STUDY OF THE DOPPLER BROADENING SPECTROSCOPY IN PMMA AFTER DOPING WITH MWNT

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ABSTRACT
Doppler broadening of annihilation radiation in PMMA/MWNT, using $^{22}$Na as a positron source, were performed to study pure Poly methail methaacrylic acid (PMMA) and doped PMMA with different concentration of MWNT(multiwall carbon nanotube). MWNT/PMMA nanocomposites membranes have been prepared by dispersing different concentration (wt% - 0.1, 0.3 and 0.5%) of multiwall carbon nanotubes (MWNT) in Poly methyl methaacrylate (PMMA) matrix using benzene as a solvent. The S –W parameter was measured for as a function of the relative weight used in the samples. The behaviour of the S-W parameter was analysed in terms of positron annihilation and positronium formation for the various samples. Results show direct correlations between these parameter and the various physical characteristics of Carbon nanotube.

Keywords- MWNT, PMMA nanocomposites, Positron annihilation, Parameters, Doppler broadening.

INTRODUCTION
Polymer have been widely used in our daily life and industrial areas not only traditional material such as wood, stone, glass, natural fabrics and metals, but they also become indispensable factor to a break through in up-to-date-technologies. The need for more so-phisticated polymeric material for the intended applications drive many researches to enhance the macroscopic properties of polymer product[1-4]. Polymer in their pure state are excellent electrical insulators, but they can be modified to be relatively semiconductors or good electrical conductors. Electrical conductivity in polymers can be improved by adding conductive materials such as metals, metal oxides, and metal salt to form a conductive polymer. The conductive polymer are presently of great interest because they offer the promise of combining metallic and semiconducting characteristics[5-10].

Important properties of solids depend on both their electronic and defect structure[11]. Therefore, an experimental and theoretical estimation of these structures is a major task of material science. The positron is a relevant atomic probe, as its resulting gamma photons carry information about the localization sites of the probe and about the electrons of the solid under investigation. Positron get trapped in open-volume defect until they annihilate and exhibit a specific sensitivity to these type of defect[12-20]. Thus positron annihilation spectroscopy has found increasing interest and growing application for studying polymeric materials. All methods of positron annihilation spectroscopy(PAS), i.e. Life time (LT), Angular Correlation of the Annihilation Radiation (ACAR) and Doppler Broadning (DB) are suited to reveal electronic and structural properties of a solids[21-27].
DOPPLER BROADENING SPECTROSCOPY

Doppler broadening study of positron-electron annihilation radiation is an important tool in the field of materials science [28-32]. Doppler broadening of annihilation radiation provides a sensitive method of defect characterization by measuring the momentum distribution of the electrons. In molecular materials, the positron preferentially forms and annihilates from a bound state called positronium (Ps) atom. The Ps forms either in the so-called para (antiparallel electron and positron spins: p-Ps) or ortho electron and positron spins: o-Ps positronium states. Positron annihilation is an experimental method by which one can obtain the microstructure, momentum of electron and defect behavior of condensed matter. The positron annihilation technique has been extensively applied in areas of polymers, solid physics, chemistry, medicine and material science and so on. The emerging gamma photon produced by the annihilation of thermal positron with electrons provide information of both momentum distribution and the electron density of materials, the related spectrum can be used to study the microstructure of materials. The width of the gamma ray annihilation spectrum depends on Doppler broadening effects and reflects the momentum distribution of the electron with which the positron annihilate. The Doppler effect describes how the frequency of a wave emitted from a moving source changes according to the relative motion between the source and the observer. Since the gamma photons emitted from Ps annihilations behave as waves, they also exhibit the Doppler Effect. The final energy spectra consist of the sum of the individual shifts from much annihilation, so the energy peak is broad [33-34]. Fig (1) shows the Doppler broadened peak resulting from the moving Ps.

The Doppler broadening spectroscopy has been widely applied to study metals and polymers in the form of S- and W- parameters. The S- and W- parameters are defined as the ratio of low momentum region and high momentum region in the DBAR spectrum to the total region. It is accepted to present the DBAR result as a ratio of the area-normalized counts in each channel of the measured DBAR spectrum to the corresponding counts from a reference spectrum. The choice of the reference spectrum is of great importance for a correct interpretation of the result. The Doppler-broadening spectrum demonstrates in Fig.(2). The S and W parameters are expressed as:

\[ S = \frac{A_s}{A_o} \]
\[ W = \frac{A_w}{A_o} \]

where

\( A_s \): the area of the central low-momentum part of the spectrum.

\( A_w \): the area in the high-momentum region far from the center.

\( A_o \): the area below the whole curve.

EXPERIMENTAL Materials

The PMMA (Poly methyl methaacrylate) having molecular weight 114.14 gm/mol was purchased from Gadra Plastic Polymer Pvt. Ltd., Bharuch, Gujrat, India. MWNT (~10-30 nm diameter, 1-2 μm length) were acquired from Helix material solution, Richardson, TX. Benzene was used as a solvent.

Synthesis of PMMA/MWNT Nanocomposites

PMMA/MWNT nanocomposite with thickness 200 μm was prepared using a simple solution casting method. To prepare nanocomposite, first granular PMMA was dissolved in benzene using magnetic stirrer and then MWNTs were dispersed in this Poly-meric solution using an ultrasonication (220W, 20 kHz) for 1 h. Solution casting
was completed by pouring the solution on flat bottom Petri dishes floating on mercury. The nanocomposites of PMMA/MWNT with different concentrations of MWNTs (wt% - 0.1, 0.3 and 0.5%) are allowed to prepare until the placed MWNT in PMMA is suspended and benzene as a solvent is completely evaporated. Fig 3 show the MWNT/PMMA nanocomposites.

**Doppler Broadening Spectroscopy**

The Doppler Broadening Spectroscopy were carried out using high purity Germanium detector. The energy resolution of detector was calibrated to be 1.1 Kev (Full width at half maximum, FWHM) at 511 Kev gamma line of $^{22}$Na and the channel width was 0.192 Kev. The positron source was set at a distance of 20cm away from detector. Signals from the detector were fed into a multichannel analyzer (MCA). The DBAR data were recorded for 24 h resulting in total counts of at least $10^4$ at room temperature. Fig. 3 show the block diagram of Doppler broadening spectroscopy.

The Doppler broadening line-shape parameters were measured for PMMA/MWNT samples of different MWNT concentration (0.1%, 0.3%, 0.5% and 0.7%). The Doppler broadening line-shape S and W-parameters are calculated using SP ver. 1.0 program which designed to automatically analyze of the positron annihilation line. The most important is to determine the channel with the maximum which is associated with the energy 511 keV. The maximum is necessary because it is a base for definition of the regions for calculations of S- and W-parameters. The motion of the annihilating pair causes a Doppler shift of this energy[6].

$$\Delta E_\gamma = \frac{1}{2} c p_z$$

where $p_z$ is the longitudinal momentum component of the pair in the direction of the annihilation gamma emission. This causes the broadening of the 511keV annihilation line. Fig.5 shows the DBAR spectrum for pure PMMA. The measured Doppler-broadening spectrum in a certain material is generally assumed to be well approximated by a single Gaussian distribution convoluted with the base line function (B.L). Therefore the S and W parameters can be calculated for each spectrum. Fig. (2) shows the Doppler – broadening spectrum.

**RESULTS AND DISCUSSIONS**

Fig 4 shown the DBAR spectrum for pure PMMA and for different concentration of MWNT on PMMA with respect to pure PMMA. It is clear from fig.5 that peak height increase after doping with MWNT in pmma compare to pure pmma. This is a good agreement with the information that the DBAR can identify the chemical environment where the positron is trapped because the core $e^-$ are tightly bound to the nuclei and are almost unaffected by the chemical bonding and crystal structure.

Figure 6 & 7 shows the calculated values of the S- and W-parameters as a function of the MWNT concentration on PMMA. The S-parameter decreases with increasing the MWNT concentration that is due to decreasing the positronium fraction corresponding to decreasing the o-Ps intensity as presented by Mohamed et al. On the other hand, the increase in the W-parameter is due to increasing of positrons annihilate at the MWNT.

The S–W plot for pure and doped PMMA with different concentrations of MWNT is shown in Figure 8. Polymers usually have poor resistance to abrasive sliding attack because of their relatively low levels of hardness and strength, high plasticity, and low thermal conductivity. Fillers will certainly improve these properties therefore promote the hardness. The mechanisms revealing how fillers improve hardness are
not well established. There appear to be two broad explanations. One of them stems from the observation that excess filler concentration is noticed on the composite surface after prolonged sliding. Based on this observation the bulk of the load is supported by the concentrated filler resulting in increased hardness of the composite. The second suggestion is that fillers may improve the adhesion of the transfer film to the counter face and thereby suppress the hardness. While the first explanation might be accepted easily by common sense, the second is complicated. it is considered to be either physical or chemical in nature. Physical interaction involves van der Waals forces and is comparable in strength with the forces between molecular chains within the polymer itself. Increasing the MWNT concentration on PMMA leads to increase the hardness and increase the W parameter as a result of increasing the chemical composite in the samples (increasing the positron annihilating at MWNT). This correlation also has two different slopes that depend on the hardness of the samples (i.e., mwnt concentration on PMMA). Fig. 6 shows the S parameter as a function of % of MWNT. The pure polymer has an S value of 0.5232, with an experimental error of 0.0011. For all fillers S decreases with increasing wt.% of MWNT. This is mainly due to a decrease in positronium formation. The S and W parameters can both be described as a linear combination of the bulk- and defect-related sites.

CONCLUSION

The results presented here demonstrate that Doppler broadening positron annihilation spectroscopy can discriminate fillers used, Multiwall Carbon nanotube. We show in Fig. 6 that the S parameter decreases with the filler. This shows how the free volume measured by DBS changes with the filler added. In Figs. 8 we show the relationship between the positron annihilation of the core and valence electrons for the fillers and samples used.

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REFERENCES

2. J. Wang1, V. O. Jobando1,2, and C. A. Quarles, Materials Science Forum 607,186 (2009)
Shilpa vijay

Study of the Doppler Broadening Spectroscopy in Poly methyl methaacrylic acid (PMMA) after doping with MWNT

Fig.(1): Doppler broadened peak

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Fig. (2): Doppler broadening spectra. The lineshape parameters S and W are determined by the indicated areas AS and AW divided by the area below the whole curve
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Study of the Doppler Broadening Spectroscopy in Poly methail methaacrylic acid (PMMA) after doping with MWNT

Fig. 3: Block diagram of HPGe-detector and electronics for Doppler broadening line shape measurements
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Fig 4 DBAR spectrum of pure PMMA.
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Fig. 5 DBAR spectrum of for pure pmma and dopped PMMA with different concentration of MWNT

![DBAR spectrum for pure PMMA and dopped PMMA with different concentration of MWNT](image)
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Study of the Doppler Broadening Spectroscopy in Poly methail methaacrylic acid (PMMA) after doping with MWNT

Fig. 6 S -Parameter as a function of MWNT concentration on PMMA various sample.
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Fig. 7 W -Parameter as a function of MWNT concentration on PMMA various sample.
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Fig 8 The S-W plots for different sample