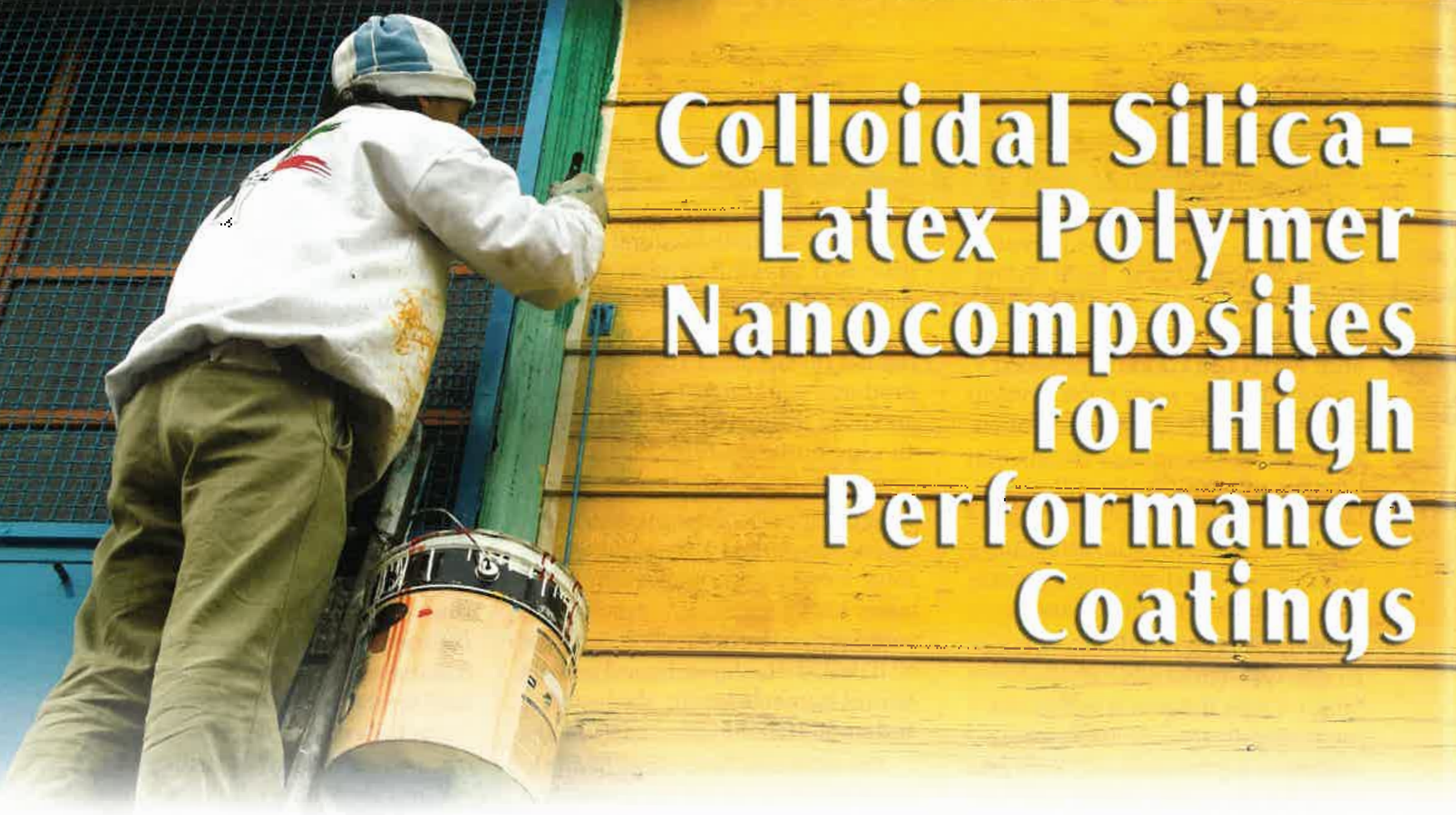

Colloidal Silica-Latex Polymer Nanocomposites for High Performance Coatings

by **Stephan Krieger, Ivan Cabrera, Marc Ratering, and Thomas Fichtner**
Celanese Chemicals Europe GmbH*
and
Rajeev Farwaha
Celanese Emulsions†

INTRODUCTION

Nanotechnology will have a significant impact on the paint and coatings market through two channels: the improvement of existing surface coatings and the innovation of new products that deliver the right blend of performance and aesthetics. Nanotechnology is the study of material properties with particle size below 100 nm. Hybrid organic-inorganic composites have attracted widespread attention in the domain of material science.[1] The controlled combination of organic and inorganic composite colloids is of increasing interest as it enables chemists to create new nano-structured materials with unusual morphology, composition, and properties originating from existing building blocks.

Long lasting performance and good aesthetics are two key performance components for exterior paint. Over time, exterior exposure leads to the accumulation of dirt, air pollutants, dust particles, and debris on the paint film. This results in a dirty appearance which no longer meets the expectations of the consumer. It is well known in the industry that a high level of dirt resistance can be achieved through the use of hard polymers. But, these polymers can also jeopardize film formation, which can then also require high levels of coalescing solvents.

Chemically, there is a wide range of nano material particles that are of interest for use in coatings. To date, the main focus in architectural coatings has been on incorporating nano SiO_2, Al_2O_3, and ZnO to produce functional properties such as scratch resistance, mildew resistance, and increased durability in the paint film. This article will document hybrid poly-

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*Industriepark Höchst, 65926 Frankfurt, Germany.
†900 Gemini St., Houston, TX 77058.

mer technology which combines the advantage of one polymer species with another to synergistically create a higher performing class of polymers. Further, this article will discuss silica-latex hybrid technology and its applications, particularly in the design of dirt pick-up resistant coatings.

BACKGROUND

In recent years, considerable effort has been devoted to the design and controlled preparation of hybrid organic-inorganic composites using colloidal particles as building blocks. Among colloidal materials, silica has been studied extensively because of its well known uses in a variety of applications including high performance coatings, photonic devices, magnetic fluids, and paper coating.[2] Furthermore, the incorporation of inorganic materials such as colloidal silica at the nanoscale level can enhance the fire retardancy and mechanical strength of organic polymers and their thermal properties.

Including an organic polymer phase in the organic-inorganic matrix reduces the brittleness found with pure inorganic materials, resulting in reduced stress cracking during the drying process of coatings. Unfortunately, the simple mixing of organic and inorganic components at the macroscopic level is tedious, very energy intensive, and usually not very successful. There are various methods to make silica/organic nano composites, but in order to achieve the desired improvement by adding nanoparticles, the targeted organic polymer must display specific interaction tendencies with the inorganic particles.

Heterogeneous polymerization, such as emulsion polymerization, has been used to prepare organic-silica composites by conducting polymerization in the presence of silica particles.[2–9] Thermodynamic and kinetic factors relating to the type of polymerization process play a key role in determining the ultimate structure.

Polymer/silica nanocomposite colloids with various morphologies have been created through emulsion polymerization using a polymerizable silane such as methacryloxypropyl trimethoxy silane (TMS) and a methacrylate-terminated macromer as a coupling agent.[3] Depending on the synthesis strategy and the nature of the mineral particle, a wide range of polymer morphologies have been obtained.[2] The anchoring TMS monomer can be simply reacted on the silica particle surface via silanol functionality. Additionally, organosilane-modified silica particles containing an active double bond have been reacted with styrene via emulsion polymerization to produce a nanosilica-latex hybrid. The resulting organic-inorganic composite latex was stable in a wide range of ionic strength environments.[5,6]

Zhang[12] and Bourgeat-Lami[5] have successfully incorporated silanol functional groups on latex particles using TMS as a functional comonomer via semi-continuous emulsion and mini-emulsion polymerization. Further, Zhang[10] discovered a controlled method of synthesizing silanol functional latex particles via mini-emulsion polymerization. These silanol functionalized latexes were reacted with colloidal silica to prepare novel hybrid particles and hollow-sphere silica polymer composites.[11] The alkyl modified-nanosilica/polyacrylate composite latex prepared by emulsion polymerization exhibited a defect free surface as measured by atomic force microscopy (AFM) and better thermal properties than a polyacrylate composition as measured by thermogravimetric analysis (TGA).[7]

The organic polymer matrix encapsulated with silica particles has also been prepared by phase-inversion emulsification.[12] Atom transfer free radical polymerization (ATRP) has also been used to make polymer-coated inorganic silica particles.[1] Styrene acrylic-silica polymers were produced by modifying silica particles with oleic acid functionality, resulting in a stable silica-organic composite.[2]

Octaphenylsilisequioxane (ONPS) has been used to react with hydroxyl acrylate emulsion.[9] These thermoset ONPS-modified nanocomposites exhibited excellent thermal and mechanical properties.

Table 1—Basic Properties of Prepared Emulsions

Emulsion Sample	Functionalized	SiO_2 Content (%)	Solid Content (%)	MFFT (°C)	T_g (°C)	Aerosol-dw (nm)	PSCS-dw (nm)
1	Yes	0	48.4	3.0	4.8	127	136
2	Yes	10	47.6	3.0	14.3	127	132
3	Yes	20	46.9	3.5	14.9	125	137
4	Yes	30	46.1	4.0	13.5	125	133
5	Yes	40	45.5	7.0	12.5	124	135
6	No	0	48.7	2.0	8.2	129	134
7	No	10	47.4	2.0	11.7	127	130
8	No	20	46.7	3.0	13.5	130	127
9	No	30	46.0	3.5	12.7	125	135
10	No	40	45.4	7.0	13.5	126	120

Figure 1—XY Elastic properties of the nano composite film. (a) latex polymer without functionalization; (b) latex polymer with functionalization.

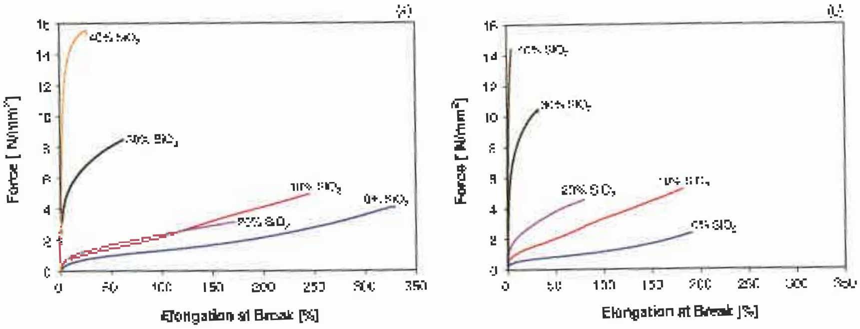


Figure 2—TEM images of cross section of the nano composite films. (a) latex polymer without functionalization; (b) latex polymer with functionalization.

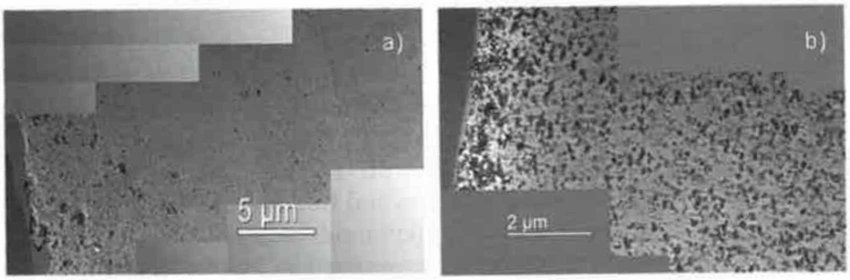


Figure 3—SEM images of film cross sections. (a) standard paint with pure acrylic emulsions as binder; (b) paint with nano hybrid emulsions as binder.

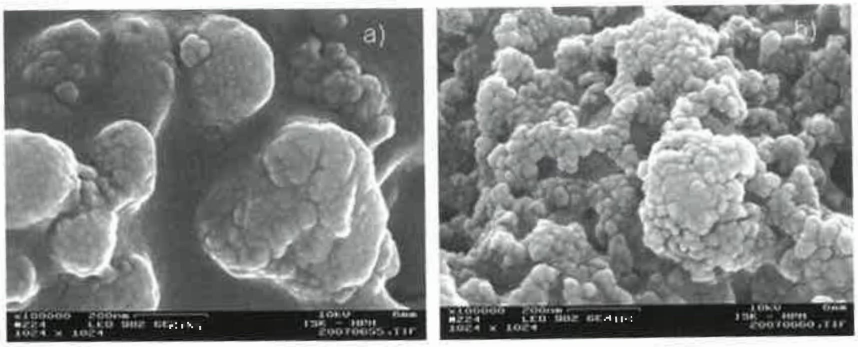
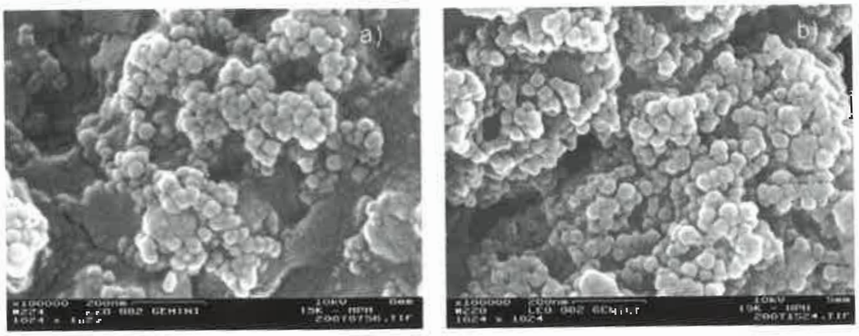


Figure 4—SEM images of film cross sections. (a) after nine months of weather exposure; (b) after 400 cycles artificial weathering.



Core-polystyrene/shell-silica nanocomposite latex particles were also synthesized using cationic silica sol.[6] The silica particles (25 nm average diameter) form a monolayer shell of 30 nm thickness on poly styrene particles. It was found that the incorporation of more than 10 wt% silica content enhances thermal stability due to the strong interaction between silica and polystyrene molecules.[6]

In another article,[1] a new class of nano SiO_2/acrylic resin composite latex was synthesized by introducing nano SiO_2 particles formed in-situ hydrolysis of tetraethylorthosilicate in emulsion polymerization.[5b] The properties of the latex were studied by scanning electron microscopy and differential thermal analysis. The results revealed that the resulting latex composite possessed an interpenetrating network structure of inorganic and organic phases.[11]

In other work, Mayer et al. reacted chlorobenzyl modified latex particles with amine and thiol function nano inorganic particles.[12]

In summary, the nano particles are so small that the bulk of the polymer matrix is in the "interphase," resulting in significantly improved coatings properties. The interphase exhibits different chemical and physical properties than either the bulk or the polymer particle. Interphase properties can be drastically different than the polymer matrix itself and therefore could become drastically different than bulk properties.

DISCUSSION

Buildings with premium architectural design or those that are historically important are in need of high quality coatings for maintenance and preservation. Many have published investigations on the development of exterior coatings with excellent resistance to dirt pick-up, mainly influenced by the hydrophilicity and hardness of the coating surface. In this regard much attention has been

Table 2—Standard Exterior Wall Paint Recipe

Ingredient	Parts (by weight)
Water	141
Tylose MH 30000 YP 2	2
Agitan 281	4
AMP 90	4
Additul VXW 6208	3
Titandioxide Kronos 2160	200
Omyacarb 2 GU	50
Omyacarb 5 GU	100
Glimmer MUN 101	100
Texanol	15
Nano hybrid emulsion (45% solids)	400
Tafigel PUR 40 (1:1 in water)	6
Total	1025
Pigment Volume Concentration (PVC)	*65.85%*

paid to organic-inorganic nanocomposites because in these hybrid systems the flexibility of the organic component can be combined with the hardness of the inorganic component. The more widely used inorganic component has typically been silica gel due to its availability. These systems have been investigated in a wide variety of application fields including medicine, electronic adhesives, separation membranes, and surface coatings.

In general, three different ways to prepare latex polymer SiO_2 nanocomposites have been described in the literature. In the first case, emulsion polymerization is carried out in the presence of colloidal silica gel compositions. In the second case, the surface of the colloidal silica gel particles is previously functionalized and then used during emulsion polymerization. In the case of the present work, a functional emulsion polymer is prepared in such a way that an effective interaction of the polymer particles with the silica gel particles is tailor-made. It is on this route that we concentrate and describe our results.

PREPARING THE EMULSIONS

To investigate the effect of the level of silica nano particles on the dispersion and resulting paint properties, a series of binders was prepared with silica levels ranging from 0% to 40% (total solids content). The base polymer consisted of butyl acrylate, methyl methacrylate, and methacrylic acid. A second series was made with a functionalized base polymer.

Dispersion properties are shown in *Table* 1. Results show that the glass transition temperature (T_g) increases with increasing silica level. This is primarily due to restricted mobility of the polymer chains near the polymer silica interface. At a 40% silica level, an increase in minimum film formation temperature (MFFT) of about 5°C was observed. Particle sizes measured by laser aerosol spectroscopy were in the range of 120–130 nm.

The influence of increasing amounts of colloidal SiO_2 on the mechanical properties of emulsion films is shown in *Figure* 1. As expected, the elongation at break is reduced with increasing amounts of SiO_2 and the tensile strength of the films is increased. This influence on the elasticity behavior is stronger when the latex polymer is functionalized. By correct selection of the latex polymer's T_g and the SiO_2 amount, flexible but tough films can be obtained.

It was also important to investigate the influence of the functionalization of the polymer on the distribution of the SiO_2 particles, both in the wet emulsion samples and in dry films prepared from them. For this purpose, transmission electron microscopy (TEM) was used to characterize the materials. This investigation showed that when the latex polymer was not functionalized (as in Emulsion Sample 10 of *Table* 1), the colloidal silica gel particles agglomerate and are not homogeneously distributed. This also leads to differences in the SiO_2 distribution in the films, which is, of course, the most decisive factor when the materials are used as a binder for coatings. Indeed, as it can be seen in *Figure* 2b, the TEM images of the cross section of the films from the emulsion sample (*Table* 1, Emulsion Sample 5) showed that the colloidal SiO_2 units are homogeneously distributed in the films only when the latex polymer is functionalized.

EFFECT ON PAINT PROPERTIES

Due to the inorganic phase, nano hybrid emulsions would be the ideal binders for exterior paints as they reduce the thermoplastic behavior of standard exterior paints, leading to less dirt pick-up and a cleaner surface.

Therefore, the nano hybrid emulsion was tested in the standard exterior wall paint recipe detailed in *Table* 2.

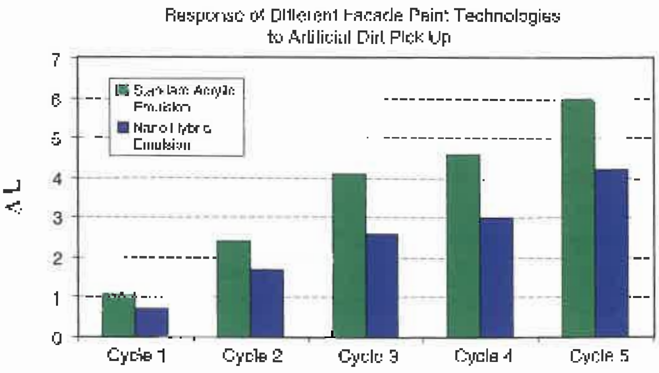
Investigations with SEM showed that by using nano hybrid emulsions it is possible to create a real nano structure on the paint surface (*Figure* 3).

Weathering tests were conducted to prove that the nano structure is still present and stable after nine months of outdoor exposure (45 degrees, south-facing) and after 400 cycles of artificial weathering including

Table 3—Water Response of Two Emulsion Systems

Binder	Water Vapor Diffusion sd (m)	Water Permeability in 24 Hours ($kg/m^2h^{0.5}$)	Contact Angle
Standard acrylic emulsion	0.88	0.01	82
Nano hybrid emulsion	0.05	0.16	70

Figure 5—Comparison of nano hybrid emulsion to standard acrylic emulsion in dirt pick-up test.



rain, freeze thaw, UV treatment, and temperature changes (*Figure* 4) from +60°C to −25°C in 240 min per cycle (Global UV tester).

The dirt pick-up behavior was also tested in comparison to a standard acrylic paint by using an artificial dirt pick-up test, which shows a significant lower dirt pick-up for a paint based on the nano hybrid emulsion (*Figure* 5).

These tests were repeated in a real outdoor environment. Outdoor exposure results from Istanbul after six months (90 degrees, south-facing, city near a broad highway) matched the laboratory data.

$$\Delta L_{\text{(Paint with Nano Hybrid Emulsion)}} = -2.70$$
$$\Delta L_{\text{(Paint with Standard Acrylic Emulsion)}} = -3.81$$

No chalking was present for either paint.

When calculating pigment volume concentration (PVC), the inorganic portion of the nano hybrid emulsions must be taken into account. Due to the inorganic portion, it is possible that the nano hybrid emulsions could be more brittle. Therefore, cracking behavior must be assessed when the binders are used in new formulations and on different substrates.

Table 3 shows the results of paints based on nano hybrid emulsions with respect to water vapor diffusion (lower Sd value) and water take-up in comparison to standard acrylic emulsion-based paints. The higher water permeability of the nano hybrid emulsion is desirable.

CONCLUSIONS

In this work, a nanostructure hybrid of acrylic latex and inorganic nano silica with controlled morphology was prepared by emulsion polymerization. It was also found that the glass transition temperature increases with an increased silica level due to restricted mobility of the polymer chains near the polymer silica interface. TEM was used to characterize the nano organic-inorganic hybrid. TEM images of the cross sections of the films synthesized showed that the colloidal SiO_2 units are homogeneously distributed in the films only if they are made from a functionalized latex polymer. Paints made with the hybrid material as a binder showed a nano structured surface. Both laboratory and real world exposure testing of these paints displayed excellent resistance to dirt pick-up, and a cleaner appearance. These functional and aesthetic properties when combined with the high water vapor permeability clearly show that the organic-inorganic hybrid systems (nano hybrid emulsions described in this article) make an excellent binder choice for high performance coatings. CT

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