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PLA coated paper containing active inorganic nanoparticles: Material characterization and fate of nanoparticles in the paper recycling process

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ABSTRACT

For paper and paperboard packaging, recyclability plays an important role in conserving the resources and reducing the environmental impacts. Therefore, when it comes to the nano-enabled paper packaging material, the recyclability issue should be properly addressed. This study represents our first report on the fate of nanomaterials in paper recycling process. The packaging material of concern is a PLA (Polylactic Acid) coated paper incorporating zinc oxide nanoparticles in the coating layer. The material was characterised and assessed in a lab-scale paper recycling line. The recyclability test was based on a method adapted from ATICELCA MC501-13, which enabled to recover over 99% of the solids material. The mass balance result indicates that 86–91% zinc oxide nanoparticles ended up in the rejected material stream, mostly embedded within the polymer coating; whereas 7–16% nanoparticles ended up in the accepted material stream. Besides, the tensile strength of the recycled handsheets suggests that the nano-enabled coating had no negative impacts on the recovered fibre quality.

1. Introduction

Incorporating Nanoparticles (denoted as NPs) in paper products has recently become a strong innovating point and therefore has attracted many research efforts, including several EU-funded projects. For example, silver nanoparticles (Ag NPs) (Martins et al., 2012) and zinc oxide nanoparticles (ZnO NPs) (Martins et al., 2013) were used as antimicrobial agents in paper coating, which holds potential application in active packaging; in a similar fashion, Ag NP-enabled cellulose absorbent pad was used in the packaging of fresh cut fruit (Fernández et al., 2010); Manda et al. (2012) proposed a sandwich-like structure for producing printing paper using TiO_2 NP-based coating layers to shield the unbleached kraft pulp in between, which enables to omit the pulp bleaching stage, and hence reducing the associated consumption of energy and chemicals as well as emissions; in the work of Steward et al. (2008), the authors explored the innovation opportunities in using NPs to enhance paper's printability and deinkability.

In the case of paper and paperboard packaging material, recycling is regarded as one of the most favourable options in terms of waste management (Directive 94/62/EC, 1994) for its important role in minimising the packaging's environmental impacts (Merrild et al., 2008). Therefore, when it comes to the nano-enabled paper packaging material, its recyclability shall be retained and not be compromised. However, only very few studies have addressed this issue: for example, a relevant research found that using NFC (Nano Fibrillated Cellulose) to replace part of the synthetic latex in paperboard coating would not cause negative impacts on paper recycling (Hohenthal et al., 2012). As reported in a recent publication (Aliaga et al., 2015), Ag NP-based ink had some noticeable impacts on the optical properties of the recovered fibres.

Nanomaterial as a new class of material, its safe and sustainable use has raised considerable attention. One major concern is the nanomaterial's toxicity (eco-system and human health). As the dimension of solid material is reduced below 100 nm, it tends to exhibit enhanced reactivity/activity/toxicity, which is associated with nano-specific physico-chemical properties, such as particle size distribution, particle shape, solubility, surface charge, and surface functionalization (Duncan, 2011). Furthermore, when nanomaterials release to the environment or expose to human, their fate and nano-toxicity strongly depends on the NPs' colloidal behaviour, e.g. the kinetics of transformation, aggregation and degradation, which is a complex mechanism and not yet fully understood (Kunhikrishnan et al., 2015; Powell and Kanarek, 2006). In a relevant study (Kaegi et al., 2010) the researchers tracked the emission

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of the NPs from a building's exterior facades that are coated with NP-containing paint. And they found that 30% of Ag NPs released after one-year exposure, and these released NPs were in binder attached colloidal form.

The objective of this study is to track the fate of nanomaterials in the paper recycling process. It will help to identify the critical stages where control measures should be implemented for the safe use of nanomaterials. The packaging material of concern is a PLA (Polylactic Acid) coated paper incorporating ZnO NPs in the coating layer. It is to be used as sandwich wrap or deli wrap to control the microbiological risk.

In the case of antimicrobial packaging application, the material shall comply with the EU regulation EC No 450/2009. The authority is taking a case-by-case approach towards the nano-agent/nano-additive (Rossi et al., 2014). Agent migration in both nano-form and ionic form is a key issue in successful authorisation (EFSA CEF Panel on Food Contact Materials, 2015).

2. Materials and methods

A white bleached kraft paper (basis weight 106 g/m^2, ash content 7.7%, top side sized) was used as substrate for coating.

2.1. Coating recipe

PLA pellets (4060D, Natureworks) were dissolved in ethyl acetate under vigorous stirring at room temperature. The final solution had a concentration of 15 wt%.

ZnO nanoparticles (Zano® 20 Plus-3) were kindly supplied by Umicore, Belgium. In accordance with the producer's information, the NPs are silane coated (ester functional group) for enhanced dispersibility in polymer. The NPs have an average particle size of 30 nm (Murariu et al., 2011). As the NPs were supplied in powder form, first they were dispersed in the solvent: adding 2 g NPs into 100 mL ethyl acetate, stirring vigorously for 10 min, and then applying ultrasonic treatment for 5 min (Sonics, microtip CV 334, 750 w 20 kHz) to break up the agglomerates/aggregates. Afterwards, the NPs dispersion was mixed with the PLA solution at the designated loadings, 0.5%, 1% and 3%, NPs over PLA in dry solids weight. The mixtures were subjected to 20 min vigorous stirring before coating.

Coating was carried out on a lab film applicator (Elcometer 4340) using a smooth bar which allows to deposit 50 μm wet film onto the substrate. Coating was applied on the sized side of the paper in order to control the polymer solution penetration. After coating, the samples were dried overnight at room temperature.

The structure of the packaging material is illustrated in Fig. 1.

In total, three different coated samples were produced. Base paper without coating was used as control. Sample identification and description are listed in Table 1.

2.2. PLA coated paper characterization

Before testing, all the samples were conditioned at 23 °C, 50% RH.

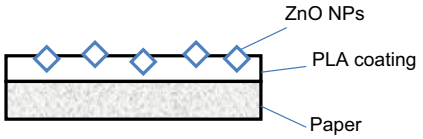

Fig. 1. Schematic illustration of the paper packaging material produced.

Table 1
Sample identification and description.

Sample identification	Description
Blank	Base paper, no coating applied
Coat-0.5	PLA coating containing 0.5 wt% ZnO NPs on base paper
Coat-1	PLA coating containing 1 wt% ZnO NPs on base paper
Coat-3	PLA coating containing 3 wt% ZnO NPs on base paper

Basis weight was determined with an analytical balance (Sartorius, CPA 225D). The measurement was done in triplicate. Data were presented as mean ± standard deviation.

Sample Coat-3 was selected for the SEM-EDX measurement (Scanning Electron Microscope and Energy Dispersive X-ray spectroscopy). The SEM images were acquired from the gold coated specimen (carried out with Cressington 108 auto), using a field emission scanning electron microscope (MIRA3, Tescan) operating at 15 kV accelerating voltage. The elemental analysis was carried out with an energy dispersive X-ray spectroscopy (Quantax EDS, detector Xflash 6/10, Bruker), which is coupled with the SEM instrument.

In order to assess the coating quality, the following tests were carried out according to their respective standards. N.B. for sample Blank, all the measurements were conducted on the sized side.

- Smoothness was measured with a Bendtsen smoothness tester following ISO 8791-2:2013. 10 measurements were made for each sample. Data were presented as mean ± standard deviation.
- Water absorptiveness was determined with Cobb-60 method (apparatus Acquati Giuseppe). The measurement was done in triplicate following ISO 535:2014.
- Contact angle was measured with an optical instrument (OCA 15EC, DataPhysics) using water as the probe liquid. The images were recorded within 1 min time span, and the measurement was done in duplicate.
- Brightness was measured with a spectrophotometer (UltraScan PRO, HunterLab). 10 measurements were made for each sample.

2.3. Recyclability test

2.3.1. Testing protocol

The testing protocol was based on the Italian method of recyclability of paper-based packaging (ATICELCA MC501-13, 2013). To accommodate our interest in tracking the fate of NPs in paper recycling line, the method was partly modified and the procedure is illustrated in Fig. 2. In brief, 25 g samples were cut into squares, approximately 2 × 2 cm, fed in a laboratory wet disintegrator (Enrico Toniolo, Italy), pulped with 1.5 L 40 °C tap water for 20 min, following ISO 5263:2004. After that, the pulp suspension was subjected to 7 min Somerville screening (L&W, Sweden, slits width 150 μm), following a modified procedure deriving from Standard TAPPI T 275 sp-12. All the "*rejects*" (material separated by the screen) and the "*accepts*" (fibrous material passing through the screen and possible coating fragments and filler particles) were collected, filtered and oven dried overnight at 105 °C to obtain the solids weight.

2.3.2. Materials from the paper recycling test

For the materials involved in the recycling test, the following tests were carried out:

- ICP-MS (Inductively Coupled Plasma-Mass Spectrometer)

Zinc concentration was determined with an ICP-MS instrument equipped with a double pass spray chamber (Sciex Elan 9000,