gram to kilogram scale

Polymer Processing Platform

Processing - Modeling - Physics - Mechanics

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General context and objectives

Developing new polymers is nearly always starting with first stages where the amount of material is very small. There is thus always a need in evaluating the usefulness of a given new polymer. In addition to the development of new oil-based polymers, the last years have seen a huge increase of the development of new biomass-based polymers, mainly associated with the consumer request of having monomers and polymers from the renewable resource.

Renewable carbon-based counterparts of existing oil-based polymers (polyesters, polyolefins, ...), new polymers coming from white biotechnologies (polylactic acid, polyhydroxyalcanoates,...), new complex polymerisation techniques, blends, mixtures with various organic and non-organic fillers, nano-suspensions, and new functionalisations are under development.

The next years will see an even larger number of new polymers due to the predictable development of biotechnologies like new fermentation techniques, bacterial or sponge biosynthesis and microalgae culture.

To fully characterise the new polymers, from physico-chemical and structural properties to their processability and final end-use properties, there is the need to work with quantities of polymers from less than one gram up to several kilograms.

The objective of CEMEF is to offer to polymer developers, chemists and biotechnologists a complete platform of techniques and expertise enabling them to select among a large number of low-amount potential candidates the ones that merit to be produced in larger quantities.

The “g to kg scale Polymer Processing Platform” combined with the wide polymer and bio-polymer expertise of CEMEF scientists and with CEMEF’s development of advanced numerical simulation techniques is the perfect and unique tool to successfully propose innovative solutions in what concerns characterization of new polymers, to assess their processing ability, to develop and optimize their processing and to analyse and understand final material properties.

CEMEF has a large experience in running research projects with industry, with more than 100 active contracts each year involving post-doctoral scientists, PhD and Post-master.

CEMEF is regularly coordinating consortium and large international programmes such as European R&D projects.

CEMEF simulation expertise is industrialised through the development of commercial software, in particular for polymer processing optimization.
Expertise of CEMEF

ARMINES-CEMEF (160 people including 70 PhD) is a joint academic research centre belonging to MINES ParisTech, CNRS and ARMINES. It is among the European leaders in the field of research on material processing. It has been ranked A+ by the French Research Ministry in 2008, the highest mark for a French research and education centre.

The main expertises of CEMEF concern the development of innovative solutions in:
- material physics
- thermodynamics and phase transformation
- mechanics
- modelling and numerical analysis
- computer engineering

Research activities are centred on the physical and mechanical understanding of the principal aspects of materials processing and forming, through both experimental analysis and numerical simulation. A large variety of materials are studied:
- synthetic and natural polymers, elastomers
- polymer blends, composites and nanocomposites
- food industry products

CEMEF focuses particularly on three research poles in order to optimize the whole processing chain:

Knowledge of processes
- Experimental background for processing: measurements on pilot processes available at CEMEF or in industry
- Construction of instruments and pilot machines.
- Analysis of thermo-mechanical phenomena during processing (pressure, temperature, stress on materials)
- Understanding of the origin of defects, and correction
- Aid to optimise tool design and to solve scale-up problems.

Knowledge of materials
- Rheology and behaviour during processing
- Processing-induced microstructures, polymer and polymer/matrix composites organisation development
- Characterisation and modelling of end use mechanical properties; Development of physically based constitutive models and specific testing machines
- Physics, physical chemistry and mechanics of surfaces and interfaces.
- Optimisation of composites and nanocomposites and of structured materials
- Physics and physical chemistry of natural and synthetic polymers.

Numerical simulation techniques
- Numerical simulation of thermomechanical flow and micro-structure evolutions during forming
- Development of new computational methods: parallel computing, optimisation, fluid structure interaction tools for studying thermal, mechanical and microstructure coupling between material flow and tools deformation.
- Dedicated software for polymer and polymer/matrix based composites: injection moulding and extrusion (Rem3D©), twin screw extrusion (Ludovic©), extrusion and mixing (Ximex©).
- Development of rheo-numerical tools for the comprehension and validation of phenomena occurring at the microstructure scale

**Unique CEMEF tools**

In addition to recent, state-of-the-art pieces of equipment in physics, processing and mechanics, CEMEF developed specific, unique experimental and numerical tools to study polymers:

**Experimental facilities**
- Capillary rheometers with controlled thermo-mechanical history
- Rheo-optical tools able to work with highly viscous polymers up to 180°C
- Dedicated small-angle light scattering software
- Crystallisation under microscope with shearing and stretching, with fast cooling
- Crystallisation under microscope under high pressure (200 MPa)
- Very high pressure polymer stamping (3GPa, available end of 2010)
- Extruders equipped with dies with transparent walls in order to observe the flow and to measure velocity (laser Doppler velocimetry) and stress fields (flow birefringence)
- Transparent mould installed on an injection moulding press
- Standard and non standard mechanical tests involving, video controlled systems, 3D strain field and 2D temperature fields measurements, tension, shearing up to high strain rate.
- Home-developed thermo mechanical biaxial testing machine

**CEMEF large-scale computing tools**

Numerical simulation provides informations on thermomechanical quantities and microstructure properties at different scales.

- At the process scale, simulations of extrusion or injection allows to access stress, temperature, deformation, deformation rates and most important, averaged properties giving information on the influence of the process on the structure development (such as average molecular or fiber orientation) and during the formation of the test samples.
- At the microstructure scale, multiphase flow and mechanical computing provide data on the validity of the macroscopic behaviour and evolution laws.

The many numerical techniques developed are highly parallelised, in order to be implemented in industry.

**Highly parallel software facilities**

CEMEF’s has been investing for fifteen years in high performance computing, through the development of highly parallel software, but also by acquiring parallel computing architectures such as clusters of PCs. Today’s configuration is composed of 1496 CPU processors and 960 GPU processors, distributed in the following way: 60 nodes of bi-processor Octo-Core 2,3GHz with 32 Gb RAM, 22 nodes of bi-processor Dual-Core 2,4GHz with 8 Gb RAM, 24 nodes of bi-processor Dual-Core 2,8GHz with 8 Gb RAM, 40 nodes of bi-processor Quad-Core 2,3GHz with 16 Gb RAM, 2 nodes of bi-processor Octo-Core 2,3GHz with 32 Gb RAM linked to the 4 node GPU of and 240 Cores with 16 Gb RAM.
“g to kg scale Polymer Processing Platform”

The purpose of the polymer processing platform is to perform a set of physical and mechanical characterizations and of processing techniques able to guide companies in their development of new polymers.

The platform is based on four sub-platforms, each tailored for a specific given amount of polymers.

**5 g of polymer and less**

With such a low amount of polymer, especially when it is less than one gram, there is no possibility to perform a classical processing in form of test (bar or film).

The approach is to use complementary physical tools to be able to measure the processing range, to characterize the main physical transformations that the polymer can experience in a given temperature range and the associated morphology (ies) and to estimate mechanical properties:

- State-of-the art calorimetry (Cemef is an application laboratory of ThermoFisher): thermodynamics, phase transition temperatures
- Optical and electron microscopies, X ray scattering: morphologies at levels from millimeters to nanometers. State-of-the-art SEM
- In-situ crystallization and structure development apparatus: optical, X ray and light scattering characterizations of structures and kinetics
- Melt or solution rheometry: flow behaviour. Cemef is a leading research center in polymer rheology
- Dynamic mechanical analysis: mechanical relaxations
- Atomic Force Microscopy with a nanoindentor (under air, in liquid environment with solvents, acid and strong basis, between -5°C et +250°C, with small or large motorised displacements): mechanical behaviour, surface structure
- Chemical analysis (Time of flight mass spectrometry, XPS, FTIR)

This first level gives an estimate of the potential usefulness of a given polymer.

**10 to 50 g of polymers**

**Processing**

At this scale, it is now possible to process small amounts of polymers and to perform some compounding and prepare test bars and films:

- Haake Minilab: twin screw extrusion, either co- or counter-rotating, with recirculation.
- Haake Minijet injection molding: coupled to Minilab, allows to inject test bar (traction, DMA) and disks

The whole Haake system allows to process neat polymers, polymer blends and suspensions with low dimension fillers.

**Physics and mechanics**

- Rheology: five rheometers are allowing performing capillary, cone-plate, plate-plate and extensional experiments in a variety of controlled environments (temperature, hygrometry, ..) and solicitations (transient, dynamic and steady state shear).
- Structure: full characterisation of structures (X-ray, optical and electron microscopies, AFM, etc…)
- Flow-induced structures: Compounds can be studied by Cemef-made optical shear devices to assess the stability of obtained morphologies under shear deformations.
• Standard mechanical tests (tension, compression, bending, toughness, hardness, …).
• Non standard mechanical tests (shearing, bi axial tension, high velocity tension / compression) and field measurements facilities.

This second level allows having a reasonable estimate of the processability of a given polymer and gives a first idea of the polymer structure-processing-property relationship.

100 g to 5 kg of polymers

Processing
• High precision injection molding press able to inject sample from 1 to 10 g from 100-200 g feeding (available in 2011)
• Internal mixer Haake Rheomix 600P: compounding, blending, mixing
• Twin screw extruder ThermoFisher PTW24, with two gravimetric, one volumetric feeders and a pelletizer
• Single screw extruder Brabender with film blowing line
• Single screw extruder Haake with cast-film line
For transparent products, the single screw extruders can be equipped with dies with transparent walls in order to observe the flow and to perform measurements of velocity field (laser Doppler velocimetry) and stress field (flow birefringence).
• Film-stretching machine (uni constant width and biaxial, sequential or simultaneous)

Physics and mechanics
As for 10 to 50 g of polymers. For rheological tests, two capillary rheometers can also be used, one with a controlled pre-shear (Rheoplast©).

This step allows to screen polymer characteristics (molar mass, branching, composition …) and to perform the first study of the structure-processing-property relationship.

5 kg to 50 kg of polymers

This step allows a full characterization of both processing and structure-processing-properties in situations close to industrial conditions. Modelling is performed with industrial dedicated software. This step allows to perform scaling-up analysis to real industrial conditions.
Cemef equipment is composed of:
• Twin screw extruder Clextral BC45, with one volumetric feeder
• Single screw extruder Kaufman (D = 40 mm)
• Injection moulding machine (DK 110 tons), mould with transparent windows
• Stretch-blow bottle moulder

For transparent products, the single screw extruder can be equipped with dies with transparent walls in order to observe the flow and to perform measurements of velocity field (laser Doppler velocimetry) and stress field (flow birefringence).

Physics and mechanics
As for 10 to 50 g of polymers.
List of recent and present research projects

The list below is a selection of research projects conducted with industry that are either on-going or that finished less than two years ago.

- Influence of shear on palm oil crystallisation.
- Influence of pressure and cooling rate on polymer crystallisation.
- Compounding of nanocomposites
- Preparation of fibre reinforced composites (glass and natural fibres)
- Micro-injection moulding
- Calandering of multilayer structures
- Extrusion of carbon pastes
- Polymer blends containing biomass-based polymers.
- Starch-based thermoplastic blends.
- Natural fibre – thermoplastic composites.
- Improvement of cellulose sponge properties.
- Ultra-light cellulose foams: preparation, structures and properties.
- Starch-polysaccharide blends as gelatine replacement for medical capsules.
- Carbonized cellulose for electro-chemical applications.
- Use of full plant for making composites.
- Lignin-based materials.
- Starch cationisation by reactive extrusion.
- Extrusion of bitumen for nuclear applications
- Dispersion of carbon black in polyamide for electrical conduction
- Mechanisms of action of fluorinated processing aids
- Modelling of dispersive and distributive mixing in extrusion processes
- Experimental study of glass fiber reinforced composites processes: internal mixer, twin-screw extruder and continuous co-kneader
- Influence of the calendering step on the adhesion properties of coextruded polymer structures
- Modelling of the foaming step of polyurethane
- Experimental and numerical investigation of coextrusion instabilities
- Rheometry of molten polymers at high shear rates
- Developments on mini (micro) injection moulding machines
- Investigation of the behaviour of molten polymers in complex flow situations by Flow Induced Birefringence and Laser Doppler Velocimetry
- Rheometry of hot-melt polymers
- Influence of enzymatic and/or chemical treatments for increasing cellulose fiber processability.
- Simulation of short fibre orientation development in injection moulding and prediction of the mechanical properties
- Development of a fluid-structure interaction numerical technique to study the impact behaviour of injection moulded polymers
- Mechanical behaviour modelling of fibre reinforced thermoplastics
- Development of innovative constitutive models for ISBM and thermoforming;
- Development of new thermo mechanical approach for polymers in structural applications.
- Numerical and experimental study of the water assisted injection moulding process
- 3D compression and injection-compression moulding simulation
- Numerical study of the “fluid buckling” during propargol injection moulding
- Fibre and particle reinforced polymers rheo-numerical study
- Representative Elementary Volume automatic generation and application to foam structure development modelling
- Permeability computation of complex fabrics through a numerical dual scale approach

**Relevant publications 2010-2005**

**2010**


2009


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SESCOUSSE R., BUDTOVA T., Influence of processing parameters on regeneration kinetics and morphology of porous cellulose from cellulose-NaOH-water solutions, Cellulose, 16(3), 417-426 (2009).


2008


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2007


EGAL Magali, BUDTOVA Tatiana, NAVARD Patrick, Structure of micro-crystalline cellulose-sodium hydroxide aqueous solutions below 0°C and the limit of cellulose dissolution, Biomacromolecules, vol. 8, p. 2282-2287, 2007


2006


2005

W. Lertwimolnun, B. Vergnes, Influence of compatibilizer and processing conditions on the dispersion of nanoclay in a polypropylene matrix, Polymer, 46, 3462-3471 (2005)


A. Allal, A. Lavernhe, B. Vergnes, G. Marin, Relation entre structure moléculaire et défaut de peau de requin pour les polymères linéaires à l’état fondu, Rhéologie, 8, 31-43 (2005)

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M. Vincent, T. Giroud, A. Clarke, C. Eberhardt, Description and modeling of fiber orientation in injection molding of fiber reinforced thermoplastics, Polymer, 46, p.6719-6725 (2005)


