# Complex Fluids & Polymer Engineering (CFPE)

## Overview

A large number of industrially important fluids have intrinsic microstructures that range from several nanometers to microns in length. It is this microstructure that ultimately results in the performance of such materials and their products. The central theme of research in the CFPE group is to engineer microstructures in complex fluids, and understand mechanistically and quantitatively the links between the structure and the properties of such fluids.
(Figure 1)

## Mission & Goals

To add value to customer's business by (i) providing fundamental understanding of structure-property relationships for their materials, (ii) developing materials/products using our understanding of structure-property-performance relations, and (iii) providing information analysis and continuing education services.

## Competencies

The salient competencies of the CFPE & PPC groups are: deep understanding of structure-processing-property-performance linkages, development of in situ experimental tools for structural characterization, modeling and simulations of polymer physics and engineering problems, and providing services such as consulting, information analysis and continuing education to the industry. Additional competencies include providing project leadership and management for contract research projects, developing business for the laboratory and participating in institutional systems planning and processes.

## Infrastructure

The CFPE laboratory is equipped with state-of-the-art rheometers which, along with a wide range of environmental chambers and accessories, allow for the measurement of rheological properties of complex fluids under shear and elongational flows. The group has assembled tools for in situ rheo-optical measurements such as stress-birefringence, rheo-SALS, rheo-SAXS, PTV and flow visualization. CFPE has nurtured a sophisticated light scattering laboratory housing 3D-DLS equipment, diffuse wave spectroscopy and zeta sizer. The group plans to add a confocal microscopy facility in the near future. Additionally, the group is engaged in developing codes for stochastic (Monte Carlo) and CFD (ALE) simulations. The Polymer Processing Centre houses unique processing and testing equipment such as a DSM microcompounder and microinjector, Haake Polylab system, Berstoff ZE-25 twin-screw extruder, Ferromatik injection molding machine, Instron UTM and Ceast Izod impact tester.
(Figure 2)

## Glimpses of current research

### *Silk based biomaterials*

*Bombyx Mori* silk has been used as a textile fiber since antiquity because of its unmatched luster, feel, comfort and mechanical properties. Recently, silk fibroin is being seriously evaluated as a potentially useful biomaterial for valued added applications such as microporous scaffolds for tissue engineering and vehicles for drug delivery because of its

biocompatibility, environmental stability, proteolytic degradability, possibility of attaching growth factors and versatility in forming it into fibers, meshes, films and hydrogels. We have investigated the phase transition of aqueous fibroin solutions into gels upon changing pH and temperature. Gelation kinetics and microstructure of the gels were probed using a combination of rheology, light scattering, confocal scanning light microscopy and circular dichroism. Our results show that gelation happens by a nucleation and growth process in which aggregates of fibroin chains associate to form a self similar microporous hydrogel. At a molecular level the association of fibroin is driven by formation of β-sheets.
(Figure 3)

### *Colloidal assembly in surfactant mesophases*

When particles are dispersed in structured, anisotropic matrices, they develop long-range interactions, mediated by the orientational elasticity of the medium. Thus, microstructured materials with a self-assembled particulate phase can be created, with implications for diverse areas such as foods, catalysis, and functional optical materials. Our work explores the organization of silica nanoparticles in a nonionic surfactant hexagonal mesophase. We have demonstrated that particles that are much smaller than the characteristic repeat distance in the mesophase are templated by the hexagonal structure, while particles of the same size as the mesophase spacing partition into a dispersed phase and aggregated phase. Larger particles phase separate from the mesophase and form particulate strands that organize into a network. We use a combination of scattering (small angle X-ray scattering) and microscopy (optical and TEM) to visualize the formation of the network structure, and show that, as the hexagonal domains form on cooling from the isotropic phase, they expel the nanoparticles that then concentrate in the shrinking isotropic regions until they jam to form the network of strands
(Figure 4)

### *Bioimplants*

Our group has successfully developed a platform technology for polyethylene maxillofacial implants, which have controlled porous morphology with interconnecting pores allowing tissue in-growth and suturing. The implants are not fragile despite having 40-50% porosity. The first product to be developed was an orbital implant, and technology for manufacturing the same was transferred to a start-up company Biopore Surgicals (www.biopore.in), Mumbai, after extensive nation-wide clinical trials. The Indian market for PE ocular implants alone is estimated to be worth Rs. 2-9 crores/ year. Presently the demand is met primarily by imports. With the development of indigenous implants we expect a 30-70% reduction in implant price, which is is 40% of total treatment cost. This will enable access of this product to poorer sections of Indian society. Subsequent to the orbital implant we have now developed several other maxillofacial implants and the same are under various stages of commercialization.
(Figure 5)

### *Depletion aggregation in colloids*

Mixtures of colloids and polymers are used in a range of products like paints, lubricating oil, cosmetics, food etc. The microstructure, phase stability and rheology of such multi-component systems are determined by the microscopic interactions between the colloidal particles and polymers in these systems. We look at controlled aggregation, phase separation and gelation in a variety of colloid polymer mixtures like milk-xanthan, lyzosyme-PEG etc. We use light scattering, rheology and imaging techniques to look at the structure and dynamics of these systems. We have found that depletion type interactions lead to phase separation in these systems for a polymer concentration above a critical value. However these interactions can be controlled to tune the microstructure and rheology of the final product as has been shown in our milk-xanthan work.
(Figure 6)

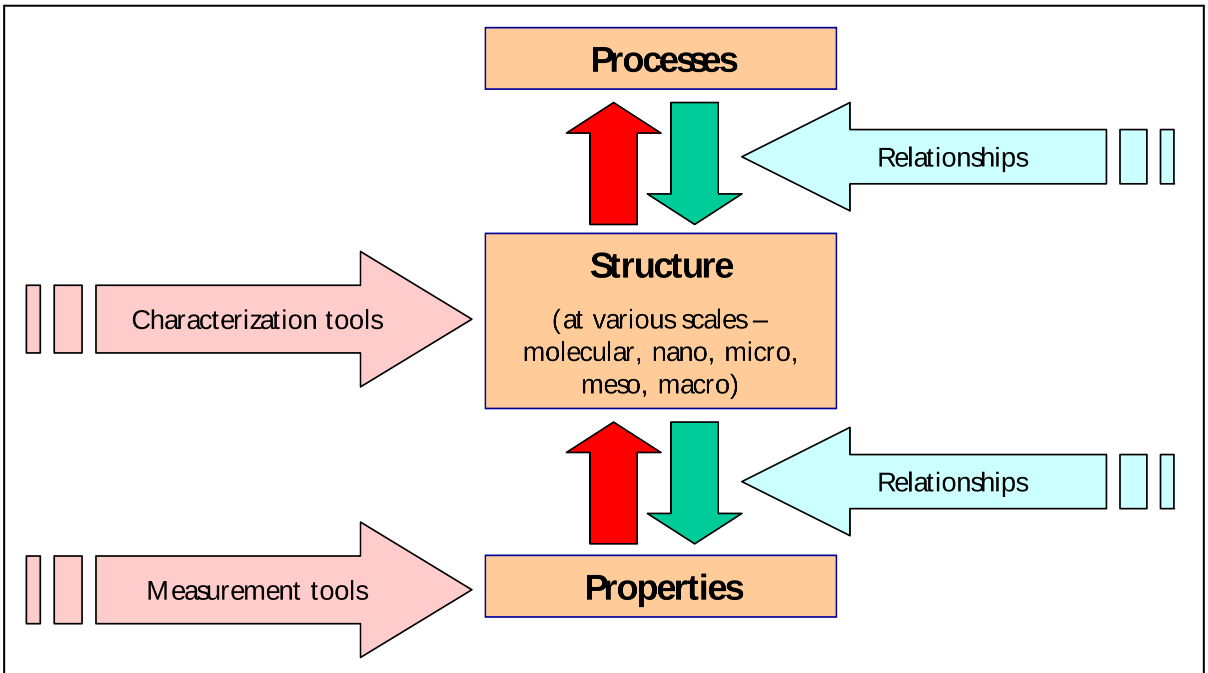
### *Flow visualization in dense suspensions*

Various industrial and consumer products come in the form of dense suspensions. While the mechanics of dilute/semi-dilute suspensions are well understood, our knowledge of dense suspensions (volume fractions > 0.5) is still incomplete despite a lot of work. The macroscopic properties of a suspension are determined by the spatial organization of particles which is known as the microstructure. When subjected to flow, the suspension microstructure can reorganize into anisotropic structures which would affect the rheological properties thereby possibly altering the flow profile itself. We plan to study the physics of such systems using a model colloidal suspension (e.g. few hundred nanometer sized monodisperse PMMA/PS/Silica micro-particles immersed in a density and refractive index matched Newtonian liquid). The micro-rheology i.e. the local dynamics, and the structure of suspension will be probed using laser induced fluorescence under a fast scanning confocal microscope while the suspension is being subjected to oscillatory shear between parallel plates. The global flow behaviour will be probed using various linear and non-linear rheology probes. Correlations between these two studies will help understand the intimate coupling between flow and microstructure. Research in this area is expected to elucidate the role of microstructure in determining the performance of suspensions as well as in controlling the manufacturing of suspensions.
(Figure 7)

### **Contact**

Dr. Ashish Lele
National Chemical Laboratory,
Dr. Homi Bhabha Road, Pune 411 008 India
Email :lele@cfpe.ncl.res.in
Phone :+91-20-2589 3300 (extn 2199)
Fax :+91-20-2589 3041

Figure 1

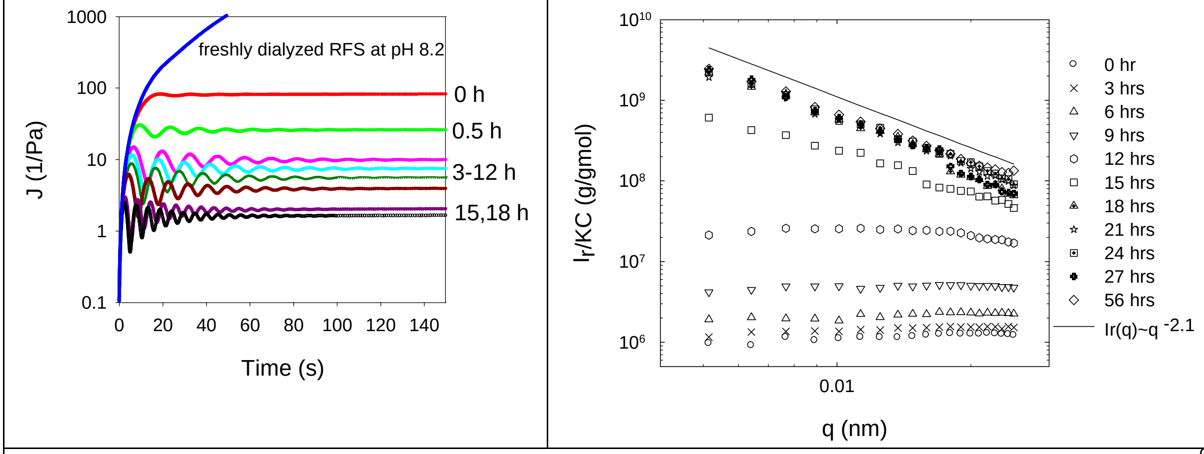


Research theme of the CFPE & PPC groups

Figure 2

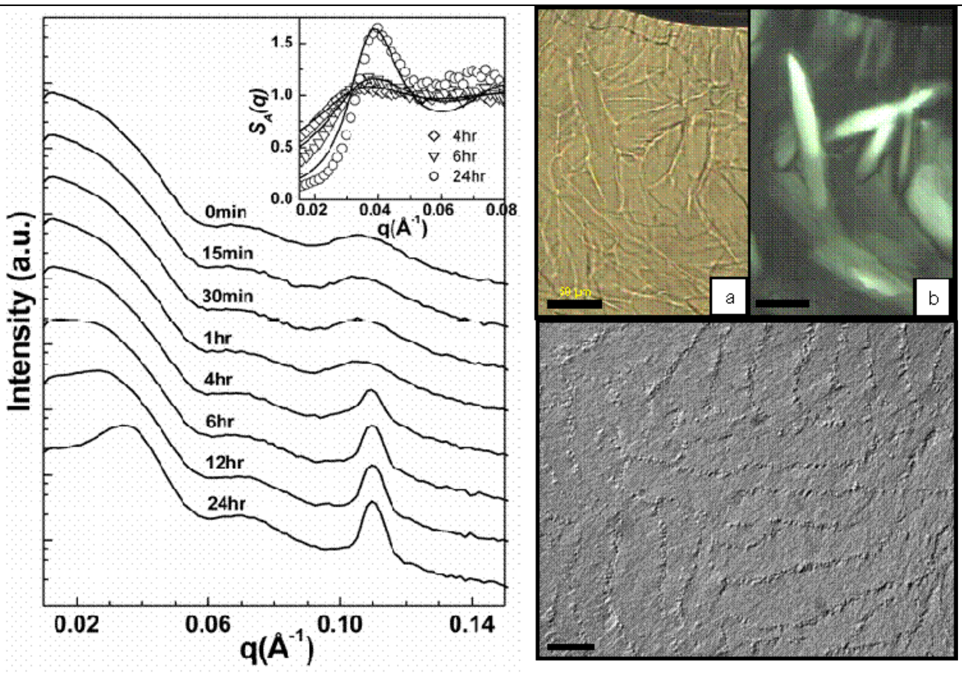
State-of-art infrastructure in CFPE and PPC laboratories

Figure 3



Creep compliance (left) and light scattering (right) of a regenerated silk fibroin solution of pH 2 at 25$^0$C undergoing gelation. The frequency of oscillations (creep ringing), which corresponds to the elasticity of the gel, is seen to increase rapidly between 12 – 15 h. In the same time period the scattering intensity also increases rapidly. The two figures show that silk protein at pH 2 forms aggregates, which grow slowly at first (till 9 h) and then rapidly to form a self similar gel.

Figure 4

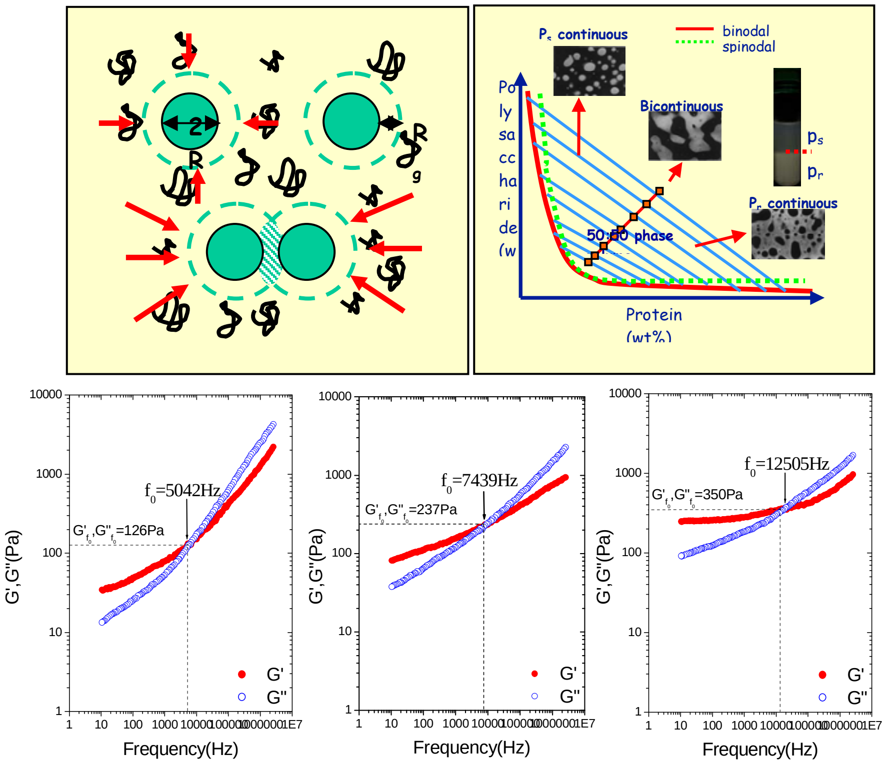


Small angle X-ray scattering (on the left) as nanoparticles jam to form a network. The resultant structure can be imaged under an optical microscope (top right, showing the structure between parallel and crossed polarizers; scale bar corresponds to 50 microns) and using freeze-fracture TEM (top bottom, scale bar corresponds to 500 nm).

Figure 5

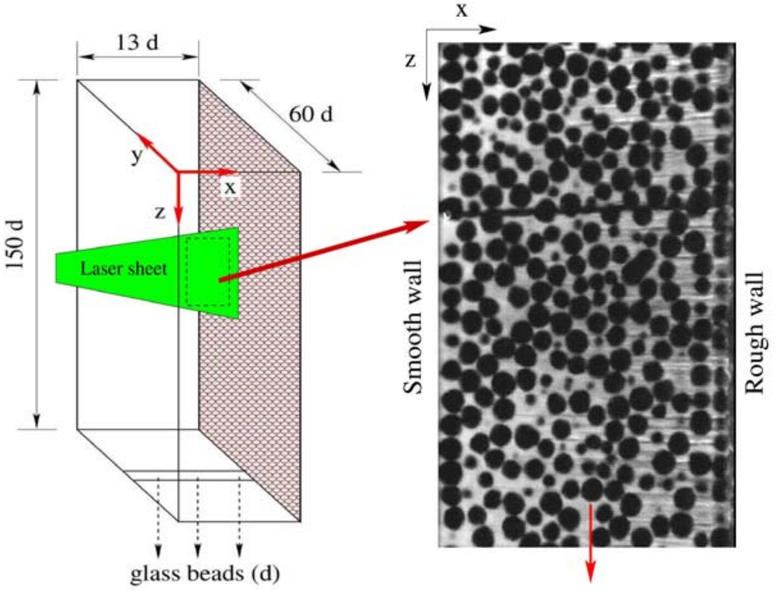
Biocompatible porous polyethylene maxillofacial implants developed at NCL using a unique non-infringing process. The implants have surface and bulk porosity enabling suturing and ingress of tissue.

Figure 6



The top left figure shows a schematic of colloidal aggregation by depletion interactions. The top right picture shows the phase diagram of a protein-polysaccharide colloidal mixture, and microscopy images of structures formed. The bottom figures show the rheology of three samples marked by red arrows in the phase diagram.

Figure 7



Laser induced fluorescence imaging of a density mis-matched non-Brownian suspension confined between a smooth and a rough wall and subjected to unidirectional gravity induced shear.