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Design colloidal particle morphology and self-assembly for coating applications

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The progressive replacement of organic solvent-based coatings by waterborne latex polymer coatings has substantially renovated the coating industry, and generated huge environmental and health benefits. Today, on top of the continuing demand for higher performance and lower costs, the coating industry faces tighter regulation and higher sustainability standards. In addition, the new waterborne coatings have created unique opportunities and challenges in terms of fundamental understanding and research development. To address these challenges, polymer latex binders with diverse particle morphologies have been developed to improve coating performance. Furthermore, colloidal self-assembly has been utilized to help manufacturers make better paint with less cost. In this report, we review the recent progress in both fundamental study and industrial application in the context of developing new generation architectural coating materials. We introduce the basic concepts in coating materials and showcase several key technologies that have been implemented to improve coating performance. These technologies also represent the most important considerations in architectural coating design.

1. Introduction

Coating materials have a wide impact in our daily life, from household paint to traffic markings on the road. Coatings not only fulfill the aesthetic needs, but also provide critical function for protecting the surfaces. Latest forecasts predict global demand for paint and coatings to rise 3.7 percent per year to 54.7 million metric tons in 2020, valued at total $193 billion.[1]

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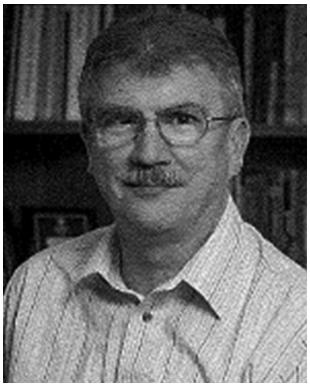
The coating industry has been through dramatic changes in the past 60 years due to the development in new technology, increasing regulations and cost pressures. In most regions around the world, the volatile organic compounds (VOC) in coatings are now under regulation. For example, in North America, due to the air basin geography and severe smog issues, some of the most stringent regulatory compliance standards are enforced in California, set by Southern California Air Quality Management District (SCAQMD). Europe and Asia have also imposed their own regulations. With the increasing environmental awareness and growing media coverage, consumers are looking more closely at paint can labels and searching for eco-friendlier products.

In order to address these challenges, advanced colloidal particle design, additives, and formulation techniques have been developed to improve coating performance while reducing VOC level and cost. In this report, we will discuss the recent progress in colloidal particle design, contrasting academic and industrial R&D approaches, with the hope to inspire more dialogue and collaboration in the future. Although academia and industry face different problems and use very different methodologies, we see the potential for concerted effort to solve challenging issues together. On the one hand, fundamental studies initiated from different perspectives may bring new ideas and inspiration for coating materials research. The results from academia may also be leveraged to solve technical difficulties in coating industries. One example is the employment of computer simulation in the field of colloids. The techniques have demonstrated powerful insight in terms of fundamental physics and understanding of colloidal systems, which can be equally useful in coating materials design. Another example is the development of self-assembly concept in academia. Actually, manufacturing of coating materials involves many assembly processes; however, these processes have not been systematically studied or categorized in the context of coating formulations. On the other hand, recent progress in industrial



Alvin Maurice

Alvin (Al) Maurice, Research Fellow, Dow Coating Materials, joined Dow/Rohm and Haas in 1982 after completing his PhD in Physical Chemistry from the University of Illinois. His primarily focus has been on emulsion polymer synthesis for Architectural Coatings. In 1992, Al was promoted to Section Manager for Architectural Coatings. In 2004, Al took on the role of Global Technology Manager with responsibility for global segments of Architectural Coatings R&D including a consulting/mentoring role with our R&D lab in China. In 2010, Al moved from the managerial to the technical ladder becoming a Dow Fellow. In 2015, Al was promoted to Dow Research Fellow.

James Bohling

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R&D may provide new inspirations and directions for academic research. In commercial applications, coating material formulations involve many additives, such as specially engineered rheology modifiers. These molecules have dramatic impact on the coating performance, as well as the assembly behaviors of the coating system. However, academic research usually embraces simple systems, which obviates the effect of additives and different components in practical applications.

We will first briefly review recent developments in the fundamental study of colloidal morphology and self-assembly of colloidal molecules and Janus particles. The concepts introduced here will help us better understand the recent development in coating technologies. Then we will highlight waterborne latex polymers and review their applications in architectural coatings. Rather than focusing on the details of polymer chemistry, we will discuss the basic rules for coating materials design, and outline how morphology and assembly provide new perspectives and opportunities to improve different aspects of coating materials. We will showcase the technologies that help lower environmental impact, improve coating performance, reduce product cost and develop new "smart coating" materials. These technologies also represent the most important considerations in architectural coating design, including sustainability, mechanical property, rheology profile, production cost and new functionality.

2. Progress in fundamental study

2.1 Colloidal molecules

Colloids have been extensively studied in many different research fields. For example, porous structures and core–shell morphology are widely used for drug delivery and controlled release.[2] On the fundamental side, colloids have been used as model systems to study the principles that guide the interaction and structure of atoms and molecules.[3] These models have been instrumental in shedding light into several fundamental problems in condensed-matter physics, such as glass transition,[4,5] crystal nucleation growth,[6,7] and phase behaviors.[8]

However, unlike molecules, which have different chemical composition and molecular geometry, conventional colloids are usually spherical in shape, homogeneous in composition, and have isotropic interactions. Considerable effort has been devoted to fabricate colloids or colloid clusters that mimic the geometry and interactions of their molecular counterparts.

The concept of colloidal molecules was initially raised to describe one of the early successes in fabricating the small uniform colloidal clusters.[9] The clusters were formed by drying the emulsion droplet that encapsulated individual colloidal particles. A more scalable approach was developed by growing polymers on the surface of silica particles as shown in Fig. 1.[10] Furthermore, different shapes of colloidal particles were fabricated using the metal–organic frameworks (MOF) methods as shown in Fig. 2.[11]

The capability of obtaining colloids similar to molecules creates opportunities for further advances in colloidal assembly. Colloidal molecules can form diverse crystal structures, which enable important applications in fabricating photonic crystals.

2.2 Janus particles

Another important development in fundamental colloidal study is Janus particle research. The Janus particle concept has created a lot of excitement in the colloidal research field.[12] Janus is the name of an ancient Roman god who has two faces looking in two opposite directions. Different from the concept of colloidal molecules, Janus particle research emphasizes the different chemical make-up on each side of a single particle. It

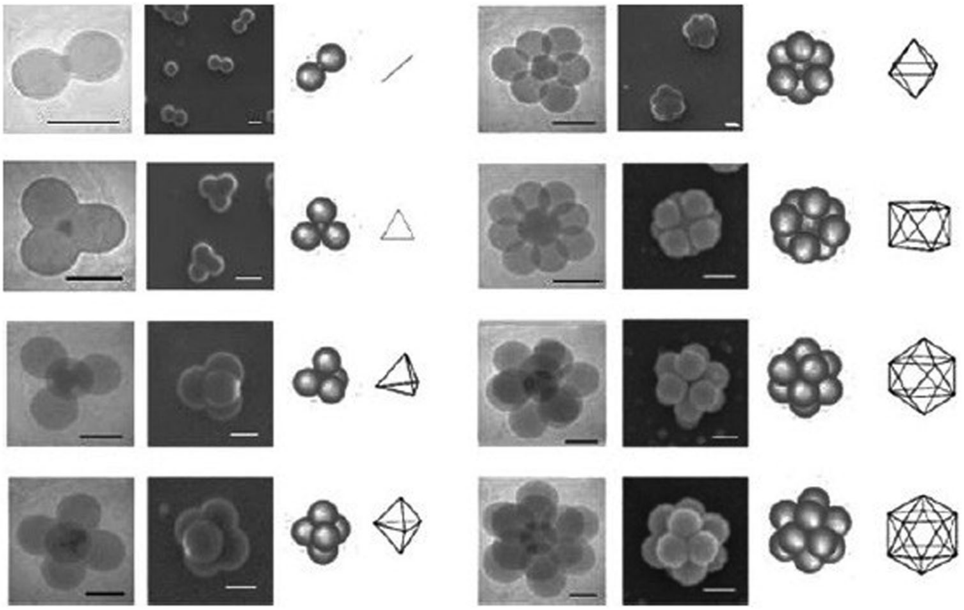


Fig. 1 Electron microscopy images of particle clusters and schematic drawings of the configuration. Reproduced from ref. 10 with permission from the Angewandte Chemie International Edition, copyright 2008.

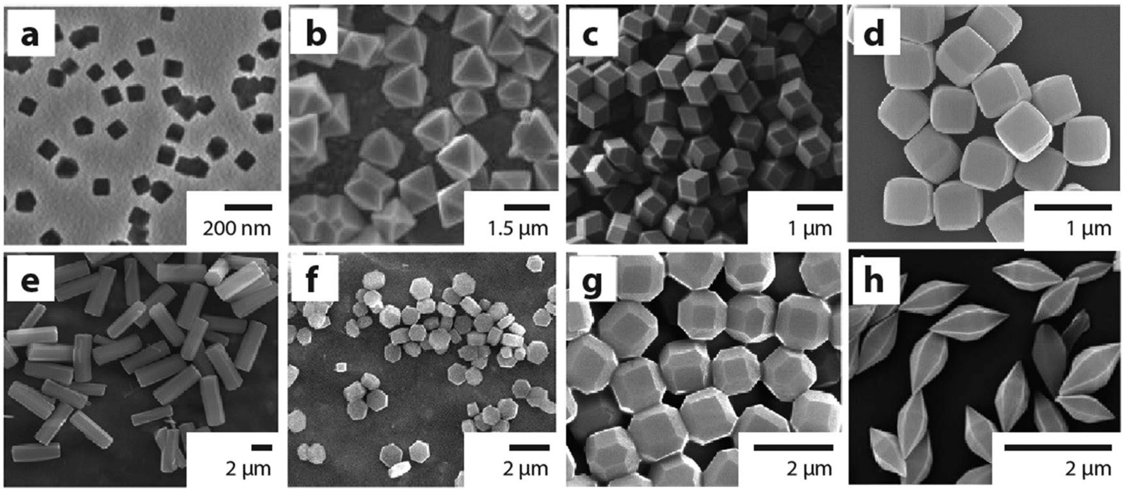


Fig. 2 Examples of polyhedral colloids synthesized from metal–organic frameworks: (a) cubes, (b) octahedra, (c) rhombic dodecahedra, (d) truncated cubes, (e) hexagonal rods, (f) hexagonal discs, (g) truncated rhombic dodecahedra, and (h) bipyramidal hexagonal prisms. Reproduced from ref. 11 with permission from the American Chemical Society, copyright 2014.

is easy to view an amphiphilic Janus particle as the colloidal version of a small surfactant molecule. Since surfactant molecules are widely used in coating formulations, Janus particles can be of particular interest for coating applications. For example, Janus particles may be used as stabilizer or emulsifier for coating materials. Janus particles may also be used as a unique binder.[13,14] The Janus geometry can be further extended to other patchy geometries, such as trivalent particles,[15] with two different chemistries on each side of the particle, and a third chemistry in between as shown in Fig. 3.

A lot of effort has been invested to synthesize Janus and patchy particles.[16] Although many different approaches have been developed recently,[17–20] and some of the methods have the potential to be scaled up,[13,14] most of the methods can hardly be mass produced economically to industrial levels. Many methods require unique chemistry and reaction conditions,[18] and some methods require an extra cleaning and separation step,[15] which cannot be easily adapted in large-scale manufacture. More versatile and scalable synthetic routes are yet to be developed. Obviously, full adoption by the coatings industry also depends on having a complete cost analysis and a compelling value proposition.

Here is a list of additional criteria that can be used to evaluate the synthetic method:

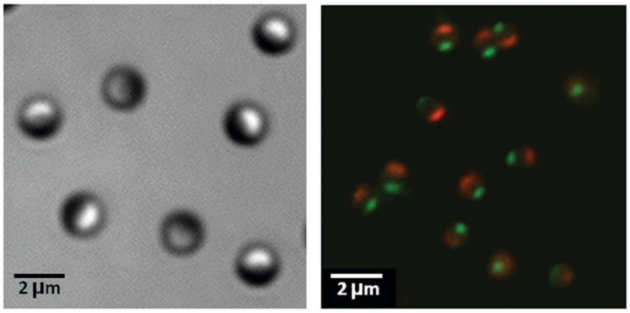


Fig. 3 Janus and trivalent particles.[15]

(1) Homogeneity: whether particles are homogeneous in size and geometry;

(2) Tunability: whether it is possible to change the shape, size of the particles and fine tune the Janus geometry;

(3) Functionality: whether it is easy to change materials of the particles and functionalize the surface;

(4) Scalability: whether it is possible to scale up the procedure for commercial production.

One important potential application for Janus particles is to stabilize emulsions.[21] Theoretical calculations suggest that Janus particles with the right geometry can offer three times more stabilizing power than homogeneous particles.[22,23] Fig. 4a shows a typical structure of a Pickering emulsion, with adsorbed particles at the emulsion droplet surface. Fig. 4b shows Janus particle with different geometry, termed as Janus balance, may stabilize different types of emulsions.

2.3 Self-assembly

Assembly structures are guided by particle interactions and dependent on the distance between the particles and the environment surrounding the particles. It is also important to emphasize that the interactions of patchy particles not only depend on the geometric shape but also the chemical shape.[24] The assembly structures may not be equilibrated structures; they can be governed by the kinetics as well.

Typical interactions between colloidal particles are electrostatic (repulsive), steric hindrance (repulsive), hydrophobic (attractive) and van der Waals (attractive). More complex interactions can be induced by the combination of these interactions. For example, roughness, capillary forces and depletion forces are employed to assemble particles.[25–27] Even more specific interactions can be programmed by DNA hybridization.[28] Fig. 5 shows the assembly structures can be precisely designed by DNA modified colloidal clusters. If particles have a magnetic component or metallic make-up, assembly can be manipulated by external magnetic or electric fields.[29,30] In addition, the

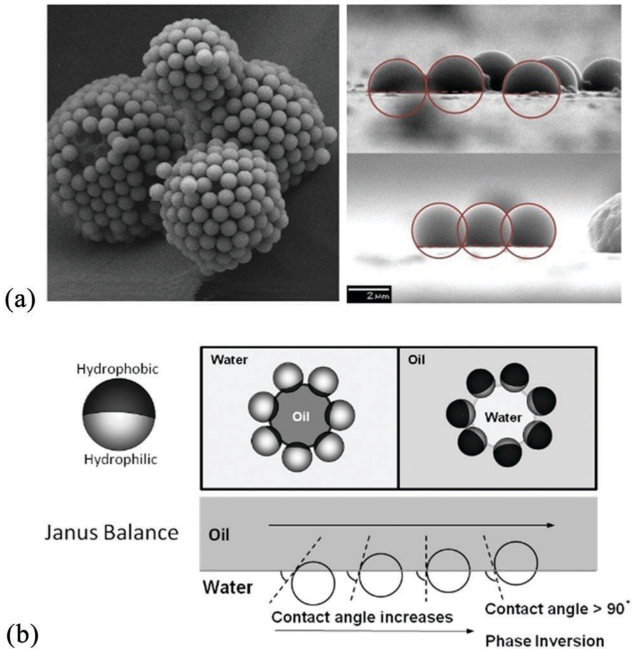


Fig. 4 Janus particles can stabilize emulsions similar to small surfactant molecules: (a) images of particles at interface; (b) emulsion type and Janus balance.[34]

assembly process can also be controlled *via* surface and interface.[31]

A plethora of assembly structures can be obtained by using the simple Janus motif. Theory and computer simulation have predicted many unique structures.[33,34] Experimentally, as shown in Fig. 6, amphiphilic Janus particles were observed to assemble into unique clusters and long chains under different conditions.[32] Janus particles can also form intriguing two dimensional crystal structures as shown in Fig. 7, adopting a hexagonal ordered position, while presenting glassy rotational dynamics.[35] Janus amphiphilic particles were also used to stabilize emulsions by assembling at the interface, similar to surfactant molecules.[12] Sensitive to geometry and surface composition of the Janus particle, the emulsion can be disrupted or inversed when Janus balance is altered.[21,36]

Most of the fundamental research on assembly has been focused on hard particles, their spatial arrangement and orientation, with the goal of achieving photonic crystal structures. Less has been done on the assembly of soft particles, which is more relevant to coating applications. There has been some effort from computer simulation on soft particle assembly;[37] however, it is much more challenging to study the structures in detail *via* experimental samples. For instance, since coating systems usually consist of many different types of small particles

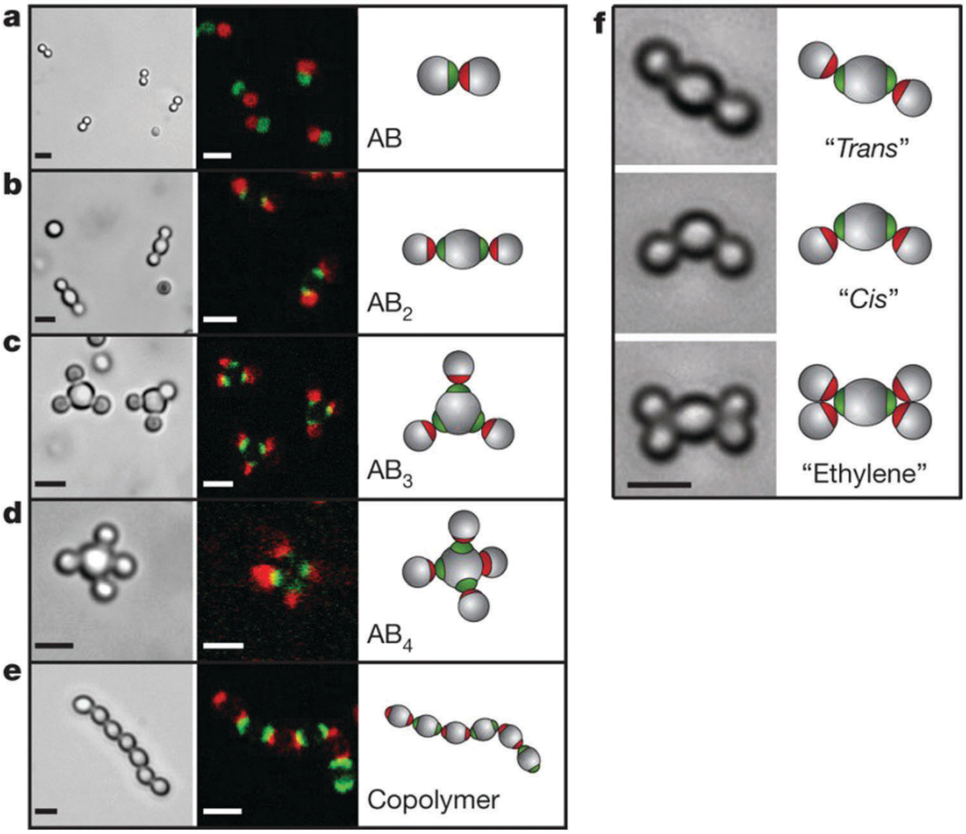


Fig. 5 Assembly structures designed by DNA modified colloidal clusters. Reproduced from ref. 28 with permission from the Nature Publishing Group, copyright 2015.

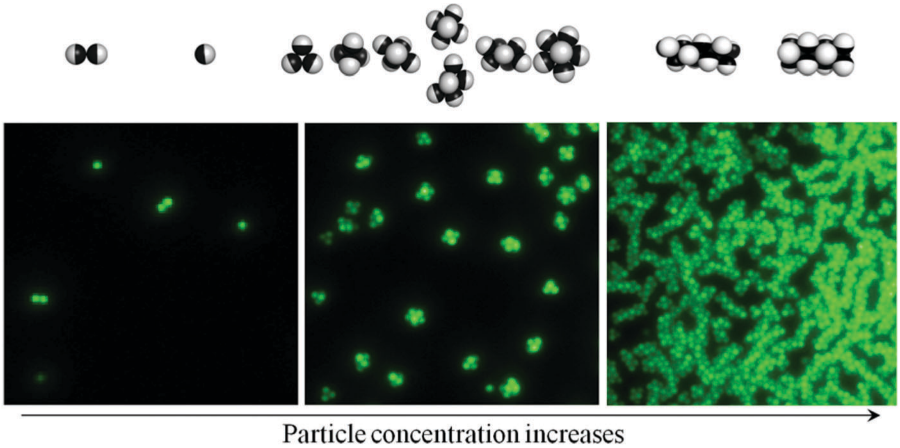


Fig. 6 Clusters and chains assembled by Janus amphiphilic particles.[32]

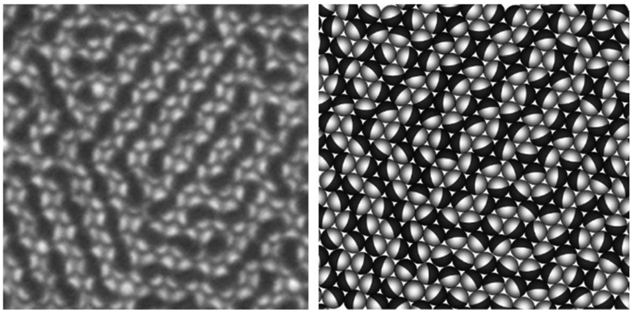


Fig. 7 2D crystal formed by Janus amphiphilic particles: left, optical microscope image, right, computer regenerated image.[35]

in 100 nm to 1 μm size range at rather high volume fraction (20 to 45%), it is very challenging to resolve the detailed structures and dynamics using conventional microscopy. Furthermore, studying the interactions between particles also becomes complicated due to the existence of rheology modifiers, dispersants and surfactant molecules. Even in the final dry state, there is additional complexity due to the phase change and migration of polymer particles from the dispersed phase into a continuous film. As a result, the whole process involves many different stages, and packing is just one step in the film formation process.

Some specialized analytical tools have been developed to study the dynamics and structures of the coating system. Small-angle neutron scattering under shear (rheo-SANS) and ultra small-angle neutron scattering under shear (rheo-USANS) have been applied to explore coating structures *in situ* in aqueous suspensions.[38–40] Real-time, ultra small-angle X-ray scattering has been used to monitor the flocculation of pigment particles during the drying process.[41] Separately, pulsed field gradient (PFG) NMR spectroscopy has been used to probe molecular level interactions on polymer latex particle surfaces.[42] The use of computer simulation has also been adopted to establish models for coating systems.[43,44] In the next section, we will discuss the important rules of material design for coating applications.

3. Development in coating applications

3.1 Basic concepts of waterborne latex polymer coating

The major components of modern waterborne latex coatings are: water, organic solvent, polymer binder, dispersant, rheology modifier, pigment, extender and additive. Polymer binder is the key active ingredient that determines many aspects of the final coating performance. As shown in Fig. 8, by simply adjusting the ratio between polymer binder and inorganic components (pigment and extender), the gloss of the coating films can be tuned. The rheology profile is controlled by the rheology modifier (a major ingredient among additives). However, due to the interactions between rheology modifier and polymer binder particles, different binders may have very different rheological responses even to the same rheology modifier. One important class of rheology modifiers are the hydrophobically modified ethylene oxide urethane (HEUR) rheology modifiers. Although widely used in the coating industry due to their superior flow and leveling performance, the mechanistic details of thickening have only been explored by experiment and computer simulation very recently.[38,40,43,44]

The polymer binder, also described as ''polymer emulsion'', refers to the polymer globules dispersed in the aqueous phase. Polymer binder particles usually range in size from 20 nm to 600 nm, and the typical concentration of the binder in suspension is 20% to 60% by weight. These binder polymer particles are synthesized by a radical emulsion polymerization process.

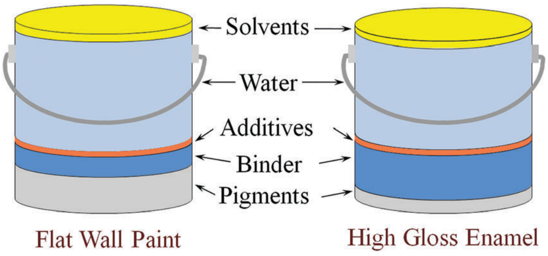


Fig. 8 Major components in a can of paint.

They are stabilized with acidic monomers and surfactants, which bring charge and steric hindrance on the particle surface.

3.2 Coating materials design

Ideally, a desired coating property may be adjusted by simply changing one or two ingredients in the formulation. In reality, due to the interactions between different components, it is much more complicated. Take the extenders as an example, which are typically used as fillers to lower formulation cost. The choice of extenders can drastically change the coating performance. Due to the interactions between extender, additives, and polymer binder particles, many coating properties can be affected, such as stability, adhesion and stain resistance. Because of these types of interactions, often times, creating a good coating formulation is considered as much an art as a science. Indeed, before we can elucidate the detailed interactions of all the components in the paint formulation, the best choice for each of the components may well depend on the experience of the formulator.

The true art in creating a good coating formulation is achieving the balance in performance and cost. Usually for product development, the choice of chemistry and raw materials are limited based on the coating system and the customer performance requirements. Many coating properties are highly correlated. For example, increasing the amount of extender may help improve the hardness, but may hurt gloss and scrub resistance performance. Increasing coalescent levels will help improve film formation, but may increase tackiness. The same is true for the polymer binder design – there is a delicate balance in engineering the optimal binder particle colloidal stability. It is necessary to design enough stability so that binder particles will endure mixing during the paint making process and provide long enough shelf life for the end application. However, making binder particles too stable will hurt film formation and several other coating properties. These examples demonstrate that coating performance is highly correlated with each individual component. Some of the correlations are easy to understand, however some correlations may only be revealed through design of experiment (DOE) and statistical analysis. Without a robust and comprehensive theoretical model, it is important to comprehensively evaluate coating properties and benchmark product performance when optimizing the coating formulation.

One unique feature of coating applications is that the desired performance is different on the two sides of a coating film. For example, tackiness and hydrophobicity are defined by the coating–air interface; however, adhesion depends on interactions at the coating–substrate interface. When designing coating materials for different applications, properties at both interfaces need to be considered.

In the following sections, we demonstrate how different binder particle morphologies, including core–shell and multilobe, can help improve performance of commercial products. We further introduce the concept of self-assembly in coating material design, and show examples of how self-assembly can help reduce product cost and improve coating properties.

3.3 Improving coating performance

3.3.1. Soft-hard elastomer morphology for reducing VOCs. There is a clear definition of VOC in Germany's Blue Angel standard. The term VOC means all volatile organic substances (*e.g.* residual monomers, solvents, coalescent, preservatives and other production-related accompanying substances). The specific value can be obtained by following total evaporation in subsequent gas chromatographic analysis, for content eluted at retention times lower than that of tetradecane (boiling point: 252.6 °C) on a non-polar separation column.

Fig. 9 shows the change of VOC level for household paint in the past 60 years. It has been a great achievement for the coating industry of continuously reducing the VOC level of architecture coatings. On the one hand, this dramatic change has been mandated by government regulations. On the other hand, the huge reduction was only made possible by constantly optimizing polymer binders and coating formulations. Originally, architectural coatings were completely made from alkyds (oil based), which used organic solvents to dissolve the polymers. Ventilation is important for confined spaces and some industrial coatings, and sometimes it is even necessary to wear a respirator during the coating application. The first big reduction in VOCs happened when waterborne latex polymers were introduced in architectural coatings in the 1940s. Since then, oil-based alkyd paint has been gradually replaced over the years. Today only specialized architectural coatings such as some trim paints, in certain regional markets, as well as a number of industrial coatings still employ large amounts of organic solvent. With the expectation that the regulations will grow even tighter in future, the coating industry has kept on improving polymer composition and paint formulations to reduce VOCs. In addition, R&D teams are actively seeking new technology to reduce VOCs. Complete removal of VOCs without negatively impacting coating performance remains a

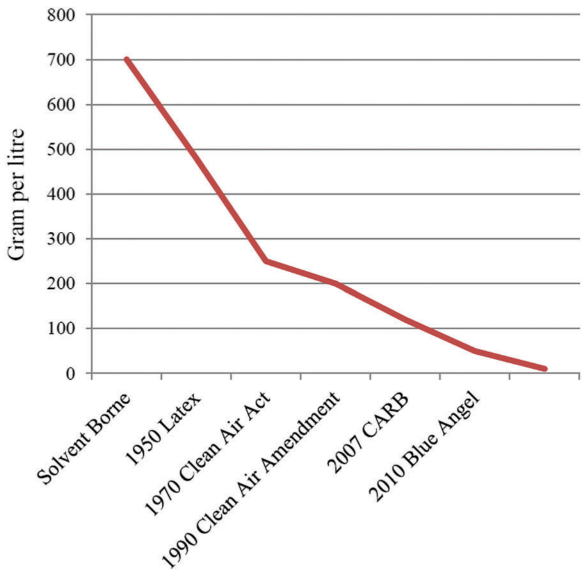


Fig. 9 VOC change of household paint over the years.[47]

significant challenge. This has driven additional studies into the morphology control of polymer latex particles and the invention of new ambient-cure crosslinking technologies.[45,46]

In order to understand the challenge in reducing VOC levels, it is important to understand the latex paint film formation process. Film formation has been extensively studied and reviewed over the past several decades.[48,49] It is generally agreed that the drying procedure contains three steps, as shown in Fig. 10. Initially in Stage I, binder particles become more and more concentrated as water evaporates. When the concentration is high enough, binder particles start to get very close to each other in Stage II, and usually begin forming a very compact and ordered packing if the particle size distribution is narrow enough. Finally, in Stage III as water continues evaporating, capillary forces push particles closer together, which overcome the electrostatic repulsions and eventually deform the particles to form a continuous film.[50]

This seemingly simple process is actually rather complicated, as demonstrated by various studies using different analytical tools and computer simulation.[51–53] With the more advanced microscopy techniques, more details of film formation have been revealed.[54] For instance, it was discovered that between Stage II and Stage III, binder particles arrange in domains with arrays characteristic of colloidal crystals, and particles coalesce first in these domains.[55] A similar phenomenon was also observed in the colloidal crystal formation in different systems.[56,57] In addition, drying of the film is never homogeneous, and film formation usually starts at the air/water interface and film edges, and propagates down to the substrate. Drying and film formation also depends on the temperature and humidity of the environment.[58,59]

The quality of film formation has a direct impact on many critical coating properties. Tensile tests show that the mechanical strength of latex films develops in the Stage III of film formation by inter-diffusion and entanglement of polymer chains across the particle boundaries.[60] Generally, the addition of solvent (coalescent) and reduction of binder polymer glass transition temperature (T_g) can help improve film formation. With stricter regulation of VOC levels, reducing polymer T_g becomes the most direct approach to ensure good film formation without the extra additives. However, when polymer T_g is low, it will have a negative impact on other coating properties, such as hardness, tackiness, block resistance and dirt pick up. In many instances, it is not convenient to adjust polymer T_g directly, so high boiling point coalescent is added to aid film formation without raising the VOC level. However, when the high boiling point coalescent remains in the coating film after film formation, it will hurt coating performance in a similar way as the low T_g binders.

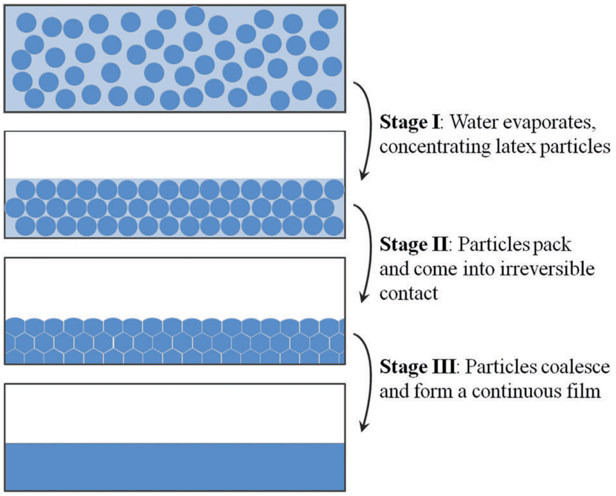


Fig. 10 Stages of the film formation process.[50]

One strategy to improve film formation while maintaining the coating performance is to introduce a hard polymer (high T_g) into a soft polymer (low T_g) matrix. This can be achieved by simply blending the soft latex particles with the hard latex particles. It was discovered that the size of the binder particle and the ratio between soft and hard components in the blend are critical to the final properties of the coating film,[61–63] but blending two different binder particles sometimes can lead to phase separation. If the refractive index is not matched, the paint film will appear hazy. A better approach to eliminate these issues is to copolymerize the hard component with the soft component, using a seeded emulsion polymerization process.

By controlling the sequence and feed rate of various monomers at different stages during the polymerization, the morphology of polymer binder particles can be varied.[64–67] A summary of different morphology discussed in the literature is shown in Fig. 11. The final polymer morphology depends on both the reaction thermodynamics and kinetics and is not simply determined by the sequence of addition. Usually the more hydrophilic monomers tend to stay on the outside of the particles, while hydrophobic monomers embed inside.[66] It is possible that the final structure can be reversed by changing the order of addition.[68] The same is also true for the control of functional site on the polymer particle surface.[69] Depending on the reaction condition, even incompatible monomers may not form very clear phase separation.[70]

It remains challenging to identify the details of the polymer particle morphology. Early electron microscopy techniques were not advanced enough to resolve the structures. More sophisticated analytical tools have since been used to probe the morphology, such as fluorescence resonance energy transfer (FRET) and liquid cell transmission electron microscopy.[71,72] Despite these challenges, these different morphologies continue to offer interesting possibilities to optimize the performance of latex binder particles.

Several studies have demonstrated that the core–shell morphology of the binder particles can help improve the final coating performance without hurting the film formation.[73,74] However,

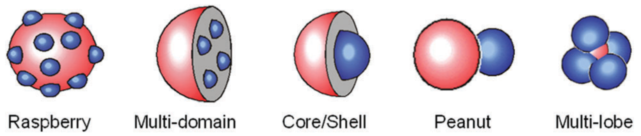


Fig. 11 Morphology of synthesized polymers.

how the binder morphology is transformed during film formation is not well understood. In another report, instead of focusing on the binder morphology, the authors put forward a model system, trying to link the final coating film morphology to the improved coating performance. In this model, a soft polymer was engaged as the matrix, while a hard polymer percolates the system, as shown in Fig. 12.[75] In order to achieve such structures, the authors proposed to blend different hard–soft polymer binders.[76] The model was validated by the experimental results. Furthermore, the authors explored both the effects of polymer microstructure and particle morphology. It was found that the compatibility of the phases has a greater influence than the morphology of the particles in determining the final film structure.

More advanced core–shell structures can help further improve the coating performance. In one report, two-component latex particles were designed to undergo a reversible morphology transformation in water as a function of pH.[77] The polymer particles consist of a high molecular weight acrylate copolymer and an acid-rich oligomer designed to be miscible with the polymer when pH is low (acid groups are protonated). Fluorescence resonance energy transfer (FRET) was employed to analyze the morphology change. Under high pH, binder particles adopt a core–shell structure when the acid groups are deprotonated. This carboxylate oligomer shell can delay coalescence for *ca.* 30 min after the passage of the drying front. In this way the binder polymer offers the coating more ''open time'' in the film formation process.

3.3.2. Multi-lobe morphology for improving rheology. The rheology profile is critical in many coating applications. It is not only directly related to the feeling of the application, but also governs the flow, leveling and final appearance. Usually the rheology is characterized by the viscosity under different shear rates, which correspond to different stages of paint application. Low-shear (1–5 s^{-1}) viscosity is indicative of the conditions when paint is in the can and after it has been applied to the wall. Viscosity at mid-shear flow (50–200 s^{-1}) corresponds to paint being loaded onto the brush or roller and as the brush or roller leaves the wall. While viscosity at high-shear flow (1000–10 000 s^{-1}) corresponds to the paint being rolled or brushed onto the wall.

There are two principal thickening mechanisms. One mechanism involves hydrodynamic volume and chain entanglement effects that act through the water phase. For this mechanism, water-soluble polymers are employed to swell and take up space in the paint. Cellulose ethers, such as Cellosize™ hydroxyethyl cellulose (HEC), fall into this category. These types of thickeners create viscosity through chain entanglement and volume exclusion. Their ability to thicken is directly proportional to their molecular weight and concentration in the paint formulation. The greater the molecular weight, the more efficiently they thicken. HEC can effectively increase mid- and low-shear viscosity, but are less efficient in increasing high shear viscosity. Paint thickened solely by HEC may suffer from poor flow, leveling, and spatter resistance.

The other mechanism is called associative thickening, which also employs water-soluble polymers. These polymers do not only thicken through swelling or taking up space. They contain hydrophobic groups that interact with each other in aqueous solution to create a three-dimensional network. The hydrophobes adsorb onto binder particle surfaces to form loops, coils, and molecular bridges. However, the bonding is only temporary and creates transient bridges between particles to produce transient aggregates of particles. The most popular associative thickeners in waterborne coatings are the HEUR thickeners. These thickeners offer substantial benefits in comparison to HEC. They provide formulators with rheological properties virtually identical to those of oil based alkyd resin coatings. However, since HEURs adsorb onto the binder particle surface, they affect other coating properties. The detailed mechanisms of HEUR rheology modifiers have been recently studied by PFGNMR, neutron scattering (rheo-SANS and rheo-USANS) and computer simulation.[39,40,42,43]

Since HEUR rheology modifiers thicken through the transient adsorption and bridging to binder particle surfaces, different binder systems may have completely different rheology response to the same HEUR rheology modifier. Usually binders with smaller particle size are more responsive, as there is more available surface for adsorption and transient bridging. Due to the same reason, one special kind of binder particle as shown in Fig. 13, with multi-lobe morphology, is highly responsive to HEUR rheology modifier.[78] Different from the conventional spherical binder particles, these multi-lobe particles have several lobes on a single binder particle. The unique geometry creates higher surface area with the same amount of binder particles of similar size.

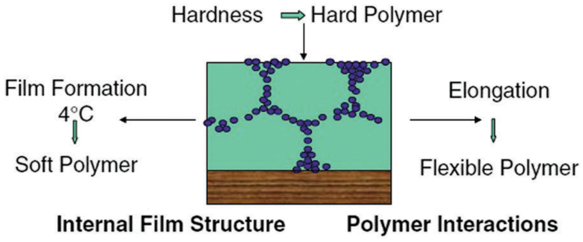


Fig. 12 Model structure for obtaining the required properties in a zero-VOC paint. Reproduced from ref. 75 with permission from the Springer, copyright 2007.

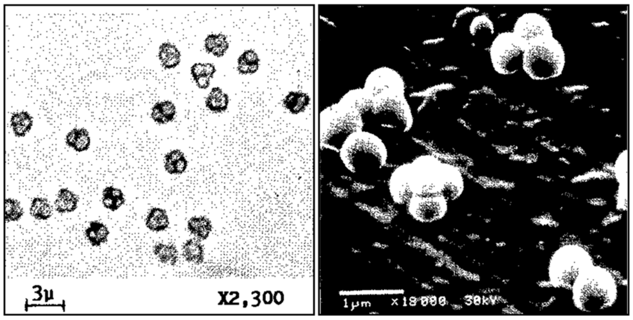


Fig. 13 Multi-lobe latex particles of different sizes: left-optical microscope image; right-electron microscopy image.[78]

Using multi-lobe structures, paint formulators can effectively reduce the usage of HEUR rheology modifier. This not only minimizes the cost, but also reduces the impact of rheology modifier on the coating performance. In addition, experiments on multi-lobe binder suggest that they can help improve adhesion performance.

3.4 Cost reduction in formulations

3.4.1. Opaque polymers for replacing TiO_2 nanoparticles. In consumer reports, one important evaluation category for coatings is the hiding performance. Hiding power describes the ability of a coating film to visually cover the features on the substrate. Imagine you need to repaint a room with a different color, if the hiding power is poor, it may require multiple coats to achieve the satisfactory result. Therefore, paint with good hiding power can help end users save cost and labor.

To improve the hiding performance, light needs to be scattered by the coating film before reaching the substrate. As shown in Fig. 14, scattering is the most important mechanism in improving the hiding performance of white and light colored coatings.

Light scattering properties were first elucidated by the Kubelka–Munk theory,[79] which is typically expressed as the scattering coefficient with the dimensions of *S* per unit thickness, either wet or dry, of a film. We will use the unit of *S*/mil, where the thickness is that of the resulting dry film. Comparative hiding can also be measured by the dimensionless value of contrast ratio (reflectance over a black substrate divided by reflectance over a white substrate) referenced to the film thickness or the nominal gap dimension of the applicator bar. This distinction will allow us to isolate the scattering from the pigments in the scattering coefficient *versus* the contribution of scattering and absorption, or undertoning, from all of the ingredients (which is contained in the contrast ratio). Another measure of hiding performance is the tint strength, which serves a dual role as it can be used to determine color matching capability as well as relative scattering efficiency. Usually scattering is used for more theoretical studies, while contrast ratio and tint strength are often measured for more practical formulating.

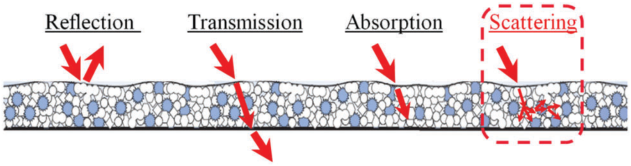


Fig. 14 Interaction of light with a coating film: scattering is the major mechanism for improving the hiding performance of white and light colored coatings.

One of the most efficient opacifiers in a coating film is the TiO_2 nanoparticles.[80] Because the efficiency of light scattering depends on the difference in refractive index, TiO_2 is selected for its very high refractive index (2.7), compared with binder polymers with low refractive indices (1.6). However, TiO_2 is also one of the most expensive ingredients in architectural coating formulations. Life cycle assessments, shown in Fig. 15, also indicate TiO_2 has a significant environmental footprint compared with other components in the coating formulation. Therefore, reducing TiO_2 usage will not only lower the coating formulation costs, but also help to minimize the environmental impact.

One smart and cost effective way to provide hiding without using TiO_2 is by introducing air voids into the coating film since the refractive index of air is 1.0,[81] *versus* the refractive index of a latex polymer of 1.6. The incorporation of air voids is usually achieved in two ways. For flat paint and economy-priced paint, the typical approach is to increase the inorganic compound, or pigment volume concentration (PVC) in the coating formulation above the critical point where binder polymer cannot cover all the vacancies between inorganic particles in a paint film. Therefore, air pockets will be created as the paint film dries. The other method is to add opaque polymer.[82]

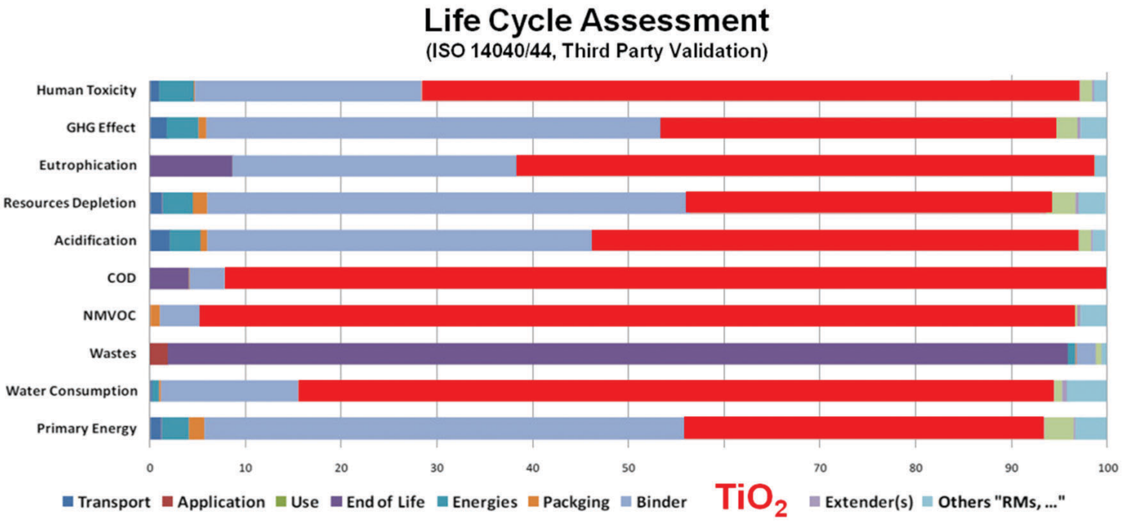


Fig. 15 Life cycle assessment for major coating component: TiO_2 has a large environment footprint.[47]

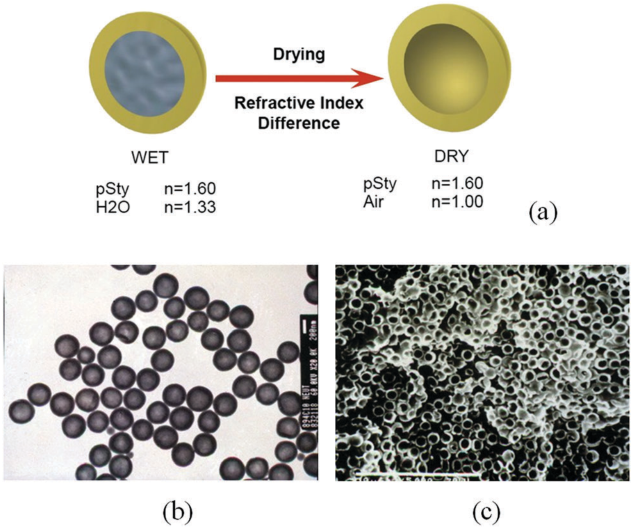


Fig. 16 Opaque polymer images (a) schematic plot; (b) under optical microscope in aqueous solution; (c) cross-section under the electron microscope.[82]

As shown in Fig. 16, opaque polymer is a spherical polymeric pigment, with an outer shell comprised of hard, high T_g polymer, and a hollow core. When dispersed in aqueous solutions, the opaque polymer core is filled with water. Water in the core diffuses out upon drying, and is exchanged with air. Due to its high T_g, the polymer shell remains intact and provides a permanently encapsulated air void. The degree of light scattering that results from the refractive differential between the void and the shell is dictated by the size of the air void. The void size of opaque polymer must be carefully controlled to facilitate optimal scattering ability and consistency. Fig. 16 shows a schematic plot of opaque polymer and the optical and electron microscope images.

Opaque polymer is known to be a cost-effective replacement for up to 20% of the TiO_2 used in architectural coatings. One advantage of opaque polymer is that its hiding power is proportional to the amount added. This is very different from the hiding power of TiO_2, which is much less efficient when the use level is increased, due to particle crowding. One newer, unique technology that can help improve the efficiency of TiO_2 particles is the pre-composite polymer technology,[83] which utilizes the self-assembly concept and designs polymer binder particles to assemble around TiO_2 particles. The assembled polymer binder particles provide spacing against aggregation and improve the scattering efficiency of TiO_2 nanoparticles.

3.4.2. Pre-composite polymers for improving TiO_2 efficiency.

Hiding has been modeled using the semi-empirical formalism from Stieg,[84] and these simple descriptions have performed well when compared to full Mie theory to determine formulation component effects on dry hiding.[85,86] According to Mie theory, scattering is the most efficient when TiO_2 particles are well dispersed, free of aggregation, and dilute (less than 1% pigment volume fraction). It has also been found that TiO_2 particles can be agglomerated even in the aqueous solutions which may lead to a decrease in scattering efficiency.[38] It is evident as shown in Fig. 17, that the hiding performance deviates significantly from a straight line as TiO_2 concentration increases in the formulation.

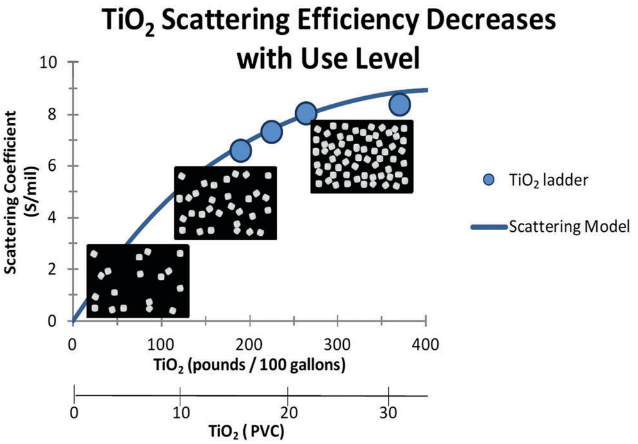


Fig. 17 Stieg curve of scattering coefficient *versus* TiO_2 concentration: scattering efficiency decreases as TiO_2 concentration increases.[38]

However, the use of pre-composite polymers can alleviate this agglomeration in both the wet and the dry states, leading to better spacing of TiO_2 and higher wet and dry hiding.

Pre-composite polymer is a latex polymer that is designed, not only to perform the traditional role of binder, but also to adsorb onto the surface of TiO_2 pigment particles. The process is shown in Fig. 18. The challenge is to control precisely the reactivity between polymer particles and TiO_2 particles. As also demonstrated in Fig. 18, if the reactivity is too slow, polymer will not adsorb onto TiO_2 surface efficiently; if the reactivity is too high, pigment aggregation, gel and grit will form.[87]

The resultant polymer–pigment composite allows for better TiO_2 dispersion and improves distribution of TiO_2.[47] Fig. 19 clearly shows a better TiO_2 dispersion and distribution, which allows for improvement in hiding in addition to scattering efficiency in paint. TiO_2 use levels in these systems can be reduced by 20% or more while maintaining the opacity and

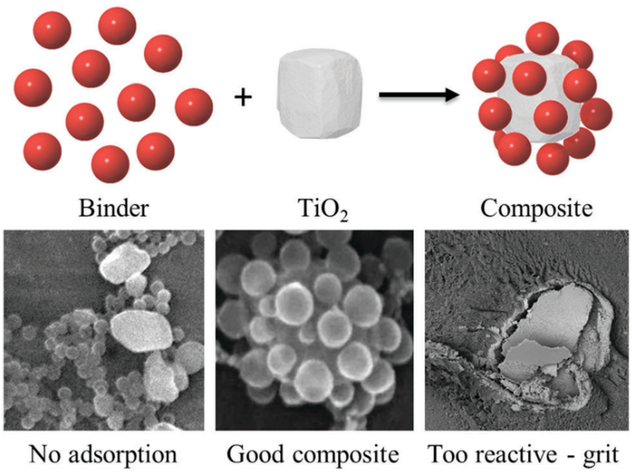


Fig. 18 Process of forming the polymer–pigment composite.[47]

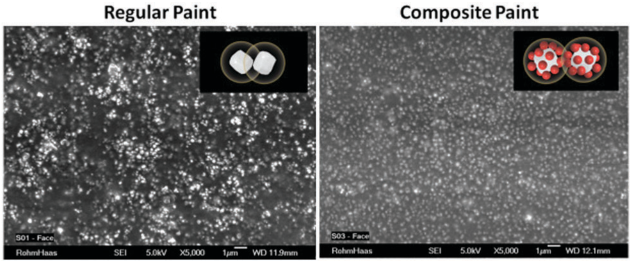
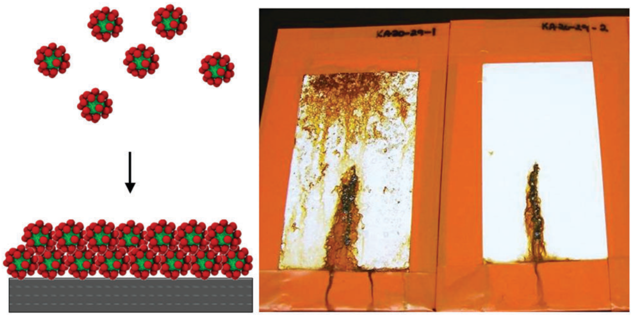


Fig. 19 Electron microscope image for regular paint *vs.* composite paint.[47]



(a) (b)

Fig. 21 (a) Schematic plot of film formation from composite polymer (red spheres) and TiO_2 (green spheres); (b) comparison of salt spray resistance of composite polymer *versus* the conventional binder.[47]

tinting strength of the final coating. In addition, the wet hiding performance of the TiO_2–polymer composites is also enhanced relative to conventional TiO_2 in liquid paint formulations as shown in Fig. 20.

There are several additional benefits for the pre-composite technology besides hiding. First, the resulting film quality benefits from these composites. Films made from composite polymer are stacked by composite particles in the sense that the alternation between binder and pigment particles is assured as shown in Fig. 21(a). The resulting film has less defects than a film formed from a conventional waterborne binder and exhibits improvements in barrier properties.

Correspondingly, we have observed that a composite-based paint film will yield improvements in stain removal, dirt-pick-up resistance, tannin stain blocking, efflorescence resistance over cementitious substrates, chalking resistance and color fading.[47] Fig. 21(b) also shows the comparison of salt spray resistance for paint film on metal coatings, where the composite film performed much better.

Pre-composite polymer technology has completely changed the precepts of binder design by introducing the concept of self-assembly within the coating formulation. Conventional binder design mostly emphasizes the binder stability, through the control of binder particle composition, deliberately aiming to avoid agglomeration that usually results in poor film performance and can be disastrous to the paint formulation. However, through careful control of assembly, pre-composite polymers are demonstrating superior performances over conventional binder polymers.

3.5 New "smart" coatings

"Smart materials" commonly refers to materials that can respond to environmental stimuli. When smart materials are incorporated in coating formulations, coating films will adapt to environmental changes and offer enhanced functionality. Smart coatings can be very beneficial to high-value applications that demand superior performance and critical protection, such as aircraft corrosion control. In addition, considerable effort has been devoted to improve anti-fouling coatings, which may find important applications in biomedical devices and marine vessels. On the other hand, smart materials have also been incorporated into low-priced architectural paint, such as air purifying paint and self-cleaning paint. The margin usually is higher for specialized coatings, and consumers are willing to pay a premium price for the additional functionality. Market analysis suggested a 10× growth in the demand of smart coatings from \$610 million in 2015 to \$5.8 billion in 2020, with a notable increase in the medical and healthcare applications.[88]

Instead of giving a comprehensive review on smart coatings, here we briefly describe three types of smart coatings: air purifying coating, self-cleaning coating and self-healing coating. They are mostly relevant to architectural coating applications.

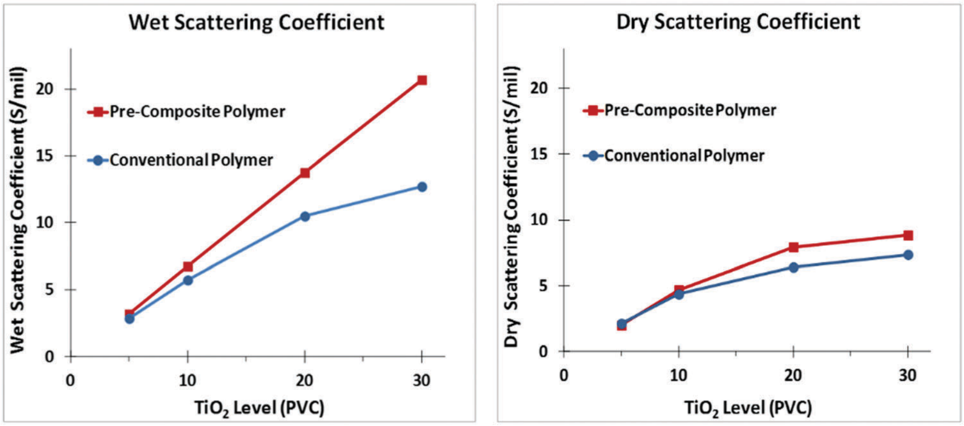


Fig. 20 Wet and dry scattering efficiency for coating formulated with regular polymer and composite polymer.[47]

The purpose is to inspire more ideas and research effort in this fast growing area. Currently, most of the research is focused on developing chemistry and functional groups for binders and additives to achieve the desired functionality. However, morphology control and self-assembly may provide alternative ideas to help further develop and improve smart coatings.

3.5.1. Air purifying coatings. As industry gradually reduces the VOC emission from paint toward zero, one step further is to eliminate VOCs and pollutants from other sources using air purifying paint, and improve indoor air quality. This can be achieved by two different mechanisms. One is to adsorb the odor or small pollutant molecules in the air by incorporating porous materials into the paint, such as silicate and zeolite.[89] This method is straightforward; however, there are several issues with this approach. First, the effectiveness of the absorbent is limited by the area of adsorbent exposed in the coating. Second, the pollutant adsorbed in the coating film will gradually saturate the adsorbent, and the effectiveness will diminish over time. Third, as the absorption becomes saturated, the pollutant may even be released when the environment changes. Since silicate is solid inorganic particles, it may also affect other coating properties, such as gloss, stain resistance, and adhesion. This may cause complication and restriction in formulation design.

The other mechanism is to include functional groups in coating films that can react with certain air pollutants. One great example is the formaldehyde abating paint. Formaldehyde is one of the most prevalent and most dangerous VOCs, also a known carcinogen.[90] Carpets, furniture, cabinetry, drapery and insulation are common household items made with glues and adhesives that may emit formaldehyde. As people spend more time indoors and buildings are more tightly sealed to improve energy efficiency, there is growing concern about formaldehyde buildup in indoor air, especially in Asian countries. The formaldehyde abating paint employs a functional monomer that facilitates interaction between paint on the wall and formaldehyde in the air. The functional group bonds with the formaldehyde and transforms it into harmless solid.[91] This approach is better than simply adding absorbent in the paint as the pollutant is practically eliminated instead of being stored.

In principle, both mechanisms may work with a wide variety of coatings, and are compatible with different binder particle morphologies. However, both mechanisms will be affected by the final structure and morphology of coating films. Control particle morphology and self-assembly in coatings may provide additional benefit to further improve air purifying performance.

3.5.2. Self-cleaning coatings. There are two types of self-cleaning surface. One type takes advantage of photocatalytic reactions, usually based on TiO_2, which can help clean off the organic substance adsorbed on the surface.[92,93] The other type originates from surface hydrophobicity, or the "lotus effect".[94] The surface is also referred as "superhydrophobic", when the contact angle of a water droplet exceeds 150° and the contact angle hysteresis is less than 10°.[95] Superhydrophobic surfaces are usually formed with the combination of surface chemistry and surface structure. Surface structures can be created by fabrication or deposition of microparticles or nanoparticles of different sizes. Air pockets trapped in the surface structure contribute to the superhydrophobicity.[96] However, superhydrophobic surfaces mainly help with stain resistance of water-soluble stains. For hydrophobic stains, the surface needs to be oleophobic, which is often achieved using perfluorinated chemicals.[97] Most self-cleaning and easy-clean paints on the market nowadays are conventional paints with slightly modified formulation or binder composition that renders the paint film more hydrophobic. There are several challenges to create superhydrophobic or superoleophobic surfaces directly using a simple can of paint. The first challenge is the cost. Perfluorinated chemicals are usually expensive. The second challenge is to create delicate surface structures. For common paint applications, the structures need to be completely self-assembled during the drying procedure. The third challenge is to maintain other paint properties, such as gloss and adhesion. Currently, most of the superhydrophobic surface is not durable, and has relatively poor adhesion to the substrate. A recent study addressed the issue by combining surperhydrophobic paint with commercial adhesives.[98] Again, particle morphology and self-assembly may be useful tools to control surface structure, and help enhance the self-cleaning function.

3.5.3. Self-healing coatings. For certain applications, such as oil pipeline and aircraft, the integrity of the surface coating is critical. Coating failure may lead to extensive damage and costly repair. Sometimes the failure will induce severe consequences. Self-healing coating offers a potential solution. Many different approaches of creating self-healing function have been developed.[99] Particle morphology and assembly play important roles in the performance of self-healing coatings. One of the most common methods is to embed the reaction agent in capsules. Usually two types of capsules are embedded in the coating film matrix. When the defect or actuation occurs, the capsules are broken with reactants released to trigger the healing reaction. For this method, core–shell morphology is usually adopted for the encapsulation. However, it would be interesting to have different reactants compartmentalized in one capsule, which may speed up their mixing and reaction time.

Another self-healing mechanism is intrinsic self-healing without the embedment of extra healing agent. The self-healing is triggered by external energy, such as UV radiation or heating, and depends on the molecular diffusion and microstructures. Again, by controlling the binder particle morphology and self-assembly, the self-healing performance may be further improved.

4. Perspective and outlook

In parallel, academia and the coating industry have developed technologies to control the morphology and assembly of colloidal particles. Academia has developed, and continues to seek new structures and new methods to control assembly in a more precise manner. Within industry, there is continued product development focus on higher performance, not only to fulfill customer needs but also to comply with regulatory requirements. The challenge is to translate academic fundamental research into commercially viable industrial applications. This requires more dialogue and collaboration between both sides to bridge the gap between the technological progress and the market demand.

For example, Janus particle research in academia already demonstrated many interesting results in emulsion and self-assembly, which may find great interest in coating applications. One potential application is to use Janus particles to stabilize binder and pigment particles. Janus particles may also affect the rheology of the coating system due to its unique geometries. In addition, Janus particles may preferentially adsorb at interfaces, which offers a unique way to render coating surface properties. Therefore, it will be beneficial for academia to prioritize effort in colloidal research, utilize funding that supports industry collaboration, and explore the potential of new colloidal particle technologies in the context of coating applications. Some of the experiments are preferably designed together with industry partners and carried out in industrial settings. It is important to include scalability and cost into consideration even at the early stage of the project.

The wide range of assembly methods already developed in academia may yet inspire new industrial applications. However, more development in scalable synthetic methods is needed to fabricate the specialized colloids. In addition, more studies are needed to advance the fundamental understanding of colloidal assembly, especially the assembly of soft polymer particles. The process of drying, and how polymer binder particles interact with different components, need to be further elucidated. Furthermore, it is critical to understand how rheology modifiers and other additives may impact the structure and properties of the coating film.

One important development in coating materials is to integrate the waterborne acrylic platform with other chemistries, such as alkyd, epoxy, and urethane. Due to the unique properties of these materials, different phase and morphology will arise in the polymer particles and coating films. In addition to functionality and performance, sustainability and bio-renewable materials become more and more important in designing the next generation of coating materials.

Research in coating materials has also generated significant impact in other industrial applications, including construction chemicals, transportation and personal care. The innovation in coating materials may also be leveraged in several newly emerged areas, such as nano-medicine and 3D printing, as these applications often share analogous formulation and compositions.

For all these reasons, it is critical to establish a comprehensive model to understand the structure–property relationship of coating materials. This is only achievable through collaborative effort involving researchers with different background and expertise, including chemical synthesis, physics, computer simulation, materials science and chemical engineering. More interactions between academia and industry will unquestionably speed up the progress.

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