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Recyclability assessment of nano-reinforced plastic packaging

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ABSTRACT

Packaging is expected to become the leading application for nano-composites by 2020 due to the great advantages on mechanical and active properties achieved with these substances. As novel materials, and although there are some current applications in the market, there is still unknown areas under development. One key issue to be addressed is to know more about the implications of the nano-composite packaging materials once they become waste.

The present study evaluates the extrusion process of four nanomaterials (Layered silicate modified nanoclay (Nanoclay1), Calcium Carbonate ($CaCO_3$), Silver (Ag) and Zinc Oxide (ZnO) as part of different virgin polymer matrices of polyethylene (PE), Polypropylene (PP) and Polyethyleneterephtalate (PET). Thus, the following film plastic materials: (PE–Nanoclay1, PE–$CaCO_3$, PP–Ag, PET–ZnO, PET–Ag, PET–Nanoclay1) have been processed considering different recycling scenarios.

Results on recyclability show that for PE and PP, in general terms and except for some minor variations in yellowness index, tensile modulus, tensile strength and tear strength (PE with Nanoclay1, PP with Ag), the introduction of nanomaterial in the recycling streams for plastic films does not affect the final recycled plastic material in terms of mechanical properties and material quality compared to conventional recycled plastic. Regarding PET, results show that the increasing addition of nanomaterial into the recycled PET matrix (especially PET–Ag) could influence important properties of the recycled material, due to a slight degradation of the polymer, such as increasing pinholes, degradation fumes and elongation at break. Moreover, it should be noted that colour deviations were visible in most of the samples (PE, PP and PET) in levels higher than 0.3 units (limit perceivable by the human eye). The acceptance of these changes in the properties of recycled PE, PP and PET will depend on the specific applications considered (e.g. packaging applications are more strict in material quality that urban furniture or construction products).

1. Introduction

Plastic production is going up and an associated overall increase in the generation of plastic waste between 2008 and 2015 of 5.7 Mt (23%) is expected. This is largely driven by a 24% rise in the packaging sector and is part of an unbroken trend of increasing plastic waste in Europe (European Commision, 2013). The use of lighter materials could, at least to some extent, solve the waste problem. Unfortunately, so far the reduction of plastic is limited because of the weak mechanical as well as poor barrier properties shown by the final plastic material. The addition of nanoreinforcements is promising for the improvement of conventional polymerś properties. A better overall performance of polymers, making them more competitive further adding environmental advantages such as reduction of waste and decrease of CO_2 emissions among others, have been found (Monteiro et al., 2011). In the case of nanoclays, they have been reported to improve thermal stability, resistance to fire and mechanical properties of several polymers like polyethylene (PE), polypropylene (PP), Nylon 6 and polylactic acid (PLA) (Silvestre et al., 2011; Duncan, 2011; Lagaron and López-Rubio, 2011; Sinha Ray and Okamoto, 2003; Baniassadi et al., 2011; Hanemann and Vinga Szabó, 2010; Akbari et al., 2007; Wang et al., 2006). Interesting antimicrobial properties have been reported when Nano-Ag is used in food and beverage packaging (PE, PP) (Silvestre et al., 2011; Tankhiwale and Bajpai, 2012; Duncan, 2011) as well as nano-titanium dioxide (TiO_2) incorporated with polyethylene terephthalate (PET) or polylactic acid (PLA) providing not only antimicrobial properties but also ultra violet (UV) protection and enhanced strength (Silvestre et al.,

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2011; Duncan, 2011; Hanemann and Vinga Szabó, 2010). Additionally, experimental tests have confirmed that the application of nanofillers can be an efficient technique for the improvement of morphological, mechanical, rheological and thermal properties of recycled polymers, composites and blends (Zare, 2013). Furthermore, nanoparticles are used as components for manufacturing intelligent inks (conductive inks), active tags, disposable power sources or other product identification and anti-counterfeiting devices in the area of intelligent packaging. Last but not least and from a more general perspective, the use of nanocomposites in packaging can lead to reduction of energy requirements for production, transport and storage and to the reduction of the volume of waste to be disposed of in landfills (Silvestre et al., 2011).

As a result of the advantages that nanomaterials entail, packaging is expected to become its leading application by 2020 (Pastemart, 2003). The robust growth in demand for rigid and flexible plastic packaging based on polymeric materials especially in sectors like drinks, cosmetics, toiletries and household and personal care products (Smithers Pira, 2012) drive to the conclusion that the amount of nanocomposites in the market is about to increase substantially over the next years and as a consequence the amount of nanocomposites waste will do likewise.

Packaging waste management is regulated by the Packaging Waste Directive (94/62/EC and 2004/12/EC). Its main objective is to reduce the environmental impact associated to packaging waste generated in the European Union. With this objective, a hierarchy in the waste management strategies was set in order to boost, in this order, the reduction, reuse, recycling and valorisation of packaging waste. Within this framework, these directives also establish increasing recycling percentages for domestic waste. Concretely, it is established that 70% of domestic paper, metal, plastic and glass waste has to be prepared for reuse, recycling and valorization by 2015.

Prevention is more related to the manufacturing practices of the companies independently of the materials they use and reuse is only possible under certain circumstances (e.g. closed loop operations). Therefore, the first priority for the nanocomposites applied for packaging purposes from the waste management point of view is to ensure their recyclability when it becomes waste being mechanical recyclability the preferred treatment option for post-consumer plastic waste (Luijsterburg and Goossens, 2013). Nevertheless, materials and especially plastics reinforced with nanoparticles could have the potential to cause problems in current recycling processes especially taking into account the increasing production volume of these innovative materials. It is needed to evaluate if the presence of some amount of nanomaterials in the final recycling material streams could to some extent affect either the recycling process or the final recycled material properties.

Studies have shown that mechanical recycling of plastic composite materials and especially packaging is possible (Cornier-Ríos et al., 2007; Kers et al., 2006; Teodorescu et al., 2008). However, it is worth to note that some studies dealing with plastic composites recycling (Augier et al., 2007; Petchwattana et al., 2012; Russo et al.,2007) reported that after a certain amount of processing cycles the molecular weight distribution in the polymeric matrix is affected (becomes shorter and narrower). This affects the viscosity and the mechanical properties of the material.

Nevertheless, information regarding the recyclability of nanocomposites is still scarce because only studies in some specific materials have been carried out up to this point. For instance, Srebrenkonska and Bogova Gaeva (2011) evaluated the properties of rice hulls reinforced-PLA after various processing cycles and concluded that it can be recycled and utilized for production of new eco-materials with acceptable thermal and mechanical properties. Nevertheless, Touati et al. (2011) evaluated the effects of reprocessing cycles on cloisite 15A reinforced-polypropylene and concluded that the recyclability of this material is more complex because it strongly affects the performance of the nanocomposites in terms of structure and therefore in mechanical properties. It appears therefore that conclusions regarding the recyclability of nanocomposites and specifically nano-reinforced packaging materials cannot be drawn yet. As a result, more studies are needed in order to obtain a more comprehensive view and adapt the existing recycling technologies to the gradually increasing production of nano-reinforced packaging materials. Moreover, final quality of the recycled plastics incorporating nanomaterials has to be assessed in order to know potential applications.

The objective of this study is to evaluate the final material main properties as well as the potential recyclability constraints in conventional recycling systems caused by packaging materials incorporating nanomaterials. The results could serve as the basis for the adaptation of technologies to the increasing production and use of these innovative materials.

This work has been focused on plastic, since this is the most common packaging material accounting for 50% of all packaged goods in Europe (Plastics Europe, 2013). Specifically, nano-reinforced films of PE, PP and PET have been selected since they are the most representative plastic packaging materials (American Chemistry Council, 2014) in the food sector (the biggest market of packaging). According to different scientific publications, market reports and industrial end-userś opinions, the most commonly used nanoreinforcements for packaging purposes are organic layered nanoclays, metal nanoparticles, metal oxide nanoparticles and carbon nanotubes. In this sense, silver, gold and zinc nanoparticles are most studied metal nanoparticles with antimicrobial function (Silvestre et al., 2011; Duncan, 2011; Tankhiwale and Bajpai, 2012). On the other hand, for mechanical and barrier properties, the polymers incorporating clay nanoparticles are among the first polymer nanomaterials that emerged in the market incorporated in a wide range of polymers such as polyolefins, polystyrene, epoxy resins polyurethane or polyethylene terephthalate. Taking all this into account four nanoparticles have been chosen: layered silicate nanoclay modified with hexadecyltrimethylammonium bromide (hereafter Nanoclay1), $CaCO_3$, Ag and ZnO.

Extrusion processing of different nano-reinforced plastic films containing different nanomaterial concentrations were compared with conventional recycling process of conventional recycling of packaging film without nanomaterials. Processing conditions as well as final material properties have been monitored and analysed to identify possible changes in parameters such as discolouration, haze, smells, degradation fumes, sticking effects, increasing number of pinholes, visual appearance, material quality and mechanical properties.

2. Material and methods

The evaluation of the recyclability constraints caused by plastics films reinforced with nanoparticles was carried out through experimental recycling tests where conventional recycled packaging films without nanomaterials were subjected to extrusion processing in combination with increasing concentrations of nano-reinforced plastic films. In this work only one recycling cycle was considered.

This evaluation was focussed on PE, PP and PET monolayer films used in the food sector reinforced with 4% in weight of four nanoparticles (ZnO, Ag, Nanoclay1 and $CaCO_3$). This percentage was decided since it is conventionally used in nano-reinforced plastics in the packaging sector (Paul and Robeson, 2008; Deshmane et al., 2007). Specifically, 6 plastic film materials were included in the study: PE + $CaCO_3$, PE + Nanoclay1, PP + Ag, PET + ZnO, PET + Ag and PET + Nanoclay1.