Journal of Materials Chemistry A

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. J. Smith, C. H. Lau, J. I. Mardel, M. Kitchin, K. Konstas, B. P. Ladewig and M. R. Hill, *J. Mater. Chem. A*, 2016, DOI: 10.1039/C6TA02603F.

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Journal Name

ARTICLE

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

Stefan J. D. Smith,^{*ab} Cher Hon Lau,^b James I. Mardel,^b Melanie Kitchin,^{bc} Kristina Konostas,^b Bradley P. Ladewig,^{bd} and Matthew R. Hill^{*ab}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Despite the exceptional separation performance of modern glassy mixed matrix membranes, these materials are not being utilized to improve the performance of existing membrane technologies. Nano-sized additives can greatly enhance separation performance, and have recently been used to overcome age-related performance loss of high performance MMMs. However nano-additives also compromise the structural integrity of films and little is known on how physical aging affects their mechanical properties over time. A solution for both physical aging and mechanical instability is required before these high performance materials can be utilised in industrial membrane applications. Here, we examine physical aging in mixed matrix membranes through mechanical properties and single gas permeation measurements using three glassy polymers, Matrimid® 5218, poly-1-trimethylsilyl-1-propyne (PTMSP), and a Polymer of Intrinsic Microporosity (PIM-1); and a range of nano-scale additives; Silica, PAF-1, UiO-66, and Ti₅UiO-66, each previously shown to enhance gas separation performance. We find polymer-additive interactions strongly influence local physical aging and play a key role in determining the overall material properties of glassy nanocomposite films. Strong interface interactions can slow physical aging, and may not correlate to reinforced or age-stable films. Whereas traditionally 'incompatible' nanocomposites exhibit mechanical properties that can improve over time and even outperform their native polymers. Tuning polymer-additive interactions is vital to achieving the physical aging, mechanical stability, and permselectivity requirements of advanced mixed matrix membrane technologies and reducing the enormous global energy cost of separation processes.

Introduction

Separation processes account for as much as 15% of global energy consumption.¹ Many industrial separations currently use high-energy processes, such as distillation, as alternative low energy processes are either technically unfeasible, or excessively costly. Improving the efficiency of separation processes will have immediate effects on the world's transition toward clean energy by reducing the need for fossil fuels to meet global energy demand. For example, large-scale carbon capture and sequestration (CCS) plants rely on solvent scrubbing systems that have struggled to make meaningful improvements on the monoethanolamine baseline performance.² This, despite the numerous publications

reporting higher performance systems based on pressure/temperature swing processes and membrane technologies for CO₂ capture.³⁻⁶ Membrane technology's potential to greatly reduce the energy costs of separation processes is not being realized.^{1,7} Mixed Matrix Membranes (MMMs), the amalgamation of additive particles within polymeric films, report significant performance enhancement and functional properties over their pure polymeric membrane equivalents.⁸⁻¹⁰ High performance additives, such as Metal Organic Frameworks (MOFs), have been utilized to achieve exceptional membrane performance,^{4,11-16} however industry remains dominated by only a select range of membrane materials.¹⁷ Mechanical stability and aging properties are core considerations for industrial applications, integral to both product and process design.^{5,12,18-20} Glassy polymer membranes offer exciting separation performance, but are hindered by their mechanical properties and physical aging.^{21,22} High additive loading generally causes severe embrittlement, though a few recent studies have reported stable MMM films through targeted polymer-additive interactions.^{12,23-26} Similarly, adsorption of polymer chains in super-porous additives have been used to stop age-related permselectivity loss in glassy MMM.^{12,27-29} To date, there is no complete model describing the complex polymer-additive interactions responsible for MMM properties and little is

^a Monash University, Department of Chemical Engineering, Clayton, VIC 3800, Australia. E-mail: matthew.hill@monash.edu

^b CSIRO, Manufacturing, Private Bag 33, Clayton South MDC, VIC 3169, Australia

^c Centre for Advanced Nanomaterials, The School of Chemistry & Physics, The University of Adelaide, Adelaide, SA, 5005, Australia.

^d Department of Chemical Engineering, Imperial College London, Exhibition Road, London SW72AZ, United Kingdom

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: Tables and figures detailing material characterization and mechanical properties of prepared nanocomposite films. See DOI: 10.1039/x0xx00000x

known about how additive incorporation affects the mechanical resilience of polymer nanocomposites with aging.^{4,12,30}

Herein we report the first detailed study of the mechanical properties of polymer nanocomposites with aging. The glassy polymers PTMSP, PIM-1, and Matrimid 5218 were selected for their different rates (in decreasing order) of physical aging and prior use in unsupported MMM films.⁴ The diverse surface chemistries of PAF-1,^{27,31} fumed silica,^{32,33} UiO-66,^{10,34} and Ti-exchanged UiO-66¹⁰ nanoparticles; each previously shown to enhance membrane performance, but not all to stop physical aging, were used to correlate observed mechanical properties with polymer interactions within composite films (Figure 1). In this figure the effect of various mechanisms found to be at play are summarized – the key point being the nature of interaction between polymer chains and the additive surface. Though generally less than optimum for mixed matrix membrane performance,⁴ nanocomposite films were prepared at 10 wt. % to balance processability, agglomeration, and permeability enhancement.^{4,10,27} Through analysis of mechanical properties with time since casting, we examine nanocomposite structure and mechanical performance with reference to chemical interactions and known mechanisms of physical aging in polymer films. H₂ and N₂ permeability measurements are included to confirm the influence of additive interactions on physical aging and their effect on the mechanical properties of nanocomposites films.

Experimental

Materials: Poly-1-trimethylsilyl-1-propyne (PTMSP), purchased from Gelest Inc. (Morrisville PA, USA), Matrimid 5218 US, purchased from Huntsman International (Salt Lake City UT, USA), and fumed silica, purchased from Cabot Corp. (Boston MA, USA), were used without purification. Details of the

synthesis methodology for PIM-1, PAF-1, UiO-66, and Ti-UiO-66 are described in the Supporting Information. Polymer and nanocomposite (10 wt. % loading) films were prepared by evaporation casting from ~2 wt. % solutions in chloroform overnight. Films were placed in a vacuum oven at 80 °C for 6 hr to remove residual solvent and then aged in ambient conditions.

Characterization: Mechanical properties were obtained by tensile tests from stamped films, prepared from at least three individually cast films, using a Mini-Instron (Instron, USA) and recorded using a 100 N load cell with BlueHill software. 10 samples of each nanocomposite were prepared and results were averaged after removal of outliers. FTIR spectra were obtained using a Thermo Scientific Nicolet 6700 FT-IR. GPC was completed on Waters Alliance e2695 liquid chromatograph, using a tetrahydrofuran eluent. DSC was undertaken with a Mettler Toledo Differential Scanning Calorimeter with a temperature range of 25 °C to 525 °C and heating rate of 10 °C/min. 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. PXRD patterns were recorded by a Bruker D8 Advance X-ray Diffractometer, using Cu K-alpha radiation (40 kV, 40 mA). BET surface areas were calculated from N₂ adsorption isotherms (77 K) recorded on an ASAP 2420. SEM images were taken using a FEI Nova NanoSEM 450 Field Emission Scanning Electron Microscope (FESEM) with an accelerating voltage of 2 kV. Small Angle/Wide Angle X-Ray Scattering was obtained on the SAWS/WAXS beam line at the Australian Synchrotron, Victoria, Australia.³¹ Gas permeation was measured on a custom fixed volume rig, used in prior works,^{10,27} with a pressure differential of 2 Bar. X-ray Photoelectron Spectroscopy (XPS) was performed using an AXIS Ultra DLD spectrometer (Kratos Analytical Inc., Manchester, UK).

Results and discussion

Here, we discuss the effects of aging and additive inclusion on MMM properties in relative terms to as-cast polymer films, as each polymer exhibits significant differences in mechanical properties. Maximum engineering stress was considerably higher for Matrimid films (56.0 ± 3.0 MPa) than PIM-1 and PTMSP films, which were comparable at 28.3 ± 1.1 MPa, and 23.0 ± 1.3 MPa, respectively. Similarly, Matrimid had the greatest strain at failure amongst pure polymers film at 11.8 ± 1.6 %, closely followed by PTMSP at 11.4 ± 1.3 %. PIM-1 was the least ductile of the polymers with a failure strain of 4.8 ± 0.9 %. Differences in mechanical properties arise from structure and functionality of the polymer; though for a given polymer, properties will improve with increasing molecular weight (ESI 4).³⁵

As expected, incorporation of nano-additives reduced the stress and strain at failure of as-cast composites under tensile load (Figure 2).^{12,13} PAF-1 (which stops physical aging),³¹ fumed silica and UiO-66 (which do not stop physical aging)³¹ exhibited almost identical losses in failure at strain performance regardless of the polymer used (Figure 2D).

Fig 1 Fracture mechanisms of polymer nanocomposites with different additive interface environments compared to freshly cast polymer embrittlement. Adhesive interaction reduces crack propagation, leading to better performance over the embrittled aged polymer. Repulsive interaction initially compromise film properties; however the localized increased aging rate isolates defects and leads to mechanical stability.

Fig 2. Effect of nanoparticle addition on maximum tensile stress (A) and strain at failure (D) of as-cast polymer composite films. Comparison of Stress (B), Strain (C), Toughness (E), and Modulus (F) of PIM-1 based nanocomposites with age. Pure PIM-1 films were too fragile for testing after 90 days whereas 180 days of data could be extracted from the nanocomposite samples. Properties of PTMSP and Matrimid based nanocomposites are included in ESI 13.

Changes in the maximum stress obtained in the freshly cast samples (Figure 2A) appear to follow the trend of the pure polymers, with PIM-1 and PTMSP weakened by additive incorporation more than Matrimid, in relative terms. However, the properties of the Ti substituted UiO-66 (which slows aging and strongly interacts with the polymer) were markedly different.¹⁰ Previously we have measured nanocomposite interaction through viscosity changes.^{31,36} The matrix polymer largely determines mechanical properties of nanocomposites; however additive choice also has a significant effect on the properties of composite films. For the same additive, PIM-1 and PTMSP formed much weaker and more brittle composites than with Matrimid. Tensile failure of glassy polymer composites generally occurred in the elastic region and before achieving the Ultimate Tensile Strength (Figure S4A, ESI). Reported stress and toughness values of the nanocomposite films are therefore dependent on the films ductility in our controlled tensile loading conditions (Figures S5-7, ESI). Some plastic deformation was observed in as-cast Matrimid and PTMSP nanocomposite films; with thicker (>100 μm) samples showing visible width reduction or “necking” from plastic deformation. Stress-strain plots of as-cast PTMSP and Matrimid-based silica composites exhibited a small plateau in the elastic region, similar to the deformation observed in rubbery materials (Figure S4B, ESI). As-cast PIM-1 films exhibited minimal plastic deformation, while all PIM-1 composites fractured during elastic deformation. Having established the baseline performance for as-cast samples, their change with time was then examined. Predictably,

mechanical properties of pure polymer films decreased over time from physical aging driven embrittlement (Figure 2 and ESI 13).³⁷⁻³⁹ Failure strains of the glassy polymers universally reduced, while PIM-1 and PTMSP also exhibited significant losses in strength. Based on stress-strain curves, Matrimid maintained a comparable degree of plasticity within the first month of physical aging. However and counter-intuitively, UiO-66 caused an increase the ductility of Matrimid and PTMSP-based composites with aging (Figures S5B and S7B, ESI). Generally, Young's modulus gradually increased with aging but differed with additive inclusion. A correlation between decreasing film thickness and increasing Young's moduli was observed, arising from the higher fraction of the stiffer, dense polymer skin layer,^{39,40} as described by Struik^{21,22} (ESI 14). Toughness closely resembles the trend in failure strain, highlighting the exciting improvement of properties of UiO-66 composites with age. Finding methods to combine the improved gas transport properties of MMMs with enhanced mechanical properties is highly sought after. As shown in Figure 2, nano-additive inclusions almost universally reduce the strength and ductility of as-cast composite films; however exhibit a wide range of aging behaviours, indicating additives have a complex influence on the polymer's physical aging mechanisms. Additives that formed weaker nanocomposites were considerably more age-stable, and even exhibited some improvement mechanical properties over time (ESI 13). PAF-1, previously shown to stop permeability loss from physical aging in PIM-1 and PTMSP MMMs,^{27,29,31} delivered a marked decrease in mechanical durability (Figures S6-S7, ESI). Silica

Table 1: Change in Hydrogen and Nitrogen Permeabilities of Nanocomposite Films over Time

Nanocomposite		Freshly Cast			Aged			Permeability Change	
Polymer	Additive	Permeability, Barrer		Ideal Selectivity	Permeability, Barrer		Ideal Selectivity	H ₂	N ₂
		H ₂	N ₂	α [H ₂ /N ₂]	H ₂	N ₂	α [H ₂ /N ₂]		
Matrimid	-	37.3	7.68	4.86	27.6	4.74	5.83	-26%	-38%
	PAF-1	283	19.0	14.9	121	8.89	13.7	-57%	-53%
	Silica	254	28.5	4.25	121	24.9	10.2	-52%	-13%
	UiO-66	35.4	10.8	2.44	26.3	7.78	4.55	-26%	-28%
	Ti ₅ UiO-66	43.3	5.46	7.92	38.7	4.38	8.82	-11%	-20%
PIM-1	-	2020	289	7.01	744	71.2	10.5	-63%	-75%
	PAF-1	4070	911	4.47	3890	237	16.4	-4%	-74%
	Silica	4100	606	11.9	3460	292	11.9	-16%	-52%
	UiO-66	2270	281	8.08	811	60.0	13.5	-64%	-79%
	Ti ₅ UiO-66	3480	255	13.7	2150	235	9.13	-38%	-8%
PTMSP	-	14200	5080	2.79	3830	813	6.38	-73%	-84%
	PAF-1	27800	6440	4.32	21200	2230	9.50	-24%	-65%
	Silica	17100	4470	3.83	6010	1350	4.45	-65%	-70%
	UiO-66	16300	3750	4.34	8870	1270	7.00	-46%	-66%
	Ti ₅ UiO-66	21200	4440	4.78	18700	3380	6.29	-12%	-24%

Permeability measurements were recorded on a custom fixed volume rig, with a pressure differential of 2 Bar, at 298 K and within +/- 5 % deviation. Nanocomposites are prepared with 10 wt. % additive. Ideal selectivity is calculated from single gas measurements, $\alpha = P_A/P_B$. Units: Barrer = 10^{-10} (cm³ STP) cm⁻¹ cm⁻² s⁻¹ cmHg⁻¹.

had a similar effect on nanocomposite strength and ductility, but greatly increased the modulus of films over time. Incorporation of UiO-66 caused an unusual improvement with age across all three polymer matrices, with strain failures increasing by 35% and 50% in Matrimid and PTMSP, respectively after 6 months (ESI 13). Addition of Ti₅UiO-66 into PIM-1 improved properties over a pure PIM-1 film after just 1 month of aging and exhibits a 20% higher failure strain after three months, confirming previous reports of PIM-1 Ti₅UiO-66's exceptional mechanical stability.¹⁰ Nanocomposite properties were more consistent over time with mechanical degradation from physical aging occurring at a much slower rate, an important property for improving polymer membranes.

As expected, H₂ and N₂ permeability for each nanocomposite decreased with aging, whereas ideal H₂/N₂ selectivity generally improved (Table 1). In each case, additives increased the initial permeability of freshly cast films, though had varied effects on the selectivity and permeability over time. Permeabilities of Ti₅UiO-66 nanocomposites were much more stable than that of the pure polymer, whereas considerably greater losses were observed in PAF-1 Matrimid and Silica PTMSP nanocomposites, than their respective polymer films. By considering small gases as molecular probes, changes to single gas permeation can be used to trace aging within films.

^{27,29,31,41} Additive interactions influence the rate of densification within interface regions, and consequently the average fractional free volume of the glassy polymer film. As shown in Figure 1, greater permeability losses with aging are indicative of a 'free surface' interface; whereas constrained surfaces reduce densification leading to more consistent permeability. These results highlight the opportunity to combine the aging mechanisms behind the enhancement of mechanical properties, delivered by UiO-66 and its Ti-

substituted analogue, with the 'ageless' gas transport properties of PAF-1 MMM (Table 1),²⁷ to overcome the barriers facing the use of MMM in industrial membrane technologies.

NANOCOMPOSITE INTERACTION MECHANISMS

Encouraged by the results showing that some additives can indeed enhance mechanical properties, we sought to derive the mechanisms underpinning the results obtained. Polymer entanglement, additive interactions, and their effects on physical aging mechanisms are each discussed with reference to observed changes to nanocomposite properties.

POLYMER ENTANGLEMENT

Polymers with high glass transition temperatures (*T_g*) are useful for gas separation as their limited chain movement and often poor chain packing generates good permselectivity through the fractional free volume elements of the films. However, this effective immobility of glassy polymer chains reduces the materials' ductility and causes brittle failure behaviour under load.^{21,42} The glassy polymers used in this study vary in chain rigidity and entanglement resulting in different mechanical responses under load (Figures 4 and S4A, ESI). PIM-1's rigid ladder structure greatly limits the polymer's packing efficiency, responsible for the polymer's microporosity.^{43,44} Under load, the flexibility of the dioxane ether bridge allows some elasticity; however the entangled rigid sections prevent chain dislocation and plastic deformation.^{42,43} Similarly, bulky trimethyl-silyl groups and double bonds lock PTMSP monomer sections in *cis/trans* configuration, which restricts chain packing, and forms a glass with high fractional free volume.^{42,45} However, unlike PIM-1, PTMSP's structure includes single bonds that allow some chain

Fig 3 Packing entanglement of glassy polymers Matrimid, PIM-1, and PTMSP.

dislocation under load without bond cleavage.^{42,44} Matrimid is the least bulky and contorted of the polymers, causing it to exhibit higher packing efficiency and form a considerably less entangled glass (Figure 3).⁴⁶ This linearity allows chain movement under load, leading to the plastic deformation, strain hardening and necking observed. Fragility often limits the attainable performance of MMM as high additive loadings compromise the mechanical stability of films.^{4,12} As nanocomposites, the most rigid and entangled polymers had the greatest loss in mechanical stability due to higher packing disruption around dispersed additives (Figure 2).⁴⁷ At equivalent loadings by weight, low-density additives represent significantly higher volume fractions in cast films. Silica and PAF-1 composites were consistently amongst the most fragile of the films tested. In these films, there is relatively less polymer volume to support the additive suspension. Additives with small particle sizes have the greatest effect on disrupting polymer packing and increasing free volume, however can agglomerate that increases the effective particle size and compromises performance.^{33,48} Agglomerates have weak inter-particle adhesion that enables crack propagation through the composite material independent of the additive's adhesion to the polymer. Larger additive particles have less pronounced effects on composites properties as increasing size reduces interfacial surface area.^{33,48-50}

NANO-ADDITIVE COMPATIBILITY

The term, "compatibility", is commonly used in literature to refer to the polymer-additive connectivity and degree of agglomeration in MMMs.⁵¹ Poorly compatible combinations are described as having a 'sieve in a cage' morphology, and often exhibit non-selectivity.⁴ However, we find that 'compatibility', as a summary of polymer-additive interactions, is a poor predictor of nanocomposite mechanical properties. PAF-1 nanocomposites were considerably less robust in the compatible polymers, PTMSP and PIM-1, though performed reasonably well in the 'incompatible' polymer, Matrimid. Viscosity provides some indication of polymer-additive interaction, where observed decreases in viscosities arise from **a)** reduced polymer entanglement by additive surface adhesion, **b)** disruption of polymer chain packing, causing an increase in

free volume, and **c)** polymer adsorption within the additive pores, if possible.^{10,27,52,53} Differences in viscosity measured before and after thorough agitation are indicative of additive interactions with the polymer in solution.³¹ Viscosities of a few composite solutions fell below that of pure polymer solutions indicating conformational changes to the polymer in solution (Table S4, ESI). Strong polymer-additive interactions may also cause a crosslinking effect, leading to higher viscosities, as observed with PAF-1 in PTMSP and PIM-1. These effects were further confirmed with DSC measurements, where endothermic shifts in the DSC curves are linked to the degree of interaction (Figures S13-15, ESI).⁵²

Ti exchanged UiO-66 based composites were strikingly different from each of the other polymer additive combinations studied; exhibiting the best properties in PIM-1, but among the worst for PTMSP and Matrimid composites (Figure 2). Structurally, $\text{Ti}_5\text{UiO-66}$ is isomorphous to UiO-66; however post-synthetic exchange (PSE)⁵⁴ has been shown to increase polymer interaction, partially separate charge, increase surface area and further expose Ti^{IV} / Zr^{IV} metal sites within the framework (Figure S14, ESI).^{10,55} XPS analysis of the MOFs indicates that titanium exchange increases missing linker concentration; with Zr:C ratio increasing to (0.116:1) from (0.079:1) and (0.084:1) for native UiO-66 and an 'exchanged' UiO-66 control, respectively (Table S3, ESI).⁵⁶⁻⁵⁸ We propose that $\text{Ti}_5\text{UiO-66}$'s exposed Ti^{IV} forms a chelation complex with PIM-1's terminal catechol groups (Figure 4).⁵⁹⁻⁶³ Ti-Catechol complexes are highly stable and are used to bind molecules to titanium and titanium dioxide surfaces.^{59,64,65} Attempts to directly measure this interaction by FTIR, DSC, and ^1H NMR have so far been inconclusive. $\text{Ti}_5\text{UiO-66}$'s distinct metal nodes moderate the terminal grafting density with PIM-1, necessary for the observed enhancement in mechanical properties.^{50,66-68} Strong additive interactions can reinforce polymer matrices,¹² but can also cause conformation changes to the polymer that

Fig 4 Proposed 'catechol complex' interaction between exposed metal sites in $\text{Ti}_5\text{UiO-66}$ and PIM-1, responsible for the nanocomposite's exceptional mechanical properties.^{26,64,65}

compromise nanocomposite properties. Like PIM-1, Matrimid has a strong interaction with $\text{Ti}_5\text{UiO}-66$ through the polymer's imide and ketone oxygens (Figure S13 and Table S4, ESI); however instead forms a brittle composite with $\text{Ti}_5\text{UiO}-66$ nucleating large spherulites (5–20 μm) in the polymer matrix (Figure S19D, ESI). $\text{Ti}_5\text{UiO}-66$'s exposed metal sites likely interacts with the PTMSP's double bond in solution, explaining the decrease in viscosity, however it appears a greater repulsion to the bulky side group causes agglomeration during casting. Similarly, adsorption of PTMSP and PIM-1's bulky methyl groups in the pores of PAF-1 fixes the polymer in a high free volume morphology, as observed with SEM (Figure S21A, ESI). This highly porous structure is responsible for the composites' high permeability,^{27,29,31} but also greatly compromises the films' mechanical properties through concentrating applied stresses (Figures S6–S7, ESI). Interestingly, additive interactions with chain terminal groups appear to reinforce nanocomposite films, whereas strong side group interactions seem to compromise mechanical performance; highlighting the influence of additive interactions on polymer conformation.^{20,23,50,67}

AGING MECHANISMS

Physical aging is the gradual densification of glassy amorphous polymers through the thermal relaxation based on the thermodynamic driving force and polymer mobility of α - and β -chain segments.^{39,49,69} For membranes, thickness dependent physical aging is usually measured through reductions in free volume or gas permeability.^{28,41,70–72} Ultra-thin films (<1 μm) age drastically faster than thicker (1–100 μm) equivalent films^{40,49,70,71} as polymer chains near the surface have a reduced glass transition temperature (T_g) and increased chain mobility.^{40,49,70,71} A denser 'skin layer' forms almost immediately, which is stronger than the bulk polymer, but also causes embrittlement through the internal stresses^{37,39} that accumulate as the film ages.^{37,73} Conversely, hydrogen bonding and functional group interactions can constrain surface polymer chains; increasing the local T_g and suppressing structural relaxation.^{27,49} Dispersed additives introduce secondary polymer surfaces to composite films,⁴⁸ which can influence aging mechanisms throughout the film's core.^{49,68,73,74} Like external film surfaces, these interfaces behave as either a constrained or free surface depending on the polymer's adhesion/repulsion to the additive surface.²⁵ Attractive polymer-additive interactions mimic constrained surfaces and suppress physical aging of the interface region;⁴⁹ whereas additives that repel the polymer chains are separated from the matrix by a 'free surface' forming around them. Locally accelerated physical aging thickens the interface layer around these voids over time and eventually isolates them from stresses applied to the film, as observed in the directionality of composite fracture surfaces (Figure 5). Distribution of these dense interface regions throughout the film also relieves internal stresses, further preventing the initiation and propagation of cracks responsible for polymer embrittlement (Figure 1).³⁹ Together, these phenomena explain the unusual increasing failure strain of PTMSP UiO-66

Fig 5 Cross-section tensile fracture surface of Matrimid UiO-66 composite by SEM. Arrows highlight directionality of fracture propagation. Circles identify dense regions (lighter) around included additives, indicative of aged interfacial free surfaces. SEM images of other composites are included in Supporting Information 18

and Matrimid UiO-66 composites over time (ESI 13). The mechanical enhancement of aged nanocomposites with 'incompatible' polymer-additive interactions is limited by loading and suspension stability within the film.^{4,12} Incompatible polymer-additive combinations are prone to agglomeration, such as PTMSP with $\text{Ti}_5\text{UiO}-66$; which introduces large defects that concentrate stresses applied to the film (Figure S21D, ESI). Similarly, extensive interconnectivity may leave insufficient 'core' polymer between dense interface regions leading to brittle failure. On the other hand, strong attraction can stop physical aging within the interface but may not prevent mechanical degradation over time. In aged composites, strongly constrained interfaces can cause embrittlement through internal stresses that arise from the difference in polymer density of the interface and aged 'core' polymer; a local reversal of aging in pure polymer films (Figure 1).^{39,49} These findings may also provide insight into the cause of changes in MOF nanocomposite properties after thermal annealing, in effect an acceleration of the physical aging process discussed here.^{20,75}

Conclusions

Herein, we report the mechanical properties of unsupported glassy mixed matrix membranes with aging, specifically focusing on additive effects on composite film properties. We confirm previous generalizations that additives and physical aging compromise the stability of glassy polymer films. Together, polymer-additives interactions can significantly influence the aging mechanisms in composite materials and can lead to mechanical properties that improve over time.

Both targeted polymer-additive interactions and traditionally 'incompatible' MMM combinations are shown to overcome the introduced mechanical weaknesses of composite films; though controlling the extent of interaction appears key to advantageous mechanical performance. Additives that improved mechanical stability over time were dependent on forming a free surface at the interface, whereas prevention of permeability loss occurs through restricting polymer chain movement. To date, age-stable permselectivity and film durability in glassy high free volume polymers have been only been examined separately in literature.

This detailed study highlights how interaction between additive surfaces, the interface, and polymer chains strongly influence physical aging and mechanical properties in glassy polymers films. As such, we highlight how tuning the polymer-additive interactions may allow ageless permeability and film stability to be realized in unison in glassy MMM; a major advancement of membrane technologies. MMM that combine resilient mechanical properties with ageless gas transport enables high performance MMM to replace existing membrane materials in industry, and greatly reduce the energy cost of separation processes.

Acknowledgements

This research was supported by the Science and Industry Endowment Fund (SIEF). The authors acknowledge Dr. Chris Easton and Dr. Guoxin Li of CSIRO for characterization support and advice. Parts of this research were undertaken on the SAWS/WAXS beam line at the Australian Synchrotron, Victoria, Australia. The authors acknowledge use of facilities within the Monash University Center for Electron Microscopy. MRH acknowledges FT 1300345.

References

1. *Materials for Separation Technologies: Energy and Emission Reduction Opportunities*, U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, 2005.
2. B. P. Spigarelli and S. K. Kawatra, *J. CO₂ Util.*, 2013, **1**, 69-87.
3. M. Boot-Handford, J. C. Abanades, E. Anthony, M. Blunt, S. Brandani, N. Mac Dowell, J. Fernandez, M.-C. Ferrari, R. Gross, J. Hallett, S. Haszeldine, P. Heptonstall, A. Lyngfelt, Z. Makuch, E. Mangano, M. Pourkashanian, G. Rochelle, N. Shah, J. Yao and P. Fennell, *Energ. Environ. Sci.*, 2013, **7**, 130:189.
4. B. Seoane, J. Coronas, I. Gascon, M. E. Benavides, O. Karvan, J. Caro, F. Kapteijn and J. Gascon, *Chem. Soc. Rev.*, 2015.
5. T. C. Merkel, H. Lin, X. Wei and R. Baker, *J. Membr. Sci.*, 2010, **359**, 126-139.
6. S. E. Kentish, C. A. Scholes and G. W. Stevens, *Recent Pat. Chem. Eng.*, 2008, **1**, 52-66.
7. D. F. Sanders, Z. P. Smith, R. Guo, L. M. Robeson, J. E. McGrath, D. R. Paul and B. D. Freeman, *Polymer*, 2013, **54**, 4729-4761.
8. H. B. Tanh Jeazet, C. Staudt and C. Janiak, *Dalton Trans.*, 2012, **41**, 14003-14027. DOI: 10.1039/C6TA02603F
9. M. G. Buonomenna, W. Yave and G. Golemme, *RSC Advances*, 2012, **2**, 10745-10773.
10. S. J. D. Smith, B. P. Ladewig, A. J. Hill, C. H. Lau and M. R. Hill, *Sci. Rep.*, 2015, **5**, 7823.
11. G. Dong, H. Li and V. Chen, *J. Mater. Chem. A*, 2013, **1**, 4610.
12. Y. Yampolskii, *Macromolecules*, 2012, **45**, 3298-3311.
13. B. Zornoza, C. Tellez, J. Coronas, J. Gascon and F. Kapteijn, *Microporous Mesoporous Mater.*, 2013, **166**, 67-78.
14. L. M. Robeson, *J. Membr. Sci.*, 2008, **320**, 390-400.
15. L. M. Robeson, *J. Membr. Sci.*, 1991, **62**, 165-185.
16. B. D. Freeman, *Macromolecules*, 1999, **32**, 375-380.
17. V. Abetz, T. Brinkmann, M. Dijkstra, K. Ebert, D. Fritsch, K. Ohlrogge, D. Paul, K. V. Peinemann, S. Pereira-Nunes, N. Scharnagl and M. Schossig, *Advanced Engineering Materials*, 2006, **8**, 328-358.
18. W. J. Koros and R. Mahajan, *J. Membr. Sci.*, 2000, **175**, 181-196.
19. R. W. Baker and B. T. Low, *Macromolecules*, 2014, **47**, 6999-7013.
20. E. M. Mahdi and J.-C. Tan, *J. Membr. Sci.*, 2016, **498**, 276-290.
21. L. C. E. Struik, *Physical Aging in Amorphous Polymers and Other Materials*, Elsevier Scientific Publishing Company, 1978.
22. L. Struik, *Polymer*, 1980, **21**, 962-967.
23. R. Lin, L. Ge, L. Hou, E. Strounina, V. Rudolph and Z. Zhu, *ACS Appl. Mater. Interfaces*, 2014, **6**, 5609-5618.
24. Y. Zhang, X. Feng, H. Li, Y. Chen, J. Zhao, S. Wang, L. Wang and B. Wang, *Angew. Chem. Int. Ed.*, 2015, **54**, 4259-4263.
25. Q. Xin, J. Ouyang, T. Liu, Z. Li, Z. Li, Y. Liu, S. Wang, H. Wu, Z. Jiang and X. Cao, *ACS Appl. Mater. Interfaces*, 2014, **7**, 1065-1077.
26. D. K. Roh, S. J. Kim, H. Jeon and J. H. Kim, *ACS Appl. Mater. Interfaces*, 2013, **5**, 6615-6621.
27. C. H. Lau, P. T. Nguyen, M. R. Hill, A. W. Thornton, K. Konstas, C. M. Doherty, R. J. Mulder, L. Bourgeois, A. C. Y. Liu, D. J. Sprouster, J. P. Sullivan, T. J. Bastow, A. J. Hill, D. L. Gin and R. D. Noble, *Angew. Chem. Int. Ed.*, 2014, **53**, 5322-5326.
28. R. Swaidan, B. Ghanem, E. Litwiller and I. Pinnau, *Macromolecules*, 2015, **48**, 6553-6561.
29. C. H. Lau, K. Konstas, C. M. Doherty, S. Kanehashi, B. Ozcelik, S. E. Kentish, A. J. Hill and M. R. Hill, *Chem. Mater.*, 2015, **27**, 4756-4762.
30. I. Erucar and S. Keskin, *Curr. Org. Chem.*, 2014, **18**, 2364-2380.
31. C. H. Lau, K. Konstas, A. W. Thornton, A. C. Y. Liu, S. Mudie, D. F. Kennedy, S. C. Howard, A. J. Hill and M. R. Hill, *Angew. Chem. Int. Ed.*, 2015, **54**, 2669-2673.
32. J. Ahn, W.-J. Chung, I. Pinnau, J. Song, N. Du, G. P. Robertson and M. D. Guiver, *J. Membr. Sci.*, 2010, **346**, 280-287.
33. T. C. Merkel, B. D. Freeman, R. J. Spontak, Z. He, I. Pinnau, P. Meakin and A. J. Hill, *Science*, 2002, **296**, 519-522.

34. O. G. Nik, X. Y. Chen and S. Kaliaguine, *J. Membr. Sci.*, 2012, **413-414**, 48-61.
35. L. J. Fetters, D. J. Lohse, D. Richter, T. A. Witten and A. Zirkel, *Macromolecules*, 1994, **27**, 4639-4647.
36. M. Kitchin, J. Teo, K. Konstas, C. H. Lau, C. J. Sumby, A. W. Thornton, C. J. Doonan and M. R. Hill, *J. Mater. Chem. A*, 2015, **3**, 15241-15247.
37. D. K. Mahajan, R. Estevez and S. Basu, *J. Mech. Phys. Solids*, 2010, **58**, 1474-1488.
38. J. M. Hutchinson, *Prog. Polym. Sci.*, 1995, **20**, 703-760.
39. J. R. White, *C. R. Chim.*, 2006, **9**, 1396-1408.
40. B. W. Rowe, S. J. Pas, A. J. Hill, R. Suzuki, B. D. Freeman and D. R. Paul, *Polymer*, 2009, **50**, 6149-6156.
41. C. H. Lau, X. Mulet, K. Konstas, C. M. Doherty, M.-A. Sani, F. Separovic, M. R. Hill and C. D. Wood, *Angew. Chem. Int. Ed.*, 2016, **55**, 1998-2001.
42. P. M. Budd and N. B. McKeown, *Polymer Chemistry*, 2010, **1**, 63-68.
43. M. D. Guiver and Y. M. Lee, *Science*, 2013, **339**, 284-285.
44. M. Carta, R. Malpass-Evans, M. Croad, Y. Rogan, J. C. Jansen, P. Bernardo, F. Bazzarelli and N. B. McKeown, *Science*, 2013, **339**, 303-307.
45. G. A. Dibrov, V. V. Volkov, V. P. Vasilevsky, A. A. Shutova, S. D. Bazhenov, V. S. Khotimsky, A. van de Runstraat, E. L. V. Goetheer and A. V. Volkov, *J. Membr. Sci.*, 2014, **470**, 439-450.
46. Y. Xiao, Y. Dai, T.-S. Chung and M. D. Guiver, *Macromolecules*, 2005, **38**, 10042-10049.
47. A. Gonciaruk, K. Althumayri, W. J. Harrison, P. M. Budd and F. R. Siperstein, *Microporous Mesoporous Mater.*, 2015, **209**, 126-134.
48. R. J. Hill, *Ind. Eng. Chem. Res.*, 2006, **45**, 6890-6898.
49. R. D. Priestley, C. J. Ellison, L. J. Broadbelt and J. M. Torkelson, *Science*, 2005, **309**, 456-459.
50. H. Chao and R. A. Riggelman, *Polymer*, 2013, **54**, 5222-5229.
51. R. Semino, N. A. Ramsahye, A. Ghoufi and G. Maurin, *ACS Appl. Mater. Interfaces*, 2015, **8**, 809-819.
52. S. Jain, J. G. P. Goossens, G. W. M. Peters, M. van Duin and P. J. Lemstra, *Soft Matter*, 2008, **4**, 1848-1854.
53. M. E. Mackay, T. T. Dao, A. Tuteja, D. L. Ho, H. Brooke Van, K. Ho-Cheol and C. J. Hawker, *Nat. Mater.*, 2003, **2**, 762-766.
54. M. Kim, J. F. Cahill, H. Fei, K. A. Prather and S. M. Cohen, *J. Am. Chem. Soc.*, 2012, **134**, 18082-18088.
55. C. H. Lau, R. Babarao and M. R. Hill, *Chem. Commun.*, 2013, **49**, 3634-3636.
56. G. C. Shearer, S. Chavan, J. Ethiraj, J. G. Vitillo, S. Svelle, U. Olsbye, C. Lamberti, S. Bordiga and K. P. Lillerud, *Chem. Mater.*, 2014, **26**, 4068-4071.
57. H. Wu, Y. S. Chua, V. Krungleviciute, M. Tyagi, P. Chen, T. Yildirim and W. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 10525-10532.
58. M. J. Cliffe, W. Wan, X. Zou, P. A. Chater, A. K. Kleppe, M. G. Tucker, H. Wilhelm, N. P. Funnell, F.-X. Coudert and A. L. Goodwin, *Nat. Commun.*, 2014, **5**, 4176.
59. B. A. Borgias, S. R. Cooper, Y. B. Koh and K. N. Raymond, *Inorg. Chem.*, 1984, **23**, 1009-1016. DOI: 10.1039/C6TA02603F
60. H. J. Lee, A. N. Koo, S. W. Lee, M. H. Lee and S. C. Lee, *J. Controlled Release*, 2013, **170**, 198-208.
61. T. J. Boyle, L. J. Tribby, T. M. Alam, S. D. Bunge and G. P. Holland, *Polyhedron*, 2005, **24**, 1143-1152.
62. Y. Chi, J.-W. Lan, W.-L. Ching, S.-M. Peng and G.-H. Lee, *Journal of the Chemical Society, Dalton Transactions*, 2000, 2923-2927.
63. Z. Tachan, I. Hod and A. Zaban, *Adv. Energy Mater.*, 2014, **4**.
64. C. Creutz and M. H. Chou, *Inorg. Chem.*, 2008, **47**, 3509-3514.
65. S. Saxer, C. Portmann, S. Tosatti, K. Gademann, S. Zürcher and M. Textor, *Macromolecules*, 2009, **43**, 1050-1060.
66. Y. Feng, N. Ning, Z. Wei, L. Zhang, M. Tian, H. Zou and J. Mi, *Polymer*, 2014, **55**, 3178-3185.
67. J. F. Moll, P. Akcora, A. Rungta, S. Gong, R. H. Colby, B. C. Benicewicz and S. K. Kumar, *Macromolecules*, 2011, **44**, 7473-7477.
68. T. V. M. Nodoro, E. Voyiatzis, A. Ghanbari, D. N. Theodorou, M. C. Böhm and F. Müller-Plathe, *Macromolecules*, 2011, **44**, 2316-2327.
69. B. W. Rowe, B. D. Freeman and D. R. Paul, *Polymer*, 2010, **51**, 3784-3792.
70. Y. Huang, X. Wang and D. R. Paul, *J. Membr. Sci.*, 2006, **277**, 219-229.
71. Y. Huang and D. R. Paul, *Polymer*, 2004, **45**, 8377-8393.
72. R. R. Tiwari, Z. P. Smith, H. Lin, B. D. Freeman and D. R. Paul, *Polymer*, 2014, **55**, 5788-5800.
73. E. Voyiatzis, M. Rahimi, F. Müller-Plathe and M. C. Böhm, *Macromolecules*, 2014, **47**, 7878-7889.
74. J. Koski, H. Chao and R. A. Riggelman, *J. Chem. Phys.*, 2013, **139**.
75. E. M. Mahdi and J.-C. Tan, *Polymer*, 2016, **97**, 31-43.

256x194mm (150 x 150 DPI)