

Multilayer NIR reflective coatings on transparent plastic substrates from photopolymerizable nanoparticulate sols

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Abstract

A new synthesis and processing route for preparing multilayer interference coatings on plastic substrates has been developed. For this purpose, alcoholic sols of surface modified (3-glycidoxypropyltrimethoxysilane, GPTS) SiO₂ and TiO₂ particles with sizes of 10 and 4 nm, respectively, were synthesized. Layers were prepared by dip coating, subsequent UV curing (2.1 J/cm²) and thermal post treatment at 80°C for 15 min. Refractive indices of $n_D = 1.47$ for SiO₂ layers and $n_D = 1.93$ for TiO₂ were measured. As an example, plastic sheets were coated by angle dependent dip coating with withdrawal speeds from 3 up to 6 mm/s and an inclination angle of 4°. By this way, one side of the substrate was coated with six quarterwave thick layers (peak wavelength at 750 nm), producing a reflective interference filter with a reflectivity of 72% between 650 and 900 nm. On the other side of the substrate, an interference filter with a reflectivity of 66% between 800 and 1100 nm was produced simultaneously. The interference coatings do not show delamination or defects after boiling water test (H₂O + 5 wt.% NaCl, 8 h) and excellent adhesion (GT 0, TT 1) was obtained in the cross cut tape test. Yellowing did not occur ($\Delta g < 3$) and the mechanical properties of the interference filters were not altered after dry sun test at 760 W/m² for 270 h. For mechanical protection a nanocomposite hardcoat can be applied on top of the NIR reflectance filters without changing the optical properties remarkably.

Keywords: Sol-gel; Nanoparticles; Photo polymerization; IR reflective coatings

1. Introduction

Near infra red (NIR) reflective coatings on plastics are useful for solar energy control and heat protection. Well known examples for their application are windshields for cars, where a coated plastic foil is embedded in the laminated glass or visors for fireman's helmets. The state of the art for their realisation is the deposition of interference layers, consisting of a metal (Ag or Au) layer with thickness about 10–20 nm in combination with dielectric layers for protection and to increase the transmittance in the visible spectral range, because the high reflectance of the metal layer is not restricted to the NIR and the infrared (IR). These interference layers are produced by PVD [1], PCVD [2] and sputtering using webcoating machines.

As an alternative, multilayer interference systems with high and low refractive index dielectric layers have been applied by Ashley and Carol [3,4] on polycarbonate (PC) substrates by hydrolysis and condensation of silanes and various metal alkoxides (sol-gel process). The layers had

to be densified at 50°C for 2 to 3 weeks, due to the low reactivity of the alkoxide derived sols. Tsucha et al. [5] have prepared high refractive index nanoparticles of different suitable oxides in order to tailor the refractive index of an organic polymer coating matrix, leading to a maximum refractive index of about $n_D = 1.75$ and a minimum refractive index of about $n_D = 1.50$. The layer can be cured rapidly by e-beam curing. However, a rather high number of layers are required for the preparation of efficient filters due to the low difference in the refractive index of the layers. Recently, a new approach with SiO₂ and TiO₂ nanoparticles, coated with an epoxysilane and dispersed in alcohol was used to prepare an optical double layer with antireflective properties (V-filter) on polycarbonate substrates [6]. The epoxysilane (GPTS) is used for steric stabilization of the nanoparticles and for covalent coupling of the particles after layer deposition (dip coating) by UV irradiation. A polymer type or ormocer type matrix is not required for the formation of stable layers [6]. Therefore, very low ($n_D = 1.47$) and also very high ($n_D = 1.93$) refractive index coatings can be obtained.

The scientific goal of this paper was to design and realize a broad band NIR reflectance filter with these photopolymerizable nano particles. In order to minimise the number

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of layers, the application of the angle-dependent dip coating technique [7,8] was investigated with this system. The durability of the filter was investigated with eraser test, UV test and boiling test.

2. Experimental

2.1. Coating preparation

The preparation of the SiO_2 nanoparticle containing coating solution was based on the synthesis route described in detail earlier in [6]. After preparation of an alcoholic (isopropanol) solution with 30 wt.% SiO_2 nanoparticles by acid hydrolysis and condensation of tetraethoxy silane (TEOS) and stabilisation with 0.5 wt.% glucose according to [6], GPTS was added in a weight ratio $\text{SiO}_2\text{:GPTS} = 4\text{:}1$ and the mixture was stirred at 50°C for 5 h. The preparation of the TiO_2 nanoparticulate solution was modified, compared to [6]. 2.1 g of tetraisopropylorthotitanate was slowly added to a mixture of isopropanol with 0.981 g conc. HCl (37 wt.%/ H_2O) and 0.105 g water under stirring at 25°C . The solution was stirred 24 h at 25°C . Afterwards, 2 g GPTS were mixed with 200 g TiO_2 -sol under reflux with vigorous stirring at 50°C for 5 h. A part of isopropanol (10 g) was removed from the sol by vacuum distillation at 14 mbar and 25°C and 14 g of 2-isopropoxyethanol were added. Finally, a mixture of GPTS, hydrolysed with 0.1 N HCl by stirring for 24 h at 25°C and 2 wt.% (in relation to GPTS) of the photoinitiator UVI 6974 (Union Carbide) was added. By this way a total TiO_2 content of 90 wt.% (related to the cured coating material) was reached.

In order to improve the scratch resistance of the NIR filter, a hardcoat as described in [9] was synthesised. The coating consists of SiO_2 and AlOOH (boehmite) nanoparticles embedded in a GPTS based matrix.

2.2. Coating process

UV stabilised polycarbonate sheets of $20 \times 30 \times 0.4$ cm were used as substrates after rinsing with isopropanol and drying with air. The coatings were applied by the angle dependent dip coating technique (ADDC) [7,8] using a constant angle of 3.7° for all layers. The withdrawal speed was varied between 3 and 5 mm/s to adjust the coating thickness which had been determined by computer simulation [10] using the TF calc programme (Software Spectra. Inc.). After each coating step, the coated sheets were dried for 1 min. at 25°C and cured by UV irradiation with 2.1 J/cm^2 on both sides. After the ADDC process with six layers, the coating stack was thermally treated at 120°C for 15 min. The hard coat was deposited on top of the interference stack by flow coating [11] and curing at 80°C for 1 h.

2.3. Characterization

The adhesion of the coatings was tested by cross cut and

tape tests [12] and eraser test [13]. In the saline-test, the coated substrates were stored in water containing 5 wt.% of NaCl at 100°C for several hours. The test was interrupted every hour. The sample was cleaned with ethanol and delamination and pin hole formation was investigated by microscopy. In the suntest, the coated polycarbonate sheets were irradiated with UV light (Hereaus sun test, 760 W/m^2 without filter) and the yellowing (Δg [11]) was determined as a function of irradiation time by UV-Vis absorption spectroscopy (Omega 30, Bruins Instruments).

For the determination of the thickness and refractive index of single layers, rectangular dip coating was realized. The layers were cured as described in Section 2.2. and refractive index and thickness were determined by spectral ellipsometry (SOPRA, ES4G).

3. Results and discussion

For application of solar energy control, it is important to obtain a broad band filter with a high reflectance in the NIR range, close to the edge of visible light. Based on the optical data of the high and low refractive index films [6], a simulation of a reflectance interference filter for each side of the polycarbonate substrate has been made, in order to estimate the volumes of the expected reflectance peaks for the chosen conditions. One filter with maximum reflectance at 750 nm was chosen. In order to obtain a wide bandwidth towards longer wavelengths, a second filter with a peak position at about 900 nm was selected. The result of the computer simulation is shown in Fig. 1.

The simulation was performed with six layers for each side of the substrate. As one can see from Fig. 1, peak reflectances of 75% at 720 nm and 78% at 880 nm were obtained. These high reflectances can be attributed to the large difference in refractive index of the layers [1], prepared from SiO_2 ($n_D = 1.47$) and TiO_2 ($n_D = 1.93$) nanoparticle containing coating solutions.

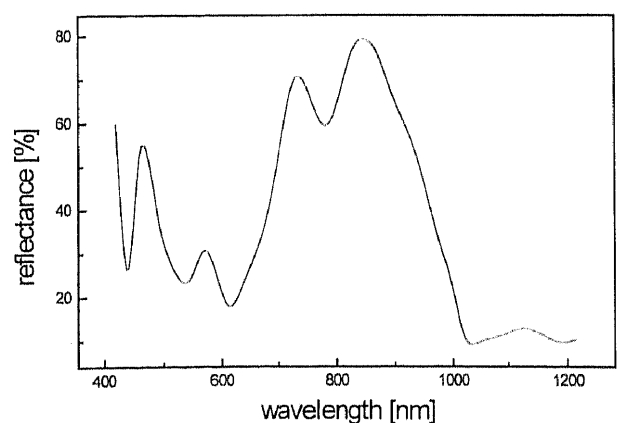


Fig. 1. Computer simulation of a NIR-filter with 6 quarterwave layers (with refractive index n_D of 1.93 and 1.47, respectively) on each side of the substrate (polycarbonate) with different filter performances on both sides of the substrate.

The filters consist of six quarterwave layers with high (n_h) and low (n_l) refractive index and the appropriate thickness t_h and t_l , respectively, which depend on the quarterwave conditions for both filters. For both peak positions (λ_1 and λ_2) the quarterwave conditions have to be fulfilled. This means that

$$n_h \cdot t_{1h} = n_l \cdot t_{1l} = \lambda_1/4 \quad (1)$$

$$n_h \cdot t_{2h} = n_l \cdot t_{2l} = \lambda_2/4 \quad (2)$$

where t_{1h} , t_{1l} , t_{2h} and t_{2l} are the thicknesses of the high and low refractive index layers for the two filters with the peak positions λ_1 and λ_2 . As one can see from Eqs. (1) and (2) the relation between the thicknesses of the high and low refractive index layers is given by Eq. (3)

$$t_{1h}/t_{2h} = t_{1l}/t_{2l} = \lambda_1/\lambda_2 \quad (3)$$

Since the filter at 750 nm should be deposited on one side of the substrate and the filter for 900 nm on the other one, the relation of the thicknesses of the high refractive index layers on both sides has to be the same as for the low refractive layers. Therefore, it seemed to be feasible (from Eq. (3)) to prepare both filters simultaneously on the two sides of the substrate sheet by ADDC with a constant angle, because it was assumed that the thickness ratio of upper and bottom side might be only a function of the dipping angle. In order to prove this hypothesis for the given sol systems, the thickness ratios t_1/t_2 of the coating on the bottom (thickness = t_1) and upper (thickness = t_2) side were determined for both SiO_2 and TiO_2 as a function of the withdrawal speed for different dipping angles. The result is shown in Fig. 2 for SiO_2 as well as for TiO_2 . The values of Fig. 2 represent an average of five single measurements each. The relative error of measurement was estimated to be about 3%.

In the case of SiO_2 , the t_1/t_2 values for 30° (5 and 6 mm/s) and for 40° could not be measured because cracks appeared in the appropriate films after the photopolymerization step.

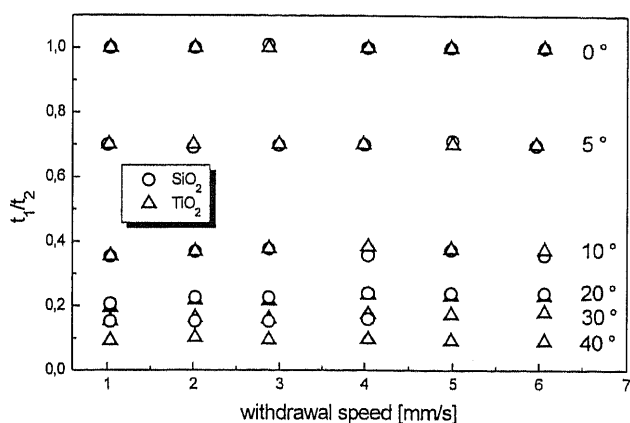


Fig. 2. Ratio between the thicknesses of TiO_2 (Δ) and SiO_2 (\circ) films of the bottom side (t_1) and the upper side (t_2) after the ADDC-dipping process and UV-curing (2.1 J/cm^2) as a function of the withdrawal speed for different dipping angles.

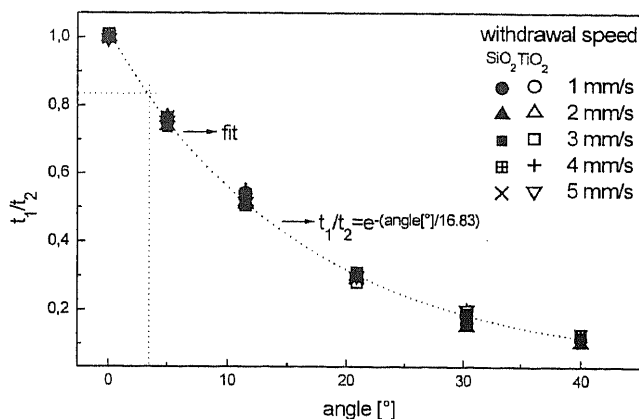


Fig. 3. Ratio between the film thicknesses (SiO_2 , TiO_2) on the bottom side and the upper side after the ADDC-dipping process and curing by UV-irradiation (2.1 J/cm^2) as a function of the dipping angle for different withdrawal speeds. For a thickness ratio of 0.833 (750 nm/900 nm) the dipping angle is 3.7°.

The thickness ratios are not depending on the withdrawal speed in the investigated range and are the same for SiO_2 and TiO_2 for a given angle. This is the prove for the possibility to prepare two different filters on both sides of the substrate by ADDC with a fixed angle, with the chosen sols. In order to find out the adequate angle for the two peak positions (750 and 900 nm), the thickness ratio t_1/t_h is plotted as a function of the dipping angle for a selected withdrawal speed of 1, 2, 3, 4, and 5 mm/s (Fig. 3).

Fig. 3 shows a strong decrease of the thickness ratio with increasing angle. The ratio, required from Eq. (3) is about 0.833, which is obtained for an angle of about 3.7°.

With this angle, a six layer filter was prepared as described in Section 2.2 and the reflectance was measured. Fig. 4 shows the result in comparison with the result of the computer simulation.

There is an excellent agreement between simulation and measurement. The prepared filter shows reflectances $>50\%$ in the range between 700 and 940 nm with peak values of 70% at about 730 nm and 80% at about 840 nm. The peaks at 570 and 460 nm are due to interference modulations and can be remarkably reduced by further optimization [14].

In order to see whether there is any absorption in the Vis-NIR-range, the transmittance spectrum was also recorded (Fig. 5).

Curve 1 of Fig. 5 shows the transmission of the uncoated polycarbonate substrate.

A steep UV-cut-off at 400 nm is clearly seen and for the NIR region absorption peaks occur at $\lambda > 1100 \text{ nm}$ occur.

The curves 2 and 3 reflect the transmitting filters on the bottom side and upper side of the polycarbonate sheet prepared by ADDC (in both cases, the appropriate other side was covered with a plastic foil during the ADDC process). Curve 4 is the transmittance curve of the filter, coated under the same conditions on both sides by ADDC. This curve shows minima at about 740 and 840 nm which

correspond very well to the maxima in the reflectance spectrum of this filter shown in Fig. 4. The appropriate transmittance values of about 30 and 20% respectively correspond also very well the values of reflectance of 70 and 80% respectively (see Fig. 4). The peaks in the NIR region ($\lambda > 1100$ nm) can also be attributed to reflectance in combination with absorption of the polycarbonate substrate, since curves 3 and 4 have the same transmittance spectrum but is different from that of curve 2. This is the prove that the filter layers do not cause absorption in this spectral range, which is important for solar energy control applications.

Fig. 5 also clearly shows that for curves 2 and 3 the minima in transmission (which is due to maxima in reflectance), (see Fig. 4) have been realized at wavelengths of 750 and 870 nm which are very close to the desired filter design.

A good adhesion and stability of the layers against UV and chemical attack are important for practical application and have therefore been characterized. The interference layers show excellent adhesion, since values of GT0-TT1 were obtained in cross cut and tape test [12]. After saline test (boiling water with 5 wt.% NaCl) no delamination or defect formation was recorded after 8 h. It was especially interesting to investigate the UV stability of the coatings, because TiO_2 nanoparticles had been used in combination with organics. The surprising result was that even for exposure times of up to 270 h in the sun test (760 W/cm^2) no degradation, defect formation or yellowing (Δg) could be observed. For longer exposure times a yellowing became evident, but this has not been investigated systematically yet, since a 270 h UV test fulfills the specifications for many applications. The TiO_2 nanoparticles in the layers are amorphous [6] and their surface is assumed to be covered with -O-Si-groups. Therefore it can be concluded that the UV-activity is suppressed. Uncoated UV stabilized polycarbonate sheets showed yellowing already after about 30 h [15] of suntest. Therefore the interference system serves as UV protection layers due to the UV absorption

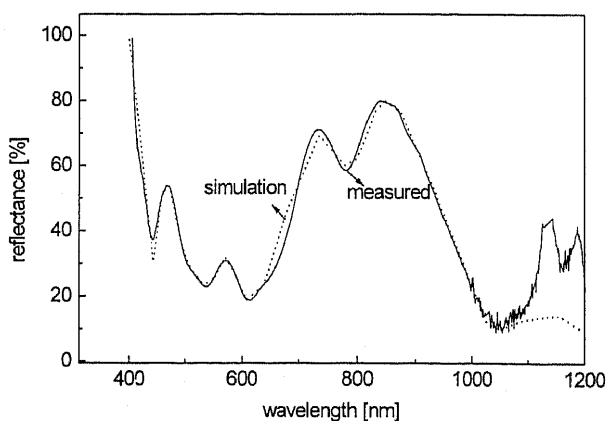


Fig. 4. Comparison between the computer simulation and the measured transmission spectra of the NIR-Filter on polycarbonate, prepared by ADDC with a fixed angle of 3.7° , using photopolymerisable nanoparticulate SiO_2 and TiO_2 coating sols.

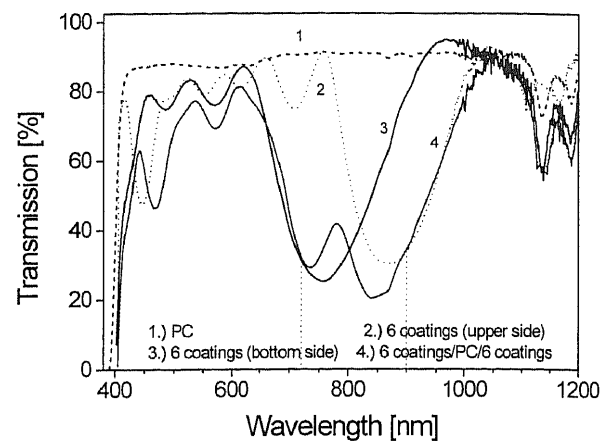


Fig. 5. Transmittance spectrum of (1) uncoated polycarbonate, (2) NIR-filter on the bottom side of the polycarbonate sheet, (3) NIR-Filter on upper side of the polycarbonate sheet and (4) NIR-Filter on bottom and on upper side of the polycarbonate sheet, prepared by ADDC with a fixed angle of 3.7° .

of TiO_2 and also due to UV reflectance, as it can be seen in Fig. 5.

With the taber test, defects were visible after a few cycles (12% haze after five cycles) already and eraser test was passed with 10 cycles, whereas 20 cycles are the specifications for optical coatings [13]. Comparable values were obtained for uncoated substrates. It is assumed that the total thickness of the layer stack of about 600 nm is not sufficient for mechanical protection of the soft substrate surface. Investigations on hardcoats derived from organic-inorganic nanocomposites (Nanomer[®]) on plastics have shown [11] that a coating thickness of at least $2 \mu\text{m}$ is required for efficient protection. In order to overcome this difficulty, such a Nanomer[®] hard coat, which had been developed earlier for polycarbonate substrates [11] was applied on top of the interference filter. After that, a haze value of 7% was obtained after 1000 cycles of taber test, which is in good agreement with the results obtained on polycarbonate substrates [11] and sufficient for many applications. The question was however, how the hardcoat layer would change the NIR reflectance characteristics. Therefore, reflectance measurements were performed with and without hardcoat. The results is shown in Fig. 6.

There is no remarkable difference in the NIR reflectance of the interference system with and without hard coat within the error of measurements which can be estimated to about $\pm 3.5\%$ reflectance. The NIR reflectance spectrum is mainly caused by the reflectance at the interfaces of the high and low refractive index quarterwave layers and only insignificantly determined by the interface with the substrate, air or hard coat respectively. The reflectance at the optical interface between the top layer and the surrounding medium depends of their refractive index difference. A hard coating decreases the reflectance of the quarterwave film on the top of the interference filter, because this refractive index difference is smaller (n_D of the hardcoat is about 1.5 compared to

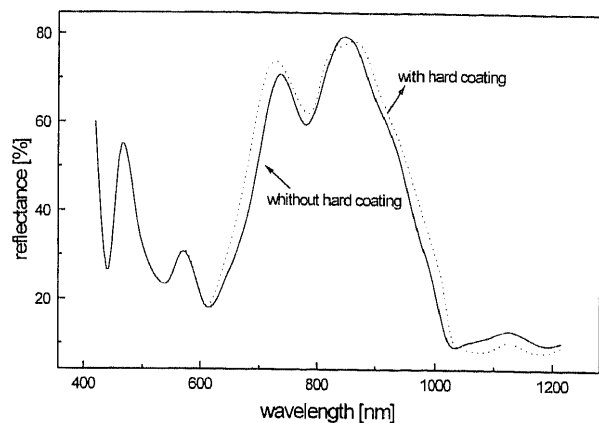


Fig. 6. Reflectance of NIR-filters with and without a nanocomposite hard coating (thickness = 5 μm , [11]) deposited on top of the interference layer stack.

1.0 for air). However, this effect is almost compensated, because the interface hard coating and air reflects about 4% of the total incident light.

4. Conclusions

The results show that the use of functionalized nanoparticles produced by sol-gel process is a very useful tool for the preparation of optical films with extreme refractive index on temperature sensitive substrates. The main advantages of this new approach are the extremely high and low refractive index, the short processing times by UV curing and the very good stability of the layers. For broadband application, the ADDC technique offers an additional cost saving by reducing the number of layers by 50%. Therefore this new coating system has a great potential for future practical application.

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