Supplementary Information

Aged layered double hydroxide nanosheet - polyvinyl alcohol dispersions for enhanced gas barrier coating performance

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Experimental and Methods

Materials. Mg(NO$_3$)$_2$·6H$_2$O (98%, Alfa Aesar), formamide (99%, Alfa Aesar), Al(NO$_3$)$_3$·9H$_2$O (99%, Acros Organics), sodium hydroxide (98%, Macron), sodium nitrate (>98%, Alfa Aesar), Bentonite powder (Sigma-Aldrich), and poly(vinyl alcohol) (PVA) (Mowiol® 8-88, $M_w$: 67,000 g mol$^{-1}$, 86.7-88.7 mol% hydrolysis, Sigma-Aldrich) were used as received without further purification. Polyethylene terephthalate (PET) film (12 μm thick) was supplied by SCG chemicals Co., Ltd. (Thailand).

Synthesis of LDH nanosheets. The Mg$_2$Al-LDH NS sample was synthesised following on literature reports$^1$. Typically, the traditional titration method$^2$ was slightly modified to directly synthesise Mg$_2$Al-LDH nanosheets in 30 vol% aqueous formamide. A 100.0 mL solution composed of Mg(NO$_3$)$_2$ (0.333 M) and Al(NO$_3$)$_3$ (0.167 M) was added drop by drop to a solution of 100.0 mL NaNO$_3$ (0.167 M) containing 30 vol% formamide. Simultaneously, a solution of 1 M NaOH was added dropwise under magnetic stirring at 65 °C to maintain the system at a pH value of ca. 10. The reaction was completed within 20 minutes. Then, the prepared sample was filtered and washed with dionised water. By repeating the process three times, a LDH dispersion in water was obtained. Sodium nitrate was added to precipitate the LDH. The solution was stirred for half an hour, filtered and washed thoroughly with deionised water to obtain the LDH wet cake. The solid content of the LDH wet cake was determined by drying under vacuum overnight at room temperature.

LDH/PVA coating dispersion preparation. PVA solution was prepared by dissolving PVA resin in water at around 90 °C under reflux for an hour. A 10 wt% PVA stock solution was used to prepare a coating dispersion. The PVA/LDH coating dispersion was prepared by mixing 10 wt% PVA solution with LDH wet cake and water with different total solid contents and LDH loadings. A uniform dispersion formed after one
hour of magnetic stirring and one hour of ultra-sonication treatment (Branson 8510R-MT, 250 W, 44 kHz). For example, a 6L4P coating solution contains 90 wt% water and 10 wt% solid where LDH is 6 wt% and PVA is 4 wt%.

**Bentonite/PVA coating dispersion preparation.** Bentonite was stirred in 30 vol% formamide aqueous solution for a day to exfoliate before centrifuged and washed with water to obtain a gel-like sample. The solid content of the bentonite gel was determined by drying overnight under vacuum at room temperature. The PVA/bentonite coating dispersion was prepared by mixing 10 wt% PVA solution with bentonite gel and water than contains 0.6 wt% bentonite and 1.6 wt% PVA (and 97.8 wt% water).

**Ageing of coating dispersion.** The coating dispersion was labelled as fresh when we first prepare it. After the dispersion was freshly coated on PET film, it was carefully sealed to prevent water from evaporation and was left standing still for various period of time. This process is defined as ageing time throughout this report. In the temperature effect study, the two coating dispersion samples were first heated at 40 °C and stirred for a week in an oil bath. The two samples were then sealed and put in a drawer to age at room temperature.

**Coating process.** A 12 μm PET substrate was coated with the coating dispersions by a semiautomatic coater (K control coater, RK PrintCoat instruments Ltd, UK) at a coating speed equivalent to 10.67 m/min. All the coating dispersion samples were usually stirred for half an hour before coating. After coating, the PET films were dried at room temperature for about 30 minutes before testing. All the coating films were prepared by a coating rod that give a 6 μm thick wet coating layer.

**Powder X-ray diffraction (XRD).** XRD data were collected on a PANAnalytical X’Pert Pro diffractometer in reflection mode at 40 kV and 40 mA using Cu Kα radiation (α₁ =
1.54057 Å, \( \alpha_2 = 1.54433 \) Å, weighted average = 1.54178 Å). The barrier films were taped on to an aluminium holder to make XRD measurements with the coated side facing the incident X-ray beam.

**Pole figure measurements.** For pole figure measurements a Panalytical X’Pert Pro MRD was used. This is equipped with a focusing mirror providing intense Cu K\( \alpha \) radiation and a Pixcel detector as a point detector with an 8.5 mm active length. The focusing mirror provides a much more intense X-ray beam which was desirable for the weak scattering response of these samples. This provides each pole figure with a 2\( \theta \) range of 1.5°. The samples were mounted on a glass slide using double-sided tape and oriented so that at \( \phi=0^\circ \) the coating layer would face the incident beam.

The pole figure measurement consists of a series of \( \phi \) scans (rotation of the sample about the surface normal) made at a number of different \( \psi \) angles (sample tilt angle). Each \( \phi \) scan was from 0 to 360° with a 2° step size and a counting time of 0.88 s per position. A phi scan was made every 2° from 0 to 40° in \( \psi \) giving a total collection time per pole figure of 1 hour. For each sample (including PET substrate film), pole figure measurements were made with the detector fixed at 2\( \theta =10.75^\circ \).

Gaussian distribution:

\[
y = y_0 + \frac{Ae^{-\frac{4\ln(2)\left(x-x_c\right)^2}{w^2}}}{\sqrt{\frac{\pi}{4\ln(2)}}}
\]

(S1)

Degree of orientation:

\[
\vartheta = \frac{180 - FWHM}{180} \times 100
\]

(S2)

where FWHM is the full width at half maximum obtained by pole figure measurements.
TEM measurements of LDHs and cross-sectional TEM sample preparation. All TEM images were obtained on a JEOL JEM-2100 transmission electron microscope operated at 200 kV. The coated PET films were first embedded into epoxy, and slices of ca. 80-100 nm thickness were cut on a Reichert-Jung Ultracut E ultramicrotome from the embedded epoxy sample. The slices were deposited on 75-mesh copper grids for imaging.

Transparency of the film. The transparency of the film samples were characterised by an Agilent Cary 4000 UV Vis Spectrometer. The transmission was taken at wavelength of 550 nm.

AFM measurements. The coating layer thickness and thickness of LDHs were measured by a NanoScope MultiMode atomic force microscope using tapping mode with a silicon tip coated with aluminium with a force constant of 40 N/m. LDH samples were diluted into ca. 0.01 mM and spin coated on freshly cleaved mica wafer for AFM imaging.

SEM imaging. SEM images were taken on a JEOL JSM 6610 scanning electron microscope operated at 5 kV with a secondary electron detector. The films were first coated with ca. 10 nm gold before imaging.

Viscosity measurements. The dynamic viscosity of the coating dispersion samples was measured on a HR-2 discovery hybrid rheometer (TA instruments) using 60 mm aluminium cone plate with an angle of 1.01° and a truncation gap of 30 μm at 25 °C.

OTR testing. The OTR of the barrier films were tested on M8001 oxygen permeation analyser (Systech Instruments, UK) at 23 °C and zero relative humidity. The instrument testing limit is 0.005 cc/m²/day. The testing complies with ASTM D-3985.

Two-dimensional X-ray scattering analysis (2DXRD) of coated films. Samples were cut into strips 3 cm in length with a width between 0.5 and 0.6 cm. The sample
was mounted horizontally such that the beam was travelling through the width of the sample. Wide-angle X-ray scattering (WAXS) measurements were made using a Xenocs Xeuss 2.0 equipped with a micro-focus Cu Kα source collimated with Scatterless slits. The scattering was measured using a translatable Pilatus 300k detector with a pixel size of 0.172 mm x 0.172 mm. The distance between the detector and the sample was calibrated using silver behenate (AgC_{22}H_{43}O_{2}), giving a value of 0.150(2) m. This setup provided a horizontal 2θ range up to 15° and a vertical range up to 31°. A radial integration of the 2D scattering profile was performed using FOXTROT software to produce the diffraction pattern. Azimuthal integrations were performed using a 2θ range of 10.28° to 13.1° to determine the orientation of the LDH diffraction. Azimuthal integrations were performed with step sizes of 1°. All WAXS data were collected at 25 °C using two 10 min detector images.

**Small Angle X-ray Scattering (SAXS)** analysis of coating dispersion samples was carried out at 1W2A station of Beijing Synchrotron Radiation Facility with a beam wavelength of 1.54 Å using a MarCCD-165 detector (resolution is 2048*2048 pixels, each pixel size is 79*79 μm). The sample to the detector distance was 5 meters.

Calculating \( d \) (nm) from \( q \) (nm\(^{-1}\))

\[
d = \frac{2\pi}{q}
\]

**IR-ATR of films.** IR spectra were recorded on a Varian FTS-7000 Fourier transform, infrared spectrometer fitted with a DuraSampIR Diamond ATR. The resolution is 0.5 cm\(^{-1}\). All the films were conditioned at 60 °C for 2 days before testing.

**Bharadwaj model to predict relative permeability:**

\[
\frac{P_S}{P_0} = \frac{1 - \phi_s}{1 + \frac{\alpha}{2} \phi_s \left(\frac{2}{3}\right) (S + \frac{1}{2})}
\]
Dil corrected model

\[
\frac{P_S}{P_0} = \frac{1 - \Phi_S}{1 + \frac{\alpha}{2} \Phi_S(1 - \sqrt[3]{2/3(1 - S)})}
\]

Where \(P_S\) is the permeability of the filled polymer composite film; \(P_0\) is the permeability of the pure polymer composite film; \(\Phi_S\) is the volume fraction of the platelets; \(\alpha\) is the aspect ratio of the platelets; \(S\) is the order parameter.
**Fig. S1.** AFM measurements of the freshly prepared Mg₂Al-LDH NS sample. Mean diameter (**a**), thickness (**b**) and aspect ratio (**c**). Aspect ratio was calculated by diameter divided by thickness of individual particles. Error bars represent the standard deviations of more than 30 measurements.

**Fig. S2.** Transmittance of PET film coated with 0.6L1.6P and 6L4P dispersion samples at different ageing time measured at wavelength of 500 nm.
Fig. S3. AFM measurements of dry coating layer thickness of films coated by freshly prepare 0.6L1.6P (a), 1.6L0.6P (b), and 6L4P (c) dispersions. All the coating films were coated with a coating rod with a coating gap of 6 μm.

Fig. S4. OTR value of PET substrate and LDH coated PET film.
Fig. S5. OTR of PET films coated with freshly prepared and aged 2.2 wt% PVA (2.2P) coating dispersion.

Fig. S6. OTR of PET films coated with freshly prepared and aged 1.6L0.6P coating dispersion, the Mg\textsubscript{2}Al-LDH NS sample was aged for 7 weeks before mixing with PVA to prepare the coating dispersion.
**Fig. S7.** Mean aspect ratio (a), mean thickness (b), and mean diameter (c) of fresh Mg$_2$Al-LDH and Mg$_2$Al-LDH aged for 6.5, 8.5, and 9.5 month. Thickness and diameter are obtained from AFM measurements of samples at more than three different spots. Aspect ratio was calculated by diameter divided by thickness of individual particles. Error bars represent the standard deviations of more than 30 measurements.

**Fig. S8.** AFM image of Mg$_2$Al-LDH NS aged in water for 6.5 month (a) and mean aspect ratio (b), diameter (c), and thickness (d). Thickness and diameter are obtained from AFM measurements of samples at more than three different spots. Aspect ratio
was calculated by diameter divided by thickness of individual particles. Error bars represent the standard deviations of more than 30 measurements.

**Fig. S9.** AFM image of Mg$_2$Al-LDH NS aged in water for 8.5 month (a) and mean aspect ratio (b), diameter (c), and thickness (d). Thickness and diameter are obtained from AFM measurements of samples at more than three different spots. Aspect ratio was calculated by diameter divided by thickness of individual particles. Error bars represent the standard deviations of more than 30 measurements.
Fig. S10. AFM image of Mg$_2$Al-LDH NS aged in water for 9.5 month (a) and mean aspect ratio (b), diameter (c), and thickness (d). Thickness and diameter are obtained from AFM measurements of samples at more than three different spots. Aspect ratio was calculated by diameter divided by thickness of individual particles. Error bars represent the standard deviations of more than 30 measurements.
**Fig. S11.** AFM image (a), mean aspect ratio (b), thickness (c) and diameter (d) of LDH in 5 weeks aged 0.6L1.6P coating dispersion (aged at 40 °C for a week before aging at room temperature).
**Fig. S12.** Ageing effect observed using glycine reconstructed LDH NS [L(Gly)] and Bentonite: OTR of PET substrate coated with 3L(Gly)2P coating dispersion (a) and 0.6Bentonite1.6P coating dispersion (b) plotted against aging time. The preparation details of the L(Gly) NS can be found in our previous publication\(^3\). All the films were coated with a coating rod with 6 μm coating gap.

**Fig. S13.** AFM images of 1.6L0.6P (a and b) and 3L(Gly)2P (c and d) coating dispersion samples aged for ca. 1 year and 7 month respectively, showing LDH surface is covered by PVA polymer chains.
Fig. S14. TEM images of 1.6L0.6P (a) and 3L(Gly)2P (b) coating dispersion samples aged for ca. 1 year and 7 months respectively, showing LDH surface is covered by PVA polymer chains.

Fig. S15. Oxygen transmission rate of barrier films tested at 38 °C and under 50% relative humidity (PVA-PET is 2.2wt% PVA dispersion coated PET film, LDH/PVA-PET is 8 weeks aged 0.6L1.6P dispersion coated PET film).
Fig. S16. IR-ATR of PET films coated with freshly prepared and aged 1.6L0.6P and pure 2.2P coating dispersions (resolution is 0.5 cm\(^{-1}\)). All the films were conditioned at 60 °C for 2 days to exclude moisture interference before experiments.
**Fig. S17.** SAXS of LDH aqueous dispersions and LDH/PVA dispersion freshly prepared and aged for several month.

![Graph showing Intensity vs 2Theta (Degrees) for Fresh, 2 days, and 4 weeks aged samples](image)

**Fig. S18.** Powder XRD patterns of PET films coated with freshly prepared, 2 days, and 4 weeks aged 1.6L0.6P coating dispersion.

**Fig. S19.** The raw $\phi$ summed intensity plotted against the $\psi$ angle for all coated film samples (a). Pole figure measurements (b) at $2\theta= 10.75^\circ$ of the PET substrate.
Table S1. FWHMs in degrees obtained from Gaussian fitted raw data for all coated films.

| Samples   | FWHM (°) at 2θ = 10.75° | Uncertainty (°) |
|-----------|--------------------------|-----------------|
| F         | 53.0                     | 1.0             |
| 2 days    | 37.3                     | 0.8             |
| 4 weeks   | 24.0                     | 1.0             |

Fig. S20. Dynamic viscosity versus shear rate of a).0.6L1.6P coating dispersion aged at 40 °C for a week then aged at room temperature; b).0.6L1.6P coating dispersion
aged at room temperature continuously; c).1.6L0.6P coating dispersion aged at 40 °C for a week then aged at room temperature; d).1.6L0.6P coating dispersion aged at room temperature continuously measured at various aging time.

**Fig. S21.** Effect of ageing on surface roughness of the coated film. AFM images and the corresponding height histograms of coated PET films prepared from a same coating dispersion that is freshly prepared (a and b), 2 days aged (c and d), and 4 weeks aged (e and f). The coating dispersion contains 1.6 wt% Mg₂Al-LDH NS and 0.6 wt% PVA (aged at 40 °C for a week before ageing at room temperature). All the films are coated with 6 µm coating gap rod.
Table S2. Barrier properties of the coated films. (STP, standard temperature and pressure; PVA with MW of 67,000 was used for all the coating films).

| Samples | Coating gap (µm) | LDH in coating layer (vol%) | Coating thickness (nm) | OTR [mL·m⁻²·day⁻¹] | O₂ permeability of coating layer \( \left[ 10^{-16} \text{cm}^3(\text{STP})\cdot\text{cm}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1} \right] \) | Relative permeabilitya |
|---------|-----------------|-----------------------------|------------------------|----------------------|---------------------------------------------------------------------------------|---------------------|
| F       | 24              | 34.6                        | 435                    | 4.55 ± 0.54          | 0.0245                                                                          | 0.2626 ± 0.0346     |
| 4WK     | 24              | 34.6                        | 323                    | 0.95 ± 0.10          | 0.0035                                                                          | 0.0496 ± 0.0052     |
| 8WK     | 24              | 34.6                        | 332                    | 0.20 ± 0.05          | 0.0007                                                                          | 0.0102 ± 0.0026     |
| 2.2 wt% PVA-PET | 6              | -                           | 43                     | 31.50                | 0.0155                                                                          | -                   |
| 2.2 wt% PVA-PET | 24             | -                           | 210                    | 19.25 ± 0.45         | 0.0462                                                                          | -                   |
| 5 wt% PVA-PET³ | 24             | -                           | 890                    | 18.25                | 0.1860                                                                          | -                   |
| PVA435-PET | -              | -                           | 435                    | -                    | 0.1260*                                                                         | -                   |
| PVA323-PET | -              | -                           | 323                    | -                    | 0.1000*                                                                         | -                   |
| PVA332-PET | -              | -                           | 332                    | -                    | 0.1020*                                                                         | -                   |

Relative permeability is calculated using the oxygen permeability of the barrier film divided by the permeability of the pure PVA coating layer of the same thickness; *Predicted value.

Fig. S22. AFM measurements of dry coating layer thickness of films coated by freshly prepared (a), 4 (b), and 8 (c) weeks aged 0.6L1.6P coating dispersion. All the coating films were coated with a coating rod with a coating gap of 24 µm (The coating dispersion was first stirred and aged at 40 °C for a week before ageing at room temperature).
Fig. S23. SEM images of PET film surface coated by (a). Freshly prepared and (b) 8 WK aged (aged at 40°C for 1 WK then aged at RT for 7 WK) 0.6L1.6P dispersion. All the coating films were coated with a coating rod with a coating gap of 24 μm.

Fig. S24. AFM measurements of dry coating layer thickness of films coated by freshly prepared 2.2 wt% PVA coating dispersion using a coating rod with a coating gap of 6 μm (a) and 24 μm (b).
Fig. S25. Prediction of OTR of pure PVA coated PET film for different coating layer thickness.
| Model              | Flake size, array type | Relative permeability \( \frac{P}{P_0}^a \) | Dil model modified\(^4 \) relative permeability \( \frac{P}{P_0}^a \) |
|-------------------|------------------------|-----------------------------------|---------------------------------------------------|
| Cussler Random array\(^5 \) | Monodisperse, Random array | \( \frac{1 - \phi}{\left(1 + \frac{\alpha}{3}\phi\right)^2} \) | \( \frac{1 - \phi}{1 + \left(\frac{2\alpha\phi}{3} + \frac{(\alpha\phi)^2}{9}\right)(1 - \sqrt{\frac{2}{3}(1 - S)})} \) |
| Gusev-Lusti\(^6 \) | Polydisperse, Random Array | \( (1 - \phi)e^{\left(\frac{\alpha\phi}{3.47}\right)^{0.71}} \) | \( \frac{(1 - \phi)}{1 + \left(e^{\left(\frac{\alpha\phi}{3.47}\right)^{0.71}} - 1\right)(1 - \sqrt{\frac{2}{3}(1 - S)})} \) |
| Nielsen\(^7 \) | Monodisperse, Regular array | \( \frac{1 - \phi}{1 + \frac{\alpha}{2}\phi} \) | \( \frac{P}{P_0} = \frac{1 - \phi}{1 + \frac{\alpha\phi}{2}(1 - \sqrt{\frac{2}{3}(1 - S)})} \) |

\( a \) is aspect ratio; \( \alpha = R/d, \sigma = \) standard deviation, \( r = \) mean value of \( R; \phi = \) volume fraction and \( \phi = 0.346 \) is used to make the plot.
Table S4. Aspect ratio predicted by different models using experimental relative permeability and S (volume fraction is set at 0.346 for all the samples).

| Sample  | Nielsen | Cussler random | Gusev-Lusti |
|---------|---------|----------------|-------------|
| Fresh   | 28 ± 5  | -              | 25 ± 3      |
| 4 weeks | -       | 44 ± 3         | 51 ± 2      |
| 8 weeks | -       | 109 ± 19       | 74 ± 4      |

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