Innovation at DSM: State of the Art Single Layer Anti-Reflective Coatings for Solar Cell Cover Glass

Pascal Buskens, Nanning Arfsten, Roberto Habets, Harm Langermans, Ad Overbeek,
Jurgen Scheerder, Jens Thies, Nicolaas Viets
DSM, P. O. Box 18, 6160 MD Geleen, The Netherlands
E-mail: pascal.buskens@dsm.com

Keywords:

1= anti-reflective coating
2= core-shell particles
3= solar cell cover glass
4= picture glazing

Abstract:

In principal, there are two approaches to lower the reflection of a substrate such as glass: the application of an interference-type multiple layer coating system or the use of one single porous graded index coating. Although the application of a single-layer anti-reflective coating (ARC) is the most efficient of both approaches, it is not yet commonly used in industry. The reason for this paradox is the high level of porosity required to obtain good anti-reflective properties with this technology. 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.

By controlling the balance of surface roughness and internal porosity, DSM managed to overcome the typical drawbacks mentioned above providing a mechanically robust and easy to clean anti-reflective glass with a transmission of 98% or higher and a low level of rest reflection. Further chemical modifications provide the coating with an excellent durability. This makes the glass suitable for outdoor applications such as solar cells and greenhouses.

Introduction:

Optical reflectance is a fundamental phenomenon when light propagates across a boundary between two media with different refractive indices. For many applications, reflection is undesired either because it affects the aesthetics or the functionality of an article. Examples of such applications are electronic displays, picture and art glazing, solar cell cover glass and green house cover glass. In principal, two approaches can be used to obtain low reflection: the technique of applying an interference-type multiple-layer system or one inhomogeneous graded-index layer.[1]

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 which the optical constants smoothly vary throughout its thickness.[1] The refractive index of the glass substrate is matched to air as closely as possible using an inhomogeneous layer of which the refractive index gradually falls from that of the substrate to unity. There are, however, no low index solid materials that display a refractive index lower than 1.37 [2] and the best method to approach unity 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.[3] 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.[4] 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 and cleanability properties of the coating.

Figure 1.

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

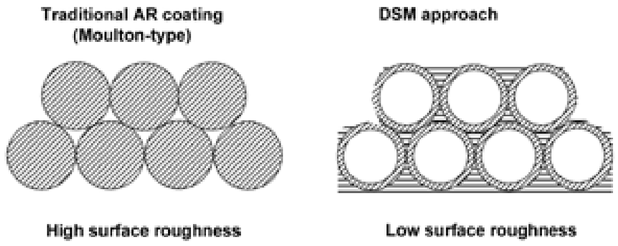
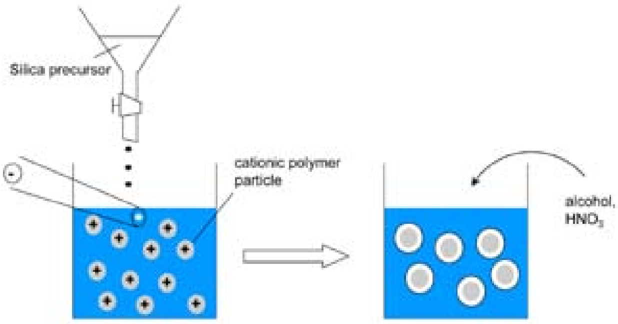


Figure 2.

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



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 [5] and in-situ produced silica nanoparticles were used.[6] As polymeric template, both cationicly stabilized micelles[7] and cationic latexes were applied.[8] 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.[9] This aqueous polymer system was treated with TMOS to form core-shell particles. At the desired shell-thickness, the reaction was stopped through dilution with alcohol and subsequent acidification with nitric acid.

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.

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.

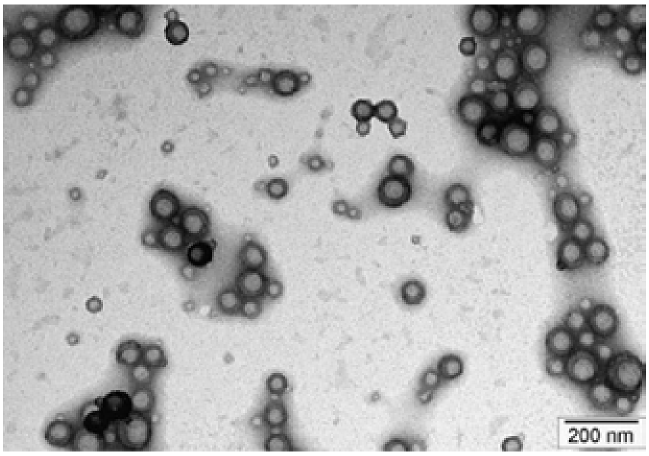
The coatings were applied on both sides of the substrate ***via*** dip-coating. The coating thickness can be controlled ***via*** the dip speed. Typical coating speeds for dip-coating are in the range of 0.5 to 1 m·min^{-1}. Currently, a horizontal process is being developed to apply these coatings on one single side of the substrate. Initial results show that coating speeds up to 20 m·min^{-1} can be achieved using this process. This is comparable to the coating speed of conventional sputtering processes.

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 4). They are steel wool resistant, easy to clean and display broad-band anti-reflective properties.

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 5.

Figure 3.

Core-shell particles.



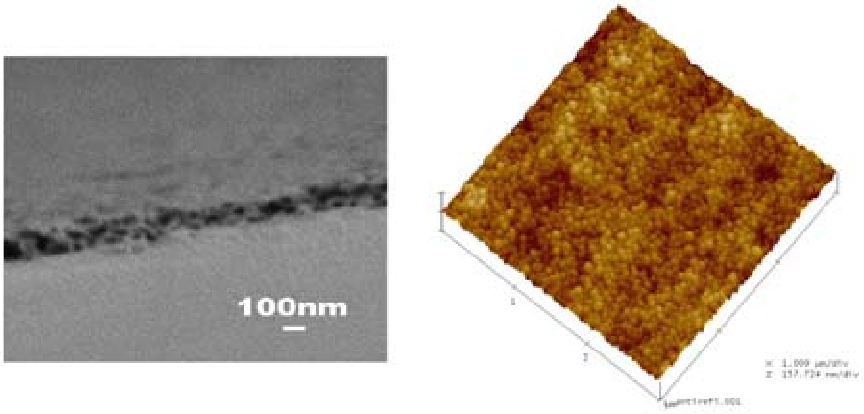
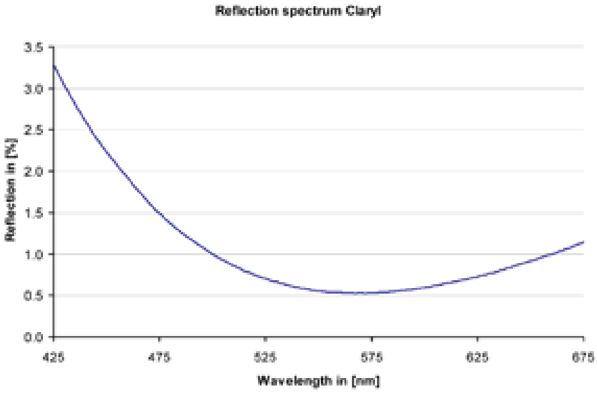


Figure 4.

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

Figure 5.

Reflection spectrum of ®claryl (VIS).



The optical properties of the picture glass are outstanding: the rest reflection VIS is 1.2 ± 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 since 2007under the brand name ®claryl and is produced by DSM.[10]

A second technology comprising core-shell particles is DSM's anti-reflective coating for solar cell cover glass - the so-called KhepriCoat™ technology. 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).[11] With respect to the optical properties, the coating was optimized for m-crystalline silicon cells. The transmission curve of a resulting two-side coated sample is displayed in Figure 6 (0° angle).

As shown in Figure 6, 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% in at 60°. Initial 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°. More accurate measurements on real-size modules are currently performed at PI.

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 7.

Figure 7 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. Currently, durability tests on real-size modules are performed at PI Berlin. DSM shortly plans to introduce its solar cell cover glass. Additionally, we aim to make the technology available to glass or module producers via licensing.

Conclusions:

In this report, we clearly demonstrate that 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 glazing 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. DSM's solar coating - KhepriCoat™ - 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. Currently, the glass is tested on real-size PV modules at PI Berlin. We aim to make the technology available to glass or module producers via licensing.

Figure 6.

Transmission spectrum of DSM's solar cell cover glass.

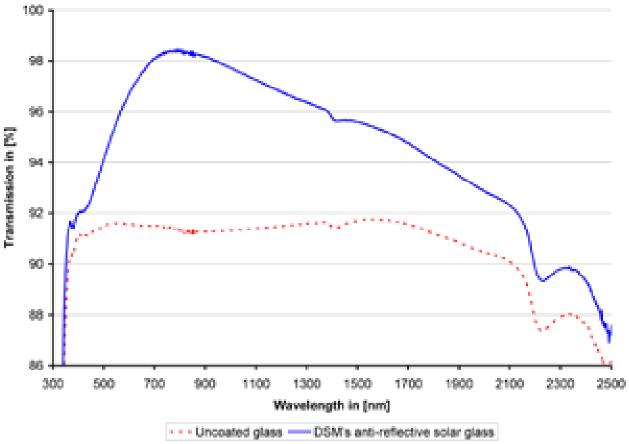
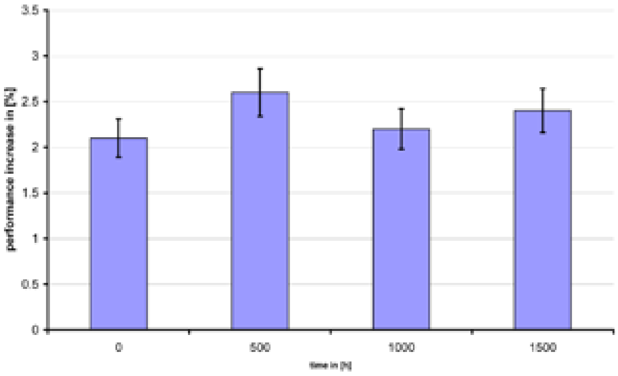


Figure 7.

Damp-heat test results on small size modules.



Acknowledgements:

The authors thank Dorina van Haeringen, Michaela Rusu and Sven Kreisig (DSM) for their support.

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[5] http://www.nissanchem-usa.com/products.php

[6] For example: (a) K. Nozawa, H. Gailhanou, L. Raison, P. Panizza, H. Ushiki, E. Sellier, J. P. Delville, M. H. Delville, Langmuir 2005, 21, 1516-1523; (b) G. H. Bogush, M. A. Tracy, C. F. Zukoski, Journal of Non-Crystalline Solids, , 104, 95-106.

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[9] Particle size determined by dynamic light scattering.

[10] See www.claryl.com

[11] Xerogel undamaged after abrasion resistance test (EN 1096-2).