Electronic Supplementary Information

Highly permeable and selective mixed-matrix membranes for hydrogen separation containing PAF-1

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1. Isotherm Adsorption Curves

A Micromeritics ASAP 2420 instrument was used for measuring adsorption isotherms of N_2 (77 K) for the prepared PAF-1. These samples were activated at 100 °C under vacuum (10^{-6} torr) for 24 h prior to analysis. The Brunauer-Emmett-Teller (BET) surface area for PAF-1 was 3905 $m^2 g^{-1}$.

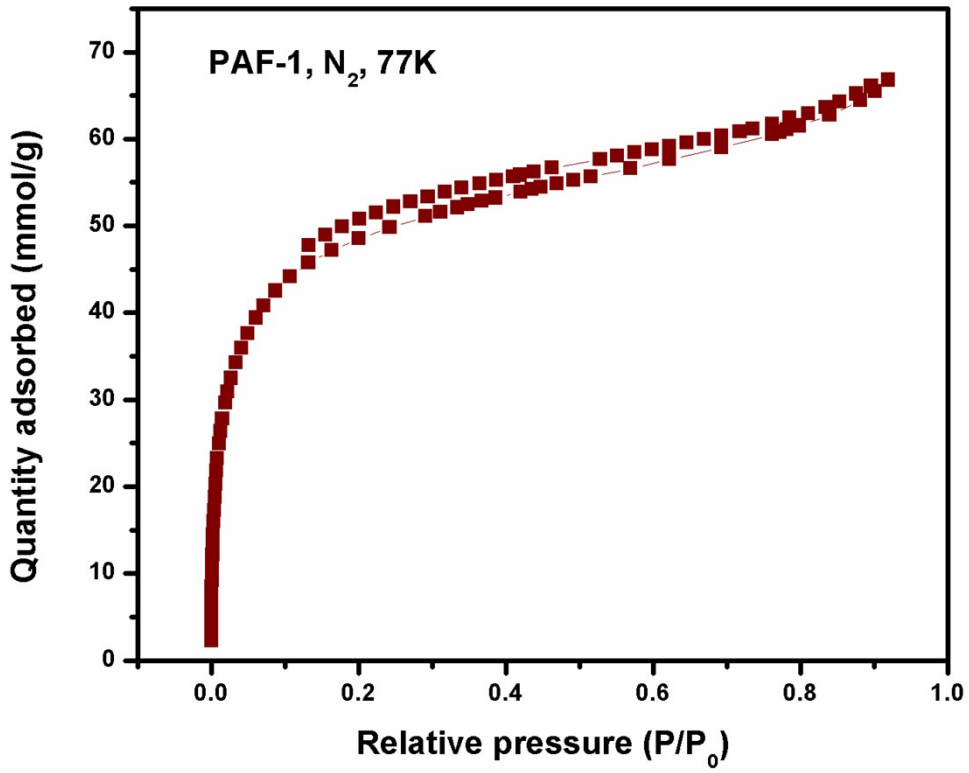

Figure S1: N_2 adsorption isotherm at 77 K for PAF-1.

2. Thermal-Gravimetric Analysis

Thermal-gravimetric analysis was carried out using a Mettler Toledo TGA 2 STAR^{e} System thermogravimetric analyser. Membranes samples were tested from 50 to 800 °C at 10 °C min $^{-1}$ under 50 mL/min nitrogen

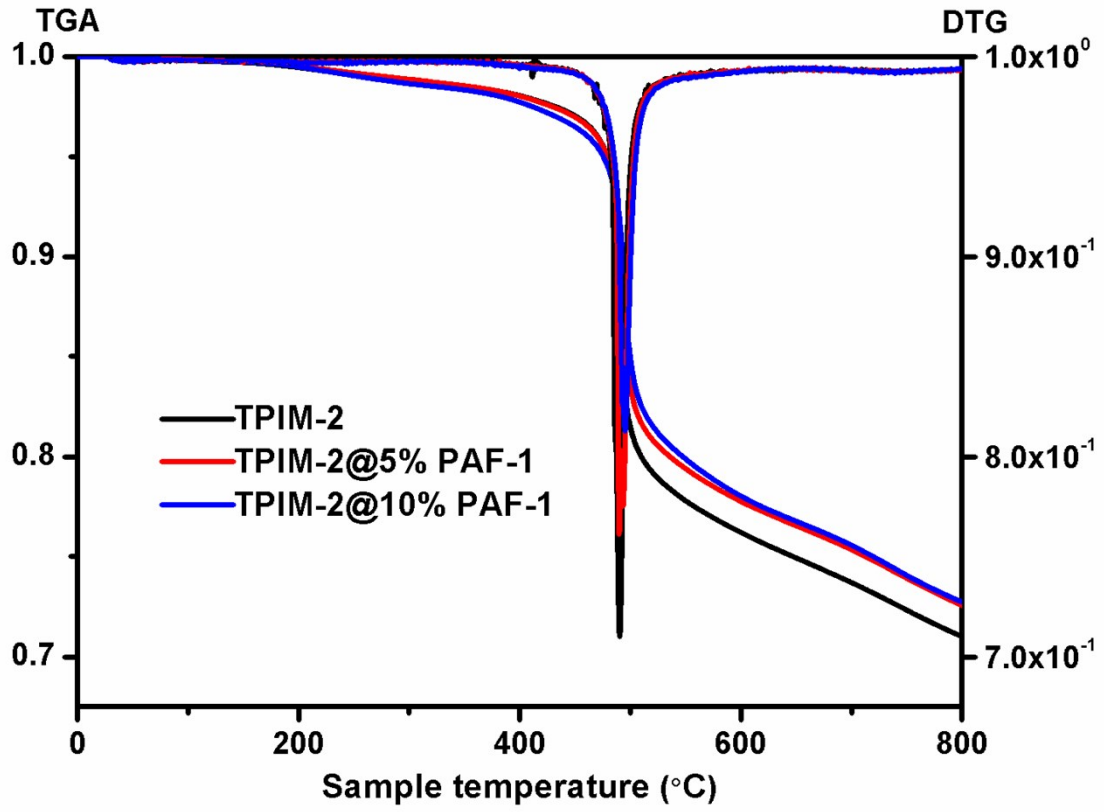

Figure S2: Thermal gravimetric analysis for TPIM-2, TPIM-2@5%PAF-1 and TPIM-2@10%PAF-1

3. Membrane Flexibility Bend Test

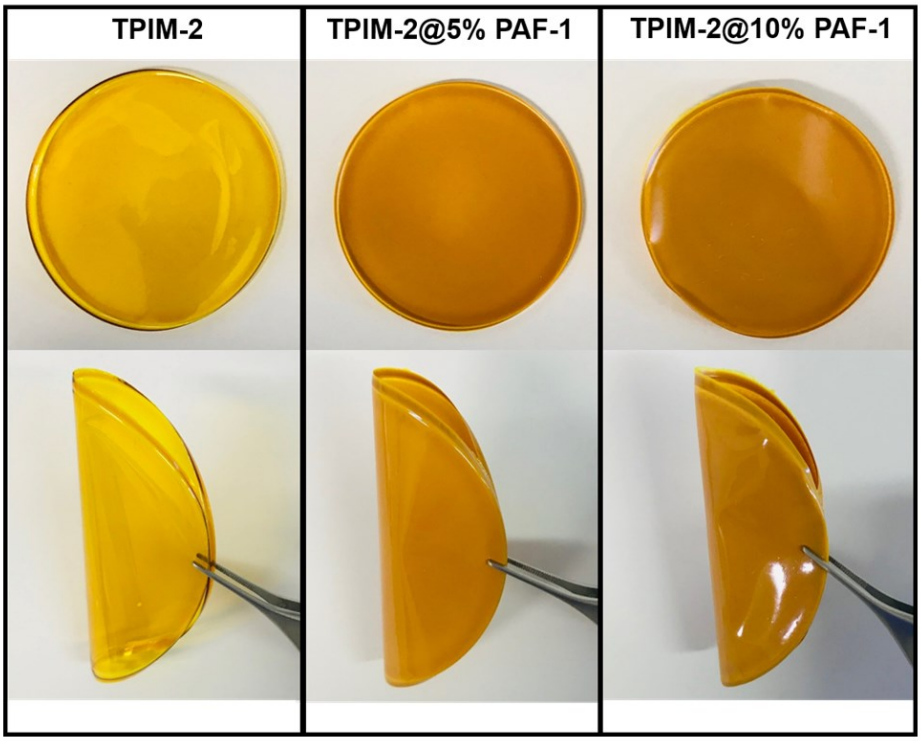

Figure S3: Membrane flexibility bend test for TPIM-2, TPIM-2@5%PAF-1 and TPIM-2@10%PAF-1.

4. Fourier-Transform Infrared (FT-IR) Spectroscopy

Fourier Transform Infrared (FT-IR) spectra of all samples including six TPIM-2 related membranes and one PAF-1 powder sample were collected using a Thermo Scientific NICOLET 6700 FT-IR.

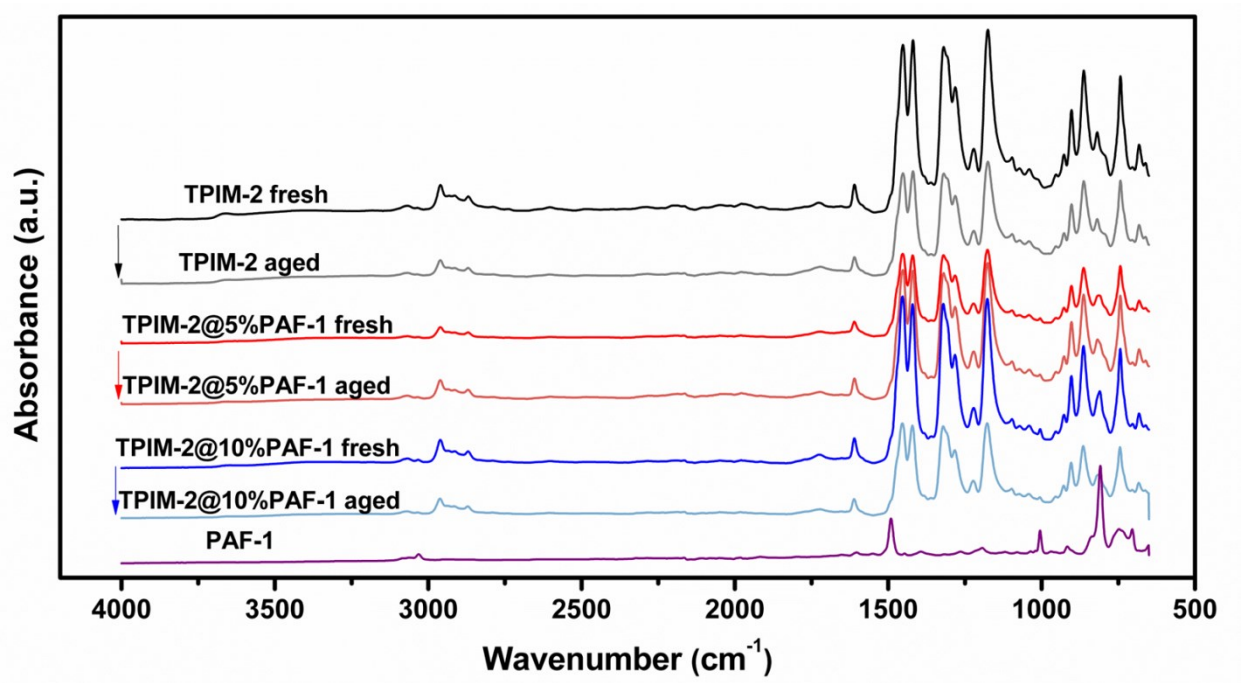

Figure S4: FT-IR spectra for PAF-1, fresh and aged TPIM-2, TPIM-2@5%PAF-1 and TPIM-2@10%PAF-1.

5. X-Ray Diffraction (XRD)

Powder x-Ray diffraction (PXRD) for PAF-1 was performed on a Bruker D8 Advance A25 X-ray diffractometer using Cu K-α radiation (40kV, 40mA) equipped with a LynxEye XE-T detector. Samples were scanned over the 2θ range from 2 to 85° with a step size of 0.02° and a count time of 1.6 seconds per step. XRD spectra for membrane film samples (TPIM-2, TPIM-2-PAF-1-based MMMs) were conducted on a Rigaku Smartlab X-ray diffractometer, operating under Cu K-α radiation (45Kv, 200mA) equipped with a HyPix-3000 detector. The samples were scanned over the 2θ range from 2 to 70° with a step size of 0.04° and scan rate of 2 degrees per minute.

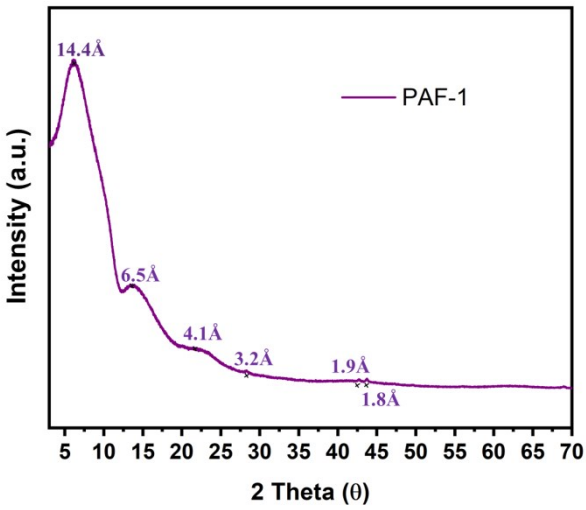

Figure S5a: X-Ray diffraction spectrum for PAF-1 powder.

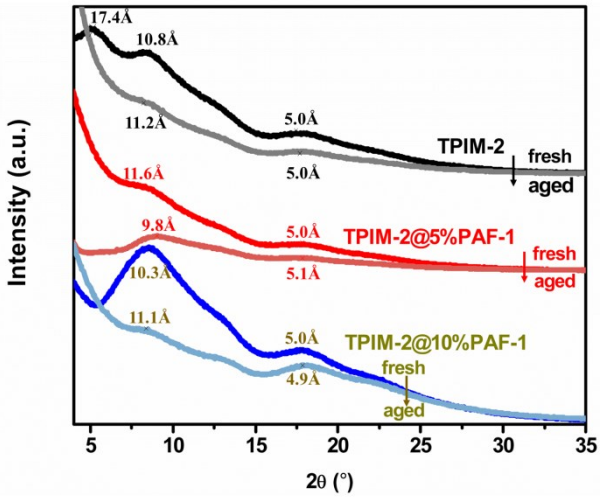

Figure S5b: X-Ray diffraction spectra for fresh and aged TPIM-2, TPIM-2@5%PAF-1 and TPIM-2@10%PAF-1 membranes.

6. Gel Permeation Chromatography

Molecular weights and polydispersity index (PDI) of TPIM-2 was measured by gel permeation chromatography in chloroform (Agilent Technologies 1200 series) using polystyrene as calibration standards.

7. Membrane Permeability and Selectivity Used for Trade-Off Comparisons.

Table S1	Permeability (Barrer)				Ideal Selectivity		
	$P(H_2)$	$P(N_2)$	$P(CH_4)$	$P(CO_2)$	H_2/N_2	H_2/CH_4	
TPIM-2	1651	85	104	1987	19.5	16.0	This work
TPIM-2@5% PAF-1	2907	108	120	2747	27.0	24.2	
TPIM-2@10% PAF-1	4886	209	260	4655	23.4	18.8	
TPIM-2*	1175	30	33	787	38.7	35.2	
TPIM-2@5% PAF-1*	1335	17	17	447	78.0	77.8	
TPIM-2@10% PAF-1*	2440	40	39	956	61.0	62.6	
Matrimid	27	0.3	0.2	7.7	97.0	83.3	Ref[1]
PTMSP	19628	4132	7030	30695	4.8	2.8	#
TPIM-1	2666	54	50	1549	50.0	53.0	Ref[2]
PIM-7	860	42	62	1100	20.5	14.0	Ref[2]
PIM-Trip-TB	8039	629	905	9709	12.8	8.9	Ref[2, 3]
PIM-SBF	5240	554	754	10400	9.5	7.0	Ref[2]
PIM-EA-TB	8114	580	774	7696	14.0	10.5	Ref
PIM-1	4902	652	1020	11427	7.5	4.8	Ref[4]
PIM-1/pDCX	9713	1127	1654	20553	8.6	5.9	Ref[4]
PIM-1/OH-pDCX	5230	304	379	8508	17.2	13.8	Ref[4]
PIM-1/PAF-1	7066	638	902	12354	11.1	7.8	#
PTMSP/PAF-1	18352	2226	3859	27317	8.3	4.8	#
PIM-1/UiO-66	3590	250	310	5340	14.4	11.6	Ref[5]
PIM-1/Ti5UiO-66	5280	660	1220	13540	8.0	4.3	Ref[5]
PIM-1/ZIF-8	10650	1090	1440	17050	9.8	7.4	Ref[6]
PIM-1/Silicalite-1	894	83	183	2530	10.8	4.9	Ref[6]
PIM-1/GCNN	3830	354	503	5785	10.8	7.6	Ref[6]

Notice: *: aged 2 months samples; GCNN: Graphitic Carbon Nitride Nanosheets, TIPM-1: aged 14 days, PIM-trip-TB: aged 100 days, PIM-EA-TB: aged 470 days, PTMSP/PAF-1: aged 15 days, #: unpublished work

8. TPIM-2 and TPIM-2/PAF-1 MMMs Permeability and Aging Studies

Pure-gas permeability calculation for He, H_2, N_2, O_2, CH_4 and CO_2 were based on the constant volume/variable pressure method. The gas permeability was determined from the rate of permeate pressure increase (*dp/dt*) once permeation reached steady state, according to equation S1. Membrane performance was conducted twice for each gas - the deviation was within 10%.

$$P = \frac{\frac{273 \times 10^{10}}{760} \quad VL}{AT\left[\frac{p_2 \times 76}{14.7}\right]}\left(\frac{dp}{dt}\right) \qquad \text{Equation S1}$$

where, *P* refers to the permeability of a membrane to a gas and its unit is in Barrer (1 Barrer = 1×10^{-10} cm^3 (STP) cm cm^{-2} sec^{-1} $cmHg^{-1}$); *V* is the permeate volume (cm^3); *L* is the film thickness (cm); *A* is the effective membrane area (cm^2); *T* is the temperature (K); and p_2 is the feed gas pressure (psia). Ideal selectivity ($\alpha_{A/B}$) was calculated as the ratio of the single gas permeability for a given gas pair.

Table S2. The aging study of the polymer films was done by storing the samples under ambient conditions after initial membrane performance measurements for as-cast samples; with periodical storage (15, 30, 45, 60 and 180 days). The permeation measurements were carried out on these aged membranes after evacuating overnight to remove any adsorbed air and any other potential impurities from storage. For each test, single gas measurements were recorded sequentially using He, H_2, N_2, O_2, CH_4, and CO_2 at 2 bar feed pressure, in duplicate (deviation with ± 10%) at 25 ± 1 °C. Before changing gases for permeation testing, the membrane and permeation system were evacuated under low vacuum for at least 2 hours to completely remove prior gas and ensure the measurement accuracy.

Table S2	Permeability (Barrer)						Ideal Selectivity			
	P(He)	$P(H_2)$	$P(N_2)$	$P(O_2)$	$P(CH_4)$	$P(CO_2)$	H_2/N_2	H_2/CH_4	CO_2/CH_4	O_2/N_2
P-1	632	1651	85	354	104	1987	19.5	16.0	19.2	4.2
P-15	544	1401	56	259	64	1411	24.8	21.7	21.9	4.6
P-30	549	1293	43	217	49	1126	30.1	26.2	22.8	5.0
P-45	518	1264	35	191	38	949	36.4	33.6	25.2	5.4
P-60	518	1175	30	163	33	787	38.7	35.2	23.6	5.4
P-180	Membrane broke									
M-5%-1	1299	2907	108	518	120	2747	27.0	24.2	22.9	4.8
M-5%-15	1012	2078	50	268	50	1224	41.5	41.4	24.4	5.4
M-5%-30	935	1801	33	192	30	797	54.3	59.2	26.2	5.8
M-5%-45	870	1593	24	142	20	554	65.4	78.2	27.2	5.9
M-5%-60	805	1335	17	104	17	447	78.0	77.8	26.0	6.1
M-5%-180	543	644	6	33	7	122	102.9	92.4	17.5	5.5
M-10%-1	2230	4886	209	941	260	4655	23.4	18.8	17.9	4.5
M-10%-15	1738	3521	91	527	94	2197	38.7	37.4	23.3	5.8
M-10%-30	1577	2973	61	380	62	1494	48.9	47.6	23.9	5.7
M-10%-45	1430	2644	48	297	46	1175	55.2	57.9	25.7	6.2
M-10%-60	1372	2440	40	255	39	956	61.0	62.6	25.5	6.4
M-10%-180	1047	1400	15	87	17	34	96.5	85.1	21.0	5.8

Notice: P: TPIM-1, M: MMMs, 5%: 5wt. % PAF-1 loading, 10%: 10wt. % PAF-1 loading, 1, 15, 30, 45, 60, 180: samples aged for 1, 15, 30, 45, 60, 180 days. Operation conditions: single gas, 2 atm, 25±1°C

9. Positron Annihilation Lifetime Spectroscope (PALS)

Mean pore size and intensity were obtained through Positron Annihilation Lifetime Spectroscopy. The membrane samples were cut and stacked into two 2 mm thick piles and each placed on either side of the positron source sealed in a Mylar envelope (^{22}NaCl, 1.8 MBq). The samples were then placed in a vacuum cell (5 x 10^{-6} torr) between two EG&G Ortec fast-fast coincidence spectrometers. The timing resolution of the system was 240 ps and a minimum of 4 files of 4.5 x 10^6 integrated counts were collected. The spectra were analysed using LT-v9 software [7] and fitted to 4 component lifetimes. The first lifetime (τ_1) was fixed to 0.125 ns and attributed to para-positronium (bound state of a positron and an electron with opposite spin) annihilation. The second component (τ_2) was due to free annihilation of the positron with free electrons within the sample. The longer lifetimes (τ_3, τ_4) were due to ortho-positronium annihilation of the positron in a bound state of an electron in the same spin state. These longer lifetimes are due to annihilation within the free volume of the membranes and indicate the presence of a bimodal porosity in the PTMSP and the composite samples. The lifetimes were calculated using the Relative Tao-Eldrup relationship.[8-10] The pore size distribution was a visual representation adapted using the PAScual software.[11] The fractional free volume (FFV) calculation[12] was based on the equation below.

$$FFV_{PALS} = CV_{PALS}I_{PALS} \qquad \text{Equation S2}$$

Where,

$$V_{PALS} = \frac{4}{3}\pi R_{PALS}^{3} \qquad \text{Equation S3}$$

Here, C is the empirical constant, 0.0018 Å, V_{PALS} is the average volume of the pore elements calculated using the radius, R_{PALS} determined from the PALS lifetime and I_{PALS} is the associated Intensity. Separate pore size FFV (FFV 3 and FFV 4) and total FFV are listed as below

Table S3 **Positron Annihilation Lifetime Spectroscopy (PALS)**

Samples name	Tau 3 (ns)	Tau 4 (ns)	I3 (%)	I4 (%)	TE Diameter3 (nm)	TE Diameter4 (nm)	FFV 3 (%)	FFV 4 (%)	FFV total (%)
TPIM-2-fresh	**1.85** (±0.14)	**6.73** (±0.12)	**5.22** (±0.18)	**11.94** (±0.28)	**0.540** (±0.03)	**1.090** (±0.009)	**0.8** (±0.1)	**14.8** (±0.7)	**15.5** (±0.9)
TPIM-2-aged	**1.98** (±0.13)	**7.12** (±0.11)	**4.66** (±0.11)	**11.00** (±0.29)	**0.568** (±0.024)	**1.124** (±0.008)	**0.8** (±0.1)	**14.7** (±0.7)	**15.5** (±0.8)
TPIM-2@10% PAF-1 fresh	**2.13** (±0.06)	**6.77** (±0.05)	**6.48** (±0.09)	**11.98** (±0.23)	**0.594** (±0.01)	**1.098** (±0.003)	**1.3** (±0.1)	**14.9** (±0.4)	**16.2** (±0.5)
TPIM-2@10% PAF-1 aged	**1.97** (±0.13)	**6.70** (±0.08)	**5.64** (±0.10)	**13.43** (±0.23)	**0.564** (±0.02)	**1.107** (±0.006)	**1.0** (±0.1)	**17.2** (±0.6)	**18.1** (±0.7)

Note: PALS was run for membrane aged 6 months

10. Solution Viscosity Measurements

Viscosity measurements were made using a SCHOTT AV350 Viscometer (standard ASTM D445) using 52610/I U-tube calibrated with a de-ionized water standard at 20 °C. Samples of pure solvent, PAF-1 in solvent, pure polymer in solvent and mixed polymer with additives in solvent were made. For pure additives in solvent: 22.5 and 45 mg PAF-1 was placed into 15 ml anhydrous chloroform. For pure polymer solution: 450 mg TPIM-2 was dissolved into 15 ml anhydrous chloroform. Mixed solutions for 5 and 10 wt. % MMMs were made by combining 22.5 mg, 45 mg PAF-1 and TPIM-2 (with total amount of 450 mg) into 15 ml anhydrous chloroform. Viscosity was measured after stirring for 24 h. Results are averaged from 10 duplicates.

Table S4 **Viscosity Measurements**

Samples	**Agitated for 24hrs centipoise, Cp**	**+/-**
Chloroform	0.42	0.0041
5% PAF-1	0.44	0.0022
10% PAF-1	0.46	0.00061
TPIM-2	3.17	0.071
TPIM-2@5%PAF-1	3.05	0.030
TPIM-2@10%PAF-1	3.04	0.024

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

11. References

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