

Title: Hybrid Materials for Application in Anti-Reflective Coatings

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Abstract: The possibility of combining properties of organic and inorganic components for materials design is an interesting area of research which found its origin in the second half of the twentieth century. Traditionally, such hybrid materials are prepared through hydrolysis and condensation of metal oxide precursors in the presence of organic molecules, polymers or bio-components. The resulting hybrid materials are then processed into micro-structured coatings. The micro-domains which are present in such coatings are generally polydisperse in size and locally heterogeneous in composition.

Further tailoring of properties can only be achieved through a higher level of control over local and semi-local structures. For this purpose, we designed structurally defined hybrid building blocks that keep their integrity in the final coating. Examples of such building blocks are polymer-metal oxide core-shell particles. These are currently produced by DSM on a multi-ton scale for use in single-layer anti-reflective coatings on glass. By incorporation of polymer-silica core-shell particles into an inorganic matrix and subsequent removal of the core material, a coating with a refractive index of about 1.23 is achieved. This coating combines a low level of rest reflection (less than 1.5%) with excellent mechanical resistance and outdoor durability. Hence, the technology is applicable to a wide variety of in- and outdoor applications like anti-reflective picture glass, glass displays, lighting covers, solar cell covers and green house covers. The technology is currently in use for DSM's anti-reflective picture glass – [®]claryl – and for solar cover glass and other (outdoor) applications under the brandname KhepriCoat[™]. The technology is available to glass or module producers *via* licensing.

Currently, we are developing a slot-die coating process for the single-side application of optical coatings at speeds up to 20 meters per minute and evaluating our coating for other single-side applications (e.g. roller coating, spray coating). Latter make it possible to use DSM's anti-reflective coating technology in large-volume applications of up to ten million square meters per year.

Introduction: In this report, we discuss the preparation of anti-reflective coatings (ARCs) for glass substrates based on a single layer system containing a coating film of a refractive index of about 1.23. There are, however, no low index solid materials that display a refractive index lower than 1.37 ^[1] and the best method to achieve lower values is to reduce the packing density. According to Moulton and co-workers, this can be achieved by the application of nanoparticles to form a nanoporous film.^[2] However, these traditional Moulton type single layer ARCs normally exhibit a sharp trade-off between optics and mechanics: a high level of porosity is required to obtain a low rest reflection.^[3] This is usually accompanied by a high surface roughness which causes poor abrasion resistance, a high degree of optical fouling and problems with cleaning. Furthermore, these coatings are typically sensitive when exposed to outdoor conditions.

To improve the properties of traditional single layer ARCs, a high level of control over the balance of surface roughness and internal porosity is required. In contrast to the Moulton approach, we use polymer nanoparticles with a silica shell to form ARCs. During the curing or tempering step, the polymer template is removed resulting in a coating with a high level of internal porosity (Figure 1). This enables us to use higher amounts of binder than for traditional Moulton-type ARCs which lowers the surface roughness and increases the scratch resistance, cleanability properties and outdoor durability of the coating.

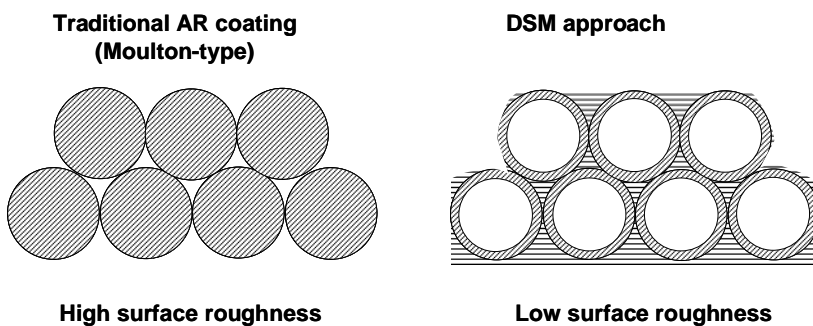


Figure 1. Schematic representation of a traditional Moulton-type ARC and DSM's single layer ARC.

Results and discussion: For the synthesis of polymer nanoparticles with a silica shell, small silica nanoparticles were deposited on a spherical cationic polymer template. For silicification, both commercially available silica nanoparticles like MT-ST from Nissan Chemicals^[4] and *in-situ* produced silica nanoparticles were used.^[5] As polymeric template, both cationically stabilized micelles^[6] and cationic latexes were applied.^[7] A schematic representation of the synthetic approach starting from tetramethyl orthosilicate (TMOS) as precursor is depicted in Figure 2. For this example, a cationic polymer with a particle size of about 80 nm is used as template.^[8] This aqueous polymer system was treated with TMOS to form core-shell particles. At the desired shell-thickness, the reaction was stopped *via* dilution with alcohol and subsequent acidification with nitric acid.

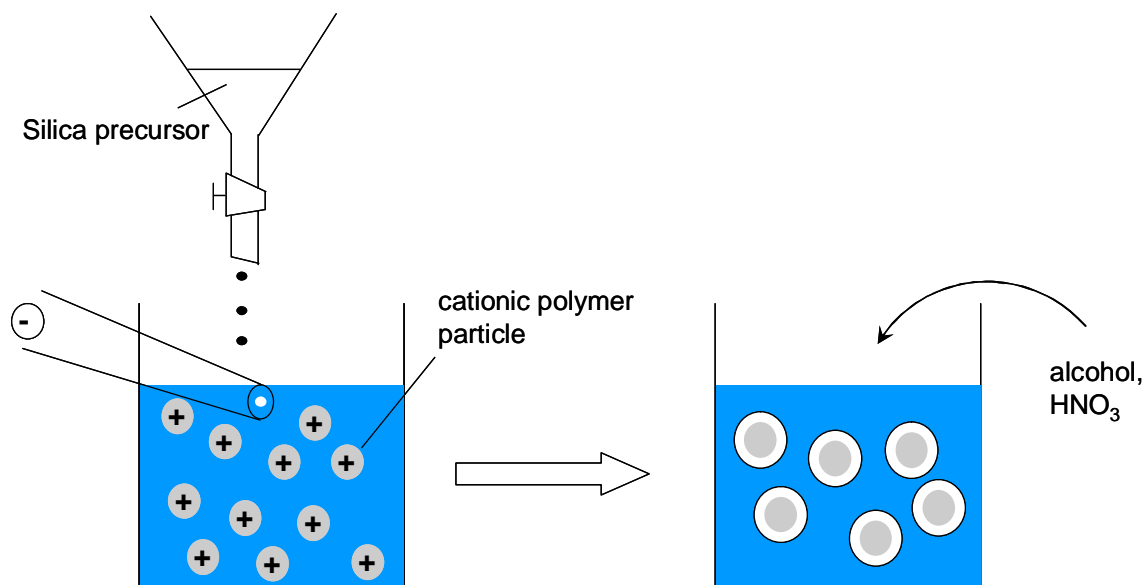


Figure 2. Schematic representation of the synthesis of polymer-silica core-shell particles.

Parameters that influence the growth rate of the particles are the concentration of solids in the reaction mixture, *pH*, temperature and the addition rate of TMOS. At optimized reaction conditions, the growth process started after a specific induction period and was nearly linear. A TEM image of the resulting core-shell particles is shown in Figure 3.

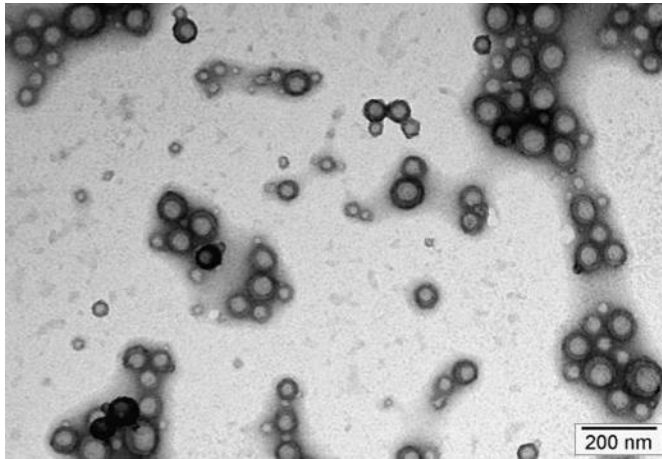


Figure 3. Core-shell particles.

The alcoholic particle dispersion was subsequently treated with a binder. A variety of inorganic silica binders were tested. For the preparation of the coatings described in this article, the above mentioned particles were combined with alcoholic dispersions of pre-oligomerised tetraethyl orthosilicate (TEOS).^[6] Under ambient conditions, the resulting coating formulations were stable for more than six months.

The coatings were applied on both sides of the substrate *via* dip-coating. The coating thickness can be controlled *via* the dip speed. Typical coating speeds for dip-coating are in the range of 0.5 to 1 m·min⁻¹. Currently, a horizontal slot-die coating process is being developed to apply these coatings on one single side of the substrate. Initial pilot-scale results show that coating speeds up to 20 m·min⁻¹ can be achieved using this process (Figure 4). The resulting coatings show an excellent optical homogeneity and are similar in performance to dip-coated samples.



Figure 4. Slot-die coating process as developed by DSM.

Directly after application of the coating material, a xerogel is formed. This xerogel has an overall reflection of about 6.6% in the visible (VIS) and is surprisingly robust. The film withstands polishing and edge working treatments which are commonly applied before tempering. During the curing (450°C) or tempering step (675°C), the cross-link density in the inorganic network is increased and the polymeric template is removed. The resulting coatings display a low surface roughness and a high level of internal porosity (see Figure 5). They are steel wool resistant, easy to clean and display broad-band anti-reflective properties.

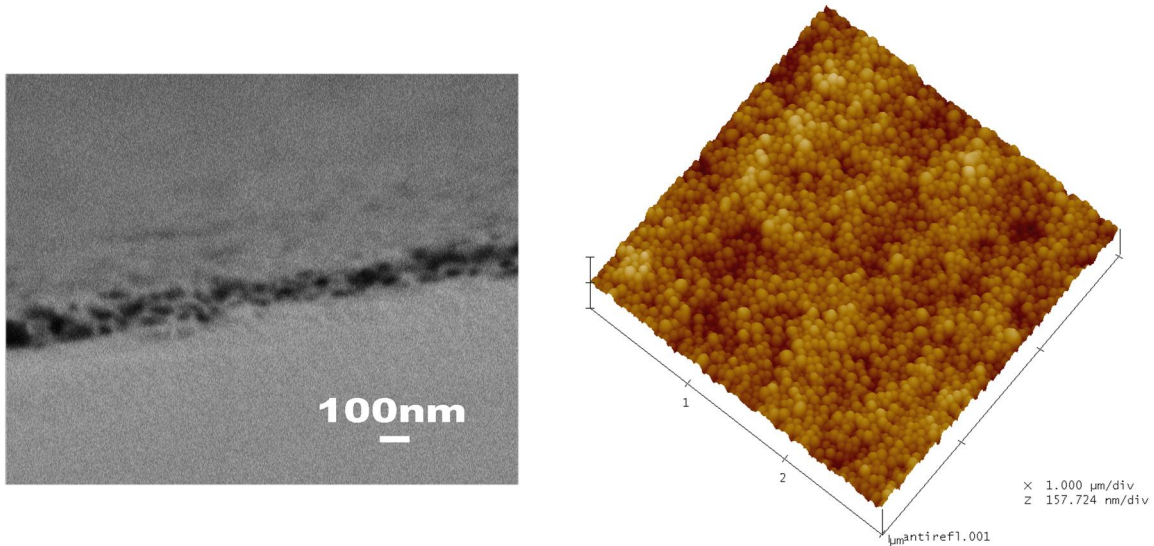


Figure 5. ARCs based on core-shell particles (SEM and AFM).

The anti-reflective coating was optimized for picture and art glazing. For this purpose, low-iron glass of a thickness of 2 mm was coated with the above mentioned formulation in a dip-coating process and cured at 450°C for one hour. The reflection minimum directly correlates to the coating thickness, which can be varied either by changing the viscosity of the formulation or the dip speed. The reflection spectrum is optimized for the sensitivity of the human eye, which is most sensitive around 550 nm. The reflection spectrum VIS is shown in Figure 6.

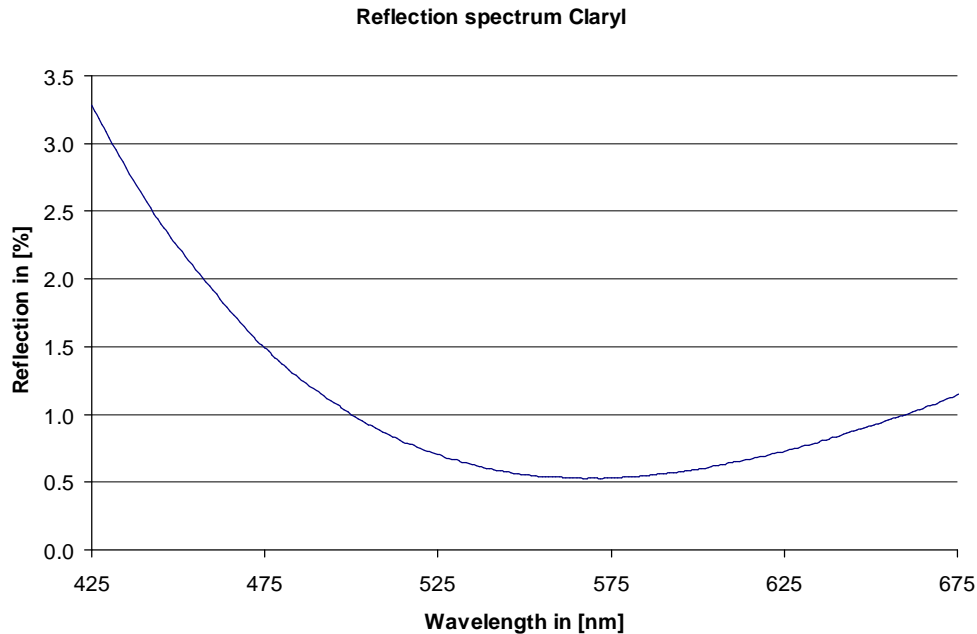


Figure 6. Reflection spectrum of [®]claryl (VIS).

The optical properties of the picture glass are outstanding: the rest reflection VIS is $1.2 \pm 0.1\%$, the transmission is higher than 98%. Furthermore, the color fastness and the viewing angle performance are excellent. The coating is mechanically robust (steel wool resistant) and easy to clean with conventional glass cleaners. This picture glass is available in Europe and the US under the brand name [®]claryl and is produced by DSM in The Netherlands.^[9]

A second technology comprising core-shell particles is DSM's anti-reflective coating for outdoor applications, like solar cell cover glass. The [®]claryl system was used as starting point for this development and optimized to reach the desired performance and durability. After formation of the xerogel, the coating was tempered. The xerogel coating is sufficiently robust to withstand edge work and polishing steps (grinding).^[10] With respect to the optical properties, the coating was optimized for m-crystalline silicon cells. The transmission curve of a resulting two-side coated low-iron float glass sample is displayed in Figure 7 (0° angle).

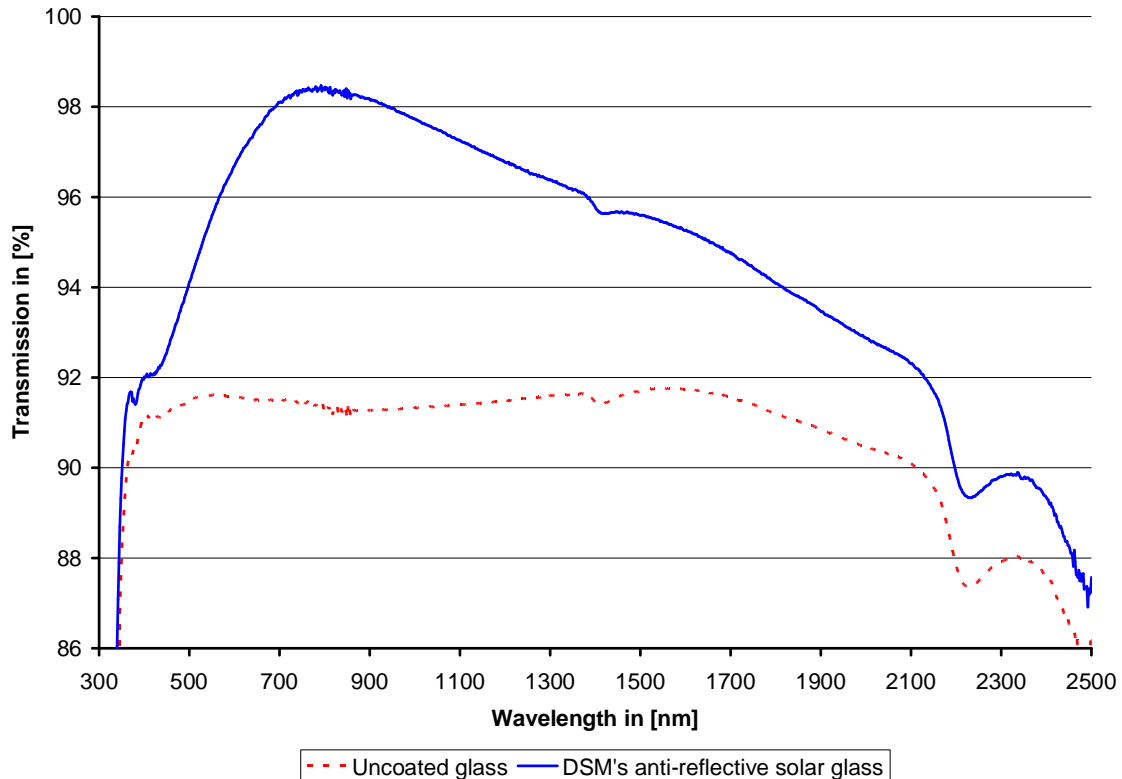


Figure 7. Transmission spectrum of DSM's solar cell cover glass.

As shown in Figure 7, the transmission increase per side is about 2.5% in the regime 400 - 1100 nm. The increase with respect to normal glass rises up to about 5% at 60°. Experiments on small size solar modules as performed by the Photovoltaik Institut (PI) in Berlin show a performance increase between 2 and 3% at 0°, which is in line with the transmission increase. The performance increase rises up to about 5% at 60°.

The durability of the anti-reflective cover glass was evaluated using following set of tests: abrasion resistance test (EN 1096-2), damp-heat test (IEC 61215), humidity-freeze test (IEC 61215), thermal cycling test (IEC 61215). During these tests, only minor changes in transmission and scratch resistance were observed (up to 0.5% decrease in transmission per side, 400 – 1100 nm). To verify this behavior, small size modules with coated and uncoated cover glass were subjected to the damp-heat test for 1500 h. The results of this test are shown in Figure 8.

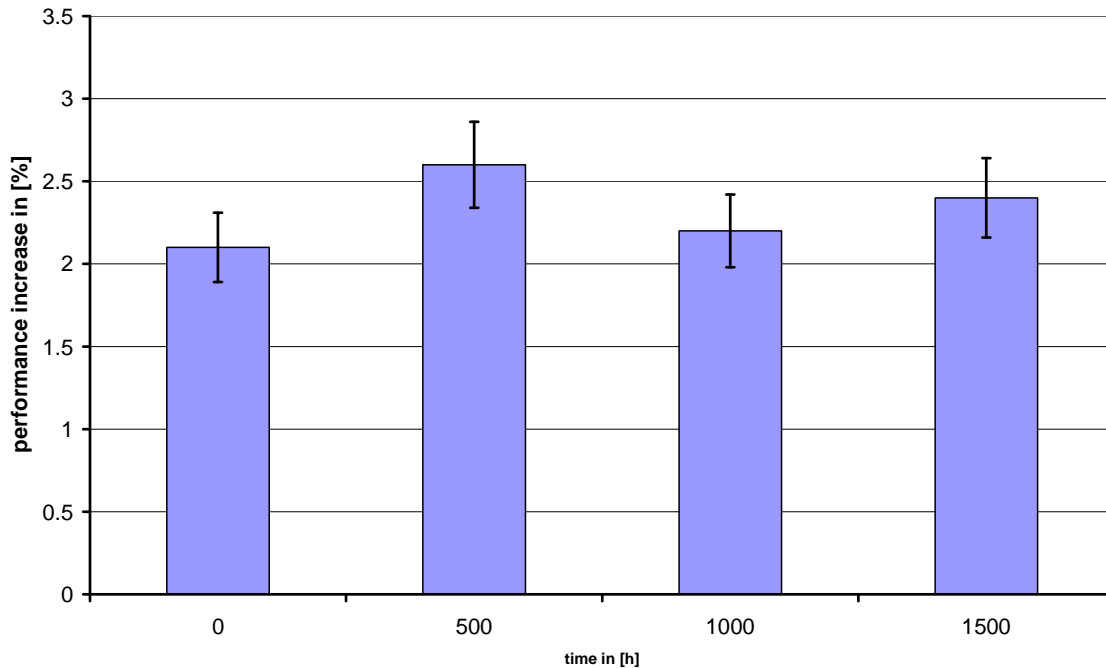


Figure 8. Damp-heat test results on small size modules.

Figure 8 clearly shows that the performance increase caused by the anti-reflective coating is constant for the total duration of the test, which is in-line with the test results on the glass itself. Durability tests on real-size modules gave similar results.

DSM has introduced its AR-coating technology for solar cell cover glass and other (outdoor) applications under the brandname KhepriCoat™. This technology is available to glass or module producers *via* licensing.

Conclusions: In this report, we clearly demonstrate that DSM's single-layer ARCs can be applied both for indoor and outdoor applications. The application of polymer nanoparticles with a silica shell provides us with a high level of control over the balance of surface roughness and internal porosity in such coatings. During the curing or tempering step, the polymer template is removed resulting in a coating with a high level of internal porosity. This enables us to use higher amounts of binder than for traditional single layer ARCs which lowers the surface roughness and increases the scratch resistance, cleanability properties and hydrolytic stability of the coating.

The coating system was optimized for picture glass and solar cell covers. ®Claryl, DSM's picture glass, has excellent optical properties, is robust and easy to clean. ®Claryl is produced since 2007 and currently commercially available in Europe and the US. DSM's solar AR-coating results in a performance increase of a solar module between 2 and 5%. Durability studies were performed both on the glass and on the modules and show that the performance of the coating in

the commonly accepted accelerated ageing tests is excellent. The coating can be applied to both sides of a glass sheet in a dip-coating step. For high-speed single-side application, DSM is developing a horizontal slot-die process. DSM's AR coating technology for solar cover glass and other (outdoor) applications is marketed under the brandname KhepriCoat™ and is available to glass or module producers via licensing. Currently, we are in the process of expanding our product portfolio towards an anti-reflective coating system suitable for plastic substrates.

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- [8] Particle size determined by dynamic light scattering.
- [9] See www.claryl.com
- [10] Xerogel undamaged after abrasion resistance test (EN 1096-2).