

A CONVERSION ELECTRON MÖSSBAUER SPECTROSCOPY STUDY OF ION BEAM MIXING AT Fe: POLYETHYLENE INTERFACE

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The effects of ion beam induced atomic mixing at the Fe-Polyethylene interface have been investigated by means of conversion electron Mössbauer spectroscopy [CEMS]. It is shown that the as deposited and ion beam mixed composites exhibit distinctly different features. In particular, the ion beam mixed composite shows the presence of Fe²⁺ state in polyethylene matrix along with the Fe-C austenite like phase.

1. INTRODUCTION :

In recent years there is a rapid growth of polymer science from the point of view of applications. Polymeric materials are used in number of applications such as adhesive coatings, electrical and thermal insulations, moisture barriers etc. /1-5/. In addition to these conventional applications, the polymers are found to be potentially useful in the solar technology. Surface processing and modification of polymers is a new emerging trend and very interesting results have been reported by irradiating the high energy ion beam on polymers /1-3/. The fact that polymers undergo dissociation and those atoms which form volatile species are selectively depleted from the polymer surface can be utilised in producing useful inorganic composites by ion bombardment of polymers. Recently, synthesis of novel inorganic films was attempted by using ion-polymer film interaction and the formation of Si-C bond was reported /1/. Ion beam mixing /6/ is yet another method to obtain novel metastable phases. In this paper, we demonstrate the potential use of ion beam induced reactions to synthesize useful materials. This, to our knowledge, is the first study of its nature in the context of ion beam modification of materials. We have chosen Fe:polyethylene system and the ion beam induced microstructural changes are characterised by using conversion electron Mössbauer probe /7/.

2. EXPERIMENTAL :

Polyethylene [PE] substrates were coated with $\sim 230 \text{ \AA}$ thick iron overlayer containing 30% of Fe⁵⁷ isotope by vacuum evaporation at a background pressure of 10^{-6} torr. Care was taken to avoid the heating of the substrates during the deposition. The evaporation unit was equipped with foreline traps [molecular sieves] and liquid nitrogen traps to avoid contamination. A number of such freshly prepared composites were subjected to 80 keV Ar⁺ ion bombardment to induce ion beam mixing. The ion doses in the range between 1×10^{15} and 1×10^{16} ions/cm² were employed. The process of ion implantation was carried out using a machine fabricated in our laboratory /8/. During the ion bombardment the pyrolysis of the polyethylene substrate was avoided by maintaining the ion current in the range 0.1-0.2 $\mu\text{A}/\text{cm}^2$. Room temperature conversion electron Mössbauer spectra were recorded for as-deposited Fe:Polyethylene composite as well as the ion beam mixed composite using the standard Mössbauer spectrometer with gas flow proportional detector. The source used was Co⁵⁷:Rh with 50 mCi strength. Experimental Mössbauer curves were least square fitted using MOSFIT programme /9/. Wherever necessary, the composite Mössbauer spectra were deconvoluted following the procedure by G. Le Caer et al./10/ to obtain information regarding the distribution of quadrupole interaction.

3. RESULTS AND DISCUSSION :

Fig.1(a) shows the conversion electron Mössbauer (CEMS) spectrum of the as-deposited Fe:Polyethylene composite. The specimen was subsequently bombarded with different ion doses. The corresponding CEMS spectra are presented in Figs.1(b)-1(e). The distribution of quadrupole interaction [P(QS)] associated with each of these spectra is presented in Figs.1(f)-1(j). The best fit CEMS spectrum of the as-deposited sample comprises of a broad doublet with an isomer shift of 0.39 mm/sec [with respect to α -Fe] and quadrupole interaction of 0.78 mm/sec. The typical nature of the hyperfine interaction indicates the presence of Fe^{3+} state

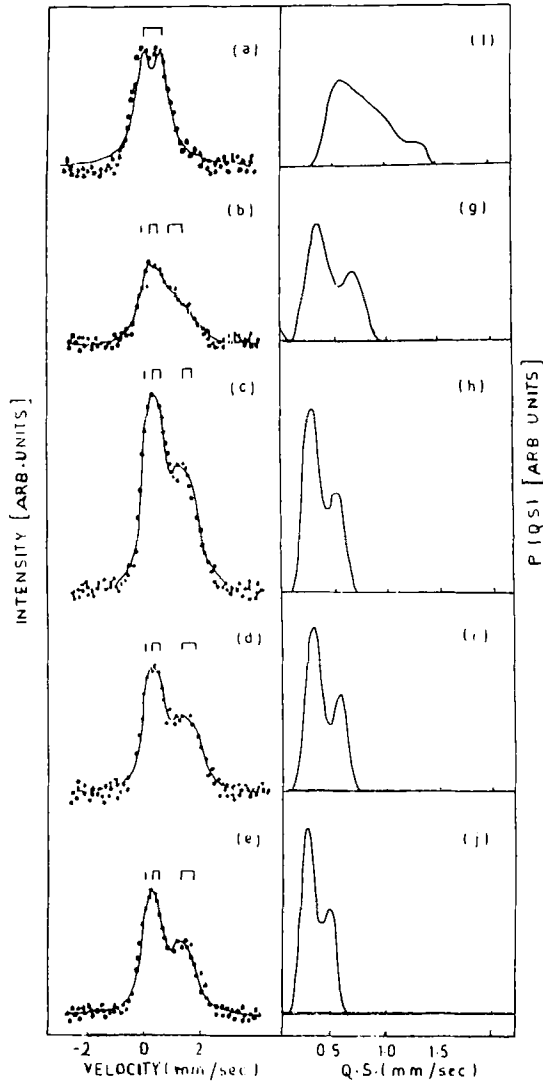


Fig.1 : Room temperature CEMS spectra and the corresponding P(QS) distributions of Fe:Polyethylene composite at various ion doses.

in the as-deposited sample. Similar result was observed in the case of iron doped polymers presumably due to the superparamagnetic behavior of Fe incorporated in the polymer chain /11,12/. The notable feature of this doublet is the broadening of the resonance lines and it can be attributed to the distribution of non-equivalent Fe sites in the polyethylene matrix. The quadrupole interaction distribution curve [Fig.1(f)] also shows clearly the variation in the electric field gradient [efg] due to slightly different bond lengths and angles of Fe³⁺ ions.

Upon ion bombardment with 80 keV Ar⁺ ions at a dose of 1×10^{15} ions/cm², the nature of CEMS spectrum [Fig.1(b)] shows a drastic change. It is clearly seen that the ion beam mixing leads to the growth of entirely different non-magnetic components. The CEMS spectra contain a singlet with small isomer shift and two doublets. The singlet along with the doublet having isomer shift 0.36 mm/sec and quadrupole interaction 0.36 mm/sec can be the result of Fe-C austenite like order /13/. The Fe-C austenite is an interstitial solid solution in which the carbon atoms are randomly distributed on octahedral voids in the fcc structure of γ -iron. Such a phase configuration is metastable in nature but can be retained at room temperature through the quenching effects /14/. It is well known that the quenching rates of 10^{10} K/s can be achieved during the ion beam mixing process leading to novel metastable phase formation /6/. It is interesting to observe that the Ar⁺ ion bombardment also produces carbon free radicals which eventually take part in ion beam mixing process to precipitate new local arrangements or compositions. It is already reported that the dominant effect of energy deposition in the polymer is the creation of free carbon radicals which are chemically highly reactive and our results are consistent with this observation /2/. The hyperfine interaction values corresponding to the Fe-C austenite like order are different than the reported values and such differences are expected in the radiation processed materials which have high concentration of defects [vacancies] and associated compressive stresses. The other doublet with a large isomer shift [1.27 mm/sec] can be attributed to the presence of Fe²⁺ state in the polyethylene network. This conversion of Fe³⁺ to Fe²⁺ may be due to the association of carbon which essentially acts as a donor of electron. Such a transformation of an ionic state due to the radiation has been reported in the case of Sn atoms in organotin compound used for the polyethylene stabilization /15/. The corresponding quadrupole interaction distribution [Fig.1(g)] also clearly reveals the ion beam induced mixing in Fe:Polyethylene composite and shows the varying environment experienced by Fe⁵⁷ atoms in polyethylene matrix.

The CEMS spectra of the samples bombarded with higher doses of Ar⁺ ions [Figs.1(c)-1(e)] basically retain all the non-magnetic component but the systematic changes in the values of hyperfine interactions indicate the dose dependent microstructural changes due to the ion beam induced reactions. The

intensity of the doublet associated with Fe-C austenite-like order is increased at a dose of 3×10^{15} ions/cm² and is observed to be stabilized at higher ion dose. This may be due to the availability of large number of carbon free radicals due to the further degradation of polymer network at high ion dose bombardment. The substantial increase in isomer shift of Fe²⁺ doublet due to the higher ion dose treatment can be attributed to the increase in the number of carbon near neighbours of Fe atoms in certain regions of polyethylene matrix. The distribution of quadrupole interaction [Figs.1(h)-1(j)] primarily reveal the same features exhibited by the corresponding CEMS spectra. Finally, it is interesting to observe the significant improvement in the overall sharpness of the quadrupole distribution curves as well as CEMS resonance lines with the increase of the ion dose. This dose dependent feature of Fe:Polyethylene interaction exhibits the microstructural changes via the local atomic order.

4. CONCLUSION :

The ion beam induced reactions in Fe:Polyethylene composite produce significant changes in the polymer matrix with the growth of a metastable Fe-C austenite-like structure. Further experiments such as resistivity measurements,

oxidation are being carried out to obtain insight in the role played by Fe atoms for the stabilization of polyethylene network. These results will be published elsewhere.

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REFERENCES :

- / 1/. T. Venkatesan, Nucl. Instrum. and Methods B7/8 (1985) 461.
- / 2/. G. Ungar, J. Mat.Sci. 16(19881) 2635.
- / 3/. M.C. Wintersgill, Nucl. Instrum. and Methods B1 (1984) 595.
- / 4/. T. Venkatesan, T.Wolf, D.Allara, B.J.Wilkens and G.N.Taylor, Appl.Phys. Letts. 43(10) (1983) 1934.
- / 5/. A.J.Lovinger, S.R. Forrest, M.L. Kalpan, P.H.Schmidt and T.Venkatesan, J.Appl.Phys. 55(2) (1984) 476.
- / 6/. J.A.Davies, in Surface Modification and Alloying by Laser, Ion and Electron Beams, eds. by J.M. Poate, G.Poti, D.C.Jacobson (Plenum Press, New York, London, 1981).
- / 7/. V.P.Godbole, S.M. Chaudhari, S.M. Kanetkar, S.V. Ghaisas, S.B.Ogale and V.G.Bhide, Phys. Rev. B 31(9) (1985) 5703.
- / 8/. S.B.Ogale, A.S.Ogale, S.V. Ghaisas, V.N. Bhoraskar, A.S. Nigavekar and M.R. Bhiday, Radiat. Effs., 63 (1982) 73.
- / 9/. This MOSFIT programme was originally written by E. Kreber from Universität des Saarlandes, Saarbrücken and it was adopted for ICL 1904S by S.K.Date from National Chemical Laboratory, Pune, India.
- /10/. G.Le Caer and J.M.Dubois, J.Phys.E:Sci.Instrum. 12 (1979) 1083.
- /11/. V.K. Inshemmik and I.P.Suzdalev, J. de Physique, Colloque Suppl. 12 (1976) C6-751. /13/. J.M. D. Coey and P.W. Readman, Nature 246 (1973) 476.
- /14/. M. Ron, in Applications of Mössbauer Spectroscopy Volume II, edited by R.L. Cohen (Academic Press, New York, London, 1980).
- /15/. V.I. Goldanskii and L.A. Korytko in, Applications of Mössbauer Spectroscopy Volume I, edited by R.L. Cohen (Academic Press, New York, London, 1976).