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SURFACE-MODIFIED POLYMER PARTICLES: PERFORMANCE ADDITIVES FOR EPOXY AND CAST PU

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SURFACE-MODIFIED POLYMER PARTICLES: PERFORMANCE ADDITIVES FOR EPOXY AND CAST POLYURETHANE

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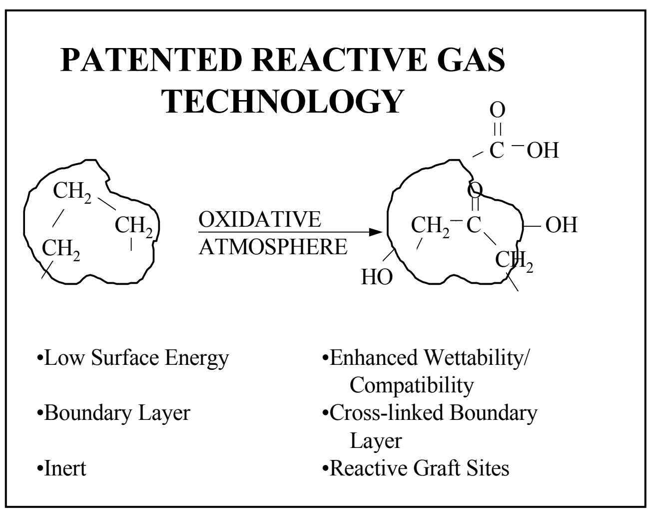
Surface-modified polymer particles are a class of performance additives for polyurethanes, epoxies, and other thermosets that has been growing in commercial use for 12 years(1-6). This family of materials promises to have much greater importance in the future. This report summarizes progress to date and predicts the direction of future growth.

Surface Modification

Surface-modification is a process whereby the chemical structure of the surface of an item is changed. "Items" can be anything such as film, reinforcement fibers, molded goods, and even particles. While numerous properties of materials are defined by surface structure, for this discussion we are concerned with those that affect compatibility and adhesion. Surface-modification facilitates the incorporation of polymer particles in epoxies and polyurethanes that normally are incompatible.

Appropriate chemical treatments of polymer surfaces result in formation of polar functional groups, such as hydroxyl and carboxylate, Figure I. These surfaces enable particles to be readily wetted by and dispersed in polar polymer precursors. As the polymer cures, these surface functionalities facilitate strong adhesion to continuous phase polymer through covalent and/or hydrogen bonding.

Figure I



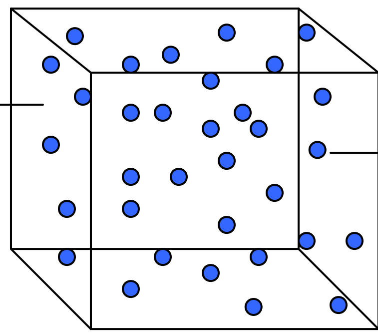
There are two types of processes in commercial use to effect surface-modification on polymer particles. These are reactive gas treatment and plasma. In the reactive gas approach, the chemistry is essentially a controlled oxidation. The reactive gas approach has a considerable depth of penetration. Because of its free radical mechanism, cross-linking of the surface molecules on the particles occurs in concert with treatment. This locks the modified areas in place, making the treatment permanent. Plasma processing, in contrast, ablates surface molecules as it modifies them. This results in a much shallower treated layer, and there are problems with loss in surface functionality over time with some substrates.

Composites Formed

Incorporation of surface-modified polymer particles in polyurethane formulations actually results in formation of composite materials. The polymer particles retain their size and shape during molding. When cured, the composite material consists of epoxy or polyurethane, as the continuous phase, and polymer particles dispersed throughout, as the discontinuous phase. Such structures are examples of *polymer-polymer composites*, as illustrated in Figure II.

Figure II

POLYMER-POLYMER COMPOSITE STRUCTURE



Facilitates Wetting & Dispersion

The oxygen-containing chemical functionalities on surface-modified particles cause high surface energy. This in turn means that the treated particles are readily wetted and dispersed in polar media, such as polyols, prepolymer, and even water. The effectiveness of surface-modification on wettability and dispersion is dramatically illustrated by comparing the dispersability of treated and non-treated ultrahigh molecular weight polyethylene (UHMW PE) particles in water (Figure III).

Figure III

ENHANCED WETTING AND DISPERSION

Enhanced wetting and dispersability; non-treated UHMW PE (left) and surface-modified UHMW PE (right) in water.

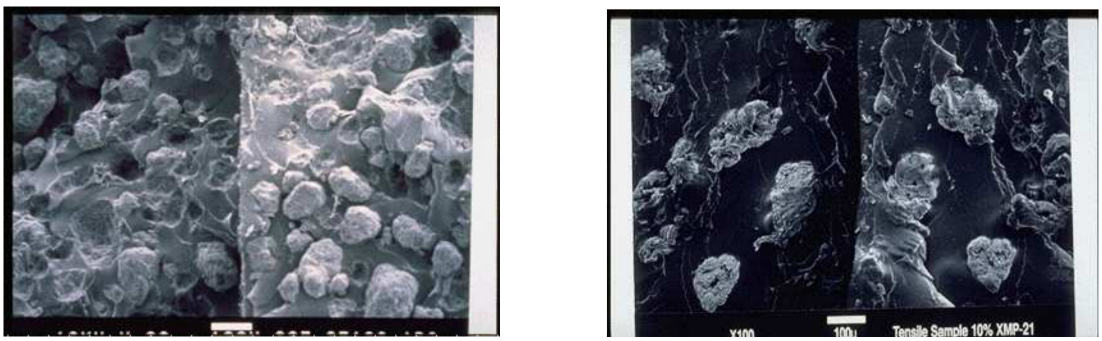
Excellent dispersability is necessary in order for composite materials to have good physical properties. If polymer particles are not well wetted and dispersed, clumps of dry particles result in the cured material. These areas function as voids and result in poor physical properties, which lead to poor performance and premature failure.

Bonding to Epoxies, PU, and Other Matrices

The surface modification is also very important because it results in much stronger bonding between the particles (or fibers) and the matrix resin. The enhanced adhesion is a result of chemical bonding with surface functionalities. The improved bonding of treated particles is illustrated via scanning electron photomicrographs comparing the failure surfaces of tensile samples made with non-treated or surface-modified UHMW PE particles in a polyurethane matrix (Figure IV). With non-treated UHMW PE particles, adhesion is so weak that the particles pull away as the sample breaks. In contrast, treated UHMW PE particles adhere so tenaciously that they tear in half and do not pull out of the polyurethane.

Figure IV

ENHANCED BONDING of PARTICLES



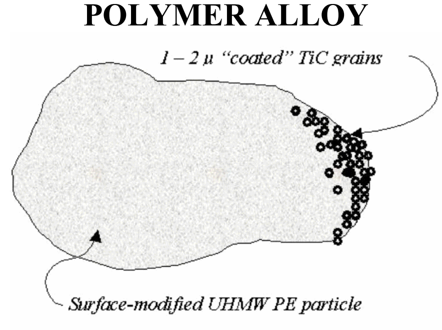
Photomicrographs of non-treated (left) and surface-modified (right) UHMW PE particles in a polyurethane matrix clearly illustrate the enhanced bonding of the latter.

Titanium Carbide Polymer Alloys

Surface-modification also creates chemical functionality that can be used to bond moieties to the surface of particles. One example of this is INHANCE™[7] titanium carbide polymer alloys. This is the first example that we are aware of whereby titanium carbide is chemically bonded to polymer chains. The structure of this family of materials consists of small grains of titanium carbide (TiC) bonded to the exterior of a surface-modified polymer particle, as illustrated in Figure V. The TiC grains are chemically bonded to a proprietary “coupling agent,” which in turn is bonded to the functionalized surface of the polymer particle. Depending on the particle size of the surface-modified polymer particle used, these materials can consist of 70% to more than 85% by weight TiC. This unique combination of polymer and ceramic-type material imparts some highly desirable properties.

Figure V

TITANIUM CARBIDE POLYMER ALLOY



USE in EPOXIES

With their polar surfaces, INHANCE™ polyethylene particles are very compatible with epoxy resins. Incorporation in epoxy formulations imparts desirable property enhancements including increased toughness and greater abrasion resistance. This enables formation of end products with outstanding performance.

Stronger Adhesives through Toughening
Perhaps the most critical characteristic for an adhesive in its end use is the strength of the bond it forms. In practice, many factors can effect adhesive joint strength, including the internal strength of the adhesive, the ability of the adhesive to wet the substrate, the bond thickness, and the adhesive bonding area. The internal strength of the adhesive is often related to its modulus, which is a measure of the stiffness of the material. As a rule of thumb, both very high and very low modulus materials are undesirable as adhesives. A material with high modulus will tend to be brittle, causing the material to crack under stress. A low modulus material is often weak and tears easily.

In theory, thermoplastics can be used as a modulus modifier in adhesives. Thermoplastics that are tough and flexible resist both cracking and tearing. Because of these desirable properties, some thermoplastics can be used to modify epoxies and other adhesives with unacceptable moduli. Unfortunately, most thermoplastics with these properties are nonpolar, which makes them incompatible with epoxies and other structural adhesives because these adhesives are polar in nature.

Now INHANCE™ polyethylene particles make it possible to enhance adhesive properties through modulus modification. These particles, having polar surfaces, are readily incorporated into structural adhesive formulations. INHANCE™ particles make it possible to combine the elasticity and toughness of polyethylene with the desirable properties of polar structural adhesives. INHANCE™ polyethylene particles can be used as a "modulus modifier" that either reduces the modulus of a brittle adhesive or increases the modulus of a weak adhesive. Thus, INHANCE™ particles can improve the strength and flexibility of structural adhesives.

Data illustrating how incorporation of INHANCE™ polyethylene particles in an epoxy increase performance as an adhesive is summarized in Figure VI. In this experiment, the shear overlap strengths of three adhesives bonding two pieces of steel were measured. The adhesive formulations were an unfilled epoxy, and two formulations incorporating 10% and 30% by weight INHANCE™ UH-1250, surface-modified UHMWPE particles. **The sample made with 30% INHANCE™ particles shows a lap shear increase of almost 50%.**

Figure VI

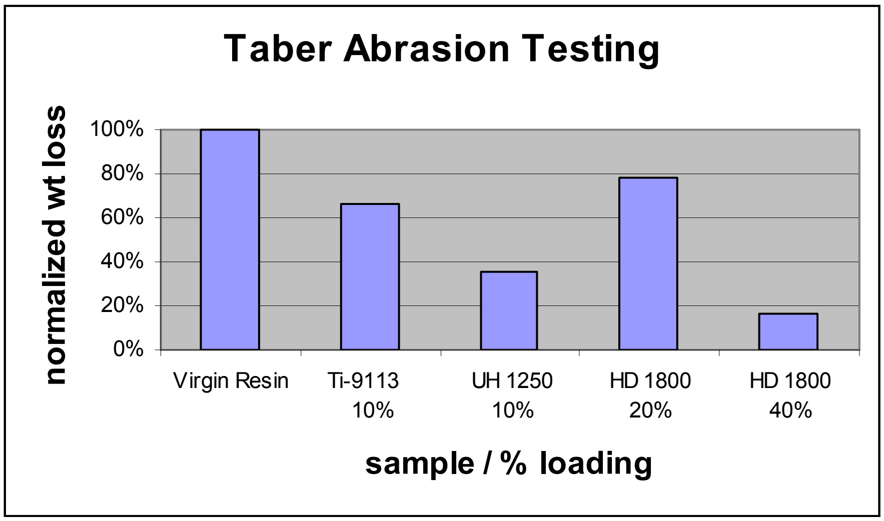
EPOXY ADHESIVE STRENGTH

Adhesive	Lap Shear Strength (psi)
Unfilled epoxy	7,500
10% (wt) INHANCE™ UH-1250	9,200
30% (wt) INHANCE™ UH-1250	11,100

Greater Abrasion Resistance

Probably the major reason that INHANCE™ particles are incorporated in formulations is to increase abrasion resistance. UHMW PE has the highest sliding abrasion resistance of all polymers[0]. Incorporation of INHANCE™ UHMW PE particles in epoxy formulations generally increases the abrasion resistance significantly. Data summarizing some Taber abrasion testing, Figure VII, shows that incorporation of 10% INHANCE™ UH-1250 in an epoxy gives abrasion resistance 300% that of the unfilled resin. Use of other INHANCE™ products also improves abrasion resistance.

Figure VII



USE in CAST POLYURETHANE

Polyurethanes, as a family, consist of an extremely broad array of chemical structures and corresponding physical properties. Thus, with most sweeping statements about physical property changes associated with incorporation of surface-modified polymer particles there are always exceptions. Nevertheless, several generalizations are apparent in most engineering cast PU systems. Figure VIII summarizes complete physical characterizations of three PU formulations. These are based on Bayer Baytec®[8] MS-242, an MDI. The data was supplied by Bayer Corp.

Problems with generalizations are underscored in this data concerning abrasion resistance. As measured by the Taber method, there is little difference in abrasion resistance with incorporation of INHANCE™ UH-1080. In contrast, when measured via the NBS abrasion test, the same samples showed a significant increase in abrasion resistance with incorporation of the UH-1080 particles.

INHANCE™ polyethylene and titanium carbide polymer alloy particles are used in numerous cast (PU) applications because of superior physical properties achieved. These include abrasion resistance, adhesion to substrates, tear resistance, and reduced coefficient of friction. These generalizations are discussed in greater detail below.

Figure VIII

INHANCE™ UH-1080 in MDI-POLYESTER

Chain Extender – 1,4 butandiol; 95% stoichiometry

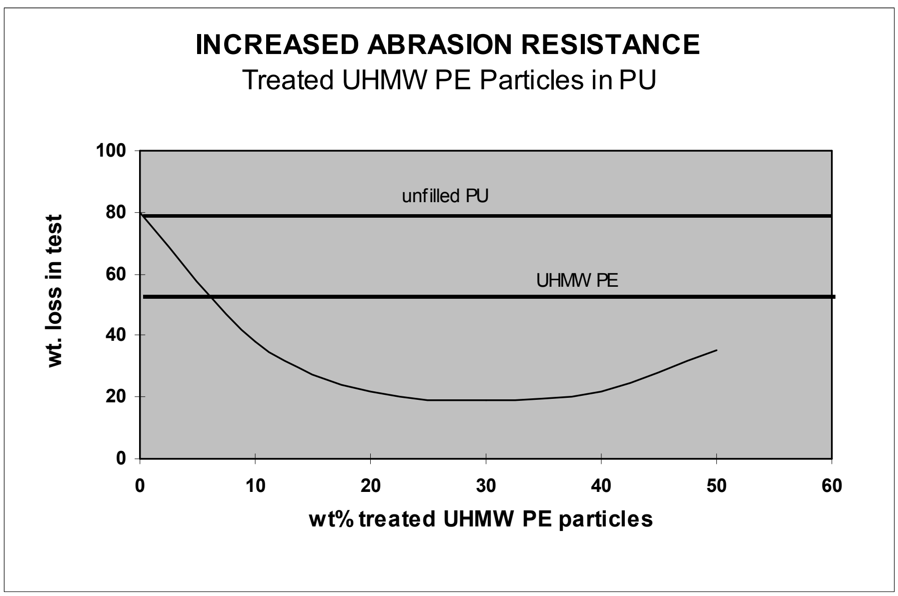
Wt % INHANCE UH-1080	0%	10%	20%
Hardness (Shore A)	85	85	88
Rebound (%)	36	36	35
Modulus			
100% Elong. (psi)	980	1300	1333
200% Elong. (psi)	1460	1905	1994
300% Elong. (psi)	2314	3136	2680
Split tear (psi)	257	323	387
Compression Set (%)			
2 weeks	45.9	39.6	45.8
4 weeks	20.6	25.2	29.5
7 weeks	16.8	20.3	21.7
Taber abrasion, (mg loss)	7.5	8.0	6.7
NBS abrasion (%)	449*	954*	1871*
Specific Gravity	1.25	1.17	1.08
Compression load deflection			
2% modulus (psi)	12.1	40.9	67.9
5% modulus (psi)	89.3	155.9	190.1
10% modulus (psi)	238.0	296.6	335.0
15% modulus (psi)	363.2	421.4	463.8
20% modulus (psi)	486.8	542.2	586.1
25% modulus (psi)	611.9	669.6	717.4
50% modulus (psi)	1569	1980	2319
Shear Strength (psi)	3786	3715	3632

* *NBS results represent revolutions required to achieve specific linear wear. Therefore, larger result indicates greater abrasion resistance. Standard is rubber at 100%.*

Abrasion Resistance from Surface-Modified UHMWPE Particles

It should be no surprise that incorporation of UHMW PE particles in polyurethane increases the sliding abrasion resistance. UHMW PE is known to have the greatest abrasion resistance of all polymers. However, the amount of increase in PU composite abrasion resistance is much more than would be expected. Figure IX shows the abrasion resistance of a polyurethane (TDI/polyether prepolymer cured with MBOCA) as a function of loading levels of INHANCE™ UH-1250 particles as determined by the DIN 53516 method. It is noteworthy that not only does the abrasion resistance improve as more UHMW PE particles are added, but beyond 5% addition level, the **PU/UHMW PE polymer-polymer composites outperform even UHMW PE itself**.

Figure IX



Tribologists' explanation for this unexpected behavior is that the polymer-polymer composite has a wear failure mechanism that is different from that of UHMW PE. When UHMW PE sheeting wears, microscopic pieces of material are chipped off. When polymer-polymer composites, consisting of INHANCE™ UHMW PE particles in PU, are exposed to sliding abrasion, the UHMW PE particles deflect into the elastomeric PU matrix and some of the energy is absorbed.

Abrasion Resistance from Surface-Modified HDPE Particles

In the past, there was market demand for smaller particle size surface-modified UHMW PE particles that can be processed on existing meter-mix casting equipment. The closest that we could come was fine particle size (18μ) high density polyethylene (HDPE) particles. Since HDPE sheeting is known to have only about 5 - 10% of the abrasion resistance of UHMW PE sheeting in numerous abrasion tests, it was expected that surface-modified HDPE particles would give little or no improvements in polyurethane formulations, in comparison to surface-modified UHMW PE particles. Nevertheless, this material was surface-modified and evaluated in cast PU.

Unexpected results were again obtained. Surface-modified HDPE particles (INHANCE™ HD-1800) in cast polyurethane formulations are virtually as good as surface-modified UHMW PE (INHANCE™ UH-1700) for increasing sliding abrasion resistance. These results are summarized in Figure X. In addition to being very fine particle size, HDPE particles are considerably less expensive than are fine UHMW PE particles. This is an important development, which opens opportunities for surface-modified polyethylene particles in high volume cast polyurethane as well as various coatings markets.

Since the mid '90's surface-modified 18µ HDPE particles have been commercially available. Today this product is being used in a broad spectrum of cast PU and coatings applications. One customer, who molds cast polyurethane parts, reports that **use of INHANCE™ HD1800 surface-modified HDPE particles increases the durability of a specific part fifteen times (15x) longer** than parts made in the same polyurethane but without the HD-1800.

Figure X

ABRASION RESISTANCE of UHMW PE VERSUS HDPE PARTICLES

Particles in Cast PU[(a)]	NBS Abrasion Results[(b)]
None	213
25% INHANCE™ UH-1700 (35µ UHMW PE)	783
25% INHANCE™ HD-1800 (18µ HDPE)	746

(a) PPT 95A/Ethacure
(b) Larger value indicates greater abrasion resistance

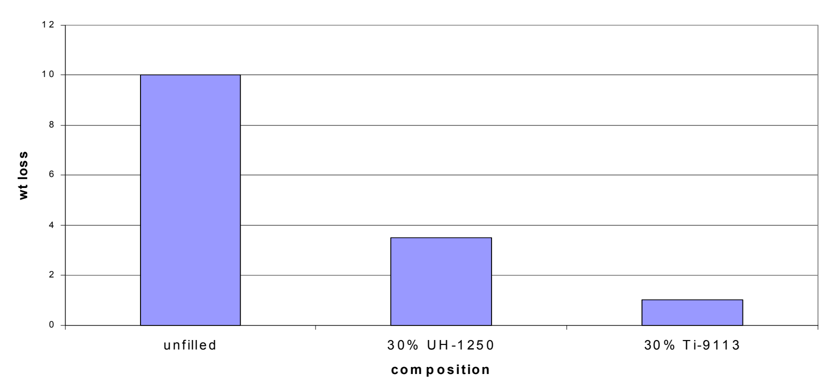
Abrasion Resistance from INHANCE™ Ti 9113

INHANCE™ Ti titanium carbide polymer alloy particles are being used in thermoplastics as well as thermosets, primarily because of the tremendous increase in abrasion resistance obtained in certain applications. Data illustrating improvement in wear resistance for a cast polyurethane is summarized in Figure XI, for a TDI polyester PU using a sand slurry test.

It is noteworthy that since the titanium carbide (TiC) grains in INHANCE™ Ti materials are rounded, there is minimal abrasion or cutting of the counter surface. This is much different from most other carbides, which are used in grinding and cutting media. This minimal counter surface wear property of INHANCE™ Ti-9113 makes it ideal for applications such as bushings, seals, pistons, and other dynamic parts.

Figure XI

GREATEST ABRASION RESISTANCE
TITANIUM CARBIDE POLYMER ALLOY



Adhesion to Substrates
Incorporation of INHANCE™ particles in cast PU and other formulations has been found to significantly increase adhesion to substrates. An example of where this is beneficial is when a PU wheel is molded to a metal hub for the bearing or bushing. Excellent adhesion between the hub and the PU is necessary. The current method for optimizing the PU-metal bond is to prime the metal surface with an adhesion promoter. This is an added step whereby the metal is coated and dried prior to casting the PU. Incorporation of INHANCE™ particles gives better adhesion to substrates with or without use of primers. In fact, some data shows that incorporation of INHANCE™ particles in cast PU gives better adhesion than does use of primer alone. Incorporation of INHANCE™ particles in addition to using a primer give even greater bond strength. Results from one such study are summarized in Figure XII.

Figure XII

T-PEEL ADHESION TEST: PU BONDED TO STEEL

Additive	Primed?	Bond Strength (lb/in)
None	No	8
None	Yes	14
INHANCE™ UH-1250	No	18
INHANCE™ UH-1250	Yes	24

Stronger Paint Adhesion
Several customers report that incorporation of surface-modified polymer particles in cast PU (and other systems) improves subsequent paint adhesion to molded parts. In fact, one customer was able to stop using primer on the cured PU prior to painting by using INHANCE™ particles in his formulation.

While it is probable that this phenomenon is related to the enhanced adhesion to substrates discussed above, the mechanism has not been determined. One postulate is that surface-modified particles near the surface alter the *interphase* continuous phase polymer around them and extending to the surface, and that the altered chain orientation is favorable for adhesion.

Enhanced Barrier Properties
There have been several reports of increased barrier properties from incorporation of surface-modified polyethylene particles in cast polyurethanes. For example, a manufacturer of industrial coatings reported that in salt spray tests, PU coatings with INHANCE™ UH particles gave greater corrosion resistance than they had ever seen before with a PU. Another example is that PU roll coats made with INHANCE™ polyethylene particles are considerably more resistant to delamination from the metal core via corrosive disbondment than is unfilled PU.

It is expected that barrier performance would be improved because of the "tortuous path" imposed by the particles, a well-know mechanism for increasing barrier properties. However, in these examples the corrosion resistance is greater than can be achieved with other "tortuous path" additives. It has been postulated that increased performance is a result of chloride ions, as they permeate through the PU, preferably associating with the functionalized surface of the INHANCE™ particles. This has the effect of reducing the concentration of chloride ions transiting the PU for some amount of time.

Reduced Solvent Swell

Incorporation of surface-modified polyethylene particles in polyurethane decreases solvent swell. This probably happens because a fraction of the material consists of polymer (UHMW PW or HDPE) that does not swell to an appreciable amount with solvents. Nevertheless, achieving this reduction in swell, along with enhancing other properties, is important in some applications. Examples of this phenomenon are summarized in Figure XIII.

Figure XIII

REDUCTION IN SOLVENT SWELL for PU[(a)]

ASTM D 471 (25ºC/48 hrs)

Volume % Increase

Solvent	unfilled	15% INHANCE™ UH-1080
Water	4.1	2.3
Methanol	46.9	35
Trichloroethylene	149	106
Toluene	150	107
Acetone	67	50

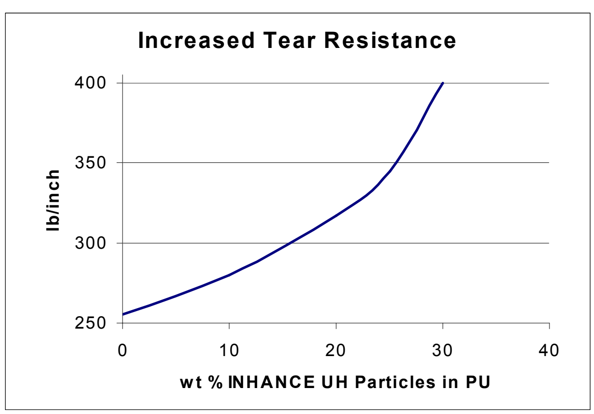
(a)Polyurethane is Airthane® PET 90A/Ethacure® 300

Tear Resistance and Cut Resistance

Incorporation of surface-modified polymer particles in cast polyurethane (PU) increases the tear resistance of these elastomers. Data illustrating this improvement is shown in Figure XIV. This is an important benefit because tearing is a major failure mechanism for PU elastomers. It is hypothesized that the increase in tear resistance is caused by the firmly bonded polyethylene particles "pinning" tears.

Although we have no specific data on cut resistance, it is clear from cutting samples that it is much more difficult to cut PU that contains surface-modified polyethylene or titanium carbide polymer alloy particles.

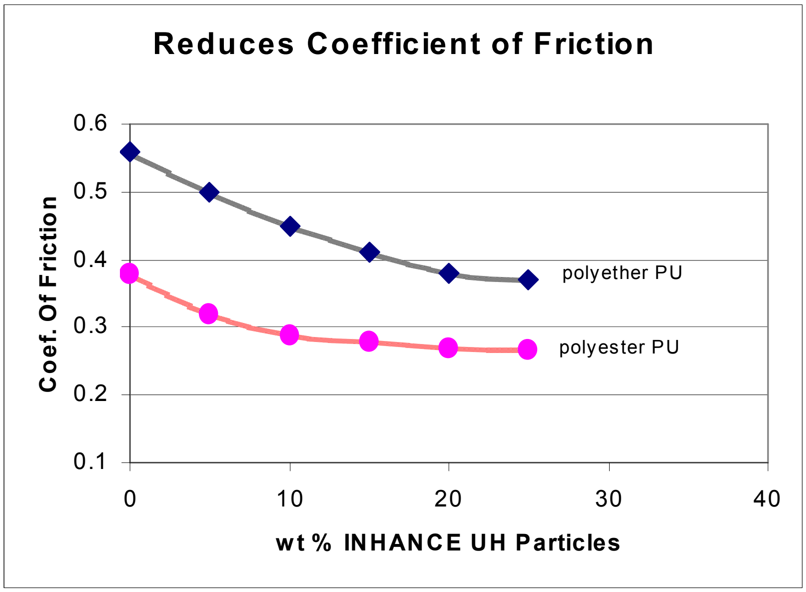
Figure XIV



Reduced Coefficient of Friction

Incorporation of INHANCE™ UHMW PE or HDPE particles in cast polyurethane gives reduced coefficient of friction. This is illustrated in Figure XV. In order to appreciate this effect, the molded part must be sanded or otherwise abraded sufficiently to expose the polyethylene particles. Cast polyurethane parts with reduced coefficient of friction surfaces are desirable for moving parts, like bushings and gears, and for material handling applications.

Figure XV



PROCESSING – HOW TO USE

INHANCE™ particles can be incorporated in cast epoxies and PU via hand mix or by use of several types of meter-mix equipment. The particles create processing changes that must be anticipated. The two biggest changes are increased viscosity and the possibility of the clogging of filters, lines and valves.

Increased viscosity means that it may take longer to homogeneously mix the curative, and it is slightly more difficult to degas. Often the amount of INHANCE™ particles that can be used is limited by viscosity-related processing issues. Sometimes the process temperature is increased above what is normally used for a given prepolymer system since higher temperatures give lower viscosity,

INHANCE™ particles can be processed on a variety of older as well as newer meter-mix equipment. Although most older meter-mix equipment was designed to process liquids and not slurries, particles can be used. Flying Wedge-type machines generally have no difficulty in processing particles because of viscosity or clogging. Machines, such as APC, which use precision gear pumps, are used successfully as long as there is sufficient clearance in the pump. Zenith and Viking pumps are used frequently with particles. Even equipment with fine metering

valves, such as those from Max Machinery, can be used as long as the particle size is small enough.
Furthermore, meter mix equipment manufacturers have begun offering equipment that is designed to be able to process particles as well as fibers. Examples of such manufacturers include Krauss-Maffei and Cannon.

Another difficulty sometimes encountered is floating of the particles in the uncured system. Since the specific gravity of INHANCE™ UH and HD particles are less than that of prepolymer or polyol, there is a tendency for the particles to float to surface. This problem can be solved by keeping the mix in constant agitation.

There are no changes required in stoichiometry for curative. Even though there are hydroxyls groups on the surface, the absolute concentration is insignificant in the overall system. Also, the hydrophilic layer of surface-modified material is so small that negligible amounts of moisture are absorbed on the particles so that pre-drying is not required.

END PRODUCTS

Most epoxy and PU end products being made with INHANCE™ UH, HDPE, and Titanium Carbide Polymer Alloy particles are those which are exposed to abrasive wear and/or benefit from low coefficient of friction. Many of these are in materials handling and mechanical equipment applications. Examples include gears, mining screens, throwing wheels, rollers, and wear surfaces. These materials also find numerous uses in liners and protective coatings.

In the future, we expect to see more usage of these particles in epoxy and PU coatings and adhesives, because of the benefits they bring.

CONCLUSIONS

Surface-modified polymer particles represent a new dimension in material engineering. Incorporation of these particles in cast polyurethane systems can help molders create unique combinations of properties desired for specific applications. The chemically-functionalized treated particles enable new types of performance-functional polyurethanes to be made. This will continue enhancing the competitive positioning of the industry.

Footnotes

[1] U.S. Patent # 4,771,110 "*Polymeric Materials Having Controlled Physical Properties and Process for Obtaining These*", September 1988
[2] U.S. Patent # 4,833,205 "*Polymeric Materials Having Controlled Physical Properties and Process for Obtaining These*", May 1989
[3] U.S. Patent #5,382,635 "*Higher Modulus Compositions Incorporating Particulate Rubber*", January 1995
[4] U.S. Patent #5,506,283 "*Higher Modulus Compositions Incorporating Particulate Rubber*", April 1996
[5] U.S. Patent #5,693,714 "*Higher Modulus Compositions Incorporating Particulate Rubber*", December 1997
[6] U.S. Patent #5,969,053 "*Higher Modulus Compositions Incorporating Particulate Rubber*", October 1999
[7] INHANCE™ is a trade name applied for by Fluoro-Seal
[8] Baytec® is a trade name registered to the Bayer Corporation
[9] Ticona literature

BIOGRAPHY -- BERNARD D. BAUMAN

Bernard D. Bauman is Vice President Special Projects and Vice President & General Manager of the INHANCE business area at Fluoro-Seal, in Houston Texas. Since joining Fluoro-Seal in July 2000, he has been establishing the INHANCE line of surface-modified polymer particles and fibers. Prior to this, Dr. Bauman was Chairman of Composite Particles, Inc., a company that he founded and managed for 7 years. Those products were sold under the VISTAMER® trademark. Although Composite Particles has ceased operations, Dr. Bauman is actively licensing the company's technology for surface-modification of rubber particles. Composite Particles' business, the manufacture and sale of advanced materials consisting of surface-modified polymer particles and fibers, and titanium carbide polymer alloys was partially based on technology acquired from Air Products and Chemicals, Inc.

For the 17 years prior to founding Composite Particles, Dr. Bauman had been with Air Products and Chemicals, Inc. His assignments there included research and development, marketing, and venture business management. Bauman is an inventor on over 20 U.S. patents. He conceived the technical foundation of surface-modified polymer particles in the early 1980's. This technology was developed, scaled-up, and introduced to the marketplace by Bauman's group at Air Products over a 12-year period. Prior to Air Products, Bauman was with the Rohm and Haas Company for 2 years, in the Pioneer Research Department.

Bauman's education includes a BS in Chemistry from Eastern Nazarene College, a Ph.D. in Physical Organic Chemistry from the State University of New York at Albany, and a postdoctoral scholarship at the Pennsylvania State University.