Electronic Supporting Information

Physical Aging in Glassy Mixed Matrix Membranes; Tuning Particle Interaction for Mechanically Robust Nanocomposite Films

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Polymer Characterization

1. PIM-1 Synthesis

Monomer reagents were purified before use, and stored under a nitrogen atmosphere prior to synthesis reaction to exclude moisture. 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1-spirobisindane, (TTSBI) 97+ %; was purchased from Alfa Aesar and recrystallized from methanol (MeOH, HPLC grade, Merck, as received) and vacuum dried at 90 °C. Tetrafluoroterephthalonitrile, (TFTPN) 99 %; from Sigma Aldrich was sublimated under vacuum at 150 °C and oven dried overnight at 120 °C. Anhydrous potassium carbonate, ($K_2CO_3 > 99$ %, AnalaR) was oven dried at 120 °C. Synthesis solvents, dimethylacetamide (DMAc >99 %, Acros Organics) was filtered before use, after drying over molecular sieves and calcium hydride. Toluene (extra pure <0.005 % H2O, Merck) and chloroform (CHCl₃, analysis grade, Merck) were used as supplied.

The synthesis of PIM-1 polymer is based on a rapid polycondensation reaction of TFTPN (25.6 mmol) and TTSBI (25.7 mmol) in the presence of excess K_2CO_3 (62.1 mmol), in DMAc (75 mL). The reaction mixture (under nitrogen atmosphere) was refluxed at 160 °C. Precipitation of a yellow solid occurred within the first 30 minutes preventing reaction propagation. To maintain product in solution, additional aquilots of Toluene and DMAc were added during synthesis. Reaction solvents were removed by solvent exchange in methanol, and vacuum filtered before being dissolved in CHCl₃. The PIM-1 solution was washed with water and dilute HCl in a separating funnel to remove excess K_2CO_3 , then vacuum dried before again dissolving in CHCl₃, recrystallized from MeOH and vacuum dried at 100 °C overnight.



Figure S1: Fourier-Transform Infrared (FTIR) spectrum of synthesized PIM-1 polymer measured by Thermo Scientific Nicolet 6700 FT-IR.

2. PTMSP

Polytrimethylsilylpropyne (PTMSP) was purchased from Gelest Inc. (Morrisville PA, USA) and used without purification.

3. Matrimid

Matrimid[®] 5218 US (Matrimid) was purchased from Huntsman International (Salt Lake City UT, USA) and used without purification.

4. Gel Permeation Chromatography (GPC)

Gel Permeation Chromatography (GPC) of polymer samples were performed on Waters Alliance e2695 liquid chromatograph equipped with a Waters 2414 differential refractometer and 3 Å[~] mixed C and 1 mixed E PLgel columns (each 300 mm Å[~] 7.5 mm) from Polymer Laboratories. The eluent was tetrahydrofuran (THF) at 30 °C (flow rate: 1 mL min–1). Number (Mn) and weight-average (Mw) molar masses were evaluated using Waters Empower Pro software. The GPC columns were calibrated with low dispersity polystyrene (PSt) standards (Polymer Laboratories) and molar masses are reported as PSt equivalents. A third order polynomial was used to fit the log Mp vs time calibration curve, which was linear across the molar mass range 2 Å[~] 10^{2} to 2 Å[~] 10^{6} g mol⁻¹.

| Table S1: Gel Permeation Chromatography of Polymers. | | | | | | | |
|--|-------------------|-------|--------|--------|--------|--------|----------------|
| Polymer | Retention time | Mn | Mw | MP | Mz | Mz+1 | Polydispersity |
| PIM-1 | 23.958 | 59993 | 126664 | 99047 | 244320 | 468658 | 2.11 |
| Matrimid | 25.500 | 6211 | 41927 | 37608 | 86867 | 149650 | 6.75 |
| PTMSP | 22.817 | 67652 | 216957 | 209321 | 419409 | 654999 | 3.21 |
| | | | | | | | |

Units: weight average molecular weight (M_w) ; number average molecular weight (M_n) ; molecular weight polystyrene equivalents weight (M_p) ; size average molecular weight (M_2) ; Polydispersity = (M_w / M_n) .

Additive Characterization

5. PAF-1 Synthesis

PAF-1 was synthesized according to Zhu and co-workers¹ to yield an off-white powder with a BET surface area of 4190 m²/g. Briefly, 1,5-cyclooctadiene (dried over calcium hydride) was added into a solution of bis(1,5-cyclooctadiene) nickel and 2,2'-bipyridyl in dehydrated DMF. The mixture was heated for 1 hour at 80 °C to form a purple solution. Tetrakis(4-bromophenyl)methane was added and the mixture was stirred overnight at 80 °C. The mixture was allowed to cool to room temperature and concentrated HCl was added. The solids were collected and washed with chloroform, THF, and deionized water. PAF-1 particle size was typically in the range of 100-200 nm.

6. Silica

Amorphous fumed silica was purchased from Cab-o-Sil (grade: M5-T) and used as supplied.

7. UiO-66 Synthesis

All reagents; terephthalic acid (98 %, Sigma Aldrich), zirconium tetrachloride (ZrCl₄) (>99.9 %, Sigma Aldrich), and solvents; dimethylformamaide (DMF HPLC grade, Merck), chloroform (CHCl₃ Analysis grade, Merck), and methanol (MeOH, HPLC grade, Sigma Aldrich), were used as supplied. UiO-66 was prepared solvothermally from zirconium tetrachloride (47.8 mmol) and terephthalic acid (47.9 mmol) with a large excess of benzoic acid (749.7 mmol) in a dimethylformamide:water (1850:92 mL) solvent. The resulting product was washed sequentially with DMF and MeOH before being drying under vacuum at 100 °C.

8. Ti₅UiO-66 Synthesis

Ti₅UiO-66 was prepared by Post-synthesis Ti Exchange of UiO-66 according to our previous work², using UiO-66 as prepared above. All other reagents, titanium tetrachloride tetrahydrofuran (TiCl₄(THF)₂, 99 %, Sigma Aldrich), dimethylformamaide (DMF, HPLC grade, Merck) and methanol (MeOH, HPLC grade, Sigma Aldrich), were used as supplied. Roughly equimolar quantities of TiCl₄(THF)₂ (7.0 mmol) and synthesised UiO-66 (2.35 g) were suspended in DMF (30 mL) and incubated at 85 °C for a period of 5 days. The resulting product was washed sequentially with DMF and MeOH before being drying under vacuum at 100 °C.

9. Powder X-Ray Diffraction (PXRD)

Powder X-Ray Diffraction (PXRD) measurements were completed on a Bruker D8 Advance X-ray Diffractometer, using Cu K-alpha radiation (40kV, 40mA) equipped with a LynxEye silicon strip detector. Samples were scanned over the 2 θ range 5° to 85° with a step size of 0.02° 2 θ and a count time of 0.4 seconds per step.



10. Additive Surface Area

Langmuir and BET surface areas were calculated from nitrogen adsorption isotherms at 77 K using an ASAP 2420. Samples were activated at 120 °C under vacuum overnight prior to analysis.

| Particle | BET Surface Area, m ² /g | Langmuir Surface Area, m²/g |
|-----------|--|--------------------------------|
| PAF-1 | 4190 | 5476 |
| Silica | 215 | 291 |
| UiO-66 | 1072 | 1398 |
| Ti₅UiO-66 | 1267 | 1609 |

11. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) analysis was performed using an AXIS Ultra DLD spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al K_a source at a power of 144 W (12 kV \times 12 mA), a hemispherical analyser operating in the fixed analyser transmission mode and the standard aperture (analysis area: 0.3 mm × 0.7 mm) The total pressure in the main vacuum chamber during analysis was typically 10⁻⁸ mbar. Survey spectra were acquired at a pass energy of 160 eV. To obtain more detailed information about chemical structure, oxidation states etc., high resolution spectra were recorded from individual peaks at 40 eV pass energy (yielding a typical peak width for polymers of 0.9 - 1.1eV). Samples were filled into shallow wells of custom-built sample holders. One lot of each sample was prepared and 2 different locations were analysed on each sample at a nominal photoelectron emission angle of 0° w.r.t. the surface normal. Since the actual emission angle is ill-defined in the case of particles (ranging from 0° to 90°) the sampling depth may range from 0 nm to approx. 10 nm. Data processing was performed using CasaXPS processing software version 2.3.15 (Casa Software Ltd., Teignmouth, UK). All elements present were identified from survey spectra. The atomic concentrations of the detected elements were calculated using integral peak intensities and the sensitivity factors supplied by the manufacturer. The accuracy associated with quantitative XPS is ca. 10 % - 15 %. Precision (i.e. reproducibility) depends on the signal/noise ratio but is usually much better than 5 %. The latter is relevant when comparing similar samples.

| Element | UiO-66 | Standard Deviation | UiO-66 "Control" | Standard Deviation | Ti₅UiO-66 | Standard Deviation |
|--------------------------|--------|-----------------------|---------------------|-----------------------|-----------|-----------------------|
| Oxygen | 30.61 | 1.53 | 30.53 | 1.35 | 35.07 | 0.28 |
| Carbon | 64.09 | 1.48 | 63.55 | 1.03 | 57.66 | 0.28 |
| Zirconium | 5.08 | 0.23 | 5.40 | 0.22 | 6.71 | 0.02 |
| Nitrogen | 0.23 | 0.18 | 0.23 | 0.08 | 0.57 | 0.02 |
| Atomic Ratio (X:C) | UiO-66 | Standard Deviation | UiO-66 "Control" | Standard Deviation | Ti₅UiO-66 | Standard Deviation |
| Oxygen | 0.478 | 0.035 | 0.478 | 0.029 | 0.608 | 0.008 |
| Zirconium | 0.079 | 0.002 | 0.084 | 0.002 | 0.116 | 0 |
| Nitrogen | 0.004 | 0.003 | 0.004 | 0.001 | 0.01 | 0 |

Table S3: Elemental Surface Composition of UiO-66, Ti₅UiO-66 and UiO-66 Control measured by XPS (atomic percentage, %).

The UiO-66 "Control" sample was exposed to the same solvothermal conditions, less the titanium reagent, used to prepare Ti₅UiO-66 as detailed in Supporting Information 8. No Titanium peak was observed in XPS analysis of Ti-exchanged UiO-66.

MMM Characterization

12. MMM Film Preparation

Membranes were cast from \sim 0.2 g/mL chloroform solutions in PTFE dishes, covered in perforated aluminium foil. Membranes were vacuum dried at 80 °C for 6 hours following casting to remove residual solvent. Aged membranes samples were stored in ambient conditions.

13. Tensile Test Measurements

Measurements were taken using a Mini-Instron with 100 N load cell at 2 mm/min, operated by Blue Hill software. Membrane samples were tested as 'dog bones', cut using a die press, with a testing region of 4.8 mm wide and 18 mm long. Sample thickness was taken as the lowest of three measurements along length of neck. Each sample was tested with 5-10 duplicates prepared from at least three individually cast films. Reported values are averaged after excluding outlier values. Young's modulus was calculated as the maximum slope of the stress-strain plot to overcome variances in starting tension.



Figures S4A, B: (Top) Normalized stress-strain plot from tensile testing measurement of polymer films. Dotted line indicates on the onset of plastic deformation, 'O' indicates Ultimate Tensile Strength (UTS). Young's modulus is calculated on the peak curve slope within the elastic region. (Bottom) Stress-strain plots of Matrimid silica nanocomposites, with dotted lines highlighting 'plateaus' discussed in as-cast films. The arrow highlights the MMM's unusual improvement in mechanical properties with age.



Figures S5A-D: Mechanical properties of Matrimid based MMMs with age.



Figure S6A-D: Mechanical properties of PIM-1 based MMMs with age. Pure PIM-1 films were too fragile after 90 days whereas 180 days of data could be extracted from the nanocomposite samples (Repeat of manuscript Figure 3).





Figure S8: Modulus variation with thickness of Matrimid composites.

A reduction in Young's modulus of the nanocomposite films can be statistically correlated with increasing thickness, as predicted by densification of glassy polymers.^{3, 4} In very large thick films, Moduli trends are expected to plateau as the ratio of aged dense surface polymer to bulk decreases toward zero, whereas ultrathin films would trend toward the moduli of a fully aged film due to the increased aging rate at this scale.^{5, 6} Correlation values are severely limited by the small number of samples measured at each additive and age combination. Analysis of film stress and strain values generally do not show consistent correlation to film thickness, as both are greatly affected by the nanocomposites' failure mechanism. Previous works⁶⁻⁸ have highlighted the change in polymeric material properties in ultra-thin films. Further studies are required to prove the relationship conditions of thickness-dependent trends observed.

15. Viscosity

Viscosity measurements were made using a SCHOTT AV350 Viscometer (standard ASTM D445) using a 52610/I U-tube calibrated with a de-ionised water standard at 20°C. Samples were prepared as 1 $\%_{w/v}$ solutions of prepared membranes in chloroform, with particle loading of 10 wt. %. Results are averaged from 10 duplicates, excluding outliers. Fresh samples are prepared by stirring for 30minutes to ensure polymer dissolution. Aged samples are stirred for 24hrs prior to testing to maximize polymer-particle interaction.

| Sample | Initial Solution | | Agitated for | or 24hrs |
|--------------------|-------------------|-------|-------------------|----------|
| | centiPoise, cP | +/- | centiPoise, cP | +/- |
| CHCl₃ | 0.433 | 0.004 | - | - |
| PAF-1 | 0.453 | 0.003 | - | - |
| F. Silica | 0.432 | 0.003 | - | - |
| UiO-66 | 0.425 | 0.004 | - | - |
| Ti₅UiO-66 | 0.425 | 0.003 | - | - |
| PIM-1 | 0.583 | 0.010 | 0.585 | 0.008 |
| PIM-1 PAF-1 | 0.649 | 0.026 | 0.629 | 0.003 |
| PIM-1 F. Silica | 0.593 | 0.017 | 0.595 | 0.006 |
| PIM-1 UiO-66 | 0.573 | 0.009 | 0.576 | 0.004 |
| PIM-1 Ti₅UiO-66 | 0.596 | 0.016 | 0.571 | 0.004 |
| PTMSP | 1.157 | 0.007 | 1.193 | 0.006 |
| PTMSP PAF-1 | 1.407 | 0.057 | 1.435 | 0.013 |
| PTMSP F. Silica | 1.294 | 0.022 | 1.320 | 0.008 |
| PTMSP UiO-66 | 1.188 | 0.015 | 1.268 | 0.006 |
| PTMSP Ti₅UiO-66 | 1.244 | 0.017 | 1.190 | 0.018 |
| Matrimid | 0.659 | 0.000 | 0.669 | 0.002 |
| Matrimid PAF-1 | 0.659 | 0.009 | 0.672 | 0.001 |
| Matrimid Silica | 0.669 | 0.004 | 0.713 | 0.004 |
| Matrimid UiO-66 | 0.656 | 0.003 | 0.668 | 0.002 |
| Matrimid Ti₅UiO-66 | 0.616 | 0.002 | 0.622 | 0.001 |

 Table S4: Viscosity of MMM casting solutions

Units: centipoise, $cP = 10^{-3}$ Pa.S; DI water standard (20 °C) = 1.0020 cP. Uncertainty is reported as one standard deviation of measured data, after excluding outliers.

16. Small Angle/Wide Angle X-Ray Scattering

MMM films and additive samples were examined on the Small Angle/Wide Angle X-Ray Scattering (SAWSWAXS) beam line at the Australian Synchrotron, Victoria, Australia. Kapton tape was used to mount powder samples, while films were mounted directly to the sample plate. Background spectra were subtracted from raw data averaged from up to four repeat scans from the SAXS and WAXS detectors, with q ranges of q = 0.18 - 1.12 and q = 0.95 - 3.17, respectively. Detector overlap (q = 0.95 - 1.12) was removed by using a transition value of q = 1.1, favouring SAXS data in this region. The resulting intensity plots are normalised to maximum values over select q-ranges for each detector range. SAXS measurements of PAF-1, Silica, and their respective nanocomposites were normalised to q = 0.53 - 0.55 in Matrimid and PTSMP; and 0.89 - 0.95 for PIM-1. Similarly, inclusions and nanocomposites of UiO-66, and Ti₅UiO-66, were normalised to q = 0.50 - 0.55 for all polymer matrices. All intensity curves for the WAXS detector were normalised to the maximum peak value in the range: q = 1.88 - 2.0. Curves depict the reduction in polymer chain spacing and pore size of in polymer composites with aging.⁹



Figures S9A-E: SAXS (right) and WAXS (left) spectra for Matrimid based MMM comparing ascast and aged films.



Figure S10A-E: SAXS (right) and WAXS (left) spectra for PIM-1 based MMM comparing as-cast and aged films.



Figures S11A-E: SAXS (right) and WAXS (left) spectra for PTMSP based MMM comparing ascast and aged films.



17. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) measurements were made using a Mettler Toledo Differential Scanning Calorimeter. Samples were encapsulated in aluminium pans and heated from 25 °C to 525 °C at 10 °C/min. All curves have weighted blanks removed to exclude the effect of the aluminium pans. Polymer-additive interaction plots are calculated by subtracting the theoretical DSC curve, calculated by summating the component curves (10 % additive and 90 % polymer), from the measured DSC curves of the respective MMM. DSC curves of PAF-1 and silica particles exhibit high background noise due to their considerably lower bulk densities, and introduce small false peaks to the calculated DSC curves.



Figure S13: (Right) DSC measurements of Matrimid based MMM and (Left) calculated effect of interaction in Matrimid MMM. Arrows highlight greatly improved thermal stability of MMM, with decomposition temperature peaks shifting above 525 °C.



Figure S14: (Right) DSC measurements of PIM-1 based MMM and (Left) calculated effect of interaction in PIM-1 MMM. Arrows highlight increased thermal stability and endothermic shift caused by addition of Ti_5 UiO-66 into PIM-1.



Figure S15: (Right) DSC measurements of PTMSP based MMM and (Left) calculated effect of interaction in PTMSP MMM. Arrows highlight exothermic shift by additives in PTMSP.



18. Scanning Electron Microscopy (SEM)

A FEI Nova NanoSEM 450 Field Emission Scanning Electron Microscope (FESEM) with an accelerating voltage of 2 kV was used for imaging the fractured cross sectional surface of membrane samples after tensile testing. Samples are mounted with carbon tape and sputter coated with iridium.



Figures S17A-C: Cross section tensile fracture surfaces of pure polymer films.



Figures S18A-D: Particle size of additives measured by SEM.

Table S5: Particle Size of additives by SEM

| | Additivo | Particle Size, | | | | |
|---|-----------|----------------|--|--|--|--|
| | Additive | nm | | | | |
| | PAF-1 | 100-200 | | | | |
| | Silica | 50-100 | | | | |
| | UiO-66 | 100-300 | | | | |
| | Ti₅UiO-66 | 100-300 | | | | |
| - | | | | | | |

Particle Sizes measured within FEI NOVA SEM interface software.



Figures S19A-D: Cross section tensile fracture surfaces of Matrimid based MMM.



Figures S20A-D: Cross section tensile fracture surfaces of PIM-1-based MMM.



Figures S21A-D: Cross section tensile fracture surfaces of PTMSP-based MMM

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