Hard and Transparent Films Formed by Nanocellulose–Titania Nanoparticle Hybrids

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Abstract
The formation of hybrids of nanofibrillated cellulose and titania nanoparticles in aqueous media has been studied. Their transparency and mechanical behavior have been assessed by spectrophotometry and nanoindentation. The results show that limiting the titania nanoparticle concentration below 16 vol% yields homogeneous hybrids with a very high Young’s modulus and hardness, of up to 44 GPa and 3.4 GPa, respectively, and an optical transmittance above 80%. Electron microscopy shows that higher nanoparticle contents result in agglomeration and an inhomogeneous hybrid nanostructure with a concomitant reduction of hardness and optical transmittance. Infrared spectroscopy suggests that the nanostructure of the hybrids is controlled by electrostatic adsorption of the titania nanoparticles on the negatively charged nanocellulose surfaces.

Introduction
Organic–inorganic nanocomposites or hybrids have attracted much interest due to their current and potential applications as they can combine useful chemical, optical and mechanical characteristics. [1,2] Traditionally, organic–inorganic nanocomposites have had a focus on the polymeric matrix, being e.g., formed from vinyl polymers, condensation polymers or polyelectrolytes filled with relatively passive inorganic components such as layered silicates, i.e., montmorillonite or hectorite. [1,2] With the strong movement towards biodegradable, renewable, sustainable, and carbon-neutral polymeric materials, it is also of importance to develop viable and facile production routes for nanocomposites using such biopolymers. In this respect, nanocellulose [3] is emerging as a cheap and sustainable polymeric material with useful functional properties such as tailored hydro/oleophilicity, optical transparency and remarkable mechanical performance both as films and aerogels. [4–9] The exploration of nanocellulose-nanoparticle hybrids is still relatively sparse but has increased pronouncedly since the pioneering report on multifunctional nanoparticle hybrids is still relatively sparse but has increased pronouncedly since the pioneering report on multifunctional nanoparticle hybrids. [10] Recent studies have suggested various applications for different nanocellulose-inorganic hybrids: nanocrystalline cellulose-amorphous calcium carbonate hybrid films resemble biogenic materials such as dentin, [11] nanocellulose-clay nanopaper has shown good fire retardancy and gas barrier functions, [12] nanocellulose aerogels coated with titania using a CVD approach display a photoswitchable hydrophobicity [13] and oil adsorption, [14] and nanocellulose-silver hybrids were evaluated as potential antibacterial agents. [15] Moreover, it should be noted that other biopolymers such as silk, [16,17] chitin, [18,19] or collagen [20] also can be utilized in the production of organic-inorganic hybrids.

Titania-based materials are very attractive due to their inherent high refractive index and UV absorbing properties. For instance, titania-polymer hybrids have been prepared with conductive polymers, [21–23] polycrylonitrile electrospun fibers [24], polycrylonitrile and carbon nanotubes [25,26], block co-polymers, [27–29] polystyrene beads, [30,31] polyamide, [32] acrylic acid or PMMA, [33–35] silicates or siloxanes, [36] polyimides, [37] epoxies, [38] and polycrylates. [39] In this work, we demonstrate the facile fabrication of nanocellulose-titania nanoparticles hybrids with high inorganic content by the adsorption of TiO2 (anatase) nanoparticles on wood-derived nanofibrillated cellulose. The nanostructure of the hybrids was characterized mainly by electron microscopy and the optical transparency and mechanical performance of the hybrids were evaluated using spectrophotometry and nanoindentation tests, respectively. We show that the effective Young’s modulus, hardness and transparency of the hybrids are determined by their nanostructure, in particular, by the homogeneity of the inorganic and organic components. The optimum range of inorganic content, where the modulus and hardness of the hybrids exceed that of pure nanocellulose and the transparency is high, is identified and the mechanisms for the nanocellulose-titania interactions and agglomeration are discussed.
Materials and Methods

Materials

Commercial TiO$_2$ (anatase) nanoparticles were dispersed in a 0.1 M HCl aqueous solution with a stock concentration $c_{\text{TiO}_2} = 30$ mg/cm$^3$. Nanofibrillated cellulose (NFC) was prepared by TEMPO oxidation of wood fibers according to a previously reported procedure which resulted in surface-functionalized fibrils with carboxylic groups with a total charge of 1.84 mmol/g. [6]

Aqueous dispersion of hybrids were prepared by adsorbing TiO$_2$ nanoparticles onto NFC in an aqueous media. TiO$_2$ nanoparticles, NFC (stock concentration $c_{\text{NFC}} = 0.75$ mg/cm$^3$) and water (Millipore, resistivity $\rho_{\text{water}} = 20$ MQ/cm) were mixed in different ratios, see Table 1, and their composition was also assessed using thermal analysis (see Supplementary Information, Figure S2). The dispersions were shaken for two hours and then the pH was adjusted to 8 with aqueous solutions of diluted NH$_3$ and HCl.

Films were prepared by depositing 0.2 cm$^3$ of an aqueous dispersion of the hybrids on circular glass slides (diameter $\odot = 1.2$ cm) and placed in a Binder atmospheric chamber at 30 $^\circ$C and 50% relative humidity. The thickness of the obtained films was approximately 20 µm. Alternatively, the aqueous dispersions of hybrids were centrifuged for 30 min at 3800 g with a Hettich EBA 21 centrifuge, the supernatant was discarded and the remaining portion was freeze-dried at $~$10$^{-4}$ mbar using a SRK GT2 freeze-drier.

Morphological Characterization

Transmission Electron Microscopy (TEM). Transmission electron microscopy (TEM) images of the titania nanocrystals were obtained using a JEOL JEM-2000 FX microscope equipped with a LaB$_6$ filament operated at 200 kV (Cs = 3.4 mm, point distribution function.

S8 62.5 1.25 5.6 67 44
S7 35 1.25 5.6 53 30
S6 25 1.25 5.6 44 24
S5 15 1.25 5.6 32 16
S4 7.5 1.25 5.6 19 9
S3 3.8 1.25 5.6 11 4
S2 1.9 1.25 5.6 6 2
S1 0 1.25 5.6 0 0

Table 1. Composition of hybrids.

Spectroscopic Characterization

UV-Visible spectrophotometry. In-line transmittance spectra of the NFC and hybrids in the form of films on glass slides and as aqueous dispersions in the visible region (400-800 nm) were obtained with a Perkin-Elmer Lambda 19 UV-Vis-NIR spectrophotometer using a clean glass slide as a background. The aqueous dispersions were filled in a 1.4 cm$^3$ semi-micro rectangular quartz cuvette using Millipore water as background.

Infrared spectroscopy. Infrared (IR) spectra of NFC, TiO$_2$ and NFC-TiO$_2$ hybrids materials were measured on a Varian 670-IR FTIR spectrometer, equipped with an attenuated total reflection (ATR) detection device (Goldedge by Specac) with a single reflection diamond ATR element. 32 scans were accumulated in the spectral region of 390-4000 cm$^{-1}$ with a spectral resolution of 4 cm$^{-1}$. To maximize the signal of the carboxylic band the pH of aqueous dispersions of NFC and was adjusted to pH = 3 with few microliters of diluted HCl and NH$_3$ prior to contacting them with the aqueous dispersions of TiO$_2$. The pH of the pristine aqueous dispersions of TiO$_2$ was also adjusted to pH = 3 before the measurements. The materials were then freeze-dried before the measurements using the protocol previously described.

Mechanical Characterization

The mechanical properties of the hybrids were evaluated using a Fischer-Cripps Laboratories Ultra-Micro-Indenteter system (UMIS) equipped with a Berkovich pyramidal-shaped diamond tip. The value of maximum applied force was chosen to be 500 µN to ensure that the maximum penetration depth was kept well below one tenth of the overall film thickness (a necessary condition to avoid having an influence of the substrate on the measured mechanical properties of the film). [41] The thermal drift during nanoindentation was kept below 0.05 nm/s. Proper corrections for the contact area (calibrated with a fused quartz specimen), instrument compliance, and initial penetration depth were applied. The hardness, $H$, and effective reduced Young’s modulus, $E_s$, were derived from the load-displacement curves at the beginning of the unloading segment using the method of Oliver and Pharr. [42] From the initial unloading slope, the contact stiffness, $S$, was determined as $S = \frac{P}{h}$ where $P$ and $h$ denote, respectively, the applied load and the penetration depth during nanoindentation. The effective reduced Young’s modulus was evaluated based on its relationship with the contact area, $A$, and contact stiffness $S = \beta \frac{E_s}{\sqrt{A}}$. Here, $\beta$ is a constant that depends on the geometry of the indenter ($\beta = 1.034$ for a Berkovich
The films are transparent at low inorganic content but tend to the films and also in between the fibrils. AFM images (Figure 1f) show the hardness was calculated as $H = \frac{P_{\text{max}}}{A_{\text{contact}}}$ where $P_{\text{max}}$ is the maximum load applied during nanoindentation. Finally, the elastic recovery was evaluated as the ratio between the elastic and the total (plastic + elastic) energies during nanoindentation, $W_{\text{el}}/W_{\text{tot}}$. These energies were calculated from the nanoindentation experiments as the areas between the unloading curve and the $x$-axis ($W_{\text{el}}$) and between the loading curve and the $x$-axis ($W_{\text{tot}}$). [43] The results presented here represent the statistical average of a set of 50 indentations for each sample, whereas up to 200 indentations were carried out on the samples with low inorganic content (<16 vol%).

**Results and Discussion**

Figures 1a and 1b show electron microscopy images of the hybrid constituents, i.e., TiO$_2$ nanoparticles and NFC fibers, respectively. Analysis of the TEM images showed that the TiO$_2$ particles had a length $l = 26 \pm 3$ nm and a width $w = 16 \pm 2$ nm, i.e., an aspect ratio $AR = 1.6 \pm 0.3$ (see Supplementary Information, Figure S1). The cellulose nanofibrils had a width distribution between 3–5 nm and length of $3 \pm 1$ nm. However, during the adsorption of TiO$_2$ the fibrils tend to agglomerate somewhat and form bundles with thickness between 10–20 nm, as can be see in Figure 1c which shows a TEM micrographs of the hybrid aerogel with 9 vol% of inorganic content. Hybrids of NFC and TiO$_2$ nanoparticles were prepared also as films. Representative SEM images of hybrid films with low (4 vol% TiO$_2$) and medium (16 vol% TiO$_2$) inorganic content are shown in Figures 1d and 1e, respectively. The images show that the amount of fibers on the surface decreases with an increase of the fraction of nanoparticles. Films with a large amount of TiO$_2$ nanoparticles ($\phi_{\text{vol}} > 16$ vol%) display an even granular surface. AFM images (Figure 1f) show that the inorganic nanoparticles are distributed on the surface of the films and also in between the fibrils.

Figure 2a shows a photograph of the films deposited on glass. The films are transparent at low inorganic content but tend to become milky as the concentration of nanoparticles increases, suggesting that light scattering becomes increasingly important. The optical transmittance, $T$, in the visible region of the different film samples with different inorganic content is shown in Figure 2b. The figure shows that the NFC film has a high optical transmittance over the visible range, as expected from its low absorption coefficient [47] and smoothness of the films. The hybrids with relatively low concentration of inorganic nanoparticles have a high transmittance in the visible area which decreases toward the ultraviolet region, when the bandgap of anatase is approached. In the case of hybrids, in the absence of significant absorption, the transmitted light across a hybrid film can be described using the Rayleigh formalism for scattering, as indicated by Eq. (1). [48]

$$T(\%) = 100\% \exp \left[ -4\frac{\pi^2}{\lambda^2} \left( \frac{n_{\text{TiO}_2}^2 - n_{\text{NFC}}^2}{n_{\text{TiO}_2}^2 + 2n_{\text{NFC}}^2} \right) d \phi_{\text{vol}} \right] \tag{1}$$

where $T$ is the transmittance, $\lambda$ the wavelength, $n_{\text{TiO}_2} \approx 2.49$ and $n_{\text{NFC}} \approx 1.58$ the average refractive indices of anatase [49] and cellulose [47], respectively, $d$ the diameter of the particles, and $x \approx 20 \mu$m the thickness of the film. Note that the model assumes that the NFC matrix is dense and nonporous and that the particles are point scatterers much smaller than the wavelength, i.e., $d < \lambda/20$.

The equation shows that the transmittance decreases with an increase of: the concentration of nanoparticles, the particle size, the difference of refractive indices, and the thickness of the films, and with a decrease of the wavelength. Indeed, as anatase and cellulose have a very low absorption in the visible region it is possible to use Eq. (1) to model the response of the hybrids using the experimental data. Figure 2c shows the optical transmittance of the films at $\lambda = 550$ nm. Plotted along the experimental points are the calculated transmittance for three particle sizes: (i) particle diameter with an equivalent particle volume as the TiO$_2$ nanoparticles used for the fabrication of the hybrids ($d_{\text{TiO}_2} = 19$ nm); (ii) particles with a diameter equal to the upper limit of the experimental particle size ($d_{\text{TiO}_2} = 30$ nm); and (iii) particles with a diameter similar to the observed agglomerates ($d_{\text{TiO}_2} = 50$ nm. The experimentally observed transmittance of the hybrid films with an inorganic content $\phi_{\text{vol}} \leq 16$% can be well described within the boundaries described by (i) and (ii) (hatched region). Alternatively, the transmittance of the hybrids with $\phi_{\text{vol}} > 16$% is between the boundaries defined by (ii) and (iii), suggesting that the number of agglomerates becomes increasingly important. Notice that both the reflectivity [39] and the surface roughness of the films [50] also contribute to a slightly lowered transmittance.

Previous work on the fabrication of poly(vinyl alcohol)-TiO$_2$ (rutile) nanoparticle (PVAL-TiO$_2$) nanocomposites have also demonstrated high transparency in hybrid films. [51] The hybrids, with a thickness $x \approx 100$ nm, were formed in a similar fashion as the ones described in the present work, i.e., by the ex-situ nucleation of nanoparticles ($d \approx 2.5$ nm) and their subsequent mixing and drying with the polymer. As a comparison, PVAL-TiO$_2$ hybrids with a $\phi_{\text{vol}} = 4$ vol% showed a $T(550\text{nm}) \approx 90\%$. Sasaki et al. prepared poly(diallyldimethylammonium chloride)–Ti$_4$O$_{20}$ nanoparticle–poly(vinyl alcohol) nanocomposite films using the layer-by-layer technique (LbLTiO$_2$). [39] The hybrids were composed of alternating layers of polymer and Ti$_4$O$_{20}$ nanoplatelets (thickness ca. 1.2 nm, lateral dimensions in the sub-μm regime). However, the LbLTiO$_2$ hybrids showed a substantial reflectivity which decreased the optical transmittance. For instance, a 10-repeat multilayer with a thickness of $x \approx 20$ nm showed a reduced $T(550\text{nm}) \approx 90\%$. Regarding the current work, it is interesting to note that despite the relatively large size of the anatase nanoparticles and the fibrillated structure of the nanocellulose, the transparency of the hybrids is very high and comparable to those systems prepared from smaller particles.

The mechanical behavior of the films was tested using nanoindentation measurements where the typical load-displacement nanoindentation curves and AFM images of the indents are shown in the supplementary information (Figures S4 and S5). Figure 3 shows the effective reduced Young’s modulus, $E_r$, and hardness, $H$, of the films as a function of inorganic content, $\phi_{\text{vol}}$. The $E_r$ value corresponding to NFC is in close agreement with the reported values of the transversal Young’s modulus of native cellulose, [52] The addition of a small amount of TiO$_2$ nanoparticles resulted in a slight increase of $E_r$. This initial increase of $E_r$ as $\phi_{\text{vol}}$ increases can be described with a simple linear rule of mixtures, i.e., $E_r \approx \phi_{\text{vol}} E_{\text{TiO}_2} \& (1-\phi_{\text{vol}}) E_{\text{NFC}}$. Figure 3a includes the estimates for hybrids with low $\phi_{\text{vol}}$ (hatched
fractions increases there is a sharp decrease of the hardness values at volume hatched area). As the concentration of nanoparticles further

The experimental value obtained for sample S1 is assigned to pure NFC, i.e., $E_{NFC} \approx 38$ GPa. However, as the concentration of nanoparticles increased further the $E$ value of the hybrid films decayed abruptly. Indeed, at higher concentration of nanoparticles, $\phi_{vol} \geq 30\%$, the films became looser and compliant, leading to a decrease of $E$. This behavior suggests that the bonding and microstructure of the hybrids change significantly with increasing anatase content. Remarkably, the NFC and hybrid films with TiO$_2$ concentrations up to 24 vol% had extraordinarily high effective Young's modulus when compared to organic-inorganic hybrids previously reported (see [41] and references therein) and some high-performance lightweight materials, such as magnesium [55] or concrete. [56,57] The linear increase in $E_r$ at low TiO$_2$ additions strongly indicates that the inorganic nanoparticles are homogeneously distributed and bonded to the NFC network, thus increasing the modulus (and hardness) with increasing amount of the stiff and hard constituent. At a critical concentration, the homogeneity of the hybrid and the anatase nanoparticle distribution decreases. Recent reports have indeed shown that nonsintered films composed of anatase TiO$_2$ nanoparticles have Young's moduli as low as 22.5 GPa. [58,59] This strong dependence of the mechanical behavior on the TiO$_2$ nanoparticle content is much more evident in Figure 3b where the hardness, $H$, of the NFC and hybrid films is depicted. The hardness of the NFC and hybrids with $\phi_{vol} \leq 9\%$ is roughly constant about 3.4 GPa (first hatched area). As the concentration of nanoparticles further increases there is a sharp decrease of the hardness values at volume fractions $\phi_{vol} \geq 16\%$ (second hatched area), with $H$ falling below 1 GPa. Note that AFM analysis of the indentations shows little pile-up and sink-in at high TiO$_2$ contents (30 vol%) thus having a reduced influence on the overall trends shown in Figure 3 see supplementary information Figure S5).

We have used IR spectroscopy to obtain more information on the bonding and interaction between the inorganic nanoparticles and the nanocellulose. The IR spectra are shown in Figure 4a for NFC, TiO$_2$ nanoparticles, and the hybrids with different inorganic content. The broad band at the low frequency end of the spectra (also partially related to the librational mode of adsorbed water) is assigned to the Ti-O band and increases with the TiO$_2$ content. To facilitate the analysis of the interactions between the nanoparticles and the NFC, the nanocellulose and the hydroxyl groups on the surface of the fibrils it is possible to correlate the reaction between the fibrils and the positively charged TiO$_2$ nanoparticles. Figure 4a shows that a decrease in the intensity of carboxyl band corresponding to the acidic C = O (1725 cm$^{-1}$) decreases with an increase of the concentration of TiO$_2$. The formation of an ester interactions are readily determined between the carboxylic group of the nanocellulose and the hydroxyl groups on the surface of the fibrils. Hence, by observing the C = O stretching region of the (protonated) carboxylic groups on the surface of the fibrils it is possible to correlate the reaction between the fibrils and the positively charged TiO$_2$ nanoparticles. Figure 4a shows that a decrease in the intensity of carboxyl band corresponding to the acidic C = O (1725 cm$^{-1}$) decreases with an increase of the concentration of TiO$_2$. The formation of an ester interaction between the carboxylic group of the nanocellulose and the hydroxyl groups on the surface of the fibrils was excluded as no C = O band was detected at higher frequencies than that corresponding to the acidic C = O. Using a difference spectra, the bands that take part in the NFC-TiO$_2$ interactions are readily observed. Figure 4b shows the spectrum of freeze-dried TiO$_2$ nanoparticles and the difference spectra of a hybrid with 16 vol% TiO$_2$ from which the spectra of NFC was subtracted. The negative band at 1725 cm$^{-1}$ shows the decrease in the amount of carboxyl groups whereas the positive band at 1595 cm$^{-1}$ (antisymmetric stretching) suggests an increase in the amount of carboxylate

Figure 1. Morphological characterization of the materials. (A) TEM micrograph of titania nanoparticles. (B-E) SEM micrographs of freeze-dried samples corresponding to (B) pristine nanofibrillated cellulose, NFC and (C) a hybrid composed of NFC-TiO$_2$ with a 9 vol% of inorganic content (S4); films of NFC-TiO$_2$ hybrids deposited on silicon wafers with (D) 4 vol% (S3) and (E) 16 vol% of inorganic content (S5). (F) Derivative and phase AFM images of the hybrids shown in (E). The scale bars represent 200 nm (50 nm in the insets).

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area) using the experimentally reported values for the elastic modulus of anatase thin films (nanoindentation), $E_{film}^{TiO_2} \approx 170$ GPa, [53,54] and nanoparticles (high pressure X-ray), $E_{NP}^{TiO_2} \approx 330$ GPa. [45] The experimental value obtained for sample S1 is assigned to pure NFC, i.e., $E_{NFC} \approx 38$ GPa. However, as the concentration of nanoparticles increased further the $E$ value of the hybrid films decayed abruptly. Indeed, at higher concentration of nanoparticles, $\phi_{vol} \geq 30\%$, the films became looser and compliant, leading to a decrease of $E$. This behavior suggests that the bonding and microstructure of the hybrids change significantly with increasing anatase content. Remarkably, the NFC and hybrid films with TiO$_2$ concentrations up to 24 vol% had extraordinarily high effective Young's modulus when compared to organic-inorganic hybrids previously reported (see [41] and references therein) and some high-performance lightweight materials, such as magnesium [55] or concrete. [56,57] The linear increase in $E_r$ at low TiO$_2$ additions strongly indicates that the inorganic nanoparticles are homogeneously distributed and bonded to the NFC network, thus increasing the modulus (and hardness) with increasing amount of the stiff and hard constituent. At a critical concentration, the homogeneity of the hybrid and the anatase nanoparticle distribution decreases. Recent reports have indeed shown that nonsintered films composed of anatase TiO$_2$ nanoparticles have Young's moduli as low as 22.5 GPa. [58,59] This strong dependence of the mechanical behavior on the TiO$_2$ nanoparticle content is much more evident in Figure 3b where the hardness, $H$, of the NFC and hybrid films is depicted. The hardness of the NFC and hybrids with $\phi_{vol} \leq 9\%$ is roughly constant about 3.4 GPa (first hatched area). As the concentration of nanoparticles further increases there is a sharp decrease of the hardness values at volume fractions $\phi_{vol} \geq 16\%$ (second hatched area), with $H$ falling below 1 GPa. Note that AFM analysis of the indentations shows little pile-up and sink-in at high TiO$_2$ contents (30 vol%) thus having a reduced influence on the overall trends shown in Figure 3 see supplementary information Figure S5).

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group. Note that the band at 1440 cm$^{-1}$ is due to ammonium ions, whereas the bands at 1405 and 1260 cm$^{-1}$ in the spectrum of TiO$_2$ are likely to correspond to nitrate and nitrite ions arising from the photooxidation of ammonia used during pH adjustment as these bands do not appear in the IR spectrum of pristine TiO$_2$ (see supplementary information Figure S3). The bands at 1460 and 1410 cm$^{-1}$ could arise from the symmetric stretching of carboxylate ions, although the presence of artifacts during spectral subtraction cannot be ruled out.

Analysis of the spectra suggests that the nanocellulose and the nanoparticles interact through electrostatic interactions between the dissociated carboxylic group and the positively charged groups on the nanoparticles, i.e., $-\text{COO}^-\cdots\text{TiO}^-$. Other groups have prepared polymer-titania hybrids using a silane groups as grafting agent, resulting in a covalent modification of titania nanoparticles (e.g., a Ti–O–Si bond) formed in-situ, whereas the formation of polyaniline-titania probably also proceeds via electrostatic interactions. The formation of hybrids using ex-situ synthesized nanoparticles allow for a larger range of inorganic content that is accessible. However, the results also suggest that a careful balance of the electrostatic interactions between the nanocellulose and titania nanoparticles and their dispersability in aqueous media is key to ensure optimized optical and mechanical properties.

Conclusions

Hybrids composed of nanofibrillated cellulose and anatase nanoparticles with variable inorganic content were fabricated through the adsorption of ex-situ prepared nanoparticles. Electron
microscopy shows that the homogeneity of the hybrids decreases towards high concentration of nanoparticles. The reduction in homogeneity resulted in a reduced hardness and reduced optical transparency. Infrared spectroscopy demonstrated that the nanocellulose and nanoparticles are bound through electrostatic interactions and not through the formation of covalent bonds. The hybrids with an optimized inorganic content presented in the current work showed extraordinary optical and mechanical properties, with high transmittances in the visible region and high effective Young’s modulus and hardness superior to previously reported materials. These properties suggest a potential use of nanocellulose-based hybrids as transparent coatings where high wear resistance and UV activity are required.

Supporting Information

Figure S1  Titanium dioxide nanoparticles and their size distribution. (left) TEM image of titanium dioxide nanoparticles and (right) histograms built from the manual determination of particle length and width. The lines correspond to a fit with a Gaussian distribution function.

Figure S2  Thermogravimetric analysis of the samples. TGA was performed on a Perkin Elmer Thermogravimetric Analyzer TGA7. Ca. 1 mg of the different hybrids (freeze-dried from the solutions) was filled in a platinum cup and analyzed under technical air from 30–900°C at a heating rate of 5 K/min. (left) The initial weight loss up to 200°C corresponds to the release of adsorbed water. The second weight loss from 200–500°C is due to the removal of NFC. (right) Derivative of the mass loss.

Figure S3  Infrared spectra of TiO2 nanoparticles before (b) and after (a) addition of ammonium ions. The band at 1630 cm−1 is due to the bending mode of adsorbed water, the one at 1440 cm−1 corresponds to the deformation vibration of ammonium ions, whereas the bands at 1405 and 1260 cm−1 are likely belong to the asymmetric stretching of nitrate and nitrite ions.

Figure S4  Load – displacement curves. Indentation curves corresponding to hybrids with different compositions deposited as films on glass substrates. The thickness of the films is ca. 20 μm.

Figure S5  Atomic force microscopy derivative images. Indentations performed on samples S2 (left) and S7 (right). The circles highlight the indentations, where no pronounced pile-up is observed.

Table S1  Additional mechanical properties of the hybrid NFC/TiO2 films obtained from nanoindentation experiments. Parentheses indicate the standard deviation in the last digits.

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Author Contributions

Conceived and designed the experiments: LW GSA. Performed the experiments: CS JS ZB EP. Analyzed the data: JS ZB EP GSA.
Contributed reagents/m-serials/analysis tools: VO AF. Wrote the paper: L. Bergström. Analysed the data and co-wrote the paper: L. Berglund.

GSA. Conceived, designed the experiments, and co-wrote the paper: L. Bergström. Analysed the data and co-wrote the paper: L. Berglund.

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