

## Thermal ageing of sepiolite/ polyamide66 nanocomposites

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Clay/polymer nanocomposites are hybrid materials in which the nanoclay is exfoliated in the polymer matrix providing remarkable physical properties suitable for sophisticated industrial applications [1, 2]. The enhancement of the technical properties has been related to the crystallographic arrangement between the clay minerals and the polymer matrix [3]. Nanocomposites have been used commercially since Toyota first auto parts in the late 1980s. However, further effort has to be done to understand the long-term thermal stability of these materials. The aim of this work is to study the influence of the temperature on the stability (and thus the technical properties) of injection molded sepiolite/polyamide66 nanocomposites. For that purpose pure polyamide66 (PA66-S-0 samples) and sepiolite/polyamide66 nanocomposites with 5 wt.% clay loading (PA66-S-5 samples) were manufactured and injected (BABYPLAST 6/10, CRONOPLAST) to simulate industrial processing. Thermal ageing was carried out at 110 °C and 150 °C during 7, 14, 21, 28 and 35 days. Thermogravimetric analyses (TG Mettler Toledo TS 0801R0) were carried out to determine the thermal stability of the materials. Crystallinity index ( $W_c$ ) was calculated with the help of Differential Scanning Calorimetry (DSC 822e, Mettler Toledo). Infrared spectra (FT-IR Bruker Tensor 27) was used to obtain the carbonyl index. The results indicate that the mass loss is not affected by the ageing. However, in PA-S-5 samples  $W_c$  decreases with the ageing and carbonyl index is higher than in pure polyamide66, thus indicating further degradation.

[1] Kojima *et al* (1993) *Mater Res* **8**, 1185-1189. [2] Wang *et al* (2004) *Appl Clay Sci* **25**, 49-55. [3] Yebra-Rodríguez *et al* (2009) *Mater Lett* **63**, 1159-1161.

## Pressure-induced polyamorphism in Amorphous Calcium Carbonate: Insights into biomineral polymorph selection mechanisms

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Amorphous calcium carbonate (ACC,  $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ ) is commonly found in the earliest stages of biomineral development and as one of the metastable phases formed during the inorganic precipitation of calcium carbonate crystalline polymorphs. Recently, the existence of different amorphous polymorphs of ACC—proto-vaterite and proto-calcite—that act as precursors of the crystalline polymorphs has been suggested [1]. It has also been shown that the presence of  $\text{Mg}^{2+}$  in ACC induces an aragonite-like local order around the  $\text{Ca}^{2+}$  ions [2]. Here we show using high-pressure high-energy x-ray diffraction experiments combined with reverse Monte-Carlo modeling that ACC undergoes a reversible structural transition at  $\sim 9.8$  GPa adopting an aragonite-like local order when its molar volume is decreased. This has been confirmed by high-pressure Raman experiments that show a discontinuous behavior of the carbonate stretching and in-plane bending modes at  $\sim 10$  GPa. This finding could be suggesting that cationic substitutions of  $\text{Ca}^{2+}$  by smaller ions, such as  $\text{Mg}^{2+}$ , control ACC polyamorphism by reducing the molar volume of the amorphous phase. The fact that the structure is hydrated and that no signs of dehydration are found throughout the compression suggests that water is a key element in the reversibility of the transition. To our knowledge, this is the first reversible amorphous-amorphous phase transition found for an amorphous ionic system. High-pressure x-ray absorption experiments have also been performed to study the evolution of the density under pressure, allowing the first determination of the bulk modulus ( $K' = 27.2 \pm 1.4$  GPa) and the density of ACC ( $2.18 \text{ g/cm}^3$ ).

[1] Lam, Charnock, Lennie & Meldrum. (2007) *Cryst. Eng. Comm.* **9**, 1226-1236. [2] Gebauer, Gunawidjaja, Ko *et al* (2010) *Angew. Chem. Int. Ed.* **49**, 1-4.