

POLYMER SOLIDIFICATION UNDER PROCESSING CONDITIONS

Solidification under processing conditions of semicrystalline polymers and blends

Polymer solidification takes place in all relevant forming routes of thermoplastic materials. It occurs under extreme conditions of all state variables involving the onset of metastable solid phases. The complexity of the phenomena occurring being under debate a systematic modelling of macromolecules solidification is still to come.

Aim of this research is to apply a newly developed experimental approach consisting in the design of “model experiments” where the effects of some relevant processing variables (namely cooling rate and pressure) on the crystallization kinetics of several semicrystalline polymers (iPP, PET, PBT, PTT, PEN, PA6, sPS) may be isolated and properly quantified. The structure developed is analysed by different means of investigation of bulk samples properly applied since the method provides an homogeneous morphology over macroscopic dimensions. The overall crystallization kinetics has so far been euristically approached in the framework of a multiphase Kolmogoroff-Avrami-Evans approach.

With respect to this topic, part of the research effort was devoted to investigate and identify the correct dependence of relevant phenomena taking place during injection moulding of glass fiber reinforced thermoplastics, such as shrinkage, warpage upon the chemico-physical features of the polymer matrix. In particular, the research interest was focused on the determination of the role played by glass fibers and by the internal stresses (owing to the differential cooling of the moulded parts).

Additionally, as a side-branch research new in-line technique was designed and developed to monitor the solidification process during the cooling stage of injection moulding of semicrystalline polymers.

Cooperation with several industrial partners (Borealis, DSM, Solvay) are still in progress, to witness the industrial interest in this type of scientific and technological research.

Preparation of polymeric scaffolds for tissue engineering

In the last few years a research interest has also been developed towards the synthesis and characterization of polymeric scaffolds to be used for therapeutic applications like tissue or organs restoration. Tissue engineering studies the functional-structural relationships of human tissues trying to restore, maintain, improve or eventually substitute the function of living tissues partially damaged. The aim of the present work is to explore a suitable route to reliably prepare porous biodegradable foams by thermally induced phase separation (TIPS) starting from polymer solutions varying the residence time and temperature in the metastable state, so as to control the final structure in terms of complex morphology, average pore size and degree of interconnection.

DEGRADATION AND STABILIZATION OF POLYMER SYSTEMS

While understanding and controlling degradation has absolutely critical to the development and commercialisation of plastic materials, particularly in high-stress uses such as automotive, film for packaging and agriculture. The degradation of the polymers or of the filled-polymer systems under normal use conditions is a major factor limiting the application of these versatile materials. The degradation ways of the polymers is a more complex phenomenon; it depends on many factors, such as the polymer type (i.e. chemical structure, crystalline degree, etc.), the processing conditions, the migration of the oxygen into the polymers, the penetration of UV radiation (in case of outdoor exposure), etc. The degradation starts with irreversible changes in the composition and structure of the polymer molecules and proceed with loss in mechanical performances and in external appearance (discolouration and loss of gloss) of the materials.

The incorporation of micro- and nano-sized fillers, such as calcium carbonate, talc, unmodified and organo-modified silicate, carbon black, CNTs, etc, into the polymer matrices, results in significant

enhancement of some mechanical, thermo-mechanical, optical and dielectric performances. Usually, the presence of all the filler types do not modifies the degradation ways of the polyolefin matrix but the filler particles are able to slow or in some cases, to accelerate the matrix degradation rate. Beyond, the micro- and nano-sized fillers are able to change the molecular arrangement and the crystalline degree, i.e. the morphologies of the polyolefin matrix with alterations of the oxygen penetration and diffusion, and consequently the fillers are able to modify the polyolefin degradation rate.

In order to extend the useful lifetime of the polymers or of the filled-polymers, it is fundamental to understand the degradation ways and to stabilize the materials. Inhibition of the degradation process by structural modification, by copolymerization, by crosslinking or by additives are different stabilization strategies to prevent both thermal- and photo-degradation. Furthermore, each stabilizer appears to work at a specific stage in the degradation mechanisms.

MACROMOLECULAR ENGINEERING OF COMPOSITES AND BIO-ACTIVE MATERIALS

Biocompatible hydrogels as functional materials for biology and medicine

Hydrogels are tridimensional polymer networks able to swell up to thousand times their dry weight in water without dissolving in it. The morphological resemblance of gels and extracellular matrices, the existence of gels throughout living systems allows one to speculate that the development of hydrogels for biological applications may become increasingly important and the integration with bioactive components (proteins, enzymes, antigens, antibodies, genes) may offer the opportunity for breakthroughs in medicine, pharmacology, material science and engineering. Depending on the desired level of bio-communication, that is molecular, cellular or skeletal, the structure and properties of the material has to be designed at the nano-, micro- or macro-scale, where biocompatibility is the first requirement.

Biocompatible hydrogels are synthesized starting from both natural or synthetic monomers and polymers and characterized to assess their structural, morphological, physico-chemical, rheological, electrical and optical properties. Hydrogel nanobeads are produced in miniemulsion conditions or by high-energy irradiation of water-soluble monomers in dilute aqueous solutions. Nano- or micro-porous hydrogel pastes, slabs or films can be made through either physical, chemical or irradiation methodologies with a wide of network mesh sizes, swelling and rheological properties.

Suitable functional groups may be present in the network and/or organic and hybrid organic/inorganic nanoparticles can be purposely incorporated in the hydrogels to obtain reversible changes in the physical form, or in the optical or electrical properties of the hydrogels, as a response to changes in the external environment (pH, temperature, redox molecules, enzymes, etc).

Optical (fluorescent) probes are used to study the micro-environment inside the network and model the uptake and release of actives with different polarity, dimensions and chemical functionalities. Incorporation and controlled release of fragrances, synthetic or biological drugs is investigated through in vitro experiments. Biocompatibility and interaction with living cells can be assessed. The research is carried out in collaboration with a team of biologists and biophysicists and with the partial support of IAEA.

Synthesis and characterization of conjugated polymers

Conjugated polymers are macromolecules with a spatially extended system of double bonds. They can be semiconductors, and as such of importance in organic electronics or, if fluorescent, they can be of great interest as sensory materials to detect metals, chemicals, proteins, bacteria, DNA, etc.

Changes in absorption or fluorescence are generally affected by the change in supramolecular structure and, thereby, the morphology.

Polyanilines are a family of conjugated polymers with different chemical structures at the variance of the oxidation state and protonation level. They can be easily synthesized in aqueous dispersion and in the presence of a variety of suspending agents, to yield nano- or micro-particles with controlled shape, size and size-distribution. Morphology of the obtained particles is investigated by high resolution microscopic methods (SEM, AFM, TEM). The supramolecular organization and the morphology of the obtained particles produced is related to the electrochemical, optical and electrical properties of their aqueous dispersions.

In particular, the immobilization of conducting polymers nanoparticles into biocompatible hydrogels matrices or nanobeads is pursued with the aim of enabling in-vivo detection of biomolecules of medical interest (such as radical oxygen and nitrogen species as a sign of inflammation).

PREPARATION AND CHARACTERISATION OF PHOTOCATALYSTS

The research activity concerns the preparation of polycrystalline bare and loaded semiconductors used as photocatalysts, also supported on concrete (research developed with industry). Some attention has been focused on preparation of nanostructured TiO₂ from TiCl₄ hydrolysis. The influence of various parameters on the obtained crystalline phases has been deeply investigated. Photoactivity under visible irradiation has also been studied, such as in the case of porphyrins and phthalocyanines loaded TiO₂ powders. The samples are characterised by using several techniques as X-Ray diffraction, X-Ray photoelectron spectroscopy, specific surface area determination, scanning electron microscopy and energy dispersive X-Ray analyses. The present research activity in this field is being devoted to the improvement of some characteristics of the photocatalyst as the extension of the absorption to the visible range.

Reactivity of photocatalytic powders

The commercial and home-prepared photocatalysts have been subjected to reactivity tests, carried out by oxidising a probe molecule in liquid and in gas phase, in order to compare the efficiency of different samples in the same experimental conditions. Semiconductor powders have been used also to degrade, under mild conditions (room temperature and atmospheric pressure), pharmaceutical drugs and recalcitrant organic species, such as cyanuric acid and benzonitrile.

Immobilization of TiO₂ thin films over various materials

Recently many efforts have been made to prepare TiO₂ thin films, by immobilization through dip-coating of materials, such as glass slides or beads and various polymers (research developed with industry), in sol precursors of TiO₂, eventually obtaining the three phases of TiO₂, pure or in mixtures. The immobilization of TiO₂ in the form of a thin film significantly reduces some of the drawbacks of practical application of heterogeneous photocatalysis; for instance the need to separate the powder or the tendency of the particles to agglomerate in aqueous dispersions. Metal-loaded films have also been prepared to improve the absorption and hence the activity under visible irradiation.

Selective photocatalytic reactions

In these last years the research was interested to the study the applications of photocatalysis as a selective reaction route. In particular home prepared catalysts have been developed by a sol-gel route to improve the selectivity in partial oxidation, by decreasing the oxidising power of TiO₂. The preparation of these catalysts takes place at very low temperature and atmospheric pressure, the inexpensive TiCl₄ being the starting precursor. All the reactions were carried out in water.

Photocatalysis coupled to other technologies

Heterogeneous photocatalysis coupled with ozonation has been widely studied in the oxidation of various compounds, whereas electrochemical-assisted photocatalysis is being recently developed by our group.

Photoreactor modelling

The determination of absorbed photon flow can be used for determining the quantum yield value for the photocatalytic oxidation reactions. The modelling of a fixed bed photoreactor has been recently developed by studying the radiation field through the Monte Carlo algorithm. The catalyst present in the reactor was immobilised in Pyrex beads through a sol-gel process exploiting the hydrolysis of TiCl_4 .

Kinetics of heterogeneous photocatalytic reactions

The research has been involved in the study of the photodegradation kinetics of organic and inorganic compounds in aqueous or in gaseous medium. The rate of photo-oxidation of new substrates is studied by varying some operational parameters as: i) initial substrate concentration; ii) catalyst concentration; iii) initial pH; iv) irradiation power; v) oxygen concentration. The rate equations, the reaction pathways and the kinetic models determined from the experimental data can be used to predict the feasibility of the photoprocess. The general models used to interpret kinetic data is the Langmuir-Hinshelwood.