Synchrotron light: a unique tool for the characterization of plastics and rubber

Plastics & Rubber, Barcelona, 7 March 2024

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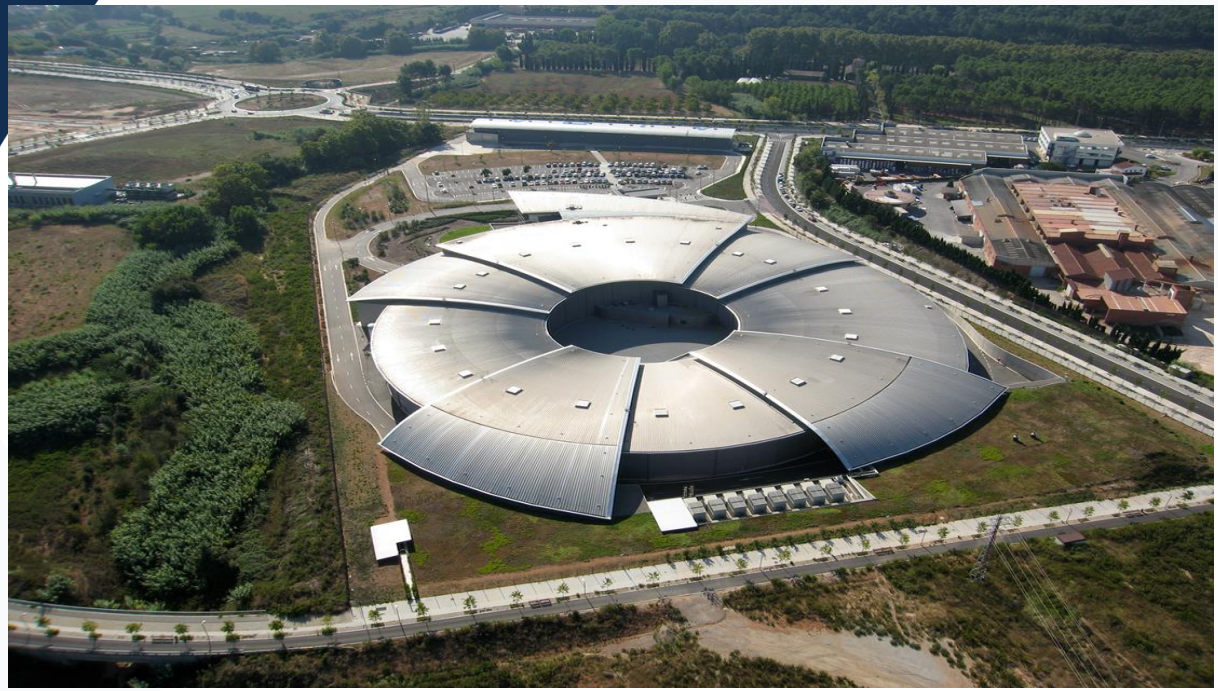
ALBA Synchrotron in short



1st SCIENCE FACILITY IN SOUTH-WEST EUROPE

300 M€ PUBLIC INVESTMENT (2022)

250 STAFF (28% INTERNATIONAL)

2500 RESEARCHERS PER YEAR (35% INTERNATIONAL)

300 EXPERIMENTS PER YEAR +
60 INDUSTRIAL EXPERIMENTS PER YEAR

4500 HOURS PER LAB PER YEAR

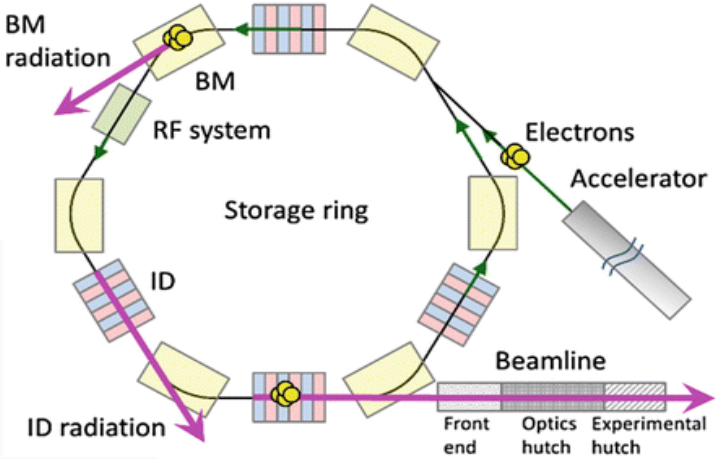
A large facility to study the structure at atomic scale of materials in:

- CHEMISTRY
- PHARMACEUTICAL
- ADVANCED MATERIALS
- ENERGY
- HEALTH
- NANOTECHNOLOGY
- AUTOMOTIVE AND AEROSPATIAL
- FOOD AND PACKAGING
- ENVIRONMENT
- CULTURAL HERITAGE & FORENSIC SCIENCES

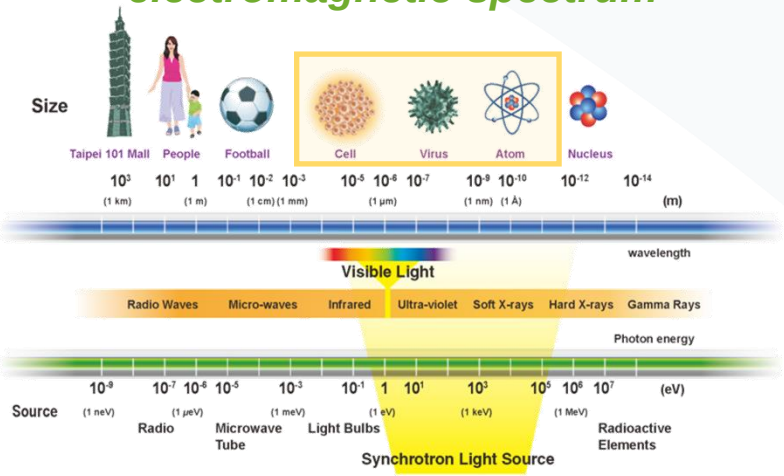
What is a synchrotron

- It is a particle (electrons) accelerator.
- The electrons travel to nearly the speed of light and generate synchrotron light: IR, UV, soft and hard X-rays.
- Synchrotron light can be used to study materials up to atomic scale

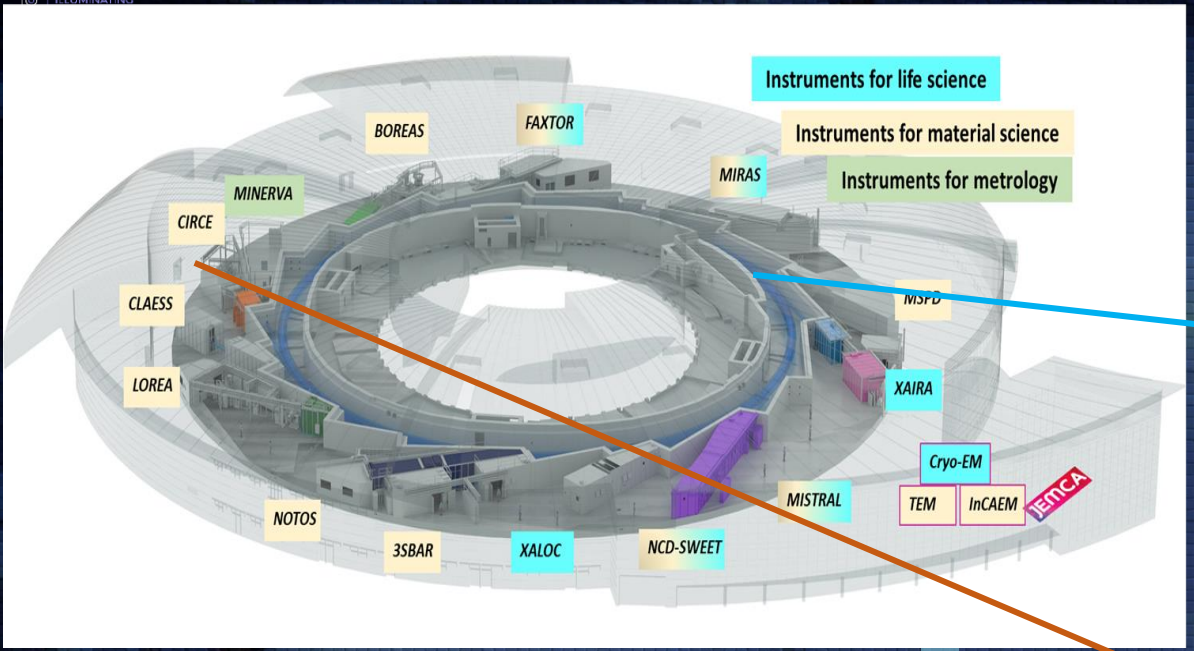
Scheme of a synchrotron



Synchrotron light range in the electromagnetic spectrum



Production of synchrotron light in the accelerator, use in the beamlines



3 GeV e- synchrotron
270 m circumference
250 mA operating current
> 98% availability

11 operating beamlines
+ 3 beamlines in construction
+ Joint Electron Microscope Center (JEMCA)

WHAT DOES ALBA SYNCHROTRON OFFERS TO INDUSTRY ?

ALBA Synchrotron offers to industry top notch characterization of materials and processes at micro and nanoscopic level by using synchrotron light, providing results focused on the companies specific needs.

Synchrotron light techniques:

- X-ray microscopy
- X-ray powder diffraction
- X-ray absorption spectroscopy
- Ir microspectroscopy
- Macromolecular crystallography
- Small and wide angle scattering (SAXS & WAXS)
- Photoemission (microscopy, near ambient pressure)
- X-ray magnetic dichroism

Plastics & Rubber

WHY ?

DO COMPANIES USE ALBA SYNCHROTRON?

ALBA Synchrotron techniques provide **outstanding results** that cannot be achieved with other equipment and techniques and which are very valuable in boosting a company's competitiveness.

- LOWER DETECTION LEVELS
- CHEMICAL MAPPING
- OXIDATION STATE DETERMINATION
- HIGHER RESOLUTION
- FASTER EXPERIMENTS
- WIDE VARIETY OF SAMPLE ENVIRONMENTS

ALBA clients

Long term contract between HENKEL and ALBA

Helix BioStructures performs first post-lockdown COVID-19 measurements at ALBA

- ✓ *85 different clients using ALBA beamlines*
- ✓ *Wide range of industrial sectors*
- ✓ *600 industrial experiments*

BASF, UPC and ALBA propose a methodology for producing better additives for concrete technology

SAMTACK benefits from synchrotron light for improving food packaging

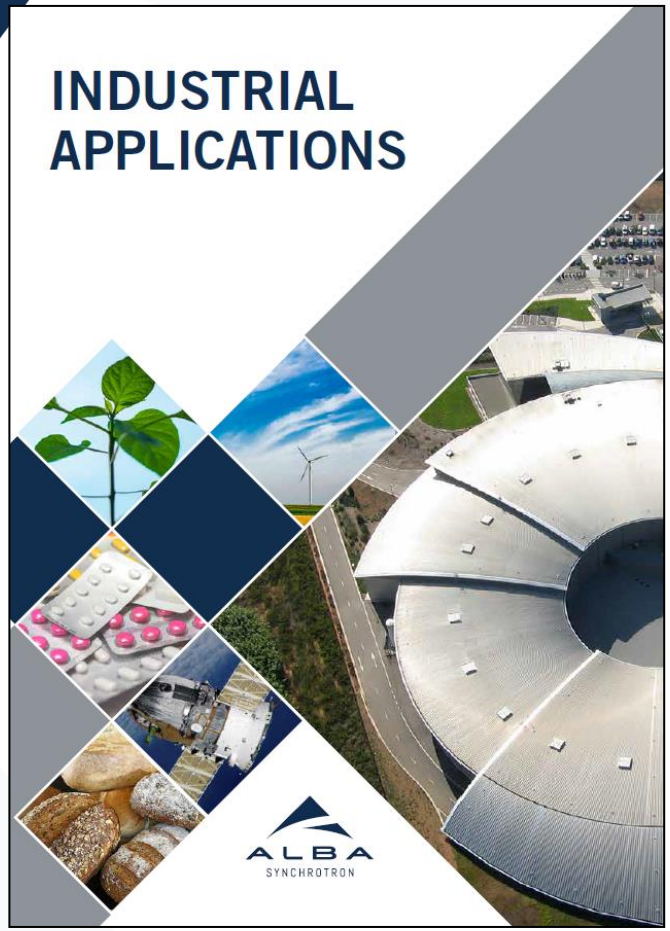
The company is analysing nanoparticles contained in a new food packaging system that will prevent food oxidation and extend its lifetime.

ESTEVE, UAB and ALBA Synchrotron join efforts to investigate the mechanism of action of new inhibitors against pain

ENANTIA uses ALBA's X-rays to detect crystalline impurities in drug products

TOYOTA and CSIC proved viability of calcium-based batteries

The Spanish Research Council (CSIC) in collaboration with TOYOTA Motor Europe (TME) demonstrates the viability of Calcium rechargeable batteries using ALBA techniques.



CHEMISTRY

WHAT CAN BE STUDIED?

- CATALYSTS
- PLASTICS, ELASTOMERS AND POLYMERS
- PAINTS AND PIGMENTS
- FIBRES
- PULP AND PAPER
- ENCAPSULATION OF ORGANIC COMPOUNDS
- HOME CARE PRODUCTS
- CHEMICAL REACTIONS

WHAT INFORMATION CAN BE OBTAINED?

- Structural characterisation of solid samples at the atomic level.
- Determination of the oxidation states and species in a wide variety of samples.
- Nanoscale characterisation of the shape, size and density of molecular aggregates.
- Characterisation of depositions, contamination and photochemical processes on surfaces.
- Microstructural characterisation of dispersions, emulsions and materials partially ordered.
- Chemical identification and characterisation of contaminants.
- Study of chemical reactions and processes in both a dynamic and steady state at the atomic level.

WHAT ALBA DOES

CUSTOM-MADE AND MORE EFFICIENT CATALYSTS

Rhodium and Palladium nanoparticles deposited on a ceria substrate are used as catalysts for the production of hydrogen. The analysis of their surfaces under working conditions conducted at ALBA showed that the oxide substrate induced a rearrangement of the nanoparticles that increased the reaction yield. This result helps to design catalysts with improved performance.

IMPROVING THE PROPERTIES OF PIGMENTS AND THEIR MANUFACTURING

The low detection limits and the possibility to determine oxidation states provided by ALBA permitted the colour properties of a commercial pigment, produced by different synthetic routes, to be correlated with its crystal and atomic structure.This information is very valuable for developing more efficient methods for pigment manufacturing.

GIVING SHAPE TO POLYMERS

Different degrees of crystallisation provide plastic materials with properties that are halfway between hard/solid and soft/flexible. ALBA characterised the degree of crystallisation of different polymers cooled down at different cooling rates, similar to those used under industrial conditions, to determine the most suitable process for tuning the rigidity or plasticity of the polymers for particular applications.

https://www.cells.es/en/industry/industrial_applications_baja.pdf

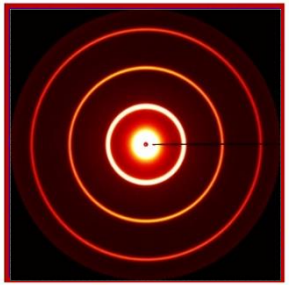
ALBA Synchrotron with plastics and rubbers

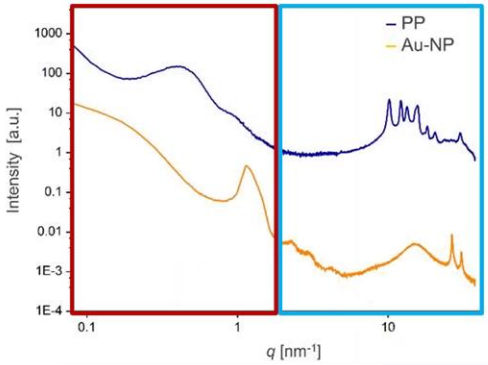
EXAMPLES

NCD-SWEET beamline: SAXS and WAXS (Small and Wide Angle X-ray Scattering)

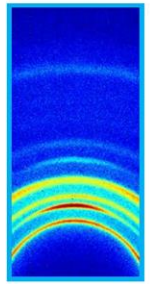
- ✓ **Provides structural information**
- ✓ **What can be studied: changes in the structure, crystallization, morphologies (lamellar stacks, spherulites…)**
- ✓ **In-situ changes can also be monitored**

SAXS





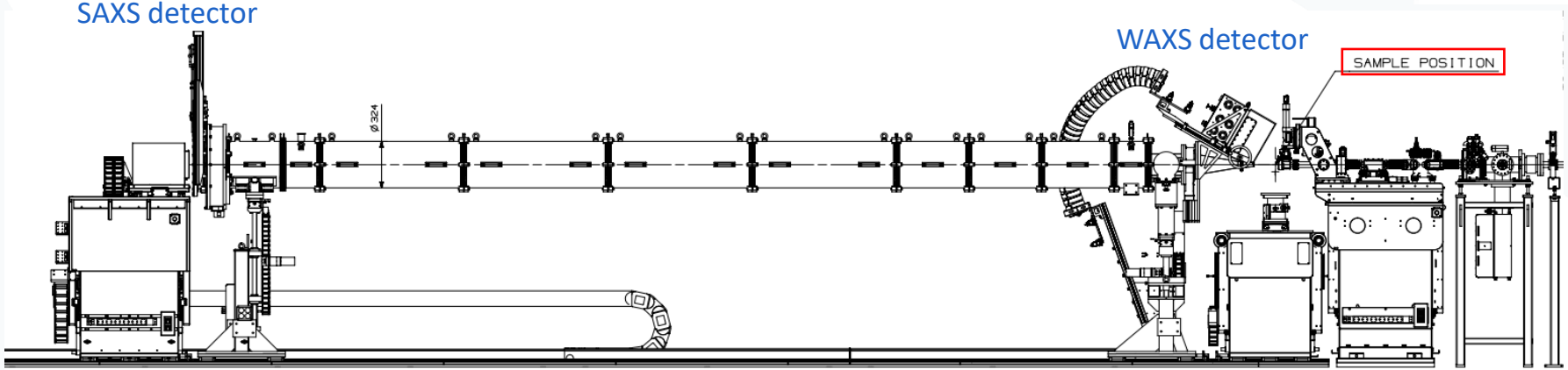
WAXS



DECTRIS webinar 15/05/2018

SAXS detector

WAXS detector



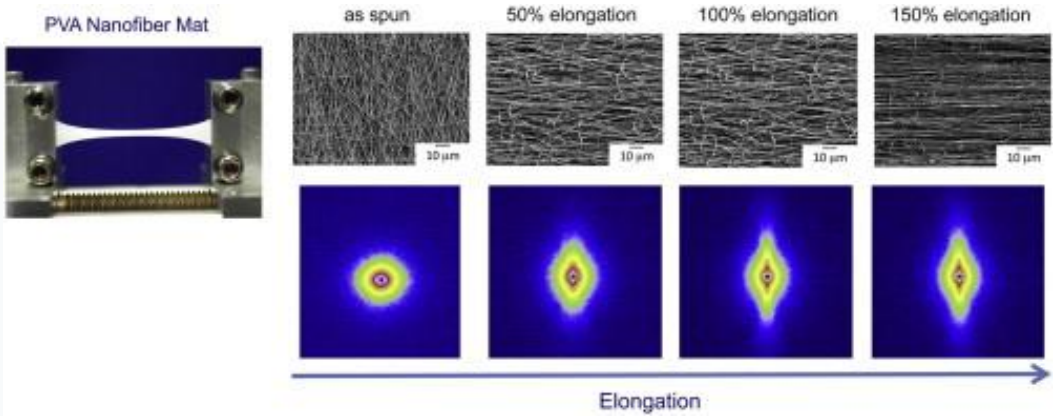
NCD-SWEET beamline

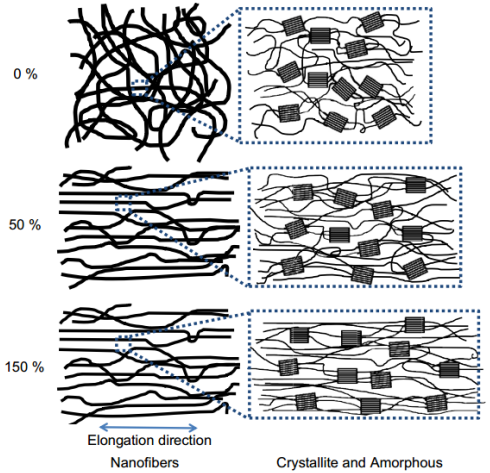
Investigation of Polyvinyl Alcohol (PVA) upon uniaxial stretching using SAXS

"In-situ stress-strain measurement with synchrotron radiation is a powerful tool for the investigation of structural development of polymer materials, enabling a wide range of structural details to be studied on a single specimen during mechanical deformation."

"The influence of crystalline orientation, orientation-induced crystallization, crystal transition, fibrillar formation and cavitation on the film deformation process has been demonstrated.

"In-situ analysis of the uniaxial stretching of an electrospun nanofiber mat: nanofiber orientation and the crystallite and molecular chain orientation. This may contribute to material design of non-woven nanofiber materials for industrial applications."

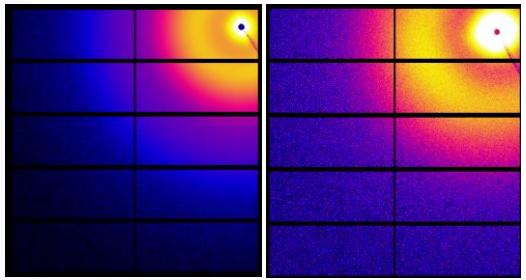


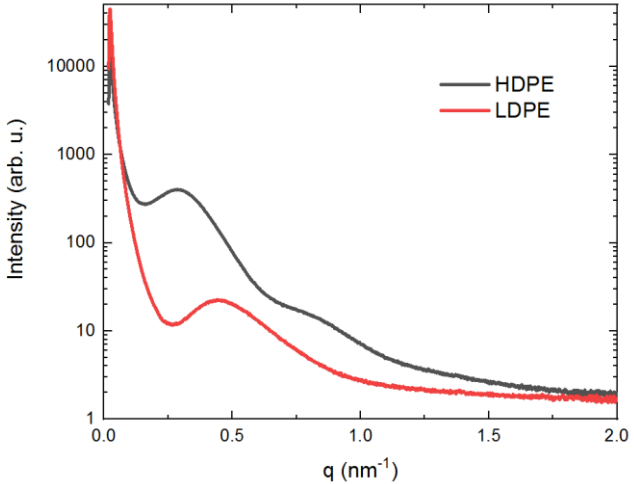


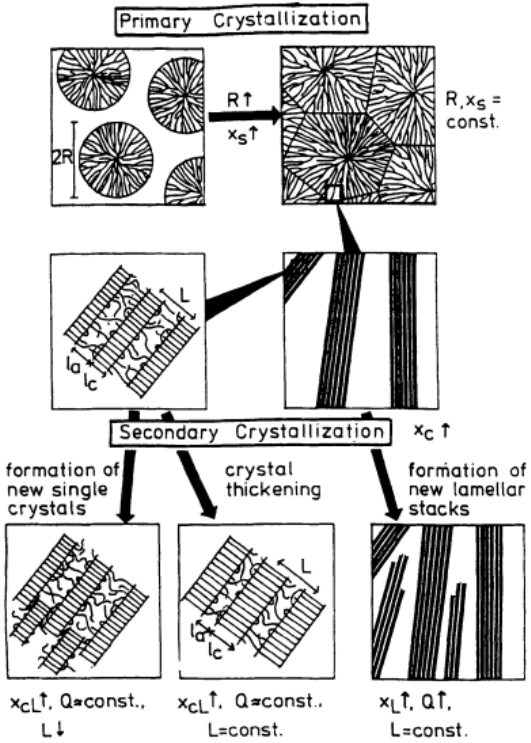
T. Yano et al. / Polymer 53 (2012) 4702-4708

Polymer crystallization studies in Polyethylene (PE) blends using SAXS

- ✓ Studies with HDPE/LDPE blends at different percentage
- ✓ Temperature changes and deformation were applied
- ✓ Changes in morphology observed; spherulites, elliptical particles and rods, crystal thickness, lamellar stacks..
- ✓ Changes in crystallization observed
- ✓ Mechanical properties of the semi-crystalline polymers are related to their crystalline morphology





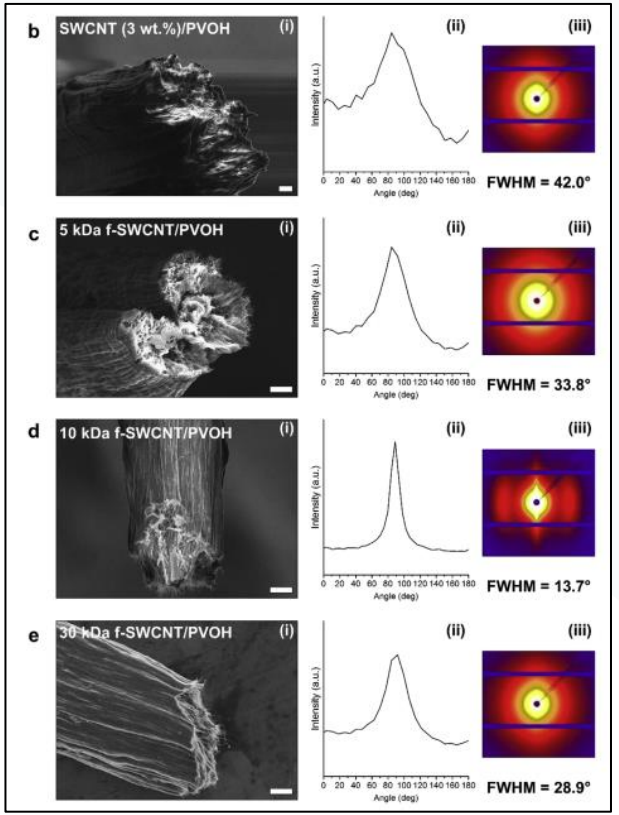


Crystallization of Polymers pp 403-414
Q. Fu et al. Polymer 44 (2003) 1927–1933

Structural studies of composite fibers using SAXS

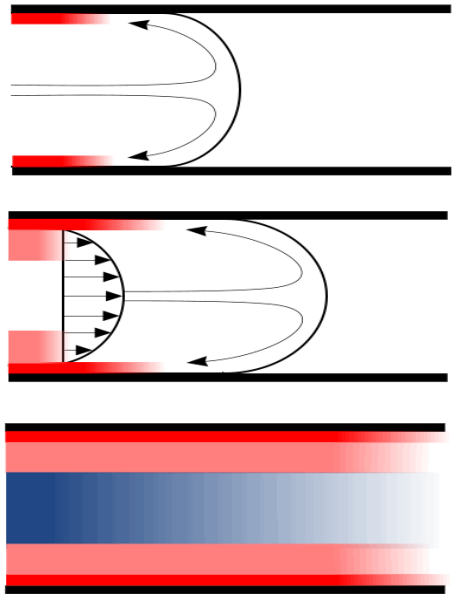
Nanocomposites are critically influenced by interfacial interactions between the reinforcement and matrix. Polyvinyl alcohol (PVOH) of varying molecular weights were prepared and grafted-to single-walled carbon nanotubes (SWCNTs), to improve the interfacial interaction with a homopolymer PVOH matrix.

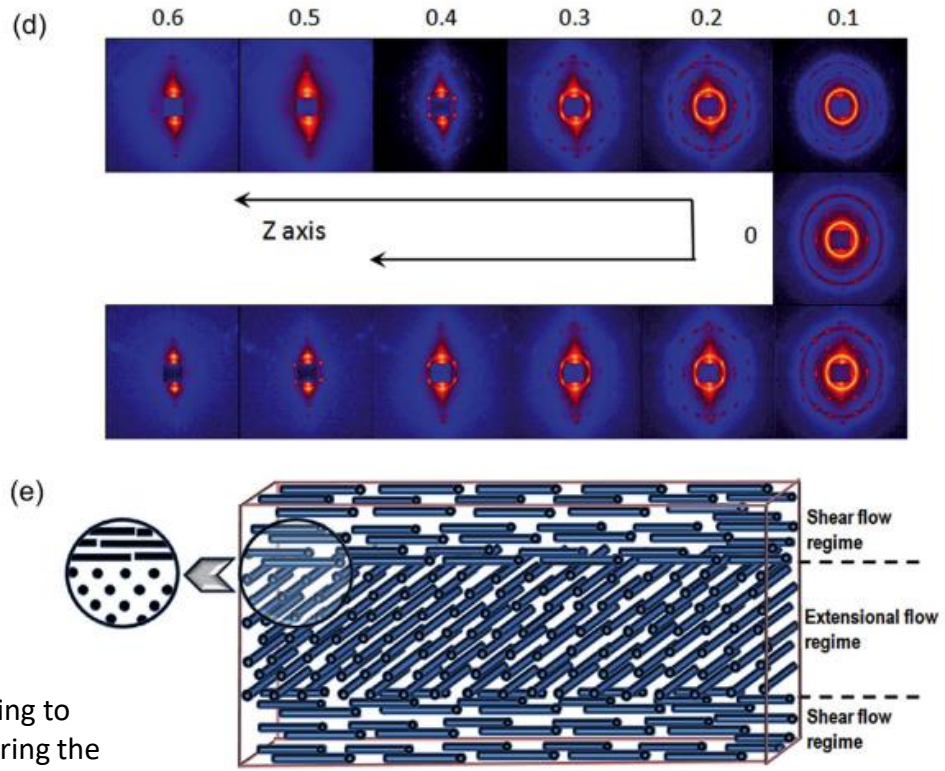
SAXS (…) can be thus conveniently used to analyze individual 30µm diameter composite fibers (…) enhanced orientation for the f-SWCNT samples, with the best alignment for the 10 kDa fibers (…). The (bulk) SAXS showed (…) that the nanotubes were indeed preferentially orientated to the nanocomposite fiber axis.



W.J. Lee et al. / Carbon 146 (2019) 162-171

Investigation of slow injection molding using SAXS



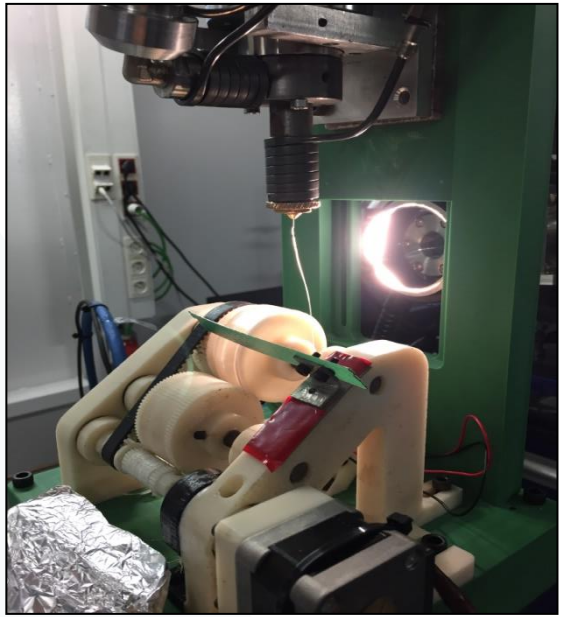


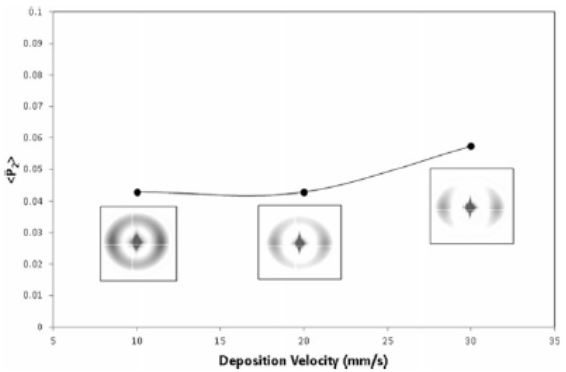
SAXS provides morphological and orientation information, allowing to investigate material heterogeneities, that could be originated during the fabrication steps

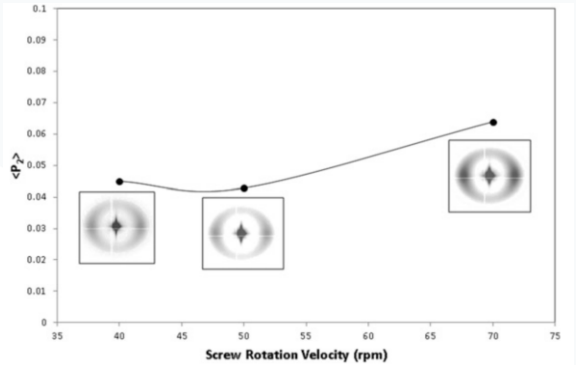
Sakurai. Polym Int., 2017 (66) 237–249

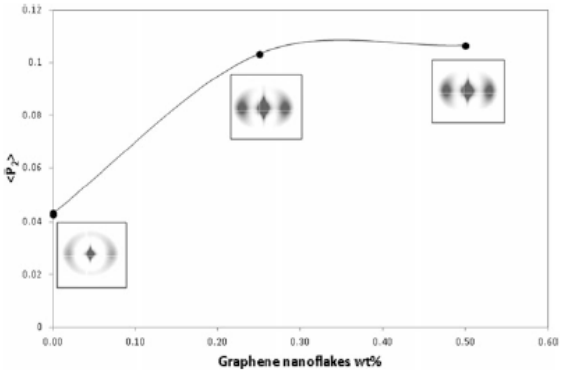
in situ 3D printing studies using SAXS

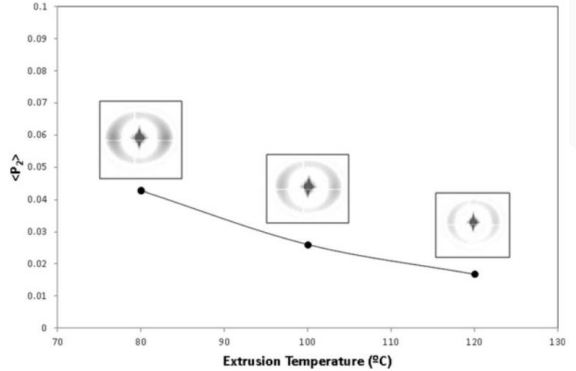
Parameters influencing the fiber orientation and hence, the final material properties











*Tojeira, A., et al. , Controlling the morphology of polymers (pp. 181-207). Springer.

Mechanical reinforcement in rubber composites using SAXS

- Mechanical performance of the rubbery components in pneumatics or other natural rubber is related to their ability to undergo strain-induced crystallization (SIC)
- Incorporation of crystallizable waste into natural rubber enhances reinforcement of the resulting composites
- Confirmation of SIC in natural rubber/ground tire rubber composites using in-situ X-rays radiation during uniaxial deformation
- Use of waste rubber particle devulcanization may be beneficial to improve the reinforcement and strain induced crystallization

- ✓ In-situ measurements
- ✓ Deformation induces crystallization
- ✓ Samples with ground tire rubber improves the properties

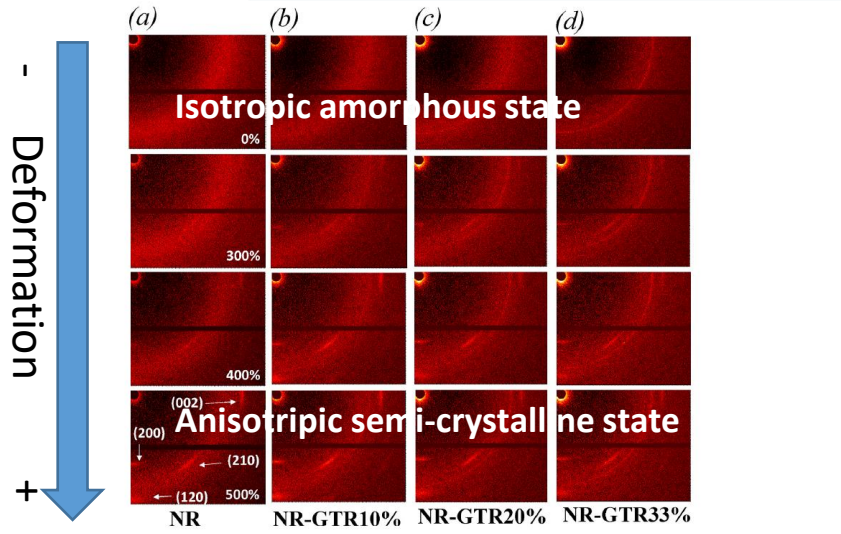


Fig. 5. 2D WAXS patterns of the NR and NR-GTR blends at different deformations from 0% to 500% (from top to bottom) for *(a)* NR, *(b)* NR/GTR10, *(c)* NR/GTR20 and *(d)* NR/GTR33. The patterns are shown after subtraction of the direct beam.

N. Candau et al. / Polymer Testing 101 (2021) 107313

MIRAS beamline: infrared spectroscopy and microscopy

- ✓ Study the **chemical and biochemical composition** of materials in different physical states
- ✓ **High spatial resolution (max 3x3 μm²) to characterize heterogeneous samples**

In-situ FTIR imaging on the plastic deformation of isotactic polypropylene (iPP) thin films

- Plastic deformation of semi-crystalline polymers is an important phenomenon which occurs during tensile deformation in film processing
- Understanding the mechanism of plastic deformation is key to guide the processing of high performance products
- To better understand such process methods with time resolved and spatial resolution are needed.
- Specific IR bands are determined to estimate the content of crystal and amorphous
- Synchrotron **FTIR technique can be used to detect spatial resolution of crystallinity**, orientations of crystals and amorphous chains

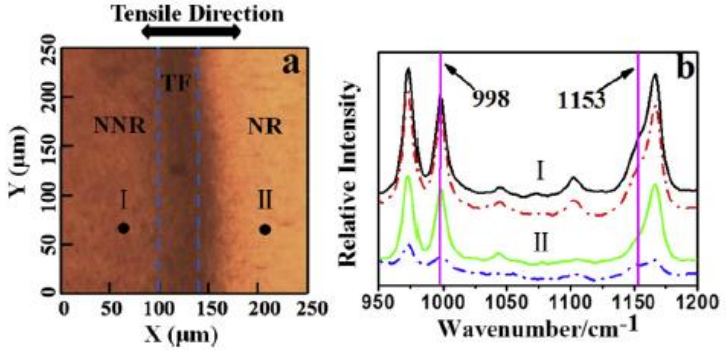


Fig. 2. (a) The optical micrograph at the macroscopic strain of 3.3 of iPP film. NNR, TF and NR are defined by the blue dash dot lines. (b) Corresponding FTIR spectra of points I and II in range of 950–1200 cm^{-1}. The solid and dashed lines are spectra with radiation polarized parallel and perpendicular to tensile axis, respectively (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

J. Li et al. / Polymer 55 (2014) 1103-1107

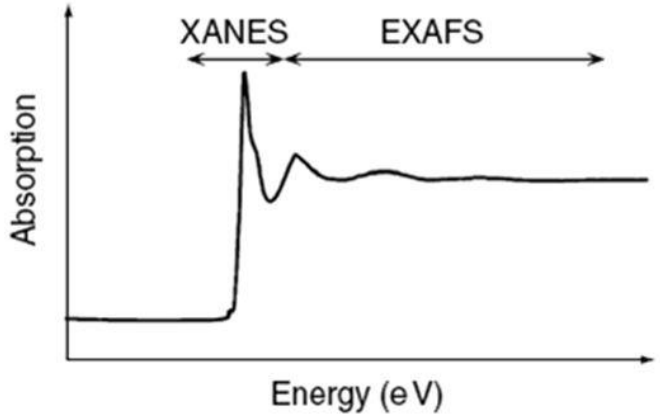
CLAESS beamline: X-ray absorption spectroscopy

EXAFS

- Bond distances
- **Coordination number**
- Static and dynamic disorder

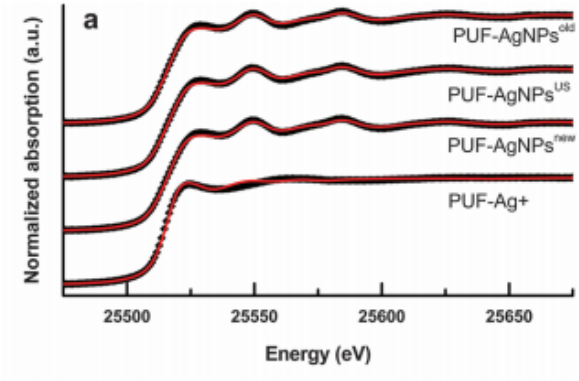
XANES

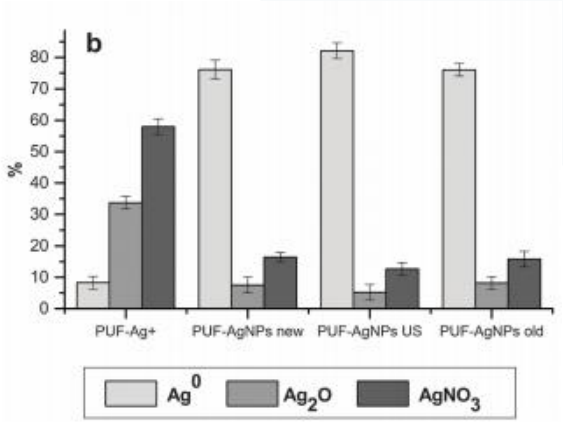
- **Oxidation state**
- Unoccupied electronic states
- Spin state
- Local structure
- Direct information about bond angles



Polyurethane foam dopped with Ag nanoparticles studies with XAS

- Polyutethane foam with **Ag nanoparticles** to be used as **antibacterial** in water treatment.
- XAS technique allows studying the **oxidation state and chemical stability of Ag**





- ✓ **Ag species of new and old simples were very similar, showing that nanoparticles were stable**
- ✓ Some oxidised species were found in all the samples ($AgNO_3$ o Ag_2O)

Doménech et al. New J. Chem., 2016, 40, 3716.

HOW ?

One-stop shop service which provides guidance and coordinates the whole process

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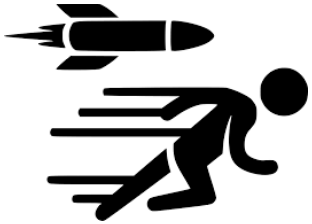
HOW ?

TO CONTACT ALBA



FAST

CONFIDENTIAL

FULL SERVICE

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Funding opportunities via European Projects

LEAPS-INNOV:

- SPECIFIC PROGRAMME FOR SMEs (TamaTA)
- FREE ACCESS TO ALBA
- CALL OPEN: https://wayforlight.eu/en/industries/

ReMade@ARI:

- PROJECTS ADDRESSINS CIRCULAR ECONOMY
- SPECIFIC PROGRAMME FOR INDUSTRIES (2 different programmes)
- FREE ACCESS TO ALBA
- CALLS OPEN

ALBA ILO (industrialoffice@cells.es) will help

Summary

- ✓ Synchrotron light is very useful and flexible for the plastics and rubber industries
- ✓ Synchrotron light can provide information on:
  - ✓ Structure, orientation, crystallinity
  - ✓ Chemical imaging information with spatial resolution
  - ✓ Oxidation state and chemical species of polymer additives
- ✓ Tailored access to different synchrotron techniques for industries. Funding available.

industrialoffice@cells.es

THANK YOU!