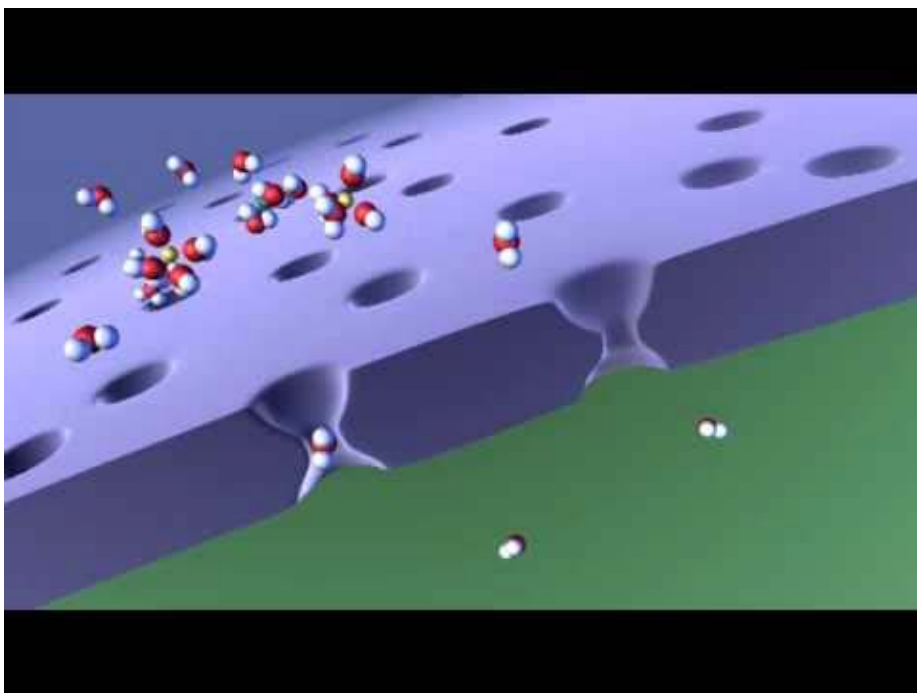


Development of a polymer inclusion membrane with high stability and adequate selectivity for Zn(II)



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Development of a stable polymer inclusion membrane based passive sample for Zn(II) and other heavy metals

- **Introduction**

- ✓ What is PIM
- ✓ Disadvantage of existing PIM
- ✓ Why are we concern about Zinc

- **Experiments**

- ✓ Components
- ✓ PIM preparation and composition
- ✓ Extraction experiments
- ✓ Morphology study

- **Results**

- ✓ Nature of PIM
- ✓ Extraction capability comparison
- ✓ Roughness data

- **Conclusion**

- **Acknowledgement**

Introduction:

- **What is PIM?**

A thin film made of polymer backbone and some active molecules are impregnated in polymer base.

Polymer : PVC (**polyvinylidene chloride**), CTA (**cellulose triacetate**), PVDF (**polyvinylidene fluoride**), PVDF-HFP (**poly(vinylidene fluoride-co-hexafluoropropylene)**)

Extractant : Aliquot 336, Phosphonium ionic liquid, Cyanex, D2EHPA

- **Disadvantage of existing PIMs**

- Leaching of carrier molecule and weight loss
- Not suitable for long term use
- Less selective
- Low flux value

Introduction:

- Why are we concerned about Zinc?

Benefits: Regulating immune function, Treating diarrhoea, Affecting learning and memory, Helping treat the common cold, Fertility etc...



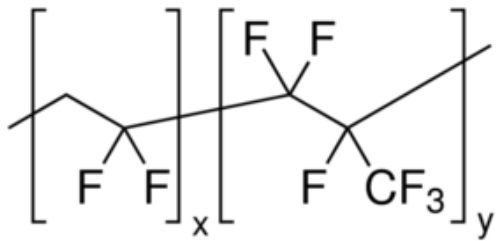
There is a LIMIT of intake.

Children (0-8yr): 3-5mg per day
Adult male: 11mg per day
Adult female: 8mg per day
Pregnant and lactating women:
11-13mg per day

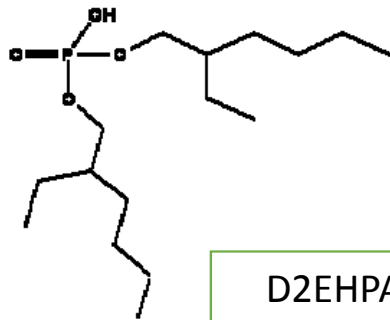
Adverse effects: Nausea, Vomiting, Loss of appetite, Stomach pains, Headaches, Diarrhoea etc..

Experiments:

Components:



PVDF-HFP



D2EHPA

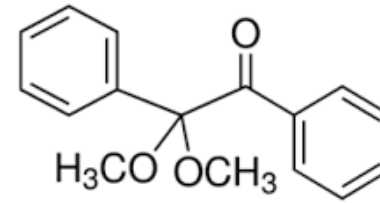
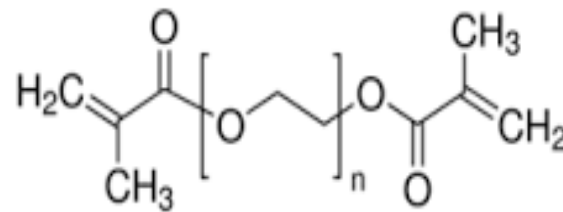


Photo initiator



PEG-DMA

Experiments:

PIM Preparation:

PIMs were casted using casting knife.

Composition:

PIM with fixed polymer ratio

PIM Id	Composition unit	PVDF-HFP	D2EHPA	PEG-DMA	INITIATOR
25%	Mass (g)	1.258	0.771	0.8278	0.2041
	Percentage	40.5	25.4	27.3	6.8
30%	Mass (g)	1.141	.904	0.9024	0.2041
	Percentage	37.9	30.0	25.3	6.8
35%	Mass (g)	1.054	1.055	0.7085	0.2006
	Percentage	34.9	35.0	23.5	6.6
40%	Mass (g)	0.961	1.205	0.6469	0.2046
	Percentage	31.8	40.0	21.4	6.8
45%	Mass (g)	0.875	1.352	0.5817	0.2043
	Percentage	29.0	44.9	19.3	6.8
50%	Mass (g)	0.781	1.504	0.5400	0.2080
	Percentage	25.7	49.6	17.8	6.9

PIM with varying polymer ratio

PIM Id	Composition unit	PVDF-HFP	D2EHPA	PEG-DMA	INITIATOR
40%-5:5	Mass (g)	0.818	1.213	0.8256	0.1506
	Percentage	27.2	40.3	27.5	5.0
40%-6:4	Mass (g)	0.991	1.208	0.6641	0.15
	Percentage	32.9	40.1	22.0	5.0
40%-7:3	Mass (g)	1.150	1.215	0.5040	0.1530
	Percentage	38.0	40.2	16.7	5.1
40%-8:2	Mass (g)	1.321	1.207	0.3307	0.1503
	Percentage	43.9	40.1	11.0	5.0
40%-9:1	Mass (g)	1.486	1.206	0.1789	0.1501
	Percentage	49.2	39.9	5.9	5.0
40%-10:0	Mass (g)	1.651	1.215	0.0000	0.1509
	Percentage	54.7	40.3	0.0	5.0

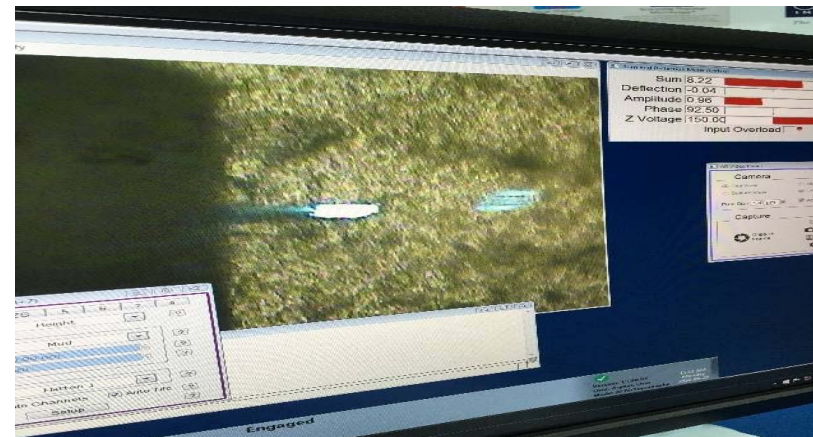
Experiments:

Extraction and Stripping of Zn (II):

- Feed solution - 35mg/L Zn(II)
- pH of feed solution – 3.1
- Stripping solution – 0.1M HCl
- Stirring rate – 150 rpm
- Concentration of Zn(II) measured by Hitachi AAS

Morphology study of PIM:

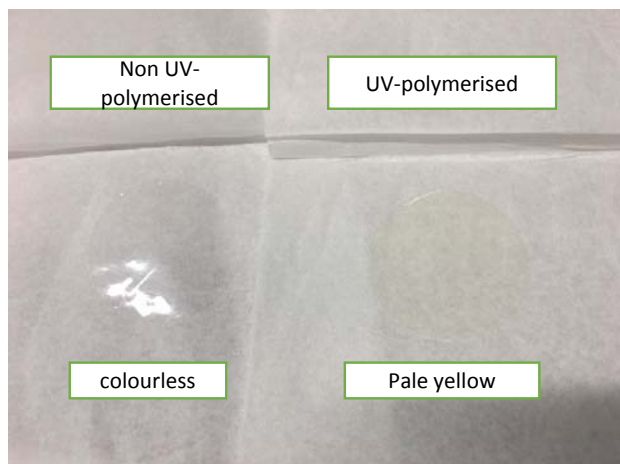
- AFM (Oxford Instruments Asylum Research's)
- Si tip of force constant 1.2-29 N/m
- Resonance frequency 76-263 kHz
- Area of $5\mu\text{m} \times 5\mu\text{m}$ was scanned
- 0.48Hz scan rate and 630.00mV set point
- Topography analysis by WSxM 5.0 software



Camera view of PIM surface

Results:

Nature of PIM:

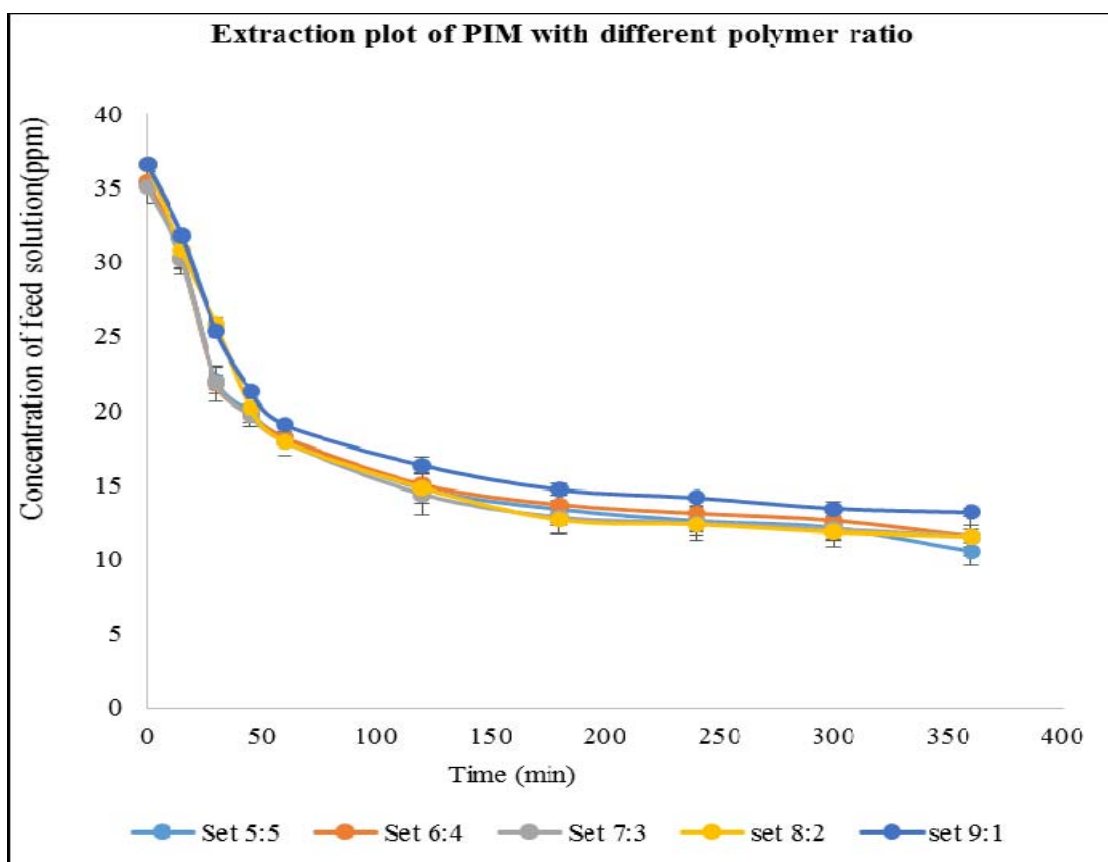


PIMs characteristics as a function of compositions

D2EHPA Polymer Ratio	50 wt%	45 wt%	40 wt%
5:5	Very soft, could not be peeled off	Soft and sticky, slightly stretchable	Slightly soft, sticky, slightly stretchable
6:4	Soft, not so sticky not stretchable,	slightly Soft, slightly stretchable	Slightly soft, Not so sticky, slightly stretchable
7:3	Slightly soft, not sticky, stretchable	Not soft, not sticky, stretchable	Slightly soft, not sticky, stretchable
8:2	Slightly soft, not sticky, stretchable	Not soft, not sticky, stretchable	Not soft, not sticky, extensively stretchable
9:1	Slightly soft, not sticky, slightly stretchable	Not soft, not sticky, extensively stretchable	Not soft, not sticky, extensively stretchable
10:0	Slightly soft, not sticky, slightly stretchable	Not soft, not sticky, extensively stretchable	Not soft, not sticky, extensively stretchable

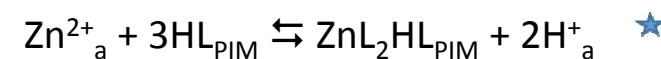
Extraction results:

Extraction result of PIMs with 40 wt% D2EHPA and different polymers ratio



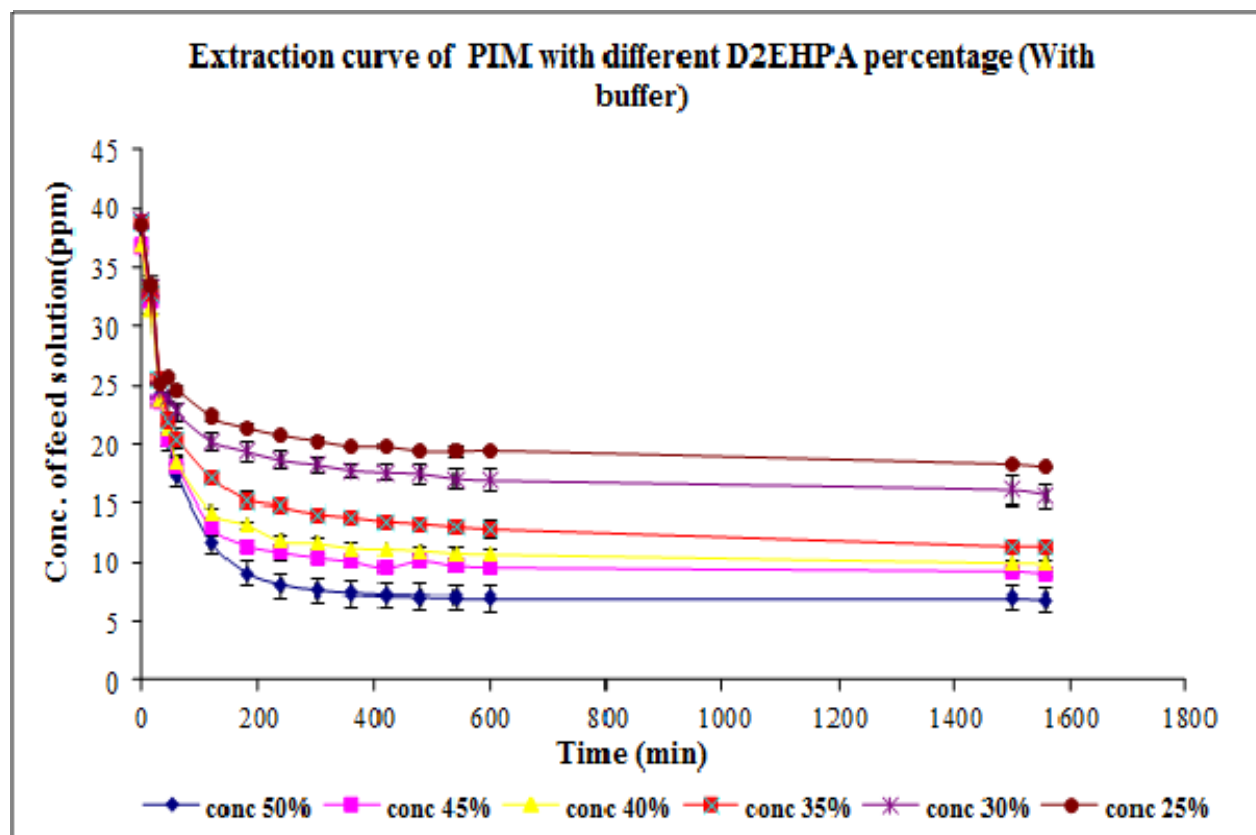
PIM Id	Amount of Zn(II) extracted		Time (h)
	Mass (mg)	% of initial Zn(II) concentration	
40%-5:5	2.6	73.2 %	26
40%-6:4	2.5	71.1 %	26
40%-7:3	2.5	70.9 %	26
40%-8:2	2.7	73.1 %	27
40%-9:1	2.5	68.0 %	27

pH changed to 2.7 from 3



Extraction results:

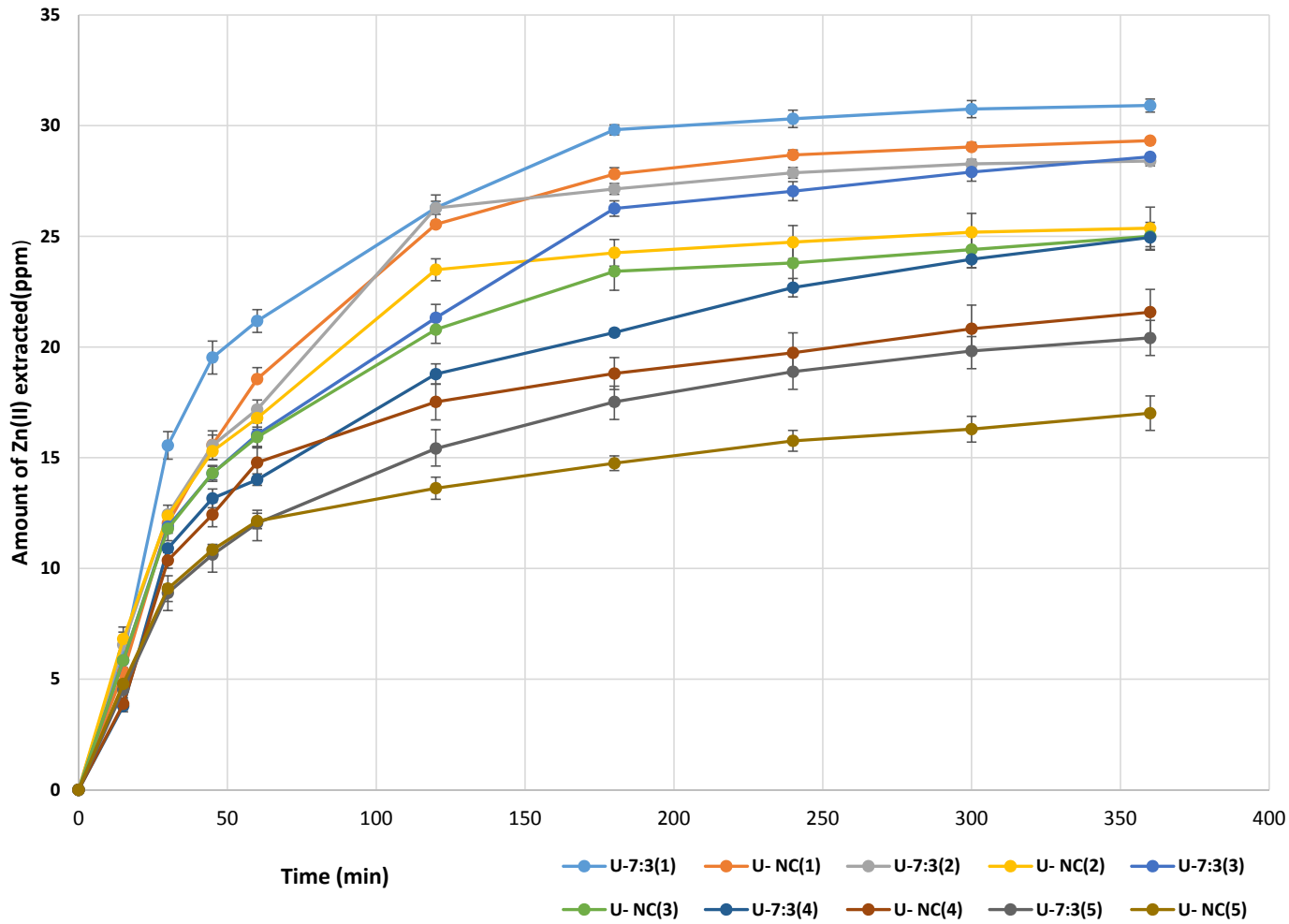
Extraction result of PIMs with 25-50 wt% D2EHPA and 6:4 polymers ratio



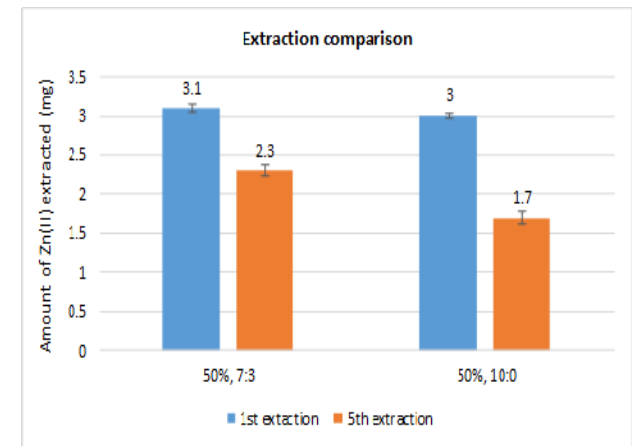
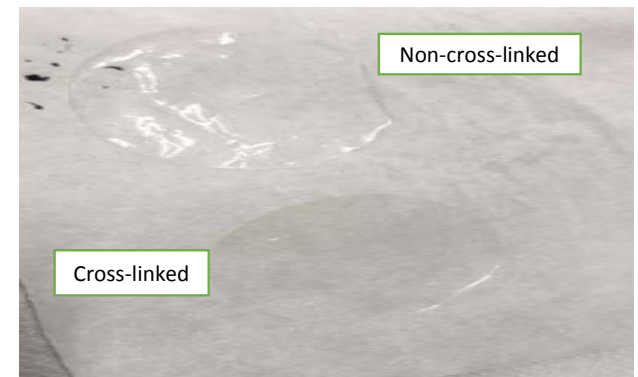
PIM Id	Amount of Zn(II) extracted (mg)		Time (h)
	Mass (mg)	% of initial Zn(II) concentration	
25%	2.04	53.2 %	27
30%	2.32	60.0 %	27
35%	2.74	70.8 %	27
40%	2.72	73.6 %	27
45%	2.77	75.5 %	27
50%	3.15	85.6 %	27

Extraction results:

Multiple extraction with 50 wt% D2EHPA PIM (cross-linked and non-cross-linked)



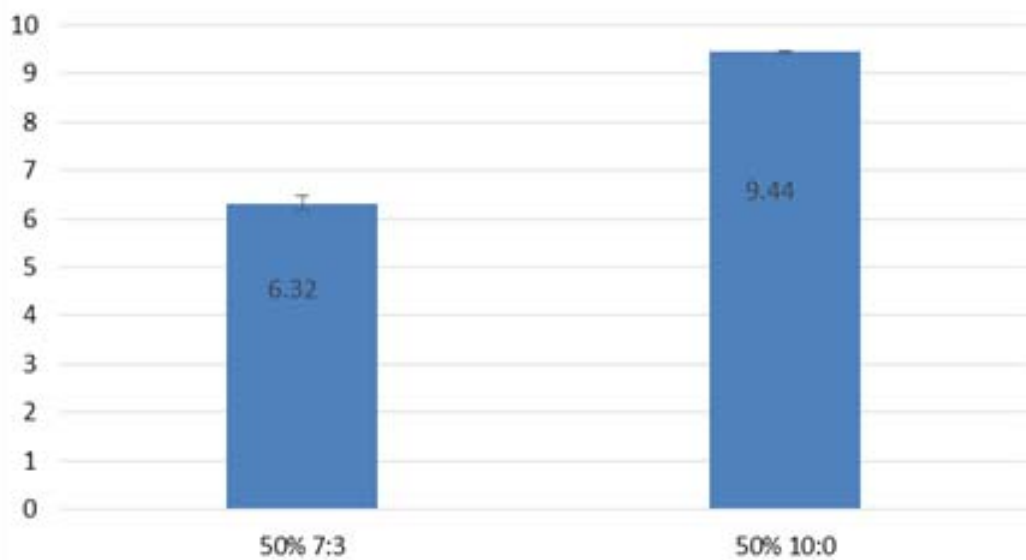
- Extraction of cross-linked PIM is better in all step
- Non-cross-linked PIM started to get folded from edge



Extraction results:

Weight loss comparison of cross-linked and non-cross-linked PIMs

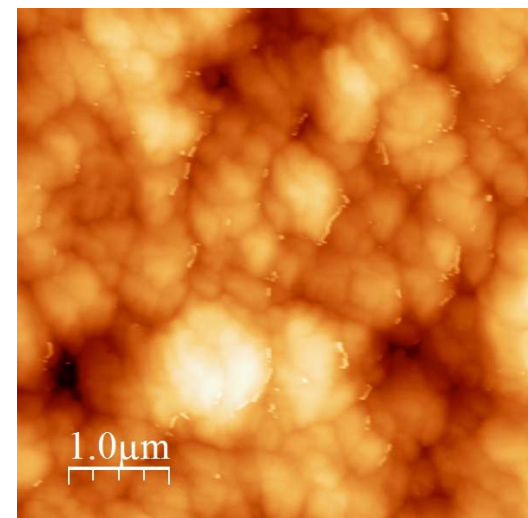
% Weight loss



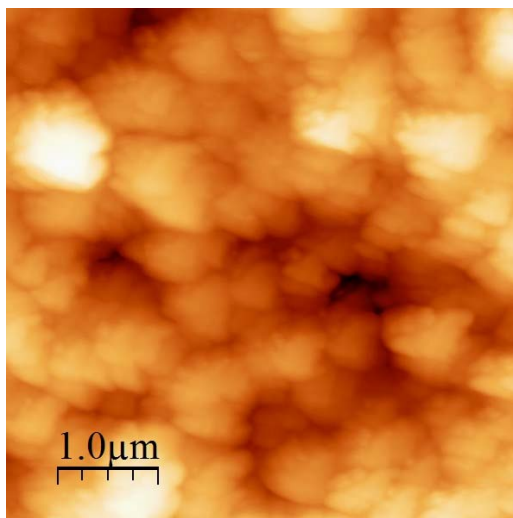
Rate constant and Initial flux

PIM Id		$k \times 10^6 \text{ (s}^{-1}\text{)}$	Initial flux (J_i) ($\mu\text{mol m}^{-2}\text{.s}^{-1}$)
D2EHPA concentration (wt%)	Polymers ratio		
40	5:5	74.82	3.82
40	6:4	76.87	3.93
40	7:3	72.68	3.71
40	8:2	83.49	4.27
40	9:1	67.49	3.45
50	7:3	102.2	5.22
50	10:0	74.71	3.81

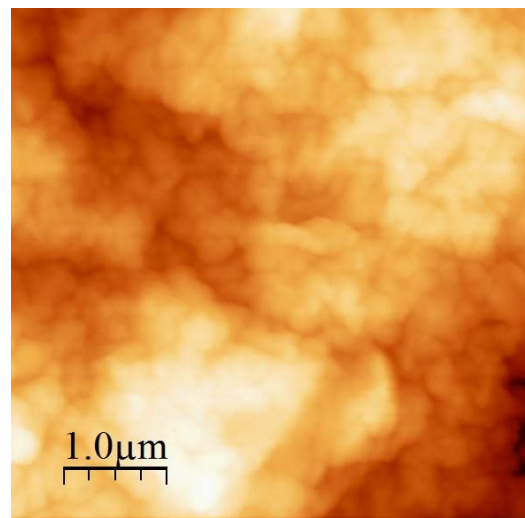
Morphology study:



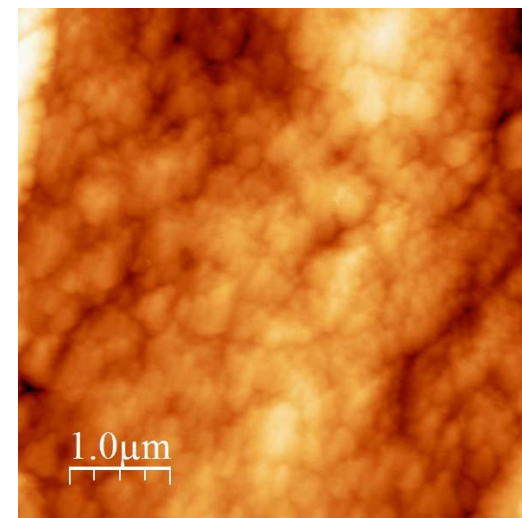
45 wt%, 6:4, UV-treated



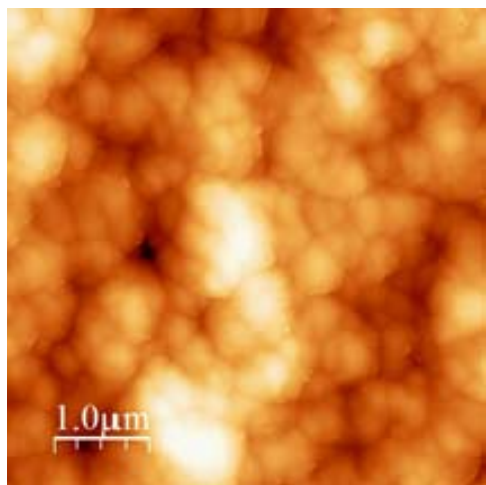
45 wt%, 6:4, UV-treated, used



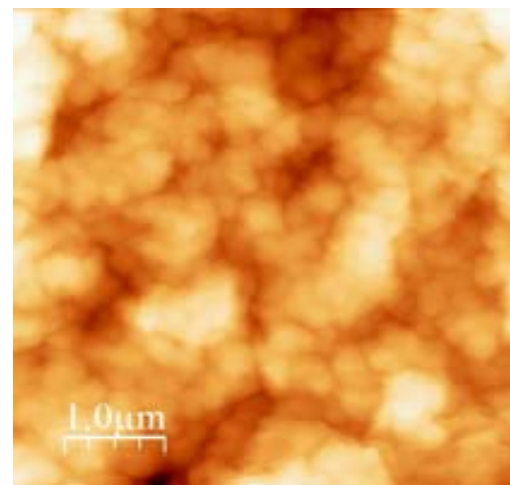
40 wt%, 6:4, UV-treated, M.used



45 wt%, 10:0



45 wt%, 6:4, Non-UV-treated

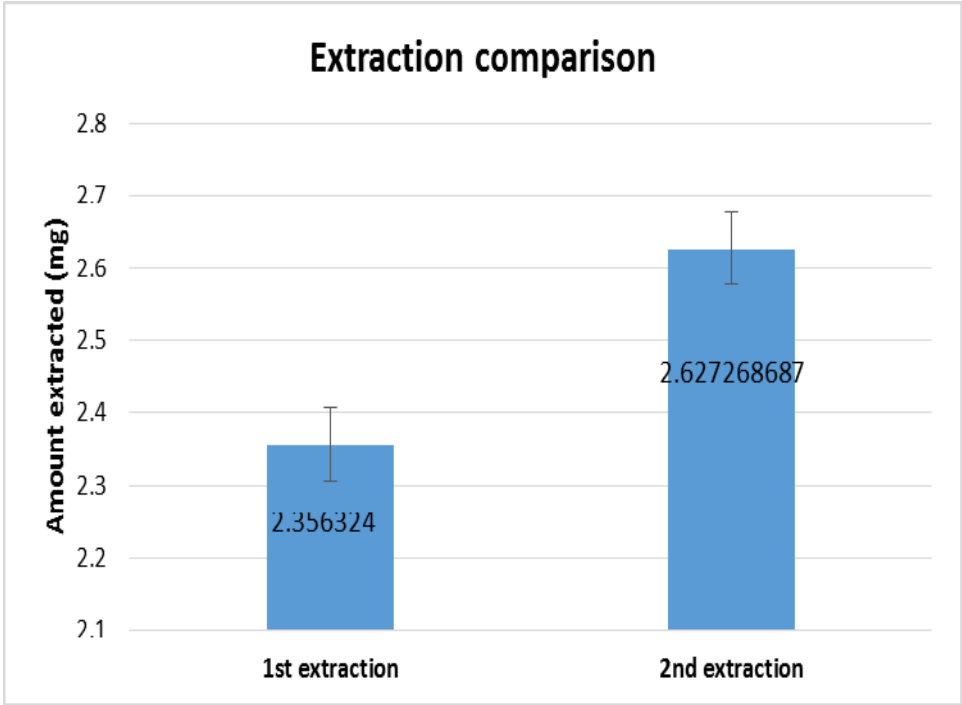


50 wt%, 7:3, UV-treated, M.used

Morphology study:

Roughness Table

PIM Id	45 wt%, 6:4 (UV)	45 wt%, 6:4 (No UV)	45 wt%, 10:0 (No UV)	45 wt%, 6:4 (S.U)	50 wt%, 7:3 (M.U)	40 wt%, 6:4 (M.U)
Roughness(nm)	145.8	149	38.9	314	378	389



Conclusion:

- ❖ PVDF-HFP : PEG-DMA ratio of 5:5, 6:4, 7:3, and 8:2 have almost same stability
- ❖ 50 wt% D2EHPA PIM has better extraction capability
- ❖ Cross-linked PIM with 50 wt% D2EHPA has better extraction capability and stability than non-cross-linked PIM
- ❖ Rougher the PIM , better the extraction capability

Acknowledgement:

- Prof. Spas Kolev and all labmates
- School of Chemistry, University of Melbourne
- Workshop team
- Dr. T.G. Gopakumar, IIT KANPUR
- Department of Chemistry, IIT KANPUR
- Advance Imaging and Nanotechnology sector, IIT KANPUR

THANK YOU