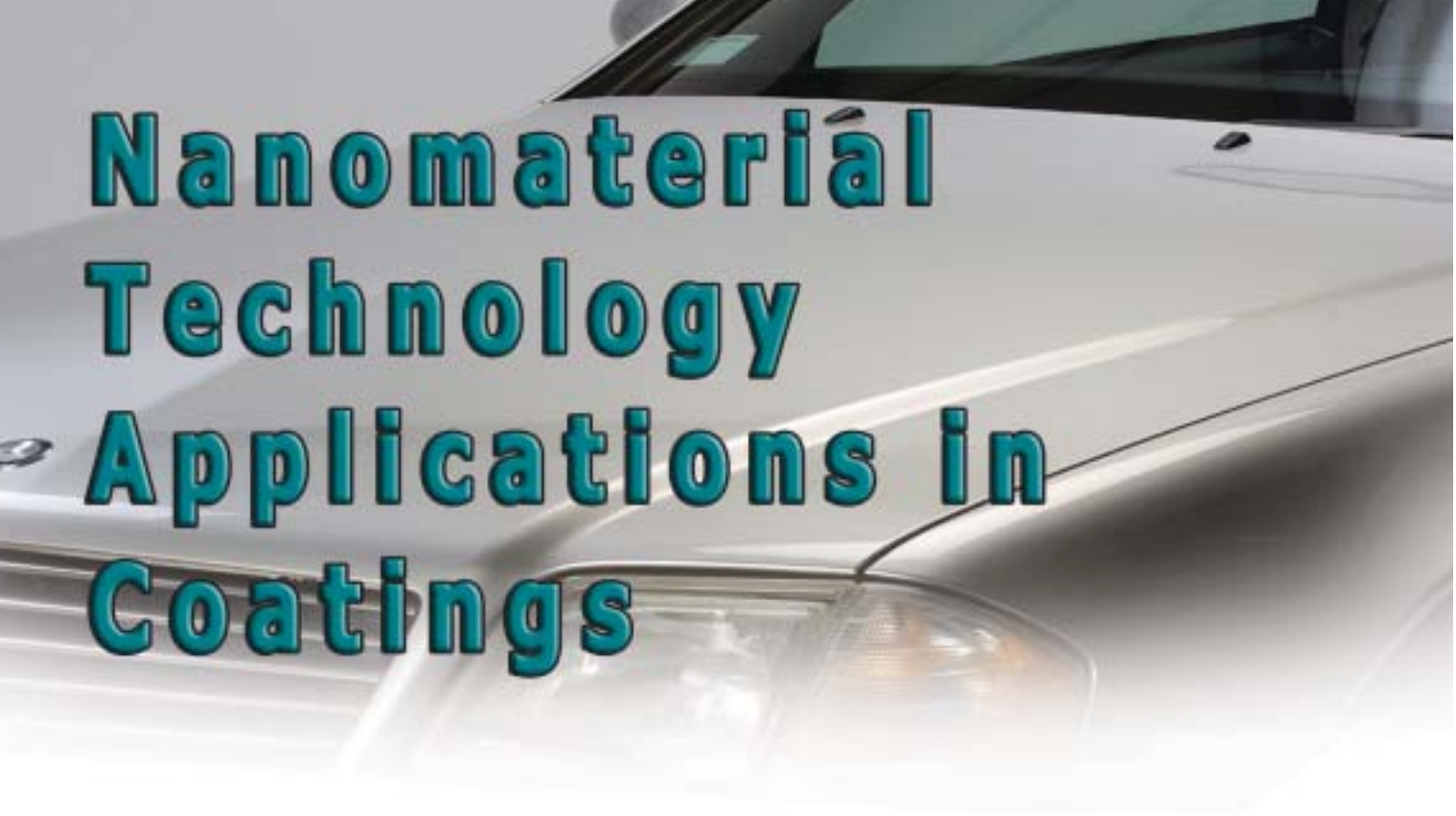

Nanomaterial Technology Applications in Coatings

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Nanomaterial technology is receiving a great deal of attention in the coatings industry today. Several approaches within this technology can be used to achieve organic-inorganic nanocomposite or nanostructured coatings. These approaches include incorporation of preformed nanoparticles in organic resin systems, in-situ generation of nanoparticles or nanophases, and other nanostructuring mechanisms. Following an overview of benefits and critical issues of nanomaterial technology, this article reviews advancements in the application of nanomaterial technology to coatings. Several commercial applications of the technology are described.

INTRODUCTION

Nanomaterial technology, a subset of more broadly defined nanotechnology, is of great interest to the coatings industry today. This interest is clearly evident if one examines the number of nanomaterial-related research publications and patents, and the number of nanomaterial companies that have appeared in recent years. The interest was clearly evident at ICE 2003 in Philadelphia last year, where the one-day workshop on "Nanotechnology" was attended by a record number of participants. Patent activities in this area were the subject of the "Nanocoating Intellectual Property" conference organized by InteCap, Inc. last year.[1] According to information presented at that conference, there were 3200 worldwide U.S. patent publications related to nanomaterials in coatings, compared to about 1200 in 1997, and about 600 in 1992. It does not matter whether you are in an industrial, government, or academic lab, you cannot escape the fact that "nano-projects" receive a great deal of attention, and a significant portion of the resources available. The primary reason for the high level of interest is the promise of

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this technology to deliver breakthrough coating performance in such areas as, for example, scratch and mar resistance, barrier properties including corrosion resistance, and mechanical properties. Promoters of nanotechnology, a technology defined on the basis of a length scale, have done a great job of selling the idea that "smaller is better."

It should be noted, however, that "smaller is better" is not an entirely new concept to coating scientists and formulators. Several decades ago, coating scientists learned that small particle size latexes are better film formers and provide superior pigment binding ability in architectural paints.[2,3] This led to the introduction of small particle (100 nm and smaller) latexes by several raw material suppliers. Polyurethane dispersions (PUDs), which are commonly used in coatings, provide another example of organic nanoparticles.[4] Early use of colloidal silica and other nanoparticles in coatings has been reported as well.[5] However, such early work on applications of nanomaterials in coatings has been sporadic and disjointed. Today, although not formally coordinated in most cases, there are many groups around the world investigating many different aspects of nanomaterial applications in coatings. As a result, conditions are mature for breakthroughs in this area over the next several years. This article reviews various nanomaterial technologies of interest to the coating industry, with particular emphasis on coating performance enhancements offered by these technologies. Overviews and reviews of the broad spectrum of other nanotechnologies can be found elsewhere.[6-9]

IMPORTANT ATTRIBUTES OF NANOPARTICLES IN COATINGS

The basic purpose of applying nanomaterial technology to coatings is to produce either a nanocomposite (e.g., inorganic nanoparticles in an organic matrix), or nanostructure within a single phase coating. The length scale of interest here is from a few nanometers to about 100 nm. The category of nanomaterials includes any material having at least one of its dimensions in the range between few nanometers and about 100 nm. From a coatings perspective the small length scale that separates this technology, say from "micro-technology" has two key effects: first, there is a relatively large amount of interfacial material and second, the materials are optically clear.

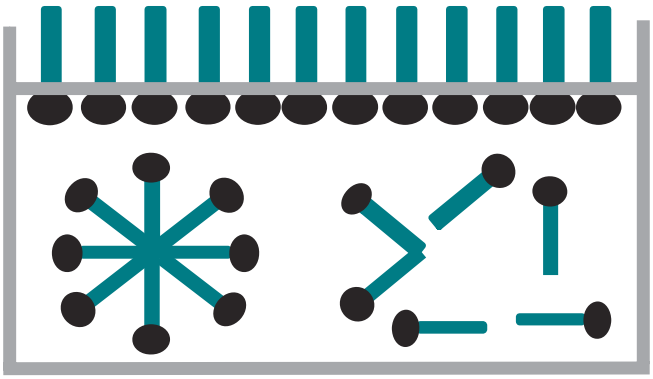
Large Interfacial Material Content

It is well established that the properties of "interfacial material" at the interface between two materials are different from the bulk properties of either material. To illustrate this, consider the interface between an aqueous surfactant mixture and air. As shown in *Figure* 1, at appropriate concentrations, surfactant molecules form a monolayer at the interface by migrating to the water/air interface and aligning as indicated in the figure in order to reduce the surface free energy. The result is formation of an interfacial layer having a very different composition from the bulk surfactant/water mixture or air. Another example is the modification of glass transition temperature (T_g) of a polymer at an interface. T_g of the polymer changes due to the steric and enthalpic effects that alter the segmental mobility of the polymer molecule at a polymer/filler interface.[10-12] How different the composition and physical properties of the interfacial layer are depends on the chemistry and the interactions between the two bulk phase materials. Thickness of the interfacial layer can also vary, but typically is in the range of 1–10 nm. In theory, the difference in properties of "interfacial material" when compared to the bulk material should alter the properties of the whole composite. However, in a typical composite (e.g., a coating filled with micron size fillers) this phenomenon has an insignificant effect on the overall properties because of the relatively small interfacial area involved. In a nanocomposite, on the other hand, this area can be at least an order of magnitude higher. As a result, the "interfacial material" content can be very significant.

Consider an example where an inorganic material made up of uniform, spherical particles is incorporated into an organic coat-

- Nanometer is a billionth of a meter.
- Nanometer is approximately 10 times the size of hydrogen atom.
- Particle size of typical hiding grade TiO_2 is approximately 200 nm.
- Automotive grade leafy aluminum flakes are approximately 100 nm thick and 25,000 nm (25 micron) long.
- Size ratio between a nanometer and a soccer ball is the same ratio as soccer ball to the planet earth.

Figure 1—Schematic of surfactant monolayer formation at the aqueous-air interface.



ing (*Figure* 2). In one case the particles are large, and in the other case they are small. In each case there is an interfacial region where several molecular layers of the two phases behave differently from bulk. Dispersing nanoparticles instead of larger particles allows a coating formulator to increase the interfacial material content significantly. This is illustrated in *Table* 1 in which the effect of particle size and the interfacial layer thickness on the volume fraction of interfacial material content is presented. The calculations apply for a dispersion of particles in a continuous polymer matrix at 30 volume% loading. For example, at a particle size of 300 nm and interfacial layer thickness of 10 nm, the interfacial material content is 3%, whereas it increases to 22% when the particle size is decreased to 50 nm. Thus, the interfacial material becomes a major portion of the composite coating. If the interfacial material has better properties that are not offered by individual materials of the composite, this approach would maximize such benefits.

What has been discussed so far is enhancing interfacial effects that are already present in a macro-composite by transforming the system into a nanocomposite. A related but different effect is that even in the absence of entropic or enthalpic effects at the interface, a nanomaterial would have altered properties because a large fraction of the material could be under unbalanced atomic scale forces. Bulk properties of a material are not scalable down to this size scale (referred as non-scalable region[8]). This aspect of a material is captured by Baer et al. in a recent review article[8] with the statement, "A distinction may be drawn between 'smaller is better' nanotechnology and a more complex and perhaps richer field of nanoscale functionality which is unobtainable in 'bulk' materials or extension of bulk material properties." Such quantum properties as electron-hole formation, photovoltaics, and nonlinear optics are attainable in this region.

Optical Clarity

Optical clarity is an essential property of a number of classes of coatings, such as automobile clearcoats, floor wear layers, and optical lens coatings. Unless the refractive index can be matched to that of the coating resin, adding inorganic particles causes light scattering that leads to reduction or elimination of film clarity. Since nanoparticles are small compared to the wavelength range of visible light (400–800 nm), they scatter very little light. Therefore, they can be added to a clearcoating formulation with little or no adverse impact on visual characteristics. This feature of nanoparticles is extremely important in expanding nanoparticle applications in coatings.

NANOCOMPOSITE AND NANOSTRUCTURED COATINGS

As mentioned earlier, approaches to produce a nanocomposite or a nanostructured coating include incorporation of preformed nanoparticles, in-situ generation of nanoparticles or nanophases, and nanostructuring by other means. These approaches are discussed in detail below with representative examples.

Incorporation of Pre-formed Particles

A critical requirement for reaping the potential benefits of incorporating nanoparticles in a coating is nanoscale dispersion of the particles. In fact, the dispersion issue is one of the major barriers to more rapid introduction of new products in this area. Early attempts to commercialize nano "titanium dioxide" (TiO_2)[13] were unsuccessful because of the high degree of agglomeration of the powder and subsequent difficulties in redispersing the particles in coatings. One approach to achieve nanoscale dispersion is to use effective grinding methods such as ball milling.[9,14] Effective dispersing requires grinding media that is much smaller than those used for dispersing conventional particles. The high surface area generated can significantly increase the dispersant demand. A recent article

Table 1—Interfacial Material Volume Fraction Dependence on Particle Size (Particle Loading—30% by volume; interfacial layer thickness—10 nm)

Particle diameter (nm)	300	250	200	150	100	50
Interfacial volume fraction	0.03	0.04	0.05	0.06	0.10	0.22

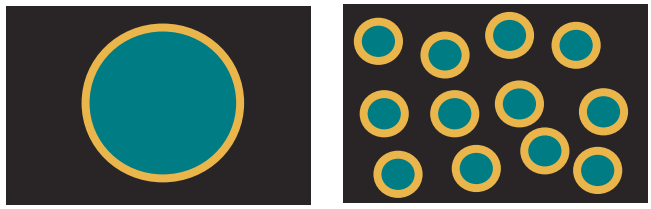
described how to optimize dispersion methods for nanopowders in coatings.[14] High viscosity caused by finely dispersed nanoparticles is another problem that needs to be addressed. The large surface area can increase viscosities due to the increase in interfacial forces (e.g., electroviscous forces) and limit the amount of nanoparticles that can be incorporated. Adding the right surface functionality to address dispersibility and viscosity rise is another approach to address the dispersion issue. In addition to promoting dispersion, functionalizing the particle surface enables the nanoparticle to be covalently linked to the organic resin matrix.

Most of the nanoparticle research and development in raw material suppliers' laboratories have been focused on functionalizing and other surface treatments of nanoparticles. Such efforts are facilitating commercialization of an increasing number of nanoparticle types for coating applications. For example, colloidal silica has been available from at least a dozen companies around the world in the particle sizes range from about 2 nm to 100 nm, in aqueous and nonaqueous media. Nonaqueous media include both solvents and polymerizable monomers. More and more grades are now becoming available with functional groups attached to the particle surface to improve dispersion and enable the particles to be covalently linked with the organic matrix. Recent advances in functionalization of colloidal silica present the greatest promise for growing the use of this material in coatings. Several studies have reported[15-18] the use of functionalized nanosilica in UV-curable resins to prepare UV-cured coatings with improved abrasion, scratch, and chemical resistance while maintaining a high gloss and film clarity. In these studies high silica loadings have been achieved by the selection of surface functional groups compatible with the dispersion medium (solvent and/or monomer) to minimize viscosity.

A European luxury car manufacturer recently announced use of nanoparticles (referred to as ceramic particles) in a clearcoat application.[19] This coating is claimed to be world's first automotive clearcoat that incorporates nanoparticles to achieve performance enhancements. The particles are reported to be less than 20 nm in diameter, and crosslinked at 140°C. Compared with conventional clearcoats, the new coating system is claimed to have 40% better gloss retention after car wash tests. A few months earlier, a major U.S. paint company announced introduction of a nanoparticle-based automotive clearcoat with the trade name "CeramiClear." The announcement made reference to the company's joint development efforts with a European luxury car manufacturer. At least two recent patent applications relate to this type of approach.[20,21]

Fumed silica represents another important nanoparticle silica technology. This material, made by flame hydrolysis of silicon tetrachloride, has also been around for many decades. However, this process produces fused or agglomerated nano silica particles, and as a result, dispersion is difficult and viscosities are high even at low loading levels. Its primary use in coatings has been as a rheology modifier. However, recently reported results on functionalized fumed silica claim measurable improvements in abrasion, and scratch and mar resistance in UV-cured clearcoats.[22]

Figure 2—Incorporation of uniform, spherical filler particles into an organic coating: (a) macro-particles; (b) nanoparticles.

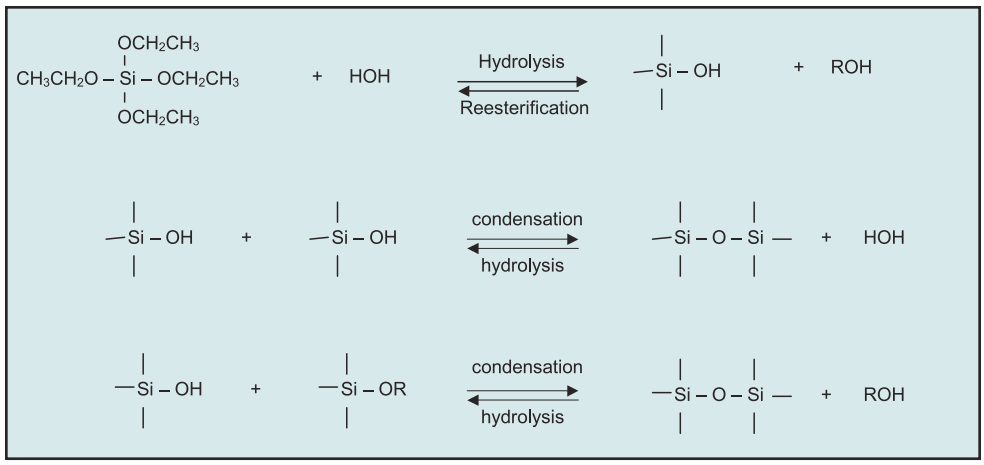


(a) (b)

Another important class of nanoparticles finding increasing commercial applications is titanium dioxide. Typical grades are supplied at approximately 200 nm average size[23,24] to optimize light scattering and hiding power when incorporated in a coating. Pure TiO_2 surface can catalyze degradation of organic compounds in the presence of UV radiation and moisture.[23] This phenomenon was exploited in old "chalking paints"[25] sold for exterior decorative applications. Upon exposure to exterior UV and moisture, the top layer of such paints would degrade and become "chalky." During a rain storm this layer would wash off with any dirt collected, thus maintaining a clean appearance. Since photocatalytic degradation is undesirable in other, more typical coatings, hiding grades of TiO_2 are supplied with a thin layer of silica, alumina or other surface treatment. There is a great deal of interest in utilizing the photocatalytic activity of TiO_2 to create germicidal,[26] and self-cleaning surfaces. An early application of this phenomenon includes clear coatings for light fixtures installed in difficult to clean locations such as traffic tunnels. In order to maintain film clarity, nano titania must be used in these applications. A more recent introduction of "self-cleaning" technology includes exterior windows coated with nano titania.[27]

Another utility of titanium dioxide's photocatalytic activity is in preparation of anti-fogging surfaces. Application of a thin layer of nano titania on a surface such as glass can make that surface highly polar in the presence of UV and a small amount of moisture. On such a glass surface, trace amounts of water would spontaneously spread to form a thin layer rather than forming tiny water droplets that make the glass foggy.

Scheme 1—Sol-gel hydrolysis/condensation reaction of TEOS.



This phenomenon is utilized to fabricate anti-fog glass for such applications as automobile windows.[28]

The ability of TiO_2 to absorb UV radiation is the primary reason for its use in sunscreen lotions. Nano TiO_2 is in increasing demand for this application because it makes the lotion clear rather than opaque once applied. In coatings, nano titania is being studied as a replacement for UV stabilizers such as hindered amines. In one such study,[29] the behavior of nanoparticle (6–92 nm rutile and anatase titania) titanium dioxide as UV absorbers in water-based acrylic and isocyanate-based acrylic coatings was investigated. Results indicate comparable or better performance compared to HALS within the system studied.

Zinc oxide and barium sulfide are two other significant materials that are available in nanoparticle form for coating applications. ZnO_2 nanoparticles' role in coatings is somewhat parallel to the role as a hiding pigment. Its use as an antibacterial agent[30] and as a light stabilizer has been reported. Raw material suppliers have announced[31] plans to increase the availability of nano zinc oxide for coating applications as well as sunscreen applications. Nano barium sulfate is promoted as a pigment dispersion stabilizer and as a functional additive for a variety of clearcoats.[32]

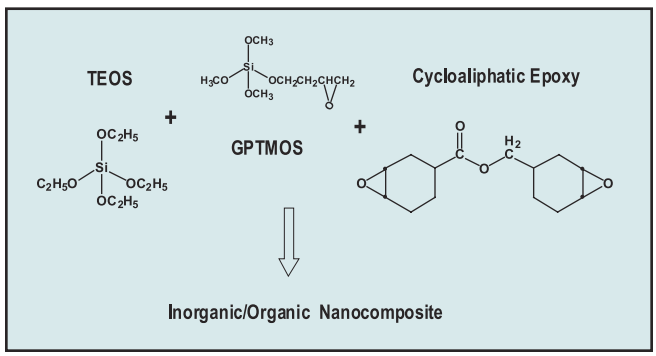
Nanoclays represent another class of inorganic nanoparticles. Incorporation of clays (layered silicates) and organoclays in polymers has been widely studied.[33] Preparation of nanocomposites with clays involve delamination and random distribution of clay platelets (exfoliation) or placement of polymer molecules between clay platelets (intercalation). Processing conditions and other aspects of preparing these composites limit their applications in coatings—clearcoats, in particular. However, a synthetic, lithium aluminum silicate clay that can be dispersed into nanosize primary particles (e.g., Laponite) has been in the market for a long time. Its primary use is as a rheology modifier. Its use as a coatings additive to improve performance has been reported as well.[5]

In-Situ Generation of Nanoparticles and Nanostructure

The most common approach to generate inorganic particles or nanophases within an organic matrix is to utilize sol-gel chemistry of silanes (e.g., tetraethoxy orthosilane, TEOS). The hydrolysis and condensation reaction of TEOS (*Scheme* 1) can yield colloidal silica particles of varying sizes including nanoparticles under alkaline conditions, or a crosslinked monolith under acidic conditions.[34] Under controlled conditions, silanes and organic molecules can form coatings containing silica nanoparticles or nanophases. In the presence of a coupling agent, the organic and inorganic phases can be covalently linked (*Scheme* 2). This approach has been in practice, including in commercial products, for more than 15 years.[35,36] Inorganic/organic hybrid coatings prepared by the sol-gel route have been the subject of extensive research since then. Several representative examples are discussed below.

Feasibility of sol-gel derived organic/inorganic hybrid coatings as a replacement for aircraft aluminum alloy primers containing chromate corrosion inhibitors has been an active area of research.[37-39] Other studies have shown improved photostability in aircraft and exterior architectural applications.[37,40] Improving scratch resistance of soft substrates such as polycarbonate and

Scheme 2—Approach to inorganic-organic hybrid films.



plastics, and steel has been the focus of other studies.[16,41,42] Properties and the nanostructure of the final coating on one hand depend on the selection of silane, coupling agent (if present) and the chemistry of the organic phase. On the other hand, to a large degree, the same attributes depend on the pH and aging conditions of the sol-gel mix and precursors. Often, the silane precursor mixture is aged under acidic conditions to favor the formation of silica clusters in the few nanometer size range. Therefore, coatings prepared with aged silica precursors may be considered under the previous section. The important point to note, however, is the fact that the nanostucture of the final film depends heavily on the processing conditions. The formation of distinct silica particles of different sizes (depending on composition) is documented.[43] However, better understanding of the nanostructure and its control continue to be active areas of research.

As the hydrolysis/condensation reaction of TEOS (*Scheme* 1) indicates, these reactions are reversible. This reversibility is a significant issue in developing hybrid coatings for applications where long-term durability is essential. Cost/benefit ratio is another significant issue for these coatings as well as applications discussed in the previous section.

Attempts to develop low dielectric constant (low k) coatings for electronics industry represent another example of an application of sol-gel chemistry. In this application, surfactants are used at high enough concentrations to form cylindrical and other mesostructures (typically in alcohol/water mixtures). These mesostructures can act as templates for organizing silica formed in-situ from appropriate silica precursors. Such systems have been shown to form nanostructured, hybrid coatings. Pyrolysis of the surfactants leaves a porous silica coating on a silicon substrate, thus forming a coating with lower k than silica itself. This area is of significant interest to today's semiconductor industry.[44,45]

Nanostructuring

In this last section, a few additional approaches to nanostructuring of coatings are discussed. One interesting approach involves attempting to mimic the skin of dolphins. Dolphin skin is known to have nanometer scale roughness that helps reduce the adhesion of barnacles, tube worms, and other marine organisms. Because of the adhesion reduction caused by the reduced contact area between the skin and marine organisms, they can be shed by water turbulence once the dolphin begins to swim. To mimic this nanostructure, two normally incompatible polymers (a hyperbranched fluoropolymer and a linear polyethylene glycol) have been mixed and applied on a substrate. As the polymers phase separate, they are crosslinked to create a nanostructured coating that has nanoscale roughness.[46] Research in this area is directed towards developing nontoxic coatings for marine coating applications.

Another example of nanostructuring a surface involves creation of nanoscale roughness on polypropylene.[47] In this approach carefully selected solvents are applied on the polypropylene substrate and dried under controlled conditions to create the nanoscale roughness. The result is a super-hydrophobic surface having a water contact angle as high as 160°. Such surfaces are attractive for applications such as antennas, self-cleaning traffic signals, etc., because of the reduced affinity to water and snow. Nanostructured coatings from both approaches discussed in this section can be developed as drag reduction coatings to marine vessels. The recently reported "lotus effect,"[48] a term coined to capture the mechanism of how water droplets help clean lotus leaves, essentially follows the same principles.

CLOSING REMARKS

Nanotechnology presents a wide range of opportunities to improve performance of coatings, and incorporate new performance features. Several different approaches to applying nanomaterial technology in coatings have been discussed in this article. Although nanomaterials are not entirely new to coating industry, advancement in this area has been limited until recent years. The heightened interest in broader nanotechnology has had a major impact on the pace of nanomaterial technology applications in coatings. CT

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