PAS : A Tool to Probe Complex Polymer Structures

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Abstract

The discovery that the annihilation characteristics of positrons and positronium (Ps), such as lifetime and energy, contain information about electronic properties within molecules and solids led to the development of Positron Annihilation Spectroscopy (PAS). PAS has emerged as a powerful tool for determining atomic and molecular defects and interfacial properties of a wide variety of materials. PAS is still in the early stages of development in terms of methodologies and technological applications. In recent years, PAS has been successfully used to determine the free volume, void and layer properties in polymeric systems. The basic principle of using PAS in polymers is based on the fact that the positron and Ps are preferentially localized in pre-existing defects, including, free volume (~ 0.1 to 1 nm) and voids (<1 nm). In the amorphous phase, a polymer contains hole free volume, which appears in the form of many irregularly shaped local free volume elements of atomic and molecular dimensions which arise because of disordered molecular packing. Only limited experimental information about the holefree volume and its microstructure is available in the literature.The free volume concept is one of the most fascinating theories to understand the physical properties of polymers and has provided a key construct to polymer scientists for understanding structure-property relationships in polymers.Despite the importance of free volume only limited experimental data has been reported about free volume of polymers, mainly due to lack of suitable probe for sub-nanometer molecular dimensions in the short time scale of many dynamic motions Recently, estimation of free volumes in polymers has been made possible using molecular simulations.

Porosity is a profound, yet, ubiquitous concept that is inherent to many materials, both, natural and synthetic. Biomaterials (skin, alveoli in the lungs), inorganic frameworks (zeolites, carbon, silica, clay), organic frameworks (supramolecular assemblies), plant materials (bamboo) and synthetic polymer membranes (water desalination membrane, kidney dialysis membrane, gas separation membranes) are all notable for their exquisite porous architectures, which are critical to its structure and functions. Porosity in polymers can be created either during its synthesis (generally called, polymers with intrinsic porosities) or by modifying pre-formed polymers using techniques, such as, phase inversion, templating with inorganic nanoparticles, self-assembly and electrospinning. Depending on the method employed, it is possible to generate micro- , meso– or macroporous polymers.

This lecture will provide an overview of the application of PAS to the study of dynamics of polymers as well as intrinsic porosity in polymers.The scope and limitations of the technique will be discussed