# Systematic study of the nanostructures of exfoliated polymer nanocomposites

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# ABSTRACT

High-performance bioinspired materials have shown rapid development over the last decade. Examples are brick-and-mortar hierarchical structures, which are often achieved via solvent evaporation. Although good properties are claimed, most systems are composed of stacked or intercalated platelets. Exfoliation is a crucial step to give ultimate anisotropic properties, *e.g.* thermal, mechanical and barrier properties. We propose a general framework for all the various types of micro-scale structures that should be distinguished for 2D-filler nanocomposites. In particular, the exfoliated state is systematically explored by the immobilization of montmorillonite platelets via (gelatin) hydrogelation. Scattering techniques were used to evaluate this strategy at the level of the particle dispersion and the regularity of spatial arrangement. The gelatin/montmorillonite exfoliated nanostructures are fully controlled by the filler volume fraction since the observed gallery d-spacings perfectly fall onto the predicted values. Surprisingly, X-ray analysis also revealed short- and quasi long-range arrangement of the MMT at high loading.

# **KEYWORDS**

Gel, Polymer nanocomposites, Platelets, Exfoliation, X-ray, Order-disorder, Immobilization

Natural materials are intriguing as they can display complex, highly regular nano- to macro-architectures, which are fabricated at ambient conditions.<sup>1</sup> A common example is the "brick-and-mortar" micro-structure of nacre, which inspired the design of polymer composites for the past decades.<sup>2</sup> In essence, the hybrid nacre-like materials consist of highly ordered inorganic platelets which are bound in a lamellar manner. Several mimetic and bioinspired materials have been constructed either from suspension/melt mixing (top-down) or in-situ techniques (bottom-up).<sup>2–4</sup> The design of hierarchically structured composites from 2D nanoparticles has already been extended to clay silicates, (reduced) graphene oxide, boron nitride, MXenes, dichalcogenides, among others.<sup>5–8</sup> In general, the anisotropic materials show desired thermal, mechanical, conductive, and barrier properties. For instance, they combine excellent stiffness and toughness.<sup>4,9,10</sup> Nevertheless, in order to achieve tailored structural properties, the right choice of building blocks and fabrication strategy become important.

Processing conditions can dramatically influence the obtained hierarchical structure. Several processes have been reported, such as suspension casting, doctor blading, vacuumassisted self-assembly, melt compounding, in-situ polymerization, etc.<sup>2,11</sup> About a decade ago, bioinspired polymer nanocomposites saw much advance with water-based and largescale methodologies, akin to paper-making.<sup>9,10,12,13</sup> Since then, the focus has shifted to the optimization of polymeric core-shell particles, followed by solvent removal.<sup>5,6,14</sup> The ideal conditions to realize aligned assemblies have been extensively adjusted. Nevertheless, these often are formed by intercalated structures, with restacking still observed at higher filler concentrations.<sup>2,15–20</sup> Above all, these efforts have led to a great number of mechanisms being proposed for polymer-particle association and (re)organization.

The main drive behind new technologies is the same: surpassing the limits of measured anisotropic properties over the in-plane arrangement. As a strategy, the logical approach should be to keep the high aspect ratio of 2D filler (exfoliated state) and, if feasible, aim for high loadings. This would ensure the nanoscale properties, and functionalities, to be translated as much as possible to the bulk material. However, as previously discussed, composites do not frequently achieve the formation of exfoliated nanostructures, with limited polymer intersection, although an exception might be made for samples from Layer-by-Layer or multilayer deposition approaches<sup>21,22</sup>, which however are mainly of scientific interest. Furthermore, many applied studies exclusively investigate whether there is polymer intercalation onto the integral layers of the 2D filler, which is accompanied by a synergetic improvement of properties. High filler contents, i.e., above 20 wt.%, are equally unexplored. Thus, the quality of (nano)dispersion needs more systematic evaluation, guiding the way to better methods and ultimate properties from all exfoliated samples.

Finally, there is still lack of consensus about the classification of composite microstructures, where the difference between intercalated and exfoliated states remains elusive. For instance, highly interlocked systems can also show a certain level of regularity due to the particles' flat geometry. In other words, there can be a positional order-disorder transition with filler concentration. So far, we have seen not seen a complete overview of the combined effects of the level of 2D material dispersion and associated positional order. In Chart 1, we illustrate how this coupling (dispersion and regularity) will lead to many more composite nano- to meso-phases. The orientational order of dispersed phase is for now ignored, even though alignment will clearly have an influence on the anisotropic properties. Thus, we introduce a general framework on all the possible phases of dispersion and positional order present in polymer/platelet composites.

### 1. Nanostructure classification based on 2D particle dispersion and positional order

# 1.1.1. Particle dispersion

Depending on the level of initial dispersion and system compatibility, 2D materials (platelets or sheets) can yield exfoliated (E), intercalated (C) or stacked (S) composite structures. Restacking into aggregates, or tactoids, is one of the most frequently addressed issues in nanocomposite preparation and processing.<sup>23-26</sup> When platelets are stacked (S) they are phase separated from the polymer matrix, indicating chains do not diffuse in between the individual layers, which remain immiscible. In X-ray diffraction, the gallery d-spacing, door, corresponds to the initial bulk material. In the specific case of sheets, additional phenomena such as wrinkling and fold-overs also come into play.<sup>27</sup> Further on, when the 2D-filler is considered intercalated (C), there is still aggregation, but an increase in the d-spacing between integral layers is observed. This is attributed to polymer diffusion or expansion of the gallery. The distance between 2D units is enlarged and, most importantly, fixed. In the case of exfoliation (E), sometimes also called delamination, there is not a fixed length between the single layers but an average spacing value. This also means the net interparticle force between the individual colloids is repulsive. A point often overlooked is that the truly dispersed state, E, only happens when there is homogeneous distribution of the 2D material in the polymer matrix. Therefore, the mean spacing of 2D units must be dictated by the total volume of separated particles. In this context a criterion for exfoliation based on some required distance is not appropriate, as the distance depends on the filler volume fraction.

# 1.1.2. Positional order-disorder

In addition to the dispersion, nacre-like composites with high aspect ratio particles can also develop a degree of periodicity. Considering samples from suspension or melt mixing, this is rare in contrast to the commonly attainable orientational order of anisotropic particles.

Nevertheless, regularity can happen in a few systems, especially if there are self-assembling molecules and particularly towards higher 2D-filler fractions. When a structure is disordered (d), there is no regular correlation between the position of individual 2D particles, however delaminated or within a stack. Short-range ordered (r) systems will show some localized structural positioning. The extent of periodicity is determined by a correlation length, calculated from fitting a Lorentz-type function over scattering profile. This length is distinct from the platelet gallery spacing (dispersion). For the special cases of (quasi) long-range order (1), the materials' structure will resemble that of a 1D crystal. In practice, these long range ordered structures will have a finite size or have a finite correlation length domain length, representing the extent of periodicity of a pile of regularly spaced platelets. The finite domain length is commonly fitted to a Gaussian distribution function. In X-ray diffraction, short- and (quasi) long-range order can also be studied from the appearance of multiple {00*l*} peaks in the scattered intensity profile.<sup>28</sup> The more narrow these peaks are, the higher is the probability of finding a scatterer at a position that matches that of a crystal lattice plane. Regardless of the degree of order in the system (d, r, l), it is imperative to notice that this distinction is relevant irrespective of the dispersion quality (E, C, S).



**Chart 1.** The structure classification of polymer nanocomposites based on level of 2D-filler dispersion and positional order-disorder. The length of 2D materials is typically between 100 and 5000 nm and exfoliated thickness around 1 to 10 nm.

In the field of high-performance nacreous materials, the mechanisms to actively achieve nanoparticle exfoliation and hierarchical structure features are still missing. Therefore, the focus herein is on a strategy to fabricate exfoliated nanostructures, even at high loading, by preventing reaggregation. We hypothesize that an earlier immobilization of platelets would enable us to preserve, initially, the exfoliated system. To test this, we have investigated a water-based system using montmorillonite clay (MMT), up to a high fraction of 80 wt.% on composite basis, in a thermo-reversible gelatin network. The fast-gelling reaction should immobilize the platelets early enough to ensure less or no virtual stacking during solvent evaporation. Therefore, a network formation that prevents filler relaxation would result in exfoliated structures and keep the MMT high aspect-ratio. The study is a systematic investigation of the evolving structures from exfoliated platelets locked in a hydrogel matrix. The underlying goals are two-fold: to reiterate the importance of achieving exfoliated nanostructures (level of dispersion) in the design of functional, nacre-like composites; and to clarify the nomenclature of 2D material organization. We refrain from addressing particle alignment here since this topic shall be discussed more extensively in a follow-up communication.

The gelatin A/MMT bionanocomposites were prepared by solvent casting 3% solids suspensions at RT (method in Supporting Text S1). The formation of an unfragmented hard gel network, like in pristine gelatin, was visually observed in hybrids up to a 20 wt.% MMT content (Figure S4). The final filler mass was determined by thermogravimetric analysis (TGA, Supporting Text S2). and converted to a composite volume fraction percentage X, herein denoted as XMMT. Curiously, the obtained films showed high translucency up to sample 11MMT, while volume fractions above 33 to 64% had increasing haziness (Figure S5). Because the aligned nanostructures are less scattering the visible light, transparency is often taken as an identifying feature of a homogeneous and well-dispersed phase. It is true transparency that can indicate the absence of 2D-filler aggregation but at times homogenous systems, for instance locally crystalline (spherulites in semicrystalline polymers) or anisotropic arrangements (nematic fluids), can show opacity.

We further examined the gelatin/MMT samples with focused ion beam scattering electron microscopy (FIB-SEM). Because of the large difference between soft/hard phases, the ion

milling step was slightly uneven in the vertical direction and image treatment was necessary (Supporting Text S3). The obtained micrograph allow for inspecting the morphology of film cross-section. All the bionanocomposite samples showed the expected in-plane orientation. No large-scale aggregation or restacking was observed up to 64MMT. In Figure 1, we show a very diluted sample, containing only 0.4% MMT in volume. At this unique regime we could see MMT platelets separately and measure their lateral dimension, of roughly 130 to 270 nm. To investigate the 2D material thickness, electron scattering techniques should not be relied upon, due to charge density and contrast blurring effects. However, they can provide for a qualitative estimation of particle width, degree of separation, and extent of exfoliation.<sup>29</sup> The 0.4MMT sample can be classified as exfoliated disordered (*Ed*), because homogeneous spreading of nanosized particles is observed, but without any observable periodicity. Only a generic evaluation could be done for higher platelet fractions, 11MMT and 64MMT, because charging effects hindered discrete particle visualization (Figure S2). For these, exfoliated or intercalated phases are probable, considering the uniform distribution of densely layered structures.



**Figure 1.** FIB-SEM cross sectional image of Gelatin/0.4MMT composite (a) and its representative nanostructure (b), classified as exfoliated disordered (*Ed*).

Wide angle X-ray scattering (WAXS) was used to investigate the basal spacing of MMT (Figure 2). The patterns were obtained with the incident beam at a glancing angle parallel to the film surface, as shown in Figure 2a. The angle applied was iterated to ensure the scattering vector properly intersects the Ewald sphere. This transmission mode is very sensitive to the local 2D material arrangement and the rather high level of in-plane orientation. We could observe distinct trends between sample groups 0.4 to 11MMT and 33 to 64MMT. A clear streak was observed up to 5MMT, while for 11MMT an ill-defined wedge shape appeared. At higher filler volume fractions, from 33MMT, there were clear equatorial arcs, typical of anisotropic MMT layers. The first detection of a basal 001 reflection was at 11MMT, corresponding to an average spacing of  $d_{001} = 120$  Å. Remarkably, a gradual change in the peak position of clay reflection was observed with increasing clay content (Figure 2b). With this, the corresponding d-spacings decreased down to 18 Å. These distances are larger than the back calculated pure MMT basal spacing of 12 Å (Figure 2c), which confirms that there was gelatin intercalation into the clay galleries for all samples. Additionally, the orientation seen in the pristine Na-MMT film likely developed from flocculation (edge-face attraction), yielding an arrangement like in a random pile of cards.<sup>30</sup>

In a defined two-dimensional space, if we consider perfectly aligned 2D nanoparticles that are not allowed to interact, the volume fraction can be defined by the summed thickness of all particles over the determined space length. By analogy, the concentration of particles should be proportional to the thickness of particles over the inter-particle spacing (Figure 2d). For this reason, the apparent d-spacing is inversely proportional to the MMT volumetric content, decreasing with filler concentration. This volumetric rule is what truly defines an exfoliated structure and is valid to any form of 2D platelet/sheet nanocomposite. Therefore, all the studied concentrations for gelatin/MMT seemed to follow the exfoliated regime. From 11MMT up to 64MMT, there is an excellent agreement between experimental and theoretical exfoliated d-spacings derived from the integrated 001 reflections ( $R^2 = 0.993$ ). Despite unusually high clay fractions, there is virtually no re-stacking and phase separation over a wide concentration range (up to 64 vol.%). This is encouraging because examples of perfect exfoliation are limited, with often high temperature and pressure required.<sup>26</sup> In comparison, other successful 2D silicate bionanocomposites have been reported, usually at lower loadings, and, even so, fall inside the intercalated regime (Figure 2c).<sup>18,31</sup>



**Figure 2.** a) 2D transmission X-ray scattering images of gelatin/MMT samples with varying volumetric MMT composite content at beam inclination parallel to the plane of the films (90.5 to 94° range of glancing angle). The scattering patterns reveal anisotropy and a

progressive change in basal reflections with increasing clay loadings. b) Wide-angle X-ray diffractograms depict a peak shift of  $d_{001}$  MMT reflections towards higher angles starting from sample 11MMT. c) Comparison between experimental and calculated d-spacings derived from the  $d_{001}$  MMT reflection. The thickness of a delaminated Na-MMT platelet was obtained by reciprocal fit of  $d_{001}$  lengths and extrapolating to origin (virtual zero concentration). Alginate and carboxymethyl cellulose (CMC) composite data respectively from Zlopasa *et al.*<sup>31</sup> and Ebina and Mizukami<sup>18</sup>. d) Illustration depicting the theoretical basis for calculating d-spacing, where a reciprocal volumetric rule of concentration of MMT is assumed;  $t_{MMT}$  is the thickness of a single platelet and  $d_{spacing}$  is the platelet interspace.

The WAXS diffraction patterns were also obtained at higher q scattering vectors by moving the detection setup (Figure 3a). Interestingly, for neat gelatin the scan showed structural arrangement that is derived from the crystallization of collagen-like helices (q 0.05 nm<sup>-1</sup>) and a broad peak related to the peptide bonds.<sup>32</sup> The WAXS patterns showed that samples 33MMT and higher have additional reflection peaks (also broad [002] and [003] features), corresponding to higher orders of the MMT lamellar planes (Figure S7). Surprisingly, the sample 64MMT showed many additional reflections, all the way up to [006]. To investigate this further the layered bionanocomposites could also be studied in X-ray analysis in Bragg-Brentano geometry, allowing for higher intensity levels (Figure 3b). The 1D diffractograms are used to better detect the presence of higher order clay reflections [007]. Additional lattice reflections ([002], [003]) were confirmed for samples 33MMT and higher around q range 0.05 – 0.20 nm<sup>-1</sup>, which can be interpreted as evidence of improved layer regularity. The sample 64MMT showed remarkable quasi long-range order (six reflection peaks). However, due to particle polydispersity, this should not be confused with a real one-dimensional lattice. The periodic systems were modelled by a Gaussian distribution function over q. The correlation length or crystal domain size were calculated via the Scherrer equation<sup>33</sup> for both 001 and 003 reflections (Table 1). In the case of gelatin/MMT composites, the length L translates into the relative extent of short- or long-range positional order. For 64MMT, a substantial length of L = 198 Å is found for the *dool* reflection (18 Å d-spacing). In other words, the 64MMT sample had a 001 polymer/clay crystallite of  $L \sim 200$  Å, of which around 11 platelets were inside. This unexpected regularity at high particle content supports the findings of a closely packed lamellar structure.

Altogether, the various gelatin/MMT compositions resulted in exfoliated structures of different lamellar spatial arrangement (regularity), as previously illustrated in Chart 1. We could identify exfoliated disordered (up to 33MMT), short-range ordered (up to 44MMT), quasi long-range ordered at 64MMT (Figure 3b). This is highly unexpected, since water-based polymer composites reinforced with high aspect ratio nanoparticles can easily present long-range orientational order (high orientation factor or  $\langle P_2 \rangle$  value), but seldomly show a significant degree of positional order. In fact, to the best of our knowledge, positional order has been only reported in silicates modified by quaternary ammonium cations and host-guest additives.<sup>26</sup>

Our exfoliation strategy depends on the formation of a continuous network to immobilize the 2D material and develop yield stress. However, the extent of gelation or network density seemed to decrease with higher MMT loadings. The thermo-reversible gelation process is not a percolative one but it is caused by aggregation of helices into a collective fibrous network.<sup>34</sup> In the X-ray diffractions, we observed the appearance of equatorial diffraction arcs up to 5MMT at q 0.06 nm<sup>-1</sup>, which were from the gelatin component (Figure 2 and 3). This nanoscale organization comes from the aggregation of renatured supramolecular helices. The crystallization was evidently hampered at elevated MMT content<sup>32,35,36</sup>, above 11 vol%, in which additions also slowly increased the pH of the system closer to the protein isoelectric point. Clay negative interference on renaturation was also supported by differential scanning calorimetry (Figure S8). This can be linked to the macroscopic breakdown of the gelatinbased physical network in the casting of gels (Figure S4). It is plausible that strong electrostatic and H-bonding interactions<sup>36,37</sup> and, particularly, the decreased amount of loose chain ends disturbed the cooperative joining of helices. At elevated MMT fractions, the macroscopic gelatin cross-linking was heavily suppressed. We speculate that by introducing the clay, there is gelatin absorption on the clay surface, thereby preventing thermal gelation. Despite the formation of weaker gels, the network in these MMT samples was apparently sufficient to avoid clay stacking and phase separation.

Curiously, the fact that the samples at elevated filler content show quasi long-range order could be linked to a platelet-driven nanoconfinement of gelatin chains. As the system settles from water evaporation, the mobility of gelatin decorated MMT is reduced. The locked gelatin molecules will progressively get confined in the interlayers and lose the ability to form secondary structures. One could consider the typical length of gelatin random coil as a radius of gyration (*Rg*) in the order of 50 to 100 Å<sup>38</sup>, coming from the rough estimate that *Rg*  $\sim aN^{1/2} \sim (10 \text{ Å})(100 \text{ units})^{1/2}$ . This radius range is reasonably close to the increment in d-spacing at 58 to 64 vol.% MMT, indicating protein confinement. We propose that the gelatin specific binding is sufficient to prevent clay restacking and instead we observe colloid positional order caused by steric repulsion from the confined gelatin coils.



**Figure 3.** a) 2D transmission X-ray scattering images at higher scattering vectors q of gelatin/MMT samples with varying volumetric MMT composite content at beam inclination parallel to the plane of the films (90.5 to 94° range of glancing angle). b) Bragg-Brentano X-ray diffractograms on films show a decrease in gelatin renaturation and appearance of multiple MMT reflections with increasing loading fractions. Multiple reflections are key to identify regularity (positional order).

**Table 1.** Equivalent correlation ( $\xi$ ) or domain length (*L*) and number of platelets (*n*) estimated using the 1D Scherrer equation on 001 and 003 basal reflections of gelatin/MMT composites.

Sample

	<i>q</i> (1/nm)	a (Å)	length (Å)	n (L/a)	Efron's pseudo- R <sup>2</sup> gaussian	q (1/nm)	a (Å)	length (Å)	n (L/a)	Efron's pseudo- R <sup>2</sup> gaussian
33MMT	0.017	37.5	216.8	5.8	0.996	0.051	12.2	42.1	3.4	0.935
44MMT	0.023	27.8	156.7	5.6	0.992	0.056	11.2	50.6	4.5	0.820
64MMT	0.035	18.2	197.6	10.9	0.990	0.107	5.9	87.5	14.9	0.970

*q*: center of basal reflection; *a*: periodicity estimated from *q*;  $\xi$  or *L*: equivalent correlation or domain length: *n*: equivalent number of platelets within periodic length; Efron's pseudo-R<sup>2</sup> gaussian: the Efron's pseudo-R<sup>2</sup> estimated for the Gaussian fit used to obtain full width at half maxima.

In conclusion, we hereby report on an easily attainable 2D material exfoliation strategy by implementing a hydrogel matrix with rapid network formation. If applied to solvent-based processes, this rationale can lead to controlled all-exfoliated systems for a wide loading range, as opposed to most reported results on nacre-like composites. For the thermoreversible gelatin/MMT nanocomposites, we report filler loadings as high as 64% volume fraction. In addition, controlled hydrogelation becomes a suitable alternative to laborious processes such as multilayer deposition, in situ polymerization, external field alignment, etc. The high level of exfoliation and alignment of the clay platelets allows for precise tuning of the sample d-spacing through the hereby described volumetric rule. Nevertheless, the extent of gelation needs to provide enough particle immobilization during the drying phase. The locking mechanism needs to sustain time scales higher than that of filler relaxation. Hence, the strategy should be applied to other systems on a case-by-case basis. Another reason for this is that the system properties are still dependent on initial polymer-particle compatibility, polymer-penetration energy, and interfacial interactions. Remarkably, particle order-disorder transitions were found to develop from these nanostructures, which requires further attention. For instance, the composites 33MMT to 64MMT were found to form very ordered phases,

with crystallite sizes about 200 Å long. Our future work shall explore the proposed hydrogelation strategy with regards to the platelet orientation mechanism and its effect on anisotropic properties.

# ASSOCIATED CONTENT

# Supporting Information

The following files are available free of charge.

Methods (gel suspensions and film fabrication, focused ion beam scanning electron microscopy (FIB-SEM), conditions for wide-angle (WAXS) and Bragg-Brentano X-ray diffraction (XRD), correlation or domain length calculations, differential scanning calorimetry (DSC) on humid films); thermogravimetric analysis (TGA); FIB-SEM image treatment and analysis. Additional figures and tables: inverted vials gelatin/MMT gel suspensions; photos of composite films; powder XRD of commercial gelatin A; integration of WAXS at higher q angles; DSC analysis gelatin/MMT films at 0.33 water activity; correlation or domain length for all composite fractions (PDF)

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# Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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# Notes

The authors declare no competing financial interest.

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# **Supporting information**

# Systematic study of the nanostructures of exfoliated polymer nanocomposites

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# **Supporting Texts**

## **Supporting Text S1. Experimental Section**

1. Materials

Gelatin from porcine skin (Type A, 78-80 mM free COOH/100 g protein, 50,000–100,000 Da, gel strength 300, relative density 1.3 g cm<sup>-3</sup>) was obtained from Sigma Aldrich and used as received. Sodium montmorillonite (Na-MMT), CLOISITE-Na+, with D<sub>50</sub> particle size <25  $\mu$ m, basal spacing d001 of 11.7 Å, and density 2.86 g cm<sup>-3</sup> was supplied by BYK Chemie GmbH, Germany, and used without further purification or surface treatment. The aspect ratio length over thickness) of the dispersed Na-MMT is typically reported as ranging from 10 to 1000 nm. All chemicals used were of analytical grade.

# 2. Gel Suspensions and Film Casting

A gelatin stock solution (3 w/v % solids content) was initially prepared by dissolving the powder in deionized water at 50 °C for 1 h using a magnetic stirrer. The pH of gelatin solution was  $5.2 \pm 0.1$  at 50 °C, which is below its reported isoelectric point of 7 – 9.5. Na-MMT was mixed in deionized water under vigorous stirring for at least 24 h to achieve a 3 w/v % delaminated dispersion. The pH of Na-MMT suspension was  $8.2 \pm 0.1$  at 50 °C.

Film-forming suspensions of protein/clay were prepared by carefully mixing (precalculated) wet ratios of the gelatin stock solution and Na-MMT suspension at 70 °C. This thermal treatment to the Na-MMT slurry was necessary to avoid lumps and re-agglomeration in the mixtures with protein due to temperature influence on its solubility.<sup>39</sup> All the Na-MMT was dispersed, without any remaining visual agglomerates. The protein/MMT suspensions were further mixed at 400 rpm for 2 hours at 70 °C to allow for gelatin-clay interaction. The pH at 50 °C of the casting gel suspensions ranged from 5.4 up to 7.7, increasing in value with higher Na-MMT addition. The hot dispersion was carefully poured into a 9 x 2 cm polystyrene petri dish and dried at ambient conditions (20 °C, 50% RH) to form a thin film. The drying step lasted around 4 days and free-standing films were obtained by peeling off the new layer. Subsequently, the films were vacuum-dried at 40 °C for 1 day to remove excess humidity. The final thickness was designed to be in the range of 200  $\mu$ m, what was confirmed using a digital micrometer at five random locations.

The study aimed at a wide range of filler loadings ranging from 1 to 80 wt. % Na-MMT, on the composite weight basis. In solid-state, this should be equivalent to up to 65 vol.% Na-MMT. Two replicates were performed for samples in region of interest, containing high clay content, where we aimed to achieve 30 and 60 vol. % MMT. The MMT content was later confirmed via thermal gravimetric analysis (TGA) (Supporting Text S2). Throughout this study, the composite clay content is expressed as volume percentage (vol. %). The samples are denoted as XMMT, where X is the volumetric MMT fraction percentage in the composite.

For the following characterization analyses, the films were additionally conditioned for a week in a desiccator containing silica gel at room temperature. This step was necessary to ensure there was absence of freely bound water, as the gelatin polymer has a hydrophilic nature.

# 3. Focused Ion Beam Scanning Electron Microscopy (FIB-SEM)

Focused ion beam scanning electron microscopy (FIB–SEM) experiments were performed in FEI Helios G4 CX microscope. A conductive thin layer of Au (~10 nm thickness) and a protective thin layer of W (0.3  $\mu$ m thickness) were deposited on the cross-sectional surface of specimens using a sputter coater and gas injection system respectively. The focused beam was operated at 30 kV and 2.5/0.24 nA used respectively to carve a trench and perform slicing up to a nominal depth of 10  $\mu$ m. After correcting for the tilt angle between specimen and SEM detector, a series of micrographs were recorded of the polished cross-sections exposed, with a secondary electron detector operated at 10 kV. When possible, the average filler size and inclination of around 50 filler particles were identified and measured (Supporting Text S3). The technique allowed to investigate micro-arrangement of MMT particles within the gelatin matrix. Image enhancement was needed, i.e. solving for "curtaining" effect in the milling direction and resolution, which was possible with the *polishEM* software tool<sup>40</sup>. Measurements and analysis of the micrographs were performed by *Gwyddion* software.

# 4. Wide-Angle (WAXS) and Bragg-Brentano X-ray Scattering

Wide-angle X-ray scattering (WAXS) was used to determine the composite nanostructure. Transmission mode X-ray diffraction was performed using a Bruker AXS D8 Discover with a VÅNTEC 2D detector and using Cu K $\alpha$  radiation ( $\lambda = 1.54184$  Å) at 50 kV and 1 mA. A point collimator of 0.3 mm was used, and the sample–detector distance was 30 cm parallel (incident beam at a glancing angle) and perpendicular to the film surface. Additional measurements were done with the detector shifted by  $2\theta = 11.5^{\circ}$  in order to obtain 2D patterns at higher angles while avoiding background noise.

Experiments were also conducted with a Bruker D8 Advance diffractometer (2theta-theta scan, often called Bragg-Brentano or focusing geometry) with Co K $\alpha$  source ( $\lambda = 1.7889$  Å, 35 kV and 40 mA) with Lynxeye position sensitive detector. The measurement range on a motorized varied divergent slit was set from 4 to 50 degrees with step size of 0.02 mm. A measuring time of 0.1 second per step was employed. For basic interpretation and data

curation of the X-ray diffraction (XRD), Bruker software (DiffracSuite.EVA version 5.1, Bruker, USA) was used.

To normalize for the different X-ray sources ( $\lambda$ ), the XRD data is shown over the scattering vector  $q = (4\pi/\lambda) \sin \theta$ , where  $2\theta$  is the scattering angle. The layer d-spacing was calculated from Bragg's law.

# 5. Correlation or Domain Length

In general, information on the size of ordered domains in composites can be extracted from the line shape of X-ray peaks. If we consider crystals with a three-dimensional lattice, the probability to find the center of mass of a molecule at a position r with respect to a test molecule (r = 0) can be described by a distribution function D(r). True dimensional positional order results in a series of Dirac delta functions along the r values. However, for quasi longrange and short-range order systems, such as nanocomposites, this distribution displays an algebraic decay with distance r, e.g.,  $D(r) \propto r^{-\eta}$  or  $D(r) \propto e^{-\frac{r}{\xi}}$ . The Fourier transform of the exponential decay corresponds to a Lorentzian expression, which is one of the distribution functions commonly fitted to the radially integrated X-ray profiles.<sup>28</sup>

In our case, the nanoplatelets will show a high aspect ratio if exfoliated, what favors the development of 1D ordered systems upon drying. Hence, distribution functions also can be fitted to estimate a correlation or domain length ( $\xi$  or L) as a measure for the degree of positional order.<sup>41</sup> To calculate this length, we applied the Scherrer equation, which is originally derived for a 1D finite stack of lattice planes:

$$\xi \text{ or } L = \frac{K \lambda}{FWHM \cos \theta}$$

where  $\xi$  or *L* are the average correlation length or domain size,  $\lambda$  is the wavelength of X-ray source, FWHM is the peaks' full width at half maxima and  $\theta$  the diffraction angle (radians), respectively. The empirical proportionality factor (K) was assumed to be 0.89. A Gaussian fit

was chosen to obtain the FWHM, since we observed quasi long-range order and possible convoluted instrumental broadening of the scattered image. The Gaussian statistical goodness-of-fit was estimated by the probabilistic parameter of Efron's pseudo-R<sup>2</sup>. The equivalent number of platelets within the period was estimated from the relationship: length over 00/ d-spacing.

# 6. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) experiments were performed to characterize the thermal behavior of gelatin/MMT composites. First, snippets from the film samples were acclimated to a 33% relative humidity environment using MgCl<sub>2</sub> saturated salt solution. The water uptake capacity at the end of two weeks was measured gravimetrically. The DSC method consisted of heating the sample from 223 to 425 K, at rate of 3 K min<sup>-1</sup>, on a PerkinElmer Pyris diamond instrument with two 1 g furnaces and calibrated with indium. Nitrogen gas was used to purge the thermal analyzer at 50 mLmin<sup>-1</sup>. Stainless steel pans with o-ring seals were used for hermetically encapsulating the equilibrated samples (20 mg). An identical empty reference pan was used. The pans were sealed according to supplier instructions (PerkinElmer). Data visualization was carried out by Python, in which the y-axis refers to endothermic transitions. Each thermogram was analyzed for the melting (or denaturation) event.

# Supporting Text S2. Thermogravimetric Analysis (TGA)

The composite samples were cut to snippets and analyzed using a thermogravimetric analyzer (TGA 8000, Perkin Elmer, USA) from 30 to 900 °C using a heating rate of 10 °C min<sup>-1</sup>. The sample weight was in the range of 4 to 6 mg. Corundum crucibles were used and air as a purge gas at a flow rate of 20 mL min<sup>-1</sup>. The method included isothermal steps at 105 and 900 °C for water removal and final weight equilibration, respectively.

In Figure S1, the thermal mass loss of gelatin, clay, and hybrids samples casted from 3 w/v % mixtures are shown. The first gelatin weight loss occurs at 270 °C, due to gelatin decomposition, and the second one around 500 °C region, due to combustion of residual organics. For the nanocomposite samples up to 5MMT, it can be clearly observed that the secondary onset thermal decomposition of the composites, around 530 to 610 °C, is higher than that of the neat protein. It can also be noted that the thermal rate of decomposition of hybrids is obviously reduced with clay concentration, specially at higher MMT loadings (> 11MMT). Thus, the well-dispersed clay inhibited the weight loss of gelatin, effectively acting as a barrier element, and because of its high thermal decomposition. Due to the usage of oxidative environment and negligible ash content of gelatin, the final residue represents the weight percentage of MMT. These concentrations were later converted into vol. % MMT, as presented in caption of Figure S1, ranging from 0.4 to 64%.



**Figure S1.** TGA of gelatin and gelatin/MMT composites fabricated from 3 w/v % suspensions at different filler loadings, shown in volume fraction,

# Supporting Text S3. FIB-SEM Image Treatment and Particle Analysis

The FIB-SEM sample images were first treated to remove typical ion beam streak artifacts or "curtaining" (Figure S2). The curtaining in the ion milling direction depends on the sensitivity of the material, being common in composites of hard and soft materials, and arising from uneven milling. This image treatment was done via 2D Fast Fourier Transformation (*polishEM* software tool).

In the case of sample Gelatin/0.4MMT, due to the low loading of MMT clay and its electron density, it was possible to observe the internal particle dispersion and composite structure. The MMT nanoplatelets are possible to be visualized only due to the high electron density contrast between the organic matrix and silicate filler. Because of the same phenomena, the visible particles are actually a blurred image of the real nanosized structure, which can only be further resolved with X-ray analysis.

Unlike previous, the FIB-SEM image of sample 11MMT was too convolved, a result from high charging interference. However, a dense and layered structure was observed, which was also free of clay aggregate traces. At 11MMT, the mean layer spacing was measured roughly 76 to 181 nm. The nanoparticles cannot be observed individually already at this volumetric content (Figure S2b and c). At high volume fraction (64MMT), the layered sample shows undulation features but it is also predominantly free of stacking.

No gelatin orientation was observed in any of the studied samples. However, during ion milling temperatures can shortly reach the onset melting point of solid gelatin ( $\geq 87$  °C or 360 K)<sup>35</sup>, what hampers the observation of possible gelatin layers from the crystallization of helices.



\* nanoparticles cannot be resolved with FIB-SEM

**Figure S2.** FIB-SEM images of gelatin/MMT nanocomposites: (a) 0.4MMT unprocessed (left) and with curtaining removed via 2D FFT (right); (b) unprocessed 11MMT and (c) unprocessed 64MMT.

# 1. Length of Na-MMT Particles

The average particle length was estimated from three micrographic pictures belonging to the 0.4MMT sample (Figure S3a). Image analysis resulted in  $212 \pm 97$  nm as average length of dispersed particle (Figure S3b). Furthermore, the (in-plane) inclination angle of particles coarsely tends to zero, suggesting sample anisotropy along this direction (Figure S3b and c).



**Figure S3.** (a) FIB- SEM images of gelatin/0.4MMT showing imaging software particle identification and data. (b) R: total planar distances of particles, in nm; and Phi: inclination angle of particles, in radians. (c) The frequency distribution of inclination angle of MMT particles, Phi.

# **Supporting Figures and Tables**



**Figure S4.** Vials containing gelatin/MMT film-forming suspensions (3 w/v % total solids). The notation XMMT classifies the suspension in terms of aimed MMT mass fraction (X%), on a gelatin/MMT basis. The inverted vials, at equilibrium, indicate that the hydrogel network starts to collapse at MMT loadings higher than 20 wt.%, which are gels resulting in composites with filler fractions above 11 vol. %.



**Figure S5**. Images of gelatin/MMT nanocomposite films. The film thickness was around 0.2 mm. The notation XMMT classifies the composite film in terms of the determined MMT volume fraction (X%), on a gelatin/MMT basis.



**Figure S6.** Powder XRD of the commercial gelatin type-A used in this study. The diffractogram shows that the *as is* gelatin is amorphous before processing into a solvent-casted film.



**Figure S7.** WAXS radial 1D integration of gelatin/MMT composites at higher *q* range and from a parallel glancing angle.



**Figure S8.** DSC analysis of the temperature dependance of heat capacity (endo up) of gelatin/MMT films equilibrated to a 0.33 water activity ( $a_w$ ). The equilibrium water uptake for each sample was measured gravimetrically and is shown in legend. The blurred area assigned to the denaturation temperature  $T_{Hel}$  was suppressed with increasing clay content, as observed via absent or decreased corresponding energetic barrier (J/g) at transition. This suggests that more amorphous gelatin structures were formed with increasing clay volume fraction. Above 373 K, the DSC pan seal integrity is broken and we observe sample water loss.

**Table S1**. Equivalent correlation ( $\xi$ ) or domain length (*L*) and number of platelets (*n*) estimated using the 1D Scherrer equation on 001 and 003 basal reflections of all gelatin/MMT composites.

Sample	001					003				
	q (1/nm)	a (Å)	length (Å)	n (L/a)	Efron's pseudo- R <sup>2</sup> gaussian	q (1/nm)	a (Å)	length (Å)	n (L/a)	Efron's pseudo- R <sup>2</sup> gaussian
33MMT	0.017	37.5	216.8	5.8	0.996	0.051	12.2	42.1	3.4	0.935
34MMT	0.018	34.6	216.7	6.3	0.999	0.054	11.7	46.1	3.9	0.941
44MMT	0.023	27.8	156.7	5.6	0.992	0.056	11.2	50.6	4.5	0.820
58MMT	0.033	18.9	148.1	7.8	0.998	n.a.	n.a.	n.a.	n.a.	n.a.
60MMT	0.035	18.1	144.1	8.0	0.960	n.a.	n.a.	n.a.	n.a.	n.a.
64MMT	0.035	18.2	197.6	10.9	0.990	0.107	5.9	87.5	14.9	0.970

*q*: center of basal reflection; *a*: periodicity estimated from *q*;  $\xi$  or *L*: equivalent correlation or domain length: *n*: equivalent number of platelets within periodic length; Efron's pseudo-R<sup>2</sup> gaussian: the Efron's pseudo-R<sup>2</sup> estimated for the Gaussian fit used to obtain full width at half maxima.

n.a. Experiment not available.

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