Cellulose Nanowhiskers Templating in Conductive Polymer Nanocomposites Reduces Electrical Percolation Threshold 5-Fold

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ABSTRACT: The creation of conducting networks within composite materials is very important to reduce the generally expensive conducting polymer content, to create conducting/nonconducting domains, and to adjust conductivity of the final composite. We developed cellulose/poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS)-based polystyrene (PS) composites with an extremely low percolation threshold of the conductive polymer. The percolation threshold of PEDOT:PSS in PEDOT:PSS/PS blends, being 2.2 wt % (2.31 vol%), was lowered to 0.4 wt % (0.42 vol%) by adding 0.8 wt % (0.56 vol %) of cheap, nonconducting cellulose nanowhiskers. Such a low percolation threshold of PEDOT:PSS is attributed to the templating effect of the cellulose nanowhiskers: the conducting PEDOT:PSS is thought to adsorb onto the cellulose surface and by doing that (at least partly) covers the network formed by the percolating, high aspect ratio cellulose whiskers in the PS matrix. UV−vis experiments indeed point to an interaction between PEDOT:PSS and the cellulose whiskers, confirming the templating of PEDOT:PSS onto the nanowhiskers during processing and film formation. This approach can be applied to other conducting composites to reduce the required conducting polymer content and increase the ease of processing as electrical percolation is directly achieved.
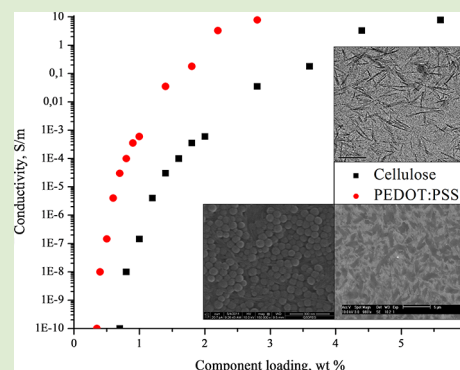
Cellulose is the most abundant macromolecule on earth, produced in nature at the rate of $10^{11}-10^{12}$ tons per year.[1] Nanocomposite materials based on cellulose nanowhiskers have attracted much attention recently due to their promising mechanical properties.[2,3] The main advantages of cellulose nanowhiskers are their renewable nature, the wide variety of source materials available throughout the world, cellulose being a nonfood agricultural product whose production can be combined with food production, their low cost and density, their high specific strength and modulus, the high sound attenuation of cellulose-based composites, their nonabrasive nature, which allows high filling levels and accordingly significant cost savings, and, last but not least, their high surface functionality and reactivity.[2,4−6]

In recent years, composite materials consisting of cellulose and conductive polymers have received significant attention.[7−13] A drawback of many such composites is that the bulk matrix material, that is, the conductive polymer, often suffers from poor mechanical properties and processability. For composite films for which the bulk mechanical properties of the conductive polymers are not sufficient for the envisioned applications, it is necessary to "dilute" the matrix material with a second polymer that intrinsically has the required mechanical and processing properties.[14] Another drawback of such systems is that often very high loadings of conductive polymer, for example, polyaniline and polypyrrole, are required for the composites to conduct in a satisfactory way. A percolation threshold at a loading of around 20 wt % of PEDOT:PSS has been reported for drop-cast blends prepared via solution mixing with poly(vinylpyrrolidone).[15] For blends containing polyaniline as a conductive component, based on chlorinated copolymer latexes Haloflex EP 262 as organic templates, a percolation threshold of 5 wt % was reported.[16] Relatively low percolation threshold values of around 2 wt % of conductive polymer have been reported for polythiophene/PS composites in which the morphology of polythiophene is whisker-like,
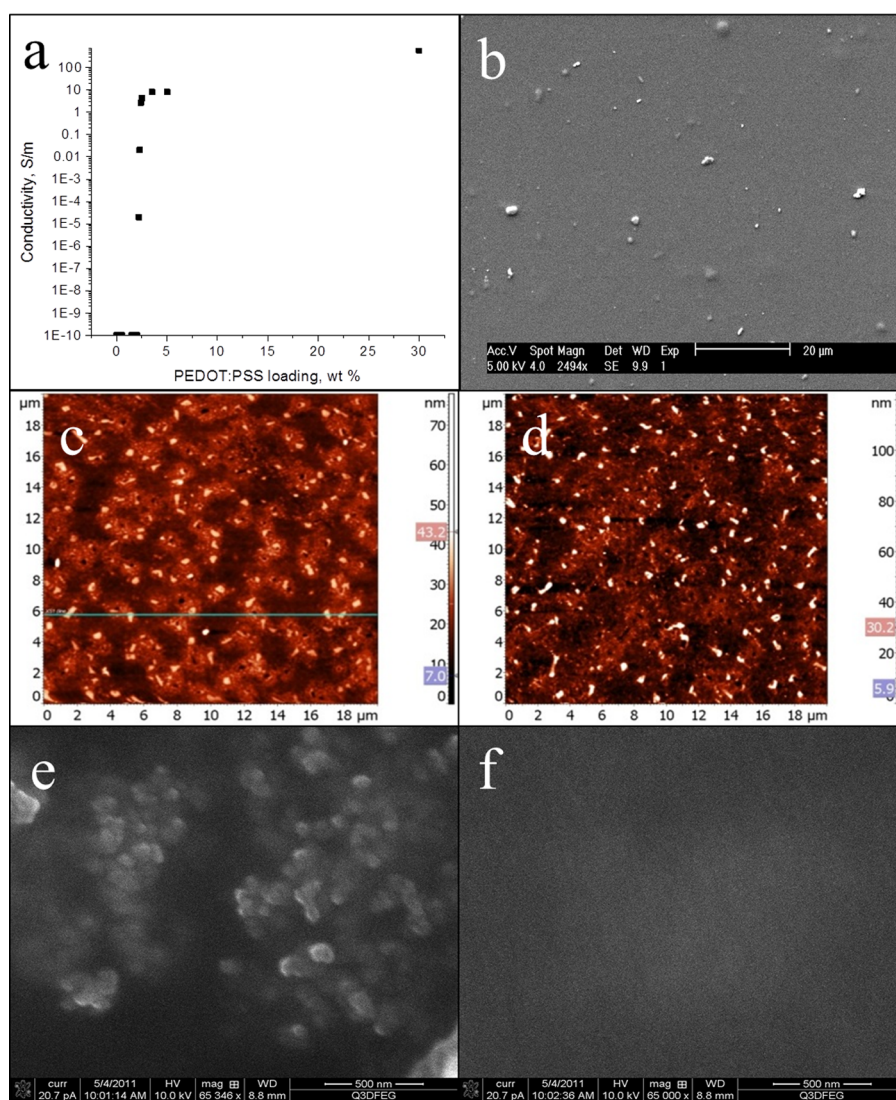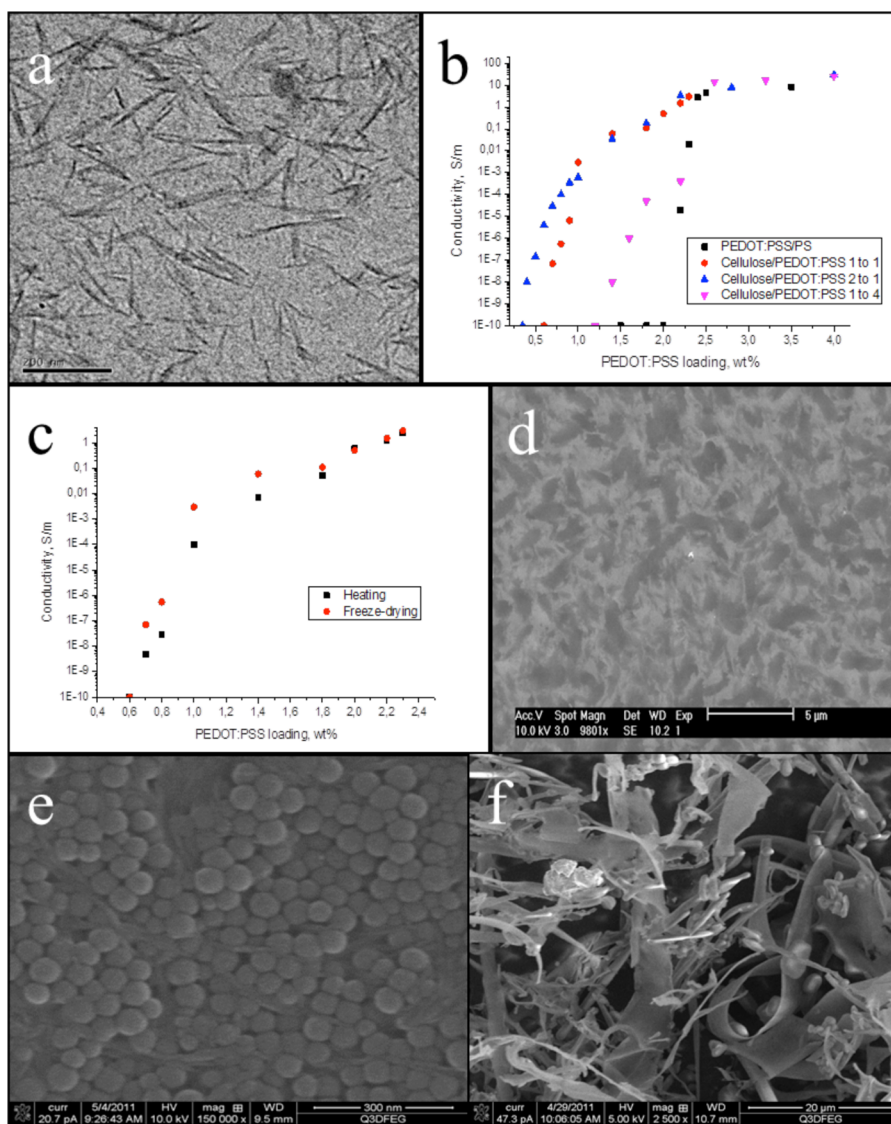
Figure 1. (a) Conductivity curve of PEDOT:PSS/PS blends; (b) SEM image of PEDOT:PSS on silicon wafer; (c, d) AFM (topographic image) of PEDOT:PSS on glass before and after annealing at 180 °C; (e, f) SEM images of different parts of a freeze-dried PEDOT:PSS/PS powder: in the majority of the PS matrix, PEDOT:PSS particles have a slightly elongated shape (e); Smooth part of the film consisting of PS particles covered with a thick layer of PEDOT:PSS (f).

indicating that similar behavior might be possible with cellulose nanowhisker fillers.[17] Work by Weder et al. has shown that it is possible to coat cellulose nanowhiskers with electronically conducting polymers in solution, making the creation of conducting polymer networks by nanowhisker templating potentially straightforward.[18,19] The conducting polymer percolation threshold was reached at around 2 vol %, close to the 2.31 vol % measured without templating in our work (vide infra). In addition, a recent study by one of the authors describes the deposition of polypyrrole onto cellulose nanowhiskers using an electropolymerization technique, resulting in a porous network homogeneously grown from the electrode surface, gave rise to a highly porous templated structure.[20] The thin polypyrrole layer (~5 nm) deposited on the nanowhiskers was found to conduct, it displayed a high capacitance with near-ideal capacitive behavior, and the negative surface charge on the oxidized nanowhiskers stabilized the polypyrrole more effectively during charge–discharge cycles than an equivalent polypyrrole/carbon nanotube composite.[20]

In this study, we prepare conductive polystyrene (PS)/cellulose nanocomposites via "latex technology" using poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS) as a conductive component. The cellulose nanowhiskers used in this work were obtained from sisal, resulting in nanowhiskers with cross sectional and longitudinal dimensions of 3.6 ± 1 and 211 ± 106 nm, respectively, when fitting the dimensional variation with a three-parameter Weibull distribution, giving rise to an aspect ratio around 60.[21] The average dimensions give a percolation threshold of 1.11 vol % or 1.58 wt % using the PS density of 1.05 g cm^{-3} and crystalline cellulose density of 1.5 g cm^{-3}.[21] The percolation threshold of "hybrid" nanocomposites with conductive polymer templated onto a percolated nanocellulose network can be extremely low with respect to the conductive polymer.[22−24] The aim is thus to prepare conductive composite materials by inducing the formation of a conductive polymer network through templating onto the percolated cellulose nanowhisker network. This should result in easier processing and conductivity at significantly lower PEDOT loading than is possible in

Figure 2. (a) TEM micrograph of exfoliated cellulose whiskers (bar in left bottom corner of picture represents 200 nm); (b) Conductivity curves of the PEDOT:PSS/PS composites, cellulose/PEDOT/PSS/PS composites prepared with a cellulose/PEDOT:PSS weight ratio of 1/4, 1/1, and 2/1 (the experimental error for conductivity values is estimated to be half an order of magnitude); (c) Conductivity curves of the cellulose/ PEDOT:PSS/PS nanocomposites with the weight ratio cellulose/PEDOT:PSS of 1/1 after applying different processing conditions for water removal: freeze-drying and drying by heating at 70 °C; (d) SEM of drop-cast cellulose/PEDOT:PSS film; (e) Freeze-dried powder consisting of cellulose and PS latex particles containing 5 wt % of cellulose; (f) Freeze-dried cellulose/PEDOT:PSS/PS powder containing 8 wt % of cellulose and 4 wt % of PEDOT:PSS. PS not covered with PEDOT:PSS shows up very bright due to charging as no coating was used, so most PS appears to be PEDOT:PSS coated.

nontemplated systems. Unlike previous work[19] where bulk polymer was used in the dissolved state to prepare composites, we produced our materials using a latex of bulk polymer. This could aid in creating a percolated network by restricting the cellulose nanowhisker/PEDOT:PSS to the latex particle interstitial space upon film formation.

A control series of cellulose-free films was prepared by mixing of PEDOT:PSS and PS to investigate at what loading of PEDOT:PSS the system becomes conductive. The preparation of the PEDOT:PSS/PS blends was performed by mixing PEDOT:PSS latex in the desired ratios with a PS latex, followed by freeze-drying to remove water and compression molding at 180 °C to make the final composite films. Polymer blends do not show true percolation thresholds as defined for fillers. Instead, for a combination of two polymers at distinct volume fractions, the morphology of the blend will be such that at least

one phase is continuous. If this phase is conductive, an insulator−conductor transition can be observed at the point where continuity is achieved.[14,25]

The results of our control experiments are shown in Figure 1a. As one can see, after mixing PS and PEDOT:PSS latex particles, PEDOT:PSS, being immiscible with PS, percolates in a PS matrix at around 2.2 wt % or 2.31 vol %, which is in good agreement with earlier reports where latex technology has also been applied to manufacture nanocomposites.[14,26] The maximum conductivity achieved for the blend is 600 S m^{-1} which can be compared with the maximum conductivity of pure PEDOT:PSS of up to 1000 S m^{-1} according to the supplier. It is known that PEDOT:PSS easily forms films on a substrate.[14,27] A scanning electron microscopy (SEM) image of a PEDOT:PSS film drop-cast on a silicon wafer (Figure 1b) exhibits a smooth structured surface with some PEDOT:PSS

particles on top. Such a morphology is probably due to the thickness of the film comprising a few layers of PEDOT:PSS particles.[27] The PEDOT:PSS film has been reported to consist of horizontal layers of flattened PEDOT-rich particles separated by quasi-continuous PSS lamellas.[28,29] Such a pancake shape of PEDOT particles, which implies an increase of their aspect ratio ($L/D > 1$ instead of $L/D = 1$ for spheres) can explain the relatively low percolation threshold of PEDOT:PSS in a blend with a noncompatible polymer such as PS because the higher the aspect ratio of the filler, the lower the percolation threshold. Particle size distribution of PEDOT:PSS also can have an impact. Although the majority of the PEDOT:PSS particles are approximately in the range of 50−100 nm, particles of much bigger size (up to 2 μm) were observed as well. The change of such big spheres to pancakes and thus big increase of L/D ratio could markedly decrease the percolation threshold. Another factor which may play a role in inducing the relatively low percolation threshold of PEDOT:PSS in PS composites can be the localization of the conductive PEDOT:PSS particles; after removal of water from the mixed latex, the conductive PEDOT:PSS particles are located in the interstitial space between the former PS latex particles, where they might already form a network structure surrounded by a large excluded volume formed by the glassy PS particles. Inspired by the work of the group of Grunlan, we believe that these conductive particles might retain their prearranged organization even after flow and fusing of the former PS latex particles.[30]

To check how the conductive blend component PE-DOT:PSS behaves upon high temperature processing, the polymer was spin-coated on a glass substrate and placed in an oven for half an hour at 180 °C to mimic the processing temperature. Atomic force microscopy (AFM) analysis of the film before and after annealing (Figure 1c,d) shows that annealing affects the morphology of the PEDOT:PSS film; the film thickness reduces due to evaporation of water, which also leads to a decrease in the distance between the particles, in agreement with an earlier report.[27] No significant agglomeration or aggregation is visible.

The morphology of PEDOT:PSS in the PEDOT:PSS/PS powder obtained after freeze-drying and deposited on a silicon wafer were further analyzed (Figure 1e,f); the PEDOT:PSS and PS latexes were mixed in such a way that the weight ratio of PEDOT:PSS to PS in the final film would be 1 to 1 in order to maximize the visibility of both polymers. As can be seen in the major part of the dark PS matrix, the lighter colored PEDOT:PSS particles have a slightly elongated (oval) shape, which also supports the earlier hypothesis that the aspect ratio of the PEDOT:PSS particles increases when this soft material is placed on a hard substrate. The film in Figure 1f looks smooth, and not any single particle can be distinguished, which can imply that the PEDOT:PSS film covers the PS particles and that the film of the conductive polymer is quite thick.

A transmission electron microscopy (TEM) micrograph of a dispersion of the sisal-based cellulose nanowhiskers in water is given in Figure 2a. The nanowhisker diameter and length estimated are 3.6 ± 1 and 211 ± 106 nm, respectively, when fitting the dimensional variation with a three-parameter Weibull distribution, giving rise to an aspect ratio around 60.[21]

For the preparation of the cellulose-based nanocomposites, the nanowhiskers were mixed with PEDOT:PSS latex at weight ratios of 1/4, 1/1, and 2/1. The obtained dispersions were then mixed with the PS latex in varying concentrations followed by the freeze-drying and subsequent compression molding to

prepare composites to determine the electrical percolation threshold and composite conductivity. The percolation threshold of the cellulose/PEDOT:PSS/PS composites prepared at the weight ratio cellulose/PEDOT:PSS 1/4 occurs at 0.35 wt % (0.25 vol%) of the cellulose loading, which is consistent with a PEDOT:PSS weight percentage of 1.4 wt % (1.47 vol%), significantly lower than the value of 2.2 wt % (2.31 vol %) reported for the binary PS/PEDOT:PSS blend (Figure 2b). The composites exhibit an ultimate conductivity of 500 S m^{-1}, achieved for a weight percentage PEDOT:PSS of 16 wt % (16.9 vol %). Percolation of the cellulose nanowhiskers-based composites prepared at the cellulose/PEDOT:PSS wt/wt ratio of 1/1 occurred at 0.7 wt % (0.74 vol % PEDOT:PSS, 0.40 vol % cellulose nanowhiskers) and the maximum conductivity measured was 650 S m^{-1} at 16 wt % (17.5 vol %) PEDOT/PSS. To find out if it is possible to further decrease the percolation threshold of the conductive component in the hybrid cellulose nanowhiskers-based PEDOT:PSS/PS composites, we prepared composites in which the weight ratio cellulose/PEDOT:PSS was 2/1. The conductivity curve with respect to the conductive polymer content is shown in Figure 2b. Figure 2b shows the system exhibits electrical charge percolation at 0.8 wt % (0.56 vol%) cellulose and 0.4 wt % (0.42 vol %) PEDOT:PSS loading, which is extremely low when compared with PEDOT:PSS/PS composites without added cellulose whiskers (lowest reported percolation at 2.2 wt % or 2.31 vol % PEDOT:PSS). So, through addition of the cheap, high-aspect-ratio cellulose nanowhiskers to a blend of PS and PEDOT:PSS, significant conductivity can be achieved at much lower PEDOT:PSS contents than is possible without cellulose nanowhisker addition. The conductivity reaches 5 S m^{-1} already at 2.8 wt % (3 vol %) of the conductive polymer. The maximum conductivity measured was 700 S m^{-1} achieved at 16 wt % (18.4 vol %) of PEDOT:PSS. As already alluded to, the lower percolation threshold may in part be due to the whiskers acting as a percolating scaffold for the conducting component. Indeed, considerations based on connectedness percolation theory predict that, under the right conditions, this lowers the conduction threshold significantly.[31,32] Normally, "latex-technology" for preparing electrically conductive nanocomposites consists of the following steps: (1) dispersion of the filler in the presence of surfactant (in the case of cellulose, it is mixing the cellulose nanowhiskers with PEDOT:PSS); (2) mixing the nanofiller dispersion with polymer latex; (3) freeze-drying followed by compression molding. To check how the processing conditions influence conductive properties of the composites we performed experiments where we replaced the freeze-drying step by a water evaporation step by means of heating the mixture of the dispersed nanofiller and the polymer latex at 70 °C, similar to the common approach to make cellulose nanowisker composites from polymer latexes.[2,3,33,34] We did these experiments for the PS composites based on merely PEDOT:PSS and for the nanocomposites based on the cellulose/PEDOT:PSS mixture with the weight ratio of the cellulose whiskers and conductive polymer being 1 to 1. The results of the experiment for the composites containing the cellulose are presented in Figure 2c. During the freeze-drying process, the removal of water occurs under vacuum by direct sublimation of the frozen water. One could suspect that at such conditions all the components of the system, namely, the cellulose, PEDOT:PSS, and PS particles, are fixed at certain positions in the frozen water and that the PEDOT:PSS particles

cannot film-form and significantly adapt their aspect ratio during the drying process as thermal energy is low and no plasticizing water is present. When drying the systems via water evaporation at elevated temperatures, the polymers have higher thermal energy and water can act as a plasticizer for PEDOT:PSS, facilitating film formation. One could thus expect that either freeze-drying or evaporation of water by heating could result in a different PEDOT:PSS morphology in the corresponding composites, which in turn would result in different percolation thresholds for the cellulose/PEDOT:PSS/PS composites prepared by the two different processing conditions. However, we did not measure any difference in percolation thresholds when measuring the conductivity of the composites (Figure 2c). However, some difference in conductivity values just above the percolation threshold can be seen. This difference is explained by inhomogeneities observed in the system by thermal motion of PEDOT:PSS and PS when evaporating water at 70 °C. The same behavior was observed for the PEDOT:PSS/PS composites, so it is not linked to the addition of the nanowhiskers. Thus, replacing freeze-drying by heating for water removal from the PEDOT:PSS/PS or cellulose/PEDOT:PSS/PS mixtures does not appear to affect the percolating system of the conductive polymer in the corresponding systems. The reason may be that when transferring the composites from the freeze-dryer to the pressing machine for production of the composite films the hygroscopic PEDOT:PSS can attract some plasticizing water from the air, or that the pressing provides enough energy to induce contact between any discrete PEDOT sections. It is also further proof that the PEDOT:PSS percolation truly occurs in the interstitial space of the PS latex particles.

To elucidate the morphology of the system and to confirm our suggestion, we took SEM pictures of the drop-cast cellulose/PEDOT:PSS films with the weight ratio cellulose/PEDOT:PSS being 2/1. During sample preparation, the initial mixture was diluted from the working concentration of the cellulose (1 mg mL^{-1}) to 0.05 mg mL^{-1} to avoid crowding. The sample was not covered with gold. As Figure 2d shows, PEDOT:PSS exhibited a visible network organization. The observed structure is similar to the electrodeposited polypyrrole on cellulose nanowhiskers,[20] and the formed structure has the appearance of a polymer-coated, drop-cast cellulose nanowhisker film.[35] Therefore, the cellulose whiskers thus indeed appear to act as a template for the PEDOT:PSS conductive polymer.

We also examined the network formed when mixing the cellulose whiskers and PS latex with SEM (Figure.2e). Mixing a nanofiller with a polymer latex is the most important step of the film forming process because it determines the effective incorporation of the filler into the polymer matrix. After mixing, the mixture of the two types of colloidal particles, that is, the cellulose nanowhiskers and latex particles, was freeze-dried. In principle, the sublimation of the water induced by freeze-drying is not expected to significantly modify the aggregated state of the cellulose nor the quality of mixing of the cellulose and the polymer latex particles.[36] Of course, drying from liquid state does induce a compaction of the nanofiller network, which becomes denser due to removal of the water. After compaction of the powder, consisting of submicrometer polymer particles and cellulose whiskers, cellulose whiskers are forced into the interstitial space between the polymer latex particles and organize themselves in a network that can be built up from individual cellulose whiskers

as well as from some smaller bundles of aggregated nanowhiskers, as seen in Figure 2e. This situation is completely comparable to the earlier noted situation described by the Grunlan group for polyacrylate latex and carbon nanotubes,[30] and numerous examples in the literature of cellulose nanowhisker reinforced composites.[2,33,34,37] If PEDOT:PSS indeed covers the cellulose nanowhiskers when mixed with them and follows the cellulose network formation in between the PS latex particles before these are deformed and fused together in the compression molding step, it explains the very low percolation threshold of this conductive polymer in the cellulose/PS composites. We also analyzed with SEM the complete system consisting of 8 wt % (5.7 vol%) of cellulose mixed with PEDOT:PSS (weight ratio of 2 to 1) in the PS latex. The sample was not covered with gold, which makes PS particles noncovered by PEDOT:PSS bright due to charging. As one can see, some network-like structure is present in the system. As this network does not appear to be significantly charged, it must form a conductive network, most likely by the cellulose covered by the conductive polymer. Templating of positively charged polypyrrole onto negatively charged cellulose nanowhiskers has previously been shown to occur very effectively and is able to create porous supercapacitor materials.[20] Three-dimensional structures of cellulose nanowhiskers into aerogels have also been made showing the ability of these nanowhiskers to form self-supporting 3D structures.[38]

To confirm interactions between cellulose whiskers and PEDOT:PSS, mixtures were monitored with UV−vis absorbance measurements, as used before to confirm cellulose−PEDOT:PSS interactions.[39] The UV−vis absorbance of a dispersion of the cellulose whiskers with PEDOT:PSS at a concentration of 1 mg mL^{-1} of cellulose nanowhiskers and a weight ratio of cellulose whiskers/PEDOT:PSS of 2/1 was measured as a function of time (Figure 3).
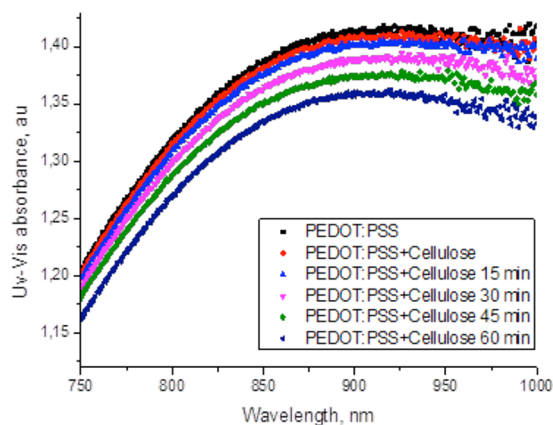
Figure 3. Following the interaction process between PEDOT:PSS and cellulose by UV−vis. The PEDOT:PSS absorbance is decreasing in time for the systems containing both PEDOT:PSS and cellulose nanowhiskers.

As a reference, an aqueous PEDOT:PSS dispersion of the same concentration as in the cellulose dispersion was also measured. The absorbance of the cellulose-free PEDOT:PSS solution was found to stay constant with time (curves not shown here). On the other hand, for the dispersion containing cellulose nanoswhiskers, the UV−vis absorbance was seen to decrease slightly shortly after mixing the conductive polymer with cellulose. This decrease continued with time, indicating an

increasing interaction between the conductive polymer and the cellulose whiskers.[39] We did not measure the absorbance after more than 1 h because this was the time we used for mixing the cellulose whiskers with PEDOT:PSS before subsequent mixing with the PS latex and freeze-drying of the final mixture. This decrease in the absorbance can be attributed to the adsorbance of PEDOT:PSS onto the cellulose surface as seen by SEM imaging of deposited material (vide supra) and the inherent decrease in absorbance of the PEDOT:PSS particles due to agglomeration around individual cellulose whiskers or their bundles. One might expect that this interaction of the cellulose whiskers and the conductive polymer can be due to the formation of hydrogen bonds between hydroxyl groups of the cellulose and sulfonate groups or other hydrogen bond acceptor groups of the conductive polymer, as well as some interaction between PEDOT and sulfate half-esters known to exist on the cellulose nanowhisker surface as they were obtained by sulphuric acid hydrolysis. Infrared spectroscopy did not show any chemical interaction between these two fillers, as there was no visible shift in peak positions or appearance of new signals indicating the formation of new bonds, suggesting that PEDOT:PSS physically adsorbs on the cellulose surface. The results of the UV–vis experiments together with the very low percolation thresholds for electrical conduction supports our hypothesis that the cellulose nanowhiskers form a template on which the PEDOT:PSS adsorbs.

In conclusion, we developed cellulose/PEDOT:PSS-based PS composites with an extremely low percolation threshold of the conductive polymer. The percolation threshold of PEDOT:PSS in PEDOT:PSS/PS blends, being 2.2 wt % (2.31 vol %), was lowered to 0.4 wt % (0.42 vol %) by adding 0.8 wt % (0.56 vol %) of cheap, nonconducting cellulose whiskers. Such a low percolation threshold of PEDOT:PSS is attributed to the templating effect of the cellulose nanowhiskers: the conducting PEDOT:PSS is thought to adsorb on the cellulose surface and by doing that (at least partly) covers the network formed by the percolating, high aspect ratio cellulose whiskers in the PS matrix. UV–vis experiments indeed point to a interaction between PEDOT:PSS and the cellulose whiskers, confirming the templating of PEDOT:PSS onto the nanowhiskers during processing and film formation.

■ EXPERIMENTAL SECTION

Chemicals: Sodium dodecyl sulfate (SDS; 90%, Merck), sodium carbonate (99%, Aldrich), and sodium peroxydisulfate (SPS; 90%, Merck) were used as received. Styrene (SC; 99%, Merck) was passed over an inhibitor remover column. The inhibitor-free monomer was kept under refrigeration for later use. Water used in all reactions was double deionized water obtained from a purification system. PEDOT:PSS dispersion, grade name Clevios P (weight ratio PEDOT to PSS is 1 to 2.5, maximum conductivity 1000 S m^{-1}) was purchased from H. C. Starck and used as received.

Cellulose nanowhiskers preparation: Cellulose nanowhiskers derived from sisal were prepared using an earlier published procedure from bleached sisal using sulphuric acid as the inorganic acid.[21] Sulphuric acid hydrolysis results in the formation of a small amount of sulfate half esters on the nanowhisker surface (ca. 250 mmol kg^{-1}), which enable the formation of stable aqueous dispersions by electrostatic stabilization. After preparation and purification, they were sonicated with a Branson sonifier at 40 W for 5 min to obtain a stable dispersion in water.

Preparation and characterization of PS latex: PS latex was synthesized via conventional free radical emulsion polymerization. The reaction was performed at 70 °C with an impeller speed of 400 rpm. The reactor was charged with the following: styrene (252 g), SDS

(26 g, 0.09 mol), SC (0.7 g, 6.6 mmol), and H$_2$O (712.2 g). The reaction mixture was degassed by purging with argon for 30 min. A solution of SPS (0.45 g, 1.9 mmol) in H$_2$O (10 g) was also degassed. The reaction was started by the introduction of the initiator in water solution to the reactor preheated to 70 °C containing the styrene/SDS/SC in water mixture. The reaction time was roughly 1 h. The average particle size as determined by dynamic light scattering was 90 nm. Size exclusion chromatography analysis showed M_n, M_w, and PDI values of 495 kg mol^{-1}, 944 kg mol^{-1}, and 1.9, respectively.

Composites processing: The aqueous cellulose dispersions (1 mg mL^{-1}) were mixed with PEDOT:PSS (12 mg mL^{-1}) and PS latex (28.16 mg mL^{-1}) in the desired ratios, the mixtures were frozen in liquid nitrogen for several minutes, and the frozen water was removed with a Christ Alpha 2−4 freeze-dryer operated at 0.2 mbar and 20 °C overnight. The resulting composite powders were compression molded into films for 20 min at 180 °C between Teflon sheets with a Collin Press 300G. The PS latex was used as synthesized, without removing surfactant.

Spin coating of PEDOT:PSS: A thin (0.17 mm) glass substrate 24 × 24 mm^2 was rinsed with acetone and exposed to a UV-ozone cleaning system from Novascan for 20 min at room temperature for the removal of molecular organic contamination. The glass plate was inserted into the spincoater (WS-650SX-6NPP/LITE, from Laurel) and was loaded with about 0.5 mL of dispersion under a nitrogen atmosphere. The rotation speed for the formation of a thin homogeneous film was set to 1500 rpm for 2 min.

Preparation of drop-cast samples of PEDOT:PSS and cellulose/PEDOT:PSS for SEM measurements: The original PEDOT:PSS dispersion was drop-cast on a silicon wafer and dried overtime at room temperature. In the case of cellulose/PEDOT:PSS, the separate dispersions of the cellulose and PEDOT:PSS at a concentration of 1 mg mL^{-1} were mixed together to obtain 50/50 wt % cellulose/PEDOT:PSS mixture. The final mixture was diluted to the cellulose concentration of 0.05 mg mL^{-1} to avoid crowding and drop-cast on a silicon wafer followed by the drying at room temperature.

Preparation of powder samples for SEM imaging: For preparation of PEDOT:PSS/PS mixtures, the original dispersions were mixed to obtain a 50/50 wt % ratio of the components and freeze-dried followed by deposition of the final dry powder on a silicon wafer. Cellulose/PS sample was prepared by mixing of PS latex (PS concentration 28.16 mg mL^{-1}) and cellulose dispersion (cellulose concentration 1 mg mL^{-1}) to obtain a mixture containing 5 wt % of the cellulose. The final mixture was freeze-dried and deposited on a silicon wafer.

For preparation of the cellulose/PEDOT:PSS/PS sample containing 8 wt % of cellulose and 4 wt % of PEDOT:PSS, the aqueous cellulose dispersion (1 mg mL^{-1}) was mixed with aqueous PEDOT:PSS dispersion (12 mg mL^{-1}) and PS latex (28,16 mg mL^{-1}) in the desired ratios, the mixture was frozen in liquid nitrogen for several minutes and the frozen water was removed by freeze-drying. The dry powder was deposited on a silicon wafer.

UV–vis spectroscopic measurements: UV–vis absorption spectra were recorded with a Hewlett−Packard 8453 spectrometer operating between 200 and 1100 nm. The blank used was the original PEDOT:PSS solution, diluted, and analyzed under the same conditions as the samples themselves.

Electrical conductivity measurement: The electrical conductivity was measured using a standard four-point method. Parallel contact lines 0.5 cm in length and with a 0.5 cm interval were drawn with conductive-silver paint (Fluka) on the composite film, and all conductivity measurements were performed at room temperature with a Keithley 6512 programmable electrometer. The voltage-current characteristics were recorded in an applied current range 10^{-9}−10^{-3} A by measuring the resulting voltage. For each sample, conductivity data represent the average value of 10 consecutive measurements.

Atomic force microscopy (AFM): AFM characterization of spin-coated films was performed with a NT-MDT NTEGRA operated in tapping mode using silicon tips NSG11 (NT-MDT). The smoothness of the films was scanned in normal tapping mode over an area of 20 ×

20 um^2. The images shown in this manuscript represent the topographic (height) profile.

Transmission electron microscopy: TEM images were taken using a Sphera type Technai 20 (Fei Co.). This was operated with a 200 kV LaB$_6$ filament and a bottom-mounted 1024 × 1024 Gatan CCD camera. A carbon-coated gold grid was used.

Scanning electron microscopy: SEM images were obtained with a Quanta 3D FEG (Fei Co.) equipped with a field emission electron source. High vacuum conditions were applied and a secondary electron detector was used for image acquisition. Additional sample treatment, such as coating with a conductive layer, has been applied when necessary before surface scanning. Standard acquisition conditions for charge contrast imaging were used. Silicon wafer without any treatment was used as substrate, due to its conductivity, for the preparation of the drop-cast films analyzed.

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Notes

The authors declare no competing financial interest.

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