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Non-linear release dynamics for a CeO_2 nanomaterial embedded in a protective wood stain, due to matrix photo-degradation☆

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ABSTRACT

The release of CeO_2-bearing residues during the weathering of an acrylic stain enriched with CeO_2 nanomaterial designed for wood protection (Nanobyk brand additive) was studied under two different scenarios: *(i)* a standard 12-weeks weathering protocol in climate chamber, that combined condensation, water spraying and UV–visible irradiation and *(ii)* an alternative accelerated 2-weeks leaching batch assay relying on the same weathering factors (water and UV), but with a higher intensity of radiation and immersion phases. Similar Ce released amounts were evidenced for both scenarios following two phases: one related to the removal of loosely bound material with a relatively limited release, and the other resulting from the degradation of the stain, where major release occurred. A non-linear evolution of the release with the UV dose was evidenced for the second phase. No stabilization of Ce emissions was reached at the end of the experiments. The two weathering tests led to different estimates of long-term Ce releases, and different degradations of the stain. Finally, the photo-degradations of the nanocomposite, the pure acrylic stains and the Nanobyk additive were compared. The incorporation of Nanobyk into the acrylic matrix significantly modified the response of the acrylic stain to weathering.

1. Introduction

The necessity to better estimate and characterize the release of engineered nanomaterials (ENMs) from products has been pointed out repeatedly these past years (Caballero-Guzman and Nowack, 2016; Mackevica and Foss Hansen, 2016; Reijnders, 2009; Som et al., 2010). Real exposure assessments are indeed still hampered by the difficulty to detect and quantify ENMs in complex natural environments (Szakal et al., 2014). While models have been developed to compensate the lack of direct measurements, they often have to rely on oversimplifications and extrapolations in order to estimate the exposure resulting from ENMs release (Caballero-Guzman and Nowack, 2016), which lowers their reliability. A more accurate determination of ENMs flows at all stages of the products lifecycle is then required.

The use phase is particularly challenging, as uncontrolled releases of ENMs can result from consumer handling or aging of the products. Such releases cannot be easily determined in the everyday life. Then the simulation of relevant aging scenarios under controlled conditions at the lab-scale appears as a good option.

The release of ENMs during the use phase will depend on the nanoproduct category. For instance, the release from liquid suspensions is inherent to use and will be around 100%, while the release from solid nanocomposites is more difficult to predict. Solid nanocomposites are materials constituted with a solid matrix and ENMs that can be either deposited at the solid surface or incorporated in the bulk as filling agents (nanofiller). The release of ENMs from a solid nanocomposite can proceed from the leaching of ENMs by a liquid, via desorption from the surface, dissolution, or diffusion inside the matrix (Bossa et al., 2017; Duncan and Pillai, 2015). But it can also arise from the degradation of the solid matrix itself, caused by a mechanical action (Bressot et al., 2017) or (photo)chemical reactions (Duncan, 2015).

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Products with an outdoor application will be especially exposed to photo-degradations due to weathering processes. The weathering of solid nanocomposites has been the focus of several studies since the release of TiO_2 nanoparticles from facades was evidenced for the first time by Kaegi et al. (2008). Outdoor weathering setups with rain collectors were developed and allowed measuring the release of silver nanoparticles from an acrylic white paint (Kaegi et al., 2010) or from wood protective stains (Künniger et al., 2014) under natural conditions. However, such realistic scenarios required long-term exposures and many other groups preferred short-term lab-scale artificial weathering, that are pre-validated to correlate with material degradation CEN standards (Podgorski et al., 2003). In the past decade, short-term artificial weathering has been performed on paint (Wang and Nowack, 2018), stains (Shandilya et al., 2015), cement (Bossa et al., 2017; Wohlleben et al., 2011) and plastic nanocomposites (Fernández-Rosas et al., 2016; Neubauer et al., 2017; Nguyen et al., 2010; Wohlleben et al., 2017), either using homemade setups (Al-Kattan et al., 2013; Bernard et al., 2011; Olabarrieta et al., 2012; Pellegrin et al., 2009) or commercial climate chambers (Fiorentino et al., 2015; Hirth et al., 2013; Vilar et al., 2013; Zuin et al., 2013). Although a variety of weathering protocols have been tested, they most often included the exposure of the material to an artificial light source, simulating the full solar spectra (Busquets-Fité et al., 2013; Wohlleben et al., 2013), or restricted to its UV-part (Al-Kattan et al., 2013; Chin et al., 2004; Fiorentino et al., 2015). It was often combined with an exposure to water such as controlled relative humidity (Nguyen et al., 2010), periodic condensation (Fiorentino et al., 2015) or water spraying phases (Fernández-Rosas et al., 2016), representative for humidity, dew or rain, respectively. Depending on the groups, different methods were applied for release assessment. Some focused on quantifying the spontaneous release of ENMs during the weathering assays, using collectors to gather particles detached by gravity (Nguyen et al., 2011), or run-off waters from spraying (Al-Kattan et al., 2015; Busquets-Fité et al., 2013). However, this involved large volumes of water (up to 5000 L (Al-Kattan et al., 2013)). As an alternative, some authors implemented external release assessment, with (Hirth et al., 2013; Hsu and Chein, 2007) or without additional mechanical stress (Zuin et al., 2013) (e.g. shaking, sonication, abrasion). Although these different approaches were found successful, the diversity of protocols and setups made difficult the comparison between studies, the understanding of the mechanisms and laws governing ENMs release.

Recently, efforts were made towards harmonization of the experimental protocols, in the framework of large pilot interlaboratory studies (Wohlleben et al., 2017, 2014). They converged towards weathering procedures in climate chambers with or without periodic water spraying, and external release assessment. This harmonized protocol yielded contrasted results, depending on the nature on the material: UV-resistant polymers such as polyethylene led to minimal release, while epoxy resins experienced strong degradations under UV, entailing an accumulation of the ENMs at the surface, and eventually their release. A comparative study on a wide range of nanocomposites estimated that release rates from different matrices were spreading across 5 orders of magnitude while the impact of the nanofiller itself on the release rate was limited to one order of magnitude (Wohlleben and Neubauer, 2016). It was then proposed that matrix degradability determined to a large extent the response of a nanocomposite to weathering and the ENMs release behavior.

In this study, we focused on a single polymer matrix and analyzed the impact of the addition of a nanomaterial to its weathering. We used an acrylic stain that offers a good resistance to UV (Chiantore et al., 2000; Forsthuber et al., 2013) and is commonly employed for wood protection. It was enriched with a CeO_2 nanomaterial, which acts as a UV-absorber and brings an additional protection to the stain. We studied the weathering of this nanocomposite to answer two questions: i) is there a potential for release of the nanomaterial upon aging of a UV-resistant matrix ? ii) is the weathering of the acrylic matrix modified in presence of the CeO_2 nanomaterial? In addition, we characterized a parameter rarely addressed in details i.e. the evolution of the release rate with the UV irradiation. Two artificial weathering procedures were applied: a standard 12-weeks weathering protocol in a climate chamber, that combined condensation, water spraying and UV–visible irradiation, close to the harmonized protocol mentioned above; and an alternative accelerated 2-weeks batch assay applying the same weathering factors (water and UV), but with a higher intensity of radiation. In both experiments, the nanocomposite was weathered along with the reference stain without CeO_2 addition, in order to evaluate the impact of the nanomaterial on the aging. Surface degradations were monitored as an indicator for weathering. The release of Ce (as dissolved and/or particulate fraction) was quantified with short time steps (e.g. 24 h–72 h), to analyze the release dynamics during weathering and relate it to the degradations of the stain surface. Finally the physico-chemical transformation of the nanomaterial within the stain with weathering duration was characterized to give an insight into aging mechanisms.

2. Material and methods

2.1. Materials

An acrylic stain commercialized by Castorama under one of its brand (Lasure Intérieur- Extérieur casto') was chosen for this study. It was deposited in three layers, on larch substrates, freshly sanded with 180 grain paper, observing 2-h drying between successive layers and 24 h final drying.

Two groups of samples were prepared. In the first group (called n-CeO_2), the stain was enriched with citrate-coated CeO_2 nanoparticles, to improve UV filtering. For this, a commercial suspension (Nanobyk-3810) was added to the stain at 7 wt%, and this mix was applied to the upper face (*i.e.* exposed face) of the substrate sample (Fig. 1). The characterization and aging of Nanobyk additive was done previously (Auffan et al., 2014). Lateral and lower faces were coated with the stain alone to protect the wood substrate during weathering.

In parallel, a second group of samples (called ACR) was painted on all faces with the Ce-free stain. It was used as a reference to evaluate the impact of ENM addition on the aging of the stain.

For the weathering experiments in the climate chamber (Suntest samples), larch blocks of 27 × 27 × 13 mm were cut. They were weighed before and immediately after the application of each layer of stain. Taking into account a 18% CeO_2 content for Nanobyk additive (Tella et al., 2014), the amount of CeO_2 deposited on each sample (upper face) was calculated, and is reported in Table 1.

For batch experiments, the stain deposit was made on a larger piece of wood (600 × 35 × 11 mm), cut afterwards into 35 × 35 × 11 mm blocks. Lateral faces were covered with Ce-free stain after cutting. This method resulted in a less accurate determination of CeO_2 content, as final samples could not be weighed individually. CeO_2 surface concentration and stain density were then assessed based on the assumption that batch samples exhibited the same final CeO_2 content (wt.%) as Suntest samples.

2.2. Artificial weathering

Two artificial weathering procedures, based on a succession of dry irradiation and immersion or water spraying phases, were tested. The two sets of experiments were both built on a cycle of 7 days