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Composite coatings with structured roughness for water repellant applications

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SoFun school "Soft Matter for Functional Materials"

Aim: to develop composite coatings with structured roughness for water-repellant applications that are cost-effective, facile to manufacture in large scale and highly adherent to glass substrates.

Part of the project: ***"New composite materials for superhydrophobic coatings with ice-repellant properties"***

Project code: PN-II-ID-PCE-4-0433/2012

Contracting agency: CNCS-UEFISCDI

Contract number 74/02.09.2013

http://www.ch.tuiasi.ro/cercetare/IDEI/dhritcu/shidrof/index_en.html

Proposed strategy:

-**Hybrid nanoparticle-polymer film preparation** to be deposited on glass surface and allowed to cure by crosslinking:

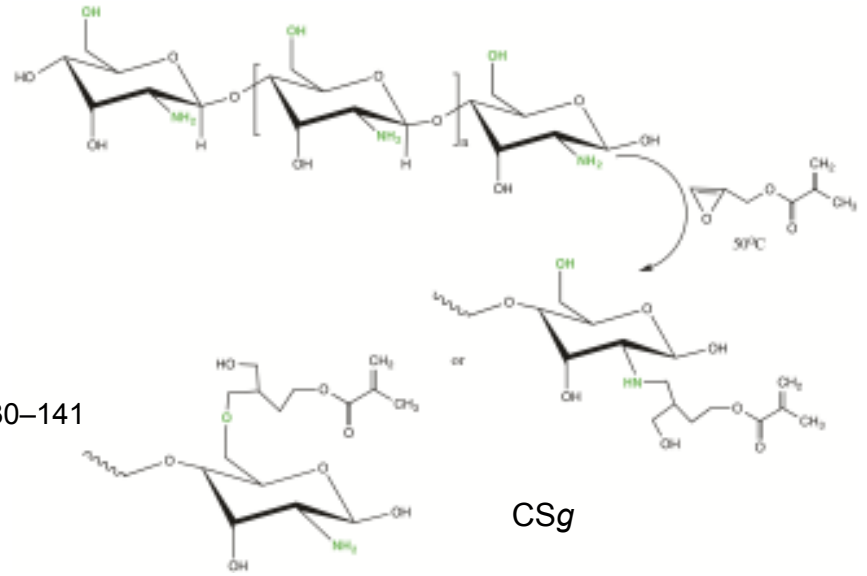
- prepare a polymeric matrix to produce patterned roughness;
- prepare iron oxide nanoparticles capable of magnetic self- assembling during the curing stage; this effect will cause colloidal aggregation and micro-scale surface protuberances.

I. Polymeric matrix

1. Chitosan

2. Chitosan surface modification through

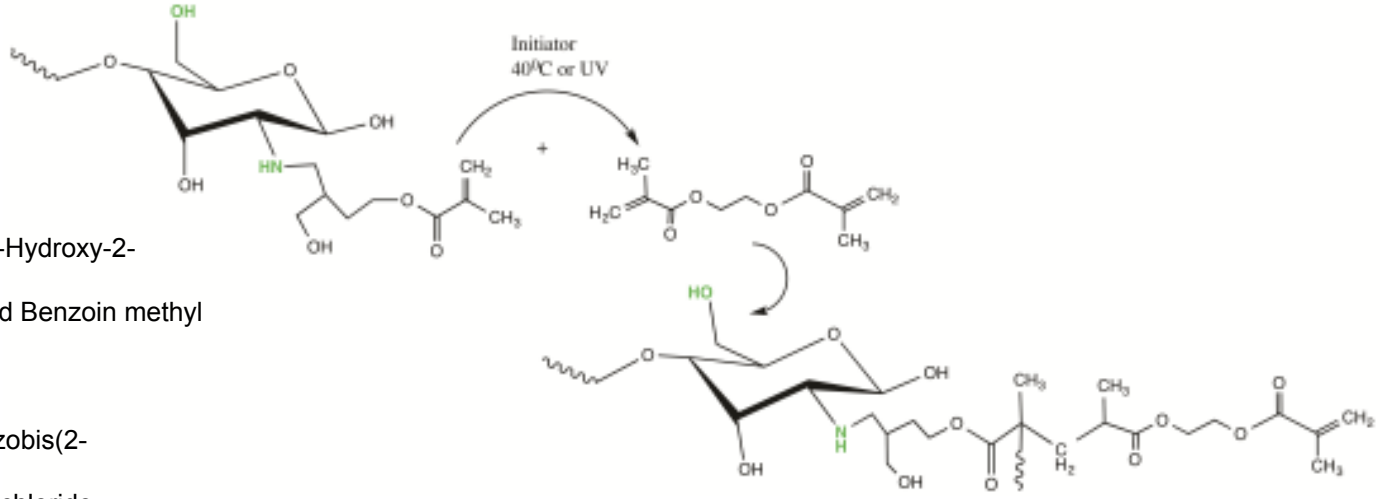
an epoxide ring opening mechanism = vinyl groups:



CS*g*

Reference: G. Dodi et al., Chemical Engineering Journal 203 (2012) 130–141

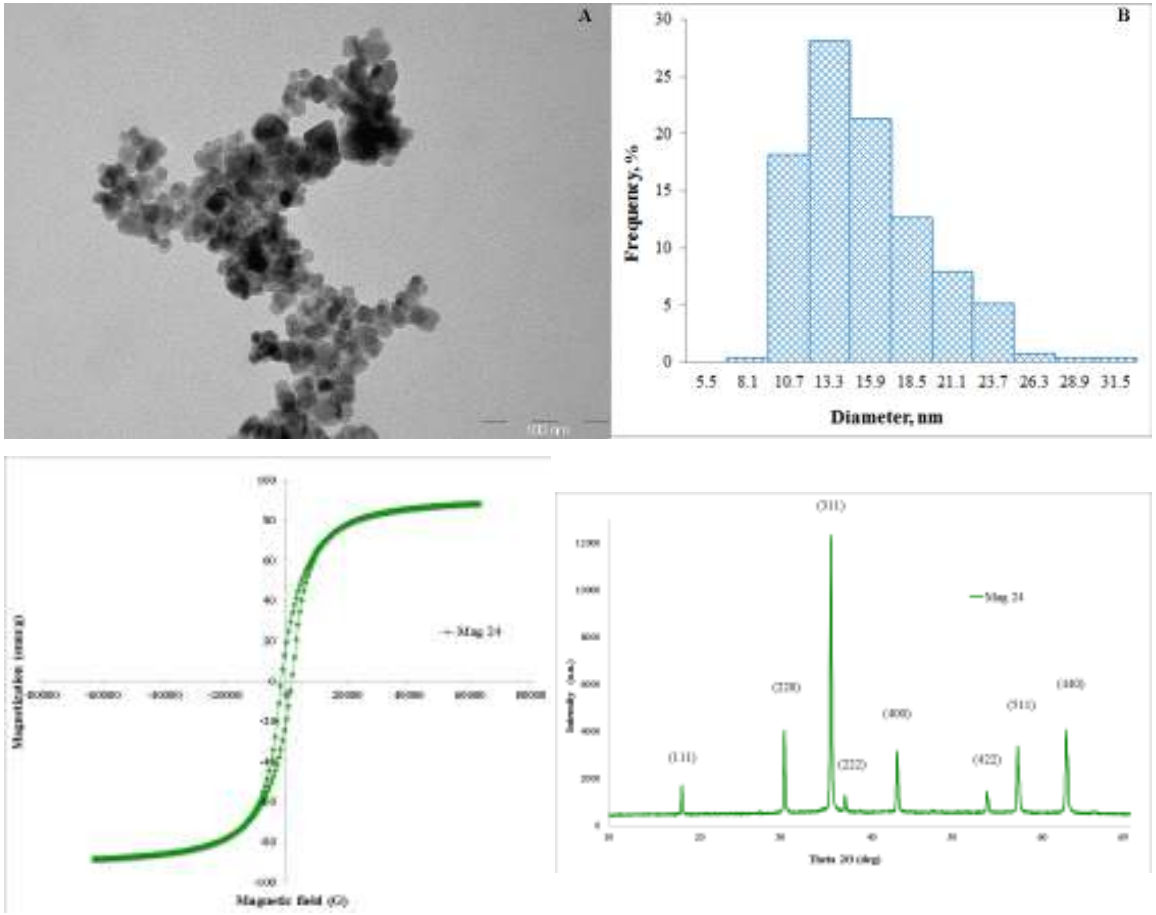
3. Radical polymerization of modified chitosan (CS*g*) with ethylene glycol dimethacrylate (EGDMA) using:



- UV initiation (366 nm): HMP (2-Hydroxy-2-methylpropiophenone 97%) and Benzoin methyl ether 99%;
- Termic initiation (40ºC): 2,2’-Azobis(2-methylpropionamidine) dihydrochloride.

II. Iron oxide nanoparticles: produced by mild oxidation of ferrous ions in alkaline solution

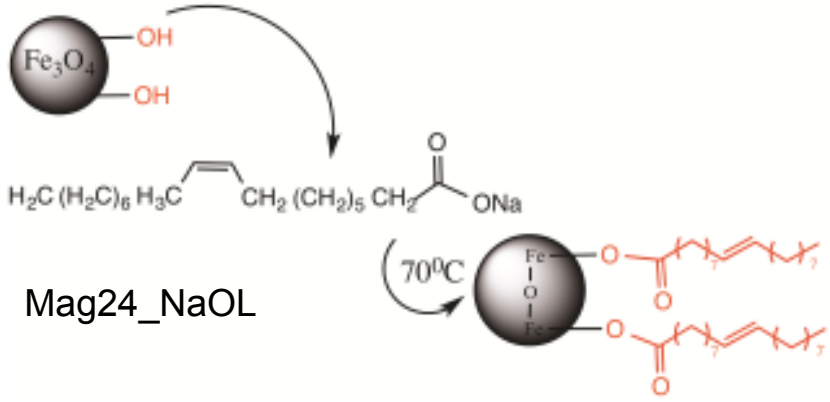
$$12\ Fe(OH)_2 + NO^-_3 = 4\ Fe_3O_4 + NH_3 + 10\ H_2O + OH^-$$



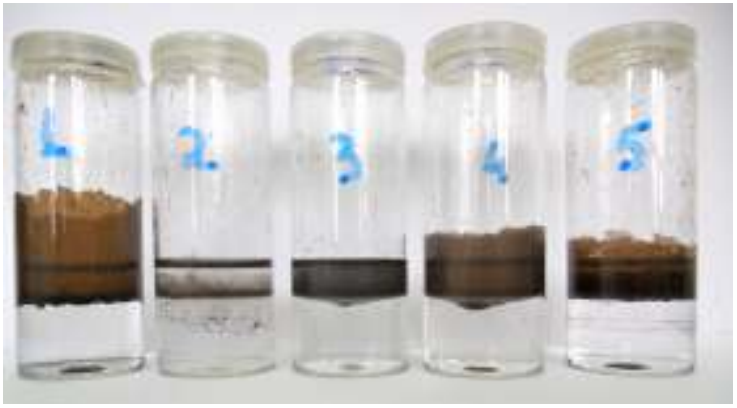
Average size: 14 nm/Saturation magnetization: 88.3 emu/g/Highly crystalline magnetite

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

1. Functionalization with various surfactants (hydrophilic-hydrophobic balance)



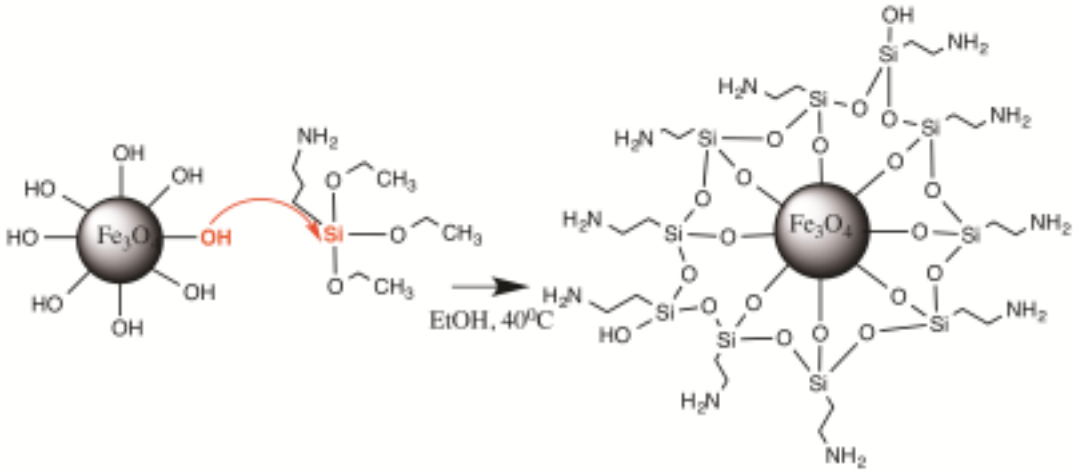
Mag24_NaOL



1: Mag24NaOl
2: Mag24 Span 80
3: Mag24 S/T 75/25
4: Mag24 S/T 50/50
5: Mag24 Tween 80

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

2. Functionalization- Amination



1: Mag24-NH_2_1
2: Mag24-NH_2_2
3: Mag24-NH_2_3

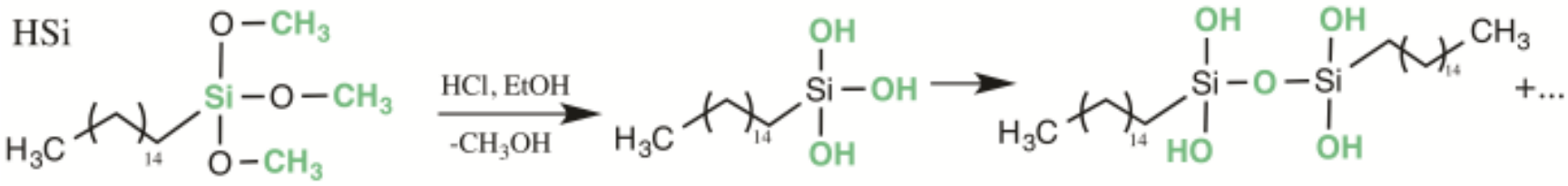
Two-phase partition- degree of functionalization uniformity

III. Hexadecyltrimethoxy silane (HSi):

- promotes interfacial adhesion

- improves the properties of composites.

1. Prehydrolyzed/precondensed sol–gel solution preparation:

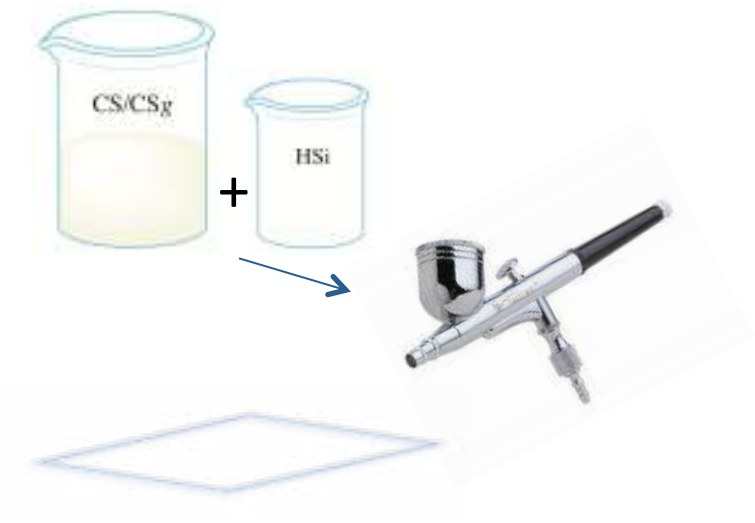


2. Complexation with polymeric matrix and iron oxide nanoparticles onto the glass slide: hybrid films.

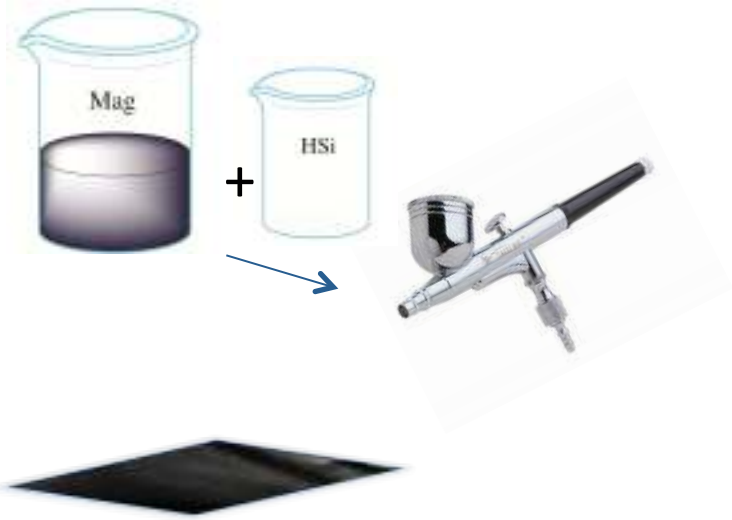
Reference: Spirk et al., Carbohydrate Polymers 93 (2013) 285–290

Film preparation: layer by layer

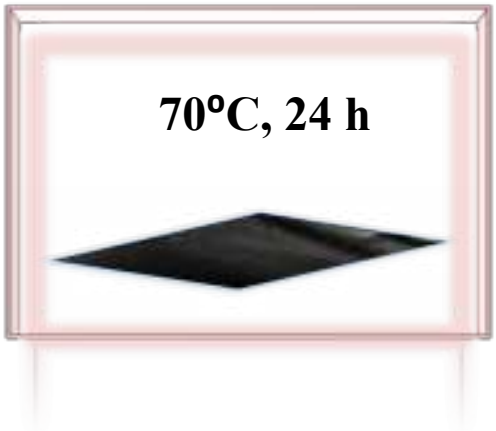
1. Hybrid matrix deposition



2. Nanoparticles deposition



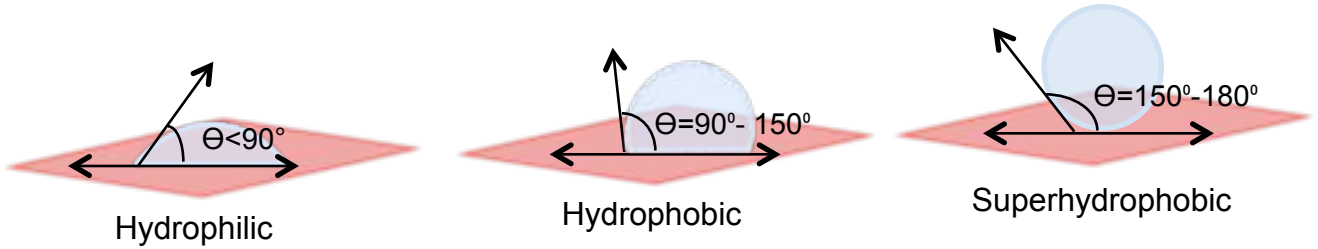
3. Hybrid film fixation

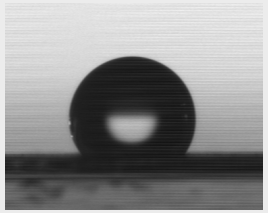
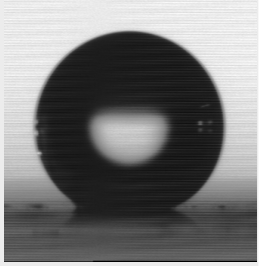
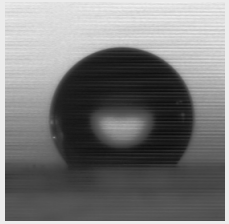
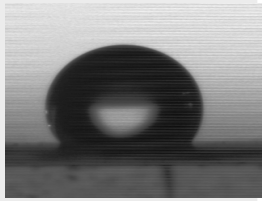


Film composition

Glass slide	Matrix, 1 mL	HSi, 250 µL	Magnetite, 1 mL
S1	CS		Mag 24
S2	CS		Mag 24_NaOl
S3	Azo2		Mag24_NH_2_2
S4	BMM2		Mag24_NH_2_2

Contact Angle and Non-Wetting Properties



Glass slide	S1	S2	S3	S4
Contact angle	134.7° 	159° 	145° 	134.8° 
Hysteresis	3.7°	0.4°	1.1°	2°

S1, S3 and S4 – 3 μL droplets;
S2 – 20 μL droplet.

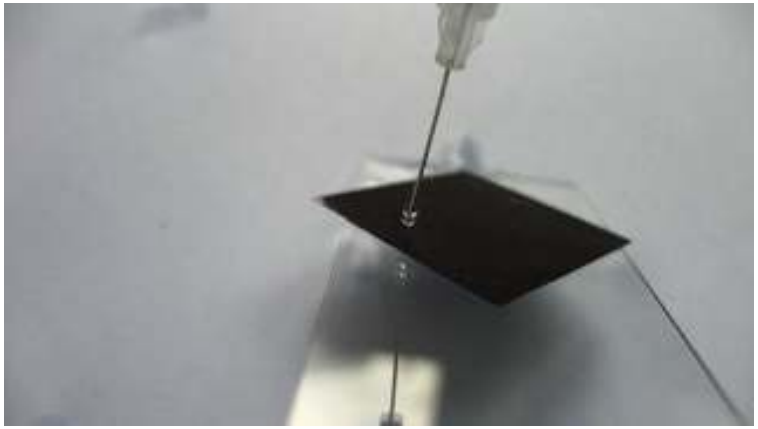
Liquid droplets wetting/non-wetting capability

S1

S2

S3

S4



Conclusions and perspectives:

- Three types of chitosan matrix derivatives were synthesized and successfully evaluated for hybrid film preparation;
- Three types of iron oxide derivatives were synthesized, characterized and successfully used for hybrid film preparation;
- Four types of hybrid materials were successfully deposited onto glass substrates;
- The water contact angle measurements evidenced hydrophobic and superhydrophobic surfaces using chitosan-silane-magnetite derivatives hybrid films.
- Future work: control of layer thickness, surface morphology.

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