Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Fabrication of Bragg Stack Films of Clay Nanosheets and Polycations via Co-polymerization of Intercalated Monomers and Functional Interlayer Cations

Dominik Schuchardt [a], Sabine Rosenfeldt [a], Hussein Kalo [b] and Josef Breu [a]*

[a] Bavarian Polymer Institute and Department of Chemistry, University of Bayreuth, Universitätsstr. 30, 95447, Bayreuth, Germany; dominik.schuchardt@uni-bayreuth.de (D.S.), sabine.rosenfeldt@uni-bayreuth.de (S.R.), josef.breu@uni-bayreuth.de (J.B.)

[b] BYK-Chemie GmbH, Plant Moosburg, Stadtwaldstrasse 44, 85368 Moosburg, Germany; Hussein.Kalo@altana.com (H.K.)

* Correspondence: josef.breu@uni-bayreuth.de

Table S1 Energy dispersive X-ray spectroscopy analysis of the freeze-dried vinylbenzyltrimethylammonium exchanged hectorite confirming complete exchange of Na^+.

Point	O / atom%	Na / atom%	Si / atom%
1	37.0	0.0	16.1
2	39.6	0.0	12.5
3	37.6	0.0	16.0
4	39.0	0.0	13.7

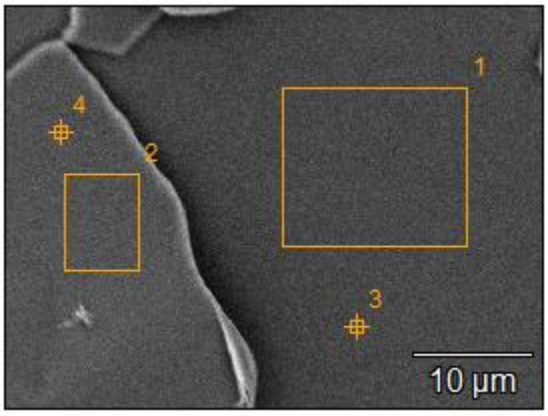

Fig. S1 Scanning electron microscope image of the EDX measurement points 1-4.

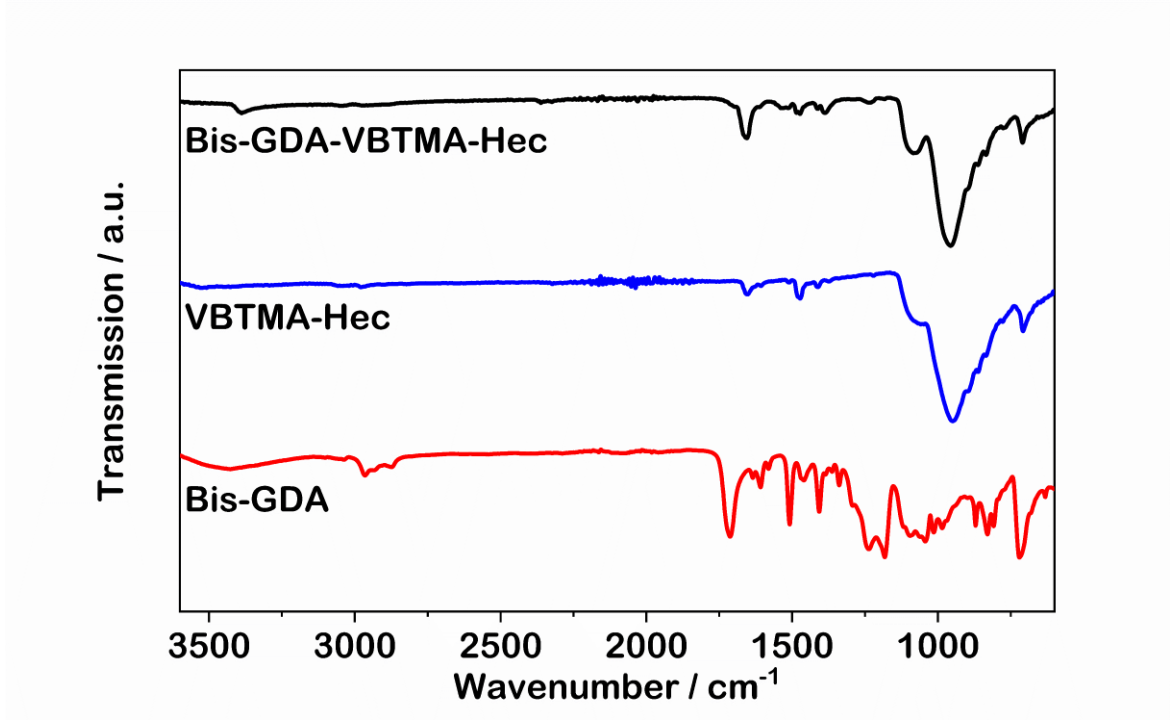

Fig. S2 Fourier-transform-infrared (FTIR) spectra of the Bis-GDA-VBTMA-Hec composite (black), VBTMA-Hec (blue) and Bis-GDA (red).

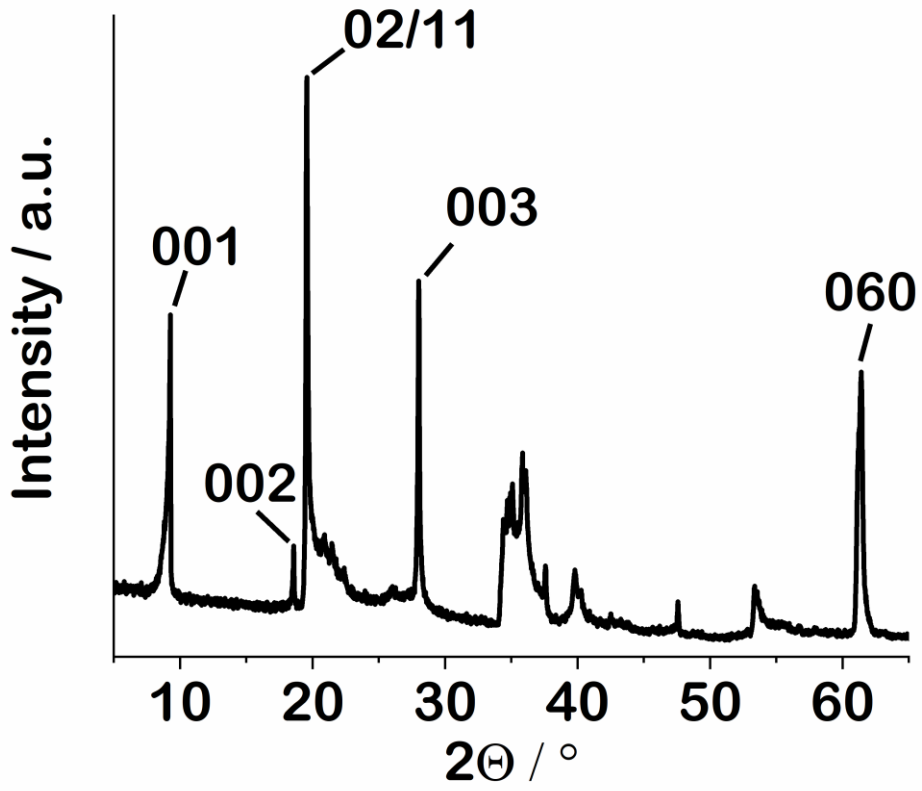

Fig. S3 X-ray pattern of dried Na-Hec indicating a d-spacing of 0.96 nm.

Thermogravimetric analysis (TGA) was measured on a Linseis STA PT 1600 (Linseis Messgeräte GmbH, Germany). The nanocomposite film was peeled off the polyethyleneterephthalat (PET) substrate and grinded to a powder by a cryogenic mill prior to the measurement. The samples were heated up to 1000 °C with a heating rate of 10 °C min^{-1} in synthetic air.

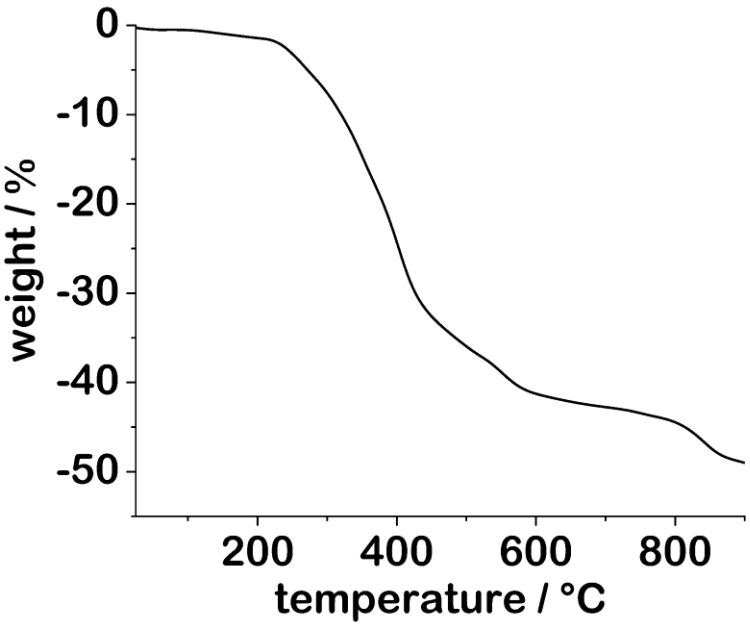

Fig. S4 TGA curve of BIs-GDA-VBTMA-Hec.

The calculation of the expected d-spacing (d001) in the polymerized and dried nanocomposite can be done using the volume content φ_{Hec} of the hectorite.

$$\varphi = \frac{wt\%\ (Hec)\cdot\rho(VBTMA+Bis\text{-}GDA)}{wt\%\ (Hec)\cdot\rho(VBTMA+Bis\text{-}GDA)+\left(100\ wt\%-wt\%\ (Hec)\right)\cdot\rho(Hec)} \quad \text{(E S1)}$$

ρ(VBTMA + Bis-GDA) can be derived through the percentage of VBTMA and Bis-GDA in the polymer matrix with With ρ(VBTMA) = 1.05 g cm^{-3} and ρ(Bis-GDA) = 1.18 g cm^{-3}.

$$\rho(VBTMA + Bis\text{-}GDA) = \frac{m(VBTMA)+m(Bis\text{-}GDA)}{\left(\frac{m(VBTMA)}{\rho(VBTMA)}\right)+\left(\frac{m(Bis\text{-}GDA)}{\rho(Bis\text{-}GDA)}\right)} \quad \text{(E S2)}$$

With ρ(Hec) = 2.7 g cm^{-3} and 54 wt% (Hec) in the dry nanocomposite, the volume content φ_{Hec} = 0.33.

$$d_{001} = \frac{1.0\ \text{nm}}{\varphi} \approx 3.0\ nm \quad \text{(E S3)}$$

The cross-sectional transmission electron microscopy (TEM) image was Fourier transformed into a two-dimensional XRD pattern (Figure S5a). Then a mask was applied, and an inverse FT was done (Figure S5b). To measure the distance of the hectorite nanosheets in the cross-section a histogram was used (Figure S5c), yielding a layer distance

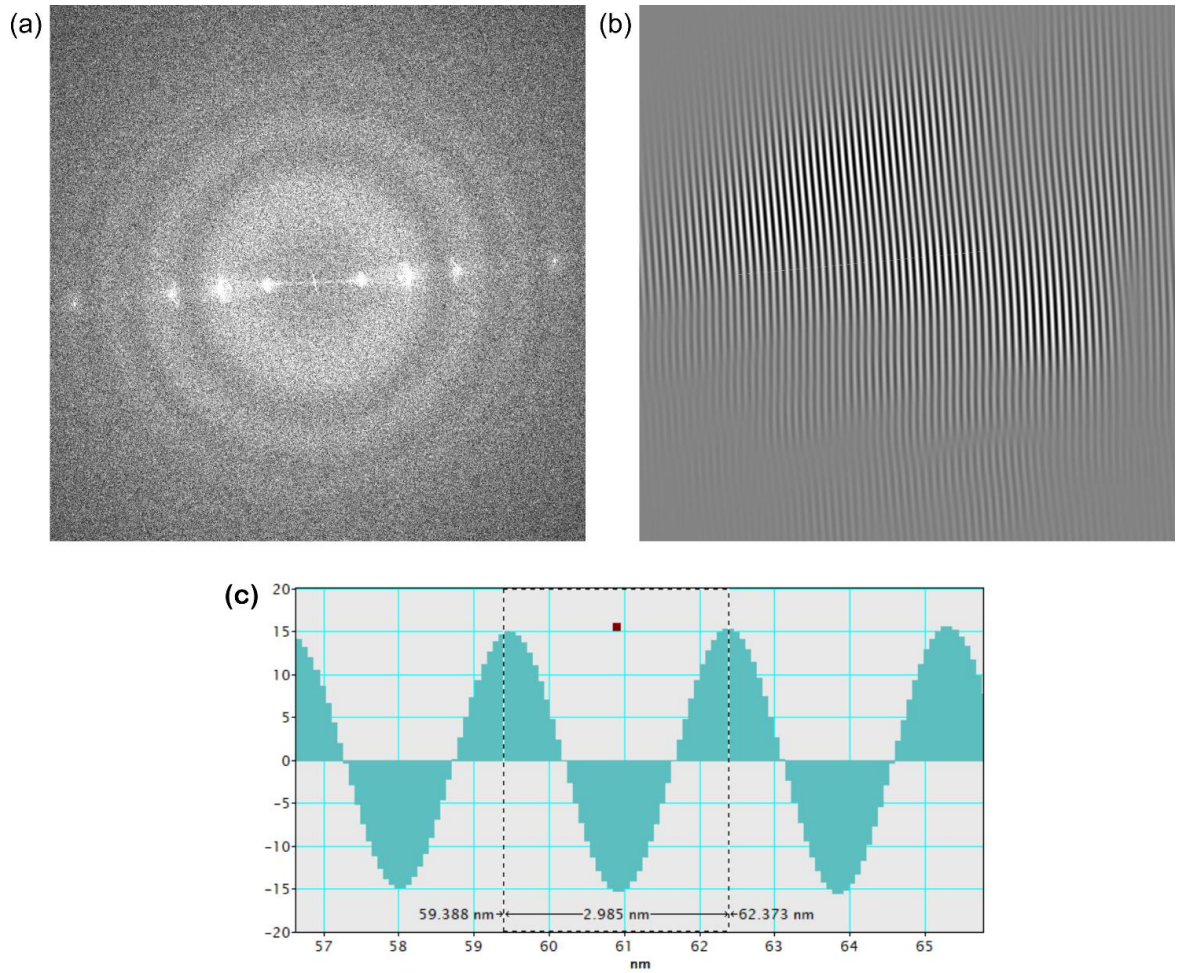

Fig. S5: (a) 2D XRD pattern of Bis-GDA-VBTMA-Hec obtained by Fourier transformation of the cross-sectional TEM image. (b) Inverse FT of the mask 2D XRD pattern of Bis-GDA-VBTMA-Hec. (c) Histogram of the grey scale analyses indicating a layer distance of 3 nm.

of 3 nm.

Preparation of neat polymer films from Bisphenol A glycerolate diacrylate (Bis-GDA)

1 g of Bis-GDA was placed in a Teflon dish and1 mol% photoinitiator were mixed and heated to 60 °C in an oven to form a homogeneous film. The sample was then polymerized by UV light for 20 minutes.

For better comparison, the oxygen transmission rate needs to be converted to the oxygen permeability (OP) by multiplying the OTR with the overall thickness of the measured sample. This is necessary because the OTR is largely influenced by the thickness of the sample. Additionally, the contribution of the PET foil to the OTR is subtracted during the conversion to the OP according to Roberts et al.2

Table S2 Oxygen (OTR) and water vapor transmission rates (WVTR) of a neat polymer film from Bis-GDA.

	relative humidity, %	**Bis-GDA**
Thickness, µm		976.2
OTR, $cm^3\ m^{-2}\ day^{-1}\ atm^{-1}$	50	3.80
	90	7.48
WVTR, $g\ m^{-2}\ day^{-1}$	50	0.51
	90	0.93

Table S3 Oxygen (OP) and water vapor permeabilities (WVP) of a neat polymer film from Bis-GDA.

	relative humidity, %	Bis-GDA-VBTMA-Hec	Bis-GDA
OP, cm^3 µm m^{-2} day^{-1} atm^{-1}	50	0.76	3.71×10^3
	90	4.41	7.30×10^3
WVP, g µm m^{-2} day^{-1} atm^{-1}	50	12.87	3.57×10^4
	90	95.52	3.59×10^4

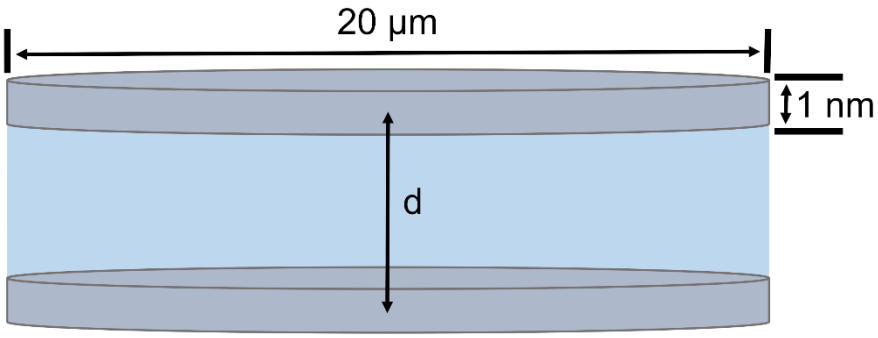

Fig. S6: Model used to fit the small-angle X-ray scattering data and to obtain the basal spacing d assuming a layer width of 20 µm (± 15 % (Gauss)) and a layer thickness of 1 nm (± 3 % (Gauss)).[1]

References

1. S. Förster, S. Fischer, K. Zielske, C. Schellbach, M. Sztucki, P. Lindner and J. Perlich, *Adv. Colloid Interface Sci.*, 2011, **163**, 53-83.
2. A. P. Roberts, B. M. Henry, A. P. Sutton, C. R. M. Grovenor, G. A. D. Briggs, T. Miyamoto, M. Kano, Y. Tsukahara and M. Yanaka, *J. Membr. Sci.*, 2002, **208**, 75-88.