One-component nanocomposites based on polymer-grafted cellulose nanocrystals

*Sandra Wohlhauser, Tobias Kuhn[§], Worarin Meesorn, Lucas Montero de Espinosa, Justin O. Zoppe, Christoph Weder**

Adolphe Merkle Institute, University of Fribourg, Chemin des Verdiers 4, 1700 Fribourg, Switzerland

[§] Department of Complex Tissue Regeneration, MERLN Institute for Technology Inspired Regenerative Medicine, Maastricht University, 6229 ER, Maastricht, the Netherlands

ABSTRACT. Cellulose nanocrystals (CNCs) are widely used as reinforcing filler in polymers, due to their exceptionally high stiffness and strength and because the biological species from which they are isolated represent renewable resources. However, aggregation of the CNCs, which is concomitant with limited reinforcement, is often difficult to avoid. One-component nanocomposites (OCNs) based on polymer-grafted nanoparticles can solve this problem, because this approach affords, by design, materials in which no such aggregation is possible. At the same time, chain entanglements between the CNC-grafted polymer chains provide stress-transfer among the particles. To demonstrate this, we investigated OCNs based on polymethacrylate-grafted CNCs. A previously un-accessed compositional space, i.e., OCNs with a CNC content of 10 or 20 wt%, was explored. Cotton linter-based CNCs were modified via surface-photoinitiated free radical polymerization, which involved the functionalization of the CNC surfaces with benzophenone moieties as photo-radical initiator species, and the subsequent surface-photoinitiated polymerization of methyl or hexyl methacrylate under UV-irradiation at 365 nm. The resulting particles readily dispersed in THF. Solvent-casting and compression-molding afforded films of homogeneous appearance, which display remarkable

improvements in stiffness or toughness and strength in comparison to conventional two-component nanocomposites of unmodified CNCs and the respective polymers.

INTRODUCTION

In order to enhance their dispersibility in solvents or solid (polymer) matrices, the surface of nanoparticles (NPs) is often decorated with compatibilizing molecules.¹ This approach has been applied to many different matrix/nanoparticle combinations.^{2,3} In addition to physisorption of small molecular surfactants or amphiphilic (co)polymers on the NPs surface, polymers can be covalently grafted to or from the surface of the NPs to compatibilize them with a given polymer, but especially at high NP loading, phase separation or de-mixing remain an omnipresent obstacle.⁴ This problem can be solved by creating so-called one-component nanocomposites (OCNs), i.e., materials resulting from the assembly of polymer-grafted or “hairy” NPs (HNPs) in the absence of any additional polymer matrix.⁵ HNPs consist of a central core that is surrounded by a polymer corona. Unlike conventional polymer nanocomposites that consist of at least two separate components, OCNs can, by design, not suffer from mixing and phase separation problems, because their components are covalently linked, and if the grafting is homogeneous, aggregation of CNCs should also be suppressed. Strictly speaking, this design feature does not qualify these materials as composites in the classical sense, but nevertheless the term “one-component nanocomposites” is used as it concisely describes their structure.⁵ OCNs can be easily processed via either solvent casting of the HNP dispersion or by melt processing the dried material at a temperature above the glass transition or the melting point of the grafted polymer. OCNs based on hairy spherical NPs have been shown to display anisotropic elastic properties, as a result of substrate-induced formation of layered assemblies.⁶ Previous works in the field of hairy nanoparticles have been mainly focused on spherical NPs,⁵ such as silica, albeit the use of high-aspect-ratio nanoparticles can

significantly enhance the mechanical properties of the final material. In this context, we surmised that OCNs based on polymer-grafted cellulose nanocrystals (CNCs) would be an interesting materials family to investigate. To the best of our knowledge, only two experimental studies^{7, 8} and two computational simulations,^{9, 10} have been published on OCNs based on hairy CNCs.

CNCs are rod-like NPs that are readily isolated through selective hydrolysis from renewable bio-sources, such as higher plants, bacteria, and tunicates, among others.^{11, 12} CNCs consist of linear homopolysaccharides composed of anhydroglucopyranose repeat units that are connected via β (1-4') glycosidic bonds.¹¹ CNCs are moderately to highly crystalline (54-88%) with an aspect ratio (10-170) that depends mainly on the raw material, but also on the hydrolysis conditions.¹² CNCs are frequently used as reinforcing filler in polymer nanocomposites, due to their low density, high tensile strength (7.5 - 7.7 GPa)¹³ and stiffness (57-151 GPa),¹² and the renewable nature of the sources from which they are isolated.¹⁴ Data also suggest that unlike other nanofillers, CNCs have a limited associated toxic potential when investigated under realistic exposure scenarios and doses.¹⁵

The use of CNCs as reinforcement agent in a polymeric matrix was pioneered by Favier et al., who observed an improvement of the mechanical properties of poly(styrene-*co*-butyl acrylate) when a latex of this polymer was combined with CNCs extracted from tunicates and processed into films.^{16, 17} Since then, CNC-polymer nanocomposites have been widely investigated and their properties are now well-understood.¹⁴ The mechanical reinforcement in polymer/CNC nanocomposites is generally accepted to take place through a hydrogen-bonded CNC network that percolates within the polymer matrix, which is responsible for efficient stress transfer.¹⁷ The reinforcement achieved is typically well predicted by a percolation model, which considers that the CNC percolating network is formed over a certain filler content (i.e.,

percolation threshold).^{18, 19} However, in many cases the actual reinforcement does not match with the prediction of this model.^{20, 21} One possible reason is that it does not take into account CNC aggregation, which we have recently shown to be important.²² The remaining challenge is thus to enhance the dispersion of CNCs within the polymer matrix. Many efforts have been directed to address this problem by increasing the hydrophobicity of the CNCs via surface modification.²³ For instance, stable dispersions of CNCs/poly(lactic acid) in chloroform²⁴ or CNCs/atactic poly(propylene) in toluene²⁵ have been reported after physically coating the CNC surface with surfactants. The physical adsorption of polymers on CNCs was also shown to improve their dispersibility.²⁶ For example, after adsorbing poly(ethylene oxide), the CNCs dispersed more readily in (hydrophobic) low-density polyethylene and the resulting nanocomposites could be processed via melt-extrusion into objects of homogeneous appearance.

Another strategy to enhance the dispersibility of CNCs is to chemically modify their surface with motifs that are similar to the polymer matrix or sites that display specific interactions with the matrix.²³ Examples include the TEMPO-mediated oxidation of the surface OH-groups,²⁷ the attachment of small molecules such as organic acid chlorides,²⁸ or acetic anhydride,²⁹ and the introduction of long polymer chains.^{30, 31}

As discussed above, one-component nanocomposites (OCNs) based on polymer-grafted nanoparticles promise to be another solution to the dispersion problem, because their architecture prevents macrophase separation. At the same time, chain entanglements between the CNC-grafted polymer chains can enable stress-transfer among the particles. Indeed, the polymer chain length, the grafting density and the polymer structure also should influence the mechanical properties of CNC-based OCNs according to the recent computational predictions reported by Hansoge et al.^{9, 10}

Polymer-grafted CNCs can be synthesized via “grafting-from”, “grafting-to”, or “grafting-through” approaches involving functional groups on the CNCs surface.^{3, 32} The grafting-from approach, which was utilized here, involves the functionalization of the CNCs with polymer brushes by way of surface-initiated polymerization from initiator groups immobilized on the NPs’ surface. This framework generally leads to polymer grafts with a well-controlled length and high polymer grafting density.³ The first example of OCNs based on polymer-grafted CNCs, using a grafting-from approach, was reported by Chen et al.,⁷ who functionalized CNCs with semicrystalline poly(ϵ -caprolactone) via surface-initiated ring-opening polymerization. OCNs with a CNC content of between 4 and 8 wt% proved to be melt-processable and the authors reported a non-linear dependence between the CNC content and the OCN mechanical properties. Unfortunately, no comparison with conventional composites was made and no correlation between the PCL graft structure and the properties of the OCNs could be established. In another study, Chang et al. reported the synthesis of CNCs-g-poly(ethynylene-fluorene) through Sonogashira coupling via a grafting-from approach,⁸ but the mechanical properties of the material were not investigated.

Here, we report the synthesis of amorphous, polymethacrylate-grafted CNCs through a synthetically undemanding free radical polymerization protocol. It involves the surface functionalization of CNCs with a benzophenone derivative that serves as radical photoinitiator for the surface-initiated photopolymerization of methyl and hexyl methacrylate upon UV-irradiation. The morphology and thermomechanical properties of the OCNs made from these “hairy” CNCs were investigated and the materials were found to display remarkable improvements in stiffness or toughness and strength in comparison to conventional two-component reference nanocomposites consisting of unmodified CNCs and the respective polymethacrylate.

RESULTS AND DISCUSSION

The synthesis of polymethacrylate HNPs (PMA-HNPs) via surface-initiated free radical photopolymerization from the surface of CNCs was performed using CNCs whose surfaces were modified with benzophenone (BP) moieties as photoactive radical initiator species (**Scheme 1**). CNCs were extracted via sulfuric acid hydrolysis from cotton according to a well-established protocol.²⁰ The CNCs thus produced had an average length of 117 ± 28 nm and an average width of 15 ± 2 nm (established by image analysis of transmission electron microscopy images, **Figure S1**) and a surface charge density of 115 mmol/kg R-OSO₃H and 21 mmol/kg COOH groups (established by conductometric titration of unmodified CNCs with 0.01 M NaOH solution, **Figure S2**), which are introduced during hydrolysis.³³ Applying conditions reported by Biyani et al.,³⁴ the CNCs were dispersed in water-free DMF and reacted with 4-benzoylphenyl-(6-isocyanatohexyl)carbamate (**1**, **Figures S3 and S4**) in order to functionalize the CNCs surface with BP moieties (**Scheme 1**). After purification by repeated ultracentrifugation and washing with DMF and THF, the resulting CNC-g-BPs were dried in vacuum and kept in an amber glass vial to protect them from light. FTIR spectra show the characteristic signals of urethane bonds at 1615 and 1576 cm⁻¹, confirming the successful attachment of the BP-containing radical initiation sites (**Figure 1**). The absence of the absorption band at 2265 cm⁻¹, characteristic of the isocyanate group, further reveals the complete removal of unreacted compound **1**. An initiator grafting density (σ_i) of 0.8 BP molecules/nm² was established by UV-vis spectroscopy following the methodology reported by Biyani et al.³⁴ For this purpose, a calibration curve was created using BP compound **1** (**Figures S5 and S6**), which was employed to determine the BP content of a CNC-g-BP dispersion. All samples were analyzed by comparing the absorbance at 285 nm and the absorbance of 100 µg/mL dispersions of CNC-g-BP was corrected by subtracting the signal of corresponding dispersions of unmodified CNCs in order to account for scattering effects.

Scheme 1. Synthesis of polymethacrylate HNPs via the surface functionalization of CNCs with 4-benzoylphenyl-(6-isocyanatohexyl)carbamate (**1**) and photoinitiated grafting of polymethacrylates from the surface of modified CNCs (CNC-g-BP). Due to the initiation mechanism (see text), free PMA is also produced.

As a next step, MMA or HMA were polymerized from the surface of CNC-g-BP via surface-photoinitiated FRP (**Scheme 1**). MMA and HMA were chosen as monomers in order to investigate the properties of CNC-based OCNs with glass transition temperatures (T_g) above and below room temperature. As a Norrish Type II photoinitiator, benzophenone undergoes

intersystem crossing to a reactive triplet excited state upon irradiation at 350-360 nm, which in turn causes the carbonyl group to abstract any nearby aliphatic hydrogen (i.e., from the surface of the CNCs, the solvent, or the monomer), yielding ketyl and carbon-centered radicals.³⁵ The initiation process can thus occur from radicals on the surface of the CNCs or from monomers/solvent radicals in solution, which affords free (i.e., not CNC-bound) polymer chains. At least for research purposes, this is an attractive feature as it affords, simultaneous to the growth of polymer-grafts from the CNCs, free macromolecules in solution, which can be easily isolated and characterized. As ungrafting polymers from CNCs is not straightforward, it has become common^{36, 37} to rely on the characterization of such free polymer populations instead of the grafted polymer^{38, 39}, but in most surface-initiated polymerizations, a sacrificial initiator (i.e., one that is not attached to the nanoparticles) must be added to the reaction mixture.

Thus, MMA and HMA were polymerized in the presence of CNC-g-BP in anhydrous DMF using two 6 Watt UV lamps emitting at 365 nm (**Scheme 1**). The reaction time was fixed to 16 h and the monomer concentration was varied to control the amount of polymer grafted onto the CNCs. The HNPs were then separated by several cycles of ultracentrifugation and washing with THF. The free polymers were isolated from the supernatant by concentration and precipitation in cold methanol (**Table 1**). The ¹H NMR spectra of the free polymers produced during the synthesis of PMMA- and PHMA-HNPs match those of PMMA and PHMA standards, respectively (**Figure S7**). For reference purposes, free PMMA (number-average molecular weight, $M_n = 161$ kDa, dispersity, $D = M_w/M_n = 1.8$) and PHMA chains ($M_n = 125$ kDa, $D = 2.3$) isolated after the synthesis of PMMA-HNP-10% and PHMA-HNP-10%, respectively, were used in this study for the fabrication of two-component nanocomposites containing equivalent weight percentage of CNCs than the synthesized HNPs, i.e., 10 and 20 wt%.

The monomer conversion into grafts was determined based on the total amount of monomer present in the reaction mixture, and the weight of the polymer grafts produced, which in turn was determined from the mass difference between the isolated HNPs and the initial amount of CNC-g-BP (**Table 1**). The monomer conversion into grafts varied between 15 and 20%, which may appear low, but due to the specific initiation mechanism (*vide supra*) a substantial amount of free polymer was produced in solution (28-60%). HNPs in which the CNC weight fraction was ca. 10 wt% (referred to as PMMA-HNP-10% and PHMA-HNP-10%) were obtained when the monomer concentration in the feed was 4.7 M and 2.5 M for MMA and HMA, respectively, and the CNC content was doubled to 20 wt% (PMMA-HNP-20% and PHMA-HNP-20%) when the monomer concentrations were cut in half (i.e., 2.34 M and 1.27 M for MMA and HMA). A further decrease of the HMA concentration to 0.6 and 0.3 M yielded HNPs with a CNC content of up to 58 wt%, but we note that the reproducibility of reactions with low monomer concentrations was, in contrast to the above reactions (**Table 1**) not very good (**Table S1**).

Figure 1. FTIR spectra of unmodified CNCs, CNC-g-BP, PMMA- and PHMA-based HNPs containing 20 wt% CNCs (top to bottom).

The presence of PMMA and PHMA grafts in the HNPs is evident from the FTIR spectra, which show intense carbonyl ester peaks at 1726 and 1723 cm^{-1} , respectively (**Figure 1** and **Figure S8**). Furthermore, the increased intensity of alkyl group peaks in the range of 2954-2858 cm^{-1} in the FTIR spectra of the PHMA-HNPs is indicative of the hexyl group of the PHMA repeating unit. ^1H NMR spectra of well-dispersed PMMA and PHMA HNPs in CDCl_3 also reflect the polymerization of MMA and HMA from the surface of CNCs by the presence of broad signals that are in good agreement with the expected structures (**Figure S9**). The formation of PMMA and PHMA grafts and the gravimetrically determined compositions were finally confirmed by elemental analysis data (**Table S2**), which show a good match between the experimentally determined and theoretical compositions based on the molecular constitution of the repeating units of CNC-g-BP and the grafted polymer and considering the gravimetrically determined graft fractions. In the light of typical variations seen for the elemental analyses of modified CNCs,⁴⁰ the experimentally determined compositions of HNPs show a good agreement with the elemental composition of the material. In the case of CNC-g-BP, the experimentally determined carbon content is higher (48.9% vs. 46.6%) than the one determined theoretically, which may be an indication that the content of BP molecules determined via UV-vis spectroscopy could have been underestimated.

In order to cleave (a portion of) the polymers from the CNCs and allow for their molecular characterization in solution, chlorosilane-induced cleavage reactions of the urethane bonds were conducted under mild conditions in the presence of tertiary amines (**Scheme 2**).⁴¹ Only a fraction of polymethacrylate chains could be degrafted through this approach (around 30 wt% of the total grafts in the case of PMMA-HNPs and up to 56 wt% in the case of PHMA-HNPs, **Table S3**), which suggests that a significant fraction of the grafted chains are linked to the CNCs surface through C-C bonds. These results are consistent with the initiation process in

which the polymerization can start from any carbon-centered radical due to the nature of benzophenone photoinitiator species (*vide supra*).

Table 1. Summary of the results of surface photoinitiated FRP of MMA and HMA from CNC-g-BP, including HNP compositions, monomer conversions, number-average molecular weight (M_n) and dispersity ($\bar{D}$) of surface-grafted and free polymers, polymer grafting densities (σ_{grafts}) and initiator efficiencies ($\sigma_{\text{grafts}}/\sigma_i$). Data are averages of three separate reactions per composition, but molecular weight data are quoted for the individual samples.

Sample	HNP composition		Surface-grafted polymer					Free polymer in solution		
	Polymer ^a (wt%)	CNC ^a (wt%)	Monomer conv. into grafts (%)	M_n^b (kDa)	$\bar{D}^b$ (-)	σ_{grafts}^c (chains/nm ²)	$\sigma_{\text{grafts}}/\sigma_i$ (-)	Monomer conv. (%)	M_n^d (kDa)	$\bar{D}^d$ (-)
PMMA-HNP-10%	92 ± 1	8 ± 1	20 ± 1	266	2.2	0.15	0.19		161	1.8
				271	2.2	0.15	0.18	30 ± 2	148	1.7
									166	1.8
PMMA-HNP-20%	82 ± 1	18 ± 1	15 ± 1	163	2.5	0.10	0.12		77	1.9
				133	2.6	0.12	0.15	28 ± 1	82	1.8
									73	1.7
PHMA-HNP-10%	90 ± 2	10 ± 2	16 ± 4	232	2.0	0.12	0.15		125	2.3
				216	2.2	0.13	0.16	60 ± 5	100	2.4
									105	1.7
PHMA-HNP-20%	80.7 ± 0.3	19.3 ± 0.3	14.6 ± 0.3	371	1.9	0.04	0.05		67	1.9
				391	2.1	0.04	0.05	32 ± 8	60	1.6
									67	1.9

^aDetermined gravimetrically by weighing the CNCs before and after the polymerization.

^bDetermined by SEC of partially degrafted polymers and calibration with PMMA standards.

^cDetermined from gravimetric analysis considering an average specific surface of 174 m² (see Supporting Information). ^dDetermined by SEC of isolated free polymer chains in solution and calibration with PMMA standards.

Scheme 2. Chlorosilane-induced cleavage reaction of urethanes bond from the surface of PMA HNPs in order to cleave the grafted PMA chains.

The ¹H NMR spectra of PMMA and PHMA degrafted from polymethacrylate HNPs containing 10 wt% of CNCs (**Figures 2a** and **S10a**, respectively) are similar to those of the reference materials obtained from the free polymer chains (**Figure S7**) isolated after the synthesis of HNPs and reveal the characteristic signals of these polymers. The SEC traces of PMMA and PHMA degrafted from PMMA- and PHMA-HNPs containing 10 and 20 wt% of CNCs are shown in **Figures 2b** and **S10b** (solid lines), and the corresponding M_n and $\bar{D}$ are summarized in **Table 1** and **Table S3**. In all cases, the dispersity corresponds to polymers grown via free radical polymerization (1.9-2.6). The M_n values of PMMA degrafted from PMMA-HNP-10% and PMMA-HNP-20% are around 266/271 and 133/163 kDa, respectively. The data are quoted for two different reactions per compositions and the similarity reflects that the process used is very reproducible. The difference of the molecular weights between the compositions is consistent with the much higher initial monomer concentration in the reaction feed for PMMA-HNP-10%. Both HNPs feature grafts of a much higher M_n than the free polymer chains isolated from the same reaction mixture, which appears to indicate that termination reactions are suppressed when the growing chains are tethered to the CNCs and display a lower translational mobility than free propagating chains. Based on the weight fraction (determined gravimetrically) and the M_n of grafts, a PMMA grafting density of 0.15

and 0.10/0.12 chains/nm² was estimated for PMMA-HNPs containing 10 and 20 wt% of CNCs, respectively, using the methodology proposed by Majoinen et al. (see **Supporting Information**).³⁶ The M_n values of PHMA degrafted from PHMA-HNP-10% and PHMA-HNP-20% are 216/232 and 371/391 kDa, respectively, resulting grafting densities of 0.13/0.12 and 0.04 chains/nm², respectively. In the case of the PHMA-HNPs, DMF is a poor solvent for the grafted chains in comparison with PMMA chains due to their larger aliphatic side chains making them less polar. As a result, the PHMA chains become more packed at a determined polymer concentration, which makes the PHMA chains inaccessible to monomer, as the propagating chains become buried by the compacted coils. This behavior explains the low monomer conversion into grafts.

Figure 2. (a) ¹H NMR spectrum of PMMA degrafted from PMMA-HNP-10% in CDCl₃. (b) SEC traces of degrafted (solid line) and free (dashed line) PMMA isolated from PMMA-HNP-10% (top) and PMMA-HNP-20% (bottom) using THF as eluent.

A comparison of the SEC data of degrafted and free PHMA polymers (**Figures 2b** and **S10b**, **Table 1**) shows that the molecular weight of the free polymers is lower than tethered polymer chains. Other authors have also reported longer chains for the grafts than for free polymers,^{39, 42} and as above mentioned the effect appears to be a consequence of the reduced mobility of the tethered propagating chains, which in turn limits chain termination. The slight broadening of the molecular weight distributions observed for the PMMA synthesized via surface-initiated

polymerization is in good agreement with the behavior predicted by Turgman-Cohen and Genzer, i.e. that the dispersity of polymers grown from flat surfaces is larger than that of polymers in bulk, and that it is dependent of the initiator grafting density, i.e., the dispersity increases with grafting density.^{43, 44}

As mentioned above, the HNPs were made from CNCs extracted via sulfuric acid hydrolysis and this process introduces sulfate half-ester groups (115 mmol/kg) on the CNCs surface. Considering the known fraction of cellulose chains on the CNCs surface (i.e., 0.19),⁴⁵ one can calculate that about 7% of the reactive surface OH groups were substituted by sulfate half-ester groups during the hydrolysis, which translates into a slight reduction of the initiator grafting density. Based on a study of Tisuji et al.,⁴⁶ one can speculate that the presence of these negatively charged sulfate ester groups on the surface of CNCs promotes the migration of free radicals across the CNCs surface by sequential chain transfer reactions, thus enhancing chain recombination. This is consistent with a tail at high elution times in the SEC traces of degrafted polymethacrylates (**Figures 2b** and **S10b**). On the other hand, such tail is absent in the SEC traces of free polymers, which supports the conclusion that chain recombination is more apt to happen on the CNCs surface on account of a higher local concentration of radicals than in the solution.

Figure 3. TEM micrographs of (a) unmodified CNCs, (b) CNC-g-BP, and polymethacrylate HNPs from dispersed (c) PHMA-HNP-10% and (d) PMMA-HNP-10%, scale bar = 500 nm.

To explore how the surface modification affected the polarity and morphology of the CNCs, the various particle types were dispersed in a range of solvents, deposited onto transmission electron microscopy (TEM) grids, and imaged by TEM (**Figure 3**). The unmodified CNCs, which readily dispersed in deionized water, had a rod-like shape with a length of 117 ± 28 nm and width of 15 ± 2 nm according to image analysis (**Figure 3a**). The CNC-g-BP, which dispersed well in DMF, displayed similar morphology and dimensions (length = 113 ± 33 nm, width = 11 ± 2 nm) as unmodified CNCs (**Figure 3b**). The CNC-based HNPs could easily be dispersed in chloroform or THF, but not in water or DMF. The TEM micrographs of these HNPs show individual rod-like cores that are surrounded by a low-contrast corona, which was ascribed to the amorphous polymethacrylate grafts (**Figure 3c-d**). The HNPs seem to have

shorter CNCs cores, but this effect is ascribed to the fact that they do not aggregate, in contrast to the neat CNCs or the CNC-g-BP.

The CNC-based HNPs were processed into OCN films with a thickness of ca. 0.2 mm by compression molding at 160 °C (PMMA-HNPs) and 130 °C (PHMA-HNPs). For reference purposes, we also produced conventional two-component composites containing 10 and 20 wt% of CNCs by first solution-casting from THF a dispersion of unmodified CNCs and free reference polymethacrylates (isolated from the synthesis of PMMA-HNP-10% and PHMA-HNP-10%), vacuum-drying and finally compression molding at 130 °C (PMMA/CNCs) and 100 °C (PHMA/CNCs). **Figure 4** shows photographs of the resulting OCN films, which clearly reveal a high level of transparency and homogeneity. This behavior contrasts that of the two-component reference composites, in which CNC aggregation is at play (**Figure S11**), and is a first indication of the excellent dispersion of the CNCs in the OCNs, which is imparted by the molecular connectivity of the building blocks. **Figure 4** also qualitatively reflects the high flexibility of the PHMA-OCNs.

Figure 4. Pictures of (from left to right) OCNs based on PMMA-grafted CNCs and PHMA-grafted CNCs with 10 wt% and 20 wt% CNCs.

The transparency of the films was assessed by UV-vis transmittance in the range between 400 and 800 nm and the results are shown in **Figure 5**. Neat PMMA and PHMA films transmitted about 97% of the incident light with very little variation throughout the visible spectrum range. As expected, the transmittance of CNC containing samples was reduced at low

wavelengths due to scattering effects, but it in the case of the OCNs it approached that of the neat polymers at higher wavelengths. Importantly, across the entire wavelength regime, the OCNs show a considerably higher transparency than the reference composites, supporting the conclusion that aggregation effects are more pronounced in the latter. In contrast to the neat polymers, which were colorless, the CNC-containing films were slightly yellow after compression molding (**Figures 4 and S11**), on account of thermal degradation of the sulfate half-ester groups present on the surface of the CNCs.^{47,48} We note that when processed at similar temperature, the conventional composites displayed considerably more yellowing than the OCNs, and thus, the processing temperature was reduced for the former (*vide supra*). This means that the thermal stability of CNCs is increased in the OCNs, arguably due to the presence of polymethacrylate grafts, as previously reported by Börjesson et al.⁴⁹

Figure 5. Optical transmittance spectra of neat polymethacrylate (black line), OCNs (solid colored line) and reference composite (dashed line) films. (a) PMMA and (b) PHMA based materials containing 10 or 20 wt% of CNCs.

In order to evaluate to what extent the crystallinity of the CNCs is impacted upon BP-functionalization and subsequent graft polymerizations, unmodified and functionalized CNCs were investigated by X-ray diffraction (XRD) experiments (**Figures 6 and S12**). The

diffraction peaks observed for a powder sample of unmodified CNCs at 14.86° , 16.48° , and 22.72° are in agreement with literature data,⁵⁰ and can be assigned to the main reflection planes ((1 $\bar{1}$ 0), (110) and (200)) of cellulose I. All diffraction peaks of cellulose I are also present in the powder diffractogram of CNC-g-BP. Based on the XRD data, crystallinity indices (χ_c) of 97 and 90% were determined for unmodified CNCs and CNC-g-BP by using the method of Segal et al.⁵¹ As this method only consider the (200) plane,⁵² χ_c does not reflect the actual degree of crystallinity, but the value serves to demonstrate that the crystallinity has been hardly impacted when the CNCs were modified with BP. Unfortunately, χ_c of the HNPs could not be determined due to the presence of pronounced amorphous halos, which result from the polymer grafts and overlap with the crystalline reflections. Nevertheless, the main diffraction peak (200) of cellulose I is visible for all materials albeit with reduced intensity due to the dilution effect of the polymer grafts (**Figures 6 and S12**).

Figure 6. X-ray diffractograms of unmodified CNCs, CNC-g-BP and CNC-based OCNs containing 20 wt% of CNCs (top to bottom).

Further examination of the OCN films using polarized optical microscopy (POM) revealed highly homogeneous, birefringent materials with larger anisotropic domains for PHMA-OCNs materials (**Figure 7a,c**). As large-scale phase separation cannot occur and the polymers used are fully amorphous, one can speculate that the anisotropic domains result from the self-assembly of the HNPs in ordered domains. The more pronounced birefringence observed for the PHMA-OCNs materials is consistent with the higher mobility of the low- T_g PHMA, which may allow a better arrangement of the HNPs than in the high- T_g PMMA. POM micrographs of the two-component PMMA/CNC and PHMA/CNC reference nanocomposites containing similar weight fractions of CNCs suggest a lower homogeneity and show less birefringence, presumably, as a result of CNC aggregation (**Figure 7b,d**).

Figure 7. POM micrographs of (a) PMMA-OCNs, (b) PMMA/CNC nanocomposites (c) PHMA-OCNs and (d) PHMA/CNC reference nanocomposites with 10 wt% (top) and 20 wt% (bottom) CNCs. Scale bar = 50 μm .

The thermal properties of the neat polymers, the OCNs, and the two-component reference nanocomposites were investigated by differential scanning calorimetry (DSC) experiments (**Figure 8a**, **Table 2**). The DSC traces of the neat PMMA and PHMA (samples used for the DSC experiments were the free polymers produced in the reactions leading to the 10% HNPs)

exclusively show glass transitions at 98 and -2 °C. These transitions are also seen in the two-component reference nanocomposites. In the case of the OCNs, an increase of the T_g of up to 20 °C, relative to the neat polymer, was observed, which may be ascribed to the reduction of the chain mobility due to their grafting on the CNCs surface.

Table 2. Thermal and mechanical properties of the OCNs based on PMMA- and PHMA-grafted CNCs, the neat polymers, and the two-component reference nanocomposites (NC).

Sample	T_g (°C)		Storage modulus (E' , MPa)		Young's modulus ^c (E , MPa)	Tensile strength ^d (σ , MPa)	ϵ at break (ϵ_b , %)	Tensile toughness (10 kJ.m ⁻³)
	DSC ^a	DMA ^b	-60 °C	25 °C				
Neat PMMA	98	95	4738 ± 58	3509 ± 62	2029 ± 64	67 ± 4	5.3 ± 0.4	297 ± 35
PMMA-OCN-10%	119	124	4728 ± 815	3168 ± 251	2026 ± 109	39 ± 4 ^e	25 ± 1	759 ± 53
NC: PMMA/10% CNC	96	95	5482 ± 213	3658 ± 107	1903 ± 113	36 ± 4	2.8 ± 0.3	61 ± 13
PMMA-OCN-20%	115	136	5227 ± 505	3658 ± 293	2560 ± 150	38 ± 2	1.7 ± 0.2	34 ± 7
NC: PMMA/20% CNC	95	93	6092 ± 115	4319 ± 50	2371 ± 173	37 ± 5	2.2 ± 0.6	57 ± 16
Neat PHMA	-2	1	1770 ± 373	15 ± 4	7.4 ± 0.4	1.8 ± 0.2	425 ± 23	420 ± 71
PHMA-OCN-10%	-1	4	2160 ± 35	59 ± 2	28 ± 1	6.8 ± 0.6	201 ± 22	801 ± 131
NC: PHMA/10 wt% CNC	-2	3	2220 ± 79	48 ± 18	15 ± 1	2.6 ± 0.2	545 ± 29	1077 ± 109
PHMA-OCN-20%	-3	11	2709 ± 208	317 ± 30	99 ± 3	10.4 ± 0.5	79 ± 7	528 ± 66
NC: PHMA/20 wt% CNC	-2	3	2748 ± 137	45 ± 3	30 ± 2	2.9 ± 0.2	248 ± 43	560 ± 121

^aDetermined by DSC. ^bDetermined from the maxima of the shear loss modulus peaks (**Figure S13**). ^cDetermined from the slope of the initial elastic region (between 0.1% and 0.25%) of the stress-strain curve. ^dStrength at break, except ^eStrength at yield. All mechanical data were established by uniaxial tensile tests.

The thermomechanical properties of all materials were investigated by dynamic mechanical analysis (DMA). The results are presented in **Figure 8b-c** and **S13**, and the most relevant

mechanical data established by these experiments are compiled in **Table 2**. All samples display a clear transition from a glassy to a viscous or rubbery regime around the T_g observed by DSC analysis. In the case of the PMMA-based materials (**Figure 8b**), the shear storage modulus (E') in the glassy regime increases slightly upon introducing CNCs from 4.7 GPa (neat PMMA at $-60\text{ }^{\circ}\text{C}$) to 5.2 (PMMA-OCN-20%) to 6.1 GPa (PMMA/20% CNC nanocomposite). As suggested by the DSC results, the T_g 's of the PMMA-OCNs, based on the maxima of the shear loss modulus peaks shown in Supporting **Figure S13** and **Table 2**, are ca. $30\text{ }^{\circ}\text{C}$ higher than those of the conventional composites. As a result, the PMMA-OCNs display at $200\text{ }^{\circ}\text{C}$ an E' of 1.4 and 7.9 MPa, whereas the reference composites are barely measurable. The behavior of the PHMA-based materials is qualitatively similar, with a lower E' and a higher relative reinforcing effect at all temperatures and a much wider (observable) rubbery regime for the OCNs (**Figure 8c**, **Table 2**). The PHMA-OCNs display an extended rubbery plateau, arguably due to massive chain entanglements between the brush-like particles, while the reference composites transition into a viscous melt. In this case, no difference of the low-temperature E' was observed between the PHMA-OCNs and the corresponding two-component reference nanocomposite.

Figure 8. (a) DSC (a) and DMA (b, c) traces of the OCNs based on PMMA- and PHMA-grafted CNCs, the neat polymers, and the two-component reference nanocomposites (NC).

In order to exclude that the improved mechanical properties of the OCNs, in particular the extensions of the rubbery plateaus, are related to covalent-cross-linking between the HNPs during melt-processing, we tested if the OCN films could be redispersed. Gratifyingly, all OCN

films fully dispersed when 0.3 wt% mixtures were stirred in dichloromethane (DCM), chloroform, THF, or acetone for 5 to 20 min (**Figure 9**). We note that neither of these solvents is useful to disperse dried unmodified CNCs. When the concentrations of OCNs were increased to higher than 1 wt%, longer times were needed to reach complete dispersion. The absence of chemical cross-linking is further supported by additional DMA experiments with the PMMA-OCNs, in which the temperature range was extended to 250 °C (**Figure S14**). For both compositions the storage modulus continues to drop as the temperature was raised above 200 °C, while no changes in the transition slope or relaxation in the transition region, which are characteristic of cross-linked networks,⁵³ could be observed.

Figure 9. Suspensions of PMMA- and PHMA-HNPs containing 10 and 20 wt% of CNCs (from left to right) dispersed in different solvents.

The tensile properties of films of the OCNs, the parent polymers, and the reference nanocomposites were investigated by uniaxial tensile tests at room temperature. **Figure 10** shows the stress-strain curves and relevant mechanical data extracted from these experiments are summarized in **Table 2**. The tensile properties of PMMA are known to depend on the strain rate⁵⁴ and temperature,⁵⁵ and the yield strength increases with the strain rate.⁵⁴ The stress-strain curves of PMMA, PMMA-OCNs films, and PMMA/CNC conventional nanocomposites, recorded at a low strain rate of 1.3 mm/min at 25 °C, are presented in **Figure 10a**. PMMA and

the conventional composites all show an initial elastic regime, characterized by a Young's modulus of the order of 2 GPa, followed by brittle fracture at low strain. The tensile strength (67 MPa) and elongation at break (5.3%) of PMMA isolated from the supernatant of the PMMA-HPN-10% synthesis are in good agreement with the data reported elsewhere.^{55, 56} The two-component PMMA/CNC reference nanocomposites with 10 or 20% CNCs (Young's modulus of 1.9 and 2.4 GPa) are embrittled and fracture at lower strain (2.8 and 2.2%) and stress (36 and 37 MPa) than the neat PMMA. Interestingly, the PMMA-OCN-10% displays an equivalent Young's modulus (i.e., 2 GPa) but a very different deformation behavior, yielding at low strain (3.3%) and exhibiting plastic deformation up to a fracture strain of 25%. While the maximum strength (observed at the yield point) of 39 MPa is reduced in comparison to the neat PMMA, the toughness of the PMMA-OCN-10% is doubled. The PMMA-OCN-20% films were stiffer and more brittle than PMMA-OCN-10%, and show a deformation behavior that is similar to that of the PMMA/CNC reference nanocomposite.

In contrast to the glassy PMMA, PHMA displays a T_g below room temperature so that the mechanical properties at ambient temperature are dominated by chain entanglements and are consequently highly strain-rate dependent; tensile tests were thus performed with a high strain rate of 130 mm/min. As expected, the stress-strain curves of the neat PHMA exhibit a very high extensibility (425%) with low Young's modulus (7.4 MPa) and tensile strength (1.8 MPa) (**Figure 10b**). In the case of the reference nanocomposites formed by combination of PHMA and unmodified CNCs, the tensile strength increased to 2.6 and 2.9 MPa, and the Young's modulus to 15 and 30 MPa, upon incorporation of 10 or 20 wt% CNCs, while the elongation at break remained very high (545 and 248%). The PHMA-OCN-10% and 20% samples are much stiffer (Young's moduli = 28 and 99 MPa) and stronger (tensile strength = 6.8 and 10.4 MPa) than the neat PHMA and also the conventional PHMA/CNC nanocomposites, and the extensibility remains rather high (201 and 79%, respectively). Thus, the data show clearly that

the mechanical properties of the new OCNs in the rubbery state are governed by the unique architecture that involves a separation of the CNCs through the attached polymer surface layer, while stress transfer among the particles is enabled by chain entanglements between them, which also depend on the grafting density and the degree of polymerization.⁵⁷

Figure 10. Stress-strain curves of OCNs based on (a) PMMA- and (b) PHMA-grafted CNCs, the neat polymers, and the two-component reference nanocomposites (NC). Data were collected at room temperature.

In order to investigate the elastic behavior of the PHMA-OCNs in more detail, tensile creep tests were performed on PHMA-OCNs and the corresponding two-component nanocomposites under two constant forces. Samples were initially loaded with 0.4 MPa or 1.3 MPa at room temperature using the same strain rate as for static tensile tests (i.e., 130 mm/min). The applied stress was then kept constant for 12 min and the change in length was recorded during this time. The data thus collected is reported as creep strain versus time (**Figure 11**). Interestingly, while most samples show considerable relaxation, PHMA-OCN-20% shows no significant creep at either of the applied loads. An analysis of the traces reveals creep moduli (E_c) of 16 kPa and 24 kPa for PHMA-OCN-20% at fixed loads of 0.4 and 1.3 MPa, respectively. Also PHMA-OCN-10% show very little deformation under a load of 0.4 MPa ($E_c = 4.3$ kPa) but

creep becomes more pronounced when the constant loading is increased to 1.3 MPa ($E_c = 2.0$ kPa). An inspection of the graphs show strikingly that both two-component reference nanocomposites show much more remarkable creep than the PHMA-OCNs. The two-component nanocomposite PHMA/10%CNC is the one that crept the most from all the materials under study, with E_c values of 0.9 and 2.6 kPa for loads of 0.4 and 1.3 MPa, respectively, while the higher CNC content in PHMA/20%CNC reduced creep a bit. The significantly reduced creep seen for the OCNs is likely related to the fact that massive “parallel” chain entanglements between the brush-like particles are at play, and confirms once more that the reinforcement achieved by fabrication OCNs is improved in comparison with conventional two-component nanocomposite due to their architectural design.

Figure 11. Tensile creep curve of PHMA-OCNs materials and the corresponding two-component reference nanocomposites at a constant loading of (a) 0.4 MPa and (b) 1.3 MPa at room temperature.

CONCLUSIONS

In summary, we have shown that polymethacrylate-grafted CNCs, in which the nature and weight fraction of the polymer graft can be easily controlled, are readily accessible functionalizing CNCs with benzophenone moieties and surface-photoinitiated polymerization with PMMA or PHMA. OCNs formed by the assembly of the HNPs -made display properties that are clearly different from those of the corresponding two-component reference nanocomposites. The PMMA-OCNs show the typical behavior of rigid, glassy polymers, with PMMA-OCN-10% being much tougher and PMMA-OCN-20% much stiffer than the neat PMMA and the two-component reference nanocomposites. By contrast, the PHMA-OCNs are rubbery at room temperature, and display a rather high extensibility, while offering higher stiffness and strength than the neat PHMA and the conventional PHMA/CNC nanocomposites. In both platforms, the rubbery regime is considerably extended, and the data suggest that stress transfer, at least above T_g , is dominated by chain entanglements between the hairy CNCs. This approach leads to a significant improvement of the mechanical properties of OCNs containing low T_g grafts. The OCNs are also highly transparent, which supports the conclusion that CNC aggregation can be avoided. The design approach should be general and applicable to other hybrid materials in which a significant mechanical performance is required without compromising the homogeneity of the final product.

EXPERIMENTAL SECTION

Materials. 4-Hydroxybenzophenone, hexamethylene diisocyanate (HMDI), dibutyltin dilaurate (DBTDL), chlorotrimethylsilane, sulfuric acid (H_2SO_4 , 95-98%) and pentane were purchased from Sigma-Aldrich and were used as received. Anhydrous DMF and THF (from Acros), and deuterated chloroform (from Cambridge Isotope Laboratories, Inc.) were used as

received. Methyl methacrylate (MMA) and hexyl methacrylate (HMA) were passed through an activated basic (Brockmann I) alumina column prior to use, in order to remove the inhibitor. Cotton-based CNCs, with an average length of 117 ± 28 nm and average width of 15 ± 2 nm (aspect ratio of 8 ± 2 , both determined by image analysis of TEM images), were extracted from Whatman no. 1 filter paper by sulfuric acid hydrolysis following a previously published protocol.²⁰ The aqueous CNC dispersion that resulted from the process was dried via lyophilization using a VirTis BenchTop 2K XL lyophilizer with a condenser temperature of -78 °C.

Methods. A Bruker Avance DPX 400 spectrometer was utilized to record ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra at 297.2 K. Data were analyzed with the MestReNova software (v 11.0), and all chemical shifts (δ) are reported in parts per million (ppm) relative to the signal of tetramethylsilane (TMS), although referencing was carried out on the basis of the residual solvent signal, i.e., deuteriochloroform (CDCl_3 , δ_{H} 7.26, δ_{C} 77.16).

Fourier-transform infrared (FTIR) spectra were recorded on a PerkinElmer Spectrum 65 spectrometer equipped with an attenuated total reflection (ATR) setup. All spectra were collected in the wavelength range between 600 and 4000 cm^{-1} after 30 continuous scans.

UV-vis absorption spectra in the wavelength range between 250 and 350 nm were recorded on a Shimadzu UV-2401 PC spectrophotometer in anhydrous DMF using quartz cuvettes with a path length of 1 cm. The transparency of films of a thickness of about 0.2 mm was measured using the same spectrophotometer above mentioned in air using a wavelength range between 400 and 800 nm. Films were cut to about 9x20 mm and were placed onto a quartz slide prior to measurement.

The determination of C, H, N and S contents was done by elemental analysis, which was performed at the ETH Zurich, Switzerland. The combustion products resulting from the sample digestion, i.e., CO₂, H₂O, were quantified by infrared spectroscopy to determine C and H contents, respectively. N and S were measured as N₂ and SO₂ by quantification of their thermal conductivity upon burning the sample at 1000 °C.

Mass spectrometry (MS) data for small molecules were provided by external analysis services at the Chemistry Department of the University of Fribourg. Electrospray ionization mass spectrometry (ESI-MS) data were collected on a Bruker FTMS 4.7 T BioAPEXII equipped with a ComiSource 1.0 and run in the positive mode.

An Agilent 1200 series HPLC system was used for size exclusion chromatography (SEC) experiments. The instrument was equipped with an Agilent PLgel mixed guard column (particle size = 5 µm) and two Agilent PLgel mixed-D columns (ID = 7.5 mm, L = 300 mm, particle size = 5 µm) and experiments were conducted at a flow rate of 1.0 mL/min, at 30 °C, and with THF as the eluent. Signals were recorded using an Optilab REX interferometric refractometer, a UV detector (Agilent 1200 series), and a miniDawn TREOS light scattering detector (Wyatt Technology Corp.). A calibration with narrow molecular weight poly(methyl methacrylate) standards (from 550 to 265300 g/mol) was utilized and Astra software (Wyatt Technology Corp.) was used to analyze the data.

Films of the OCNs having a thickness of 0.2 mm were prepared by compression molding the HNPs in a Carver CE press between two metallic plates of 15x15 cm and using 0.2 mm spacers and 7 metric tons of pressure for different times (5 min or 10 sec) and temperatures (160 °C or 130 °C) according to the material under press (see Synthesis Section for more details). Polymethacrylate/CNC nanocomposites with 10 wt% or 20 wt% of CNCs were prepared by casting from THF. Thus, the dry CNCs were dispersed in THF (10 mg/mL) by stirring for 20

h at room temperature before the mixture was sonicated for 3 h in a Sonoswiss SW3H ultrasonic unit. The CNC dispersion was then combined with a solution of the polymethacrylate (PMMA or PHMA) isolated from the supernatant of the corresponding HNPs in THF (30 and 40 mg/mL, respectively), which had been stirred at room temperature for 24 h and heated the last hour at 50 °C. The volume of the CNC dispersion was controlled in order to achieve the desired CNCs concentration in the nanocomposites. The final mixture was stirred for 10 min at 50 °C, sonicated again for 30 min at room temperature in a Sonoswiss SW3H ultrasonic unit, before it was finally cast into a Teflon Petri dish with an inner diameter of 10 cm. The solvent was evaporated in an oven at 50 °C for 48 h. Finally, the dried films were compression molded in a Carver CE press between Kapton sheets at 130 °C or Teflon sheets at 100 °C (for PMMA and PHMA, respectively) for 30 or 15 sec. A pressure of 7 metric tons was applied and spacers were used to adjust the film thickness to 0.2 mm. To minimize moisture absorption the films were then stored at ambient temperature over drierite in a desiccator, until they were used.

X-ray diffraction (XRD) measurements were carried out with a XRD Rigaku Ultima IV. Powder and film samples were loaded onto a rectangular glass sample holder and scans were obtained using CuK α radiation ($\lambda = 1.5401 \text{ \AA}$) under a voltage of 30 kV with a scan rate of 0.5 °/min. The 2θ parameter was varied between 10 ° and 50 ° in steps of 0.02 °.

Differential scanning calorimetry (DSC) measurements were performed under N₂ using a Mettler-Toledo STAR system operating at heating/cooling rates of 10 °C/min in the range from -80 °C to 150 °C and two heating/cooling cycles were routinely applied. The T_g values were determined from the second heating scan, and the midpoint of the transition was reported.

The mechanical properties of the neat polymethacrylates, the OCNs, and the two-component reference nanocomposites were studied using a TA Instrument, DMA Q800. The experiments were performed in a tensile mode with a strain amplitude of 15 μm , at a frequency of 1 Hz and

a heating rate of 5 °C/min in the temperature range from -70 °C to 200 °C or 250 °C using a film tension clamp. The testing specimens were cut in rectangular shape of approximate dimensions: 15 mm x 3.5 mm x 0.2 mm. The data reported were the average of 3 independent measurements and all errors were standard deviations. The storage moduli were determined with a $\pm 1\%$ precision according to the manufacturer specifications. Standard deviations are reported as the variance in a set of samples compared to the average (mean) of the measurement.

Microtensile specimens with an initial overall length of 38 mm in dog-bone shape and of approx. 0.2 mm thickness were cut using a die-cutting tool according to ASTM D1708 from compression-molded films of the neat polymethacrylates, the OCNs, and the two-component reference nanocomposites. All materials were dried under vacuum for at least 2 days before testing. The testing procedure followed the standard method described in ASTM D1708, but no extensometer was used. Tensile measurements were performed at room temperature using a static material testing machine from Zwick/Roell with a 200N Xforce HP load cell. The reported data are averages of 5 independent measurements and all errors quoted are standard deviations. The strain rate was 1.3 and 130 mm/min for PMMA and PHMA containing materials, respectively. The Young's modulus of materials was determined from the slope of the linear portion of the stress-strain curve, more specifically between 0.1 and 0.25 % of strain. This value is subject to accuracy limitations due to the type of specimen used during the measurement (i.e., microtensile specimens). In addition, tensile creep measurements were performed at room temperature using the same machine and specimen type than for uniaxial tensile tests. The measurements were executed at levels of stress (i.e., 0.4 and 1.3 MPa) with an initial strain rate of 130 mm/min. Once the loading was achieved, it was maintained constant and the variations in the length of the specimen were recorded for 12 min. In order to avoid a significant variation in the applied load, the variation of about $\pm 2\%$ was pre-established. The

reported data are average of 3 independent measurements and all errors quoted are standard deviations. The creep modulus was determined as the ratio between the initial stress and the final strain. The confidence interval of all measurements was 0.13% according to the last calibration of the instrument (September, 2019), performed under DIN EN ISO 75001 standard. Standard deviations are reported as the variance there is in a set of samples compared to the average (mean) of the measurement.

The average length and width of unmodified CNCs were determined by images analysis of transmission electron microscopy (TEM) micrographs, using a 0.001 wt% dispersion of CNCs, due to the well-known tip broadening effects on AFM images. The analysis resulted a length of 117 ± 28 and a width of 15 ± 2 (**Figure S1**). It is important to note that even in a well-dispersed suspension of neat CNCs, they are commonly found by pairs, which may alter the width value here determined. Nevertheless, the particle size analysis of CNCs by AFM and TEM are well-established methods to quantitatively determining the dimensions of CNCs. The average height of unmodified CNCs were obtained from images recorded by atomic force microscopy (AFM). First, a freshly peeled mica was functionalized with an aqueous solution of poly-L-lysine by drop-casting (40 μ L). After 5min, the poly-L-lysine was washed off with milli-Q water and dried under a flow of nitrogen. Aqueous CNCs suspensions (0.001 wt%, 40 μ L) were then spin-coated onto the functionalized mica surface at 2000 rpm and subsequently dried under nitrogen flow. The images were acquired with a JPK NanoWizard II, in tapping mode with PPP-NCSTR probes at room temperature and using silicon cantilever. Images were recorded with 2048x2048 pixels of resolution in a 5x5 μ m square. The analysis resulted a height of 6 ± 1 nm (**Figure S15**).

TEM micrographs of unmodified CNCs, CNC-g-BP, and the HNPs were recorded on a Tecnai Spirit transmission electron microscope (TEM, FEI/ThermoFischer, Hillsboro, Oregon,

United States) operating at 120 kV using a 2k Veleta camera (Olympus, Shinjuku, Tokyo, Japan). A bandpass filter (ImageJ, settings 80/3) was applied to reduce noise. 5 μL of sample suspensions (i.e., 0.01 wt% of CNCs in water or CNC-g-BP in DMF and 0.3 wt% of HNPs in chloroform) were spin-coated at 2000 rpm on a previously plasma treated carbon film 300 mesh copper TEM-grids (Electron microscopy science, USA). The samples were allowed to dry at 60 °C overnight before imaging. Optical microscopy images were captured with an Olympus BX51 microscope equipped with a DP72 digital camera and between crossed linear polarizers. Photographs were taken with a Nikon D7100 digital camera fitted with an AF-S DX Zoom-NIKKOR 18-135 mm lens.

The specific surface area (SSA) of CNCs was determined as follows. Considering the average dimensions of cotton CNCs determined by TEM and AFM images, i.e., a width of 15 nm and height of 6 nm, and assuming their density to be equivalent to $1.5 \times 10^6 \text{ g/m}^3$ as reported elsewhere,⁵⁸ and an ellipsoidal cross-section model of cotton CNCs, the SSA was calculated to be $174 \text{ m}^2/\text{g}$. This value is in good agreement with the SSA reported by Lin and Dufresne of $191.2 \text{ m}^2/\text{g}$ using same cross-section model.⁵⁸

The surface charge density of cotton CNCs was determined by conductometric titration according to a well-known procedure.³³ First, a dialyzed suspension of 0.71 wt% CNCs was passed through a previously washed strong acid cation exchange resin (DOWEX Marathon C hydrogen form, Sigma-Aldrich) column. Then, 20 mL of the resultant suspension, containing 1 mM NaCl, was titrated against 0.01M standardized NaOH solution using a SevenCompact Duo S213 pH/conductivity meter. The first equivalence point was assigned to the sulfate half ester groups content (115 mmol R-OSO₃H/kg CNCs), while the second equivalence point corresponds to the carboxylic groups (21 mmol/kg CNCs) (**Figure S2**).

Synthesis.

Synthesis of 4-benzoylphenyl (6-isocyanatohexyl) carbamate (1). Compound **1** was synthesized according to the procedure reported by Biyani et al. with some modifications.³⁴ In a 100 mL three-necked round-bottom amber flask equipped with a reflux condenser and a stirring bar, 4-hydroxybenzophenone (10.0 g, 50.5 mmol) and HMDI (40.5 mL, 252 mmol) were added. The reaction mixture was stirred at 100 °C under N₂ atmosphere for 24 h. After cooling the reaction mixture to room temperature, it was added drop-wise to an excess of cold pentane (150 mL) under mechanical stirring in order to remove any excess of residual HMDI. After 5 min of stirring, the resulting suspension was allowed to settle down and the supernatant (pentane) was decanted. The remaining product was dissolved in 20 mL of ethyl acetate, the solution was filtered, and the liquid phase concentrated under reduced vacuum. The above process was repeated three times in order to remove all residual HMDI. The resulting white viscous liquid was dried in a thermal bath at 50 °C and under high vacuum for 2 days to obtain **1** as a white oily product (12.9 g, 70 %). ¹H NMR (CDCl₃, 400 Hz): δ = 7.78-7.84 (m, 4H, ArH), 7.56-7.61 (m, 1H, ArH), 7.46-7.50 (m, 2H, ArH), 7.24- 7.26 (d, 2H, ArH), 5.14 (br, 1H, -NHC(O)O-), 3.27-3.33 (m, 4H, -NCH₂-), 1.58-1.66 (m, 4H, -(CH₂)₂CH₂-), 1.38-1.46 (m, 4H, -(CH₂)₂CH₂-). ¹³C NMR (CDCl₃, 100 Hz): δ = 195.8, 154.6, 153.9, 137.8, 134.5, 132.5, 131.8, 130.1, 128.4, 121.4, 43.0, 41.3, 31.3, 29.9, 26.4, 26.3. MS (ESI): m/z calc. for C₂₁H₂₂N₂O₄, [M + Na]⁺ 389.15, found 389.2.

Surface functionalization of CNCs with benzophenone (CNC-g-BP). CNC-g-BP was synthesized according to the protocol of Biyani et al.³⁴ In brief, lyophilized cotton CNCs (1.5 g) were dispersed in anhydrous DMF (595 mL) under nitrogen atmosphere by sonication with a Sonoswiss SW3H ultrasonic unit for 3 h. Then, the flask was covered with aluminum foil and compound **1** (3.7 g, 10.2 mmol) and DBTDL (220 μ L) were added. The mixture was stirred at

100°C for 16 h. Then the product was sedimented by centrifugation (10 min at 7000 rpm), the supernatant was decanted, and the product was washed with DMF (2x, 40 mL), and then THF (3x 40 mL). Finally, CNC-g-BP were transferred into an amber glass vial and dried in high vacuum resulting in a pale yellow powder.

Synthesis of polymethacrylate HNPs via surface-photoinitiated grafting of polymethacrylates from the CNCs surface and their self-assembly into OCNs materials.

In a 25 mL Schlenk tube equipped with a stirring bar, CNC-g-BP (60 mg) were dispersed in anhydrous DMF (8 mL) by sonication in a Sonoswiss SW3H ultrasonic unit for 3 h. Then, the amount of monomer necessary to reach the desired CNC content (i.e., 4 or 2 mL of monomer for the synthesis of HNP-10% or HNP-20%) were added to the reaction mixture. The mixture was degassed by the freeze-pump-thaw method. In brief, the mixture was frozen in liquid N₂, the Schlenk tube was evacuated and the vacuum was maintained for 15 min. Then, the tube was closed and the mixture was allowed to thaw in a water bath at room temperature. This process was repeated until no gas bubbles were observed during thawing, but in any case a minimum of three times. Subsequently, the Schlenk tube was placed between two 6 Watt UV lamps irradiating at 365 nm to start the surface-initiated polymerization. After 16 h, the reaction mixture clearly separated in two phases (i.e., liquid and highly viscous gel). The reaction mixture was diluted with THF (about 10 mL), stirred in a vortex mixer until complete dispersion was achieved, before it was transferred into a falcon tube and the HNPs were separated by ultracentrifugation (20 min at 7000 rpm). The supernatant was collected, replaced with THF (20 mL) and the centrifugation/washing process was repeated 3 times. The final white HNP product was dried under high vacuum and the grafted amount of polymer was determined gravimetrically from the amount of CNC-g-BP used and the weight of the dry product isolated (i.e., 823 mg and 332 mg for PMMA-HNP-10% and PMMA-HNP-20%, 530 mg and 317 mg for PHMA-HNP-10% and PHMA-HNP-20%, respectively. See **Table 1** for

more information). Free polymethacrylates were isolated from the supernatant of the synthesis of the HNPs by concentration under reduced pressure and precipitation in cold methanol. The precipitate was collected by filtration, diluted in a minimum amount of THF, and precipitated again in cold methanol. This dilution/precipitation process was repeated three times. Free PMMA was obtained as white solid (1.1 g, 29% and 0.5 g, 28% for free polymers isolated from PMMA-HNP-10% and PMMA-HNP-20%, respectively), while the free PHMA was obtained as a rubbery transparent solid (1.9 g, 56% and 0.6 g, 35% for free polymers isolated from PHMA-HNP-10% and PHMA-HNP-20%, respectively) (**Table 1**).

In order to form OCNs, the dried HNPs (about 300 mg) were redispersed in THF (40 mL) by mechanical stirring, the dispersions were cast into round Teflon Petri dishes with an inner diameter of 77 mm, and dried at 50 °C. After the films had been dried, they were re-processed by compression molding in a Carver CE press at 160 °C or 130 °C for 5 min and 10 sec, depending on the grafted polymer (PMMA or PHMA, respectively) to obtain homogeneous films with a thickness of ca. 0.2 mm. To minimize moisture absorption the films were then stored at ambient temperature over drierite in a desiccator, until they were used.

General procedure for the degrafting of polymethacrylate grafts from HNPs. The degrafting of polymethacrylate grafts from HNPs through selective urethane cleavage was performing based on the procedure reported by Greber and Kricheldorf.⁵⁹ In brief, a 5 mL 2-necked round-bottomed Schlenk flask fitted with a reflux condenser and a stirring bar, the HNPs (150 mg) were dispersed under nitrogen atmosphere in anhydrous THF (4 mL) and vigorous stirring. Then, dry trimethylamine (2.2 equivalent of urethane present in the HNPs) was added and chlorotrimethylsilane (2.2 equivalent of urethane present in the HNPs) was dropwise added. The mixture was placed into an oil bath and stirred at 70 °C for 4 hours. After this time, the mixture was cooled to room temperature, diluted with 5 mL of THF, and the

CNCs were separated by ultracentrifugation. The supernatant containing the cleaved polymer was concentrated under reduced pressure, and then precipitated into 10 mL of cold methanol. The precipitate was dissolved in THF (1 mL) and precipitated into 10 mL of cold methanol. This procedure was repeated 3 times to afford a white precipitate corresponding to the cleaved polymethacrylate (**Table S3**).

ASSOCIATED CONTENT

Supporting information

The supporting information is available free of charge from the **XXX** website at DOI: **XXX**. It includes all Supporting Figures, Tables and calculations employed within this work.

AUTHOR INFORMATION

Corresponding Author

*(C.W.) E-mail: christoph.weder@unifr.ch. Telephone: +41 26 300 9465

ORCID

Sandra Wohlhauser: 0000-0001-5155-1118

Worarin Meesorn: 0000-0003-0554-6910

Lucas Montero de Espinosa: 0000-0003-3616-0287

Justin O. Zoppe: 0000-0002-3599-9227

Christoph Weder: 0000-0001-7183-1790

Notes

The authors declare no competing financial interest

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