COLLOIDAL IONIC SELF-ASSEMBLY BETWEEN ANIONIC NATIVE CELLULOSE NANOFIBRILS AND CATIONIC BLOCK COPOLYMER MICELLES INTO BIOMIMETIC NANOCOMPOSITES

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There are plenty of composite materials in nature with excellent mechanical properties, such as mollusk shells, bone, silk, antler, tooth enamel, or wood, in which hierarchically ordered self-assemblies with a brittle interplay between the hard and soft domains are commonly observed \cite{1-3}, where typically a large fraction of hard and reinforcing aligned segments are surrounded by a soft biopolymer matrix, i.e. proteins or polysaccharides. It would be fascinating to realize how biology creates synergistic material properties combining high stiffness, strength and toughness from mostly relatively simple components. Interestingly, the soft domain often only acts as an advanced binder, allowing crack guidance and deflection and nanoscale lubrication between the spatially closely located reinforcing segments, thus benefiting for toughness. Nanoscale friction reduction under high load enables dissipative relative movement of the reinforcing domains, thus suppressing catastrophic fracture. For instance, proteins and fibroins provide soft separation of inorganic sheets in pearl of naacre, and lignin and hemicellulose are the biological lubricants between the reinforcing native cellulose microfibrils in wood. \cite{3}

Explores of transferring such biological building concepts into synthetic materials within the field of biomimetics resulted in combination of stiffness, strength and toughness with lightweight structure \cite{4-5}. The main challenge is to construct composites with high fractions of reinforcements that are hierarchically ordered into hard/soft mesostructured materials. Most importantly, we have to find pathways, components and compositions, which allow synergetic properties beyond the common rule of mixtures. A specific challenge is to identify routes for dissipative polymer layers between the reinforcements. In terms of efficient materials synthesis, we also need to develop strategies that allow their preparation with energy-efficient and rapid processes. The most elegant approach is based on assembly of the components as encoded by their architecture to overcome the laborious sequential deposition techniques or multi-step templating approaches. Recently we demonstrated such a progress for technologically-relevant naacre mimics based on the self-assembly of core-shell (hard/soft) polymer-coated nanoclay sheet-like building blocks. \cite{6-7}

In this study, the hypothesis was to overcome the nanoscale dispersion problem and to produce hard/soft biomimetic composites by ionically complexing two oppositely charged colloidal level objects, i.e., negatively charged nanofibrillar cellulose and positively charged block copolymer micelles with soft cores. We hypothesized that the micelles could promote dissipation of fracture energy upon deformation, lubrication between the NFC domains, and potentially even allow sacrificial
bonding interactions.\[8-9\] Previous literature demonstrated that, in the molecular (smaller) length scale, oppositely charged polyelectrolytes can easily mutually complex or adsorb onto surfaces through electrostatic attraction, a phenomenon widely used for the electrostatic layer-by-layer growth of lamellar composite materials.\[10\] In our work, we use an amphiphilic diblock copolymer that carries one cationic, water-soluble function and another hydrophobic part with softness and deformability as a functionality. Such polymers are commercially available or can be synthesized in a large range of compositions and polymer sequences, thus giving rise to a platform concept. Herein, we studied the composite materials with three different block copolymers and nanocellulose and present a facile ionic self-assembly between fibrillar and spherical colloidal objects towards biomimetic nanocomposites with majority hard and minority soft domains based on anionic reinforcing native cellulose nanofibrils and cationic amphiphilic block copolymer micelles with rubbery core. The concept is in view of ionic complexation of carboxymethylated nanofibrillated cellulose (NFC, or also denoted as microfibrillated cellulose, MFC) and micelles formed by aqueous self-assembly of quaternized poly (1, 2-butadiene)-block-poly (dimethylaminoethyl methacrylate) (PB-b-PDMAEMAq) and two different molecular weight of polyisoprene (1, 4 addition)-block-poly (2-vinylpyridine) (PI-b-P2VP) with high fraction of the NFC reinforcement. Such amphiphilic block copolymers self-assemble in polar solvents, forming colloidal nanoparticles (micelles) \[11\] where the hydrophobic segments collapse into a core, \[12\] surrounded by a stabilizing corona of hydrophilic chains. We aimed at a beneficial lubricating effect of the hydrophobic rubbery polybutadiene/polyisoprene phase because of its low glass transition temperature ($T_g \approx -15^\circ C$ and $-60^\circ C$, respectively) and hence soft character at room temperature. The cationic part of the block copolymer serves as a binder to NFC whereas the hydrophobic rubbery micellar cores are designed to facilitate energy dissipation and nanoscale lubrication between the NFC domains under deformation. As the concept allows wide possibilities for tuning, the work suggests approaches for nanocellulose-based biomimetic self-assembled nanocomposites combining high toughness with stiffness and strength. We will present detailed results on the adsorption process and complex formation toward micelle/NFC colloidal complexes, along with the structure of the resulting nanocomposites after drying. The adsorption of block copolymer micelles onto nanocellulose is indicated by atomic force microscopy imaging, and fluorescent optical microscopy. The physical properties are presented using electron microscopy, thermal analysis, and mechanical testing.

**Experimental Materials**

Cellulose nanofibrils were disintegrated from bleached sulphite pulp by using a high-pressure fluidizer (Microfluidizer M-110EH, Microfluidics Corp., Newton MA) at Innventia, Stockholm, Sweden (formerly STFI-Packforsk) essentially following the procedures described in ref \[13\]. The anionic NFC was prepared from bleached sulfate softwood dissolving pulp (Domsjö ECO Bright). The pulp was carboxymethylated in a chemical pretreatment step and then run once through the microfluidizer.\[14-15\] The initial NFC dispersion concentration was 1.87 wt%. Poly (1,2-butadiene)-b-poly(2-dimethylaminoethyl methacrylate) (PB-b-PDMAEMA) was prepared by anionic polymerization in THF with molecular weight $M_n = 35,200$ g/mol with $M_n/M_w = 1.06$ with 80 wt % of PB and 20 wt % of PDMAEMA blocks. \[16\] Two different molecular weights of polyisoprene (1,4 addition)-b-poly (2-vinyl pyridine) (PI-b-P2VP) were purchased from Polymer Source Inc. (Canada). One had the molecular weight $M_n = 12,500$ g/mol with $M_n/M_w = 1.05$ with 53 wt% of PI and 47 wt% P2VP (denoted as PI-b-P2VP12.5) and the other one had the molecular weight $M_n = 31,400$ g/mol with $M_n/M_w = 1.03$ with 61 wt% PI and 39 wt% P2VP (denoted as PI-b-P2VP31.4). $N$, $N$-dimethylformamide (DMF) ($\geq 99.9\%$), Tris(hydroxymethyl)aminomethane (TRIS) with pH 8.3 and Nile Red dye were purchased from Sigma Aldrich (Germany).

**Quaternization and preparation of block copolymer micelles in water**

The block copolymers were dissolved in DMF to give a 2 g/L solution, which were deoxygenated by bubbling with nitrogen gas. A five-fold excess of methyl iodide, compared to the nitrogen content of block copolymer was added with a syringe to the polymer solution and the quaternization reaction was kept in water bath at 50 °C for 24 hours. \[16\] After quaternization, the polymer solution was filled in a dialysis tube (Spectra/Por 3500Da MWCO, Canada) and dialyzed against Milli-Q water in a 10 liter...
beaker for 36 hours. The water was refreshed once during dialysis. This process yields spherical micelles with a PB (or PI) core and a cationic polyelectrolyte corona of quaternized PDMAEMA (or P2VP), termed PB-b-PDMAEMAp (or PI-b-P2VPqt) (to be shown later). The polymer is selected to have three large different weight fraction of the soft hydrophobic polybutadiene or polysisoprene block coupled to a comparatively short cationized binder segment. The presence of large soft domains was expected to be beneficial to facilitate energy dissipation in the resulting composite materials. The amphiphilic balance of the diblock copolymer was designed to approach the so-called crew-cut regime, but still kept in a ratio so that the formation of spherical micelles is favored in contrast to worm-like ones or vesicles. [12]

Preparation of nanofibril dispersion for AFM
The NFC dispersion was diluted to 1.67 g/L and ultrasonicated using a micro tip (Branson Digital Sonifire) for 10 min at 25% amplitude. After ultrasonication the dispersion was centrifuged at 10400 rpm for 45 min. The clear supernatant fraction was used to prepare ultrathin films on substrates. The end concentration of anionic fibril dispersion was 1.2 g/L and it was further diluted to the 0.2 g/L at the desired pH.

Preparation of nanocomposites
Typically 100 µL of Nile Red solution in acetone with a concentration of 0.5 g/L were added to 10 mL block copolymer solution in order to stain the micelles with a fluorescent dye. The hydrophobic dye migrates into the core of the micelles. After sonication for 30 min, the solution was left open overnight to evaporate the acetone. The pH of the micellar solution was adjusted to 8.3 using 1mM Tris buffer before mixing with NFC. Different mass ratios of NFC (pKa ≈ 4.8) [14] and block copolymer (1:1, 2.5:1, 5:1, and 10:1) were prepared via mixing with an Ultra-Turrax (IKA, T25 Basic) at 11000 rpm for 2 min. Subsequently, all entrapped air bubbles were removed by centrifugation at 2500 rpm for 5 min. Finally, composites were prepared by removing the water using vacuum filtration with 1.2 µm Millipore filter membranes.

Atomic Force Microscope Imaging (in air and water)
AFM imaging in tapping mode was used to characterize the quaternized block copolymer micelles in never-dried state adsorbed onto freshly cleaved mica and to characterize the morphology of the adsorbed block polymers on NFC surface in air. A Nanoscope IIIa multimode scanning probe microscope (Digital Instruments Inc., Santa Barbara, CA) was used. For imaging in air, silicon cantilever (NSC15/AIBS) delivered by MicroMasch, Tallinn Estonia, with a driving frequency around 300 - 360 kHz were used. The radius of the tip according to the manufacturer was less than 10 nm. A liquid cell was used for imaging the micelles in never dried state. Soft silicon cantilever with a driving frequency between 7 - 11 kHz (Noncontact ultrasharp silicon cantilevers NSCS12, NT-MDT) were used. The image analysis was done with help of Scanning Probe Image Processor (SPIP) software (version 4.5.3, Image Metrology, Lyngby, Denmark). Only flattening was performed, no other image processing was applied.

Optical Microscopy
A Leica DM4500 microscope (Leica Microsystems GmbH, Germany) was used to detect the binding of micelles on NFC in both transmission and fluorescence mode.

Field-Emission Scanning Electron Microscopy (FE-SEM)
A JEOL JSM-7500 FA field-emission scanning electron microscope was used to characterize the morphology of composites and determine the cross section thickness of composites. A thin Pt/Au layer was sputtered onto the specimens before imaging.

Transmission Electron Microscopy (TEM)
TEM imaging was performed with a JEOL JEM-3200FSC TEM operating at liquid nitrogen temperature. Zero-loss filtered images were acquired at an acceleration voltage of 300 kV with a Gatan Ultrascan 4000 camera in bright field mode. The double bonds of the polybutadiene segments of the micelles were stained using OsO₄ prior to imaging. For cryogenic TEM, a plasma-treated holey carbon grid was placed into a FEI Vitrobot and a small droplet of NFC dispersion was applied onto it. After blotting, the grid was plunged into a liquid cryogen of propane/ethane (1/1) and transferred into the TEM microscope under cryogenic conditions and imaged close to liquid nitrogen temperature.

Thermal Gravimetric Analysis (TGA)
A Mettler M3 TG50 thermo-balance gravimetric analysis (Mettler Intrumente AG., Switzerland) was used to determine the thermal stability of
composites. All samples were heated from 40 °C to 500 °C at a heating rate of 10 °C/min in air.

**Mechanical Testing**
Mechanical tests were performed on a DEBEN minitester equipped with a 200N load cell. All measurements were carried out at room temperature with a humidity of 30-60%. The specimen had dimensions of 2 cm x 2 mm x 70-200 µm. The exact specimens’ width and cross section thickness were determined by optical or scanning electron microscopy. At least five specimens were tested for each sample. A nominal strain rate of 0.5 mm/min was used. Digital speckle photography (DSP) was used to monitor the displacement of the sample upon applying stress. The speckle pattern was sprayed onto the sample surface. The Aramis Software of GOM GmbH (Germany) was used for digital image correlation and data computation.

**Results and Discussion**
The characterizations of the two kinds of colloidal level components were summarized in Figure 1. And the combination of two components has shown in optical microscope images. (Fig. 1b) The NFC in aqueous is displayed in the cryo-TEM image in Figure 1a. The micrograph indicates micrometer-long NFC nanofibrils with an average diameter at 7.5 nm (standard deviation = 2.3 nm) and a length distribution in the range of a few microns. The carboxymethylation of the pulp during the processing leads to a degree of substitution of DS ≈ 0.1 in the nanofibrils [14] and a charge density of ca. 575 µeq/g. The diblock copolymers after quaternized spontaneously form micelles by self-assembly in aqueous medium [17], see Figure 1c (PB-b-PDMAEMAq selected). The spherical nature of the micelles was further confirmed by liquid AFM imaging of never dried micellar dispersion adsorbed onto freshly cleaved mica in water (Figure 1c). A rather uniform size of spherical micelles can be observed. The diameters measured from AFM images were found to be 80 - 100 nm and the height was around 11 - 14 nm (Figure 1d). Considering the overestimation of the diameter due to tip deconvolution of the AFM-tip, this dimensions point to some flattening of the micelles for the soft character of the polybutadiene core block with a low glass transition temperature, $T_g$ ≈ -15 °C.

For the sake of controlling the composite structure, we need to understand the binding between the cationic block copolymer micelles and the anionic NFC nanofibrils. Both colloidal objects exist opposite charges and thus we expect a tight binding via ionic complexation, similar to interpolyelectrolyte complexes at the smaller molecular length scale. The main driving force for the complexation in both molecular and colloidal cases is the entropic gain due to the counterion release. Since anionic NFC is a weak polyelectrolyte with a pH-dependent ionization of the carboxylic acid groups, thus an increase of pH favors the dissociation and complexation. Therefore, we bind the block copolymer micelles onto the NFC nanofibrils with a TRIS-buffered solution at pH = 8.3. It is sufficiently above the pKa value of typical carboxylic acids (3.0 – 5.5) [18] and that of our NFC (4.8) [14] thus ensures a near quantitative degree of ionization to promote the complexation. Note that depending on the ratio of micelles to NFC fibrils, different binding scenarios can be imagined. At low content of micelles, the micelles can act as multifunctional binders between several NFC fibrils. On the other hand, if the micelles are considerably in excess, individual NFC fibrils are assumed to be coated by a layer of micelles in the aqueous medium. We expect this to be important in the final packed assembled composites to promote nanoscale lubrication between the NFC domains then allowing toughening of the composites. The binding of the micelles to NFC is visible from fluorescence microscopy upon incorporation of a hydrophobic fluorescent dye (Nile Red) into the non-polar core of the micelles (Figure 1b). The fluorescence micrograph in aqueous medium depicts fibrils and fibrillar aggregates, indicating a strong coordination of the dye-stained micelles with the NFC fibrils. The high contrast between dye-stained fibrils and non-fluorescing background demonstrates a strong affinity as free micelles would diminish the contrast. Due to the diffraction limit, it is not possible to resolve the individual nanoscale fibrils with their true diameter. Since the NFC is in large excess compared to the micelles (10/1 w/w), some clustering of nanofibrils into elongated aggregates can be observed at this particular ratio. An undesirable aggregation into large spherical agglomerates does not occur, most likely owing to the stiffness of the NFC fibrils.

We focus on the biomimetic compositions with a large fraction of the reinforcing NFC domains as separated by a small weight fraction of soft dissipative block copolymer domains. Therefore, we chose the NFC/micelles compositions in a range of 10/1, 5/1, 2.5/1 and 1/1 w/w. The composites are translucent on the macroscale having similar
appearance as pure NFC film (not shown in this paper). This indicates the absence of macroscopic phase separation of NFC and block copolymer, which would lead to opaque appearance. Obviously, the macroscopic phase separation is prevented by attractive ionic binding between the oppositely charged nanofibrillar and spherical colloids. Note that a simple mixing of polybutadiene or polyisoprene and NFC would lead to macroscopic phase separation, poor interfacial bonding and little interaction between both components. Scanning electron microscopy shows a nanofibrillar network structure (Figure 2a) and a layered internal structure on the mesoscale (Figure 2b). The NFC/PB-PDMAEMAq colloidal complexes are orientated in a random plane fashion to form a web-like fibrous network along the substrates during the vacuum filtration. Some holes and protuberances are shown in the fracture surface between the various nanocellulose layers, thus indicating that the intralaminar NFC interaction is stronger than the interlaminar one. Although the composites may have a certain limited void-content, previous work indicates that this is not critical to mechanical performance. [19] This is a consequence of the random-in-plane orientation distribution of NFC. We can find similar layered structures for all studied NFC/micelle composites. Thus only few selected examples are displayed in this work.

To investigate the structural details down to the nanoscale, we used cross-sectional TEM, where the contrast of the PB domains of the block copolymer was increased via selective staining of the double bonds with OsO4. The TEM micrograph for a NFC/PB-b-PDMAEMAq block copolymer nanocomposite is presented in Figure 2c and 2d, showing approximately periodic structure with alternating NFC and PB-b-PDMAEMAq domains with a periodicity of around 160 - 200 nm. Interestingly, the micrographs also indicate rather equally-spaced darker spheres within the PB-b-PDMAEMAq domains. Since the darker parts in the micrograph originate from the stained PB double bonds, we conclude that the PB-b-PDMAEMAq micelles are observed also in the composites upon drying and are aligned in a pearl-necklace fashion on NFC strands (see Figure 2c). This observation also coincides with the AFM imaging of the intact micelle layer in the NFC web (Figure 2c). Figure 2e shows roughly globular structures on the NFC, where the diameter is in the range of 80 - 150 nm and height in the range of 8 - 14 nm (Figure 2f).

Such structures point towards adsorbed micelles on the NFC network layer. Although the micelles have soft cores with low PB glass transition temperature (ca. -15 °C), we do not observe evidence of opening and film formation of the micelles on the surface. This result has major implications for the composite structure and behavior.

The micellar shape is retained although the low glass transition temperature of the PB part could in principal allow for sufficient dynamics and a disintegration of the micelles. Note that the dark domains coincide well with the size range of the micelles, especially considering that, staining with the bulky OsO4, flattening and microtome cutting can increase the observed size in the dried state. The micelles are well separated and do not form a continuous film. Since the periodicity perpendicular to the lamellae is closer to the diameter of a micelle than to individual NFC fibrils, it is likely that the micelles dominate the formation of the assembly at this length scale.

The thermal stability of the NFC/micelle composites was investigated by thermogravimetric analysis (TGA, Figure 3). The selected series of composites and pure NFC have similar thermal stability. The onset of degradation for all composites starts around 260 °C and exhibits a second degradation step just above 400 °C. This is in the typical range of cellulose paper with a degradation range of 230 – 360 °C. [20-23] By adding block copolymer up to 5/1 w/w of NFC/micelles do not change the thermal stability of NFC and the composite materials.

The stress-strain curves, work of fracture, Young’s modulus and strain-to-break of the composites series are indicated in Figure 4 and summarized in Table 1. For pure NFC paper, the Young’s modulus can reach 12.5 GPa (Table 1), which is a commonly found value for nanocellulose paper. [19] Upon small addition of micelles the Young’s modulus normally decreases (Table 1). For PB-b-PDMAEMAq composites series their stress-strain curves are very similar, indicating an only minor influence of the amount of PB-b-PDMAEMAq, see Fig 4a. Still, both curves are remarkably different to the pure NFC, thus pointing to different interaction between the nanofibrils. Further increase of PB-b-PDMAEMAq towards the composition 1/1 leads to a decrease of the modulus to 6.2 GPa. The modulus decreases as expected as a function of added softer PB domains. The same tendency has seen in the other two micelle composites materials which have PI softer domains. And also for the tensile strength and strain-to-failure level mostly reduced with increasing the amount of micelles in the composite.
materials. This trend is especially shown in composites with short block polymer PI-b-P2VPq (12,500 g/mol).

Nevertheless, we find strong nonlinearities when looking at stress at break, maximum extension and in particular at toughness as a function of the composition with polymer PB-b-PDMAEMAq (Figure 4a). Toughness can be defined as the work of fracture as obtained from the area under the stress-strain curve. [24] We identify a synergetic behavior of the mixture at a ratio of 2.5/1. The extension at break and also the toughness are reproducibly 2-3 times higher than those of the other compositions. Even compared to the pure NFC, we still find a more than 20% higher strain-to-failure. The suppressed brittleness of this synergetic mixture also allows reaching a high strength. We tentatively ascribe the synergy to the PB-b-PDMAEMAq micelles between the reinforcing NFC domains, where the cationic micellar shells serve as anchors to create assembled domains, while the soft PB part dissipates energy and allows friction reduction between the reinforcing NFC domains under stress.

It has been demonstrated in literature that the crack propagation in the nanofibrillated TEMPO-oxidized celluloses with hydroxypropylcellulose matrix is similar to fracture-toughened intercalated clay-epoxy nanocomposites, [25] in which cracks follow a torturous path. Within the context of our work, we suggest that the soft PB phase serves two purposes. First, it enables a more effective crack deflection at the hard/soft (NFC/PB-b-PDMAEMAq) interface as compared to polymers with high \( T_g \) and therewith it extends the crack path. [2] Additionally, the lubrication of the nanoscale fibers by synthetic block copolymer with low \( T_g \) can favor a fiber pullout vs. a fiber fracture and henceforth contribute a second attractive benefit for toughening. Though the PI parts are even more softer than PB (\( T_g \approx -60^\circ C \)) but not benefit for the reinforcement. It hints that with a high molecular weight block copolymer (35,200 g/mol) and a soft core (\( T_g \approx -15^\circ C \)) gives the synergy effect for composites materials. In order to find the optimal block copolymers and compositions which give the best mechanical properties more work has to be done in the future.

We have performed a new, facile and versatile platform concept to complex native nanofibrillated cellulose with block copolymers via non-covalent interactions, thus allowing assembled biomimetic nanocomposites that contain a large fraction of NFC reinforcements separated by rubbery domains. The concept is demonstrated using anionically charged carboxymethylated NFC as ionically complexed using quaternized poly(1,2-butadiene)-block-poly(dimethylaminoethyl methacrylate) block copolymer (PB-b-PDMAEMAc) or polyisoprene (1,4 addition)-block-poly (2-vinylpyridine) (PI-b-P2VP) micelles, possessing a cationic polyelectrolyte corona and a rubbery micelle core. The colloidal nanofibrils and colloidal micellar spheres complexation prevents macroscopic phase-separation and leads to composites with an alternating nanoscale hard/soft architecture. As a consequence of the improved mesoscale order, we identify a synergetic performance of the components beyond the simple rule of mixture with one polymer. For a ratio of NFC/PB-b-PDMAEMAc of 2.5/1 w/w, significantly larger strain and toughness could be achieved than in the other studied compositions, potentially due to the nanoscopic control over fracture energy dissipation and the interfibrillar lubrication between the NFC domains by using low \( T_g \) amphiphilic block copolymers. Since block copolymer structures can be widely tuned for different molecular weights, block constituents and architectures, we expect great possibilities to pursue biomimetic nanocomposites with significantly increased fracture toughness, while maintaining stiffness and strength.

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References


Fig. 1. Morphology of starting material and adsorption of quaternized micelle onto anionic NFC: (a) Cryo-TEM micrograph showing anionic NFC nanofibrils in aqueous medium. (b) Fluorescent optical microscopy images in aqueous medium upon mixing an aqueous dispersion of NFC with PB-b-PDMAEMAq micelles in a ratio of 10/1 w/w. (c) Liquid AFM height image of PB-b-PDMAEMAq micelles adsorbed onto mica imaged in water (z-range 30 nm). The concentration of the block copolymer was 0.2 mg/L. (d) Height profile corresponding to the section analysis shown in (c).

Fig. 2. Structures of NFC and micelle composites: (a) SEM images of the top surface and fracture surface of nanocomposites for the NFC/PI-b-P2VPq31,4 sample with the weight fraction 5/1 w/w and NFC/PB-b-PDMAEMAq sample with the weight fraction 2.5/1 w/w (b). Since all composites have similar structure in SEM and these two are selected as examples. (c-d) A cross-sectional TEM image of NFC/PB-b-PDMAEMAq sample with the weight fraction 2.5/1 w/w and section analysis. (e) AFM height image (size 2×2 µm) of adsorbed PB-b-PDMAEMAq micelles onto the NFC film imaged in air (z-range 15 nm). (f) Height profile of the section analysis indicated by the line in image (e).

Fig. 3. TGA analysis of the thermal degradation of pure NFC film and NFC/micelle composites materials in the weight fraction of 5/1 w/w. P1, P2 and P3 denoted to PB-b-PDMAEMAq, PI-b-P2VPq (31,400 g/mol) and PI-b-P2VPq (12,500 g/mol), respectively.
Fig. 4. Stress-strain curves for NFC and micelle composites. (a) NFC/PB-b-PDMAEMq (b) NFC/PI-P2VPq (31,400 g/mol) (c) NFC/PI-b-P2VPq (12,500 g/mol).

Table 1. Tensile Properties of the NFC/micelles composites where the fraction of rubbery block copolymer increases toward the top. Data refer to mean values of pure NFC and with micelles composites and corresponding standard deviations in brackets of at least five samples.

<table>
<thead>
<tr>
<th>mass ratio (MFC/polymer)</th>
<th>Young’s Modulus (GPa)</th>
<th>Tensile strength (MPa)</th>
<th>Strain-to-failure (%)</th>
<th>Work of fracture (MJ/m²)</th>
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</thead>
<tbody>
<tr>
<td>MFC 1:0</td>
<td>12.5 (1.0)</td>
<td>202.2 (21)</td>
<td>6.8 (1.4)</td>
<td>9.8 (3.0)</td>
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<td>MFC/PB-b-PDMAEMq 1:1</td>
<td>6.2 (0.2)</td>
<td>95.8 (1.2)</td>
<td>4.6 (0.5)</td>
<td>3.3 (0.5)</td>
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<td>MFC/PB-b-PDMAEMq 2.5:1</td>
<td>7.3 (1.0)</td>
<td>165.2 (21.8)</td>
<td>9.1 (0.7)</td>
<td>10.5 (2.1)</td>
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<tr>
<td>MFC/PB-b-PDMAEMq 5:1</td>
<td>11.1 (1.2)</td>
<td>144.8 (16.2)</td>
<td>2.4 (0.5)</td>
<td>2.5 (0.8)</td>
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<tr>
<td>MFC/PB-b-PDMAEMq 10:1</td>
<td>10.4 (1.2)</td>
<td>166.2 (13.7)</td>
<td>4.5 (0.9)</td>
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<td>MFC/PI-b-P2VPq31,4 1:1</td>
<td>5.3 (0.8)</td>
<td>65.7 (5.1)</td>
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<td>1.0 (0.4)</td>
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<td>9.9 (0.7)</td>
<td>144.6 (10.7)</td>
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<td>2.7 (1.0)</td>
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<tr>
<td>MFC/PI-b-P2VPq31,4 5:1</td>
<td>11.1 (1.2)</td>
<td>164.5 (8.3)</td>
<td>3.7 (0.7)</td>
<td>4.5 (1.1)</td>
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<td>MFC/PI-b-P2VPq31,4 10:1</td>
<td>12.6 (8.8)</td>
<td>196.8 (31.6)</td>
<td>4.4 (0.3)</td>
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<tr>
<td>MFC/PI-b-P2VPq12,5 1:1</td>
<td>9.5 (0.6)</td>
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<td>1.9 (0.06)</td>
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<td>MFC/PI-b-P2VPq12,5 2.5:1</td>
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<td>118.6 (13.2)</td>
<td>2.3 (0.6)</td>
<td>1.6 (0.6)</td>
</tr>
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<td>MFC/PI-b-P2VPq12,5 5:1</td>
<td>10.1 (0.8)</td>
<td>129.3 (9.7)</td>
<td>2.2 (0.7)</td>
<td>1.9 (0.8)</td>
</tr>
<tr>
<td>MFC/PI-b-P2VPq12,5 10:1</td>
<td>13.6 (1.7)</td>
<td>165.3 (17.9)</td>
<td>2.0 (0.2)</td>
<td>2.2 (0.4)</td>
</tr>
</tbody>
</table>