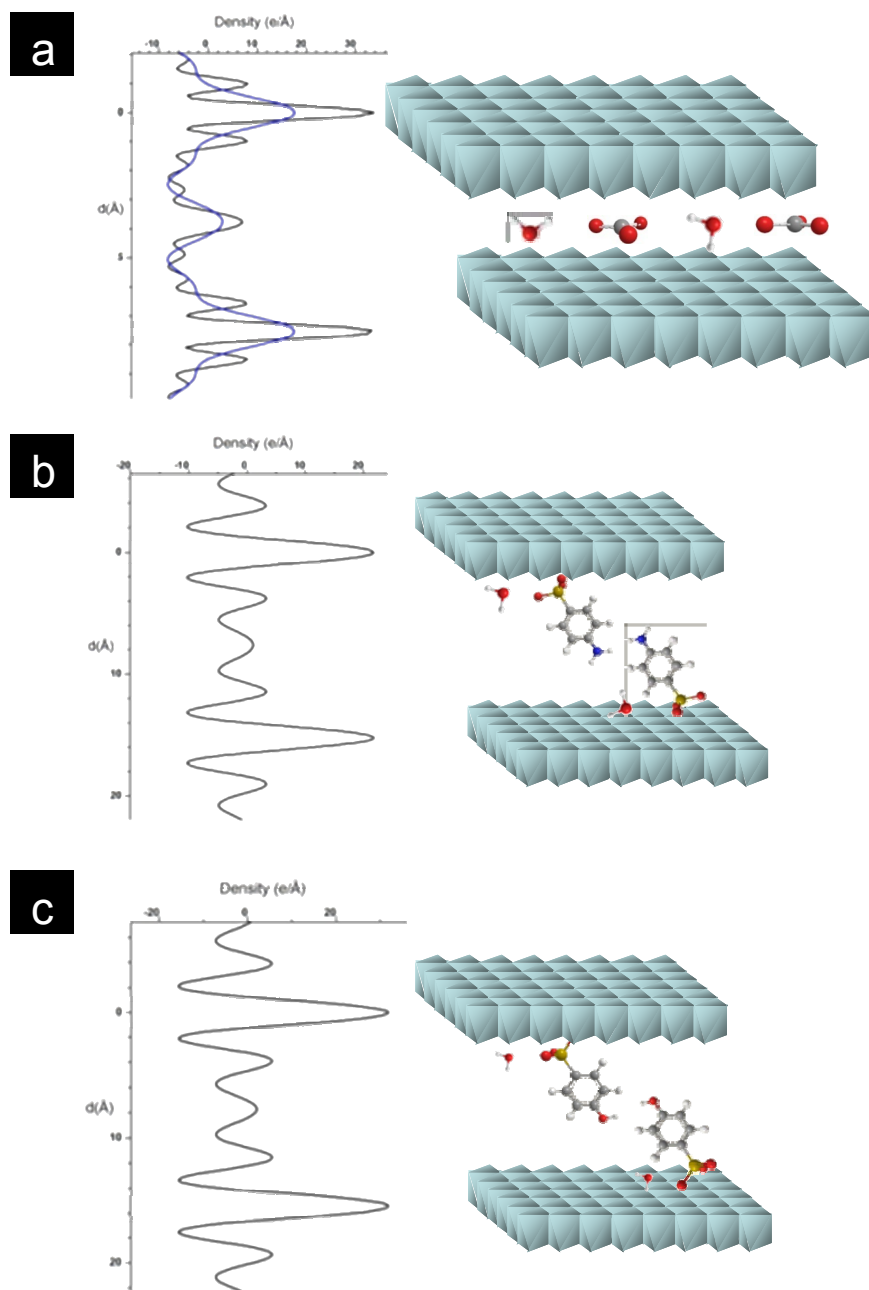


Supporting Information

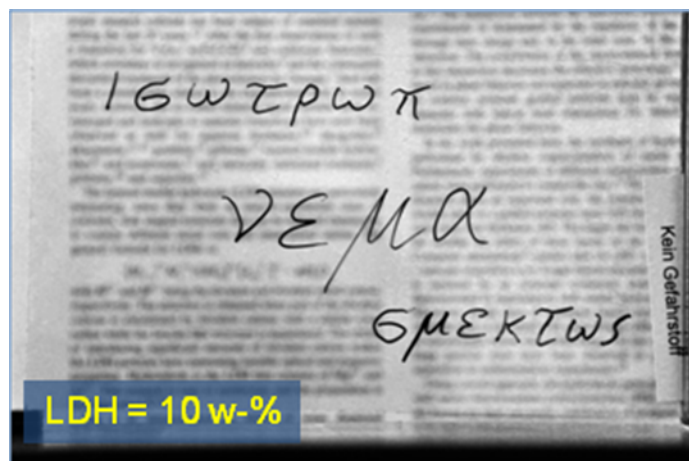


SEI 1. One-dimensional electron density distribution along the c-stacking axis for LDH

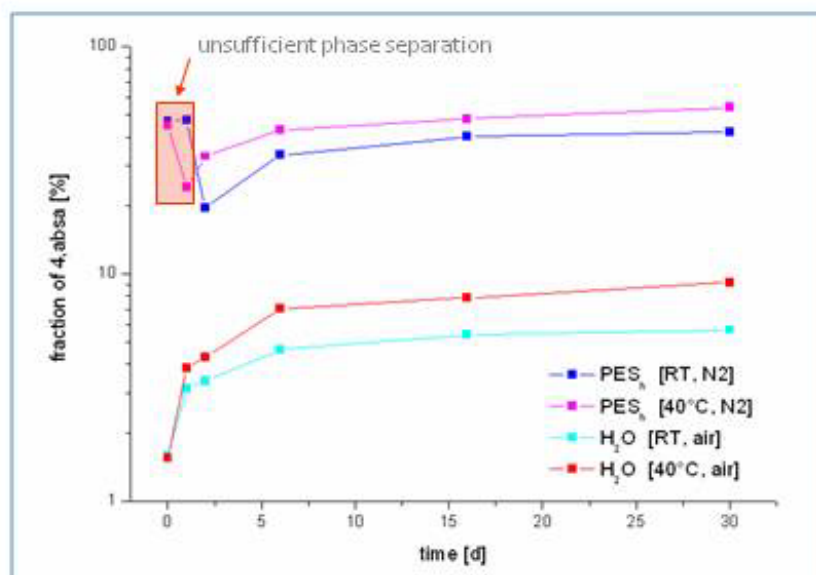
phases. a, Zn_2Al/CO_3^{2-} . b, $Zn_2Al/4$ -ABSA. c, $Zn_2Al/4$ -HBSA. One-dimensional electron density calculations based on X-ray diffraction are often carried out to probe the structure of the incorporated species in two-dimensional inorganic hosts (Bauer, J., Behrens, P., Speckbacher, M. & Langhals, H. *Adv. Funct. Mater.* **13**, 241 (2003) – Itoh, T., Shichi, T., Yui, T., Takahashi, H., Inui, Y. & Takagi, K. *J. Phys. Chem. B* **109**, 3199 (2005) – Whittingham, M. S. & Jacobson, A. J. *Intercalation Chem.*, Acad. Press, NY (1982)). The electron density maps were obtained from equation $e(z) = 1/c \sum [2 \cdot F_{00l} \cdot \cos(2\pi \cdot l \cdot z)]$. The structure factors of the $00l$ were derived from their intensities corrected for Lorentz polarization effects. C is the unit cell parameter.

SEI 2. For LDH phases Zn_2Al/CO_3^{2-} , $Zn_2Al/4$ -ABSA and $Zn_2Al/4$ -HBSA, positions of the main hkl Bragg diffraction peaks extracted from the corresponding powder X-ray diffraction pattern in the 2θ range 2 - 70° (Figure 1 a) using FULLPROF program for the peak picking

LDH phase	Bragg reflections $2\theta(^{\circ})$								
	003	006	009	0012	012	015	018	110	113
Zn_2Al/CO_3^{2-}	11.85	23.72	34.83	-	-	39.47	47.06	60.52	61.88
$Zn_2Al/4$ -ABSA	5.82	11.67	17.46	23.40	34.16	-	-	60.66	-
$Zn_2Al/4$ -HBSA	5.78	11.49	17.22	23.17	34.58	-	-	60.61	-

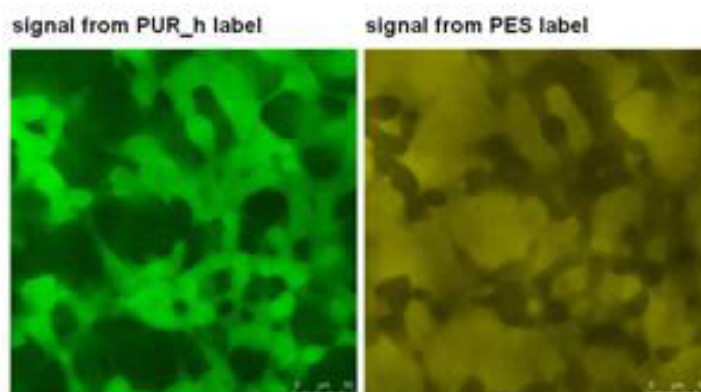


SEI 3. Transparent and smooth coating layer via drawing or spraying and a subsequent drying and curing step obtained from aqueous paste of 4-ABSA LDH dispersed into a 2-butoxyethanol containing aqueous solution of the polymer PES_h in which an aqueous dispersion of a carboxylate stabilized polyurethane PUR_h was added.



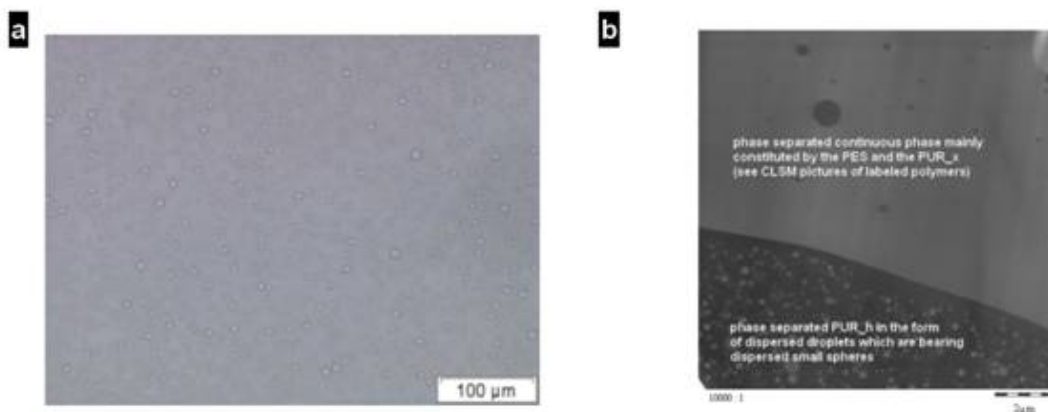
SEI 4. Variation of the concentration of liberated 4- ABSA ions in the serum phase of centrifuged samples of the intermediate PES_h – LDH mesophase as a function of time and temperature. For comparison graphs are shown of a reference dispersion without PES_h which was treated under air

instead of under nitrogen. The values represent the liberated amounts of 4-ABSA anions due to a carbonization of the LDH phase. The evaporated amounts of water was refilled over time. 4-ABSA was analyzed in the serum by determining the sulfur content.

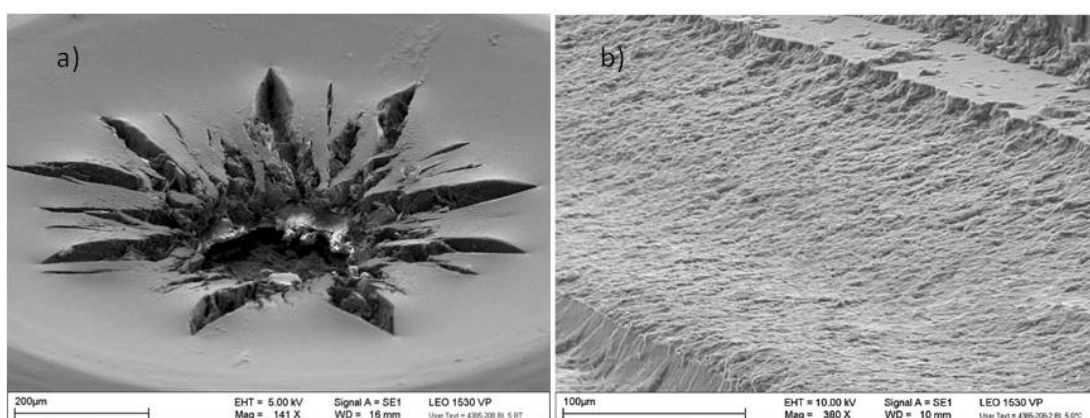


SEI 5. Morphology of an air dried film of the particle free phase separated ternary polymer mixture. The CLSM pictures showed two complementary phases each of them visualized by the signals of the covalently labeled PES (rhodamine marker shown in yellow) and the covalently labeled PUR_h (nitrobenzofurazane marker shown in green), respectively. The morphology resulted from a spinodal demixing process. The signals of the labeled PES as well as of the PUR_x (also covalently labeled with the nitrobenzofurazane) yielded congruent patterns besides the dark areas constituted by the unlabeled PUR_h. Synthetic details for the labeling of the polymers were described elsewhere.²⁰ Scale bars are 10 μm.

Confocal laser scanning microscopy (CLSM) was performed on a Leica TCS SPE microscope. The excitation / detection wave lengths were 488 / 500-530 nm and 532 / 550-620 nm for the fluorescent marker moieties 4-nitrobenzofurazane (labeled PUR, PUR_h and PUR_x) and rhodamine (labeled PES and PES_h) respectively.



SEI 6 Morphology of the MF resin cross linked cured film of the particle free phase separated ternary polymer mixture. **a**, Optical microscopy picture of a drawn film on glass showed huge dispersed droplets within a featureless continuous phase. **b**, Same material drawn on a polypropylene panel and baked simultaneously (as the film shown in a) yielded large islands of a less dense material as visualized by the dark field TEM image obtained from a lateral cut. It revealed that this phase which was mainly constituted by the PUR_h comprises numerous spheres of uneven diameters below one micron. The chemical nature of this phase is yet unknown.



SEI 7. Crater produced by a single spherical impact on a coated steel test panel. **a**, A section of the circular crater wall was shown by SEM. From the lower left corner to the upper right corner, fracture

surfaces of: the phosphate pretreatment layer, the step of the fractured cathodically electrodeposited coating layer, the readily inclining rough fracture surface of the LDH composite layer (the LDH phase was $Mg_2Al/3$ -ABSA dispersed within the ternary polymer matrix, crosslinked with MF resin), the smooth interfacial fracture surface between the composite layer and the base coat layer and finally the steep step of the fractured base coat layer, respectively. **b**, A magnified section of the composites fracture surface showed the tortuous crack path through the LDH particle comprising continuous phase.