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POLYMER-POLYMER COMPOSITES MADE WITH SURFACE-MODIFIED POLYMER PARTICLES AND FIBERS

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ABSTRACT

A new dimension in polymer engineering is made possible with surface-modification of polymer particles and fibers. Compatibility and bonding characteristics are dramatically changed with the reactive functional groups created by treatment. Novel polymer-polymer composites are custom designed with optimal properties for specific applications. Physical properties are tailored through control of variables that include type and percentage of particles, particle size, and matrix material. Examples of new polymer-polymer composites include proven applications of surface-modified ultra high molecular weight polyethylene (UHMW PE) and high-density polyethylene (HDPE) particles. This has important commercial implications as new materials are being created for the paint, coatings, and molded goods industries.

A new class of materials has also been created utilizing surface-modified particles – titanium carbide polymer alloys. In these, titanium carbide grains are bonded to polymer particles, enabling incorporation of titanium carbide in polymer systems. Plastic end-products made with titanium carbide polymer alloy are replacing metal parts because their special properties include being more abrasion-resistant than steel, being lightweight and corrosion-resistant, and being easily formed by normal plastic conversion processes such as injection molding.

OVERVIEW

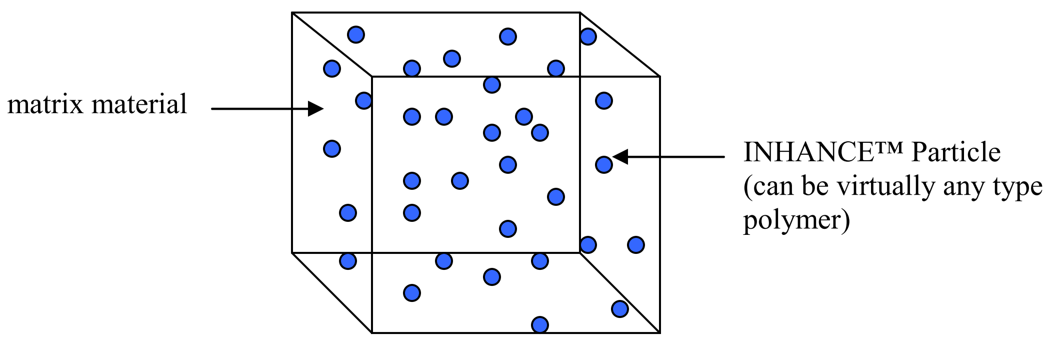
Surface-modified polymer particles and short, chopped fibers (INHANCE™ particles and fibers) represent a new dimension in material engineering. These particles and fibers can be combined with other types of polymers because their surfaces have been chemically altered to enhance compatibility and bonding. Surface-modification enables formation of unique polymer-polymer composites through combination of polymers that are normally incompatible. These novel polymer-polymer composites can be custom tailored to give desirable combinations of physical properties, resulting in superior end products. [1 – 6]

The first examples of commercially available surface-modified polymer particles are ultrahigh molecular weight polyethylene (UHMW PE) and high density polyethylene (HDPE) with highly polar surfaces. Reactive gas processing creates hydroxyl, carboxylate, and halogen groups on the surfaces. The resulting surface energy is so high that the particles are water-wettable. This makes INHANCE™ particles particularly

amenable for use in polar matrix polymers such as polyurethane, epoxy, nitrile rubber, and various water borne and latex systems.
The concept of polymer-polymer composites is illustrated in Figure I. In such structures the discontinuous phase (particles) retain their identity on a macro scale. The diameters of the particles are in the range of 1μ to 1mm, making this distinctly different from nanomaterials.

Figure I

POLYMER-POLYMER COMPOSITE STRUCTURE



Examples of Matrix Materials

epoxy	polyamides	rubber	phenolics
polyurethane	polyesters	silicone	polycarbonate
latex polymers	polysulfone	polyvinyl alcohol	polystyrene
acrylics	PVC	urea formaldehyde	acetal
melamines		polyolefin	concrete

One attractive aspect of this approach to material engineering is the ability to control properties via several variables. Important variables that can be adjusted to control properties include 1) type of continuous phase matrix, 2) type of polymer particles, 3) particle size (distribution), 4) percent particle loading, and 5) two or more types of particles. Obviously the number of possible permutations is almost infinite.

Polymer particles with functionalized surfaces can be further modified by grafting other materials onto the surface. The first example of such a structure is a family of products in which titanium carbide grains are bonded to the surface of HDPE and UHMW PE particles. These are referred to as INHANCE™ Ti Polymer Alloys in this paper.

NEW FAMILIES OF COMPOSITES

Surface-modified polymer particles and short-chopped fibers are more than just fillers or additives. Incorporation of these materials in various polymers results in creation of new classes of composites. Figure II illustrates this new class, *polymer–polymer composites,* in relation to other polymer systems.

Figure II

NEW FAMILY of COMPOSITE MATERIALS

Fillers / Resins ↓	none	common fillers[1]	high performance continuous fibers[2]	surface-modified polymer particles and fibers[3]
Commodity resins (polyolefins, PVC,	monolithic	filled resins		polymer – polymer composites
High performance, **Engineering resins** (polyamides, epoxy, polyurethane, PEEK, PPS, PPA, PTFE, polyimide, etc.)	monolithic	performance compounds	advanced composites	

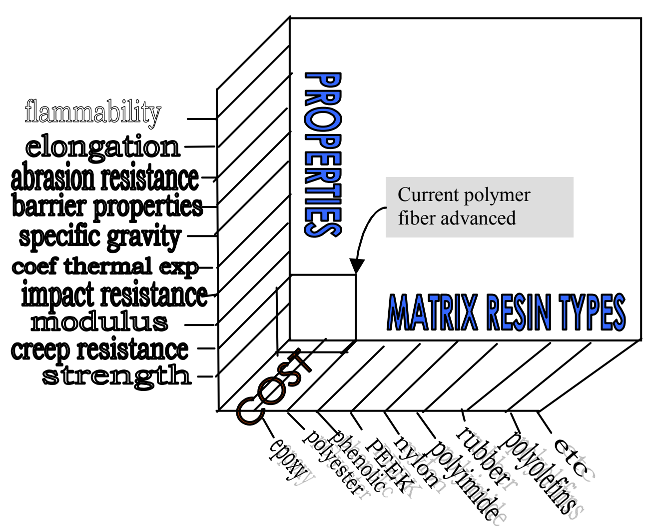
1) Common fillers include calcium carbonate, mica, silica, carbon black, glass fibers, talc, and molybdenum disulfide
2) High performance fibers include continuous or discontinuous aramid, graphite, carbon, and ceramic fibers.
3) Surface-modified polymer particles can be based on practically any type of polymer particles or fibers.

Huge Potential Market for Polymer-Polymer Composites

With appropriate surface-modification, polymer-polymer composites can be formed with virtually any combination of continuous phase (matrix) and polymer particles. Of course, such composite materials will have unique combinations of physical properties. This can have impact on materials selection for numerous applications. The potential market impact is huge. Figure III illustrates this in comparison to conventional advanced composites in terms of properties affected, amenable resins, and system costs.

Figure III

POLYMER-POLYMER COMPOSITES

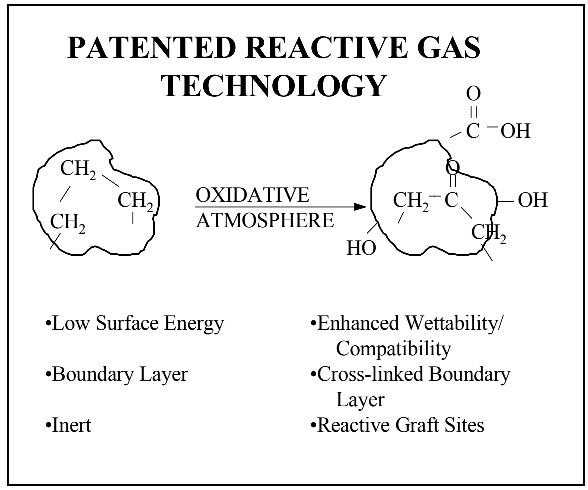


Facilitated by Surface-Modification

Surface-modified polymer particles and short, chopped fibers can be combined with other types of polymers because their surfaces have been chemically altered to enhance compatibility and bonding.

The surface-modification technology currently being used by Fluoro-Seal is basically a controlled oxidation using reactive gas atmospheres. Only the outermost molecular layers on the particles or fibers are reacted. The treatment causes the molecular backbone and/or side chains to react, resulting in formation of polar functional groups on the surface, such as hydroxyls and carboxylates, Figure IV. The feasibility of imparting different functionality through different surface-modification chemistry has been demonstrated, and will be exploited in the future.

Figure IV



The oxygen-containing chemical functionalities cause the treated particles to have high surface energy. This in turn means that the treated particles are readily wetted and dispersed in polar media, such as polyols or even water. The effectiveness of treatment on wettability and dispersion is dramatically illustrated by comparing the dispersability of treated and non-treated UHMW PE particles in water (Figure V).

Figure V

ENHANCED WETTING AND DISPERSION

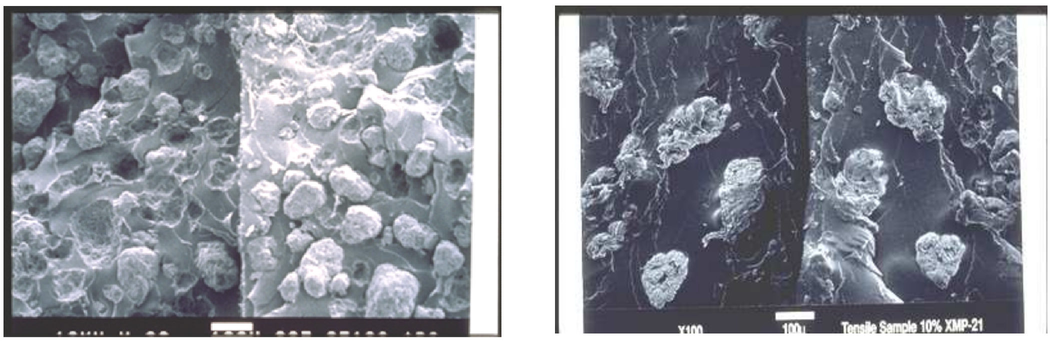
Enhanced wetting and dispersability; non-treated UHMW PE (left) and surface-modified UHMW PE (right) in water.

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.

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 and hydrogen bonding. 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 PU matrix (Figure VI). With non-treated UHMW PE particles, adhesion is so weak that the particles pull away as the sample is torn. In contrast, treated UHMW PE particles adhere so tenaciously that they tear in half and do not pull out of the PU.

Figure VI

ENHANCED BONDING

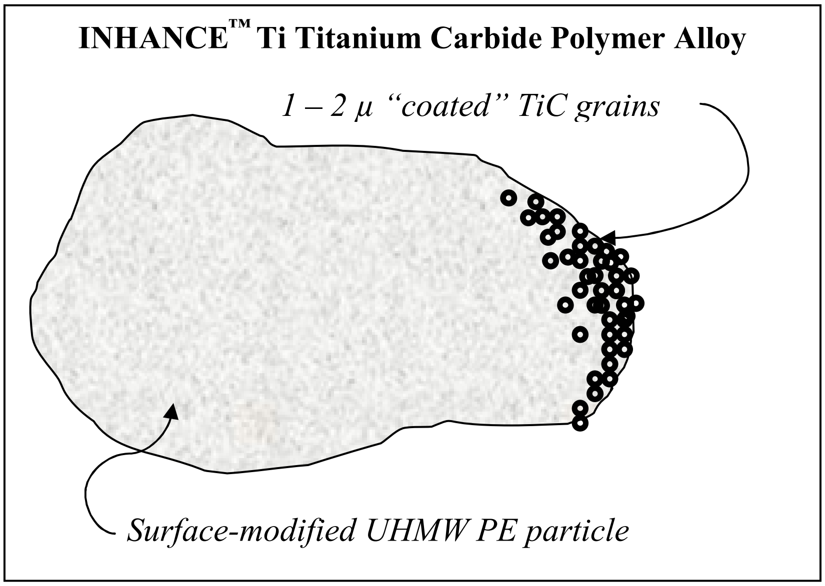


Photomicrographs of non-treated (left) and surface-modified (right) UHMW PE particles in a polyurethane matrix clearly illustrate the enhanced bonding of the latter.

Titanium Carbide Polymer Alloys

The ability to bond moieties to the surface of surface-modified polymer particles makes possible formation of INHANCE™ 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 VII. 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, as will be described later in this paper.

Figure VII



PROPERTIES AND APPLICATIONS

Applications and market potential for various materials are defined by the combination of physical properties, material costs, and end-product manufacturing (molding) costs associated with each. Often the properties of polymer-polymer composites are predictable, being a weighted average of the component polymers. Occasionally one gets unexpected results – some properties are much better than would be predicted. The material costs for polymer-polymer composites are reasonable, since they are based on existing commodity polymers. Their costs are also projected to decrease over time as volume increases. Conversion costs are quite low since they utilize conventional mixing and molding processes used in high volume manufacturing.

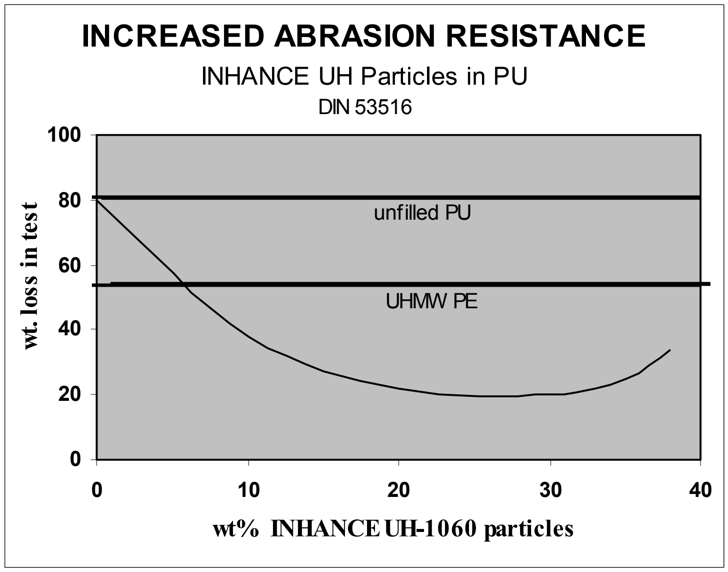
The commercial amenability of polymer-polymer composites is illustrated by the following examples of commercial applications for surface-modified UHMW PE, HDPE particles, and INHANCE™ titanium carbide polymer alloys.

Cast Polyurethane Parts

INHANCE™ polyethylene particles are used in numerous cast polyurethane (PU) applications because of superior physical properties achieved. These include abrasion resistance, adhesion to substrates, tear resistance, and reduced coefficient of friction.

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 VIII shows the abrasion resistance of a polyurethane (TDI/polyether prepolymer cured with MBOCA) as a function of loading levels of surface-modified UHMW PE particles as determined by the DIN 53516 method. It is noteworthy that not only does the abrasion resistance improve as more UHMW PE is added, but beyond 5% addition level, the PU/UHMW PE polymer-polymer composites outperform even UHMW PE itself.

Figure VIII



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.

Surface-Modified HDPE Particles

There was market demand for finer particle size surface-modified UHMW PE particles that can be processed on existing meter-mix casting equipment. The closest that we could come was a source of 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, it was decided that this material should be surface-modified and evaluated.

Unexpected results were again obtained. Surface-modified HDPE particles (INHANCE™ HD-1800) in cast polyurethane formulations are nearly as good as surface-modified UHMW PE (INHANCE™ UH-1700) for increasing abrasion resistance. These results are summarized in Figure IX. This was an important discovery that opened opportunities for polymer-polymer composites in high volume cast polyurethane as well as various coatings markets.

Figure IX

ABRASION RESISTANCE
UHMW PE VERSUS HDPE PARTICLES

Particles in Cast PU[1]	NBS Abrasion Results[2]
None	213
25% INHANCE™ UH-1700 (35µ UHMW PE)	783
25% INHANCE™ HD-1800 (18µ HDPE)	746

(1) PPT 95A/Ethacure (2) Larger value indicates greater abrasion resistance

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.

Concerning abrasion resistance, it is important to remember that relative results vary tremendously as a function of test procedures and actual end-use. Several failure mechanisms are involved in the phenomenon of abrasive wear. INHANCE™ particles in specific systems may greatly improve resistance to one type of wear while having negative effects concerning different types of wear.

Tear resistance
Incorporation of surface-modified polymer particles in cast polyurethane (PU) has been shown to increase the tear resistance of these elastomers. Data illustrating this improvement is shown in Figure X. 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.

Incorporation of surface-modified UHMW PE particles in cast polyurethane gives reduced coefficient of friction. This is illustrated in Figure XI. 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 X

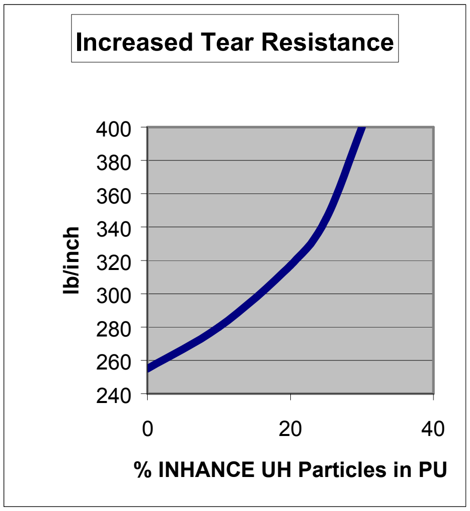
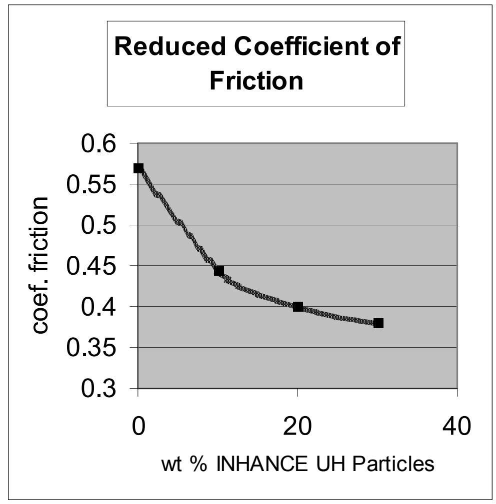


Figure XI



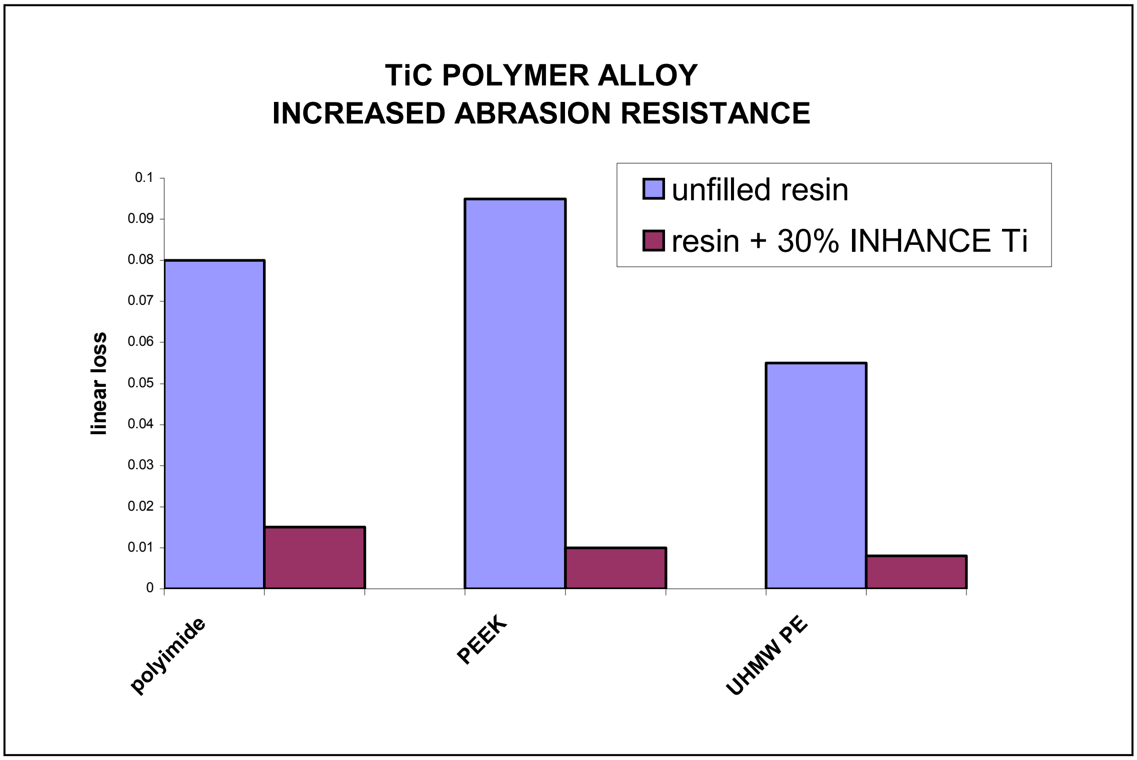
Thermoplastic Molded Goods

Polymer-polymer composites, formed through the combination of INHANCE™ particles with thermoplastics, are in commercial demand. INHANCE™ Ti titanium carbide polymer alloy particles are being used in some important thermoplastic applications. It has been demonstrated that incorporation of INHANCE™ Ti-9113 particles in a broad variety of polymers significantly increases abrasion resistance. Data illustrating improvement in wear resistance for a few examples is summarized in Figure XII. 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.

Oil Well Sucker Rod Guides

One example of INHANCE™ Ti-9113 use that we are allowed to discuss is the manufacture of rod guides. These are devices that keep oil well sucker rods centered in the casings. Initially sucker rod guides were molded in a polyphthalamide compound (Amodel®) made by Amoco Chemical Company. In some wells with very aggressive sand and with sharp curves in the casing, the rod guides wore out quickly – in as little as a few weeks. For the past three years, high performance rod guides molded with 20 – 25% INHANCE™ Ti-9113, have been used in problematic wells with excellent results – lasting for the normal time period between scheduled maintenance.

Figure XII



Reduce Coefficient of Friction

Several companies in the business of making thermoplastic compounds use INHANCE™ UH particles as additives to reduce the coefficient of friction. Many of these uses are in nylons. The INHANCE™ particles bond well to the resin and do not pull out like PTFE particles or molybdenum disulfide.

Latex Paint / Coatings

Paints and coatings are large markets for surface-modified polymer particles. INHANCE™ particles are used in paints and coatings because of the properties they enhance, which include increased abrasion/scrub resistance, greater mar resistance, stronger adhesion to substrates, reduced coefficient of friction, and gloss reduction. The polar surfaces on INHANCE™ particles allows these materials to easily disperse in aqueous latex systems.

Upgrading the performance of latex coatings with INHANCE™ particles sometimes enables these systems to equal or even exceed the performance of two-part (epoxy, polyurethane) and solvent-based coatings. Once target performance levels are achieved, it is almost always desirable to use latex because of ease of application and avoidance of solvents and hazardous chemicals.

INHANCE™ polyethylene particles are used in latex paint formulations to improve abrasion resistance, mar resistance, and scrub resistance. Data in Figure XIII, developed by an outside laboratory, illustrates the increase in scrub resistance.

Figure XIII

LATEX PAINT SCRUB RESISTANCE

ASTM Test Method D 2486

INHANCE™ content →	none	10% HD-1800	10% UH-1250
Cycles until breakthrough	110	160	385

Surface-modified polymer particles are also used in paints and coatings to impart profile for slip-resistance. These particles are used in a broad range of polymer types, including latex, polyurethane, polyurea, and epoxy. The particles are either included with other ingredients in the formulation or they are broadcast after the coating has been applied.

Future Prospects

For initial commercial applications, surface-modified polymer particles are being used as performance additives. The particles are being added to polymer systems currently being used to make specific end products. However, we predict that in the future, polymer-polymer composite materials will be selected to displace materials that are currently used to make specific items. For example, we see combinations of INHANCE™ Ti titanium carbide polymer alloy and various polymers displacing metal in the manufacture of numerous automotive components currently made in metal. These polymer-polymer composites offer benefits that include greater durability, lighter weight, and corrosion resistance. They can also be mass-produced by injection molding.

CONCLUSIONS

Surface-modification of polymer particles enables them to be combined with and to bond to polymer systems with which they are normally incompatible. By combining surface-modified polymer particles with various polymers, novel polymer-polymer composites are formed. Because of the several degrees of freedom that one has in creating these composites, this is a powerful approach for custom tailoring the properties of materials. Polymer-polymer composites have been developed to achieve combinations of physical properties that make them ideal for specific applications.

References

[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