Effect of Modified Silica Materials on Polyvinyl Chloride (PVC) Substrates to Obtain Transparent and Hydrophobic Hybrid Coatings

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Abstract: In this research, we report a simple and inexpensive way to prepare transparent and hydrophobic hybrid coatings through deposition of different silica materials on polyvinyl chloride (PVC) substrates. The silica materials were prepared using an acid-catalyzed sol–gel method at room temperature (25 ± 2 °C), using alkoxysilanes: tetraethoxysilane (TEOS), as the silica source, and ethoxydimethylvinylsilane (DMVES), triethoxyoctylsilane (OTES), and trimethoxyhexadecylsilane (HDTMES), as modifier agents. The obtained materials were characterized (either as powders or as thin films) by Fourier-transform infrared spectroscopy (FTIR), UV/Vis spectroscopy, transmission electron microscopy (TEM), thermogravimetric analysis (TGA), atomic force microscopy (AFM), spectroscopic ellipsometry (SE), and water contact-angle measurements. UV/Vis spectra showed that the PVC substrate coated with the silica material containing TEOS/DMVES/OTES had a transmittance of about 90% in the wavelength range of 650–780 nm. The water contact angles increased from 83° for uncoated PVC substrate to ~94° for PVC substrates coated with the sol–gel silica materials. These PVC films with hybrid silica coatings can be used as the materials for outdoor applications, such as energy-generating solar panel window blinds or PVC clear Windmaster outdoor blinds.

Keywords: sol–gel method; silica materials; hydrophobic coatings; PVC substrate

1. Introduction

In recent years, substantial progress has been made in the development of hybrid coatings with good functionality and performance for potential applications in the fields of catalysis, optics, and sensing [1–3]. Due to the environment- and human-friendly nature, silicon dioxide (SiO2) is a component that can be used in protective layers for anti-sticking, antifogging, self-cleaning, or water repellency [4]. Different techniques, such as deposition, self-assembly, lithography, and etching, have been used to prepare silica materials for hydrophobic/hydrophilic or superhydrophobic surfaces. Spin-coating, spray-coating, dip-coating, chemical vapor deposition, chemical bath deposition, atmospheric plasma, atomic layer deposition, and the sol–gel process were used as deposition methods in the literature [5]. The preparatory steps toward the realization of transparent and self-cleaning surfaces have been investigated. Chemin et al. [6]
reported the preparation of transparent and self-cleaning titanium dioxide/silicon dioxide (TiO$_2$/SiO$_2$) thin films on polymer (poly(ethylene 2,6-naphthalate (PEN)) substrates through plasma-enhanced chemical vapor deposition (PECVD). It was demonstrated that the addition of the hexamethyldisiloxane (HMDSO) precursor ensured a decrease in the water contact angle of the deposited films and promoted the formation of an adherent matrix coating. Jeon et al. [7] developed organic–inorganic hybrid materials with incorporated transition metal ions using a two-step spin-coating method. It was observed that the fabricated substrates showed good transparency (over 95%) and stable hydrophobicity (contact angle above 100°). Nagappan et al. [8] prepared superhydrophobic and transparent polymethylhydroxyisiloxane (PMHOS)/silica ormosil aerogel hybrids by spin-coating on glass substrate. They showed that the rough surface can be realized through the formation of hierarchical surface morphology. Wang et al. [9] obtained transparent hydrophobic silica-based coatings via a dip-coating process on glass substrates and aluminum foils, using hexamethyldisilazane (HMDS) and tetraethoxysilane (TEOS).

Compared with the mentioned methods, the sol–gel process is the most used method for preparing the hybrid silica coatings due to its main advantages, such as easy preparation at room temperature, low cost of process, reproducibility, high flexibility in composition and selectivity, good mechanical adherence to the substrate, high purity of the resulting materials, and high thermal stability [10–12]. Iline-Vul et al. [13] obtained fluorine-conjugated silica microparticles using the sol–gel technique. The final material was deposited on the different polymeric films (polyethylene (PE), polypropylene, (PP), polycarbonate (PC), and polyurethane (PU)) to obtain superhydrophobic thin coatings. The results indicated that fluorine-conjugated silica microparticles presented a good adhesion to the films, especially PU films. Chan et al. [14] prepared the hybrid coatings composed of surface-modified silica nanoparticles embedded in poly(2-hydroxyethyl methacrylate) (PHEMA) matrix. They demonstrated that the abrasion resistance of PHEMA/silica hybrids coated on poly(methyl methacrylate) (PMMA) was enhanced when silica nanoparticles were incorporated. Zhang et al. [15] achieved coatings with transmission of 96.86–97.34% through silica nanocomposites obtained using the sol–gel technique. Al-Bataineh et al. [16] showed that polyvinyl chloride (PVC)/polystyrene (PS) hybrid films containing silica nanoparticles could be achieved through the dip-coating method. The obtained films presented a high transmittance (>80%). Abdel-Baset et al. [17] prepared homogeneous PVC–silica nanocomposite films, using silica nanoparticles synthesized via the sol–gel method. Youn et al. [18] fabricated hydrophobic and transparent (T > 80.0%) films using electrospun nanofiber scaffolds made of polystyrene (PS). Tao et al. [19] reported the fabrication of the nanoporous silica coatings with high transmittance (>99%) through a one-step base-catalyzed sol–gel process using tetraethoxysilane (TEOS) and hexamethydisilazane (HMDS). Shokuhfar et al. [20] showed that SiO$_2$–TiO$_2$ nanostructured films were coated on automotive windshields through the sol–gel technique for self-cleaning and photocatalytic applications. The obtained results revealed that the surface wettability of these films can be changed as a function of the heat treatment temperature and UV irradiation time. In another study, Pingan et al. [21] examined the properties of the silica/polyvinyl alcohol (PVA) hybrid films, including transmittance, thermal stability, mechanical strength, adhesive strength, and hygrothermal resistance. They showed that the transmittance of the hybrid solution prepared via a sol–gel process is controlled by its morphology. Hegde et al. [22] developed hybrid sol–gel coatings for cavitation erosion protection of aluminum alloys, using 3-methacryloxypropyltrimethoxysilane (MAPTMS) and zirconium (IV) propoxide. The obtained results revealed that the coatings were thermally stable and have potential for marine applications. Picolo et al. [23] prepared the superhydrophobic self-cleaning surface (static contact angle of ~151°), using silica nanoparticles functionalized with perfluorooctyltriethoxysilane (POTS) on a polymeric substrate polymethyl methacrylate (PMMA). Lattie et al. [24] reported the fabrication of superhydrophobic silica nanoparticle coatings on various substrates (body of motorcycle, building wall, mini boat, solar cell panel, window glass, cotton shirt, fabric shoes, paper (currency notes), plastic, metal, wood, marble, and sponge). The results indicated that
all prepared coatings exhibited strong repellant behavior toward water (contact angle of ~160°). Sriramulu et al. [25] obtained thin films from perylene functionalized silica particles, using trimethoxy(octadecyl)silane (TMODS). They showed that the resulted coatings can be used to protect various heat sensitive substrates. In another research, Zhang et al. [26] showed that the hybrid films with photoresponsive and photosensitive properties can be prepared through combining the low-temperature sol–gel process and spin-coating technique, using solutions containing TiO₂, γ-glycidoxypropyltrimethoxysilane (GLYMO), and 3-methacryloxypropyltrimethoxysilane (MEMO).

In our previous study [27], we showed that the transparent and antireflective coatings on polyvinyl chloride (PVC) substrates can be obtained through the sol–gel method under mild conditions, using methyltriethoxysilane (MTES) and vinyltrimethoxysilane (VTMES). The obtained results indicated a reduction of reflectance (10%) for the sol–gel silica coatings, at the wavelength of 550 nm, compared with uncoated PVC substrate.

In the present study, different silica materials were synthesized using the acid-catalyzed sol–gel method, using silane precursors with various alkyl groups (tetraethoxysilane (TEOS), ethoxydimethylvinylsilane (DMVES), triethoxycyclsilane (OTES), and trimethoxyhexadecyilsilane (HDTMES)). The sol–gel method was chosen to obtain the silica materials due to its cost-effectiveness, low processing temperature, and the possibility of controlling the product’s chemical composition. These silica materials were deposited onto plastic substrates (polyvinyl chloride (PVC)) in order to obtain transparent and hydrophobic hybrid coatings. Physicochemical and morphological properties of final silica materials and of hybrid coatings were examined by Fourier-transform infrared spectroscopy (FTIR), UV/Vis spectroscopy, transmission electron microscopy (TEM), thermogravimetric analysis (TGA), atomic force microscopy (AFM), spectroscopic ellipsometry (SE), and water contact-angle measurements. Treating clear PVC films with hybrid silica coatings will increase photo- and thermal stability and transparency, improving their properties for outdoor applications, such as energy-generating solar panel window blinds or PVC clear Windmaster outdoor blinds.

2. Materials and Methods

2.1. Materials

Alkoxysilanes used were tetraethoxysilane (TEOS, 98%, Aldrich, St. Louis, MO, USA), ethoxydimethylvinylsilane (DMVES, 95%, Aldrich, St. Louis, MO, USA), triethoxycyclsilane (OTES, 97%, Fluka, Philadelphia, PA, USA), and trimethoxyhexadecyilsilane (HDTMES, 85%, Aldrich, St. Louis, MO, USA). Titanium(IV) isopropoxide (TIP, 97%, Aldrich, St. Louis, MO, USA) was used as a crosslinking agent. Maleic anhydride (MA, Fluka, Philadelphia, PA, USA) was used as a complexing agent. Isopropanol (iPrOH, 99.9%, Chimreactiv S.R.L., Bucharest, Romania) was used as a solvent. Hydrochloric acid (HCl 0.1N, Sigma-Aldrich, St. Louis, MO, USA) was used as a catalyst. Benzaldehyde dimethyl acetal (FIN, 99%, Sigma-Aldrich, St. Louis, MO, USA) was used as a UV photo-initiator. The structural and compositional information of alkoxysilanes is shown in Table 1. The chemicals were used as received. The plastic standard (polyvinyl chloride (PVC), FabTech, Bucharest, Romania) was selected due to its low-cost, flexible, lightweight, and durable properties. Before their use, the PVC substrates were washed with ethanol, vacuum-dried, and stored in a desiccator for 24 h in order to avoid the contamination with different reagents.
Table 1. Detailed information of alkoxysilanes used in this experiment.

| Alkoxysilane | Structure | Molecular Formula | \( M_w \) (g mol\(^{-1}\)) |
|--------------|-----------|------------------|-----------------------------|
| TEOS         | ![Structure TEOS](image) | C\(_4\)H\(_{20}\)O\(_4\)Si | 208.33 |
| DMVES        | ![Structure DMVES](image) | C\(_6\)H\(_{14}\)OSi | 130.26 |
| OTES         | ![Structure OTES](image) | C\(_{14}\)H\(_{32}\)O\(_3\)Si | 276.48 |
| HDTMES       | ![Structure HDTMES](image) | C\(_{19}\)H\(_{42}\)O\(_3\)Si | 346.63 |

2.2. Synthesis of Sol–Gel Silica Materials

The silica materials were prepared using the sol–gel method in a similar way to that previously reported [27]. In this work, tetraethoxysilane (TEOS) was used as a silica source, and silane precursors (ethoxydimethylvinilsilane (DMVES), triethoxyoctylsilane (OTES), and trimethoxymethyldecysilane (HDTMES)) were used as modifying agents (see Table 1).

In the first step, TEOS and silane precursors (DMVES, OTES, or HDTMES) were pre-hydrolyzed with iPrOH (15 mL) and HCl (0.1 M, 0.46 mL) for 4 h, under continuous stirring at room temperature (25 ± 2 °C). The solutions were prepared by mixing TEOS/silane precursors in a molar ratio of 1:1. As a second step, MA (0.1 g) was added to the solutions in order to start the condensation reactions. After complete dissolution of MA, a well-defined amount of TIP (0.4 mL) was slowly added. The crosslinking agent (TIP) was added in the second part of the recipe to avoid the formation of precipitation. Further amounts of HCl (0.1 M, 2 mL) and FIN (0.2 mL) were introduced to the solutions in order to continue the sol–gel process and initiate the photopolymerization reaction. The mixtures were stirred for another 2 h, at room temperature (25 ± 2 °C), obtaining two stable, transparent, and homogeneous solutions: TEOS/DMVES/OTES (A) and TEOS/DMVES/HDTMES (B) (see Table 2).

Table 2. Alkoxysilanes used for the preparation of the sol-gel silica materials.

| Sample | TEOS (mL) | DMVES (mL) | OTES (mL) | HDTMES (mL) |
|--------|-----------|------------|-----------|-------------|
| A      | 4.2       | 1.52       | 2.9       | -           |
| B      | 4.2       | 1.52       | -         | 0.7         |

Two different powders were obtained when these mixtures were placed into plastic vials. Furthermore, two films were realized when these mixtures were deposited onto the PVC substrates through draw-down sample coating with the manual applicator. All samples were irradiated under a UV lamp (\( \lambda = 365 \) nm, 10 min, irradiance of 2290 mW/cm\(^2\)) in order to initiate the photopolymerization reaction. After that, all final materials were dried, kept (overnight) at room temperature (25 ± 2 °C), and then characterized.

The obtained powders were analyzed by Fourier-transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA). The properties of final thin films were determined through UV/Vis spectroscopy, atomic force microscopy (AFM), spectroscopic ellipsometry (SE), and water contact-angle measurements.
2.3. Characterization of the Sol–Gel Silica Materials and of Thin Films

2.3.1. Photopolymerization

Photopolymerization of the sol–gel silica mixtures (placed into plastic vials and deposited on the PVC substrates) was performed using a UV lamp (from S.C. Promidea SRL, SK-818, Voluntari, Romania). Samples were irradiated for 10 min (at $\lambda = 365$ nm). The irradiance of 2290 mW/cm$^2$ was measured at the surface of samples using a Delta OHM-HD 2302.0 Light-meter (Delta OHM Srl, Padova, Italy) equipped with an LP 471 P-A radiometric probe for effective irradiance measurement in the spectral range of 315–400 nm.

2.3.2. Fourier-Transform Infrared Spectroscopy (FTIR)

The sol–gel silica materials (obtained as powders) were characterized using a Jasco FT-IR 6300 instrument (JASCO Int. Co., Ltd., Tokyo, Japan). The attenuated total reflectance (ATR) accessory of a diamond crystal was used. Data were collected in the wavenumber interval of 400–4000 cm$^{-1}$ (at room temperature, 30 scans, resolution of 4 cm$^{-1}$).

2.3.3. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) of the sol–gel silica materials (obtained as powders) was carried out using a TA TGA Q5000 IR instrument (TA Instruments, New Castle, DE, USA). The samples (14–16 mg), placed in aluminum pans, were heated from 30 to 700 °C at a 10 °C/min rate in nitrogen atmosphere (three TGA runs were performed for each sample).

2.3.4. Transmission Electron Microscopy (TEM)

The sol–gel silica materials (as powders) were contacted with lacey formvar/carbon film and copper grids (Ted Pella Inc., Redding, CA, USA) and thoroughly shaken afterward to remove large or loose particles from the grid. Micrographs (bright-field mode (BF-TEM)) were obtained using a TECNAI F20 G$^2$ TWIN Cryo-TEM (FEI Company, Phillips, The Netherlands) at an accelerating voltage of 200 kV.

2.3.5. UV/Vis Spectroscopy

Obtained samples were also characterized as thin films (deposited on the PVC substrates) using a UV/Vis/NIR Jasco V-570 spectrophotometer equipped with a large integrating sphere ILN-472 (JASCO Int. Co., Ltd., Tokyo, Japan), in order to analyze the transmittance in the range of 380–780 nm. Each sample was measured three times (standard deviation ± 0.2%, at 550 nm).

2.3.6. Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) measurements were carried in noncontact mode, using an XE-100 apparatus from Park Systems (Suwon, Korea), with PPP-NCHR sharp tips (from Nanosensors$^\text{TM}$) with less than 8 nm tip radius, ~125 μm length, ~30 μm mean width, thickness ~4 μm, ~42 N/m force constant, and ~330 kHz resonance frequency. XEI Image Processing Program (V.1.8.0, Park Systems, Suwon, Korea) was used for displaying the purpose and roughness evaluation.

2.3.7. Spectroscopic Ellipsometry (SE) Measurements

Spectroscopic ellipsometry (SE) measurements were performed using a VASE equipment (J.A. Woollam Co., Lincoln, NE, USA), at 60° angle of incidence, with a 10 nm wavelength step, in the 400–800 nm spectral range at room temperature. Analysis of ellipsometric data was carried out using the WVASE32 software package (version 3.920), assuming a three-layer model (roughness/sol-gel layer/substrate).

2.3.8. Contact-Angle (CA) Measurements

Contact angles of the coating surfaces were measured in a static regime, at room temperature on a CAM 200 contact-angle tensiometer (KSV Instruments, Helsinki, Finland) equipped with a high-resolution camera (Basler A602f, Ahrensburg, Germany) and an auto-
3. Results and Discussion

3.1. FTIR Spectroscopy

The functional groups present in the sol–gel silica materials (obtained as powders) were identified by FTIR spectroscopy (see Figure 1).

![Figure 1. FTIR spectra of the sol–gel silica materials (TEOS/DMVES/OTES (A), TEOS/DMVES/HDTMES (B)) (as powders).](image)

The spectra of all samples showed a prominent characteristic band situated at ~1039 cm\(^{-1}\), which was attributed to stretching vibrations of the Si–O–Si group. The C–H bonds from –CH\(_3\) and –CH\(_2\)– were noted in the sol–gel silica materials and identified in the 2960–2850 cm\(^{-1}\) range (stretching vibration) and at 719 cm\(^{-1}\) (rocking vibration). The peak at ~950 cm\(^{-1}\) was attributed to the bending vibration of the Si–O–Si group. The band observed at ~833 cm\(^{-1}\) could be assigned to Si–O stretching vibration. The peak at 1258 cm\(^{-1}\) indicated the presence of Si–C [28]. The peaks identified at ~1408 cm\(^{-1}\) and 1460 cm\(^{-1}\) were attributed to the CH\(_2\) group (in-plane bending deformation for SiCH–CH\(_2\)) [29].

The presence of these peaks indicates that the hydrolysis and condensation reactions between TEOS and silane precursors occurred successfully inside the silica materials.

3.2. Thermogravimetric Analysis (TGA)

The thermal degradation events of the sol–gel silica materials, realized via the sol–gel route in acidic medium, were observed by thermogravimetric analysis (TGA) under nitrogen atmosphere. The results are presented in Figure 2. Table 3 shows the weight loss (wt. loss %) and maximum decomposition temperature (T\(_{\text{max}}\)) of the sol–gel silica materials.
3.3. TEM Analysis

From Figure 2, it can be seen that all samples exhibited a weight loss at ~200 °C, which may have been due to the loss of physisorbed water and residual organic solvent. The weight loss that occurred in the temperature range of 350–700 °C may have been due to the thermal decomposition of organic moieties functionalized on the silica skeleton. This result reveals that the alkyl chains of silane may have been decomposed at the temperature of 650 °C. Thus, the silanol groups could remain on the surface of silica networks [30].

The obtained results show that the silane-coupling agents were covalently attached to the silica matrix.

Analyzing Table 3, it can be seen that the weight loss (below 700 °C) was 22.18 wt.% for sample B (TEOS/DMVES/HDTMES) and 29.75 wt.% for sample A (TEOS/DMVES/OTES). These results demonstrate that a chemical reaction occurred between TEOS and silane precursors.

3.3. TEM Analysis

The morphology of the samples (as powders) was characterized by transmission electron microscopy (TEM) (see Figure 3).
The TEM images show the amorphous nature of the samples and reveal that the silica matrix was crosslinked through covalently bonded Si–O–Si structures [31]. An enlarged view of the TEM image of sample B indicates that this material presented a more disordered structure compared with sample A.

The stacked organization of the alkyl chains may have occurred to maximize the van der Waals interactions of the chains [32]. Moreover, it was shown that the morphology of the silica material could be modified as function of the hydrophobization of silica surface with silane precursors. The density of amorphous silica may have been responsible for the textural porosity of the silica powders [33].

3.4. UV/Vis Spectroscopy

The optical properties of the coatings containing different sol–gel silica materials were investigated by UV/Vis spectra. The results are depicted in Figure 4.

Figure 3. The TEM images of the sol–gel silica materials (TEOS/DMVES/OTES (A), TEOS/DMVES/HDTMES (B)) (as powders).

Figure 4. Transmittance spectra of the PVC substrates: uncoated and coated with the sol–gel silica materials (TEOS/DMVES/OTES (A), TEOS/DMVES/HDTMES (B)).
The transmittance of uncoated PVC substrate was about 89% at 600 nm. For the PVC substrate coated with the sol–gel silica material containing TEOS/DMVES/OTES (sample A), the transmission remained relatively unchanged at 600 nm compared with the uncoated PVC substrate, but increased (>90%) in the wavelength range of 650–780 nm. In the case of the PVC substrate coated with the sol–gel silica material containing TEOS/DMVES/HDTMES (sample B), the transmittance was 86% at 600 nm. Analyzing the UV/Vis spectrum of this coated PVC substrate, it can be seen that the transmittance was lower in the wavelength range of 650–780 nm, in comparison with the uncoated PVC substrate and PVC substrate coated with sample A. This may have been due to the condensation mechanism that became favorable. In this way, the networks were branched more locally, leading to narrow pore sizes and small pore volumes. Thus, dense networks were created, and the coating surface presented a low transparency [34].

It was demonstrated that the transparency of the coating improved with nanoscale roughness [15]. Furthermore, it was shown that the refractive index of the coating must match the refractive index of the substrate as best as possible in order to obtain a coating with excellent transmittance [30].

The clarity of films is an extremely desirable feature for various industrial applications (e.g., self-cleaning, solar panels, roof tiles, and agricultural applications) because it indicates good quality and contributes to the progressive visibility of the product [13].

3.5. AFM Analysis and Spectroscopic Ellipsometry (SE) Measurements

Atomic force microscopy measurements were performed in order to evaluate the morphology and the roughness of the samples. Figure 5 shows the 2D AFM images (topography) at the scale of 1 × 1 µm², together with characteristic line-scans (surface profiles) collected along the fast scanning direction, at the position indicated in each image by a horizontal red line. Due to the fact that the AFM images were very smooth, they are presented in the so-called “enhanced color” ™ view mode, which uses the change of a pixel relative to its neighbors. Representative line scans are shown below 2D AFM images, presenting in detail the surface profile of the scanned samples.

![AFM Images](image)

**Figure 5.** The 2D AFM topographic images at the scale of 1 × 1 µm² together with random line scans, plotted below each image, for the sol–gel silica materials (TEOS/DMVES/OTES (A), TEOS/DMVES/HDTMES (B)) deposited as films on PVC substrates.
At the investigated scale, of $1 \times 1 \mu m^2$, both samples were smooth, as can be observed from the z-scale of the images and of each plotted line scan (see Figure 5).

The PVC substrate coated with the sol–gel silica material containing TEOS/DMVES/OTES (sample A) exhibited a root-mean-square (RMS) roughness of 0.47 nm and a peak-to-valley parameter (the height difference between the lowest and the highest points in the image) of 2.76 nm, while the PVC substrate coated with the sol–gel silica material containing TEOS/DMVES/HDTMES (sample B) had a slightly higher RMS roughness of 2.52 nm and a higher peak-to-valley parameter of 13.42 nm. The low corrugation degree of each sample is also well reflected by the line scans plotted below each image, which exhibited surface features in the nanometer range of ~2 nm for sample A (from $-1$ to 1 nm, see the z-scale) and of ~10 nm (from $-7.5$ to 2.5 nm) for sample B, reflecting the same tendency, with sample B being slightly rougher than sample A.

The thickness and roughness of the PVC substrates coated with the sol–gel silica materials (TEOS/DMVES/OTES (sample A) and TEOS/DMVES/HDTMES (sample B)) were obtained, together with the mean squared error (MSE), and the results are shown in Table 4.

| Sample | Film Thickness (nm) | Roughness (nm) | MSE |
|--------|---------------------|----------------|-----|
| A      | 426.96              | 2.90           | 0.89|
| B      | 513.91              | 6.63           | 0.70|

The results in Table 4 show that the thickness of sample A was higher than that of sample B. From Figure 4 and Table 4, it can be concluded that the transmittance for the PVC substrate coated with the sol–gel silica material TEOS/DMVES/HDTMES (sample B) decreased as the thickness increased, because of increasing reflectance [35].

The results shown in Figures 4 and 5, and Table 4 reveal that increasing the thickness and roughness of the hybrid film led to a decrease in the transmittance.

3.6. Contact-Angle Measurements

It was demonstrated that the wettability is an important property of the coating because it can have an important impact on the coating durability during its use [36,37]. Furthermore, it was proven that a hydrophobic coating can be achieved by using a low-surface-energy material to modify a rough surface [38].

The wettability of the uncoated PVC substrate and of the PVC substrates coated with the sol–gel silica materials was characterized by the measurement of static contact angles against water. The values of water contact angles and profiles of water droplets on the uncoated PVC substrate and coated PVC substrates are presented in Figure 6.
Furthermore, materials with low angles were replaced by hydrophobic organic groups (octyl or hexadecyl). This phenomenon is consistent with previous data reported in literature showing that long alkyl groups facilitate the formation of a more ordered structure and of lower-surface-energy materials [39].

In previous papers [40–43], it was demonstrated that the incorporation of nonpolar groups (e.g., methyl, trimethylsilyl (–Si(CH$_3$)$_3$)) into the coating materials can prevent the collapsing of pores throughout solvent evaporation and lower the surface energy of the coatings. In this way, extra functionalities are provided, such as high surface area, good antireflective property, and hydrophobic character.

4. Conclusions

In this paper, we demonstrated that transparent and hydrophobic hybrid silica-based coatings can be deposited onto polyvinyl chloride (PVC) substrates, through a simple, facile, and suitable method. The silica materials were synthesized via an acid-catalyzed sol–gel process under mild conditions, using tetraethoxysilane (TEOS) as the silica source and silane precursors (ethoxydimethylvinylsilane (DMVES), triethoxycyctilsilane (OTES), trimethoxyhexadecylsilane (HDTMES)) as modifying agents. FTIR spectra revealed that

![Figure 6. Values of water contact angles and profiles of water droplets on PVC substrates: uncoated and coated with the sol–gel silica materials (TEOS/DMVES/OTES (sample A), TEOS/DMVES/HDTMES (sample B)).](image-url)
the process of condensation between TEOS and silane precursors successfully occurred. The UV/Vis results showed that the hybrid coatings presented different transmittance in the wavelength range of 600–780 nm due to the silica materials applied on the PVC substrates. Moreover, the water contact angles of these coatings were about 94°, exhibiting a good hydrophobic property, comparing with the uncoated PVC substrate. Since AFM analysis and SE measurements proved that the silica-based coatings were smooth, it can be assumed that the hydrophobic character of the films was related to the chemical bonds of the hybrid silica-based matrices. Therefore, this study provides a feasible method for the preparation of the PVC films with hybrid silica coatings that can be used as the materials for outdoor applications, such as energy-generating solar panel window blinds or PVC clear Windmaster outdoor blinds.

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