

## SUPPORTING INFORMATION

### S1. Grand canonical Monte Carlo calculations

Grand canonical Monte Carlo simulations were performed with DL\_MONTE to saturate polymer-containing systems via oxygen insertion. This was achieved by using the 'use gaspressure' directive - using a 1 atm partial O<sub>2</sub> pressure - where activity and hence chemical potential is derived according to the following equation:

$$a = \gamma \frac{P}{P_0} = \exp\left(\frac{\mu - \mu_0}{RT}\right)$$

Where  $a$  is the activity,  $\gamma$  is the gas fraction assumed to be 1,  $P$  and  $P_0$  is the pressure and reference pressure, and  $\mu$  and  $\mu_0$  the chemical potential and reference chemical potential.

### S2. Statistical analysis

Throughout this manuscript we have alluded to the improved statistics of our methodology, whereby oxygen diffusion was predicted from 20 x 200 ns molecular dynamics simulations. The statistical requirements adhered to in this research were established in our previous study, whereby oxygen diffusion was characterised in polyethylene terephthalate (PET) and polyethylene furanoate (PEF).<sup>1</sup>

Predictions of oxygen transport in PEF were averaged from between 1 and 20 repeats of a 200 ns simulation. It was observed that a single simulation was not sufficient to obtain an accurate representation of oxygen diffusion. This was due to the high variation in oxygen displacement between simulations, linked to the low concentration of oxygen dissolved in solid plastics and their low transport rates at ambient conditions. In PEF, where oxygen diffusion is in the order of 10<sup>-9</sup> cm<sup>2</sup>/s, diffusion coefficients were seen to converge when averaged across 15+ duplicate simulations.

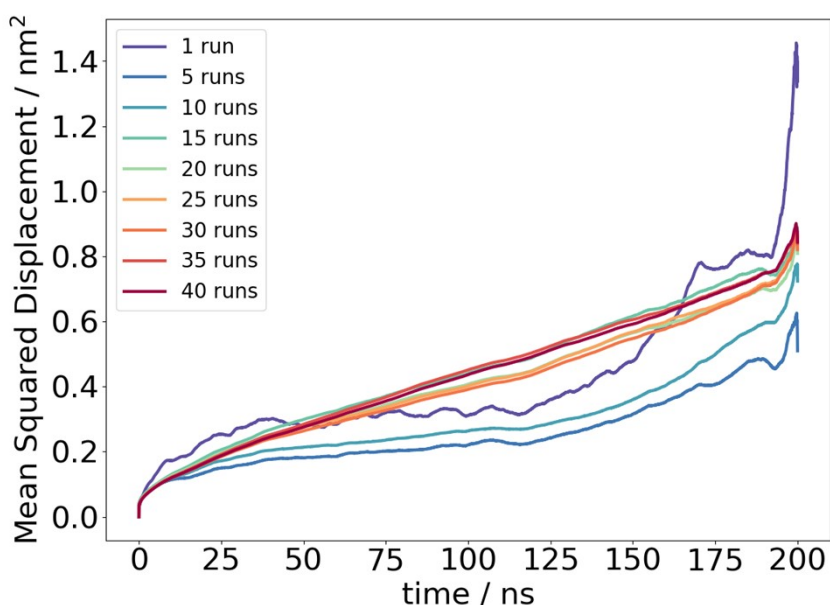


Figure S2.1. Oxygen Mean squared Displacement in PEF over time, calculated from an average of an increasing number of repeat simulations.

In order to ensure that Einstein diffusion was indeed achieved during this timescale, simulations were extended to 600 ns. No notable difference was observed between the calculated diffusion rates, as shown in table S2.1. Finally, 40 simulations of 600 ns were analysed, across which mean squared displacement was calculated. The consistency of oxygen diffusion in all cases indicated that 20 x 200 ns is suitable to quantify non-anomalous diffusion, providing a balance between statistical robustness and computing cost. For further reading, we direct the reader to our previous manuscript.<sup>1</sup>

Table S2.1. Oxygen diffusion in PEF, calculated from 20 x 200 ns, 20 x 600ns and 40 x 600 ns molecular dynamics simulations.

| Simulation length / nm | Number of duplicate simulations | $D_{O_2, PEF} \times 10^9 / \text{cm}^2/\text{s}$ |
|------------------------|---------------------------------|---|
| 200                    | 20                              | $2.89 \pm 0.62$                                   |
| 600                    | 20                              | $3.30 \pm 0.86$                                   |
| 600                    | 40                              | $2.88 \pm 0.47$                                   |

In modelling PLA, we therefore calculate diffusion from 20 x 200 ns simulations, following the conclusions of our previous work. This is more thorough than in previous studies, where oxygen diffusion has been derived from a single simulation, just several nanoseconds in length. We observe that when averaged over 15 or more duplicate simulations, oxygen diffusion is converged – with all subsequent calculated transport coefficients within error of one another. The cited error, which is calculated as the standard error over all repeats, decreases exponentially with the size of the dataset.

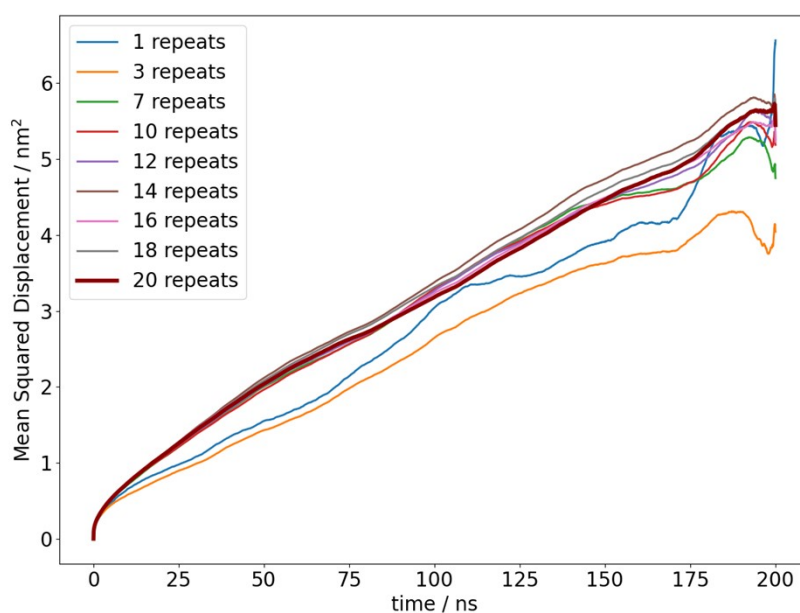


Figure S2.2. Oxygen Mean squared Displacement in PLA over time, calculated from an average of an increasing number of repeat simulations

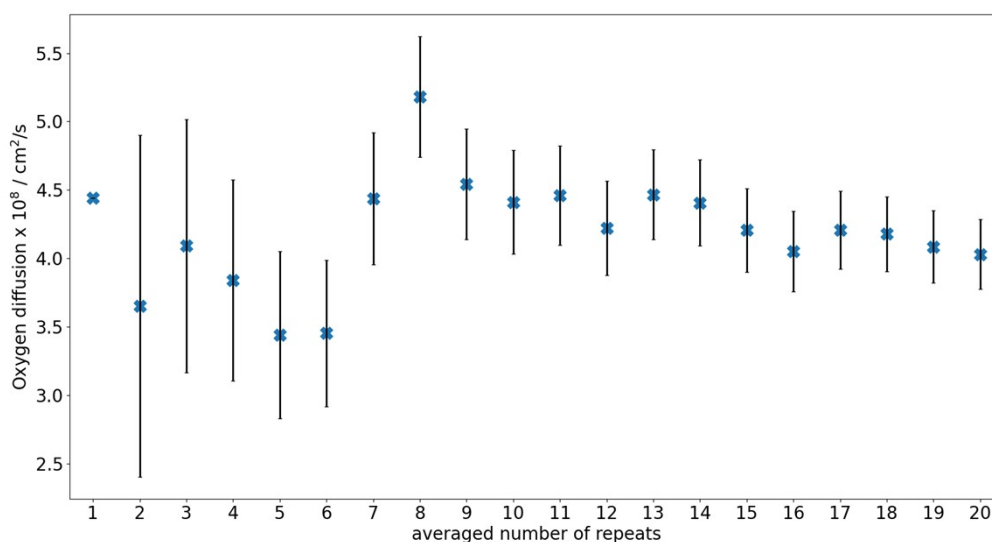


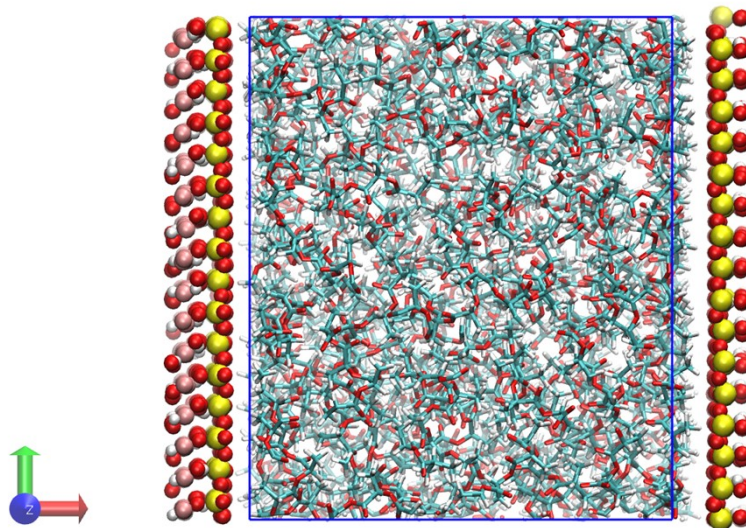
Figure S2.3. Oxygen diffusion coefficients as calculated from the average MSD over an increasing number of simulations.

### S3. Fractional Free Volume

Table S3.1. Fractional free volume, characterised in neat PLA systems and in the PLA phase of composite systems.

| System            | Fractional Free Volume |
|-------------------|------------------------|
| Neat PLA          | 0.197                  |
| Pyrophyllite/ PLA | 0.179                  |

Fractional free volume was analysed over 20 x 200 ns simulations in the NVT ensemble, quantified using the same trajectories from which diffusion was derived. Composite systems were cropped, in order to analyse only the free volume contained in PLA domain. Hence any contributions to free volume from the clay domain or directly at the interface were excluded. This is depicted in Figure S3.1. Figure



S3.1. Depiction of the cropping performed on PLA/pyrophyllite systems to quantify the fractional free volume of PLA in polymer regions. Borders of the volume considered in FFV calculations is depicted in blue.

#### S4. Radial distribution function (RDF)

In addition to density distributions, the radial distribution function was analysed between silicon atoms of the pyrophyllite layer and the carbonyl oxygens of PLA. Although the RDF curve is broad due to the amorphous nature of PLA chains, a distinct peak is observed at approximately 6 Å. This corresponds to the higher density of PLA in this region, consistent with the density analysis.

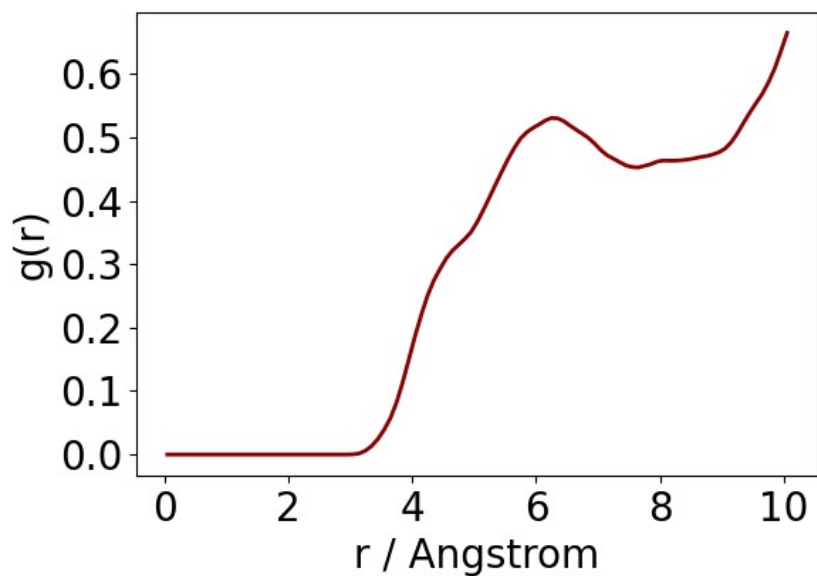


Figure S3.1. A plot showing the radial distribution function between pyrophyllite silicon atoms and carbonyl oxygen atoms of PLA.

The RDF of silicon and penetrant oxygen, analysed over 20 duplicate 200 ns trajectories, also reflects the preferential retention of oxygen at the clay surface, and entrapment of gas molecules between clay and polymer at  $\sim 4$  Å.

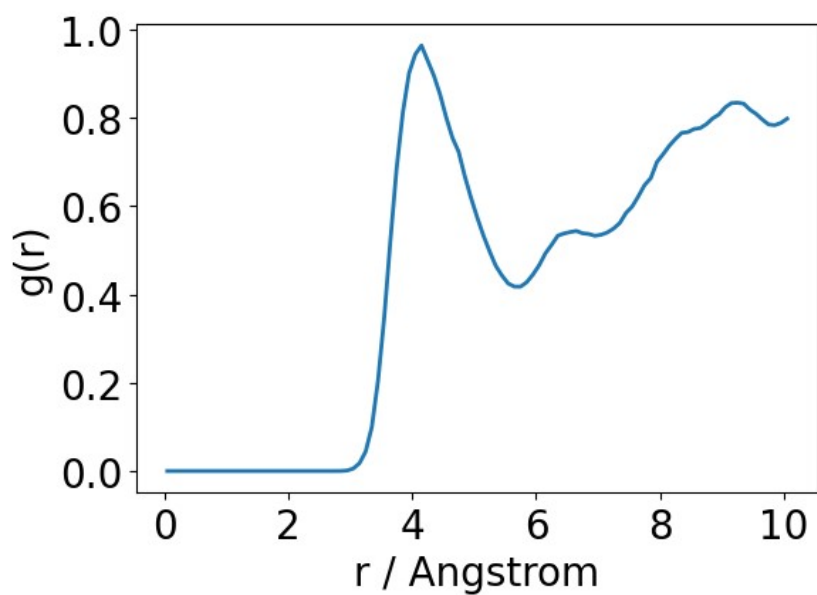


Figure S3.2. A plot showing the radial distribution function between pyrophyllite silicon atoms and penetrating molecular oxygen.

**References:**

1. J. C. Lightfoot, A. Buchard, B. Castro-Dominguez, and S. C. Parker, "Comparative Study of Oxygen Diffusion in Polyethylene Terephthalate and Polyethylene Furanoate Using Molecular Modeling: Computational Insights into the Mechanism for Gas Transport in Bulk Polymer Systems," *Macromolecules*, vol. 55, no. 2, pp. 498–510, Jan. 2022, doi: 10.1021/acs.macromol.1c01316.