

## In situ polymerization of polyolefin (nano)composites using sepiolite as support of metallocene co-catalyst

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A study concerning the use of sepiolite (fibrillar clay) as support of the co-catalyst (methylaluminoxane, MAO) for a process of in situ polymerization was performed. The formation of an ether bond on the clay surface was necessary to achieve the heterogenization of MAO over sepiolite's surface. In this sense, the experimental variables used during the process of grafting of MAO onto sepiolite's surface were studied. Therefore, it was demonstrated that the structure of modified clay and the structure of grafted MAO were kept because they were able to form the active species for polymerization in presence of catalyst and monomer.

In order to assess the effectiveness of this anchor process, a small group of polymerization test was performed. Four different (nano)composites based on polyethylene were synthesized with modified sepiolite. The presence of clay in the polymerization medium, in either case, increases the nanocomposite fusion temperature and the chain's length and is able to narrow molecular weight distributions leading to significant improvements of mechanical properties such as elongation at break ( $\% \epsilon_b$ ) and Young's modulus.

It is important to highlight that the improvements on properties of synthesized polymers with this supported catalyst are dependent on the type of treatment applied. If small amounts of anchored MAO are used, low reaction productivities are obtained. This fact is due to the few active sites available for polymerization. As a consequence, the molecular weight increasing and monodispersity are exacerbated, thus, the chains lose the ability to crystallize and finally major losses in mechanical performance are obtained.

These preliminary data have demonstrated the importance of the study of the variables that influence the process of chemical anchoring of MAO onto sepiolite surface for nanocomposite polymerization processes. Furthermore, this procedure may be easily transferred to conventional polymerization processes for obtaining polymers in which the chains are synthesized onto the surface of the filler, maximizing the interaction of matrix–nanofiller and leading to (nano)composites with better performance than the ones obtained by melt intercalation.

A more advanced study is presented by our research group in the WO2013-167764A1 patent.