Convegno Tematico AIAr 2019
Museo Archeologico Nazionale Reggio Calabria, 27-29 Marzo 2019

PEO-based nanostructured polymer systems as a cleaning agent of artworks

Maria Teresa Caccamo[a], Domenico Lombardo[a], Salvatore Magazù[b]

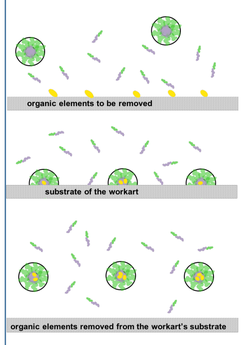
[a]IPCF - Istituto per i Processi Chimico-Fisici CNR di Messina, Viale F. S. D'Alcontres 37, 98158 Messina, Italy

[b]Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, Università di Messina, Viale Ferdinando Stagno D'Alcontres n°31, S. Agata, 98166, Messina, Italy

mariateresa.caccamo@ipcf.cnr.it

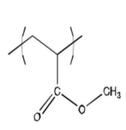
The search for innovative, smart and performing cleaning agents in the field of cultural heritage is one of the main issues of modern conservation science. The development of novel smart nano-structured cleaning systems requires the comprehension of their structural behaviour and interactions with other materials down to the nanoscale in a fluid environment. Complex fluids based on amphiphilic formulations such as micelles, microemulsions and (hydro-gels) represent emerging materials, in the field of conservation of artworks, as safe and effective nano-structured systems for the removal of hydrophobic polymeric coatings. In this respect the comprehension of the cleaning mechanism represents a key information for the design and engineering of tailored fluids for this purpose. Despite the number of recent studies in this field, the mechanism and the interaction processes between nanostructured fluids and hydrophobic polymer films is still poorly understood. We report on some recent results from a study about the mechanism of the cleaning process (organic components removal) using nano-structured materials consisting of PEO-based micellar polymer systems of block copolymer polydimethylsiloxane-b-polyethyleneoxide (PDMS-PEO). The main features of the obtained results may help to identify the main relevant parameters that influence the increase of the rate and efficiency of the cleaning process. A full understanding of these complex processes will open new possibilities for a novel approach to conservation of cultural heritage.

Some formulations based on amphiphiles employed for the cleaning of workart



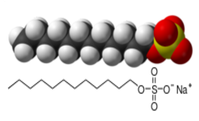
Paraloid B72 is one of the most important acrylic copolymers used in the conservation of cultural heritage and as a consolidating agent for wood. It is soluble in esters (ethyl and amyl acetate), ketones, aromatic hydrocarbons (toluene), chlorinated hydrocarbons (trichlorethylene, etc.). It is insoluble in aliphatic hydrocarbons (white spirit) and in alcohols

methyl acrylate (30%) ethyl methacrylate (70%)

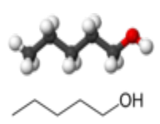


Classic formulation		Conegliano formulation		Mayapan formulation	
component	composition	component	composition	component	composition
water	86.2 (wt%)	water	69	water	73.3
SDS	3.9	SDS	5.1	SDS	3.7
1-PeOH (1-pentanol)	6.5	1-PeOH (1-pentanol)	3.9	1-PeOH (1-pentanol)	7
p-xylene	1.8	Propylene Carbonate (PC)	22	Propylene Carbonate PC	8
nitro diluent	1.6			ethyl acetate	8

Sodium Dodecyl Sulfate (SDS - an anionic surfactant)



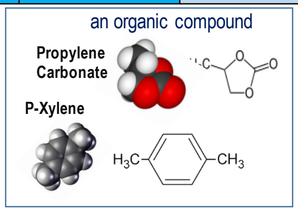
1-Pentanol (alcohol with 5 C)



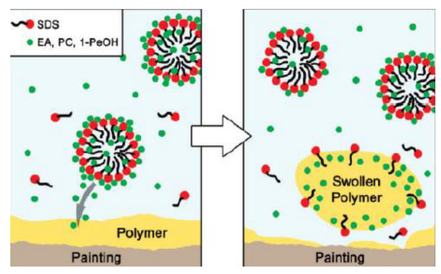
an organic compound

Propylene Carbonate

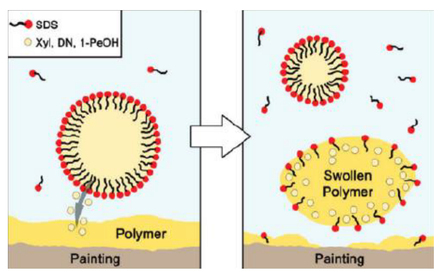
P-Xylene



- p-xylene
- nitro diluent (ND)
- ethyl acetate



Classic Detergency Mechanism
Solvents, partially soluble in water, like ethyl acetate (EA) and Propylene Carnate (PC) are divided between the micellar phase and the aqueous phase. During the interaction with the substrate to be cleaned, SDS incorporate the polymer (insoluble) detaching it from the substrate and bringing it into solution.

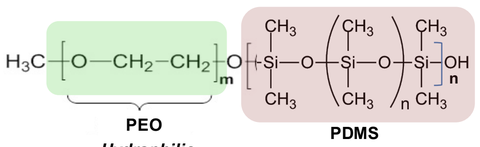


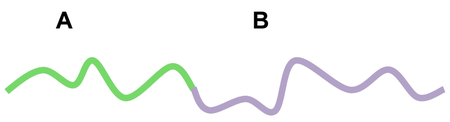
Mayapan Cleansing Mechanism
A microemulsion is formed in which the core of insoluble oil is dispersed in water by the amphiphilic system. Mayapan microemulsions act as solvent carriers and stimulate interaction with the polymer, which through a "micellar" self-assembly mechanism portions of the Polymer to be removed by the creation of Nano-aggregate

P. Baglioni, et al. New Methodologies for the Conservation of Cultural Heritage: Micellar Solutions, Microemulsions, and Hydroxide Nanoparticles, Accounts of Chemical Research, 43(6), 695-704, 2010

Innovative amphiphilic systems based nano-structured systems for the cleaning and conservation of workart

[poly-ethylene oxide] - [Poly-dimethylsiloxane]

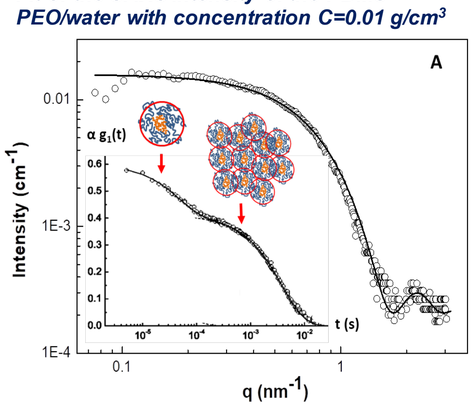




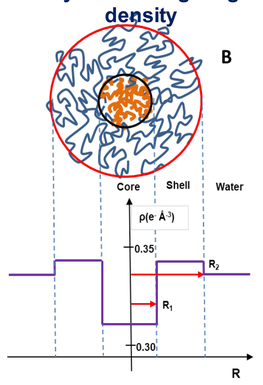
inert, non-toxic, non-flammable

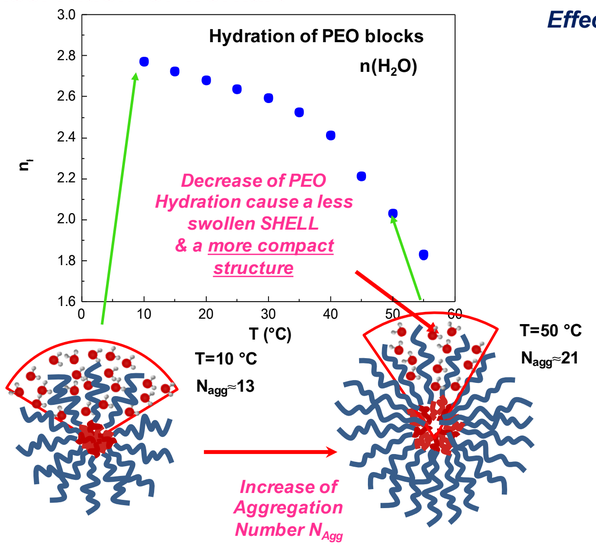
$$I(q)_{CS} = N_M V_S^2 \left\{ (\rho_C - \rho_S)\frac{V_C}{V_S}\frac{3[\sin(qR_1) - qR_1\cos(qR_1)]}{(qR_1)^3} + (\rho_S - \rho_0)\frac{3[\sin(qR_2) - qR_2\cos(qR_2)]}{(qR_2)^3} \right\}^2$$

Fit of the SAXS intensity of the PDMS-PEO/water with concentration C=0.01 g/cm³

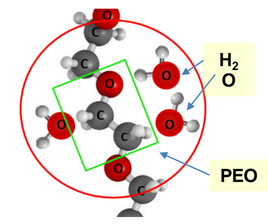


X-rays scattering-length density





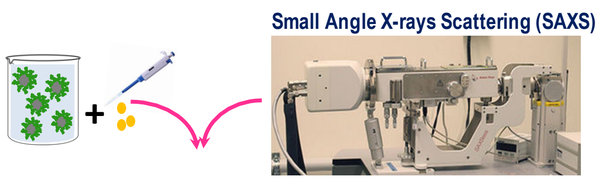
Effect of the Temperature (10≤T≤55 °C)

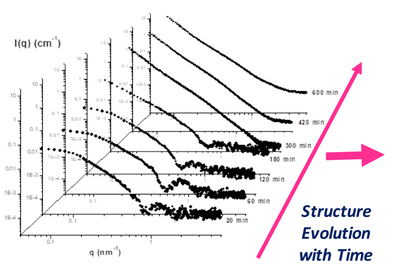


Increase of N_{agg} is connected with the PEO de-Hydration with Temperature !!

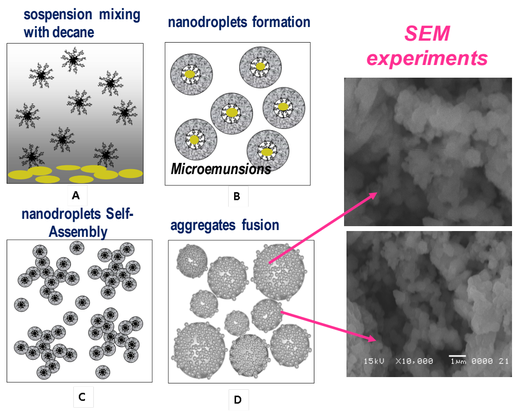
PDMS-PEO/water (C=0.02 g/cm³) - Decane (1%wt)

Small Angle X-rays Scattering (SAXS)



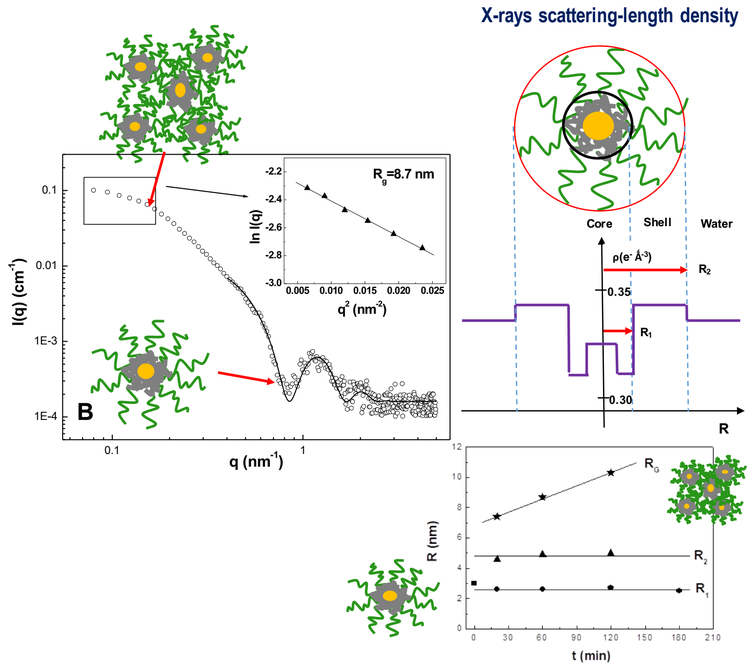


Structure Evolution with Time

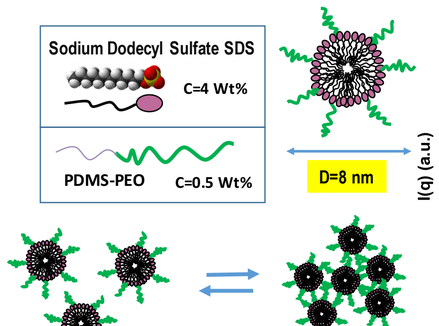


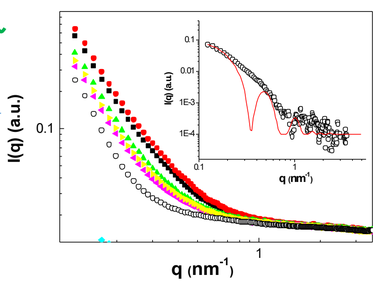
SEM experiments

X-rays scattering-length density



BINARY System



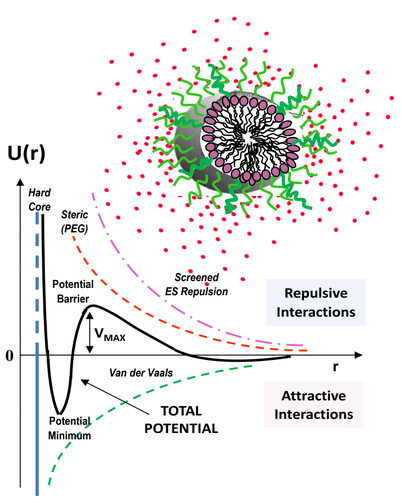


SAXS time evolution of PDMS-PEO/SDS cleaning system

- Polydisperse aggregates
- More colloidal stability of aggregates
- Aggregates fusion after 34 hour

Conclusions

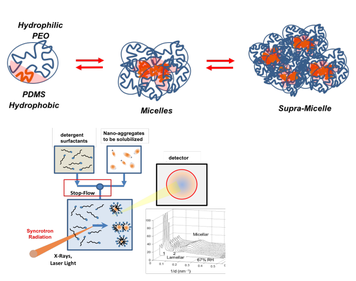
We investigate the self-assembly and detergency process of innovative formulations for the cleaning and the conservation of worksart, based on the use of nanostructured fluids (i. e. block copolymers amphiphilic systems). A full understanding of the complex mechanisms of interaction and the identification of the key factors that govern the involved supramolecular processes can open new possibilities for a scientific approach to the problems of detergence connected to the preservation of cultural heritage. The choice of appropriate theoretical models allows to analyze the basic processes of detergency at the molecular level in order to understand the parameters that most influence the detergent processes.This approach allows to reach a predictive knowledge of the effectiveness of a detergent system before testing it, based on its chemical-physical properties.



Future prospects

Development of theoretical models to identify the key parameter that influences the efficiency or the cleaning process

Time resolved experiments (SAXS + Stopped Flow)



Test on prototypes of paintings