FABRICATION OF LARGE AREA MICROPATTERNED POLYOLEFINE BLEND COATINGS HAVING FOUL RELEASE PROPERTIES

H.Y. Erbil, N.A. Gengec, I.O. Ucar,
M. Dandan and C.E.O. Cansoy

Gebze Institute of Technology (GYTE),
Chemical Engineering Department, Turkey

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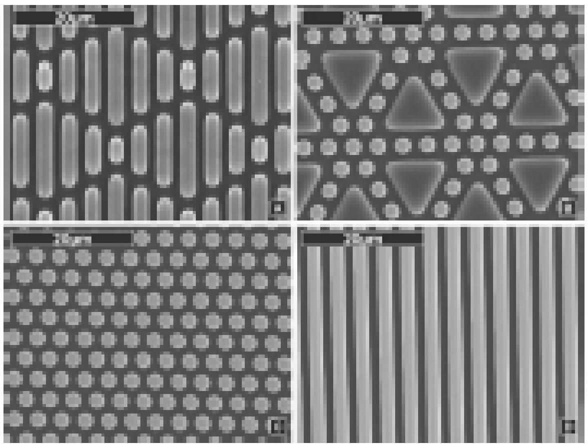
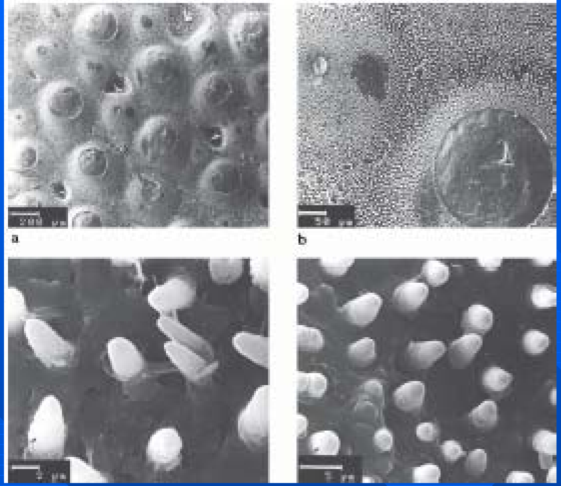
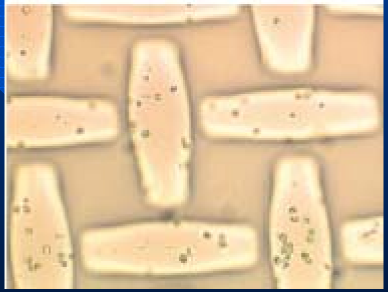
Role of Surface Roughness in Marine Foul Release





Andersson, M. Et al., Biofouling, 14, 167, 1999.
Petronis, S. et al. J. Bimater. Sci.-Polym. Ed., 11, 1051, 2000.
Baum, C. et al., Marine Biology, 140, 653, 2002.
Thomason, J. C. et al., Biofouling, 18, 293, 2002.
Kerr, A. And Cowling M. J., Phil. Mag., 83, 2779, 2003.
Scardino, A. et al., Biofouling, 19, 221, 2003.
Bers, A.V. And Wahl, M., Biofouling 20, 43, 2004.
Granhag L. M. et al. Biofouling, 20, 117, 2004.
Schumacher, J. F. et. al, Biofouling, 23, 1, 2007.



Some Polymer Surface Modification Methods

Coating of Pre-patterned Surfaces
Plasma Treatment,
Surface Grafting,
Film deposition under vacuum, etc.

Most of these methods are comparatively expensive and difficult to apply on a large scale.

Polymer blending: A potential cheap surface modification method

A polymeric component is blended with another cheap polymer by using solvent cast method to modify surface roughness. Possible processes are:

Homopolymer-homopolymer blending
Homopolymer-Statistical Copolymer blending
Homopolymer-Block Copolymer blending
Statistical Copolymer- Statistical Copolymer blending

Polymer Blending Process

When a low surface tension polymer is added to another polymer, it is expected that the first one will migrate to the air/coating interface during the film formation by a phase separation process and will change the surface roughness and free energy characteristics of the latter cheap polymer.

Polymer mixtures demix during the rapid solvent evaporation process due to intrinsic immiscibility of polymer macromolecules within the blend.

Parameters of Blending

- = Surface free energy of involved polymers
- = Miscibility of involved polymers
- = Viscosity of involved polymers at the process temperature
- = Solubility of each polymer within the chosen common solvent
- = Molecular weight (or chain length) of the polymers
- = Solvent evaporation rate and its effect on polymer film forming properties
- = Film thickness (the domination of bulk properties or substrate effects)

Non-Equilibrium Conditions Dominates

When an industrial volatile solvent is used to cast the blend films, the surface is not in thermodynamical equilibrium since the solvent evaporates relatively quickly and the polymer chains are mostly immobilized within the film before attainment of a thermodynamically favorable state.

In conclusion, the surface tension forces and polymer-solvent interactions play a more important role in the surface separation of polymers.

Walheim, S. Et al., Macromolecules 30, 4995, 1997.
Khayet M. et al., Surface Science, 601, 885, 2007

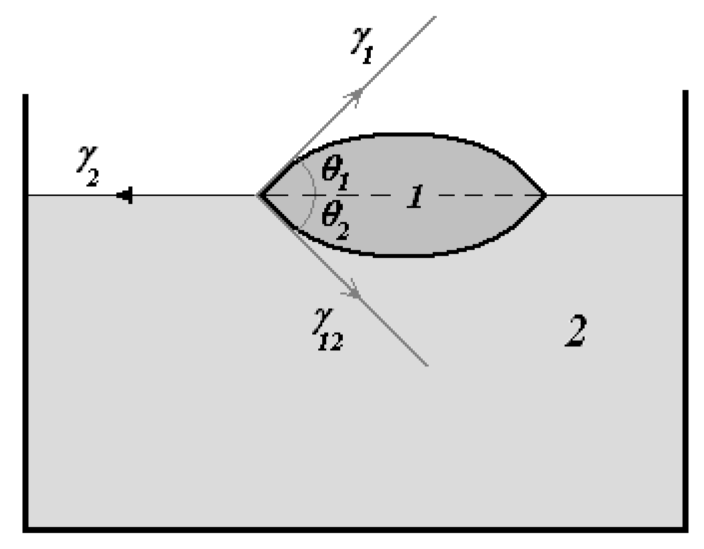
Definition of Spreading Coefficient (S) for Liquids

The conditions of wettability for immiscible liquids is dictated by the spreading coefficient, S:

$$\gamma_2 = \gamma_1 \cos\theta_1 + \gamma_{12} \cos\theta_2$$

$$S_{1/2} = \gamma_2 - (\gamma_1 + \gamma_{12})$$

$$S_{O/W} = \gamma_W - (\gamma_O + \gamma_{OW})$$



Oil spreads spontaneously on the water when $S \geq 0$, and it forms a lens when $S < 0$. Spreading occurs when a liquid of low surface tension is placed on one of high surface tension.

Harkins, W. D., The Physical Chemistry of Surface Films, Reinhold, 1952.
Erbil, H. Y., Surface Chemistry of Solid and Liquid Interfaces, Blackwell, 2006.

Use of Spreading Coefficient (S) Concept for Polymer Blending

$$S_{1/2} = \gamma_2 - (\gamma_1 + \gamma_{12})$$

$$S_{P_1/P_2} = \gamma_{P_2} - (\gamma_{P_1} + \gamma_{P_1P_2})$$

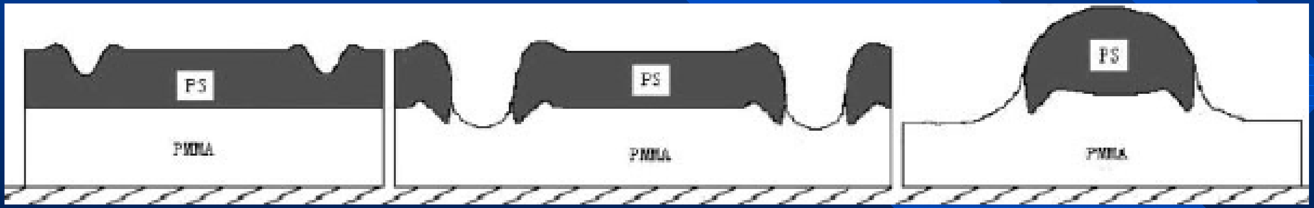
Polymer-1 spreads spontaneously on Polymer-2 when $S \geq 0$, and it forms a lens when $S < 0$. Spreading occurs when a polymer of low surface tension (Polymer-1) is placed on one of high surface tension (Polymer-2), with large surface tension differences.

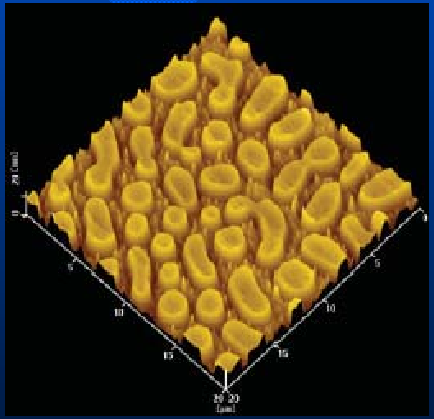
Paul D. R. and Newman, S., Polymer Blends, Academic, 1978.

A numerical example for S application:

$$S_{P_1/P_2} = \gamma_{P_2} - \left(\gamma_{P_1} + \gamma_{P_1P_2}\right)$$

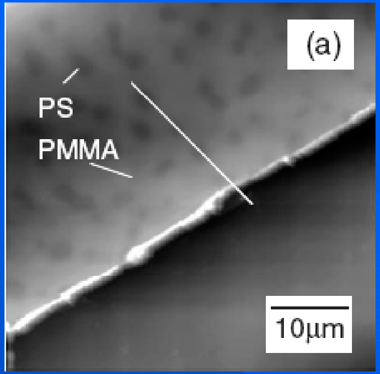
For PS-PMMA blends where PS solution was spin coated on a PMMA layer where “Polymer-2” is PMMA with γ_2= 41.2 mJ/m^2, “Polymer-1” is PS with γ_1 = 40.2 and their interfacial tension is γ_{12} =3.3. Thus, S= - 2.3 mJ/m^2 was calculated and PS protrusions were seen to form on the PMMA layer.



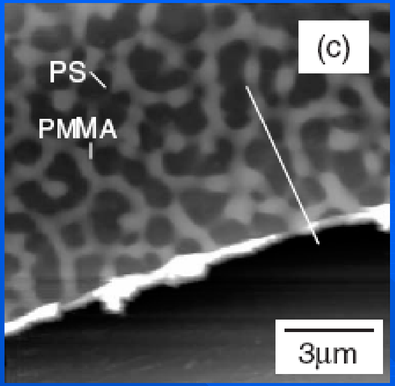


Li. Y. Et al., J. Polymer Sci., Part B, Polym. Phys., 44, 9, 2006.

Solvent Type Effect

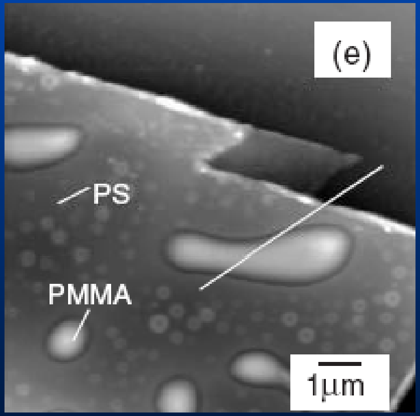


Dichlorometane

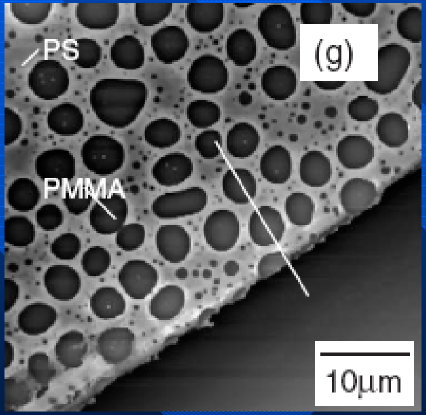


THF

PS/PMMA (50:50) 2 wt. % spin coated on Si-wafer from different solvents.



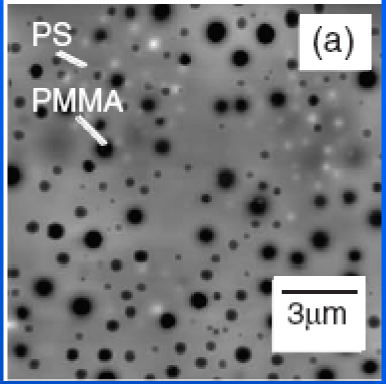
Toluene



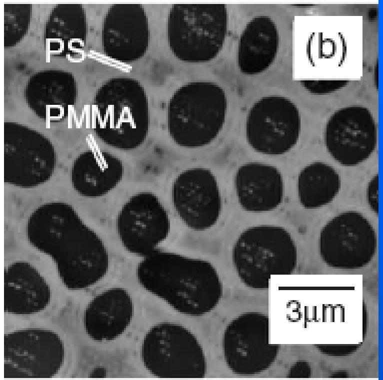
Ethylbenzene

Jackson, S. T. and Short, R. D., J. Mater. Chem., 2, 259, 1992.

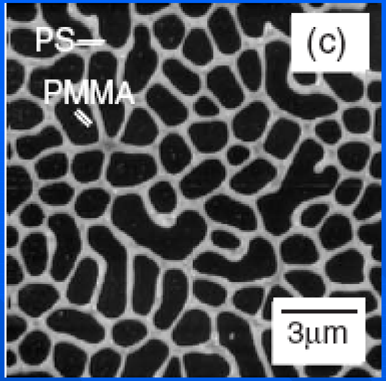
Polymer Concentration Effect



4 wt. %

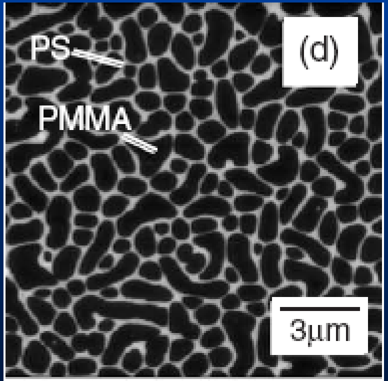


2 wt. %

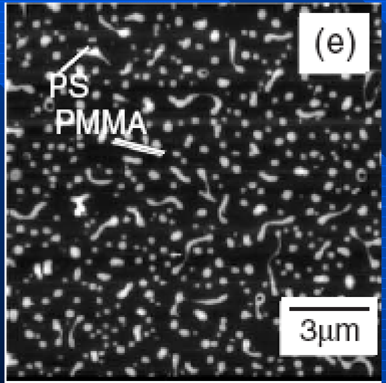


1 wt. %

PS/PMMA (50:50) spin coated on Si-wafer from etyhylbenzene solution at different polymer concentrations.



0.5 wt. %



0.2 wt. %

Jackson, S. T. and Short, R. D., J. Mater. Chem., 2, 259, 1992.

Recent Research in GYTE on Polymer Blends

= Surface roughness control by applying phase separation method to medium surface energy polymers for foul-release:

Blends of hydrophobic polyolefin copolymer coatings were prepared.

= Surface energy minimization by using low surface energy copolymers for foul-release:

Fluorocarbon-acrylate copolymer coatings which can adhere to the polyepoxide primer layer were prepared.

Why polyolefines were selected?

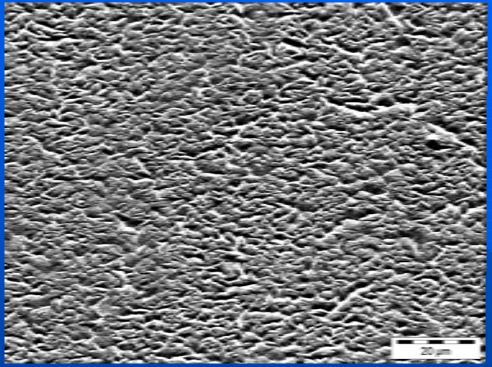
- These crystalline and hydrophobic polymers are cheap and commercially available
- The surface topology and crystallinity percentage can be controlled by selecting suitable solvent + poor solvent mixture and also by controlling the temperature in the phase-separation process
- The surface topography can be further modified by mixing with other suitable polymers.

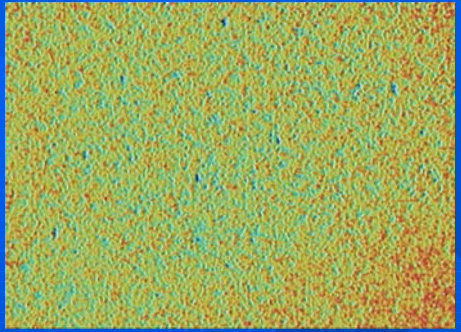
[Polypropylene (PP) in xylene solvent]

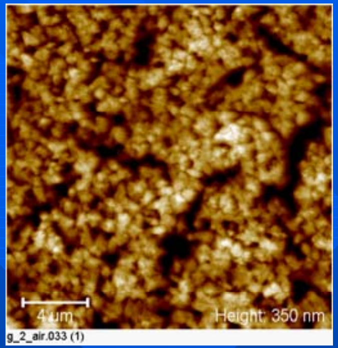
SEM Images

Confocal Images

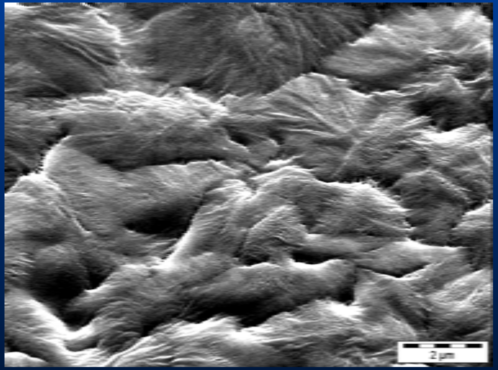
AFM Images

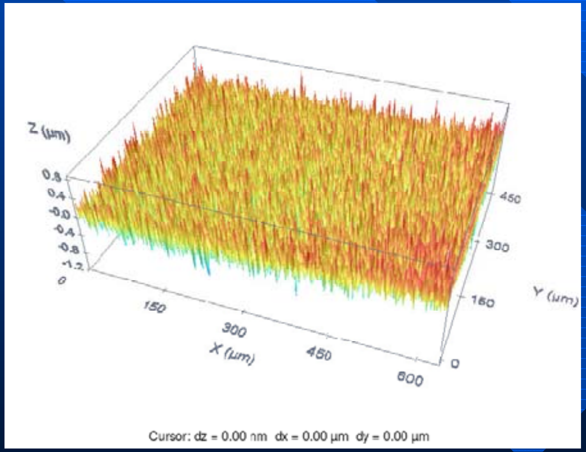






IN AIR

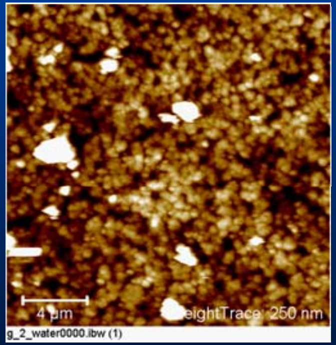




IN SEA

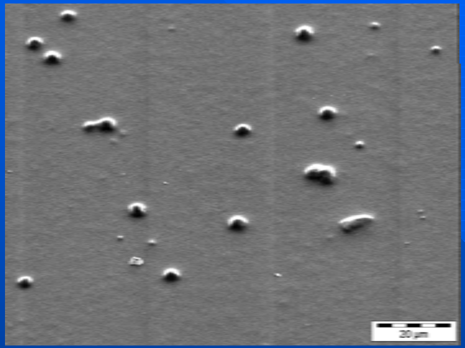
WATER

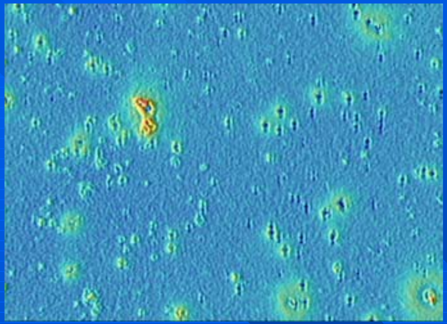
(high coarsening effect)



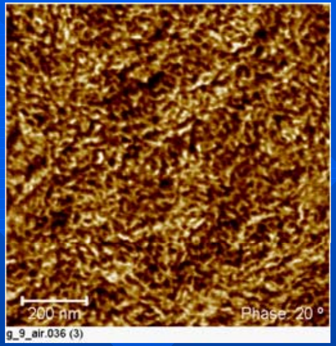
[Ethylene Vinyl Acetate Copolymer (EVA-12)]

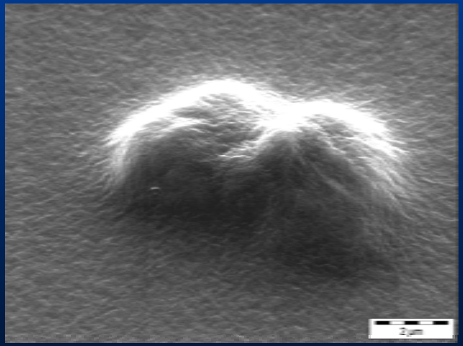
SEM Images | **Confocal Images** | **AFM Images**

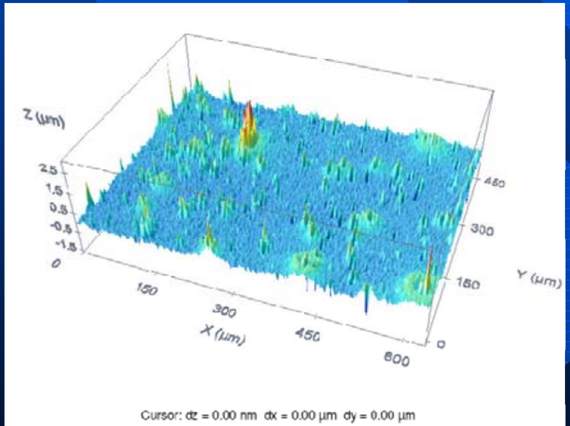




IN AIR

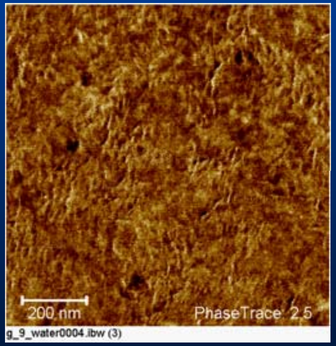






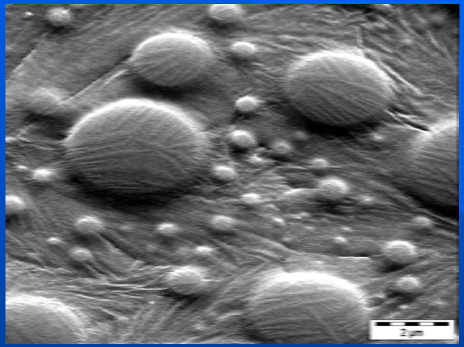
IN SEA WATER

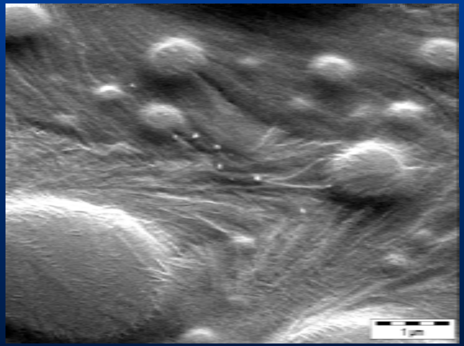
(strong moisture expansion)



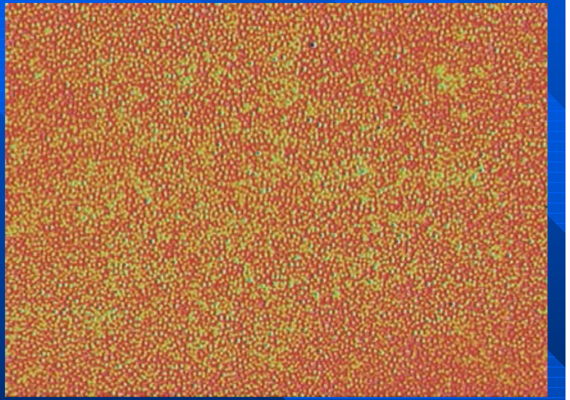
Blend of Polymers [COC (50 %) + PP (50 %)]

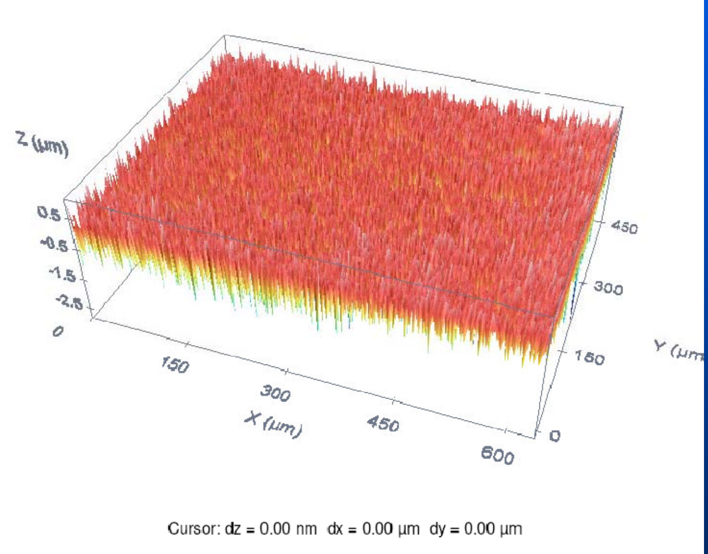
SEM Images





Confocal Microscopy Images





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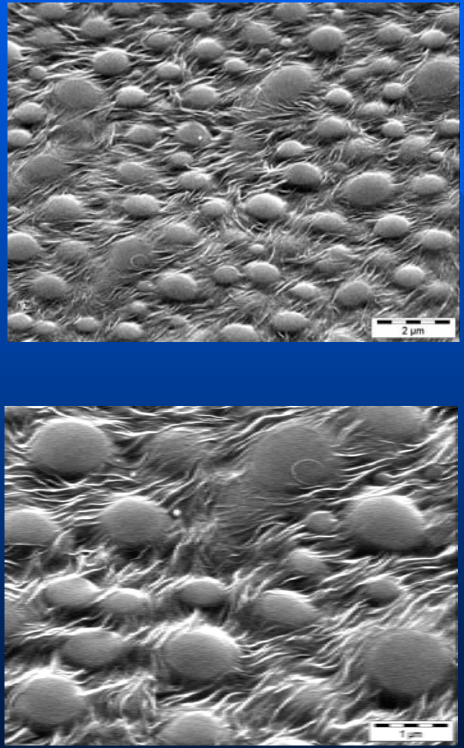
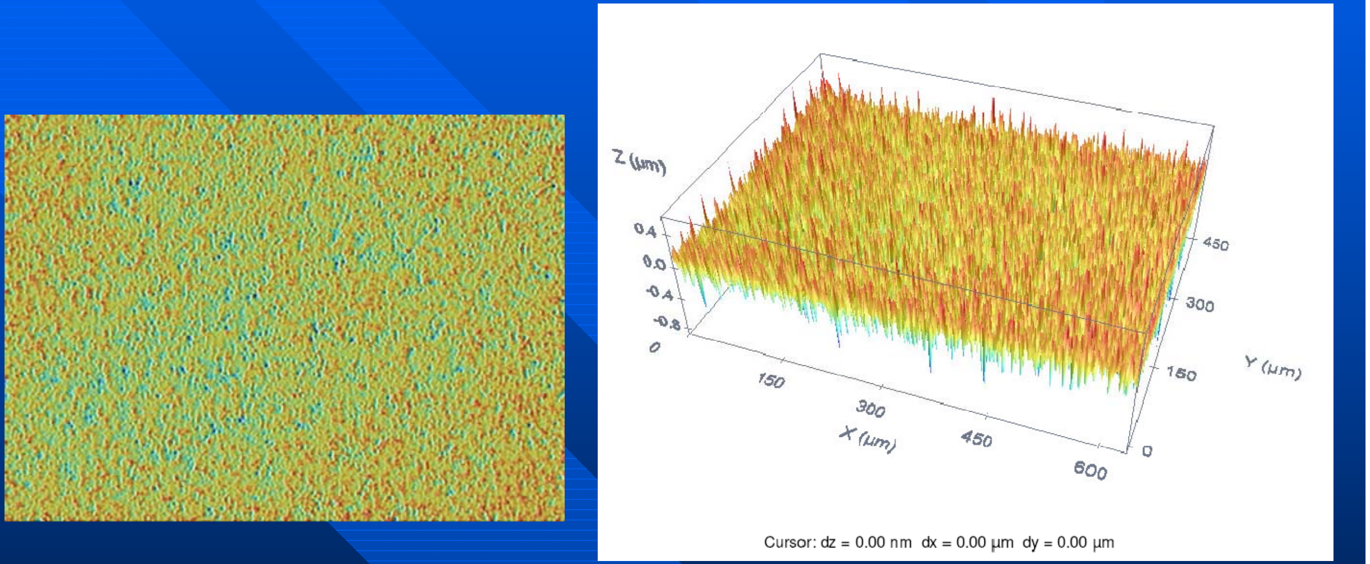
[COC (50 %) + HDPE (50 %)] Blend

SEM Images



Confocal Microscopy Images



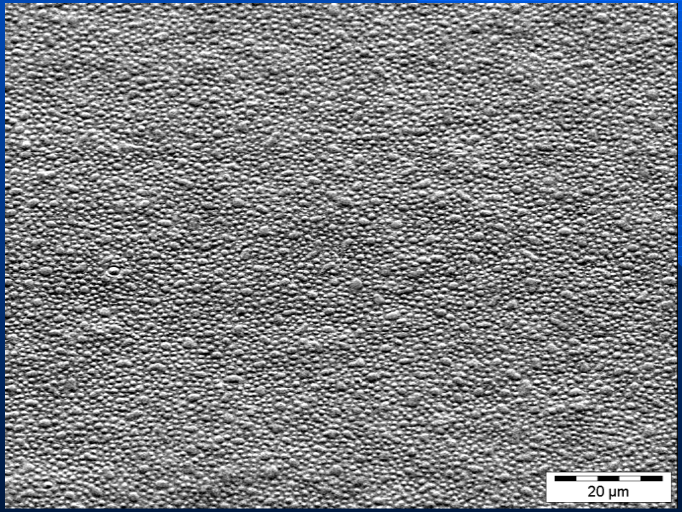
Large Area Rough Coating

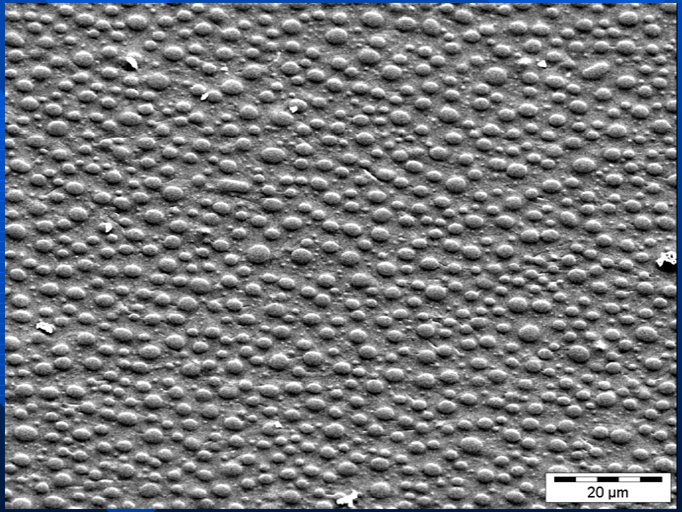
Polyolefin Blends ⟷ **Roughness Control**

(Protrusion Size Decrease)

←

[COC (50 %) +HDPE (50 %)] **[COC (50 %) +PP (50 %)]**





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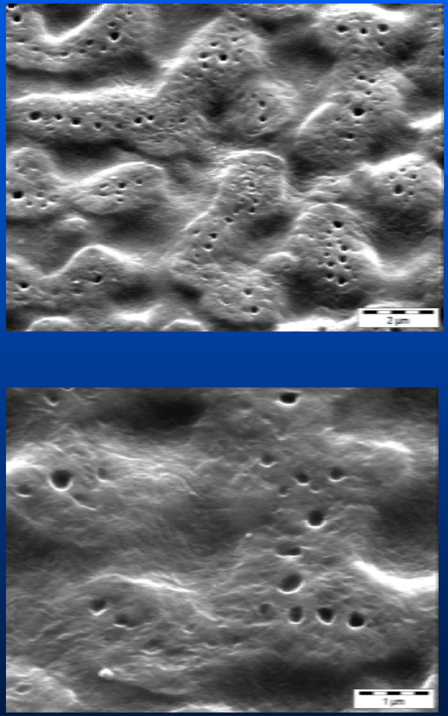
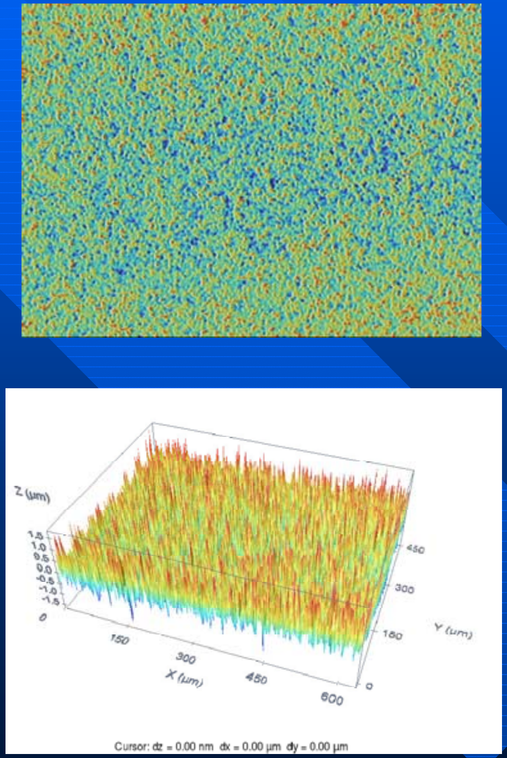
Polarity Effects: Blend of [PP (50 %) + EVA-12 (50 %)]

SEM Images

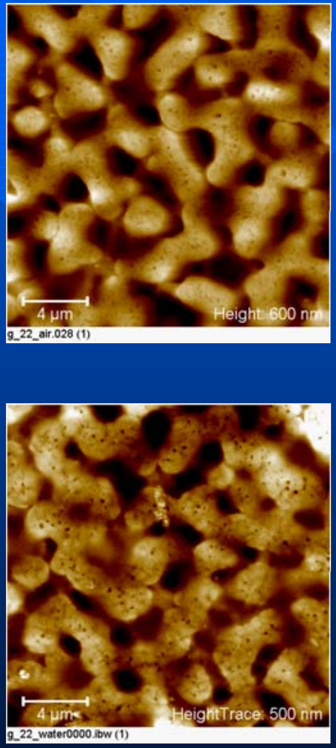


Confocal Images



AFM Images

IN AIR



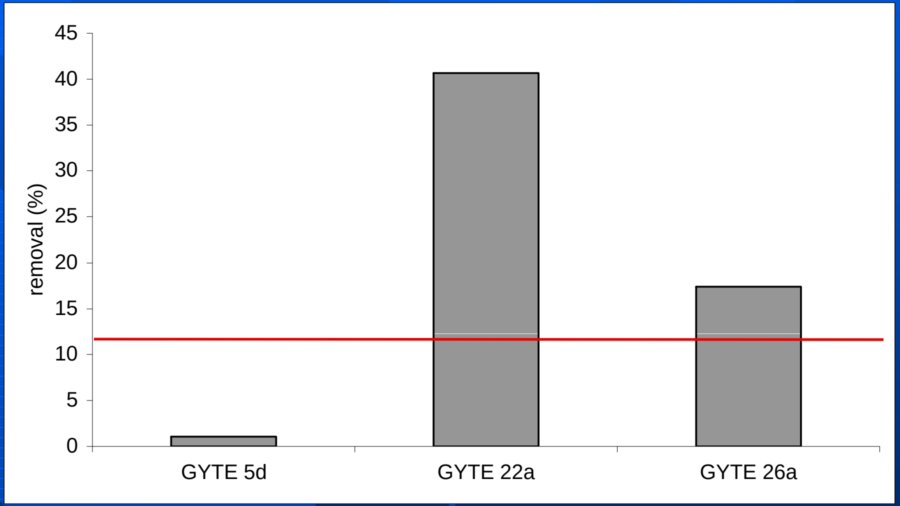
IN SEA

WATER

(very small
coarsening)

Foul Release results of Ulva Linza for a thick polyolefin blend coating (University of Birmingham)

Chemistry	*Standardised to T2 (%)*
T2 Silastic	100
GYTE 22a	347.21



CONCLUSIONS:

= Polymer blends can be used to produce large area micropatterned surfaces and can be applied as foul release coatings.

= Surface and interfacial tension forces of polymers play a dominant role rather than entropic forces to obtain phase-separated surfaces.

= Solvent selection and application temperature is important to control the surface roughness.

= Biological evaluation of polyolefin coatings with controlled roughness seems promising for freshwater applications. (Poor resistance to barnacles).