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Review

Role of free volume characteristics of polymer matrix in bulk physical properties of polymer nanocomposites: A review of positron annihilation lifetime studies

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Polymer nanocomposites which have one or more nano-dimensional phases dispersed in polymer matrix show enhancement in bulk physical properties. In order to achieve the desired properties, a large number of polymer nanocomposites have been prepared by choosing different polymers and nanofillers. These studies showed that interfacial interaction between polymer molecules and nanofillers is the most important factor to achieve the synergistic effect towards enhancement in the bulk physical properties. The strong interfacial interaction also promotes the fine dispersion of nanofillers in a polymer matrix which consequently enables the preparation of polymer nanocomposites with higher loading of nanofillers. The polymer matrix constitutes a large volume fraction of polymer nanocomposites and hence the molecular packing of the polymer matrix itself plays a deterministic role in governing the physical properties of the nanocomposites. The strong interfacial interaction brings severe changes in the original molecular packing. In order to establish the structure-property relationships for polymer nanocomposites, characterization of molecular packing of polymer matrix in its nanocomposites is essential. In this aspect positron annihilation lifetime spectroscopy (PALS) is a highly suitable technique for characterization of free volume holes in polymers or polymer nanocomposites. The present review briefly describes the positron annihilation lifetime spectroscopy technique and relevant models for calculations of free volume hole's size, density and their size distribution in polymer nanocomposites. We present a summary of the recent studies focussed on investigation of free volume structure (molecular packing) of polymer nanocomposites using PALS and its impact on transport, thermal and mechanical properties of the nanocomposites.

Contents

Abbreviations: PALS, positron annihilation lifetime spectroscopy; PNCs, polymer nanocomposites; DMA, dynamical mechanical analysis; XRD, X-ray diffraction; DSC, differential scanning calorimetry; SANS, small angle neutron scattering; PMTs, photomultiplier tubes; CFDD, constant fraction differential discriminator; TAC, time to amplitude converter; SCA, single channel analyzer; MCA, multi-channel analyzer; PVA, polyvinyl alcohol; FFV, fractional free volume; PMP, poly (4-methyl-2-pentyl); fMWCNTs, functionalized multiwall carbon nanotubes; SEM, scanning electron microscopy; EVA, poly (ethyl-co-vinyl acetate); TGA, thermal gravimetric analysis; GO, graphene oxide; r-GO, reduced graphene oxide.

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1. Introduction

Polymer nanocomposites (PNCs) are hybrid materials consisting of one or more nano dimensional phases distributed in polymer matrices [1]. Various types of nano-fillers such as carbon based (nanodiamonds [2–7], nanotubes [8–24], reduced graphene and graphene oxide [25–42]), metal or metal oxide nanoparticles [43–52], double layered hydroxide [53–62], clays [63–73] and silica [74–86] have been used for preparation of PNCs with a variety of polymer matrices. The bulk physical properties of PNCs such as electrical [87–94], mechanical [95–106], thermal [107–113] and transport [114–120] properties are shown to be superior compared to the pure polymer matrix. In the case of PNCs, visoelastic properties of the polymer matrix are combined with the hardness of the nano-fillers resulting in variation of the bulk physical properties. It is shown in literature that enhancement in the bulk physical properties of a PNC mainly depends on (i) type and loading of the nanofiller (ii) dispersion of the nanofiller in the polymer matrix and (iii) interfacial interaction between polymer matrix and nano-filler particles. [3,4,6,7,15,28,29,32,33,37,54,64,68,70,76,87,85,101] Various studies have been carried out to investigate the role of these parameters on the bulk properties such as thermal [107,110,113], mechanical [98–102,105], electrical [87,88,91] and transport [114,115,120] etc. It has been shown that ultimate properties can be achieved by loading a higher amount of nanofillers without its aggregation in the polymer matrix. In order to minimize the aggregation at higher loadings, a strong interfacial interaction between polymer matrix and nanofiller is highly desirable [24,121]. Hence, it has been concluded that a strong interfacial interaction e.g. hydrogen bonding or covalent bonding is vital for preparation of PNCs having enhanced bulk physical properties. In addition to the improvement in dispersion of the nanofiller, the interfacial interaction between polymer matrix and nanofillers slows down the polymer chain dynamics in the vicinity of nanofillers resulting in the modified thermal as well as transport properties of PNCs [107,110–112,114]. The strong interfacial interactions between polymer molecules and nanofillers also permit an efficient load transfer from polymer matrix to the nanofillers leading to an enhancement in mechanical properties [98–101,111].

In order to establish a structure-property relationship for PNCs, main focus has remained on the factors which affect the nanoscopic fillers' morphology in the polymer matrix whereas limited attention has been given to the second ingredient i.e. polymer matrix itself. Polymer matrix constitutes a large volume fraction of PNCs and its microscopic structure is equally important for understanding the structure-property relationship of PNCs [86]. Various techniques such as X-ray and neutron scattering [86,122–124], electron microscopy [125], dynamical mechanical analysis (DMA) [97], X-ray diffraction (XRD) [111,112] and differential scanning calorimetry (DSC) [102,111,112] etc. are employed to characterize the structure of polymer matrix at different length scales in PNCs. These techniques infer the changes in the polymer structure in an indirect way. For example, any change in glass transition temperature of polymer matrix in its PNCs measured using DSC is correlated to the changes in polymer structure. In some cases, a special method is required for the sample preparation. For example, radius of gyration of polymer chains is measured using the small angle neutron scattering (SANS) by mixing the hydrogenated and deuteriated polymer chains under the zero average contrast condition [86]. In this regard, positron annihilation lifetime spectroscopy (PALS) is a highly suitable technique to investigate the free volume characteristics i.e. size of free volumes, their density and size distribution (an index of molecular packing) of a polymer matrix [126–131]. Studies of PNCs have confirmed that PALS can be efficiently used for monitoring the changes in size, density and size distribution of free volumes [132–134]. In the recent years, considerable efforts have been made for the measurements of free volume characteristics of various PNCs with the aim of studying its role on transport, thermal and mechanical properties [135–139]. These studies have shown significant changes in the free volume characteristics of PNCs depending on the amount and dispersion of the nanofillers. The free volume characteristics were also shown to be highly dependent on the interfacial interaction between polymer matrix and nanofillers. These studies have confirmed that in addition to morphology of dispersed nanofillers, understanding of molecular packing of polymer matrix is equally important for the establishment of structure-property relationship of PNCs.

In the present review, we describe the basics of positron annihilation lifetime spectroscopy along with the relevant models used for the calculations of free volume size, density and size distribution. Following this, we discuss the findings from the recent studies on free volume characteristics using PALS and their role in bulk physical properties of PNCs.

2. Positron annihilation lifetime spectroscopy (PALS)

Positron being antiparticle of electron annihilates with a certain lifetime in materials emitting two or three gamma photons depending on the spin orientations of annihilating electron-positron pair. The positron lifetime in a material (inverse of annihilation rate) depends on the electron density of the material. In case of polymers, in addition to the free positron annihilation, thermalized positron combines with an electron to form a bound state (binding energy = 6.8 eV) called positronium, Ps, atom. The ground state of Ps can exist either as triplet or singlet form depending on the spin orientations of positron and electron. The intrinsic lifetimes of triplet (*ortho*), *o*-Ps, and singlet (*para*) *p*-Ps states are 142 ns and 0.125 ns, respectively. The formation rate of *o*-Ps is three times of the singlet state i.e. *p*-Ps. *o*-Ps during its lifetime interacts with the surrounding material that causes the changes in its lifetime. Hence, *o*-Ps is used as a probe to characterize the local structure of materials.

On implantation of positrons from a radioactive source e.g. ^{22}Na into the polymeric materials, a significant fraction of positrons is converted to Ps. The formation probability of Ps depends on free volume holes density as well as the functional groups presents in the polymeric backbone. The chemical groups with highly electronegative or electropositive character may influence the Ps formation by scavenging either positron or electron from the electron-positron pair. This process is known as *inhibition* of positronium formation. In absence of *inhibition* process, the Ps formation in polymers is directly correlated to the free volume holes' density. A Ps atom in