## SUMMARY

The main objective of this thesis is to provide knowledge about the influence of nanomaterials as additives for packaging purposes. They may influence final packaging performance but also environmental impact of the whole packaging & product system, waste management once the packaging is empty and product safety. This work attempts to give data about main nanomaterial applications to a specific packaging purpose that is the food packaging. Moreover, knowledge on how the recycling process and final recycled material quality once the nanoadditivated package is managed is given. Besides, the environmental impacts not only considering global environmental impacts but ecotoxicity effects are analysed when nanomaterials are incorporated as additives for packaging.

The work carried out has been compiled into trhee scientific papers which complete content has been attached to this document. The first was published in the journal "Packaging Technology and Science", the second in the journal "Waste Management" and the third one in the "Journal of Cleaner Production". The journal selection was made considering the different areas of knowledge that each one of the different works addressed. The common link between the research articles is according to the main objective intended of this thesis. This objective is to provide novel data and specific research work and results regarding nanomaterials on their application to packaging from different perspectives; functional but mainly environmental. The research activities carried out and detailed in each one of the published papers aim at providing valuable scientific contribution to such ambitious objective commented.

Thus, it was considered a key starting point to carry out an exhaustive analysis of the State –of-the-Art on nanomaterials and their applications to food packaging. Due to the huge diversity of existing nanomaterials and that they can be applied not only to the package but to the food product, the analysis was made considering the final properties improvement of the package compared to those only considering conventional materials. The analysis considered three main categories for the properties studied: Technical, active and intelligent. The qualitative evaluation results were specific applications considered (e.g. packaging applications are more strict in terms of material quality and mechanical properties than urban furniture or construction sector). Nevertheless, even if current applications accept these properties, it should be also taken into account that the increasing amount of nanoparticles in the packaging sector as well as the cumulative effects of these particles in the materials could amplify these variations.

The last analysis was focused on the environmental assessment of a nanomaterial in a specific application. Life Cycle Assessment was addressing three main objectives: (1) to solve the problem of a comparative assessment of different packaging materials considering different mechanical properties considering the same functional unit applying Ashby's index, (2) to provide an inventory for calcium carbonate production process, a novelty in the available scientific literature, and (3) to effectively apply USEtox method for evaluating the impact for inorganic nanoparticles, in this case, calcium carbonate. Concretely, a comparative life cycle assessment was carried out between a LDPE nanocomposite film (4% nanoclay) with a virgin LDPE film. The practical application of the USEtox method is a key novelty of this work due to: (a) the adaptation of the method to a specific case of the toxicological analysis carried out to the nanoparticle and (b) the absence of quantitative information of this method application for the impact assessment of nanomaterials. Results show that the use of nanomaterials can help to reduce the environmental impacts due to the functional properties improvement around 40% for impact categories not related to toxicity as well as 38% material savings. Moreover, characterization factors have been calculated for this nanoparticle being them very low what reflects high values for EC50 around 100mg/l, what means low toxicity.

Therefore, the results obtained allow identifying future research areas that will provide novel contributions in the nanomaterials and their application to packaging, products contained and their environmental and safety aspects.

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grouped to identify the ones with the most relevant potential actual and future for food packaging. That was made applying Multicriteria Decision Analysis (MCDA). Although some constraints were identified, such as no availability of specific applications for some nanomaterials, case by case analysis demands, it could be concluded that those nanomaterials have had been focused on barrier properties improvement, microbial activity reduction, mechanical functionality, and water permeability minimisation. Among the more than 84 publications reviewed, it could be observed that the one with the highest application potential was calcium carbonate or the chitosan, due to their combination of active and improved properties. Besides, nanoclays (caolinite), carbon nanotubes/nanofibres, and nanobiocomposites based on bioplastics like PLA and PHB were in the first ranking positions of the MCDA. Nonetheless the good ranking carbon nanotubes/nanofibres, there are still great uncertainties due to their citotoxicity and the non-desired migration potential to the food product. Another interesting result was that metallic particles like ZnO, TiO2 and Ag were not in the first ranking positions of the MCDA carried out.

The potential influence of the presence of nanomaterials in the packaging recycling process as well as their influence on the final recycled material properties were evaluated in the second paper. Combinations of three different film polymers (polyethylene (PE), polypropylene (PP) y polyethilenterephtalate (PET) reinforce with four different nanomaterials (nanoclays, calcium carbonate, zinc dioxide and nano silver) were anaylised. Tested combinations were: PE-nanoclay, PE-CaCO<sub>3</sub>, PP-Ag, PET-ZnO, PET-Ag, PET-nanoclay. The experimental recycling tests show that smells and degradation fumes appears in the processing of PET reinforced with nanoclay, as well as increasing number of pinholes when this polymer is reinforced with Ag. Moreover, colour deviations were visible in most of the samples in levels higher than the limit perceivable by the human eye. Additionally, regarding material quality, slight changes in brightness and vellowness index were observed (brightness especially in nano-reinforced PET and yellowness in nano-reinforced PE, PP as well in PET with Ag). Finally, also several mechanical properties suffered variations: tensile modulus (PE with nanoclay, PP with Ag), tensile strength (PE with nanoclay1), elongation at break (PET with Ag) and tear strength (PE with nanoclay1 and PP with Ag). The acceptance of these changes in the properties of recycled PE, PP and PET with the progressive integration of nano-reinforced polymers in the packaging sector will depend on the

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