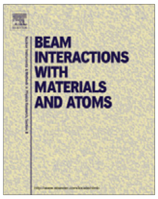
Nuclear Instruments and Methods in Physics Research B 268 (2010) 3155–3159

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb



BEAM INTERACTIONS WITH MATERIALS AND ATOMS

Radiation hardness of polysiloxane scintillators analyzed by ion beam induced luminescence

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ARTICLE INFO

Article history:
Received 9 October 2009
Received in revised form 25 May 2010
Available online 31 May 2010

Keywords:
Ion beam induced luminescence
Organic scintillators
Polysiloxane

ABSTRACT

The radiation hardness of polysiloxane based scintillators has been measured by ion beam induced luminescence (IBIL). The light intensity as a function of the irradiation fluence with an He^+ beam at 1.8 MeV (1.0 $\mu A/cm^2$) has been measured on undoped polymers synthesized with different amounts of phenyl units and on polysiloxanes doped with two different dye molecules (BBOT and Lumogen Violet) sensitizing the scintillation yield.

1. Introduction

Polymer-based scintillators are widely used in many fields, from nuclear physics experiments to medical applications, due to their low cost, ease of fabrication and fast response times. The main drawback of these materials is their poor radiation hardness. As a matter of fact, the radiation energy released to the polymer matrix not only excites the luminescence centers but also breaks chemical bonds, thus drastically modifying the polymer properties.

Polysiloxane based scintillators have been studied between the end of the 1980s [1] and the beginning of the 1990s [2–4] since they proved to be 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 Polystirene (PS). Besides the radiation hardness, polysiloxanes exhibit further advantageous properties. In fact, at room temperature they are in the rubbery state and 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 [5,6]. Moreover, their surface is resistant to the formation of microcracks, which is a typical effect observed upon handling commercial PVT based scintillators.

Previous work on polysiloxanes as organic scintillators was performed at the University of Florida [1–3]. The samples exhibited a stable transparency in the visible range upon exposure to 18 Mrad of gamma irradiation in argon atmosphere [1]. The dyes were chosen in order to reach a good solubility in the aromatic polymer. By dispersing dyes like PMP (commercially unavailable) or OLIGO 347A and tetraphenylbutadiene (TPB) as primary and secondary fluorophore, the authors obtained a yield up to 90 or 55% with respect to BC-408 [1].

More recently, Z. Bell and co-workers renewed the interest on polysiloxanes for scintillators by producing and testing silicone rubber scintillators for the detection of neutrons. They synthesized a cross-linked polymer consisting of 23% diphenylsiloxane and 77% dimethylsiloxane, obtained from a two-part system with part A containing vinyl terminated polydiphenyl-co-dimethylsiloxane (23% in moles of diphenyl units) and part B containing methyl-terminated poly(dimethyl-co-methylhydro)siloxane (8:1) [7,8]. Suitable fluors for dissolution in the polysiloxane network were chosen, such as 2,5-diphenyloxazole (PPO) and triphenyl pyrazoline (TPY). Organic compounds containing boron (m-carborane) and gadolinium (gadolinium nitrate tributylphosphate) were dispersed in the polymer in order to sensitize the scintillator to thermal neutrons.

The aim of this work is to study the radiation hardness under ion beam irradiation of polysiloxane scintillators with different amounts of phenyl groups. Cross-linked polydimethyl-co-diphenylsiloxane scintillators with different molar percentages of phe-

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doi:10.1016/j.nimb.2010.05.077

nyl units have been synthesized following a procedure similar to that of Bell and co-workers, in order to obtain a rigid, self-supporting rubber structure with a high amount of phenyl groups. 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.

2. Experimental

Polysiloxane scintillators were synthesized by mixing vinyl terminated polydimethyl-co-diphenyl siloxane (component A in Fig. 1) with hydride terminated polymethylphenyl-co-methylhydrosiloxane (component B in Fig. 1). Hydrosilylation, the addition of an Si–H bond across a π-bond —which in silicone chemistry is generally an alkene (C = C)— occurs in the presence of Pt(0) catalyst (Karstedt's catalyst). The B resin (cross-linker) also contains phenyl groups (about 50% mol of phenylmethyl moieties), thus a greater solubility – and a better homogeneity- of B resin in A resin can be expected, as a result of stronger chemical affinity. 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%) henceforth named Pt(2.1%). 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 vacuo ($1x10^{-1}$mbar) in order to remove all the trapped air bubbles. Afterwards, the resin was heated in vacuo 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.

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.

Fluorescence measurements were performed in front face geometry with a Jasco FP-770 spectrofluorimeter, equipped with a 150 W Xe lamp. Emission and excitation spectra were collected with 5 nm of spectral bandwidth and corrected for the spectral responsivity of the detection equipment.

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 mm^2 and the current density of about 1.0 $\mu A/cm^2$. 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, $20 \times 20\ \mu m^2$ 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. By measuring the total irradiation fluence and the spot area, the irradiation time was converted in fluence units (ions/cm^2).

IBIL measurements were also performed on pure PS and on NE102 plastic scintillator (EJ-212 from Eljen Technology) as a comparison.

3. Results and discussion

In Fig. 2 are shown the normalized fluorescence spectra of pure polysiloxanes (excitation wavelength $\lambda_{ex} = 260$ nm), synthesized with 4% and 22% of phenyl units of component A. With the lower amount of aromatic groups the emission band has a main component at 290 nm with a broad shoulder at 320 nm. By increasing the concentration of phenyl rings the relative intensity of the feature at 320 nm increases, living the 290 nm component as a shoulder. This behavior can be explained by assigning the peak at 290 nm to single phenyls in the polymer and the peak at 320 to the excimers formed between an electronically excited aromatic ring and a second, identical, chromophore in its ground state. The formation of excimers in aromatic polymers is a well known mechanism [9,10]. The excimer emission feature can be observed together with the single phenyl band or, by increasing the concentration of aromatic rings, can dominate the fluorescence spectrum, as it occurs for PS [9].

In organic scintillators part of the energy released by the ionizing radiation is collected by the network as electronic excitation states. A fraction of the excitation energy is then transferred to a fluorescent dye (usually dissolved in about 1% by weight), through a resonant dipole–dipole interaction. The energy transfer rate is

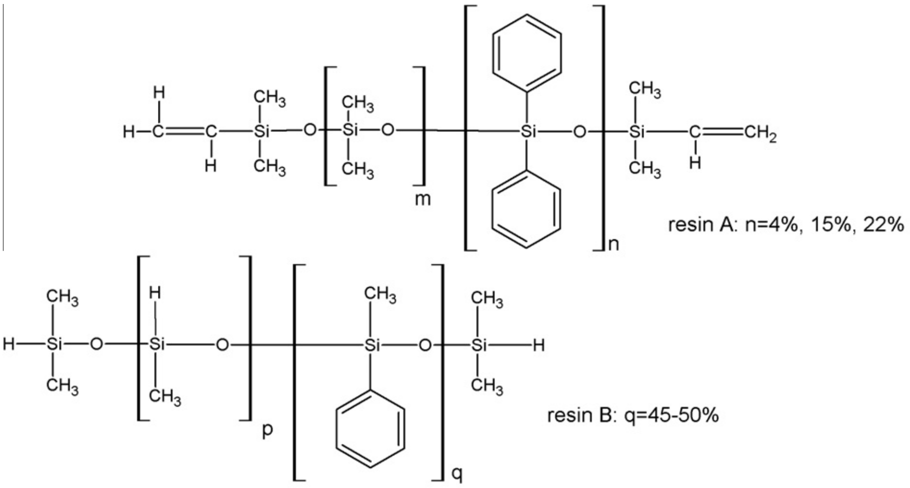

Fig. 1. Structure of the two components used for the synthesis of polysiloxanes. For component A the available percentages of phenyl containing units are indicate.