

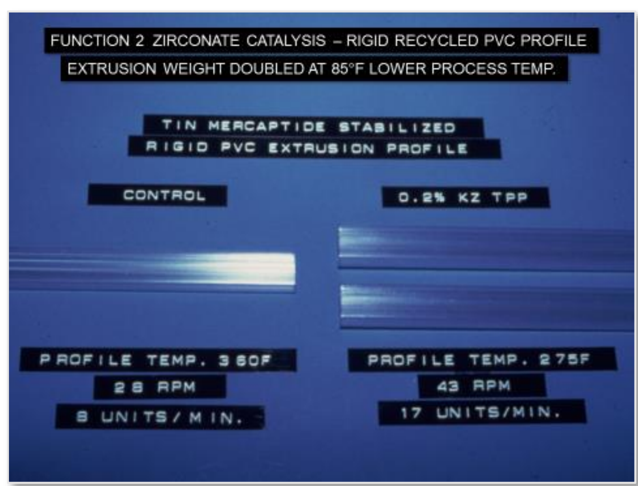


Figure 12: Phosphato titanate catalyzes LDPE/PP blends to sustain molecular weight through six extrusion cycles.

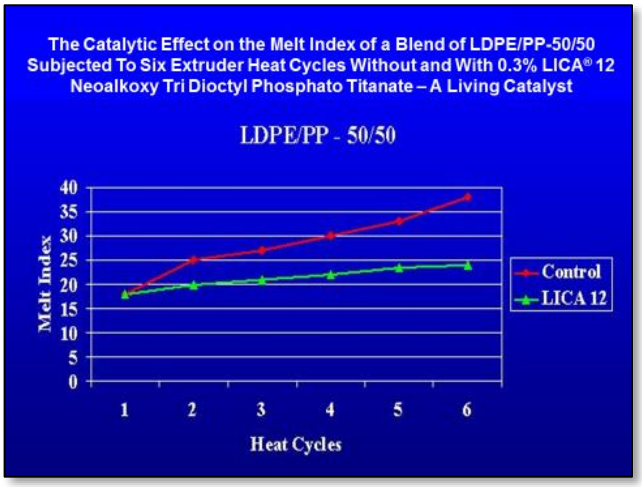


Figure 13: Typically > 5% PP in PE creates delamination. Phosphato titanate regenerates LDPE/PP-80/20 Regrind. In situ catalysis allows melt screw to become a reactor.

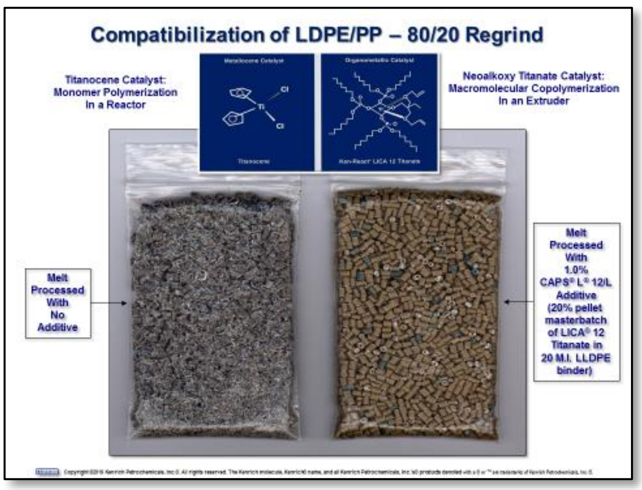


Figure 14: PET & PC are Condensation polymers. Phosphato titanate catalyzes Recycled PET/PC-80/20 Blend while maintaining transparency and strength.

Figure 15: 0.2 Titanate compatibilizes unfilled HDPE (Addition Polymer)/Nylon (Condensation Polymer) blend.

Figure 16 shows the effects of 0.2 phr titanate on FG/PC. Upper half is control; Lower half has 0.2% titanate.

Figure 17: The dispersive effect of a neopentyl (diallyl)oxy, tridodecylbenzenesulfonyl titanate emulsified into water to disperse Cabot XC-72R conductive carbon black without any mechanical stirring. Carbon/organics can be coupled in situ.

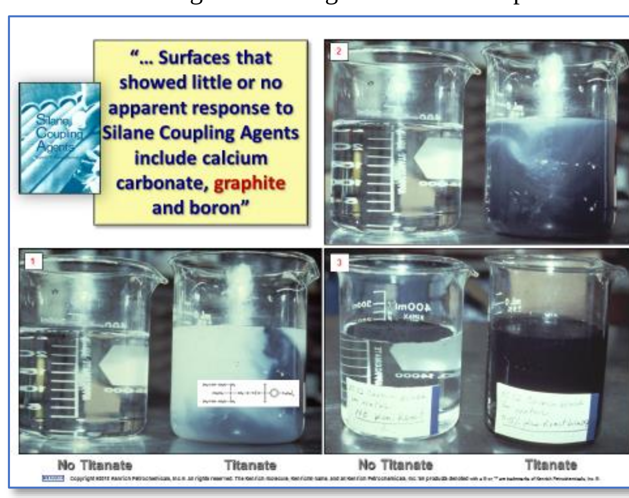


Figure 18: Patented compatibilization of oil soaked sea water sand/Portland cement composition made compatible with a proprietary titanate and is predictive of the compatibilization of all manner of inorganics and organics in recycle; and polymer modification of Portland cement based concrete.

Figure 19: 30% Talc/PP with/without phosphato titanate.

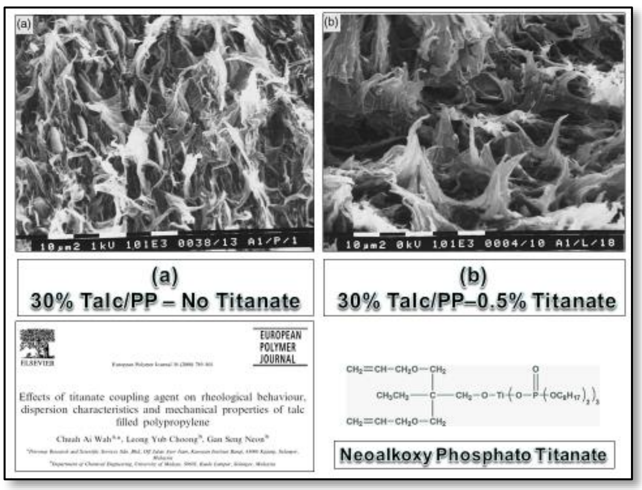


Figure 20: Adhesion of silane sized E-Glass in ETFE without and with a Neoalkoxy Aliphatic Amino Zirconate.

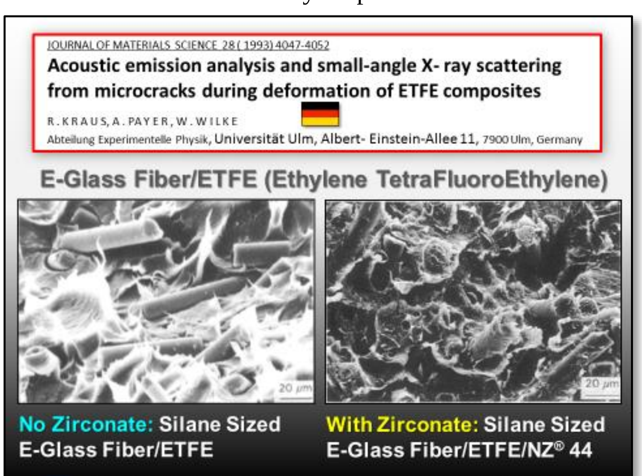


Figure 21: Post consumer and post industrial recycle need compatibilizers. There are 7-classes of plastics because they are incompatible with each other. Fillers inhibit strength. Bipolar and maleated copolymer compatibizers have limitations. Result, expensive sorting and cleaning is needed.

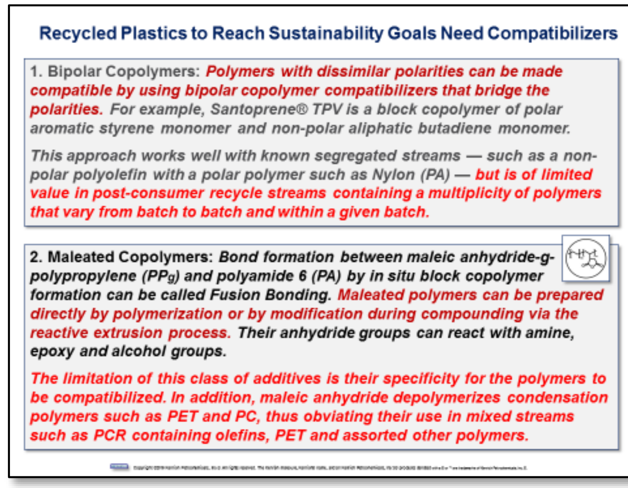


Figure 22: Conventional Catalysis art based on Ti, Zr & Al.

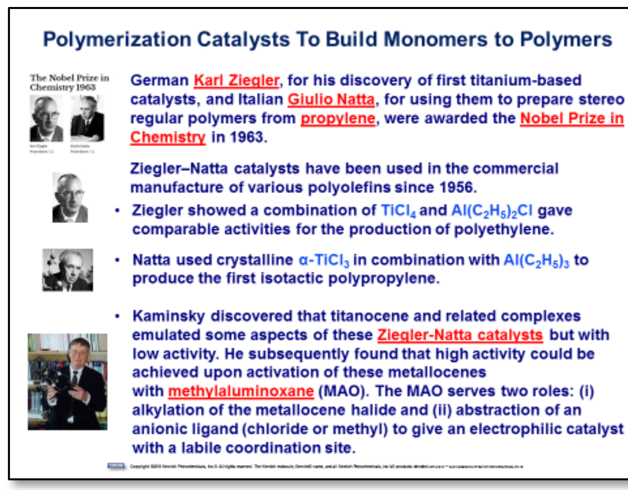


Figure 23: Monte uses Ti, Zr, and Al art to create additives in pellet/powder form to couple and catalyze in situ in the melt.

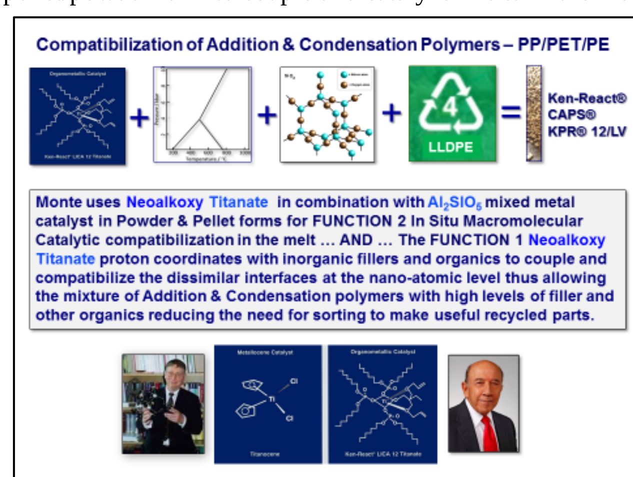


Figure 24: 1.5% Ken-React® CAPS® KPR® 12/LV compatibilizer pellet – melt processed at 10% lower temperature – compatibilizes LLDPE extruded film/PP injection molded bottle caps/PET thermoformed clam shells.

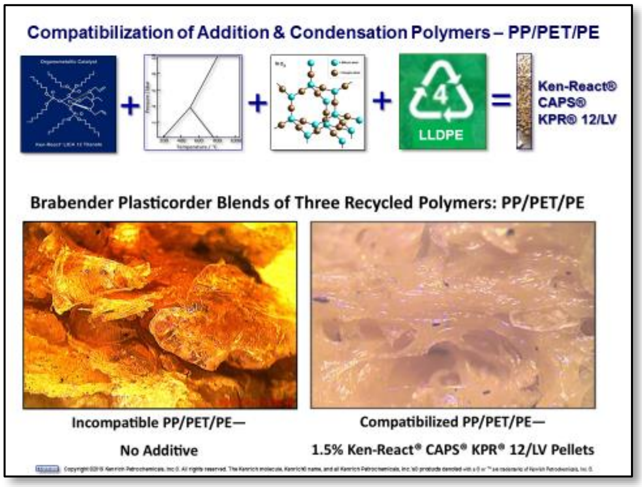


Figure 25: Reactive compounding shear needed in the melt. A common mistake is run tests under the same conditions.

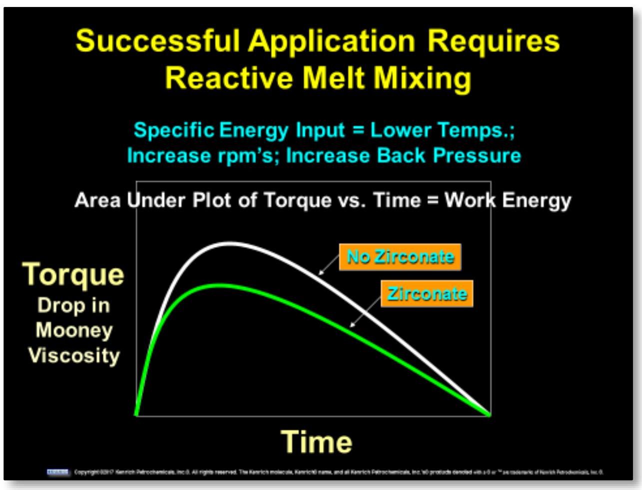
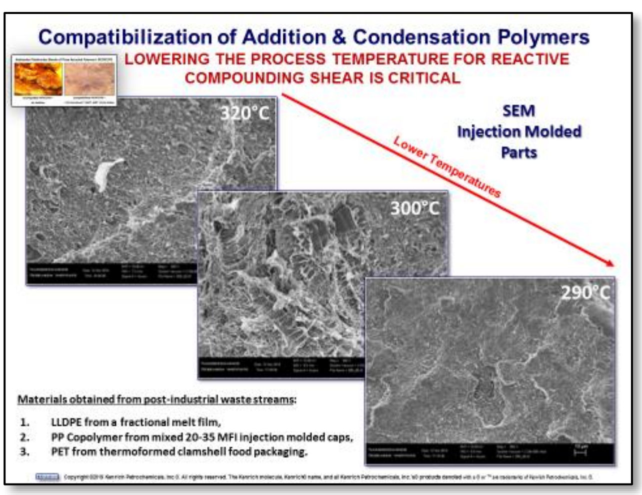


Figure 26: Compatibilization of PP/PET/PP enhanced as melt process temperature is lowered to optimize Ti/Al catalysis at the 1.5-nanometer atomic level – 290°C better than 320°C.



Conclusion

26-Figures and 3-Tables were used to focus on catalysis and coupling to achieve compatibilization and regeneration of filled and unfilled plastics during melt processing so as to achieve more efficient use of polymeric compound materials through Ti, Zr and Al catalysis and coupling. I trust this paper will prove useful in overcoming the many sustainability challenges associated with recycling.

The author is notorious for showing over a hundred slides in a half-hour presentation when the topic is expanded to include the variants of: The SIX FUNCTIONS of titanates and zirconates; compounding equipment and melt processing conditions; the need for various additive forms; thermoset catalysis effects; interaction with other additives; additive selection; dosage considerations; sequence and methods of addition; inorganic and organic filler coupling; filler and fiber geometry and effect on reinforcement; chemistry at the nano-interface compared to silanes and the silane mindset; the concept of Critical Pigment Volume Concentration and effects on filler thermoplastic strain properties; coupling via hydrolysis creating water boil delamination at the fiberglass interface; adhesion to polar and non-polar substrates; solubility parameters in aliphatic and aromatic vehicles; emulsification for waterbased systems; flame retardance and hydration synergism using nano-titanium intumescence to control burn rate and burn rate exponent; anti-corrosion; hydrophobicity; anti-aging; conductivity; rheology; reduced plasticizer content; endo and exothermic foaming; using bio-based materials in compounds; and the thousands of commercial applications developed since my first titanate invention in 1973.

The SPE template says the author should limit the paper to 5-pages, and is allowed 8-pages if needed. So, I am going to fill the balance of this paper with web links and 100 of the 1,000's of Science IP ACS CAS Search Service references based on key words: "Ti/Zr Coupling Agents".

Web Links and References

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