

Condensed Matter Physics

Fernanda Margaça

The Group's main field of research is the development and characterisation of materials with new or improved properties. For this purpose, radiation is used as a tool to investigate the structure and to induce structural modifications in particular samples.

Special polymeric materials have been investigated in collaboration with groups from the Universidade de Aveiro, Universidade de Coimbra and Universidade Nova de Lisboa, Laboratoire Léon Brillouin (CEA-CNRS-Saclay) in France, Paul Scherrer Institute, Villigen in Switzerland and the Budapest Neutron Centre in KFKI, Hungary.

The main effort has been made to characterise the hybrid materials as well as the co-polymers, both prepared by gamma irradiation using the ^{60}Co source of UTR, to optimize the processing protocol in order to improve the properties of the obtained materials.

The systems studied involve the development of new copolymers (HEMA grafted on LPDE thin films) suitable for bioapplications and hybrid materials prepared from mixtures of a polymer (PDMS) and different metallic alkoxides.

During 2010 progress continued in the copolymers development. A new methodology for determination of the grafting yield in gamma induced grafted copolymers, based on thermal analysis data, was

developed. A report for registration of a National Patent for the new polymeric material and its method of preparation is being elaborated.

The project entitled *Hybrid materials for biomedical applications*, with funding from the Foundation for Science and Technology, was started in May 2010.

Hybrid materials for biomedical applications were prepared by the sol-gel process with the addition of a new alkoxide (calcium nitrate). Some selected samples of these new materials were measured by small angle neutron scattering in the Paul Scherrer Institute, in Switzerland. They have also been characterised by other more conventional techniques, most of them available at ITN.

In collaboration with researchers from Universidade Nova de Lisboa, the synthesis and characterization of novel γ -induced porous HEMA-IL composites is being investigated. Work is also progressing towards the development of catalytic membranes of poly (vinyl alcohol) containing sulfonic acid groups.

A project entitled *Preparation of polymeric materials catalytically actives on biodiesel production by vegetable oils methanolysis*, was approved and obtained funding from the Foundation for Science and Technology. It is due to start in February 2011.

Research Team

Researchers

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A new methodology for the determination of the grafting yield on γ - induced grafted copolymers

L.M. Ferreira, J.P. Leal and A.N. Falcão

Objectives

The development of an expeditious and consistent experimental and mathematical methodology for the determination of the grafting yield in gamma induced grafted copolymers, based on thermal analysis data.

Results

Polymer crystallinity can be determined by thermal analysis techniques, namely by *Differential Scanning Calorimetry (DSC)*, which has become a fundamental tool in the study of phase transition temperatures, providing precious data about the structural organization of the matter. The melting enthalpy of a material is related to the energy required to break the intermolecular bonds, and it can be used to evaluate its crystallinity. Thus, polymer chains more ordered, i.e., more crystalline, have stronger intermolecular bonds and in greater number, and therefore, higher temperatures and enthalpies of fusion. The degree of crystallinity of a polymer (X_c) can be calculated from its enthalpy of fusion, according to the relation:

$$X_c = \frac{\Delta_f H}{\Delta_0 H} \times 100$$

where $\Delta_f H$ represents the melting enthalpy of the polymer sample measured by DSC and $\Delta_0 H$ is the melting enthalpy of the polymer in “completely” crystalline form.

In PE-g-HEMA films, a polyethylene based copolymer grafted with methacrylate 2-hydroxyethyl, we observed the existence of a consistent correlation between the grafting degree and the crystallinity of the copolymers (Figure 1).

The data are fitted by a first order exponential decay function of the type:

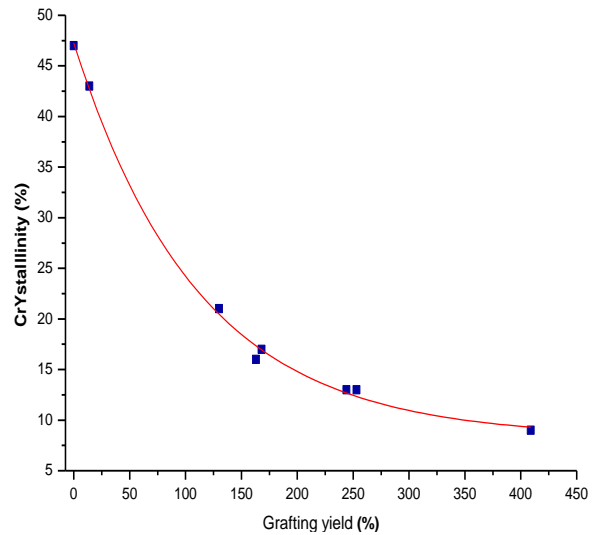
$$y = y_0 + A_1 \cdot e^{(-x/t_1)}$$

which in this case takes the form:

$$X_c = 8,30 + 38,96 \cdot e^{(-x/111,60)} \quad (R^2 = 0,998)$$

The good agreement between experimental data and the mathematical fit function ($R^2 = 0,998$), is a good evidence that the structural damages induced in polyethylene backbone depend strongly on the graft of poly(HEMA).

Moreover, this fact also allows to considerer DSC analysis as an alternative to the gravimetric method, to determine the grafting yield in copolymers. A DSC assay makes possible to determine, promptly and accurately, the melting enthalpy and the degree of crystallinity of a sample, and thereby to obtain its graft degree.



Evolution of the crystallinity degree of the PE-g-HEMA films with its yield of graft.

For our PE-g-HEMA copolymeric films, the above equation can be rewritten as follows:

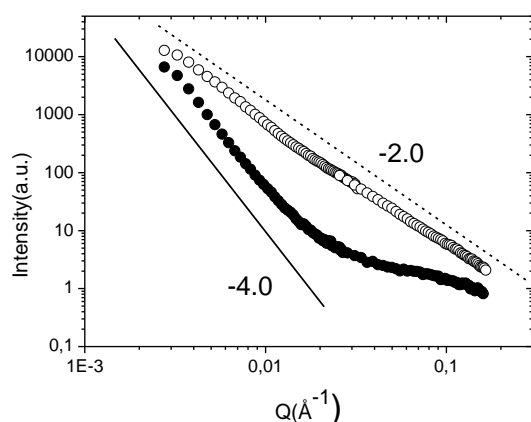
$$Yield\ of\ graft\ (\%) = \ln\left(\frac{X_c - 8,30}{38,96}\right) \times (-111,60)$$

This provides a new way to quickly calculate the copolymers grafting yield, from its degree of crystallinity.

Hybrid Materials for Biomedical applicationsF.M.A. Margaça, I.M. Miranda Salvado¹, J.J.H. Lancastre, L.M. Ferreira, A.N. Falcão, L. Almásy²

Hybrid materials PDMS-modified CaO-SiO₂-ZrO₂ were prepared and studied as to the bioactivity behaviour after immersion in SBF for different periods of time. It was found that both the addition of ZrO₂ and the thermal treatment promoted the deposition of a hydroxyapatite surface layer on the synthesised materials [1]. They were

characterised by TG, DTA, XRD and small angle neutron scattering (SANS). Figure 1 shows the SANS spectra for the sample prepared with no zirconia, before heat treatment (full circle) and after (open circle). The results showed that in the material prepared without Zr the oxide network evolved by RLCC aggregation, resulting in smooth interfaces at the nanometric scale. The oxide network of samples with PrZr grew by RLCC aggregation presenting a mass fractal structure, at the nanometric scale. The observed correlation between nanoscale structure and bioactivity should be further investigated in order to improve the processing conditions of materials for biomedical applications.



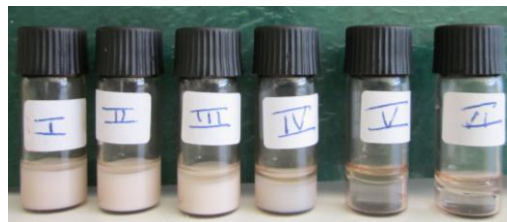
[1] Portela Marques MM, Miranda Salvado IM, Margaça FMA, Ferreira LM., *J. Therm. Anal. Calorim.* **100** (2010) 557–561

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Synthesis and characterization of novel γ -induced porous HEMA-IL compositesM.H. Casimiro¹, M.C. Corvo¹, A.M. Ramos¹, L.M. Ferreira, F.M.A. Margaça

In collaboration with researchers from REQUIMTE-DQ/FCTUNL we have synthesized and characterized a novel polymer-ionic liquid composite with poly(2-hydroxyethyl methacrylate), PHEMA, and 1-butyl-3-methylimidazolium hexafluorophosphate, BMIPF₆, obtained by γ -irradiation at room temperature. The ionic liquid has a porogenic role during the γ -induced polymerization. The resulting composites can be converted into an organogel by addition of DMSO, and converted back to a porous composite by immersion in water. These properties turn the obtained composites suitable for diverse biomedical and green industrial technology applications.

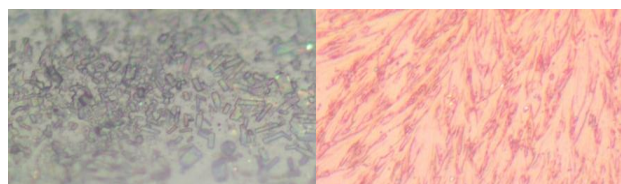


HEMA-IL composites (after irradiation)

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Development of catalytic membranes of poly(vinyl alcohol) containing sulfonic acid groupsM.H. Casimiro¹, A.G. Silva¹, A.M. Ramos¹, J. Vital¹, L.M. Ferreira

We have developed solid acid catalysts consisting in membranes of poly(vinyl alcohol) functionalized with sulphonic groups. These groups are introduced into the polymer matrix by gamma irradiation anchoring of methanesulfonic acid. These membranes show good catalytic activity in the reaction of isoamyl acetate production. Although, due to the formation of complex structures during irradiation, these membranes are still being object of a more exhaustive characterization.



(Before catalytic reaction) (After catalytic reaction)

Functionalized PVA membranes

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Laboratory of Polymers Characterization

L.M. Ferreira, F.M.A. Margaça

In 2010 the *Laboratory of Polymers Characterization* changed its location to a new and better suited place, in the ground floor, in the extension of the UFA main building. It also changed name to *Laboratory of Macromolecular Materials (LMC)*. It consists of two main parts. One dedicated to the chemical and physical manipulations of samples and the other to the mechanical and other physical analysis. This change was necessary in order to improve the working conditions, namely allowing the use of all our experimental and analytical resources in a safer and more efficient way. The significant development of activities requiring manipulation and characterization of macromolecular materials was the other important reason for this move.



Photographs of the facilities of the LMC in its final stage of installation at the new location.