Supporting Information

Spontaneous Delamination of Affordable Natural Vermiculite as a High Barrier Filler for Biodegradable Food Packaging

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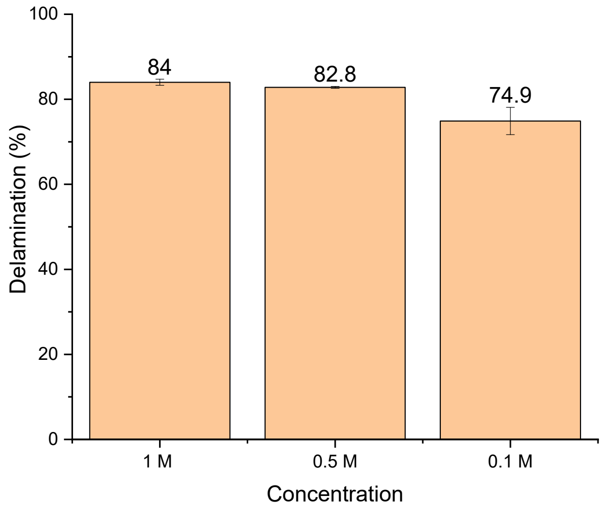

Figure S1. Comparison of the delamination yield depending on concentration of the cation.

CHN analysis

Table S1. Experimental wt% of C and N in exchanged organoclays

	$C_4 Cl^-$	Na to $C_4 Cl^-$	$C_4 Ac^{2-}$
C, wt %	3.9	4.78	7.6
N, wt %	1.08	1.31	2.21

$C_4 Cl^-$ is the sample prepared via single exchange using butylammonium cation and chlorine as a counter anion.

Na to $C_4 Cl^-$ denotes the two step sequential exchange with sodium and then with $C_4 Cl^-$.

$C_4 Ac^{2-}$ denotes the single exchange using the butylammonium cation and citrate as a counter anion.

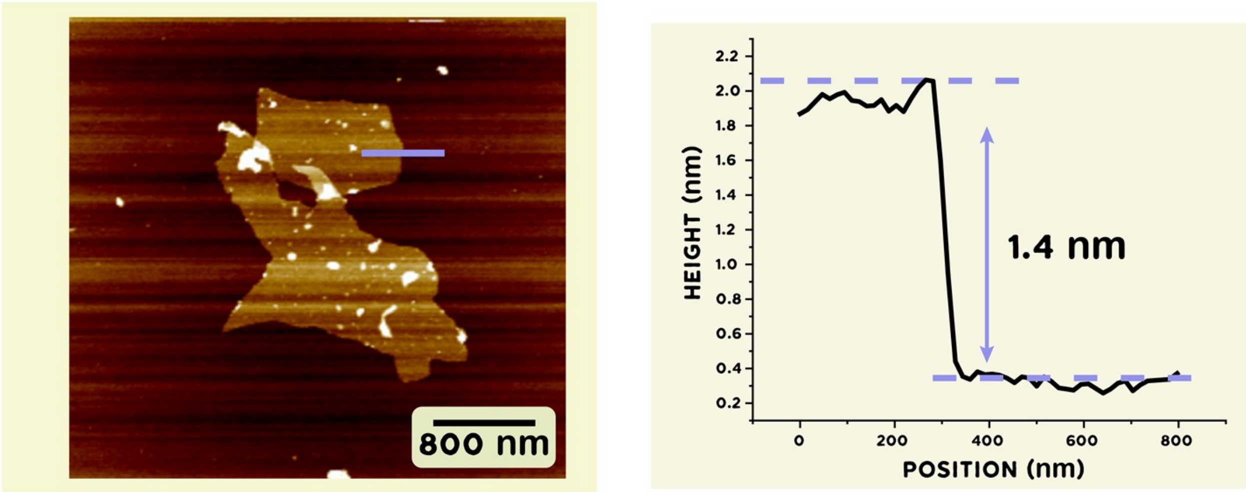

Figure S2. Topographic AFM image of a single nanosheet from an aqueous suspension with the height profile

Cussler's theory for permeability:

$$P_{rel} = P/P_0 = (1 + \mu\left(\frac{\alpha^2 \phi^2}{1-\phi}\right))^{-1}$$

Equation S1

Where P is the permeability of the nanocomposite, P_0 is the permeability of the neat polymer, ϕ is the filler content (volume fraction), α is the aspect ratio of the filler, μ is a geometrical factor dependent on filler shape (in case of platelet shape filler it is 4/9)[1]
To calculate theoretical improvement factor for different nanosheet sizes: μ is 4/9, aspect ratio is 30 for Laponite, 150 for Montmorillonite, 4000 for Vermiculite.

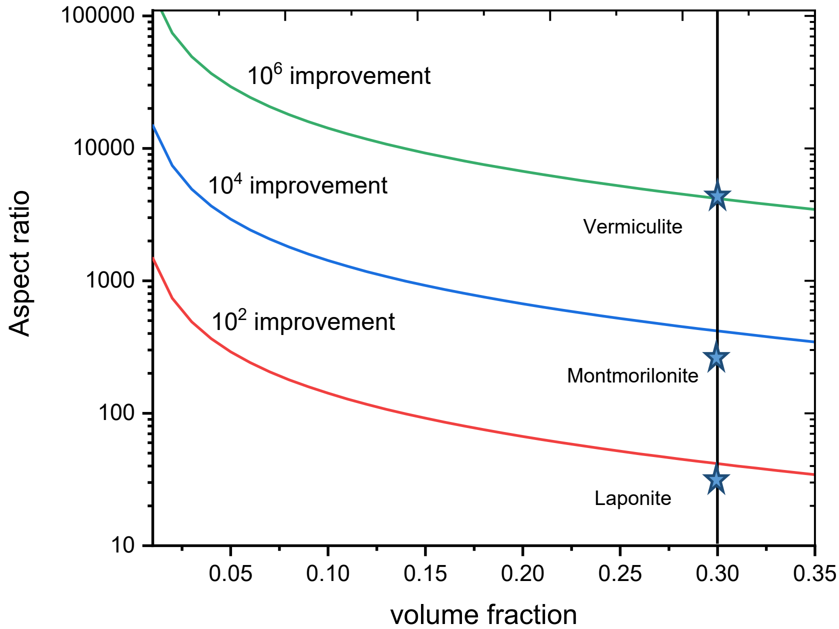

Figure S3. Improvement based on different aspect ratio nanosheets. The vertical line corresponds to a filler content as applied in the PLA-verm/CNF foil stressing the superiority of the vermiculite nanosheets compared to more common clay fillers.

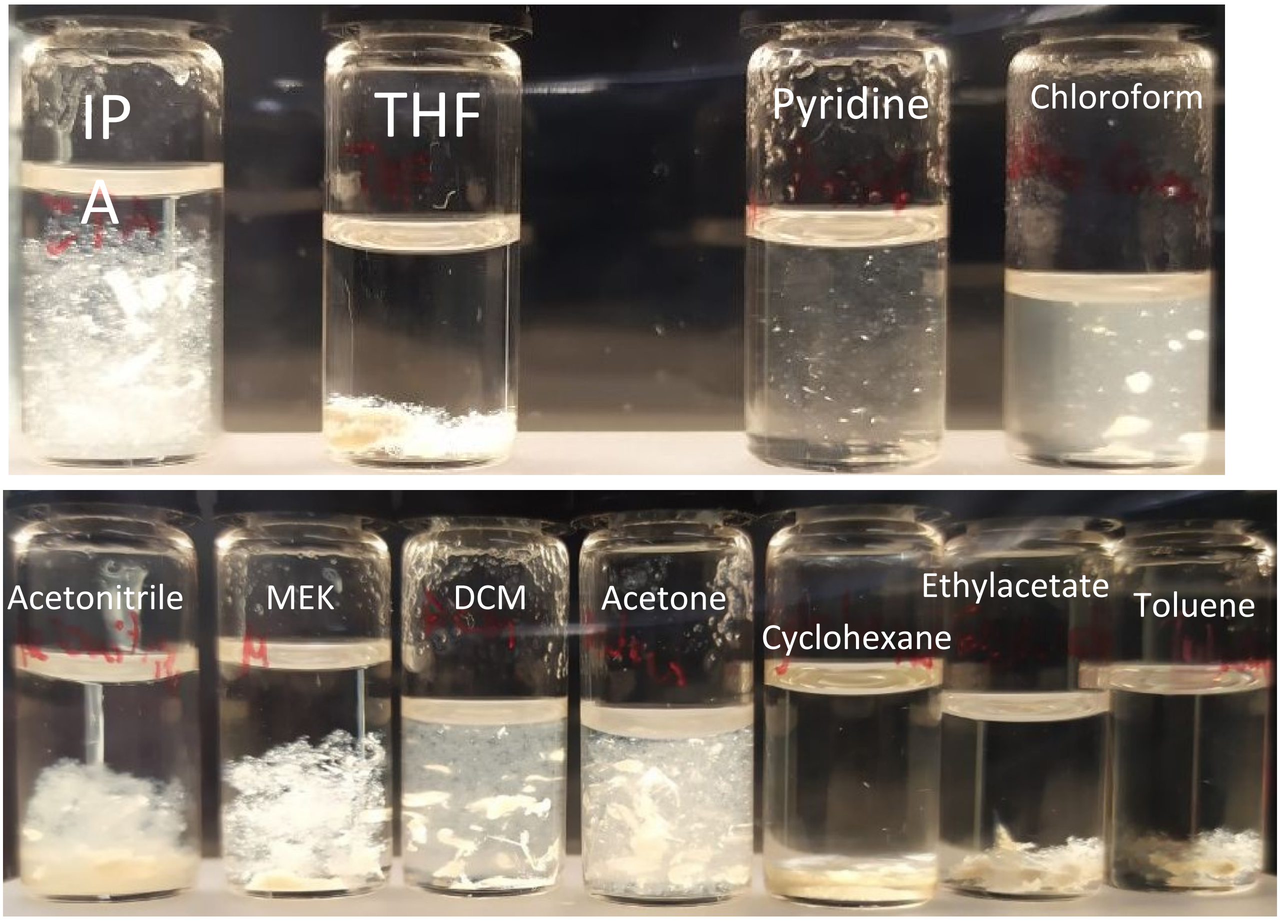

Figure S4. Photos of flocculated vermiculite samples in different solvents

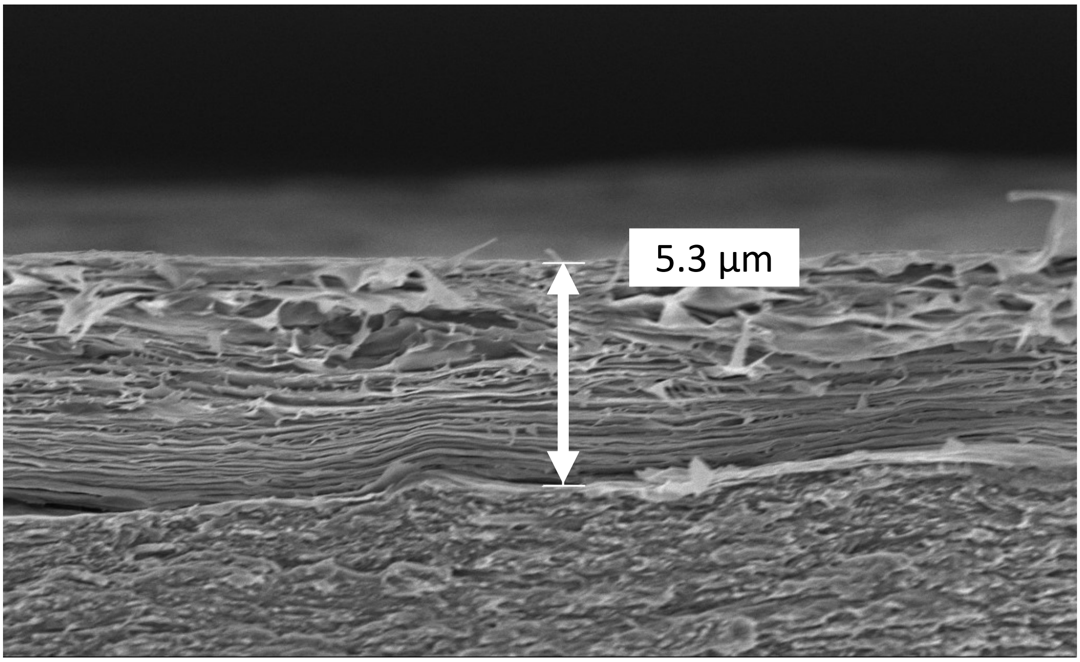

Figure S5. SEM photo of PLA-verm/CNF foil cross section. Marked bar denotes the thickness of the coating

Table S2. Summary of the solvent properties of the solvents used in the studies of natural vermiculite swelling

Solvents	Relative dielectric constant[2]	Dipole moment, D [2]	δD[3] $[Mpa^{1/2}]$ [3]	δP $[Mpa^{1/2}]$	δH $[Mpa^{1/2}]$	Swelling
Ethanol	24.5	1.66	15.8	8.80	19.4	yes
Methanol	32.6	2.87	14.7	12.3	22.3	yes
DMac	37.8	3.72	16.8	11.5	9.40	yes
DMSO	46.7	4.10	18.4	16.4	10.2	yes
NMF	171[4]	3.83	17.4	18.8	15.9	yes
Water	80.1	1.87	15.5	16.0	42.3	yes
N-methyl-acetamaide	179[4]	4.12	16.9	17.0	13.0	yes
FA	111	3.71	17.2	26.2	19.0	yes
γ-BL	41.0	4.27	18	16.6	7.40	yes
Propylene carbonate	64.9[5]	4.94	20	18.0	4.10	yes
NMP	32.2	4.09	18	12.3	7.20	yes
DMF	36.7	3.79	17.4	13.7	11.3	yes
Isopropanol	19.9	1.59	15.8	6.10	16.4	no
Cyclohexane	1.88	0	16.8	0	0.20	no
Pyridine	12.5	2.37	19.0	8.80	5.90	no
Acetonitrile	38.8	3.44	15.3	18.0	6.10	no
Methylethyl ketone	18.5	2.78	16.0	9.00	5.10	no
Acetone	21.4	2.69	15.5	10.4	7.00	no
Toluene	2.38	0.31	18.0	1.4	2.00	no
Chloroform	4.81	1.15	17.8	3.1	5.70	no
Dichloro-methane	8.93	1.14	17.0	7.3	7.10	no
Tetra-hydrofuran	7.58	1.69	16.8	5.7	8.00	no
Ethylacetate	6.40	1.88	15.8	5.3	7.20	no

DMac-Dimethylacetamide, DMSO- Dimethyl sulfoxide, NMF- N-Methylformamide, FA-Formamide, γ-BL- gamma-Butyrolactone, NMP- N-Methyl-2-pyrrolidone, DMF- Dimethylformamide, δD dispersive, δP polar, δH hydrogen bond component of Hansen parameters.

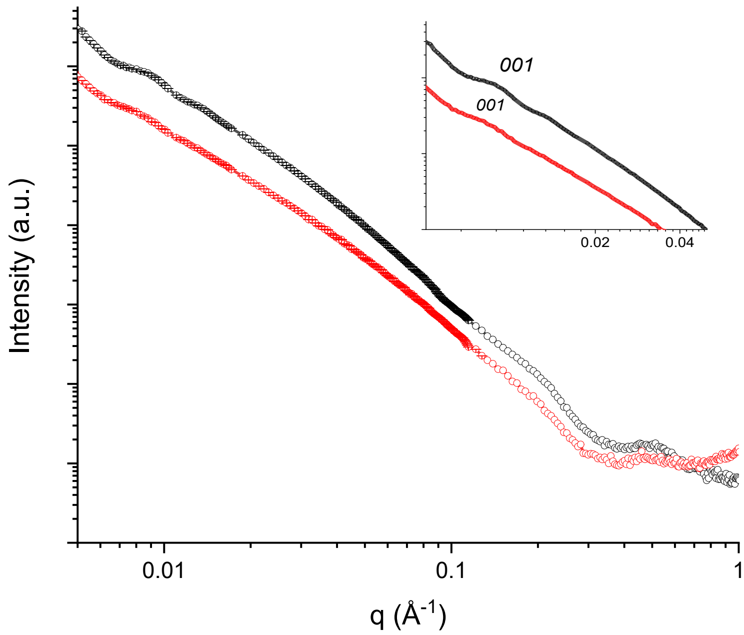

Figure S5. SAXS pattern of the vermiculite in gamma-bl (black) and vermiculite + PLA in gamma-bl (red), showing the *001* oscillation in similar positon of q, showing that addition of PLA to vermiculite suspension do not compromise the colloidal stability of nanosheets. Insert shows the q range from 0.005 to 0.05 Å^{-1} with higer magnifications.

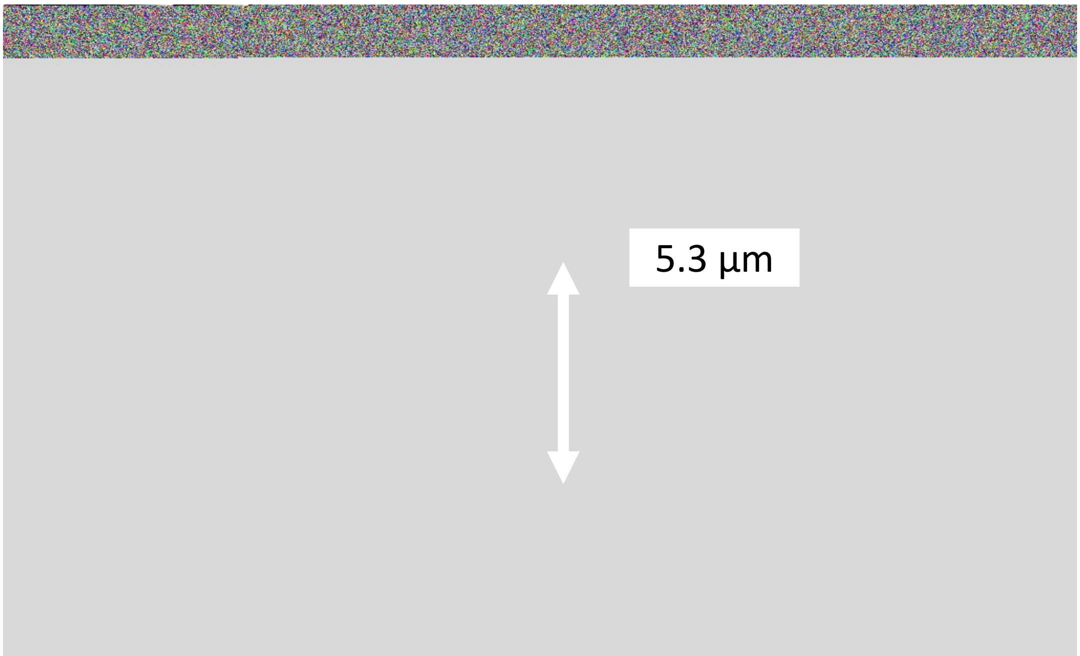

Figure S6. SEM photo of PLA-verm/CNF foil cross section. Marked bar denotes the thickness of the coating

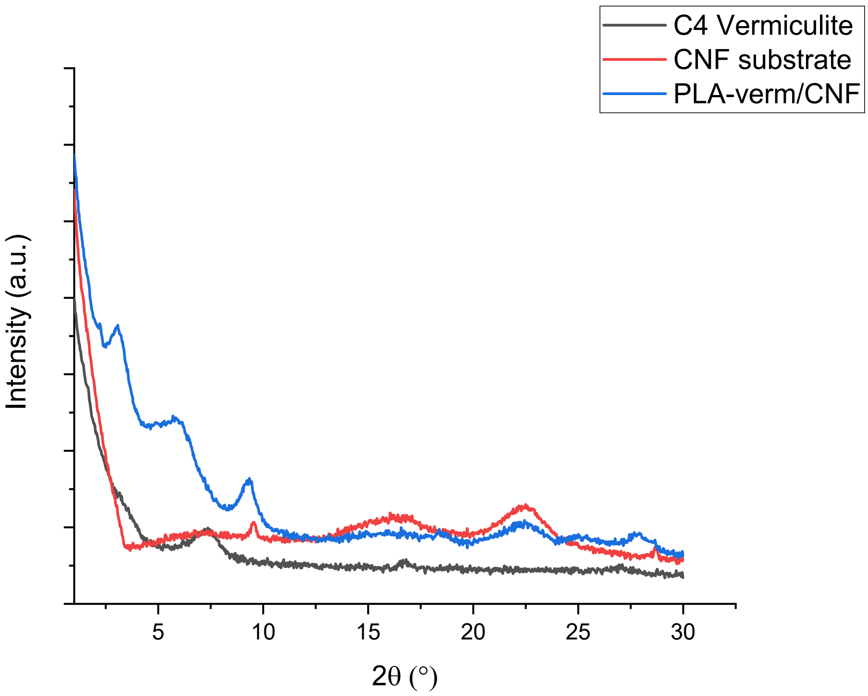

Figure S7. XRD pattern of the C4 exchanged vermiculite, CNF foil and PLA-verm/CNF nanocomposite.

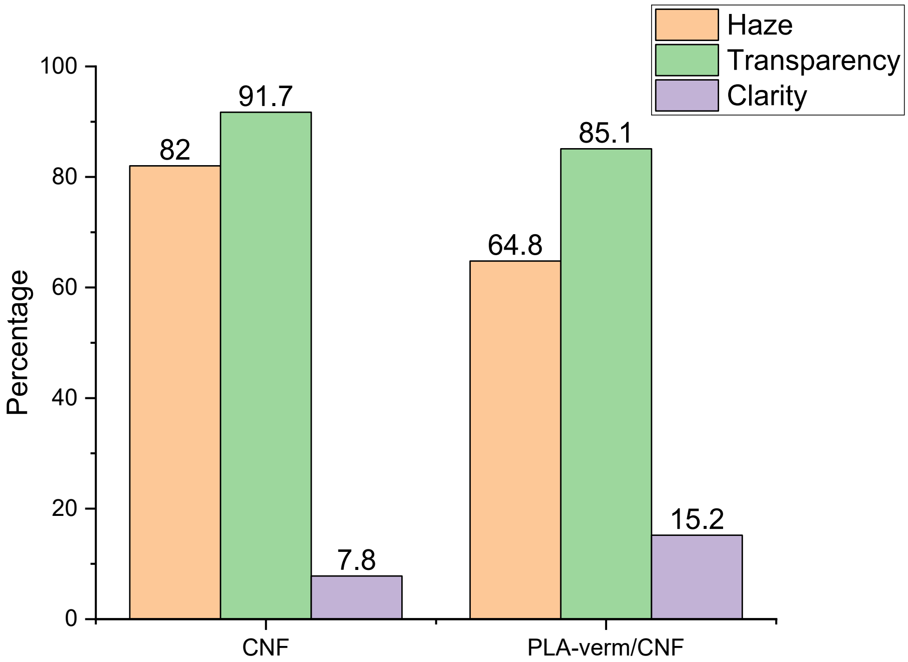

Figure S8. Optical properties (transmittance, haze, clarity) of the neat CNF substrate and CNF/Verm foil.

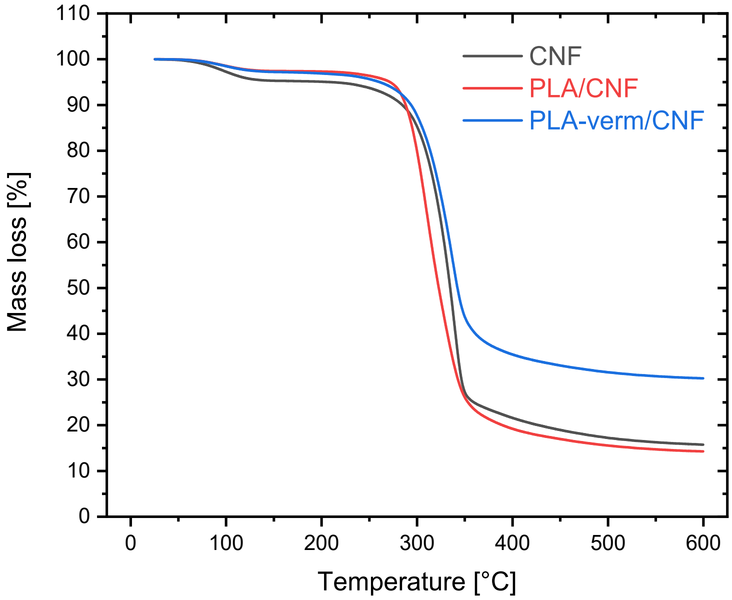

Figure S9. Thermal gravametric analysis of CNF substrate (black), CNF coated with PLA (red), and CNF coated with PLA-verm nanocomposite (blue)

Calculation for barrier improvement factor

The OTRs for the coatings can calculated by;

$$OTR_{coating} = \frac{1}{\frac{1}{OTR_{total}} - \frac{1}{OTR_{substrate}}}$$

Permeability (*P*) of both the neat polymer coating and the nanocomposite coating are calculated using their respective thicknesses (*d*);

$$P = OTR * d$$

For water vapor permeability, the water vapor partial pressure (Δp) must be considered. At 100% RH and 23°C, Δp is 0.0277 atm, which corresponds to Δp = 0.020775 atm at 75% RH and 23 °C. The new equation is;

$$P = \frac{OTR * d}{\Delta p}$$

Barrier improvement factor (BIF) is the ratio of the permeability of the neat polymer coating (P_{neat}) to the permeability of the nanocomposite coating (P_{nc});

$$BIF = \frac{P_{neat}}{P_{nc}}$$

Equation S2

Calculation for theoretical shelf life[6]:

For 500 g of powder material that is 2 wt% water content,

$weight_{dry} = 500 * 0.98 = 490\ g$

$weight_{water} = 500 * 0.02 = 10\ g$

For a critical moisture content of 8 wt%, the final weight of water in the powder is,

$weight_{max} = \frac{490}{0.92} - 490 = 42.6\ g$

The weight of water to permeate into the powder is,

$42.6 - 10 = 32.6\ g$

For a rectangular package of dimensions 3 x 15 x 10 cm, the surface area is 0.045 m^2

The amount of water permeating into the package per day is

$weight_{water\ per\ day} = 0.045\ m^2 * OTR$

The time to reach the critical moisture content (i.e. shelf life) is,

$shelf\ life = \frac{32.6\ g}{weight_{water\ per\ day}}$

References:

[1] E. L. Cussler, S. E. Hughes, W. J. Ward, R. Aris, *J. Membr. Sci.* **1988**, 38, 161.
[2] W. M. Haynes, *CRC Handbook of Chemistry and Physics*, CRC Press, **2011**.
[3] C. M. Hansen, *Hansen Solubility Parameters*, CRC Press, **2007**.
[4] J. Barthel, R. Buchner, B. Wurm, *J. Mol. Liq.* **2002**, 98-99, 51.
[5] Y. Chernyak, *J. Chem. Eng. Data* **2006**, 51, 416.
[6] G. L. Robertson, *Food packaging and shelf life: a practical guide*, CRC Press, **2009**.