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Report on the dissertation of Ms Sonia BUJOK entitled :

« Microwave-assisted preparation of polymer materials »

This PhD work was carried out at the Institute of Macromolecular Chemistry of the Czech Academy of Sciences, in the department of Polymer Processing and was supervised by Dr Hynek Benes. This study was focused on the synthesis of nanocomposite based on biodegradable polyesters such as polycaprolactone combined with layered double hydroxides (LDH) by using a clean polymerization process, *i.e.* microwave-assisted in situ ring opening polymerization of ϵ -caprolactone which can lead to shortening of the process time. The use of ionic liquids (IL) for modifying the clay nanoparticles brings a catalytic effect on the polymerization and a specific function due to the chemical nature of ionic liquid. This proposed strategy is environmentally friendly. The introduction of the review reports the concepts required for this work : the microwave -assisted ring opening polymerizations, the anionic clay such as LDH, ionic liquids, IL. Four subsections are then proposed. This manuscript is very easy to read. Congratulations because very few typographic mistakes can be found in the review. Please just correct 'to synthesize' p18, l 21, remove 'sizes' p 41, l8

The first subsection describes the modification of Mg^{2+}/Al^{3+} LDH with three types of IL different by the chemical nature of the anion : phosphinate, decanoate and phosphate. The modified clay was characterized by X-Ray diffraction, IR spectroscopy and TGA analysis.

Question : Is possible to fully modify the LDH ? Did you change the modification process ?

Question : By increasing the concentration of IL, is it not possible to increase the d-spacing and to get well ordered layers ?

Question : An anionic change takes place in the LDH modification but where is the cation ? Did you try to use a less sterically hindered cation ?

Question : To your mind, why the IL weight contents is lower for phosphinate IL ?

Question : How to separate the part of confined IL from physisorbed one on the edges ?

The second subsection focuses on other type of LDH based on Ca^{2+}/Al^{3+} LDH modified with IL based on the phosphonium cation combined with the decanoate anion. This section describes mechanism, kinetics and thermodynamics of the polymerization process by using IR, XRD, SAXS. In this section, a comparison is made between the hydrated form of LDH and its calcinated form. The modification of the hydrated clay takes place between the layers and on its surface whereas on a calcinated LDH, the author claims the modification only happens onto the surface.

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Question : Why the modification takes place too on the surface of the calcinated LDH since the OH groups disappeared ?

Question : Did you calculate the steric hindrance of the intercalated anion and compare with the measured d-spacing ?

Question : Could you show us the TGA analysis on this modified LDH ?

Question : What is the chemical group responsible in IL making it sensitive to microwaves ? Are they all sensitive to microwaves ?

Question : are you sure that the anions are released during the exfoliation of LDH ? Don't forget the ionic interaction strength ?

Question : have you an idea how to follow the location of anion/cation pairs ?

The third subsection makes a comparison between the *in situ* synthesis of nanocomposite and the melt intercalation by investigating the effect on the mechanical, thermal and barrier properties.

Question : What is the morphology of nanocomposites dedicated to barrier properties and containing the calcinated fillers in comparison with the non calcinated ones ?

The fourth subsection carries out on the $\text{Zn}^{2+}/\text{Al}^{3+}$ LDH more relevant to antibacterial properties which are described in this part.

Question : How do you explain the effect of these fillers on the molecular weight decrease ? Is the residual monomer left ?

Question : How do you explain the influence of the LDH ions nature on the properties of the resulting material ?

This work is a successful since it paves the way for processing in a sustainable route biodegradable polycaprolactone films for active bio-packaging. The large amount of data and the high quality of this work let me to give my agreement to the defence of Ms Sonia BUJOK.

Lyon, 2021 Sept 19



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