

Improving the mechanical performance of HDPE employing dendrimer-like silica nanospheres and halloysite natural nanotubes as promising nanofillers through *in-situ* polymerization

Duarte M. Cecílio^a

María L. Cerrada^b, Auguste Fernandes^a, M. Rosário Ribeiro^a

^aCentro de Química Estrutural (CQE), Instituto Superior Técnico, Av. Rovisco Pais 1, Lisbon, Portugal

^bInstituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC), Juan de la Cierva 3, 28006, Madrid, Spain
duarte.cecilio@tecnico.ulisboa.pt

Polyolefin nanocomposites, and more specifically, polyethylene/inorganic oxides nanocomposites are promising materials that combine the ductility, flexibility and easier processibility of their polymer matrix with the stiffness and rigidity of their inorganic filler. The main challenge in preparing these nanocomposites is achieving a suitable compatibilization of the interfacing components, as the hydrophilic nature of the inorganic filler results in a tendency for the nanoparticles to aggregate and thus reduce the reinforcing effect. There are several techniques to prepare nanocomposites, out of which *in-situ* polymerization provides a good dispersion of the filler. In this study, we report the synthesis of HDPE nanocomposites via *in-situ* polymerization reinforced with dendrimeric silica nanospheres (DS) which has previously proved a promising support for metallocene catalysts in ethylene polymerization, and natural halloysite nanotubes (HNT), a cost-effective and naturally abundant aluminosilicate which presents a tubular morphology. The polymerization reactions were performed by preparing a heterogeneous catalyst made up of a zirconocene catalyst immobilized onto MAO-pretreated supports (DS-MAO and HNT-MAO). A reference non-reinforced HDPE was prepared via solution polymerization with the homogeneous zirconocene. The materials were characterized regarding the polymer's crystalline features, morphology, and filler dispersion. The mechanical reinforcement of the nanocomposites was assessed by stress-strain measurements and compared against the remaining properties. We observe both fillers present good dispersion within the polymer matrix, as well as high crystallinity of the matrix. We obtain highly reinforced nanocomposites regardless of the filler employed, with increasing stiffness proportional to the filler content. Remarkably, the limit properties of the nanocomposites do not decrease significantly with reinforcement content, in some cases retaining the elongation at break values of pristine HDPE.

REFERENCES

- [1] João M. Campos, João Paulo Lourenço, Ernesto Perez, Maria L. Cerrada and M. Rosário Ribeiro, *Journal of nanoscience and nanotechnology*, 6 (2009) 3966
- [2] Duarte M. Cecílio, Auguste Fernandes, João Paulo Lourenço and M. Rosário Ribeiro, *ChemCatChem*, 10 (2018) 3761
- [3] Katarzyna Szpilka, Krystyna Czaja and Stanislaw Kudla, *Polimery*, 06 (2015) 359

FIGURES

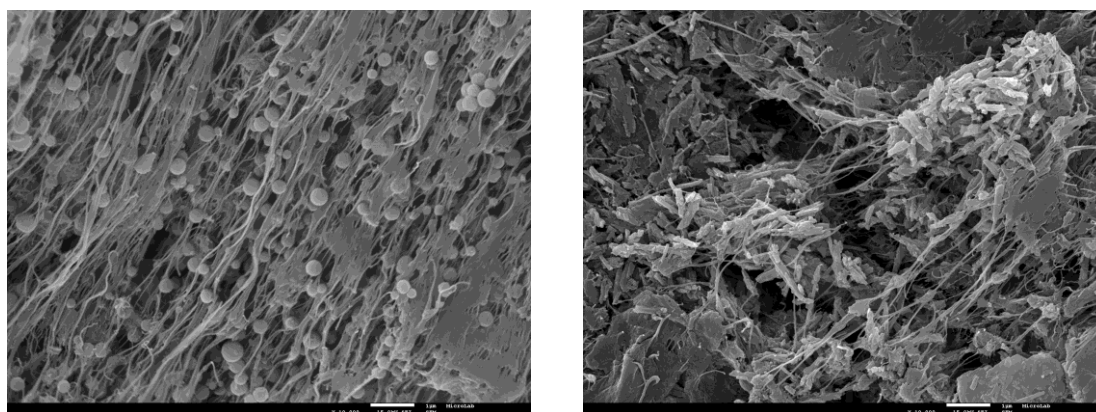


Figure 1: SEM micrographs of DS (left) and HNT (right) dispersed within the HDPE matrix.