

Analysis by ATR-FTIR of the curing process in epoxy resins modified with two different Polyhedral Oligomeric Silsesquioxanes (POSS).

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Polyhedral Oligomeric Silsesquioxanes (POSS) can be dispersed in thermosetting resins at nanometric scale to form inorganic/organic hybrid nanocomposites. In contrast to conventional inorganic fillers, POSS have the advantages of monodispersed size, low density, high thermal stability and controlled functionalities. [1]

In the present work, the mechanism of polymerization of an epoxy-diamine system, when it is modified with several percentages in weight of two different POSS, was studied by Attenuated Total Reflection Fourier Transform Infrared, ATR-FTIR. The epoxy-diamine system was formed by diglycidylether of bisphenol A (DGEBA), as epoxy resin and 4,4'-(1,3-phenylene diisopropylidene) bisaniline (BSA), as hardener. The two selected POSS were the octaepoxy-cyclohexyldimethylsilyl-POSS (OECh) and the epoxy-cyclohexylcyclohexyl-POSS (EChCh). Both of them contain eight and one epoxy groups in their structure, respectively, which can take part into the curing reaction so that, the POSS remains chemically connected in the final product. The figure 1 shows the structures of all materials.

A curing process optimized by differential scanning calorimetry analysis, DSC, was applied to the modified samples, which consists on an initial heating during 3h at 130 °C and a post-curing process during 4h at 150 °C, in a conventional oven. At designated time intervals, small portions of the sample were withdrawn from the oven and the reaction was suddenly stopped by freezing, in order to be tested by ATR-FTIR.

In the figure 2, the results of the ATR-FTIR analysis for the two epoxy-diamine samples modified with a 2,5 wt% of both POSS can be seen. As the cure reaction advances, the diamine reacts with the two epoxy groups present in the mixture, the epoxy from the thermosetting resin (DGEBA) and the epoxy from the POSS (EChCh/OECh), until the secondary amine groups are generated. It can be observed that the reaction with the thermosetting resin is more favourable than with the epoxy POSS, because the absorbance of the band corresponding to the bending of epoxy from DGEBA, at 917 cm^{-1} , disappears along the curing process, contrary to the bending band of epoxies belonging to POSS molecules, at 745 cm^{-1} for OECh and 743 cm^{-1} for EChCh. Moreover, the diamine reacts in a mayor proportion with the monofunctional POSS, EChCh, than with the octafunctional, OECh. This can be explained by means of steric hindrance, as more voluminous the epoxy containing molecule is, more difficult will be the approaching of the amine. [2, 3]

As the primary amine groups have been consumed, polyetherification reactions begin to appear as a result of the reaction between the hydroxyl groups, resulting of the opening of the oxirane rings, and the epoxy groups remaining. This phenomenon is confirmed by the presence of the stretching band of aliphatic ether groups around the 1100 cm^{-1} . So, competition phenomena exist between both kind of polymerization, the reaction with the hardener and the homopolymerization.

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References:

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Figures:

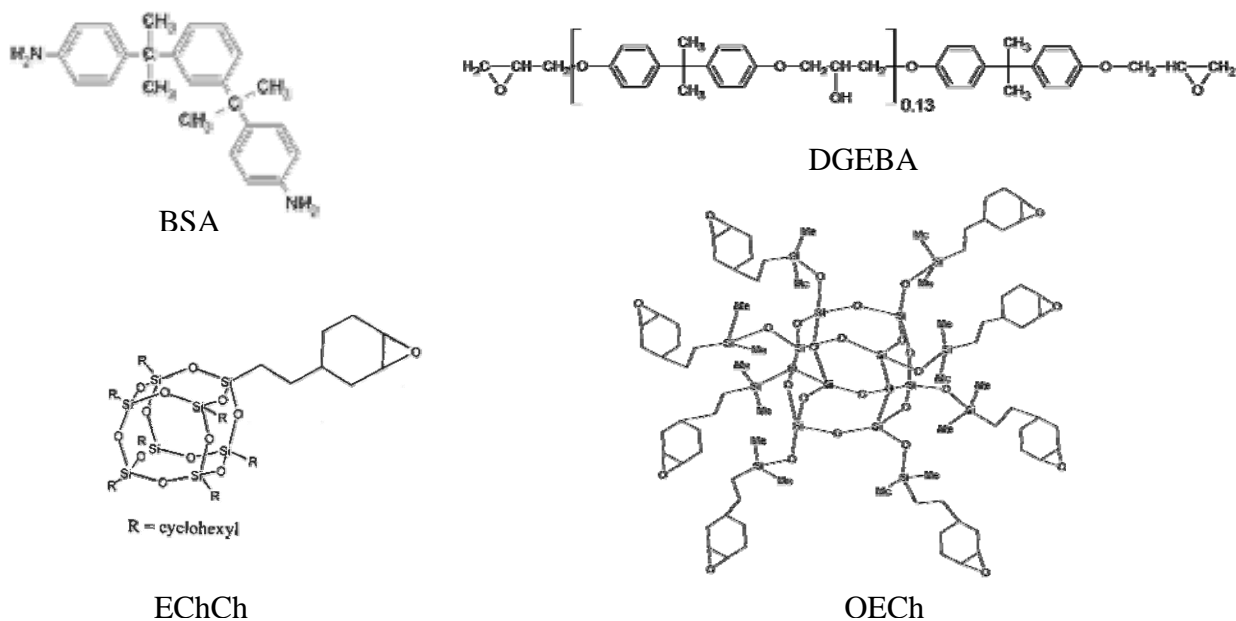


Figure 1. Structures of different materials forming the final nanocomposite.

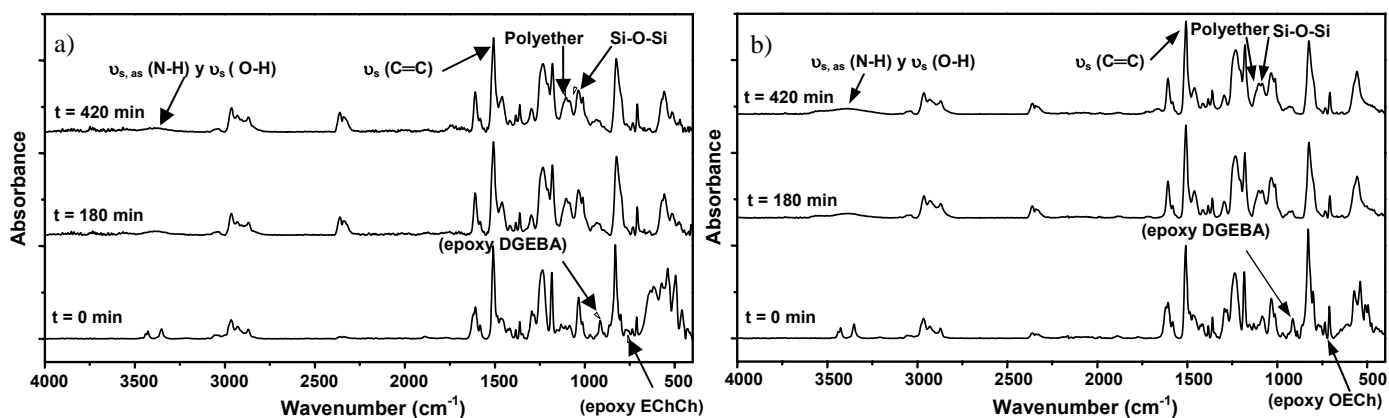


Figure 2. ATR-FTIR spectra obtained for samples with 2,5 wt % of a) EChCh and b) OECh.