

Hybrid Materials Prepared by Irradiation at a ^{60}Co source

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Objectives

The purpose of the project is the preparation and characterisation of hybrid materials with new properties by irradiation using the ITN ^{60}Co source.

Results

Irradiation with gamma rays produces cross-linking in polymers. The method is used to prepare organic-inorganic hybrid materials by irradiating samples at the ITN ^{60}Co source. The precursors are polydimethylsiloxane, PDMS, and the metallic alkoxides tetraethylortosilicate, TEOS, and zirconium propoxide, Pr-Zr, in different relative concentrations.

Earlier, hybrid materials of the same composition were prepared by the chemical sol-gel process.

The characterization of sol-gel prepared materials by conventional techniques as well as by Small Angle Neutron Scattering, SANS, showed that the polymer binds to the growing oxide regions during gelation, being well distributed inside the matrix. The local organization of low molecular weight polymer is more disturbed than that of the high molecular weight hybrids. When the Si alkoxide alone is present, the polymer arranges itself in an elaborated structure, during the gelation process. The microscopic structure consists of an open mass fractal oxide network, where the well distributed extended polymer is linked. When the highly reactive Zr alkoxide is present, gelation occurs so rapidly that the structure of the hybrid appears to be the quenched structure of the sol mixture. SEM confirmed a good homogeneity in all samples. The hybrids prepared by sol-gel show no swelling in a good solvent of the polymer.

On the other hand, hybrids of similar composition prepared by gamma irradiation are able to swell in a good solvent of the polymer. Their microscopic structure was found to be formed by oxide particles interconnected by polymer structures.

In either case – sol-gel process or gamma irradiation – the addition of PrZr was observed to alter the microscopic structure of the hybrid sample. This has also been confirmed at a smaller scale by Positron Annihilation Spectroscopy, PAS [1].

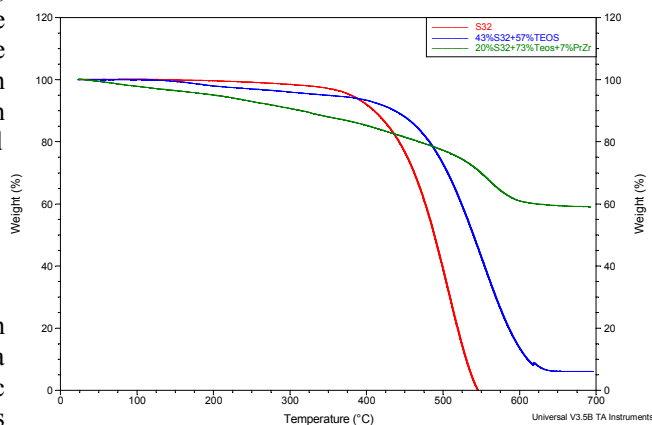
To investigate the role played by the different variables, hybrid samples have been prepared by irradiation of the precursors for different polymer concentrations, polymer average molecular weights and alkoxide mixtures.

The samples prepared by irradiation are macroscopically homogeneous, transparent, and show different degrees of flexibility.

The samples have been characterized by conventional techniques and by SANS measurements carried out in a selected few cases. The characterisation work performed so far showed the following results.

The molecular weight of the polymer has no significant role on the properties of samples prepared by irradiation. This is quite different from what had been found in sol-gel prepared samples. The reason is that gamma irradiation cross-links polymer chains. Thus, for the same mass of polymer in the sample, the cross-linking erases any differences in polymer average molecular weights.

The formation of inorganic oxide depends strongly on the presence of even a small amount of Pr-Zr rather than on the polymer/alkoxide ratio. Thermal Gravimetric Analysis, TGA, in hybrids of PDMS and TEOS (blue line) show that only a small fraction of the initial sample mass is left at 600 °C. This means that only an incipient oxide network is formed, unable to withstand higher temperatures. However for 7 % Pr-Zr (green line), up to 60 % of the initial mass remains at 600 °C. The irradiated pure polymer (red line) completely degrades before 600 °C.



Further investigation is in progress.

Published, accepted or in press work

1. N. Djourelov, T. Suzuki, M. Misheva, F.M.A. Margaça, I.M. Miranda Salvado, Positron Annihilation Lifetime Study of Organic-inorganic Hybrid Materials Prepared by Irradiation *J. Non-Cryst. Sol.* (2004) in press.

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Preparation and characterization of a suitable new material to be used in a multichannel collimator

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Objectives

The purpose of the project is to develop a suitable composite material for the production of strips to be used in the construction of a multichannel neutron collimator.

Results

A variable geometry multichannel collimator has discontinuous walls formed by sets of interlaced horizontal and vertical plans of strips. The material to be used in the production of the strips must ensure that cross-talk between neighbouring channels is negligible. The strip material has to meet the requirements of having very high absorption cross-section for cold and thermal neutrons, small total reflection probability, high resistance to intense radiation fields and mechanical properties that allow easy shaping into thin strips.

A previous theoretical study made under the assumption that the strips were made of Gd_2O_3 powder agglomerated with an epoxy resin showed that if the critical angle for total reflection is higher than a few milirad, total reflection processes would lead to cross-talk between neighbouring channels damaging the performance of the collimator. An experimental test showed, however, that the effect was not severe and that the addition of Titanium powder to the preparation mixture led to an improvement in the performance.

Homogeneous composite samples were prepared from mixtures of Gd_2O_3 and Ti powders prepared under a continuous argon flow and then agglomerated with an epoxy resin. Different weight fractions of Ti were tested (up to 57% Ti). Upon complete cure of the epoxy resin, composition and homogeneity of the samples were evaluated using PIXE, and gravimetric methods combined with XRF. For all samples the particles were found to be well distributed in the matrix.

The bulk neutron absorption cross-section of the composite was evaluated through transmission experiments performed on very thin samples.

To evaluate the neutron reflection properties of the strip material measurements were carried out at a neutron reflectometer of Laboratoire Léon Brillouin, Saclay, France. Pure epoxy samples were measured as reference. Results confirmed that the intensity reflected by the Gd_2O_3 /Ti samples is always small, and is reduced by the addition of Ti.

To evaluate the effect of reflected neutrons on the overall performance of the apparatus an existing Monte-Carlo simulation code was rewritten. Treatment of the data obtained shows that cross-talk

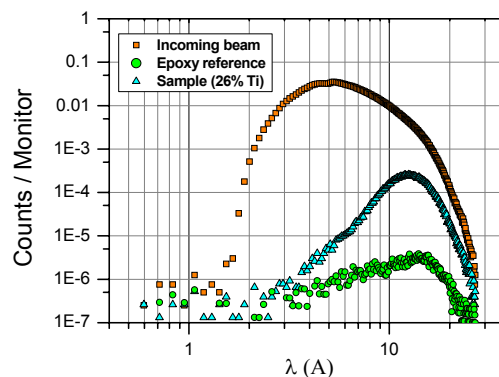


Fig. 1. Neutron reflection data, collected at an incoming angle of 4 mrad as a function of wavelength.

can be effectively prevented with little contribution to the background.

Under normal operation conditions, the material will be exposed to intense neutron and capture gamma ray fields. In a first step, the effect of the radiation on the mechanical properties of the strips was evaluated by estimating the energy deposition in the material using the MCNP Monte-Carlo code.

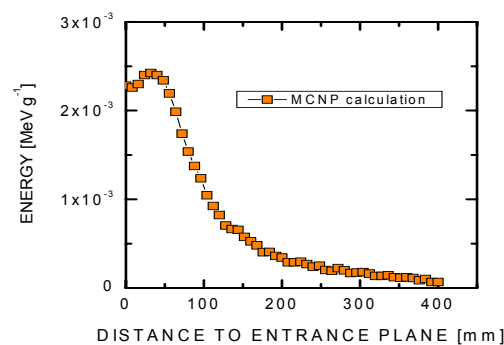


Fig. 2. Energy deposited in the collimator strips as a function of distance to the entrance plane of the collimator for the 26% Ti sample.

This study will be complemented by a series of test irradiations to be carried out at the ITN ^{60}Co facility.

Published, accepted or in press work

1. F.M.A. Margaça, A.N. Falcão and F.G. Carvalho, Guidelines for the Implementation of XY variable-geometry Converging Multichannel Collimation in a Specific SANS Facility, *J. Appl. Cryst.* **37** (2004) 210-215.

Design and Construction of In-Pile Collimators for Beam Tubes #4 and #6 of the Greek Research Reactor

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Objectives

To design and construct two in-pile collimators to be installed at beam ports #4 and #6 of the 5 MW Greek research reactor facility of the National Centre for Scientific Research, Demokritos.

Results

The overall geometry of the collimators is cylindrical (three cylinders with different outer diameters and a common axis). The external diameters of the 3 cylindrical sections were chosen in such a way that contact between the in-pile collimator and the aluminium beam tube of the housing is made at the level of the intermediate section. The equipment is composed of two sections bound together by screws: (i) section A, containing the rotating shutter; and (ii) section B (closer to the reactor core). Both sections have an outer stainless steel (SS) structure that holds the beam channel. The free space between the SS structure and the beam channel is filled with adequate shielding materials.

The shutter is made of two components, the *carter* and the *rotor*, and occupies all section A of the in-pile collimator. The rotor rotates around the axis of the beam port, and is essentially supported by a single bearing. The rotor can easily slide in and out of the carter, in order to enable maintenance operations. The correct operation of the shutter is guaranteed by a set off four positioning elements (operation guides) rigidly bound to the outer flange of the carter. The shutter can be operated either by a remotely controlled motor or manually.

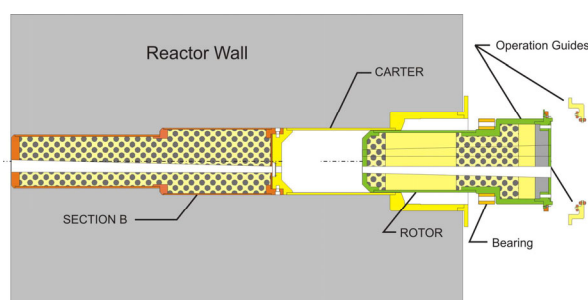


Fig. 1. Schematic representation showing that the rotor can be installed and removed, leaving the bulk of the in-pile collimator in the reactor wall.

Design parameters, and data relevant for the safety analysis were obtained by means of Monte-Carlo simulation codes. Beam profile characteristics were estimated by a locally developed code, whereas the MCNP code was used to calculate: (i) energy deposition by radiation in the section of the in-pile collimator closer to the reactor core; (ii) estimates of

the subsequent heating and swelling of the structure; (iii) activation of the smaller diameter section of the in-pile collimator; (iv) estimate of doses at the level of the reactor wall with the shutter closed and the reactor at full power. The energy distribution of the source neutrons used in the simulations was constructed semi-empirically from the given total thermal, epithermal and fast neutron fluxes, assuming, respectively, a Maxwell distribution, an $E^{-1/2}$ law and the energy distribution of the fission spectrum. The energy spectrum of the gamma flux used was also semi-empirical based on estimated total dose values and assuming a distribution typical of a light water nuclear reactor.

Results were obtained for different arrangements of shielding materials, allowing for a final decision on the overall dimensions of the equipment as well as the shielding composition (materials and material distribution along the axis of the tubes).

Construction was carried out by the Portuguese company ARSOPI, Indústrias Metalúrgicas Arlindo S. Pinho, Lda under ITN supervision.



Fig. 2. Pictures of the in-pile collimators. Top -view of the outer carter and rotor flanges; bottom – rear view of one of the in-pile collimators.

Published, accepted or in press work

1. D. Silva, M. Carrapiço, I.F. Gonçalves, A.N. Falcão, In-Pile Collimators for Beam Tubes #4 and #6 of the Greek Research Reactor, ITN report (2004).

Neutron Spectrometers at the Portuguese Research Reactor

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Objectives

The purpose of the present programme is the implementation at the ITN campus of a set of basic instruments for neutron beam work, open to external users, using neutrons from the RPI reactor. This infrastructure is expected to help developing the use of neutron scattering techniques both for research and training, while contributing to a better utilisation of the RPI reactor.

Results

Installation work of the SANS spectrometer EPA continued during the year with emphasis on command and control hardware and software. Construction and test of the electronic modules associated with the movements of the PSD detector, beam stop and sample changer were completed. The command software was implemented using Labview. The set of signal and power cables necessary for the operation of the spectrometer were laid inside the detector chamber and tests of the signalling functions, vacuum tests and preliminary tests of the state of the neutron position sensitive detector were carried out. The electronic modules associated with the PSD Detector from ORDELA were tested and the DATAVIEW software supplied by the same firm, was put to work.

Preliminary measurements of the slow neutron beam profile after the neutron velocity selector were carried out but could not be completed because of problems with the Hungarian made selector. These problems probably due to ageing of a number of electrolytic capacitors were overcome through an extensive replacement of these sensitive circuit elements.

Beam profile measurements are expected to be completed early in 2005.

Upgrading of the Two-Axis Diffractometer DIDE proceeded during the year. A cryostat that enables cooling down the sample to 1.5 K was received. However the operation of the cryostat requires the availability of a Helium recovery line that will have to be installed. This waits adequate funding.

On the other hand, an extensive evaluation of the 800-channel detector electronics that equips the two-axis diffractometer was completed. Since the persistent problems related to electromagnetic noise could not be

solved, this has led to a decision to replace the detector. A new detector system has been designed. It will be based on a detector bank with 8 linear position sensitive ^3He detectors. Placed at a sample-to-detector distance of 1.5 m, the new system will detect neutrons scattered over an angular range that is roughly half of that covered by the former detector, with the same resolution, and with double count rate. The performance of the new system is thus comparable to that of the former. The new system will further allow changing the balance intensity/resolution by changing the sample-to-detector distance. Purchase of the equipment is expected to take place in early 2005.



Fig.1. EPA - View of the EPA Spectrometer data acquisition and command and control electronics

Published, accepted or in press work

1. I.F. Gonçalves, J.F. Salgado, A.N. Falcão, F.M.A. Margaça F.G. Carvalho, MCNP Simulation to optimize In-pile and Shielding Components of the Portuguese SANS Instrument, Communication presented at ICRS-10, Funchal, Madeira, 9-10 May 2004. Paper accepted for publication in the Conference Proceedings in *Journal of Radiation Protection Dosimetry*