Magnetic chitosan-*g*-acrylate/styrene composites for hybrid coatings with nanostructured morphology

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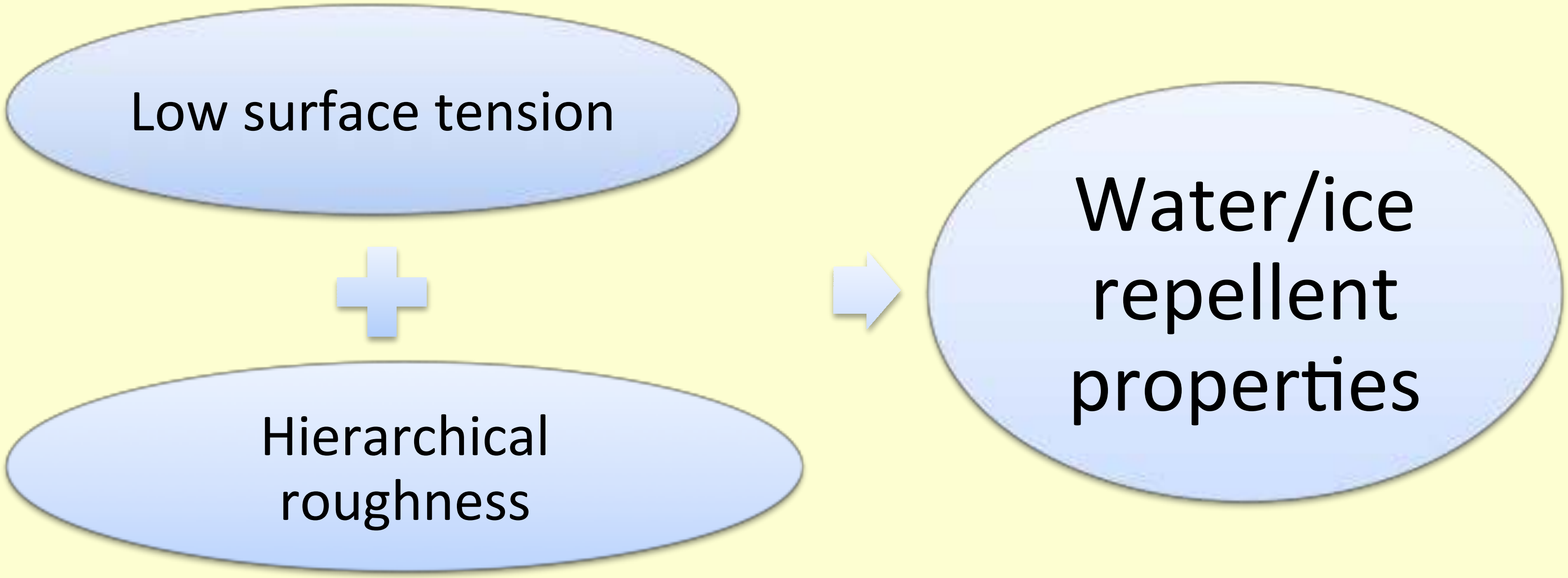
Introduction/motivation



- Textured surface facilitates air pocket entrapment -> minimize contact area with water drop
- Nanoparticle aggregation: facile method for producing patterned morphology
- Proposed strategy: Patterned surface by composite iron oxide-grafted chitosan particle assembly

Objectives and Outline

Main objective: Prepare hybrid coatings with patterned roughness and controlled wettability

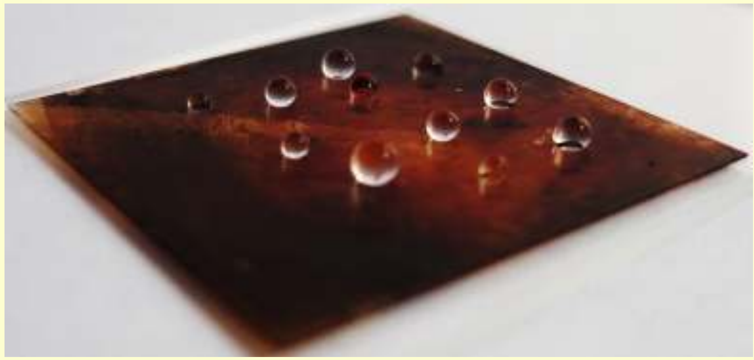
- Composite particle synthesis and characterization
- Coating formulation and deposition technique optimization
- Coating characterization
- Conclusions and future work

Textured coating components

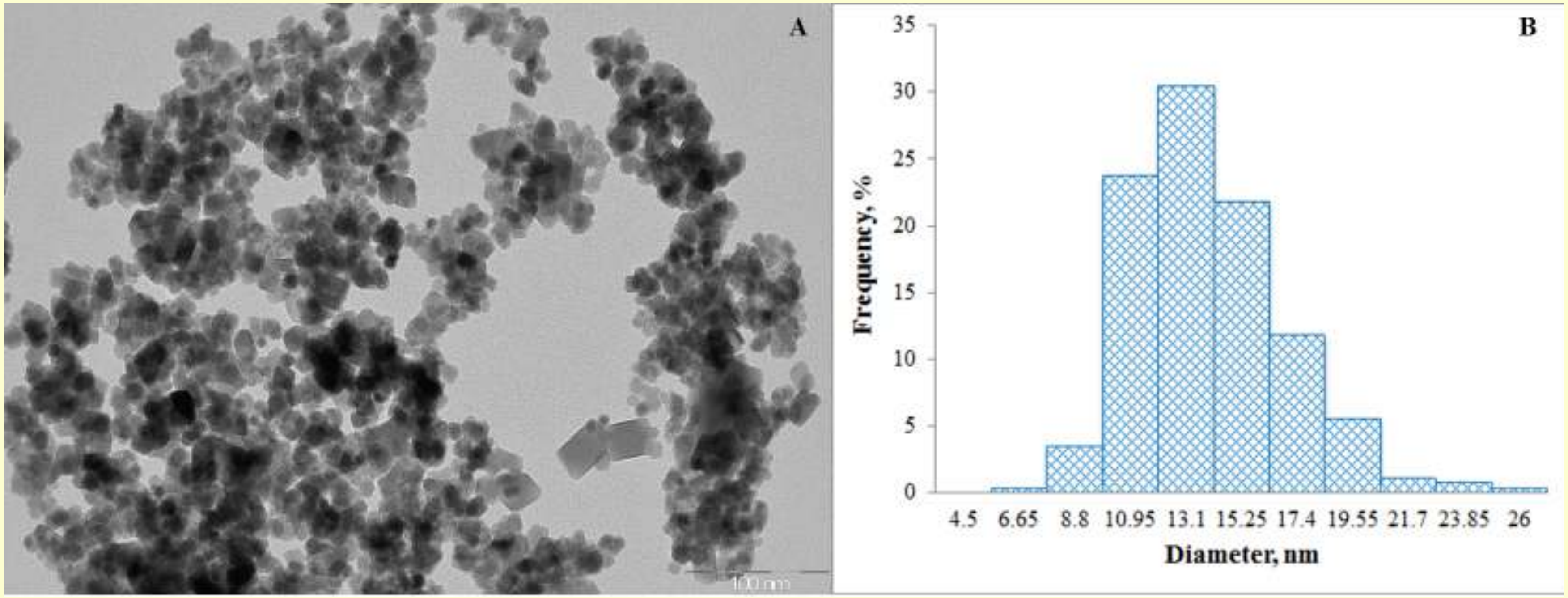
1. Composite particles: magnetic chitosan-g-acrylate (BMA/EGDMA; BA/EGDMA; HA/EGDMA) or styrene/EGDMA
2. Polymeric binder: chitosan
3. Crosslinking/coupling agent: hexadecyltrimethoxy silane

Spray or spin coat on glass slide

Curing, treatment, rinsing



Magnetite nanoparticles synthesis

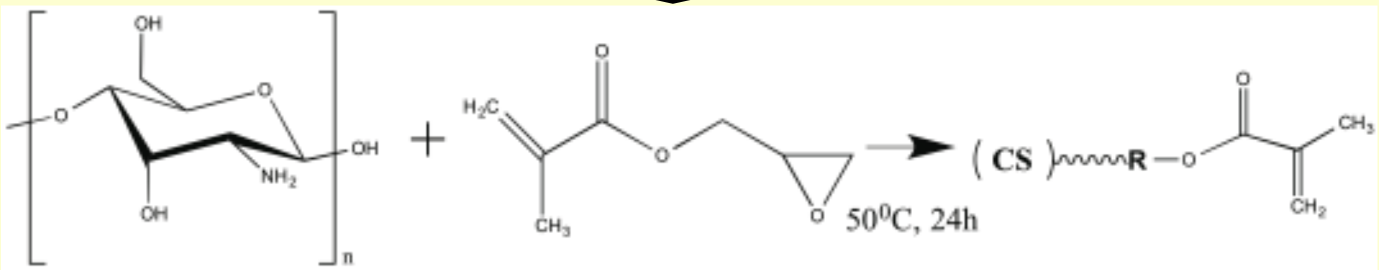


- Synthesis by co-precipitation from aqueous solution containing Fe^{3+}/Fe^{2+} ions
- Average size: 13nm

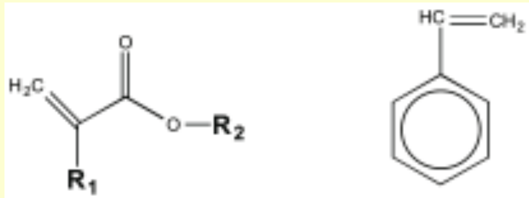
Reference: G. Dodi et al. / Journal of Magnetism and Magnetic Materials 388 (2015) 49–58

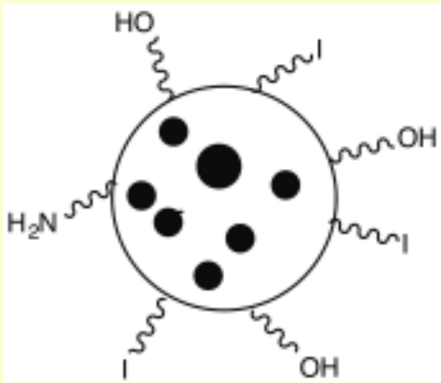
Composite particles synthesis

CS+GMA



Fe$_3$O$_4$
NANOPARTICLES

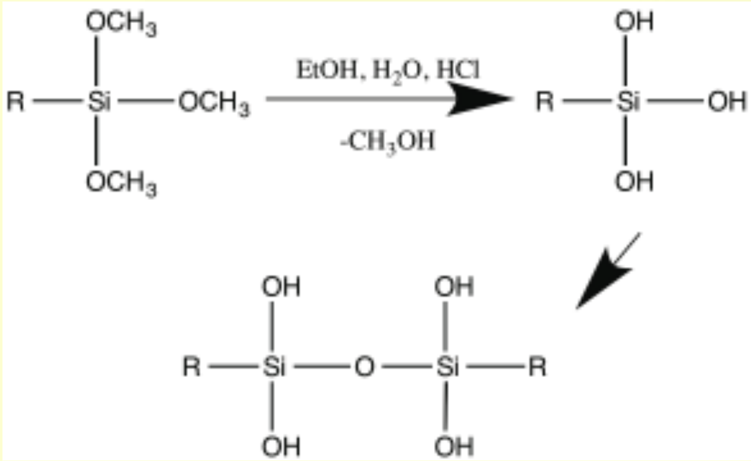




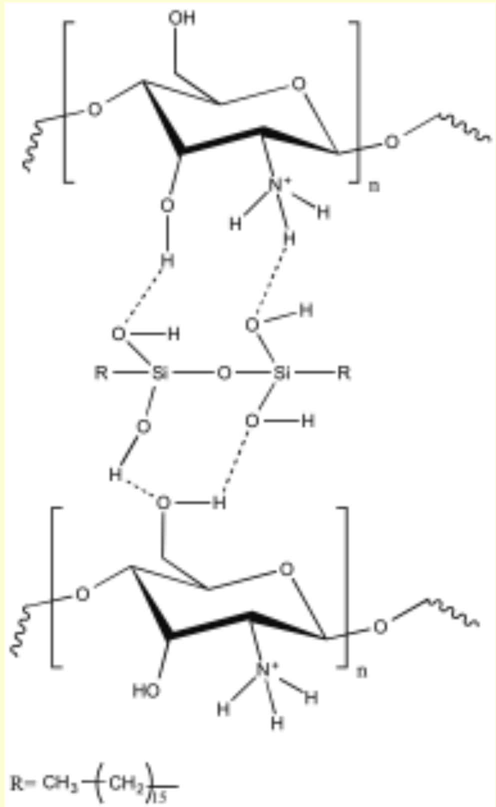
Reference: G. Dodi et al., Chem. Eng. J. 203 (2012) 130–141

Silane coupling

1. Silane hydrolysis

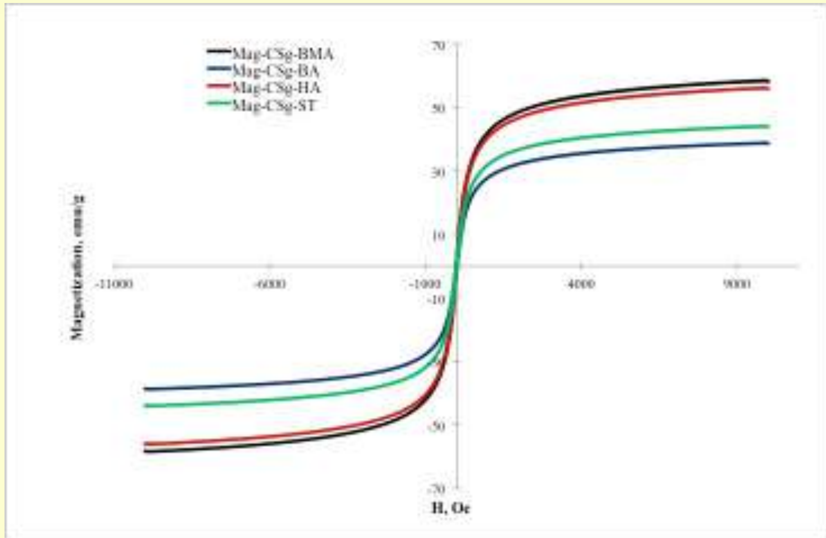


2. Polymeric binder/composite particles crosslinking/coupling



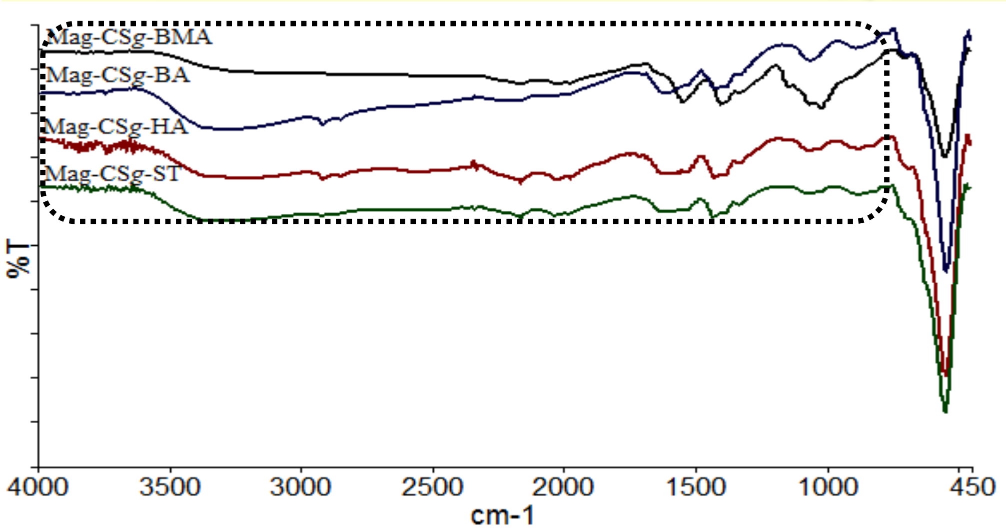
Reference: Spirk et al./Carbohydrate Polymers 93 (2013) 285– 290

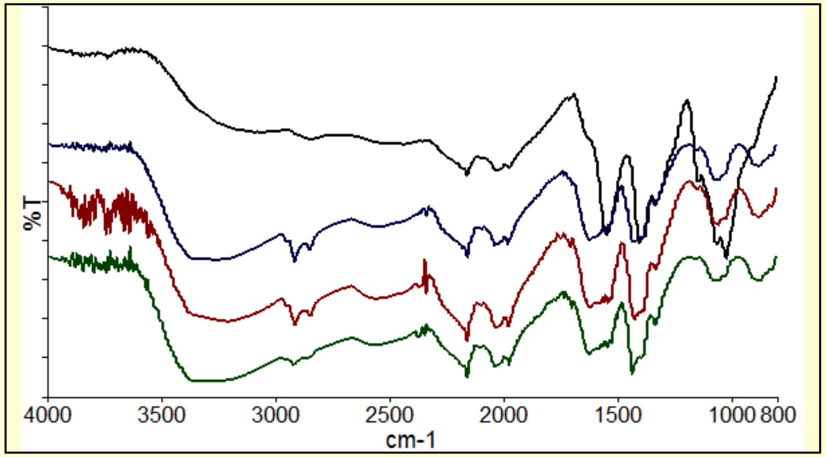
Composite particles characterization (magnetization)



Batch	Magnetization, emu/g	Magnetite % (theoretical)	Magnetite % (experimental)
Mag20	65.8	100	NA
MagCSgBMA	58.2	55.5	88.4
MagCSgBA	38.6	55.5	58.7
MagCSgHA	55.9	55.5	84.9
MagCSgST	43.8	55.5	66.6

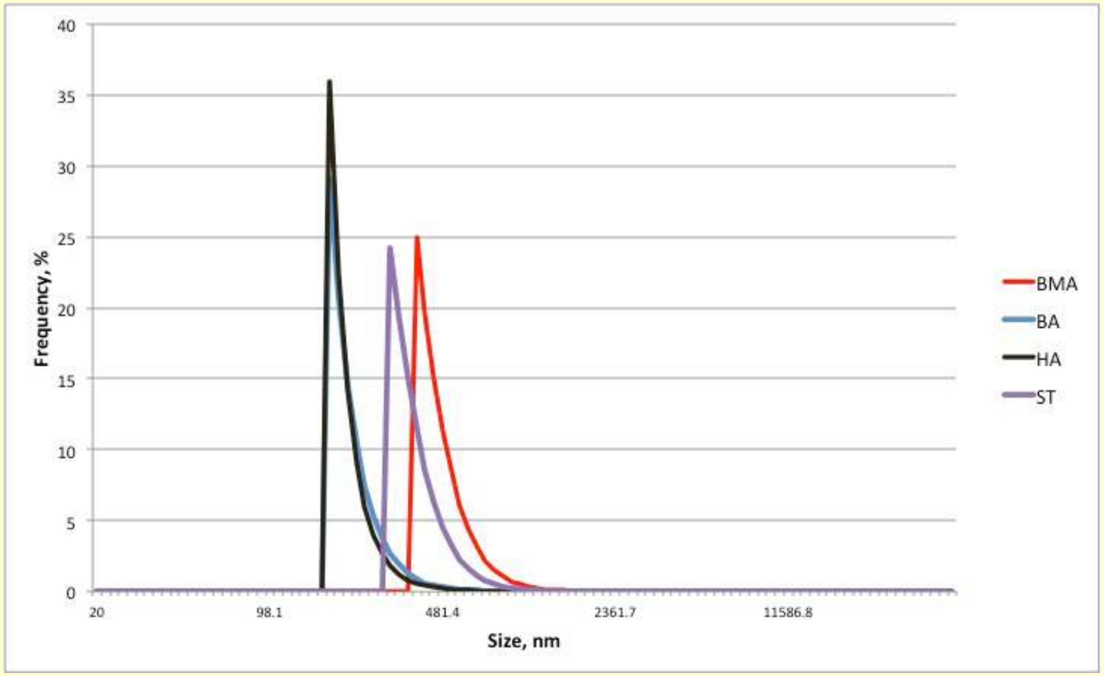
Composite particles characterization (FTIR)





Batch	**Fe-O (cm^{-1})**	**C-O (cm^{-1})**	**C-H (cm^{-1})**	**C=O or N-H (cm^{-1})**	**C-H (cm^{-1})**	**O-H, N-H (cm^{-1})**
Mag-CS*g*-BMA	547	1019 (-COO-)	1402	1543 (N-H)	-	-
Mag-CS*g*-BA	539	1054(-COO-)	1428	1617 (C=O)	2923	3351
Mag-CS*g*-HA	543	1053(-COO-)	1425	1623 (C=O)	2923	3370
Mag-CS*g*-ST	543	-	1436	1624 (C=O)	2928	3371

Composite particles characterization (size: DLS)



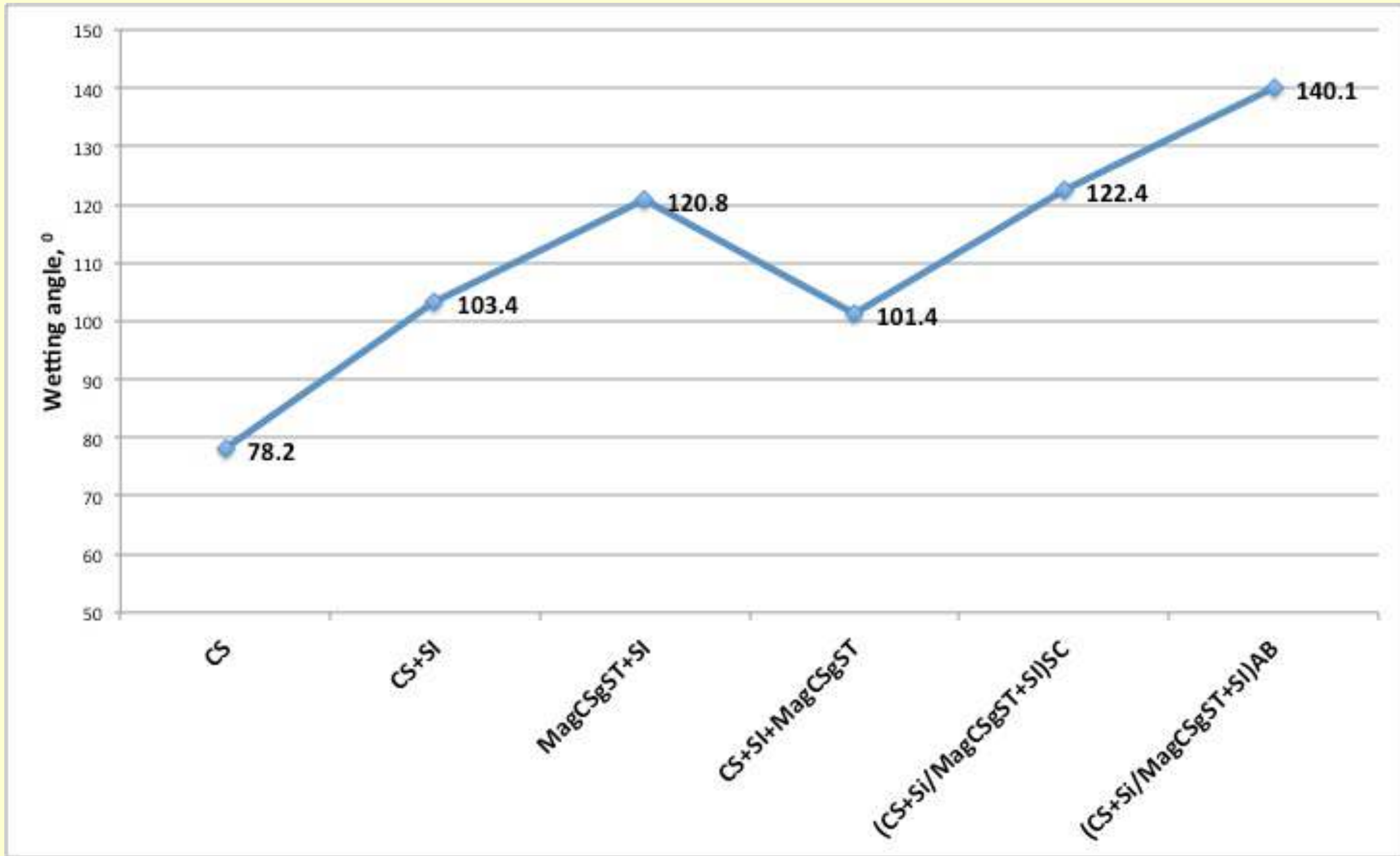
Batch	Size, nm
MagCSgBMA	422
MagCSgBA	198
MagCSgHA	203
MagCSgST	328

Coating optimization

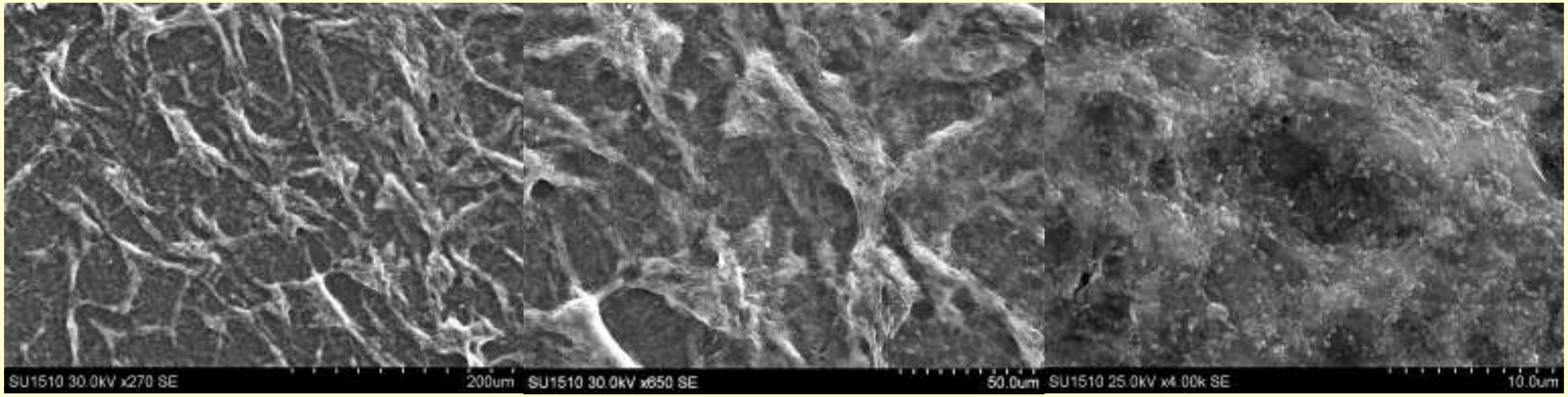
PLATE #	MONOMER	COATING COMPOSITION			DEPOSITION METHOD	COATING MORPHOLOGY	WATER WETTING ANGLE, °	HYSTERESIS, °	OBSERVATIONS
		Composite, %	CS, %	Silane, %				(30s)	
13	ST	1	0	0.03	SC	one layer	120.8	6.9	
14	ST	1	0.2	0.03	SC	one layer	76	3.7	
15	ST	1	0.5	0.03	SC	one layer	79.9	3.7	
16	ST	1	0.5	0.06	SC	one layer	88.3	4.2	
16A	ST	1	0.5	0.06	AB	one layer	101.4	3.1	
34	ST	1	1	0.03	SC	layer by layer	91.7	2.8	
38	ST	1	1	0.17	SC	layer by layer	113.4	1.9	24h, untreated
38a	ST	1	1	0.17	SC	layer by layer	105.9	2.8	78h, untreated
38t	ST	1	1	0.17	SC	layer by layer	122.4	1.8	treated
49	ST	1.7	1	0.17	SC	layer by layer	108.9	3.2	new batch
54	ST	1.7	1	0.17	AB	layer by layer	137.9	2.6	
66	ST	1.7	1	0.17	AB	layer by layer	140.1	1.5	two layers each

ST: styrene
CS: chitosan
SC: spin coater
AB: airbrush

Coating comparison



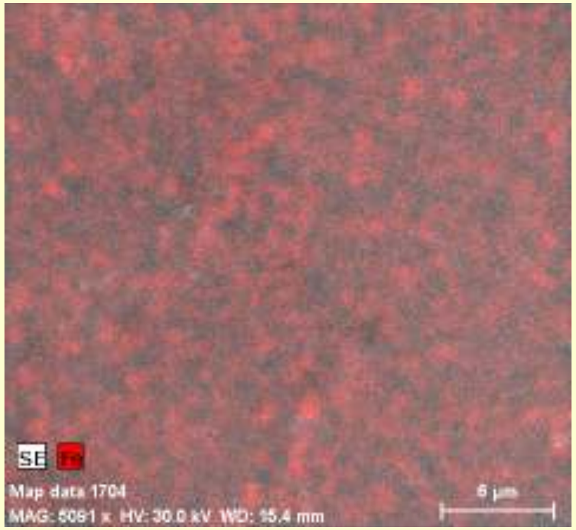
Coating morphology: SEM slides

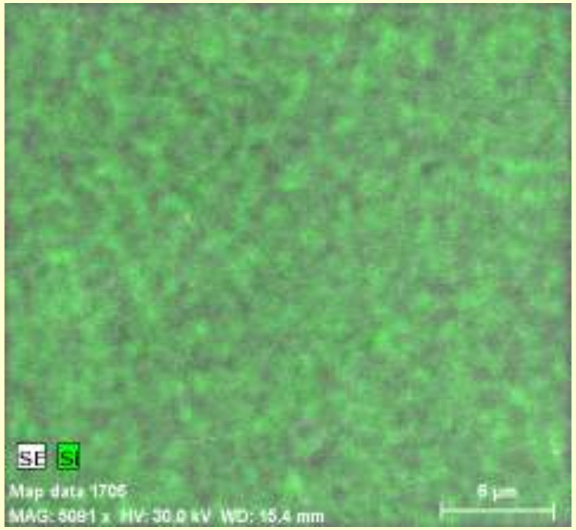


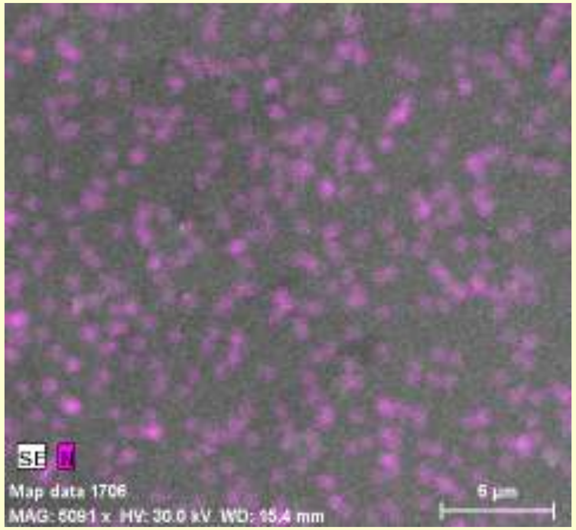
Hierarchical roughness:

1. Composite particles assembled in micro-scale interpenetrating chain-like aggregates
2. Nano-scale protuberances

Coating composition: EDX

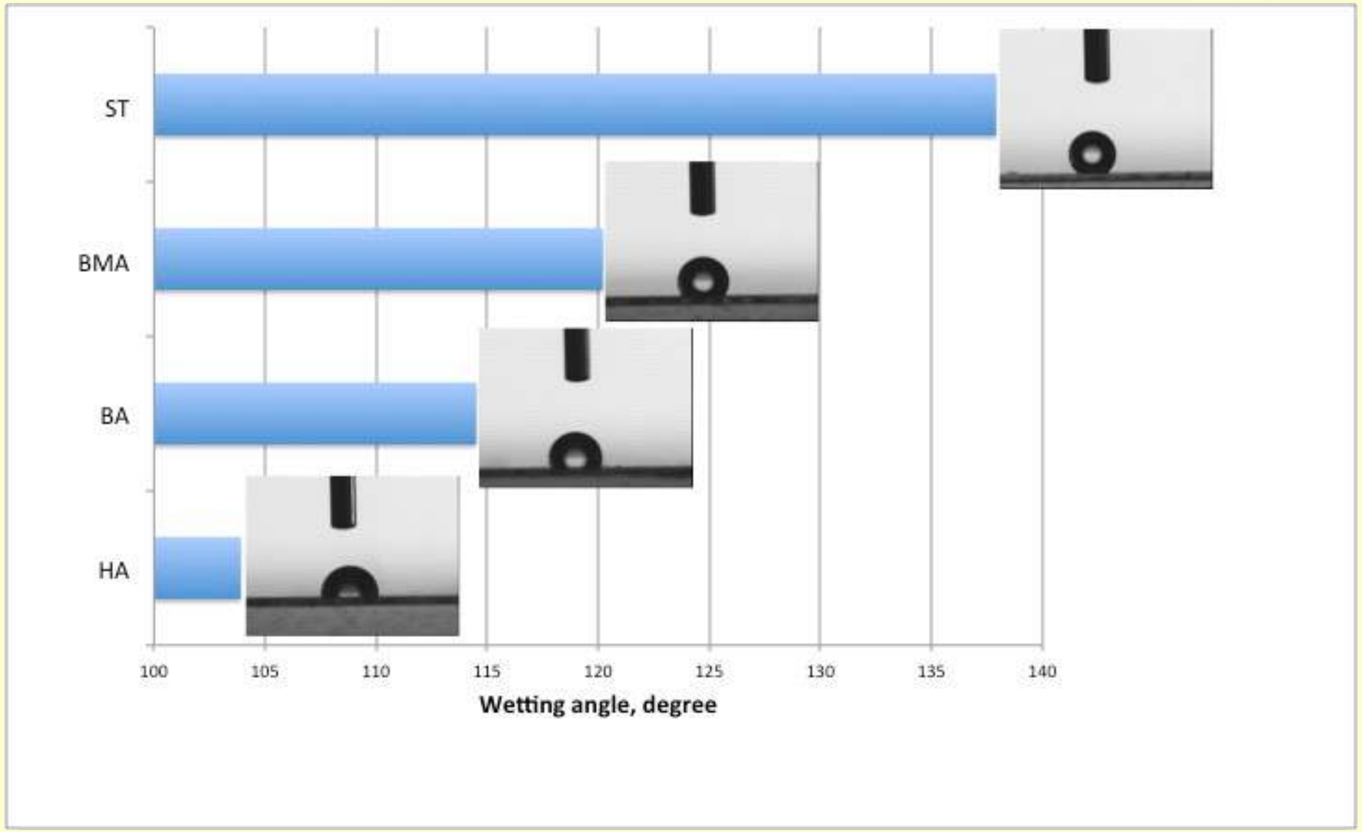






Element	Weight, %	Normalized, %
Oxygen	53.11	61.85
Silicon	21.6	25.15
Nitrogen	5.16	6.01
Carbon	2.79	3.24
Iron	3.21	3.73

Coating properties: wetting angle versus monomer type



Conclusions

- Synthesis method proposed and optimized
- Coating formulation and deposition method optimized
- Composite films with controlled wettability demonstrated
- Future work: improve reproducibility; test ice-repellent properties

Acknowledgements

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THANK YOU FOR YOUR ATTENTION!