UNIVERSITÀ DI PISA

POLYMER SCIENCE AND ENGINEERING

GIUSEPPE CARMINE DOMENICO SAVIO GALLONE

Anno accademico	2021/22
CdS	MATERIALS AND NANOTECHNOLOGY
Codice	733II
CFU	6

Moduli	Settore/i	Tipo	Ore	Docente/i
POLYMER SCIENCE AND ENGINEERING	ING-IND/22	LEZIONI	48	GIUSEPPE CARMINE DOMENICO SAVIO GALLONE

Learning outcomes

Knowledge
The student who successfully completes the course:

- will be aware of the specific characteristics of the materials included into the class of polymers, particularly with respect to structure and properties;
- will acquire knowledge of both mechanisms for synthesizing polymeric materials and relevant industrial production and processing technologies;
- will acquire basic knowledge of the principal experimental techniques for characterizing physical-chemical properties of polymeric materials.

Assessment criteria of knowledge
The acquired knowledge will be assessed by means of:

- Final oral examination

the final exam is aimed at assessing the advancement level reached by the student in terms of knowledge, skills, behaviours.
During the assessment of knowledge the student will be assessed also on his/her demonstrated ability to discuss the course contents with critical awareness and with property of expression.

Skills
The student who successfully completes the course will be able to analyze and interpret experimental results from the principal characterization techniques (for ex. DSC, GPC, various spectroscopic methods) about polymeric materials and polymers in solutions.

Assessment criteria of skills
The acquired skills will be assessed by means of:

- Final oral examination

the final exam is aimed at assessing the advancement level reached by the student in terms of knowledge, skills, behaviors.

Concerning, in particular, the assessment of skills, the student must demonstrate his/her ability to put his/her knowledge into practice by solving the proposed problems/exercises.

Behaviors
The student who successfully completes the course will acquire perception of the importance of a correct selection of polymeric materials within a design task. Moreover, he/she will be able to analyze and correlate all the aspects concerning structure, properties and processing techniques of polymeric materials in order to make the proper choices within either a design task or other possible technological scenarios.

Assessment criteria of behaviors
The acquired behaviors will be assessed by means of:

- Final oral examination

the final exam is aimed at assessing the advancement level reached by the student in terms of knowledge, skills, behaviors.

Concerning, in particular, the assessment of behaviors, the student will be required to both make appropriate choices and justify them in the frame of a possible technological scenario where a proper selection of polymeric materials would be critical.

Prerequisites

For a fruitful attendance to the lessons and for the study of the arguments of the course, it is fundamental that the student possess a solid knowledge of:

- Linear algebra
- Mathematical analysis
- General physics
- Chemistry
- Thermodynamics

It is also suggested as a useful prerequisite that the student possess a base knowledge of the mechanical behavior of materials.

Teaching methods

- Teaching is delivered by face to face lectures with the aid of computer presentations and videos, the use of a blackboard and demonstrations by means of real models.
- It is possible to download from the web the presentations slides and the notes by the teacher on specific arguments.
- The teacher suggests an interaction based on face to face discussions during his office hours, both in the period of lectures and while preparing for exams.
- No intermediate tests are foreseen.
- The course is delivered in English language.

Syllabus

Introduction to the course.

- Subject, tentative program, goals.
- Introductory survey on the universe of polymers, classification in plastics and elastomers, recyclable and not recyclable polymers.
- Historical milestones of polymer science and engineering.

Basic review of general concepts in polymer science.

- Molecular structure, homo- and co-polymers, functionality of a monomer, possible skeletal configurations: linear, branched and crosslinked polymers.
- Classification of polymers as thermoplastics, elastomers and thermosets. Semi-crystalline and amorphous thermoplastics. Melting and glass transition.
- Survey on the typical values of properties (mechanical, electrical, density, thermal stability) of most employed thermoplastics, thermosets and elastomers.
- Deformation mechanisms acting in polymers at the microscopic scale and factors that influence the mechanical response. Viscoelasticity of polymers.
- Molecular weight, molar masses and degree of polymerization.

Generalities of step-growth polymerization.

- Linear step polycondensation and polyaddition reactions.
- Control of degree of polymerization in step-growth reactions: Carothers theory and statistical analysis.
- Kinetics of step polymerization and methods for controlling reactions.
- Network step polyaddition. Gelation: significance, problems in the quantitative definition of the gel-point, consequences at microscopic and macroscopic scales. Carothers theory and Flory theory of gelation.
- Brief mention about dendrimers and hyperbranched polymers.

Generalities of chain-growth polymerizations.

- Stages of a linear chain-growth polyaddition. Production of free radicals activators by thermolysis, photolysis and redox reactions. Propagation stage. Termination by combination and disproportionation. Termination by intra- and inter-molecular chain transfer.
- Kinetics of linear chain polyadditions and steady state conditions. Degree of polymerization. Diffusion constraints and diffusion controlled reactions. Autoacceleration. Effects of chain transfer. Molar mass distribution. Effects of temperature. Ceiling temperature.
- Industrial methods for polymerization: bulk, solution, suspension and emulsion processes.
- Network radical polymerization by crosslinking monomers.
- Network radical polymerization of unsaturated (pre-)polymers.

Thermodinamics of ideal solutions.

- Liquid lattice, Gibbs free-energy for mixing, configurational entropy.

- The Flory-Huggins theory and its limitations. Chemical potential.
- Dilute polymer solutions. The cohesive density approach for predictions of polymer solubility.
- Chain dimensions: the freely-jointed chain model, bond angle constraints and short-range steric restrictions, stiffness of a polymer chain. Long-range steric interactions and chains with excluded volume. Expansion parameters for the end-to-end distance and for the gyration radius of a polymer molecule coil.
- Frictional properties of polymers in solutions. Free-draining and non-draining regimes. Hydrodynamic volume and intrinsic viscosity of a polymer in solution in the non-draining limit: the Flory-Fox and the Mark-Houwink-Sakurada equations. Diffusion process in the non-draining limit. Behaviour of polyelectrolytes in solution.

Characterization of polymers at molecular level.

- Techniques for measuring the number average molar mass based on colligative effects. Membrane osmometry. Vapour pressure osmometry. Ebulliometry and cryoscopy. End-group analysis.
- Scattering methods for characterization of polymers: static light scattering by liquids and solutions of small molecules and scattering by large molecules in solution. Effect of molar mass dispersity. The Zimm-plot method for analysis of data. Dynamic light scattering. Photon correlation spectroscopy. Small-angle X-ray and neutron scattering. Purposes, limits and methods for SAXS and SANS analysis.

Measurement of frictional properties of polymers in solutions.

- Dilute solution viscometry. The intrinsic viscosity, the Huggins equation for the reduced viscosity and the Kraemer equation for the inherent viscosity.
- Determination of average molar mass and expansion parameter for polymer molecules in solutions.
- Use of capillary viscometers for measuring the relative viscosity of a polymer in solution.
- Differential viscometer.

Molar mass distribution.

- Fractionation of dilute Polymer Solutions by Phase-Separation.
- Gel permeation cromatography: separation by size exclusion, GPC calibration and data analysis, universal calibration for GPC. Porous gels and eluants for GPC. Instrumentation and procedures for GPC.
- Mass spectroscopy (MS). Mass spectra of polymers. ESI and MALDI methods for soft ionization. Time-of-flight (ToF) mass spectroscopy. Analysis of MALDI-TOF mass spectra of polymers. Use of MALDI MS for examining the chemical structure of polymers.

Spectroscopic methods for characterization of chemical composition and molecular microstructure of polymers.

- The principles of spectroscopy and the Lambert-Beer law.
- Principles of UV-vis spectroscopy, applications in polymer science, essential apparatus and experimental procedures.
- Principles of IR spectroscopy, applications in polymer science, apparatus and experimental procedures, interpretation of IR spectra.
- Principles of Raman spectroscopy, applications in polymer science, interpretation of Raman spectra. Brief mention about Raman microscopy.
- Principles of NMR spectroscopy, interpretation of NMR spectra, absorption splitting by J-coupling. Applications of NMR spectroscopy in polymer science.

The amorphous state of polymers.

- The glass transition and its characteristics. Free volume theories. Factors controlling Tg.
- Macromelucular dynamics in the amorphous state. The Rouse-Bueche theory. The de Gennes reptation theory.
- Different paths to a glass transition: cooling, compression, polymerization.

The crystalline state in polymers.

- Evidences and characteristics of polymer crystal structures. Crystals structures for most common polymers.
- Characteristics of crystals obtained from either dilute solutions, melt cooling or solid-state polymerization. Polymer single crystals. Lamellae and spherulites. Semi-crystalline polymers and determination of the degree of crystallinity. Crystal thickness. Oriented crystals and polymer fibres.
- Defects in polymer crystals.
- Kinetics and thermodynamics of crystallization.

Melting of crystalline polymers.

- Equilibrium melting temperature. Factors that influence melting of polymers. Effects on the melting temperature of crystal thickness, chemical structure, molar mass, branching, copolymerization, annealing.
- Relationship between Tm and Tg.
- Differential scanning calorimetry (DSC): traditional power-compensation and heat-flux apparatuses, experimental procedures and calibration. Qualitative and quantitative interpretation of DSC thermograms.
- Modulated-temperature DSC (MTDSC), separation of reversing and non-reversing thermal events. Crystal perfection before melting.

Elasticity of rubbers.

- Molecular structural requirements for a polymer to show elastomeric properties. Elastomers as entropic springs.
- Natural rubber. Vulcanization.
- Mechanical behaviour of elastomers. Thermodynamics of elastomer deformation. The thermoelastic inversion effects. Statistical theory of elastomer deformation. Effects of entanglements, loops and chain ends. Stress-strain behaviour of rubbers. Strain

induced crystallization.

Electrical properties of polymers.

- Survey on the variety of possible electrical properties within the class of polymeric materials. Brief review of the classical and the band models for current transport in conductors and semi-conductors.
- Inherently conducting polymers. Conjugated polymers and their molecular structure. The case of polyacetylene: structure, explanation of its conductivity, doping, polarons and solitons.
- Ionic conduction in polymers: electrophoresis of ionic species from ionomers or from impurities.
- Electrical properties of insulating matrix/conducting fillers composites. Percolative behaviour of the electrical conductivity. Factors influencing the critical value of the filler volume fraction.
- Polymers as insulators: the dielectric breakdown phenomenon and the dielectric strength of polymers.
- Polymer dielectrics: the different mechanisms of electric polarization occurring in polymers, behaviour under time varying electric fields, the complex dielectric permittivity and the dielectric spectrum. Dielectric relaxation processes and models for their description.
- Dielectric spectroscopy methods for measuring and analysing the complex permittivity spectrum.
- Dielectric spectrum of a glass former: recognizable patterns in the behaviour of dielectric constant and loss factor; multiple relaxations, dielectric parameters, ionic conduction.
- Discussion about the influence of temperature on the spectra and on the dielectric parameters of a supercooled glass former.
- Evolution of the dielectric spectra and of the dielectric parameters in time-varying systems: the case of polymerization reactions.
- Dielectric analysis of chemically, thermally and mechanically induced glass transition: differences, analogies and attempts for a unified description of the glass transition.
- Microwave heating.

Processing of polymers.

- Principles of the techniques for processing of polymers.
- Flow properties of polymer melts: bulk deformation, elongational flow (tension stiffening and tension thinning), shear flow (shear thinning). Melt flow index. Apparent viscosity as a function of temperature and molar mass. Viscoelasticity of molten polymers and swell ratio.
- Cooling and solidification of polymer melts.
- Extrusion. Injection moulding. Thermoforming. Blow moulding. Compression moulding. Transfer moulding.

Bibliography

Recommended readings include the following works:

- R.J. Young, P.A. Lovell, Introduction to Polymers 3rd ed., CRC Press.;
- N.G. McCrum, C.P. Buckley, C.B. Bucknall, Principles of Polymer Engineering 2nd ed., Oxford Science Publications;
- Notes provided from the lecturer concerning specific arguments of the course.

Further readings can be proposed during the course.

Assessment methods

The final exam is composed of a final oral examination which has a duration averaging between 40 and 60 minutes. During the oral exam the student can be also required to solve open questions/exercises/problems. The student will be assessed on his/her demonstrated ability to discuss the course contents with critical awareness and with property of expression by starting from problems/exercises/questions proposed by the exam commission. The oral test is not passed if the candidate demonstrates to not be able to express him/her-self in a clean and proper language and if the candidate does not correctly answer at least to those questions concerning the very basic parts of the course.

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