

Why titanates and zirconates are different than silanes

By Salvatore J. Monte
Kenrich Petrochemicals Inc.

(First of two parts)

The reason why titanates and zirconates may be different or even better adhesion promoters than silanes lies in the intrinsic multi-functional chemistry of tetravalent organometallic titanium and zirconium as compared to silicene at the nano-interface where dissimilar materials meet. The titanate/zirconate six functions is a useful collective method to teach why they do what they do where silane three functions do not (Fig. 1).

TECHNICAL NOTEBOOK

Edited by John Dick

If one looks at the Periodic Table in Fig. 2, according to the atomic number, there seems to be little in common between Si (silanes), Ti (titanates) and Zr (zirconates).

But look at the Periodic Table according to valence in Fig. 3, as drawn by Dow's James Franklin Hyde, and there is much in common between tetravalent Si, Ti and Zr. Hyde has been called the "Father of Silicones" and is credited with the launch of the silicone industry in the 1930s.

To silanes, titanates and zirconates are tetravalent, but different because of the six functions.

Function 1 'coupling' Ti vs. Si difference

Until his death in 1991 at the age of 75, Edwin P. Plueddemann was considered the world's foremost expert on silane coupling agents. In 1982, Ed wrote the book, "Silane Coupling Agents" (Fig. 4) and said on page 114: "Surfaces that showed little or no apparent response to Silane Coupling Agents include calcium carbonate, graphite and boron." Note: organic substrates such as cellulose, Kevlar, azodicarbonamide blowing agents, nitramine explosives, nitrides, sulfates, sulfur, polymers, etc. are not listed.

The 1985 340-page reference manual by the author of this paper starts by claiming:

"Coupling agents are molecular bridges at the interface between two substrates, usually but not limited to an inorganic filler and an organic polymer matrix. Titanium-derived coupling agents are unique in that their reaction with the free protons at the inorganic interface results in the formation of organic monomolecular layers on the inorganic surface. The absence of polymolecular layers at the interface together with the chemical structure of the titanates create novel substrate surface energy modification and polymer phase interactions often resulting in viscosity reductions in unfilled, as well as filled polymer composites.

"Typically, titanate-treated inorganics are hydrophobic, organophilic and organofunctional. When incorporated into polymer systems

they often promote adhesion; catalyze; improve dispersion and rheology; improve strength; do not create embrittlement; improve mechanical properties; make inorganic loadings above 50 percent desirable; prevent phase separation; inhibit corrosion, etc.

"Reactivity is possible with diverse substrates such as CaCO_3 , BaSO_4 , carbon black, azodicarbonamide, nitrates, hydrates, cellulose, phthalate and lake pigments, peroxides, aramid and carbon fibers, organics and polymers, as well as classical mineral and metal oxide-derived inorganics." (Fig. 5).

Fig. 6 shows in situ function 1 titanate coupling and function 2 titanium catalysis allow 70 percent, 3-micron filled PP homopolymer to
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Executive summary

In 1973, after more than a decade servicing the rubber industry with aromatic plasticizers and dispersions, Salvatore Monte, author of this paper, invented the first of many organometallic titanate or zirconate coupling agents while working on a zinc oxide masterbatch. He has spent 50 years teaching how they provide significantly different alternative coupling mechanisms when compared to silanes.

The differences are explained through their chemistry and six functions. It will be shown that the interfacial coupling mechanism of a neoalkoxy organometallic via in situ surface proton (H^+) coordination may be superior to silane (OH^-) pretreatment condensation mechanisms because of the number of bonds and the differences in interfacial hydroxyl group availability.

In addition, silane hydrolysis leaves water of condensation on the interface during siloxane formation, which may be detrimental to long-term aging. For example, when inorganic and organic composites are subjected to a 240-hour, 10-percent saltwater boil, silanes often fail while zirconates and titanates do not. The paper will show why a zirconate can enable silane-sized E-Glass adhesion to a non-polar fluoropolymer.

The research also addresses questions such as: How can a silane couple CNTs, graphene, sulfates, carbonates or cement that have no hydroxyl groups? How can nano-intumescence be achieved with a silane with no phosphato heteroatom functionality built into its ligands?

Current work from the literature will be shown and some of the more interesting developments in the field of alternate interface technologies such as graphite, graphene and CNTs will be reviewed using recent ACS CAS abstracts.

Fig. 1: Comparison of the titanate/zirconate six functions and silane three functions.

Titanates and Zirconates – They Are Different Than Silanes	
Titanate/Zirconate Six Functions	Silane Three Functions
(1) (2) (3) (4) (5) (6) $(\text{RO})_n\text{-Ti-(-O-X-R'-Y)}_{4-n}$	(1) (2) (5) $(\text{RO})_3\text{-Si-(R'-Y)}_1$
1. $(\text{RO})_n$ = Proton [H] Reactive	= Hydroxyl [OH] Reactive
2. $-\text{Ti-O}$ = Catalytic Reactive	= $-\text{Si}$ - Stable Carbon Bond
3. $-\text{X}$ = Heteroatom	= None
4. $-\text{R}'$ = Thermoplastic	= Carbon bond to-Y
5. $-\text{Y}$ = Thermoset	= Thermoset
6. $)_{4-n}$ = Hybrid, Quat, Chelate Coordinate	= Monofunctional

Fig. 2: Comparison of the titanate/zirconate to silane according to atomic number.

The Periodic Table according to Atomic Number	
Silane = Si	Carbon = C
Titanate = Ti	Oxygen = O
Zirconate = Zr	Hydrogen = H
An Atomic Number Mindset Does Little to Connect the Coupling Relationship between Ti = Zr and Si = C	

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bend 180° without stress cracking. In the first decade—up until the mid-1980s—the high filler

loading was thought to be because of the function 1 dispersion effect—until field tests and plant trials showed flow effects and faster injection mold cycles at lower temperatures in unfilled thermoplastic parts. Eureka—polymer flow was also caused by function 2 catalysis.

Fig. 3: Comparison of the titanate/zirconate to silane, according to valence.

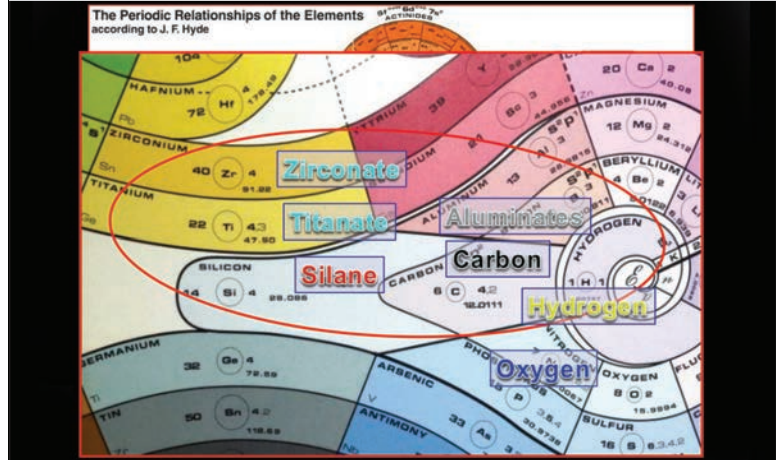


Fig. 4: A chart from page 114 of "Silane Coupling Agents" produces a chart showing silane effectiveness on silica—but not on carbon black and CaCO₃.

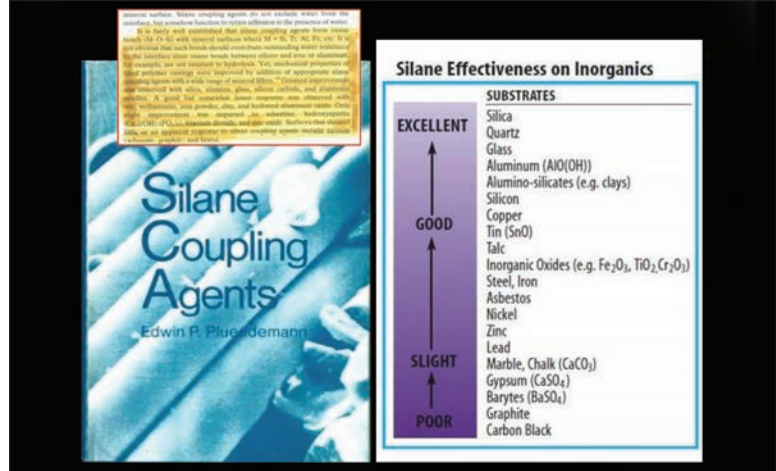


Fig. 5: Page 1 of 340-page reference manual published in February 1985 by Monte. Patents by Monte held under DOD secrecy orders for 11 years for solid rocket fuel (Al/AP/HTPB PU) and for 15 years for enhanced energetic composites (RDX/HMX/Al/CAB) to prevent unplanned detonation, solving the challenges of the insensitive munitions program.

TITANATE COUPLING AGENTS

Coupling agents are molecular bridges at the interface between two substrates, usually but not limited to an inorganic filler and an organic polymer matrix. Titanium derived coupling agents are unique in that their reaction with the free protons at the inorganic interface results in the formation of organic monomolecular layers on the inorganic surface. The absence of polymolecular layers at the interface together with the chemical structure of the titanates create novel substrate surface energy modifications and polymer phase interactions often resulting in viscosity reductions in unfilled, as well as filled polymer composites.

Typically, titanate-treated inorganics are hydrophobic (see Figure 1), organophilic and organofunctional. When incorporated into polymer systems they often: promote adhesion; catalyze (see Figure 2); improve dispersion and rheology; improve impact strength; do not create embrittlement (see Figure 3); improve mechanical properties; make inorganic loadings above 50% desirable (see Figure 4); prevent phase separation; inhibit corrosion (see Figure 5); etc.

Reactivity is possible with diverse substrates such as CaCO₃, BaSO₄, carbon black, azodicarbonamide, nitrates, hydrates, celluloses, phthalate and lake pigments, peroxides, aramid and carbon fibers, organics and polymers, as well as classical mineral and metal oxide-derived inorganics.

Figure 1. The hydrophobic effect on the flexural fracture surface of a glass fiber treated with 0.5% KR 138S in polystyrene matrix after 48 hour water boil.

Figure 2. Off-the-road tire filled with titanate containing 2 component urethane filling compound having many patented features.

Figure 3. 70% calcium carbonate filled polypropylene with KR TTS is shown on the right and is compared to virgin polypropylene on the left.

Figure 4. Proprietary pigmented virgin HDPE copolymer (left) and 50% CaCO₃ (Atomite) 0.5% KR TTS filled HDPE homopolymer (DMDJ-7006 Natural 7) (right) injection molded milk crates having equal impact strength.

Figure 5. The corrosion protective effect of KR 138D Quat on mild cold rolled steel after exposure at 100% relative humidity at 50°C for 3 hr. Control (left), KR 138D-15 min. dry (center), KR 138D-16 hr. dry (right).

Figure 5A. Space Shuttle booster rocket coating uses KR 112S to meet stringent NASA performance requirements. New generation solid rocket fuel containing Ken-React organometallics is under development.

Fig. 7 shows the function 1 dispersion effect of 0.35 percent titanate on non-silane reactive 80-percent BaSO₄-filled non-polar mineral oil.

Space limits providing a reference for every reactable interface claim made above, so **Fig. 7** is taken from my 31st patent, EP 2 614 040 B1 granted in the European Union on April 12, 2017, in which a titanate was added to water and dispersed followed by spent drilling mud (BaSO₄ saturated with hydrocarbon oil), and then Portland cement admixed to make a useful composition.

ASTM C150-Type I Portland cement consists of the following interfaces—some of which are non-silane reactive—and many used in polymeric compositions (**Fig. 8**).

Fig. 9 is taken from the author's 32nd patent on Portland cement issued on March 5, 2020, the same day we landed from a flight from Frankfurt, Germany, where the author presented in Darmstadt on March 3 a paper entitled "Repolymerization and compatibilization of thermoplastics in post-consumer recycling processes by using titanate ester catalysts." (**Fig. 10**).

Fig. 9 shows titanate-modified ordinary Portland cement (ASTM C150 Type I) composition containing oil-soaked sea water sand made into a useful composition. Titanate-treated Portland cement (ASTM C150 Type I) mortar mix (ASTM C778) preparations in order to conduct ASTM C305 cube compression tests showed the cement to H₂O ratio is reduced by 31 percent to equivalent slump (flow) using a dynamic tap table. Just

like plasticizers in polymers, the reduction in water to equivalent flow leads to higher compression strength/physical properties.

The author claims the window of efficacy in Advanced Mechanical Recycling of Polymers Nos. 1-7 fillers, carbon and ground rubber will make sustainability goals in recycle more obtainable. See link for more information:

https://vantagevinyl.com/wp-content/uploads/2021/07/Monte_Kenrich.pdf

Fig. 11 shows an emulsified titanate in water disperses added conductive carbon black (Cabot XC-72R) completely absent mechanical stirring and shows conductive carbon is well-dispersed into non-polar 20 M.I. LLDPE on a 2-roll mill increasing volume conductivity (Ω.cm) twofold.

The effects of the nano-titanium organo-functionality in ASTM concrete lab tests and by analogy extrapolated from past materials experience and inventive skills results in, or will result in:

- greater compression strength;
- efflorescence elimination; faster mix cycles; polymer compatibilization with epoxy, hydrocarbons such as oil, asphalt and plastics 3-D printing;
- improved adhesion to PE reinforcing fibers and fabric;
- adhesion to graphite, aramid, and nano-reinforcements such as clays, graphene, rCB, etc.;
- allow the incorporation of spent sulfur from refineries;
- prevention of rebar corrosion;
- less static build due to friction while flowing down metal chutes;
- more uniform cell structure in cement foam;
- more flexible structures for improved earthquake resistance; and
- the creation of ageless and beautiful concrete structures and composites.

Note: We are seeking a modern cement producer to license the technology since nano-titanate application requires precise cement plant applications that are not practical in the field.

The fiberglass interface: Si vs. Zr

Practical commercial use of



Monte

The author

Salvatore J. Monte, a veteran of more than six decades in the rubber industry, is president of Kenrich Petrochemicals Inc.

He received his bachelor's degree in civil engineering from Manhattan College in 1961 and his master's degree in polymeric materials in 1969 from New York University's Tandon School of Engineering.

During his career, Monte has been awarded 32 U.S. patents that have been filed worldwide, the most recent in March 2020. He has more than 450 ACS CAS abstracted patents, technical papers, journal articles and book chapters on applications of organometallics and reactive diluents in thermosets and thermoplastics. In addition, he authored a Ken-React-brand reference manual on titanates, zirconates and aluminates; testified on several occasions before the U.S. Congress on intellectual property and trade issues; and lectured around the world on coupling agents.

He was named in 2020 to be inducted into the Plastics Hall of Fame, but because of the COVID-19 pandemic the ceremony will be held May 2 in Chicago.

Among his many honors and awards, Monte is a board governor of the Plastics Pioneers Association; a fellow of the Society of Plastics Engineers; past chair of the ACS Rubber Division's New York Rubber Group; a two-time honoree of the C. Homer Flynn Award for Technical Excellence from the Federated Society of Coatings Technology; and a life member of the National Defense Industrial Council.

Fig. 6A: 70-percent, 3-micron CaCO₃-filled PP homopolymer showing 180°-bend with no white stress cracking. CaCO₃ treated with 0.5 weight-percent triisostearoyl titanate invented by Monte in 1973.



Fig. 6B: 80-percent, non-silane reactive BaSO₄ in mineral oil without and with 0.35-percent titanate.



Technical

“coupling agents” began in 1953 using silane-sized fiberglass reinforced unsaturated polyester parts for the Corvette automobile. Let’s revisit fiberglass where silanes are proven performers and discuss function 1 coupling at the glass interface.

Fig. 12 shows the one-step coupling proton coordination of a neoalkoxy titanate vs. the four-step hydrolysis of a trisalkoxy silane leaving water of condensation deposited on the silane coupled interface. Water at the interface is the Achilles heel of

aged compositions.

As per **Fig. 12**, Plueddemann² states on page 114: “From the above observations 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.”

According to G.R. Kritchevsky⁴, the islands of water shown on the

surface of silica (glass fiber) are the points at which delamination, adhesive failure and corrosion begin. Kritchevsky concluded: “...boiled polystyrene samples show evidence of the diffusion of water through the resin. Islands are evident on fiber fracture surfaces in all polystyrene samples except for the titanate.”

Zhi-Wen Wang et al. provide an

instructive discussion of organic modification of nano-SiO₂ particles with pyrophosphato titanate.⁵ “Org. modification of nano-SiO₂ particles was performed with supercrit, CO₂ as solvent and a titanate coupling reagent KR 38S as the modification reagent. The surface of the nano-SiO₂ particles was changed after modification by the titanate coupling reagent from hy-

drophilic to hydrophobic. IR and thermo-gravimetric analyses indicate that the interaction between the titanate coupling reagent and the particle surface is mainly through chemical bonding.

“The influence of the apparent concentration of the titanate coupling reagent on the modification at 60° and 20.0 MPa was studied, in which the apparent concentration is the weight percent of the titanate coupling reagent added in the supercrit solvent. The quantity of the titanate coupling reagent reacted on the particle surface reaches a maximum of 19.81 x 10⁻⁷ mol/m², i.e. 1.19 mol titanate coupling reagent/nm², when the apparent concentration of titanate coupling reagent is 0.6 percent (weight).”

In **Fig. 13**, Monte states: “You do not want water boiling at the nano-interface between fiber and polymer in a composite. In contrast to silanes, titanates and zirconates work better in the absence of water on the interface. Nano-hydrophobicity is critical to anti-aging.”

R. Kraus et. al. stated:⁶ “The ETFE matrix was a copolymer of ethylene (38.5 percent) and tetrafluoroethylene (61.5 percent) with a low fraction (0.4 percent) of perfluoropropylvinylether (PPVE) produced by Hoechst.

The fibers were glass fibers (E glass) with an average diameter of 10 µm and an average length of L = 60 µm. One fraction of the fibers was treated with the coupling agent NZ 44 (neopentyl(diallyl)oxytri(N-ethylenediamino) ethylzirconate) to improve the fiber-matrix interface. The specimens were prepared by melting the mixture of matrix and a weight fraction of 10 percent of fibers under pressure (p = 25 bar) at a temperature of 295°C, followed by cooling to RT (cooling rate ~ 3 K min⁻¹).

“The influence of the coupling agent on the fiber-matrix interface was studied by breaking composites at low temperature (T = -190°C, liquid nitrogen) and analyzing the fracture surface by scanning electron microscopy. Electron micrographs show that in the composite made of fibers without coupling agent, the matrix is removed from the fibers. In the composite made of the fibers treated with coupling agent NZ 44 most of the fibers are covered with polymer matrix. This indicates that the fiber-matrix interface is improved by the coupling agent.” See **Figs. 1 and 2** in **Fig. 14** from their work entitled, “Acoustic emission analysis and small-angle X-ray scattering from microcracks during deformation of ETFE composites.”

The rest of this paper will be published in the April 4 issue of Rubber News.

Fig. 7: Spent drilling mud (BaSO₄) compatibilized with ordinary Portland cement and water.

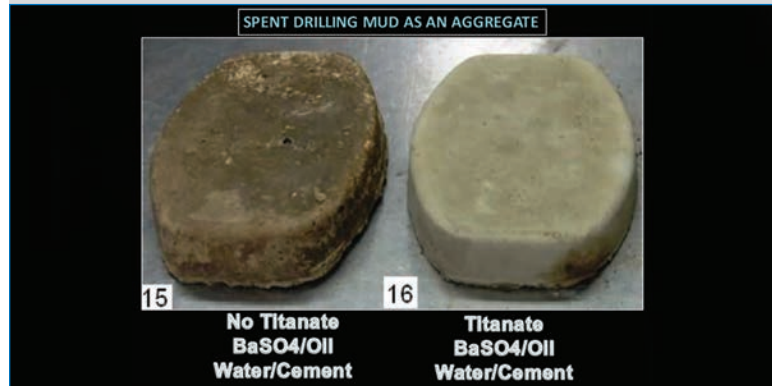


Fig. 8: SEM of Portland cement and its metal oxide makeup.

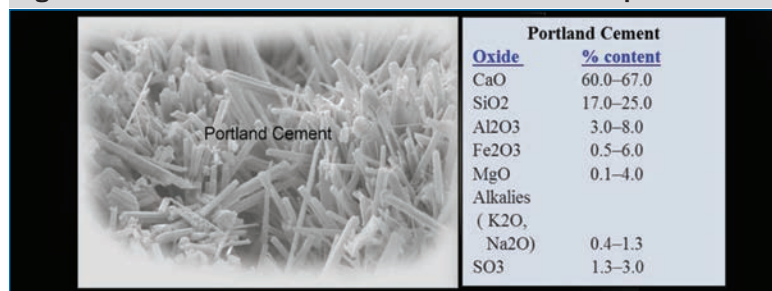


Fig. 9: The compatibilization effect of titanate on oil-soaked seawater sand mixed with ordinary Portland cement and water—U.S. patent 2020/0071230, S.J. Monte.



Fig. 10: SEM of compatibilized PP/HDPE/PET using a Ti/Al catalyst masterbatch.

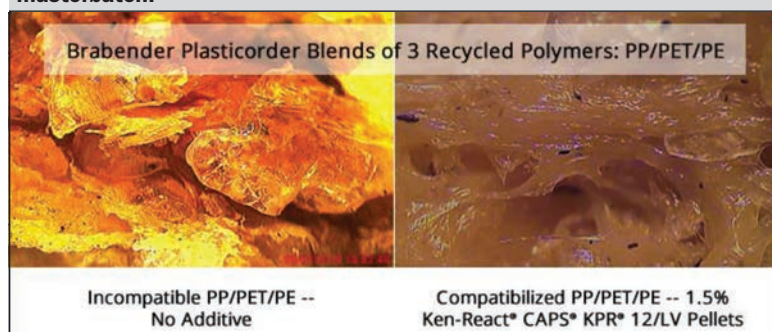


Fig. 11: Demonstrates the dispersion of conductive carbon black in water with no mechanical stirring or shear and smoother dispersion of polyethylene on a 2-roll mill sheet.

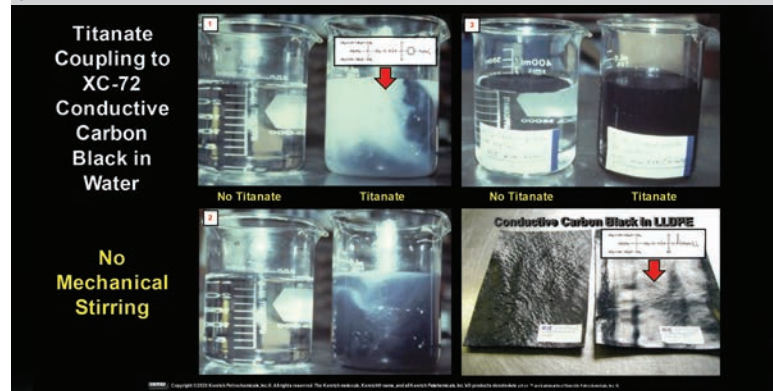


Fig. 12: The one-step proton coordination coupling of a neoalkoxy titanate as compared to the four-step hydroxyl hydrolysis mechanism of a trisalkoxy silane.

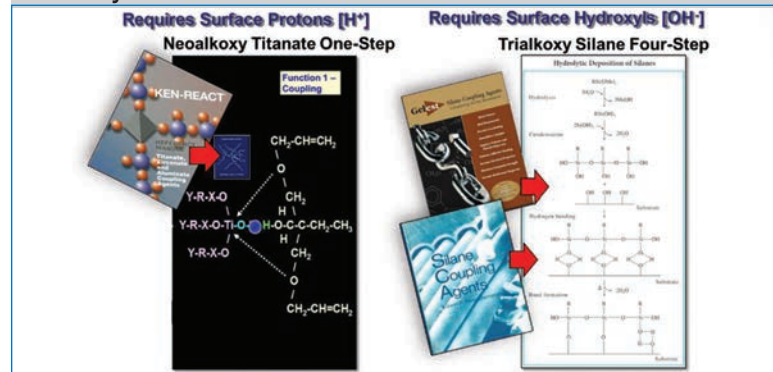


Fig. 13: Silane water of condensation left on the nano-interface is aging’s Achilles heel.

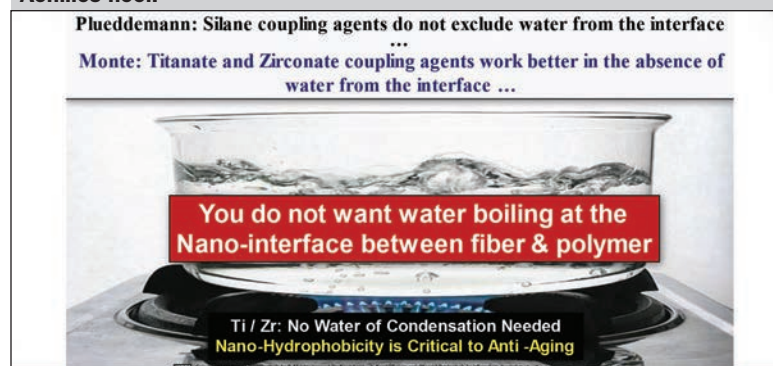
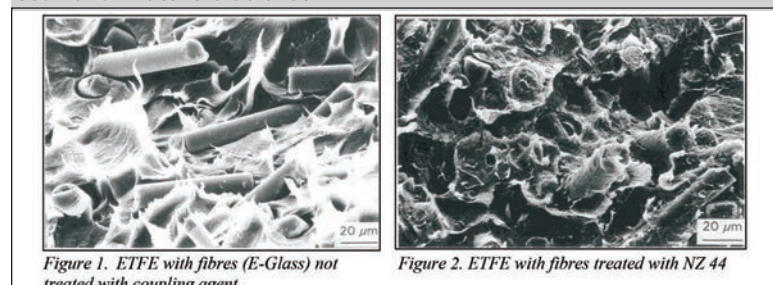


Fig. 14: “Acoustic emission analysis and small-angle X-ray scattering from microcracks during deformation of ETFE composites,” from the Journal of Materials Science.



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