Polymer Analysis

Chapter 1. Introduction/Overview

The focus of this course is analysis and characterization of polymers and plastics. Analysis of polymeric systems is essentially a subtopic of the field of chemical analysis of organic materials. Because of this, spectroscopic techniques commonly used by organic chemists are at the heart of Polymer Analysis, e.g. infra-red (IR) spectroscopy, Raman spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and to some extent ultra-violet/visible (UV/Vis) spectroscopy. In addition, since most polymeric materials are used in the solid state, traditional characterization techniques aimed at the solid state are often encountered, x-ray diffraction, optical and electron microscopy as well as thermal analysis. Unique to polymeric materials are analytic techniques which focus on viscoelastic properties, specifically, dynamic mechanical testing. Additionally, techniques aimed at determination of colloidal scale structure such as chain structure and molecular weight for high molecular weight materials are somewhat unique to polymeric materials, i.e. gel permeation chromatography, small angle scattering (SAS) and various other techniques for the determination of colloidal scale structure. The textbook, Polymer Characterization covers all of these analytic techniques and can serve as a reference for a general introduction to the analysis of polymeric systems. Due to time constraints we can only cover a small number of analytic techniques important to polymers in this course and these are outlined in the syllabus.

Structure/Processing/Property:

Generally people resort to analytic techniques when confronted with a problem which involves understanding the relationship between properties of a processed material and the structure and chemical composition of the system. Plastics are typically complex morphological systems being composed of many phases and additives, even the polymer itself being disperse in molecular weight, tacticity, crystallinity, orientation and sometimes chemical composition. Dispersion of structure and chemical composition means that the best tools to describe polymeric materials are always statistical in nature. For example, a low molecular weight organic has a specific melting point, while a polymer displays a range of melting with an onset, a peak and a maximum melting temperature. Such a melting spectrum might best be described by a Gaussian function with a standard deviation and mean. Additionally, the complication of enormous macromolecular chains means that simplified descriptions are often needed to characterize polymeric materials, for example group contribution methods in spectroscopy where the chain structure is decomposed into chemical groups which contribute to the absorption spectrum. A detailed understanding of many of the analytic descriptions of polymeric materials is often precluded by the complexity of the situation.

Analytic Techniques:

All analytic techniques used in polymer characterization are based on specific physical principles which serve as a guide to understanding the basic limitations of the techniques. Often multiple techniques are available to describe the same property of a material and it is only through understanding the physical basis of characterization techniques that one can pick the **"right tool for the job"**, the job being understanding the relationship between structure and chemical composition and properties. For example, it is often found that blown films of polyethylene display different tear strengths in the machine and transverse directions. This can lead to failure of parts made from blown films such as plastic bags. It is often assumed that this directional nature of the tear strength is related to orientation induced by processing of these plastics. There are several analytic techniques available to describe orientation. These include construction of pole-figures from x-ray diffraction scans, calculation of orientation functions from XRD data, calculation of orientation functions from IR, NMR or Raman data, and measurement of the optical birefringence for the blown films using polarized light. *Each of these techniques will yield a different value for the orientation function!*

Similarly, even the value for the degree of crystallinity in these blown films will depend on the technique which is used, i.e. XRD, differential scanning calorimetry, density, or IR for example. This makes a firm understanding of the physical basis of analytic techniques critical to their application in polymeric systems.

Levels of Structure:

The analytic description of a complex material is strongly dependent on the size scale on which an observation is made. For example, a semi-crystalline polymer such as polyethylene is composed of chemical units similar to olefinic waxes. These chemical units give rise to spectroscopic absorption patterns which are largely indistinguishable from their lower molecular weight counterparts. Similarly, the crystalline structure, which is usually of low symmetry in polymers, mimics the crystalline structure seen in lower molecular weight analogues such as waxes.

The monomer structure combined with the topological arrangement of monomers in a polymer chain give rise to helical coiling of polymer chains. This helical coiling and the weak chemical associations related to it give rise to some mechanical and vibrational features which can often be observed spectroscopically. Generally, the helical coiling of monomers in a chain are evidenced by colloidal scale structure, chain persistence (local linearity) and enhancement of the ability of long chain polymers to crystallize. NMR is a technique particularly suited for the characterization of the topological arrangement of monomers in a chain (i.e. tacticity).

In polyethylene, local chain structure is sufficiently regular to give rise to a crystalline phase. Entanglement of chains, chain branching and the presence of endgroups prevents complete crystallization of a polymer. Polymeric materials which display crystallinity are always described by a multi-phase model, i.e. semicrystalline, which includes an amorphous and crystalline phase in coexistence. Low transport coefficients and chain folding give rise to nano-scale crystallites which are best observed by TEM, small-angle x-ray scattering (SAXS) and to some extent by Raman spectroscopy (Longitudinal Acoustic Modes, LAM).

Fibrillar crystallites in polymers lead to colloidal to optical scale structures, spherulites, which are generally centro-symetric and which display radially oriented birefringence. These micron scale structures are best observed using optical microscopy, SEM, small-angle light scattering (SALS) and give rise to certain features in the mechanical and transport properties of semi-crystalline polymers.

Thus, is one in interested in a specific analytic feature of a processing operation such as film blowing on a polymeric material such as high density polyethylene (HDPE), one is immediately faced with the issue of structural level, i.e. for transport properties one might need to characterize the orientation of chains or crystallites (lamellae), for mechanical properties, orientation of spherulites and the amorphous component of these biphase materials. Additionally, it is expected that any analytic determination of these materials will be subject to a large range of statistical variation between samples as well as an innate distribution associated with the polydispersity of the material of itself.

Course Contents:

Statistics:

All properties of polymeric systems display dispersion due to 1) the limited ability of synthetic chemistry to produce monodisperse and perfect chemical structure as well as 2) the dominance of kinetics in processing of high molecular weight materials. Statistical analysis is critical to understanding and describing plastics. This course begins with a survey of the important tools to describe statistically distributed systems which includes the major distribution functions and mathematical descriptions of the propagation of error in data sets. Analytic descriptions of polymers are of no use unless some description of the expected error associated with the analytic results are presented.

Thermal and Mechanical Testing:

Thermal analysis is useful in describing solid state transitions in polymers and is of pivotal importance to understanding mechanical properties and processing of plastics. The measurement of the glass transition and crystalline transitions using typical analytic techniques will be discussed. Polymeric systems are dominated by kinetics and this is emphasized in the use of dynamic mechanical, thermal analysis techniques to describe mechanical absorption phenomena associated with the glass transition and other mechanical transitions.

Absorption Spectroscopy:

The major techniques for the determination of chemical composition and molecular topology involve the absorption of electro-magnetic radiation by polymers. The major techniques are IR, Raman, and NMR spectroscopy and the bulk of this course will involve these major analytic techniques. Absorption is a quantized inelastic phenomena involving the transfer of energy from EM radiation to a material.

Diffraction and Scattering:

In addition to inelastic absorption phenomena, elastic interaction between EM radiation and a material is possible and this gives rise to diffraction and scattering phenomena. The small crystallite size and dominance of crystalline orientation in processed plastics lead to several unique analytic approaches in the analysis of x-ray diffraction data in these materials. The focus in this course will be on those tools used in diffraction which are specific to polymeric materials.

Small-angle x-ray scattering is a critical technique for the description of polymeric materials since diffraction at small angles is associated with the colloidal to nano-scales which is the size range of a typical polymer chain. The colloidal scale is also associated with polymer crystallites (lamellae) and microphase separated block copolymer structures. Further, light scattering has been widely used in polymer science to describe disordered micron scale structure as well as a primary technique for the determination of molecular weight from dilute solutions.