Radiation Hardness Characterization by Ion Beam Induced Luminescence of Polysiloxane Scintillators

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INTRODUCTION

Polysiloxane based scintillators are promising for the employment in harsh environments. In fact, silicone rubbers preserve their transparency even after 10 Mrad dose exposure, against the exposure limits (1-3 Mrad) of standard organic scintillators matrices, such as polyvinyltoluene (PVT) and polystyrene (PS) [1]. Besides the radiation hardness, their physical properties are constant over a wide range of temperature, from -100 up to 250°C, while PS and PVT are plastic materials with a glass transition temperature of about 90°C. Moreover, their surface is resistant to the formation of microcracks, which occurs upon handling commercial PVT based scintillators.

In this work [2] the radiation hardness under ion beam irradiation of polysiloxane scintillators with different amounts of phenyl groups is studied. Cross-linked polydimethyl-co-diphenylsiloxane scintillators with different molar percentages of phenyl units have been synthesized. As dopants, 2,5-diphenyl oxazole (PPO) was chosen as primary dye, while 2,5-bis(5-tert-butyl-2-benzoxazolyl)thiophene (BBOT) and Lumogen Violet® (LV) were employed as secondary fluors.

The radiation hardness has been measured by ion beam induced luminescence (IBIL), by recording the decrease rate of the light intensity as a function of the fluence. The analysis has been performed both on undoped and doped polysiloxanes and the results have been compared with PS as polymer matrix and with NE102 plastic scintillator.

EXPERIMENTAL

Polysiloxane scintillators were synthesized by mixing vinyl terminated polydimethyl-co-diphenyl siloxane with hydride terminated polymethylphenyl-co-methylhydrosiloxane. Karstedt’s catalyst was used for the cross-linking reaction, namely platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Pt content 2.1-2.4%). The amount of Pt(0) used for each silicone formulation was kept constant at 20 ppm. The fluorophores were dispersed in the desired amounts in component A and, after complete dissolution, Pt catalyst and component B were added. The mixed resin was poured in polyethylene vials and kept in vacuum (1x10⁻¹ mbar) in order to remove all the trapped air bubbles. Afterwards, the resin was heated in vacuum at 60 °C overnight. The resulting samples were easily extracted from the vials, in form of 2 cm in diameter and few mm thick pellets [3].

Fig. 1. IBIL spectrum of a sample containing 1.0% of PPO and 0.05% of LV (22% of phenyl units).

The phenyl concentration (molar % of diphenyl siloxane groups) was determined by the composition of component A. In particular, three concentrations were chosen for the synthesis of undoped polymers: 4%, 15% and 22%. Doped polymers, giving rise to scintillating systems, were synthesized with component A containing 15% and 22% of phenyl groups, since samples with 4% were too opaque and sticky for applications in radiation detection.

Fig. 2. Normalized intensity of the light yield, as a function of the released energy density, for undoped polysiloxanes with 4%, 15% and 22% of phenyl units and for pure PS.

IBIL spectra were obtained by irradiating the samples with a 1.8 MeV He⁺ beam at the AN2000 accelerator of the INFN Laboratori Nazionali di Legnaro. The spot was of about 1.5 mm² and the current density of about 1.0 μA/cm². A quartz fiber bundle, connected to a spectrometer with a nitrogen cooled CCD detector, collected the spectrum in front of the sample. The spectrometer was an Acton 308i, (focal length 300 mm) equipped with a 150 g/mm grating. The CCD (Princeton) is made by 1340×100 pixels, 20×20 μm² each. The use of a
CCD for the detection of IBIL spectra allows collecting the full spectrum (from 300 to 780 nm) at once. With the same equipment operating as a monochromator, a selected wavelength can be sent to a photon counting detector recording the emission intensity as a function of irradiation time. IBIL measurements were also performed on pure PS and on NE102 plastic scintillator (EJ-212 from Eljen Technology) as a comparison.

RESULTS

IBIL spectra of doped samples, collected in the front-face configuration, show the contributions of the polymer at about 300 nm, and of the two dispersed dyes, at 380 and 430 nm, respectively, as can be observed in figure 1 for a PPO–LV doped sample. The higher yield observed for LV evidences the energy transfer occurring from the primary to the secondary dopant.

Under ion beam irradiation the light emission of polymers decreases very fast with the fluence due both to the formation of quenching defects or color centers and to the cleavage of the dyes dispersed in the network. In fact, it has been observed that the radiation hardness under ion beam, monitored by IBIL, is related mainly on the dye species than on the host polymer [4]. In figure 2 the normalized intensity curves of undoped polysiloxanes as a function of the released energy density are reported. While the curve of pure PS is also shown for comparison.

Table I. List of the samples examined in this work, with the amount of phenyl units in component A, with the dye concentrations and with the values of halving energy density.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phenyls %</th>
<th>PPO %</th>
<th>BBOT %</th>
<th>LV %</th>
<th>$\rho_{E}^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4%</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>19</td>
</tr>
<tr>
<td>15%</td>
<td>15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>22%</td>
<td>22</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>BBOT1</td>
<td>15</td>
<td>1.5</td>
<td>0.15</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>BBOT2</td>
<td>22</td>
<td>1.5</td>
<td>0.15</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>LV1</td>
<td>22</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
</tr>
<tr>
<td>LV2</td>
<td>22</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
</tr>
<tr>
<td>PS</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>23</td>
</tr>
<tr>
<td>NE102</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>19</td>
</tr>
</tbody>
</table>

We choose the energy density ($\rho_{E}^{1/2}$) at which the light yield is decreased to one half, obtained by the interpolating curve with a bi-exponential function, as a reference parameter to evaluate the degradation yield [5]. In Table 1 the $\rho_{E}^{1/2}$ values for all the examined samples are reported, with the concentration of phenyl groups and dye molecules. As can be observed, this value increases with the amount of phenyl units. For the samples containing 4% and 15% of diphenyl siloxane groups, $\rho_{E}^{1/2}$ is very similar to PS, while for the sample with 22% of diphenyl units it is 1.7 times the corresponding value of PS. Concerning dye containing samples, the light yield collected from dyes dispersed in the polymer decreases at a higher rate with respect to the polymer matrix, as shown in figure 3. The halving energy density is reported in Table 1. As can be observed, the values for BBOT containing samples are lower than NE102, and are independent on the amount of aromatic rings in the network. On the other hand, LV exhibits a higher resistance, reaching values 1.8 times higher than NE102. At present it is not possible to relate the observed resistance to the molecule structure, since LV is proprietary. This application evidences a quite stable structure for this fluorophore, which can be successfully employed in the production of organic scintillators characterized by a high radiation hardness.

CONCLUSIONS

In this work the radiation hardness of polysiloxane based scintillators has been analyzed by means of IBIL. It has been found that the radiation hardness increases by increasing the phenyl units in the polymer. After doping with dye molecules, the radiation hardness as measured by IBIL depends on the dispersed fluorophores. In particular, BBOT has a resistance lower than NE102, whereas Lumogen Violet®, exhibits a resistance to ion beam irradiation which is 1.8 times higher than NE102.

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