

Condensed Matter Physics

Fernanda Margaça

The Group's main field of research has been the development and characterisation of materials with new or improved properties. These are prepared and/or modified using mainly gamma irradiation from the ^{60}Co source of UTR.

The studied systems involve the development of new polymeric materials, catalytically actives, and hybrid materials prepared from mixtures of a polymer and different metallic alkoxides.

The preparation and characterisation of the studied materials has been performed in our Laboratory of Macromolecular Materials. The nanoscale structure has been investigated by neutron scattering in collaboration with colleagues at the Laboratoire Léon Brillouin (CEA-CNRS-Saclay) in France, Paul Scherrer Institute, Villigen in Switzerland and Budapest Neutron Centre of KFKI, in Budapest, Hungary.

The Group has also strengthened and widened its scientific collaborations with national research groups during the year of 2011. Namely, important work was carried out in collaboration with the Nuclear Reactions Group (ITN-UFA/ FCT-UNL), that involved the production of an Ag^{36}Cl standard for the AMS technique. Furthermore, thermal analysis has been performed in collaboration with groups from UCRS/ITN, from the Dep. of Ceramic and Glass Engineering of University of Aveiro and from Universidade Nova de Lisboa (FCT-UNL).

During 2011 progress continued in the research and development of hybrid materials, in collaboration with Aveiro University under the project *Hybrid materials for biomedical applications*, with funding from the Foundation for Science and Technology, FCT, contract PTDC/CTM/101115/2008. New applications for these materials are currently being investigated in collaboration with Universidade Nova de Lisboa.

Progress has also been made in 2011 in the project *Preparation of polymeric materials catalytically*

actives on biodiesel production by vegetable oils methanolysis, under the FCT contract PTDC/CTM-POL/114579/2009. Work on this project is carried out in collaboration with Universidade Nova de Lisboa.

The *Macromolecular Materials Laboratory, M3L*, after being moved in 2010 into a suitable room in the ground floor, in the extension of the UFA main building, was further upgraded during 2011. In fact, it now offers a range of improved possibilities for chemical and physical manipulations of samples as well as for their characterization and simulation.

In 2011 the following equipment was installed in the Macromolecular Materials Laboratory: a *workstation* to perform numerical simulations of the prepared materials, whose software is being installed; a *Universal Testing Machine* for mechanical properties of materials that is now being tested; an *hydraulic press* with temperature control that is ready to operate. Furthermore, the installation of a Positron Annihilation Lifetime Spectrometer (PALS) is underway, which is a sensitive non-destructive tool for studying pores and free-volume holes in materials.

This significant upgrading of the laboratory is a major breakthrough for our group. Now we are reaching the suitable working conditions that will allow us *i)* to extend the characterisation of materials to mechanical properties beyond the thermal analysis and in a short period also to measure the porosity; *ii)* to simulate the molecular structure and dynamics of materials, *iii)* to receive and supervise MSc and Ph.D. students, on a regular basis, to perform experimental as well as simulation work, for their thesis and *iv)* to apply to a wider variety of agencies for funding to carry out research and development in the area of macromolecular materials. Finally, such a laboratory will make us focus on this type of materials and therefore it is the right time to change the name of the group into a more realistic designation as Group of Macromolecular Materials, GM3.

Research Team

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Study of PDMS conformation in Hybrid Materials prepared from PDMS-TEOS-PrZr precursors by gamma irradiation

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Objectives

Investigation of PDMS conformation in hybrid materials of the system PDMS-TEOS-PrZr prepared by gamma irradiation.

Results

All ATR/FT-IR spectra from hybrid materials show bands similar to those found in the spectrum of the irradiated PDMS. Slight differences (marked by the arrows in Fig. 1) were found in the Zr containing samples where an increase in intensity of the base line is observed with increasing Zr content.

This increase in intensity is compatible with the presence of Zr-silicate regions whose FT-IR spectra show broad bands in $600\text{-}1300\text{ cm}^{-1}$ (Rayner Jr et al., Microelectron. Eng. 72, 304, 2004). In fact, combining that spectrum with that of irradiated 33PDMS-66TEOS-1PrZr it is possible to reproduce the experimental data by simply applying a scaling factor to the reported Zr-silicate spectrum. This suggests that, at least above certain Zr content, regions of inorganic Zr-silicate oxide are formed.

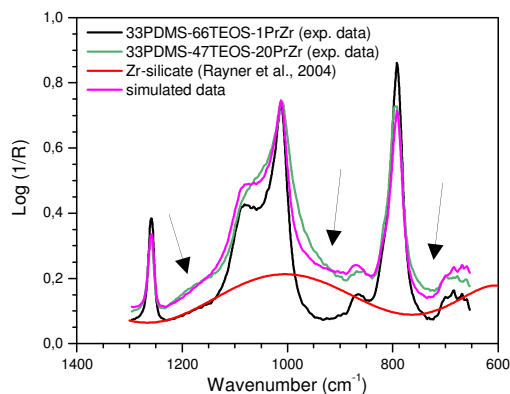


Fig.1 - FT-IR spectrum simulated (magenta line) combining the experimental data from Zr-silicate (red line) with that of irradiated 33PDMS-66TEOS-1PrZr (black line), normalized to the 1012 cm^{-1} peak. The arrows mark the differences existing in the $500\text{-}1500\text{ cm}^{-1}$ region.

Fig. 2 shows XRD diffractograms representative of the 33PDMS-(67-x)TEOS-xPrZr system. All diffractograms show two peaks: the first ($2\theta \sim 11^\circ$) is due to the presence of regions of ordered polymer chains, and the second broader one, ($2\theta \sim 21^\circ$), is associated to the distance between Si atoms in the PDMS backbone.

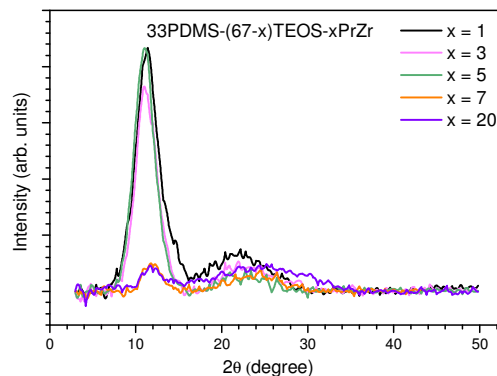


Fig.2 - XRD diffractograms of 33PDMS-(67-x)TEOS-xPrZr ($x = 1, 3, 5, 7$ and $20\text{ wt}\%$) hybrid materials.

The distance between folded chains (d), the total peak intensity and the crystallite size (L) calculated from XRD results, are shown in Fig. 3 as a function of the PrZr content.

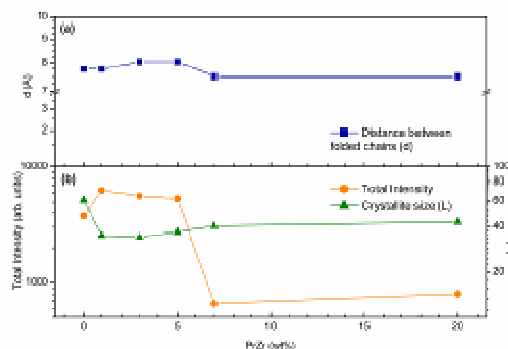


Fig. 3- Variation with PrZr content on a semi-log scale of: (a) distance between folded PDMS chains (blue); and (b) peak total intensity (orange) and crystallite size (green).

The crystallite size is smaller in samples containing Zr than in irradiated PDMS. The distance between folded chains, shows no significant change with increasing Zr. The total peak intensity, associated to the PDMS crystallites, increases with Zr for PrZr $\leq 5\text{ wt}\%$ whereas for larger contents it almost disappears. This suggests that Zr, for smaller contents, might be uniformly dispersed in the material probably linked to end positions of the polymer chains. Such a link explains the formation of smaller crystallites than in the reference sample. For larger Zr contents, the saturation of available chain ends for Zr bonding, can lead the excess Zr to bond to PDMS backbone and/or to precipitate preferably on the ordered regions, inhibiting the chain ordering.

Further work will involve mechanical analysis and bioactivity tests in these materials.

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Preparation of polymeric materials catalytically actives on biodiesel production by vegetable oils methanolysis

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In collaboration with researchers from REQUIMTE-DQ/FCTUNL we have synthesized and characterized solid acid/basic catalysts and acid/basic catalytic composite matrixes: The catalytic materials consist of mesoporous silica MCM-41 and SBA-15 bearing different functional groups. The catalytic composites are made by the organic/inorganic solid base loaded in a polymer matrix. Transesterification catalytic tests in classical batch reactor showed materials with different catalytic activity and stability.

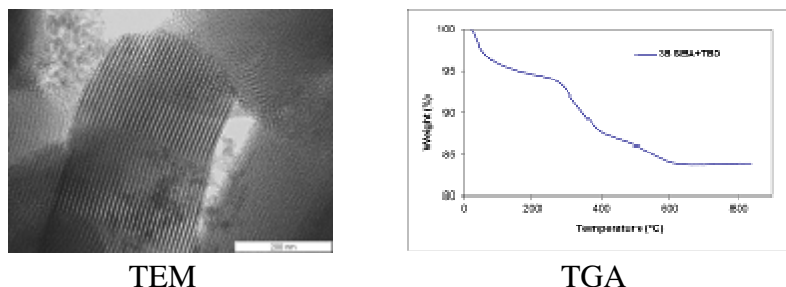


Fig 1- TEM image and thermogram of solid basic catalyst (mesoporous silica SBA-15 loaded with TBD (1,5,7-triazabicyclo [4,4,0] dec-5-ene)).

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Characterization of PE-g-HEMA films prepared by gamma irradiation through nuclear microprobe techniques

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PE-g-HEMA films with different grafting yields prepared by mutual gamma irradiation method at the ITN ⁶⁰Co facility have been characterized with ion beam analytical techniques (RBS, STIM and PIXE) using the nuclear microprobe from UFA - Ion Beam Laboratory.

Qualitative analysis showed a random and heterogeneous distribution of contaminant elements, independent of the grafting degree, suggesting the existence of several sources of contamination at different stages of their preparation. Results also suggest that this “phased” contamination occurs simultaneously with mechanisms of agglomeration/entrapment of impurities during the gamma induced copolymerization reaction. Moreover, quantitative data showed that all contaminants found in the copolymeric films are natural contaminants of their reagents of preparation, although at concentrations without toxicological hazard, which points to a low cytotoxic potential.

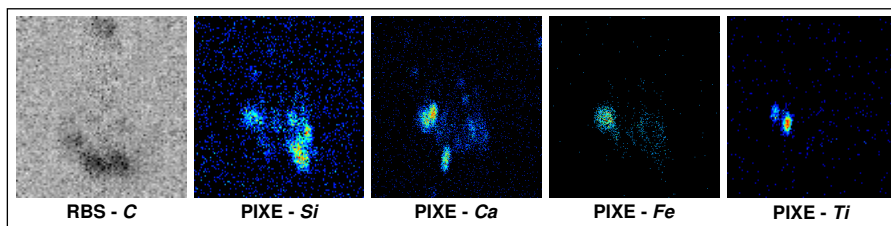


Fig 1- Maps of RBS (Carbon) and PIXE of impurities found in the PE-g-HEMA film grafted at 166% (35 hours of irradiation; $D_{abs} = 10.5$ kGy). Maps dimensions: $100 \times 100 \mu\text{m}^2$.

The use of these techniques for materials contamination characterization has worked as a quality benchmark of the experimental development of this materials and, simultaneously, reducing the level of failure of biological tests required by the international standard ISO 10993 - *Biological Evaluation of Medical Devices*, for materials biomedical applications, which are very expensive and time-consuming. The simultaneous use of RBS, STIM and PIXE allow us to know, at a time, “who, where and how” are contaminating our samples.

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Synthesis and characterization of novel γ -induced porous PHEMA-IL composites

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The synthesis and characterization of novel γ -induced porous PHEMA-Ionic Liquid composites is still being investigating. The resulting composites can be converted into an organogel by addition of DMSO, and converted back to a porous composite by immersion in water. Work in progress involves the use of different ionic liquids and evaluation of PHEMA-IL conductivity.

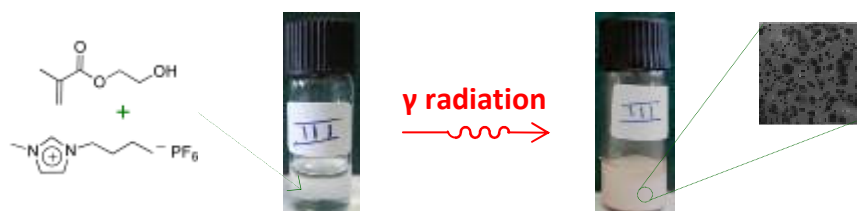


Fig 1- BMIPF₆ (1-butyl 3-methylimidazolium hexafluorophosphate) and HEMA (1:1) before and after gamma irradiation.

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Laboratory of Macromolecular Materials – Lab II (Physical Characterization)

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The Laboratory of Macromolecular Materials gained a second room that is devoted to the physical characterization of polymeric and hybrid materials. In this new room, a Universal Mechanical Testing Machine (Zwick 1435) was installed and subsequently automated. It is fully functional to study mechanical properties including flexibility, tensile and compression tests.



Fig 1- Laboratory views showing the main equipment installed during 2011.

As a complement of this equipment it was also installed an hydraulic press (12 ton) with thermal mordents (temperature controlled by programmable water and compressed air mixer). This equipment allows the preparation of polymeric specimens for mechanical testing as well to carry out thermal and compression stress routines in materials.



Fig 2- Laboratory views showing details of the equipment installed in 2011.

Furthermore, a PALS – *Positron Annihilation Lifetime Spectrometer* is in its final stage of installation. Its nuclear instrumentation as well as the software are already assembled, installed and tested. Only the gamma detectors are lacking. These should be acquired and installed next year. This facility will extend our ability to study the material porous dimensions and respective distribution as well the distance between the long chains in polymers and hybrid materials.

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