

# Crystalline Details in Decorated MCM-41/Polyethylene Hybrids

M. L. Cerrada, C. Serrano, J. Arranz-Andrés, R. Benavente, J. M. Pereña, A. Bento<sup>1</sup>, M. R. Ribeiro<sup>1</sup>, J. P. Lourenço<sup>2</sup>, S.S. Funari<sup>3</sup>, E. Pérez

*Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC). C/ Juan de la Cierva 3, 28006 Madrid, Spain*

*<sup>1</sup>ICEMS, IST, Universidade Técnica de Lisboa– UTL, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*

*<sup>2</sup>CIQA. Faculdade de Ciências e Tecnologia-Universidade do Algarve. Campus de Gambelas, 8005-139 Faro, Portugal*

*<sup>3</sup>Beamline A2 at HASYLAB, Notkestr. 85, D-22603 Hamburg, Germany*

In-situ polymerization of ethylene with mesostructured MCM-41 allows obtaining different polyethylene-based nanocomposites [1]. In this investigation, two approaches to improve interfacial adhesion between components, PE matrix and MCM-41, are tested. These methods consist of: (A) introduction of undecenoic acid, UA, in the polymer chains via copolymerization and (B) surface functionalization of the MCM-41 particles with UA molecules to increase the hydrophobic character and/or to react with polymer matrix. Three hybrids for each method varying MCM-41 content are obtained: A1, A2 and A3 with 6.8, 7.9 and 28.4 wt.%, and B1, B2 and B3 with 8.6, 11.9 and 30.2 wt.%, respectively. FTIR data suggest that independently of the synthesis strategy, using decorated or non-decorated MCM-41, similar type of aluminium carboxylate complexes are involved in the interactions established between the MCM-41 filler and the polymer matrix. Then, these methodologies are effective for improving interfacial adhesion.

Figure 1 shows the MAXS diffraction profiles at 25 °C for the different nanocomposites modified with UA. The MCM-41 exhibits its characteristic mesoporous hexagonally arranged structure that consists of a strong reflection at around 2.2° and two weak reflections at 3.8° and 4.4°, which correspond to (100), (110) and (210) planes of MCM-41, respectively. As expected, the copolymer cEUA, which does not contain mesoporous MCM-41, does not exhibit this mesoporous hexagonal arrangement. The different functionalized nanocomposites show the diffractions characteristic of MCM-41 [2], indicating that the well-ordered long-range structure is retained after decoration of MCM-41 in the approach B and after polymerization, method A.

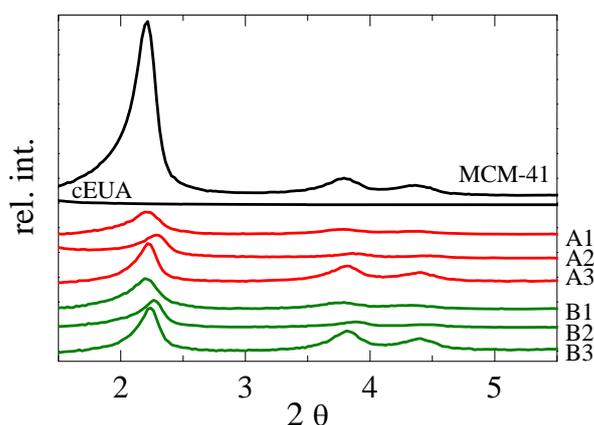


Figure 1: MAXS profiles at room temperature for the synthesized hybrids as well as for MCM-41 and copolymer cEUA, these two used as references.

WAXS patterns show that cEUA copolymer and all of hybrids display the orthorhombic lattice common in polyethylene and derivatives, characterized by the two main (110) and (200) diffractions. The location of these two diffractions is rather constant for the different samples and, consequently, dimensions of crystal lattice remain practically unchanged in these diffraction planes by incorporation of MCM-41. Diffraction intensity decreases in the hybrids when compared with cEUA, this effect being more evident for the A3 and B3 composites, those with the highest MCM-41 content.

Figure 2 displays real-time variable-temperature SAXS profiles for cEUA and two hybrids. The patterns show that as the temperature rises, approaching  $T_m$ , the SAXS peak related to long spacing shifts to lower  $1/d$  values and its intensity is increased. These features indicate the enlargement of crystallite size and thickness with temperature. According to these results, initial smaller and thinner crystals become larger and thicker. In the case of cEUA, the long spacing increases from 30.1 nm to 52.4 nm, as depicted in the left plot of Figure 3. This enhancement also comes out in the nanocomposites; then, long spacing rises from 33.2 nm to 52.8 nm and from 35.2 nm to 51.2 nm in the A1 and B1 hybrids, respectively. It is clear from these results and from the left plot in Figure 3 that cEUA crystallites undergo the highest dependence on temperature. Then, it seems that the mesoporous structure of MCM-41 leads to a confinement of some polyethylene chains inside its pores and channels. This effect is also evident from the variation of the relative invariant represented in the right plot of Figure 3.

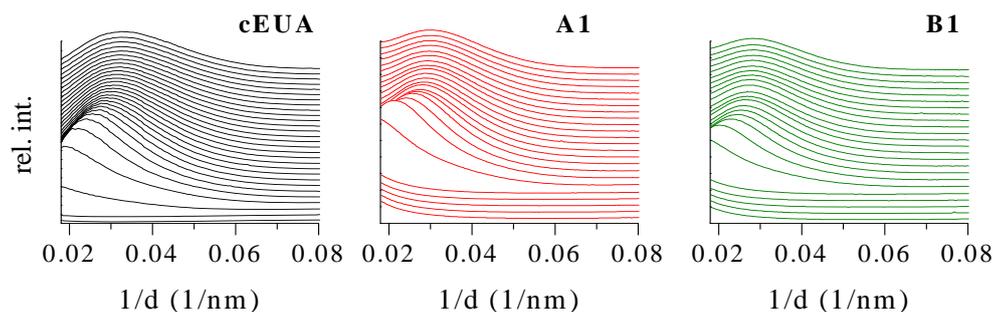


Figure 2: Real-time SAXS profiles for cEUA copolymer and two of the hybrids in a melting experiment at 8 °C/min. Only one frame every three is plotted, for clarity.

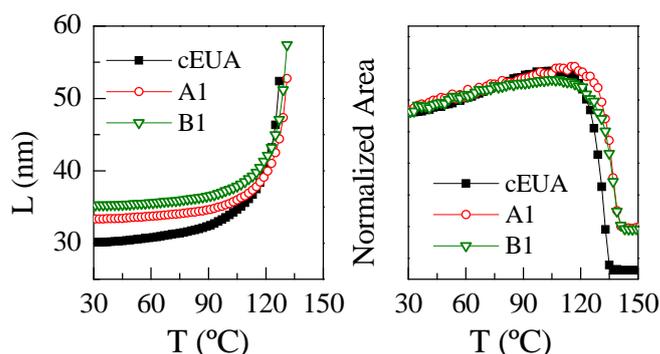


Figure 3: Temperature dependence of the long spacing ( $L$ , left plot) and relative SAXS invariant (right plot) for the cEUA copolymer and some hybrids.

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## References

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