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# Dry Processing and Recycling of Thick Nacre–Mimetic **Nanocomposites**

Francisco Lossada, Baolei Zhu, and Andreas Walther\*

Bioinspired nanocomposites with high levels of reinforcement hold great promise for future, green lightweight, and functional engineering materials, but they suffer from slow, tedious, and nonscalable preparation routes, that typically only lead to very thin films. A rapid and facile dry powder processing technique is introduced to generate bioinspired nanocomposite materials at high fractions of reinforcements (50 wt%) and with millimeter scale thickness. The process uses powder drying of vitrimer-coated nanoplatelets (nanoclay and MXene) from aqueous solution and subsequent hot-pressing. As a method of choice in industrial lightweight composite materials engineering, hot-pressing underscores a high potential to translate this approach to actual products. The use of the vitrimer chemistry with temperature-activated bond shuffling is important to facilitate smooth integration into the nanocomposite design, leading to layered nacre-inspired nanocomposites with nanoscale hard/soft order traced by X-ray diffraction and excellent mechanical properties investigated using flexural tests. Recycling by grinding and hot-pressing is possible without property loss. The compatibility with existing composite processing techniques, scalable thickness and dimensions, and recyclability open considerable opportunities for translating bioinspired nanocomposites to real-life applications.

# 1. Introduction

Bioinspired nanocomposite materials inspired by the loadbearing structures of biological materials, such as wood, bone or nacre, hold great promise for engineering the next generation

F. Lossada, Prof. A. Walther Department of Chemistry University of Mainz Duesbergweg 10-14, 55128 Mainz, Germany E-mail: andreas.walther@uni-mainz.de Dr. B. 7hu Key Laboratory of Special Functional and Smart Polymer Materials of Ministry of Industry and Information Technology Northwestern Polytechnical University Xi'an 710072 P. R. China Prof A Walther Cluster of Excellence livMatS at FIT University of Freiburg Georges-Köhler-Allee 105, 79110 Freiburg, Germany

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.202102677.

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oped materials out of the laboratory and into the real world.

Herein we introduce a facile dry hot-pressing route allowing

to obtain thick bulk materials with an internal nacre-mimetic

structure at high levels of reinforcements. The prepared mate-

rials even allow for a recycling-a key feature to promote

sustainability in lightweight high-performance materials.

The process involves freeze-drying suspensions of polymercoated nanoplatelets, followed by ball-milling and subsequent

6163028, 2021, 30, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/adfm.202102677 by Cochrane Germany, Wiley Online Library on [171/10/2022]. See the Terms and Conditions (https://onlinelibrary.wiley.com/doi/10.1002/adfm.202102677 by Cochrane Germany, Wiley Online Library on [171/10/2022]. See the Terms and Conditions (https://onlinelibrary.wiley.com/doi/10.1002/adfm.202102677 by Cochrane Germany, Wiley Online Library on [171/10/2022]. See the Terms and Conditions (https://onlinelibrary.wiley.com/doi/10.1002/adfm.202102677 by Cochrane Germany, Wiley Online Library on [171/10/2022]. nanocomposite materials uniting high stiffness, strength, and toughness together with ease of processing.<sup>[1]</sup> Such materials are critically needed to promote energy and cost efficiency in production, as compared to, e.g., carbon fiber composites, and would promote energy efficiency in mobile applications. At the same time, some better recycling might be expected as particlebased nanocomposites may be more applicable for secondary use scenarios in cyclic economies as compared to fiber-reinforced Within the last decade, significant developments have been made in the field of nacre-mimetics regarding both mechanical and functional properties.<sup>[1e,2]</sup> The preparation of nacre-mimetic structures started with time consuming and hardly scalable layer-by-layer assembly.<sup>[3]</sup> This was later on simplified by colloidal self-assembly procedures using doctorblading,<sup>[4]</sup> filtration,<sup>[5]</sup> and evaporation.<sup>[6]</sup> While those methods are relevant for model materials and can potentially be applied for continuous coatings,<sup>[4a,7]</sup> it is unrealistic to foresee thick bulk materials as needed for real-life composite applications. Lamination procedures were suggested to make thick films, yet this method is also poorly scalable as the preparation of the individual films is too time-consuming due to long solvent evaporation.<sup>[8]</sup> As an alternative, ceramic-type processing using freeze-drying of particle suspensions, followed by infiltration and polymerization of monomers stands out as one method to produce thick bulk nacre-mimetic samples.<sup>[9]</sup> Even though this can produce thick specimens, such processing is energy and time-intensive, and hardly compatible with established processing strategies in classical composite science. Consequently, despite progress, the big challenge remains to transfer nacre-mimetic nanocomposite design at high fractions of reinforcements (50 wt%)-which is incompatible also with classical polymer processing such as injection molding-into scalable methods, potentially compatible with industrial composite procedures to push the devel-



**Scheme 1.** Schematic preparation route of the dry processing of bulk-like nacre-mimetic nanocomposites. a) EMA vitrimer prepolymer structure obtained by RAFT polymerization. The indices denote the molar fractions of each component. b) Waterborne mixture of reinforcements and vitrimers to obtain polymer-coated core/shell nanoplatelets, subsequently freeze-dried. c) Griding and milling process at low temperatures provide the mixture as the finest possible powder. d) Hot-pressing the nanocomposite powder delivers homogeneous nacre-mimetic disks. e) Schematic representation of the transesterification reactions in the vitrimer system.

hot-pressing of the powders into thick nacre-inspired nanocomposite films. A critical aspect is the selection of an appropriate polymer concept, whereby we focus on vitrimers that allow crosslinking and reshuffling of crosslinks at high temperature to enable tight adhesion, crosslinking and strain release during hot pressing. We demonstrate this approach for nanoclay platelets of different aspect ratios, and underscore the generic principle by also using MXene nanoplatelets. The obtained mechanical properties are excellent and similar to film-cast materials. The final nacre-inspired nanocomposites can be recycled. The compatibility of the proposed techniques—freeze-drying/spray-drying, grinding, and hot pressing—with industrial composite manufacturing methods makes this approach a highly promising starting point for a further transfer into industrial applications.

# 2. Results and Discussion

The selection of the polymer component is a critical aspect, as the polymer needs to ideally provide i) good adhesion to the reinforcement for efficient stress transfer, ii) chances for crosslinking to boost mechanical performance and also iii) the ability for reorganization, flow, and strain-release when hot pressing into bulk materials. Therefore, we chose a vitrimer system. Vitrimers are a special class of dynamic covalent crosslinked polymer networks that undergo temperatureinduced bond shuffling reactions, hence enabling stress release during hot-pressing, as well as shaping.<sup>[10]</sup> In order to integrate them with nacre-mimetics, we chose a waterborne vitrimer prepolymer system based on a methacrylate-methacrylamide polymer structure (labeled as EMA for poly[(ethylene glycol methacrylamide)-co-hydroxy (ethylene glycol) methacrylate-co-N-(2-hydroxyethyl) methacrylamide)]; structure in Scheme 1a). The used EMA prepolymer has a  $M_{\rm p}$  of 36 kDa, D of 1.6 and a glass transition temperature,  $T_{\rm g}$ , before crosslinking of -23 °C. It is fully water soluble, but can be crosslinked at high temperature in bulk via metal-catalyzed transesterification

reactions between the side chain hydroxy groups and backbone ester groups. We previously showed that EMA polymers have vitrimeric character in presence of Lewis acids to catalyze transesterification reactions.<sup>[11]</sup> Additionally, they are useful to make bioinspired nanocomposites by waterborne classical film casting,<sup>[12]</sup> yet the critical aspect of making thick films via dryprocessing as introduced herein had not been considered by us or others. As reinforcing nanoplatelet, we selected majorly synthetic nanoclays (varying aspect ratios between 230 and 10 000), and extended the concept to a MXene to show the general applicability (**Table 1**).

Scheme 1 illustrates the dry processing route towards nacreinspired nanocomposites. First, a dispersion of EMA vitrimer prepolymer and is prepared at a 1/1 w/w ratio by stirring in water, and zinc acetate (Zn(OAc)2; 10 mol% with respect to the ester groups in EMA) is added to later catalyze the transesterification reactions (Scheme 1b). The prepolymer is physiosorbed onto the nanoplatelet surface via van der Waals forces, hydrogen bonds, and hydrophobic effect, forming well-defined polymer-coated core/shell nanoparticles.<sup>[6a,e,13]</sup> The formation of the core/shell particles prior to powder preparation is crucial to guarantee the intrinsic hard/soft character within the nacremimetic structure, and to prevent later aggregation of the nanoclay during melt processing. Subsequently, the dispersions are freeze-dried and the resultant powder is further ground using cryo ball-milling, making it easier to manipulate and homogeneously disperse an ultrafine powder inside a metal mold for further pressing of the sample (Scheme 1c). Finally, hotpressing the fine powder for 1 h at 170 °C and 10 bar results

 Table 1. Overview of nacre-mimetic nanocomposites.

Nanocomposites	Reinforcements	Nanoplatelet aspect ratio (d/t)
NC1/EMA	Synthetic nanoclays	10 000
NC2/EMA	Synthetic nanoclays	750
NC3/EMA	Synthetic nanoclays	230
MX/EMA	MXene (Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> )	1500

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Figure 1. Dry Processing of nacre-mimetic nanocomposite bulk disks. The processing technique is shown with preparation of freeze-dried mixtures, ball-milled fine powders and the obtained homogeneous pristine and fully recyclable bulk disks for a) NC1/EMA, b) NC2/EMA, c) NC3/EMA and d) MX/EMA.

in homogeneous nanocomposite disks, typically prepared at a thickness range between 0.5 and 2 mm (Scheme 1d). We emphasize that this thickness is order of magnitudes higher than typical nacre–mimetics obtained by film casting,<sup>[6d,13a,14]</sup> and that the thickness of the sample depends purely on the amount of the powder that is filled into the mold. The technique already offers homogeneous disks at 130 °C, but 170 °C accelerates the crosslinking and transesterification reactions between the vitrimeric phase,<sup>[11]</sup> which diminishes voids, releases stress, and homogenizes the whole material (Scheme 1e). A recycling can be done by cryo ball-milling and restarting the hot-pressing procedure.

Figure 1 shows the obtained freeze-dried mixtures, ballmilled fine powders (with a wide size distribution centered  $\approx$ 40 µm, Figure S1, Supporting Information), homogeneous bulk pristine nanocomposites, as well as fully recycled disks. To demonstrate the general applicability of the technique we show reinforcements of different aspect ratio, i.e., nanoclays (NCs) with different aspect ratios (NC1 with an average aspect ratio  $(d/t) \approx 10\ 000$ , NC2 with  $d/t \approx 750$ , NC3 with  $d/t \approx 230$ ), and Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene (MX, with  $d/t \approx 1500$ )). Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene (where T<sub>x</sub> represents -OH, =O and -F) is a more functional reinforcement and features high electrical conductivity and hydrophilic character.<sup>[15]</sup> Regardless the reinforcement, the processing works flawless and without visible limitations for disks prepared with thickness up to 2 mm. The slight yellowish color in the nanoclay-based materials originates from the EMA component. The good macroscopic translucency is a strong indication for the absence of voids and other inhomogeneities that would result in substantial light scattering and opacity at this thickness (Figure 1a–c). The black color for MX originates from the intrinsic color of the MX (Figure 1d).

We characterized the internal structure of the nanocomposites via X-ray diffraction (XRD, **Figure 2**). All NCx/EMA and MX/EMA nacre–mimetics show well-ordered lamellar structures with defined primary diffraction peaks ( $q^*$ ) and their corresponding second-order diffraction peaks ( $2q^*$ , long-range order; Figure 2b).<sup>[13a,14c]</sup> The lack of additional peaks corresponding





Figure 2. XRD for vitrimer-based nacre-mimetics of synthetic nanoclays. a) Bulk nacre-mimetic disks for NC1/EMA, NC2/EMA and NC3/EMA with their representative aspect ratios. XRD measurements for b) pristine and c) recycled bulk nacre-mimetic disks.

to non-exfoliated synthetic nanoclays (at  $q \approx 5 \text{ nm}^{-1}$ ) indicates full delamination and a proper polymer-coating at the nanoplatelet surface during the mixing in aqueous dispersion, which is maintained through drying and milling.<sup>[13a]</sup> We believe that these aqueous delamination and coating steps are critical to achieve a properly stacked nanocomposite and that simple vitrimer and nanoclay powder mixing and subsequent hotpressing can certainly not give ordered structures with polymer intercalation due to lack of dynamics. The NCs separation (d-spacing) is governed by the polymer content between the nanoplatelets, and can be calculated using  $q^*$  to  $\approx 1.8$  nm for the three NC/EMA nanocomposite systems and 2.8 nm for MX/ EMA. Additionally, the diffraction peak width decreases slightly for larger NC (d/t), indicating a higher order (larger grains) of the structure. The higher content of polymer between MX sheets relates to their greater thickness (1.4–1.6 nm),<sup>[15a,16]</sup> compared to nanoclay (ca. 1.1 nm).<sup>[13a,14b]</sup> Finally, Figure 2c shows the efficiency of the recycling step in the nanocomposites, maintaining the original, ordered lamellar structure with the same *d*-spacing values for all nanocomposites (≈1.8 and 2.8 nm for NCs/EMA and MX/EMA, respectively).

Next, we turn to scanning electron microscopy (SEM) to better understand the internal structure of our bulk nacremimetic disks (Figure 3). It is well known that for all the chosen reinforcements, a globally aligned lamellar structure can be obtained by previous preparation techniques, e.g., layer-bylayer (LbL), doctor-blading, filtration, and film casting.<sup>[6c,13a,15a]</sup> Interestingly, here we show that hot-pressing the reinforcements provides bulk materials that reveal grain alignment with internal lamellar structures. This alignment is supported by the flow and topological rearrangements of the vitrimer (Figure 3a-d). All the recycled bulk nanocomposites preserve a similar lamellar architecture, thus showing once again the efficiency of the recycling step (Figure 3e-h).

We proceed to the study of the mechanical properties of the bulk nacre-mimetic nanocomposites by mechanical tests and discuss them as a function of the aspect ratio in the synthetic nanoclays together with a comparison to the MX/EMA. As a reference, pure EMA behaves as a crosslinked elastomer with a stiffness, tensile strength, and strain-to-failure of  $\approx 3$  MPa, 870 kPa, and 60%, respectively.<sup>[11]</sup> Since the specimens are thick, we are here in a position to carry out flexural tests, rather than typically used tensile tests. All flexural tests were conducted at 55% relative humidity (RH) at room temperature. Table 2 summarizes the mechanical property values.

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Figure 4a shows the flexural stress-strain curves for the as-prepared nacre-mimetic nanocomposites. Let us start with the nanocomposites based on synthetic nanoclays, where the aspect ratio plays an important role in the overall behavior.<sup>[13a]</sup> In general, a stiff and strong behavior prevails for large aspect ratios. NC1/EMA ( $d/t \approx 10~000$ ) achieves a high flexural modulus (*E*<sub>f</sub>) of  $\approx$ 20 GPa, flexural strength ( $\sigma_{\rm b}$ ) of  $\approx$ 80 MPa and an elongation to break ( $\varepsilon_{\rm b}$ ) of 0.4%. Lowering the aspect ratios to 750 (NC2/EMA) and 230 (NC3/EMA) leads to a loss of stiffness to 11 and 8 GPa and strength to 50 and 60 MPa, respectively. The MX/EMA sample behaves similarly as the NC/EMA samples, yet with a slightly lower stiffness and strength, which is probably rooted in the unclear reinforcing ability of MXenes (platelet modulus). All materials show a brittle behavior with their respective fracture, which is however expected for such highly reinforced nacre-mimetics with a nanoconfined and crosslinked polymer network.

Most importantly, we retested the flexural mechanical properties after recycling all the broken samples into new homogeneous films, as shown in Figure 1. Figure 4b depicts the flexural stress-strain curves for recycled nanocomposites and show how all the recycled nanocomposites stay within the same property area values as the pristine ones. This recovery of properties once again shows the possibility of recycling nacre-mimetics via dry processing technique. Slight increase of strength and elongation could relate to minor variations within the structure such as the improvement of the vitrimer coating on the reinforcements during the second heating step or small variations within the d/t due to the milling process.

Finally, we investigate the crack propagation and the fracture toughness (K<sub>eff</sub>, Equation 1 and Supporting Information) for all the pristine and recycled bulk nanocomposites.

$$K_{\rm eff} = \sqrt{E' \cdot J} \tag{1}$$

where  $E' = E_f/(1 - v^2)$ , v the Poisson's ratio and J the J-integral. The obtained values are in the range of 0.9–2.4 MPa  $m^{1/2}$ (Figure 4c).

Figure 4d, e shows SEM micrographs revealing the crack pathways and propagation during the fracture of flexural tests. The grains dominate the fracture behavior for all nanocomposites,



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Figure 3. Cross sectional SEM micrographs of bulk vitrimer-based nacre-mimetic a-d) pristine and e-h) recycled nanocomposites. SEM micrographs for pristine and recycled a,e) NC1/EMA, b,f) NC2/EMA, c,g) NC3/EMA, and d,h) MX/EMA.

presenting toughening mechanisms due to crack deflection at their boundaries (red arrows). Moreover, multiple constrained microcracks are visible within the fractured samples (blue lines), forming next to the major cracks and indicating delocalization of stress. A slight increase of the fracture toughness for lower d/t values (NC3/EMA) suggests possible deformation mechanisms via platelet pull-outs.

It is important to compare the first obtained mechanical properties of this new preparation routes to established values of nacre–mimetic nanocomposites using similar materials. The flexural properties set a good starting point for our processing technique when compared to other preparation methods. NC1/EMA with the highest aspect ratio NC (10 000) has the best mechanical performance. The flexural

Samples	Condition	E <sub>f</sub> [GPa]	$\sigma_{ m b}$ [MPa]	£ <sub>b</sub> [%]	K <sub>eff</sub> [MPa m <sup>-1/2</sup> ]
NC1/EMA (P)	Pristine	$20.4\pm0.7$	77 ± 9	$\textbf{0.41} \pm \textbf{0.05}$	1.3 ± 0.2
NC1/EMA (R)	Recycled	$19.0\pm1.0$	$92\pm5$	$\textbf{0.58} \pm \textbf{0.03}$	$2.4\pm0.4$
NC2/EMA (P)	Pristine	$11.0 \pm 2.0$	$49\pm7$	$0.45\pm0.08$	$\textbf{0.9}\pm\textbf{0.1}$
NC2/EMA (R)	Recycled	$10.0\pm0.4$	$51\pm4$	$\textbf{0.55} \pm \textbf{0.05}$	$1.1\pm0.1$
NC3/EMA (P)	Pristine	8.0 ± 1.0	$56\pm7$	$0.7\pm0.2$	$1.2\pm0.1$
NC3/EMA (R)	Recycled	$8.4\pm0.7$	$55\pm 8$	$1.0\pm0.3$	$1.9\pm0.4$
MX/EMA (P)	Pristine	$5.5\pm0.9$	$48 \pm 4$	$0.9\pm0.1$	$1.0\pm0.2$
MX/EMA (R)	Recycled	$4.9\pm0.4$	57 ± 10	$1.3\pm0.2$	$1.2\pm0.2$

Table 2. Overview of mechanical properties for nacre-mimetic nanocomposites.







**Figure 4.** Flexural mechanical behavior for bulk vitrimer-based nacre-mimetic nanocomposites. Flexural stress-strain curves for a) pristine and b) recycled nanocomposites. c) Flexural property values for nacre-mimetic nanocomposites. d,e) Cross section SEM micrographs of the fractured NC3/EMA samples. The arrows illustrate the crack propagation and deflection path during the flexural tests.

strength, stiffness and toughness are within the range of previous bulk-approaches for nacre–mimetic materials (e.g., by lamination of many thin films),<sup>[8,17]</sup> and even compare to the stiffness of some polymer composites reinforced with glass fibers.<sup>[18]</sup> Although this underscores the potential of this new processing concept, even better mechanical properties and tunable properties should be accessible by further tailoring of the components—in particular on the polymer/vitrimer side.

# 3. Conclusion

In summary, we introduced the first dry processing technique for bulk bioinspired nacre-mimetic nanocomposites-an approach clearly breaking with classical film formation strategies for highly reinforced bioinspired nanocomposites. The key concepts are to provide well-defined hard/soft polymer-coated building blocks by drying and the use of specifically engineered polymers-vitrimers-that allow both tight crosslinking at room temperature and topological bond rearrangement and flow at high temperature. We believe that this work takes a critical step towards translating light-weight high-performance sustainable bioinspired materials from the lab into real-life materials applications. Due to the presence of the vitrimers allowing for stress relaxation, it appears rather straightforward to move into hot-pressing for shaping such materials into more complex curved parts, and we herein already also demonstrated recycling as a key concept to promote sustainability in cyclic economy.

Yet, this new area of research in the bioinspired nanocomposite field also comes with additional challenges that need to be addressed in the future. In particular improvements to the processing are needed. While we herein used the drying of rather dilute dispersion at 1 wt% solid content (to provide best defined core/shell colloids), it is obvious that higher solid contents would be beneficial for the drying, while still realizing the polymer coating on the reinforcements to predefine the hard/soft nanostructure in bulk. To this end, we have previously shown that well-defined polymer-coated nanoclays can be achieved by powder mixing at higher concentrations of suspensions if the colloidal interactions between the components are well controlled (>10 wt%).<sup>[4a]</sup> Additionally, the drying process would need to be moved towards more favorable continuous spray drying. Another challenge is to achieve a more global alignment, which is likely to be addressable by shear forces. The tuning of the mechanical property space will benefit from further advances in vitrimer science and technology, or also using other concepts of dissociative covalent bonds, such as hydrogen bonds. We expect that the approach should however be generalizable to other nano/microplatelet and nanofibrillar bioinspired composites with high degrees of order and at high fractions of reinforcements.

# 4. Experimental Section

*Materials*: Nanoclays were obtained from Topy Industries and BYK/ Altana. Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene (MX) was prepared by etching aluminum atoms from Ti<sub>3</sub>AlC<sub>2</sub> MAX phase).<sup>[15a]</sup> The synthesis of the EMA prepolymer is documented in ref. [11]. Zn(OAc)<sub>2</sub> was obtained from ABCR.

Preparation of Reinforcements: NC1 and NC2: NC1 and NC2 were dispersed, separately, in MilliQ water (5 wt%) and then centrifuged at 12 000 rpm for 90 min. The centrifuged dispersions exhibit three separate phases, a lower one with sediments, a middle one with clean viscous nanoclay solution ( $\approx$ 2 wt%) and an upper one with water excess. The middle phase was used to prepare exfoliated nanoclay dispersions at 1 wt% of solid content.

NC3: A solution of NC3 in MilliQ water (2 wt%) was centrifuged at 6000 rpm for 30 min. The centrifuged dispersion showed two phases, a

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lower one with sediments and an upper one with cleaned and dispersed NC3 in water. The upper one was used to prepare exfoliated NC3 dispersions at 1 wt%.

 $MX\!\!:\!MX$  was dispersed in MilliQ water (1 wt%) and then sonicated for 30 min.

Preparation of Bulk Nacre–Mimetic Nanocomposites: The reinforcement dispersions (1 wt%) were added to the EMA prepolymer solution (1 wt%) while stirring vigorously to reach a 1/1 w/w solid content. Zn(OAc)<sub>2</sub> (10 mol%/ester groups) was added subsequently as powder. The nanocomposite solutions were freeze dried in centrifuge tubes (50 mL capacity each). The dried polymer-coated reinforcements were ground at -200 °C using a Retsch CryoMill to obtain the finest possible nanocomposite powder and then hot-pressed for 1 h, at 170 °C and 10 bar using a Collin PCSII 200P plates press, aiming at a diameter of 25 mm and a thickness from 0.5 to 2 mm by changing the powder mass in the mold.

*X-Ray Diffraction (XRD)*: Wide-angle X-ray diffraction was performed using a Bruker D8 Discover. The measurements were carried out in Bragg-Brentano geometry, Cu radiation at 40 kV, with a wavelength of 1.5406 Å and a LynxEye XeT detector.

*Scanning Electron Microscopy (SEM)*: Cross sectional surfaces were observed with a FEI Scios DualBeam FIB/SEM at 5 kV. The samples were sputter-coated with an ultrathin Au layer.

*Flexural Tests*: Three-point bending flexural tests were performed on a Hegewald & Peschke Inspect Table 5 Universal Testing Machine with a 1 kN load cell at room temperature and 55% RH. The support span had a length of 10 mm and the bending anvil a diameter of 2 mm. Specimens had a width of 2 mm and a thickness range between 0.5 and 1 mm. The chosen support span/thickness ratio allowed failure through bending moment. The displacement of the beam was measured from the moment the anvil touches the sample. The flexural modulus is calculated from the linear elastic region. At least six samples were tested at a rate of 5 mm min<sup>-1</sup>.

*Optical Microscopy*: The powder size distribution was measured with a VWR International GmbH binocular optical microscope coupled with a Moticam 2.0 MP digital camera.

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### **Conflict of Interest**

The authors declare no conflict of interest.

### Data Availability Statement

Research data are not shared.

### **Keywords**

bioinspired nanocomposites, bulk specimens, cyclic economy, hotpressing, nacre mimetics, recycling, vitrimers

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