

# Nanoparticle Release from Polymer Nanocomposites Used for Potable Water Infrastructure and Food Packaging: Current Progress & Beyond

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## ABSTRACT

Nanoparticle (NP) enhanced polymers have the potential to revolutionize food packaging and water pipe performance, though release of NPs from these materials has gone relatively unstudied. A literature review was conducted to identify potential NP release pathways from nanocomposite materials into food and water. Results show little is known, and this lack of knowledge prevents responsible commercialization of safe and innovative nano-enhanced products, development of predictive health risk models, and generation of science-based environmental, health, and safety focused regulation. Common limitations of past studies are that quantitative results were not described, NP detection methods were lacking, and metal ions were not differentiated from NPs. Science has not quantitatively determined if and under what conditions nanocomposites release NPs into food and water matrices. Future research needs are also identified.

**Keywords:** nanoparticle, water, food, release, infrastructure

## 1 INTRODUCTION

Polymers are increasingly being selected for potable water infrastructure and food packaging applications because they are inexpensive, lightweight, and easy to handle. Because of the unique physical and chemical properties manifested at the nanoscale, nanoparticles (NPs) are increasingly being integrated into polymers (e.g., polymer nanocomposites) used for infrastructure and packaging materials [1–3]. Nanocomposites exhibit improved performance characteristics such as mechanical properties, durability, flame retardancy, biodegradability, antimicrobial properties, and oxygen barrier compared to analogous materials that lack nanoscale components.

Many polymers used for water infrastructure and food packaging applications are quite similar and both industries share a mutual technology obstruction: long-term environmental, health, and safety (EHS) issues associated with NP release into drinking water and foods have not been elucidated. Moreover, while NP toxicological effects and environmental impacts have received much scrutiny, an equally important, but overlooked question is to what extent NPs enter the environment/workplace from materials that

contain NPs. Absence of this information prevents responsible wide-scale commercialization of innovative nanoenhanced products, development of predictive health risk models, and generation of science-based EHS focused regulation. This manuscript provides an up-to-date assessment regarding NP release from polymeric materials intended for water and food contact applications.

## 2 WATER & FOOD CONTACT POLYMER NANOCOMPOSITES

### 2.1 Similar Polymers

Many different polymers are used for potable water pipe, water asset coatings, and food packaging. Polymers commonly used for these functions are semi-crystalline (e.g., high density polyethylene), amorphous (e.g., polyvinyl chloride), and thermoset materials (epoxy, polyurethane) (identified in Table 1). For potable water pipes PVC is the most popular plastic in North America [4] followed by PE. The most widely used food packaging polymers are (in order of volume used): LDPE > HDPE > polypropylene (PP) > polyethylene terephthalate (PET) > polystyrene (PS) > PVC [5].

Table 1: Common polymers used in water infrastructure and food packaging applications in North America

Material Abbreviation	Function		Material name
	Water	Food	
<i>Thermoplastics</i>			
HDPE	X	X	High-density polyethylene
MDPE		X	Medium-density polyethylene
LDPE		X	Low-density polyethylene
LLDPE		X	Linear LDPE
PEN		X	Polyethylene naphthalate
PVC	X	X	Polyvinyl chloride
PB	X		Poly(1-butene)
PP		X	Polypropylene
EVA		X	Ethylene-vinyl acetate
PET		X	Polyethylene terephthalate
PS		X	Polystyrene
PVdC		X	Polyvinylidene chloride
PC		X	Polycarbonate
PA		X	Polyamide
<i>Thermosets</i>			
Epoxy	X	X	-
PU	X	X	Polyurethane
PEX	X		Crosslinked polyethylene

## 2.2 Technology Status – Food Contact

Nanoparticle-based food packaging materials closest to commercialization are the polymer-clay nanocomposites (PCNC). These materials incorporate nanoscale platelets composed of natural phyllosilicate clays (e.g., montmorillonite) into food-compatible polymers. When fully exfoliated and homogeneously dispersed, nanoclay particles create a tortuous molecular diffusion pathway, which lowers the oxygen and water vapor transmission rates of the host polymer. Because oxygen and water are critical agents for food spoilage and microorganism growth, PCNCs increase packaged food shelf life.

PCNC materials have been made with virtually every synthetic and natural polymer in commonplace use. Polymers relevant to the food packaging that have received PCNC attention include PE, PS, PA, PET, ethylene vinyl alcohol and PP [2]. In addition, due to the mechanical property advantages that incorporated NPs provide, PCNCs based on “environmentally friendly” biopolymers (such as poly(lactic acid), wheat gluten or thermoplastic starch) have also become popular because these polymers tend to be brittle and possess poor gas barriers. Other current research directions include improving fabrication techniques for good dispersion and exfoliation, bottom-up engineering of more effective PCNC materials using layer-by-layer assembly strategies, and evaluation of PCNC materials with real food systems.

Montmorillonite and similar clays are generally believed to be non-toxic, and because exfoliated clay platelets are only nanoscale in a single dimension, they have also been predicted to pose a minimal migration risk from PCNC food contact materials [6]. PCNC resins are already commercially available and have been incorporated into some beverage containers. Yet, only a few studies have probed whether nanoclay platelets can migrate into packaged foods. While these studies have shown evidence of trace elements (e.g., Si, Mg) migrating from PCNCs into foods [7,8], the work is fragmentary at best and dedicated research initiatives need to become a higher priority.

Nanoparticulate silver (AgNPs) and metal oxides (MONPs: TiO<sub>2</sub>, MnO, or ZnO) could also be incorporated into food contact polymers. These NPs have pronounced antimicrobial activity against a variety of food- and water-borne pathogens. Antimicrobial nanoscale fillers based on carbon nanotubes (CNTs) and chitosan have been reported. Antimicrobial activity of numerous AgNP- and MONP-polymer nanocomposite systems have been evaluated [2]; factors including types of polymer and nanoparticle, as well as multiple fabrication methodologies have been investigated. Antimicrobial nanocomposites been tested with real food systems, and longer shelf lives, lower microbial counts and improved sensory characteristics have

been confirmed [2]. Unlike nanoclay platelets, AgNP and MONPs are nanoscale in multiple dimensions; therefore, it may be necessary for antimicrobial NPs to be located directly on the food contact surface in order to induce an effect. As a result, antimicrobial NPs may pose a greater migration potential than PCNCs [6].

## 2.3 Technology Status – Water Pipe & Coatings

Several nanocomposite potable water pipes and coating materials are close to commercialization. The introduction of NPs is proposed to improve pipe cyclic fatigue, slow crack growth rate, and extend service life. Patent filings demonstrate next-generation polymer water pipes and coatings could contain up to 5% mass fraction of NPs. A search revealed the invention of a ZnO enhanced crosslinked PE (PEX) type A potable water pipe [9], along with several thermoplastic water and wastewater pipes that incorporate phyllosilicate clays [10,11]. In the PEX matrix, the inventors proposed that ZnO acts as a secondary light stabilizer, improves pipe long-term stability and chlorinated water resistance. An unplasticized PVC-/montmorillonite nanocomposite potable water pipe has also been invented [12], though its manufacturing method was not readily available. A polyurethane based pipe lining material that utilizes up to 5% mass fraction of nanoclay has also been developed [13], along with several other nonpotable water pipes and coatings that utilize nanoclays. Nanocomposites most frequently described in the literature were for nonpotable applications (e.g., drainage pipe, geotech, landfill liners), and these composites used other NPs (e.g., silicon dioxide (SiO<sub>2</sub>), and multi-walled CNTs). It is possible that these other NPs could be transitioned into future composites for potable water.

Discussions with several potable water pipe resin manufacturers revealed that NP formulations have not yet been embraced because of dispersion difficulties, lack of historical migration data, and lack of published studies documenting its cost-benefit. Overall, the literature is dominated by studies focusing on mechanical or other property performances, not NP release during the life cycle, of nanocomposites.

## 3 LITERATURE CRITIQUE

NP release data remains very limited and this uncertainty poses the greatest challenge to nanocomposite commercialization and acceptance. Further, the deficiency of data on NP release also hinders our ability to comprehensively assess and manage the risk associated with nanoscale materials in drinking water and food packaging areas. One concern is whether the analytical methods used in NP release studies can adequately detect and quantify the level of consumer exposure. New or modified test protocols may need to be developed for

measuring NP migration under actual conditions of use [14]. At present, test methods for potable water pipes and coatings do not include NP migration analysis [15]. FDA recommends test methods for food systems (aqueous and acidic, low- and high- alcoholic, and fatty foods) should involve water, 3% C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>, aqueous C<sub>2</sub>H<sub>6</sub>O, and unsaturated food oils [16]. A recently completed contaminant migration review for polymer water pipes also demonstrates certain water characteristics (e.g., pH, ion content) can affect contaminant release [17]. These water quality characteristics should be considered for NP release assessments.

### 3.1 Nanoparticle Migration

There have been relatively few investigations of NP diffusion through polymers, and many claims have been made regarding NP release, but most studies report dissolved metal ion concentration, not aqueous NP concentration. Migration of functionalized CaCO<sub>3</sub> filler from PP nanocomposites (3% mass fraction) into water (40°C, 10 days) has been examined [18]. To detect NP migration, these investigators evaporated their test water and gravimetrically weighed plates after drying. This approach is suspect because CaCO<sub>3</sub> is slightly soluble in water, water solubility of functionalized CaCO<sub>3</sub> was not reported, and even if NPs were released into water their mass would be miniscule compared to the mass of the dried plate. A spectroscopic technique would be more reliable, presuming NPs did not dissolve and were present at detectable concentration. A claim of ZnO NP release from LDPE nanocomposites was based on Zn ion quantification in salty test water [19]. Unfortunately, NP concentration was not quantified. AgNP and ZnO NP LDPE composites (up to a mass fraction of 5%) caused Ag and Zn ions to be present in orange juice under typical food storage conditions (4°C, 56 days), and nanocomposites reduced bacterial concentration compared to NP-free composites [20,21]. Investigators did not quantify NP concentration in the orange juice. Fe, Mg, and Si ion release (40°C, 10 day polymer-lettuce contact period) from PS and PE montmorillonite nanocomposites into lettuce has also been investigated [7]. An increased Si ion concentration in lettuce was attributed to leaching from the polymer nanocomposite. Unfortunately, no statistical validation of results was conducted. In another example, a AgNP/cellulose nanocomposite was used as an absorbent pad for meat storage, and results showed silver ions leached from the nanocomposite into the meat exudate but not onto the meat itself [22]. In another work, a nanocomposite layer of AgNP (25 nm in average diameter) and PE was deposited on a five-layer barrier film. The Ag ion diffusion rate from the nanocomposite layer into water was greater from samples with small surface voids formed by the deposition method, which facilitated the penetration of humidity throughout the layer [23]. In summary, there have been few systematic attempts to evaluate release of AgNPs

or MONPs from nanocomposite materials intended for water or food use. The nanocomposite layer example also raises questions with regards to water's role in penetrating the polymer and extracting/dissolving NPs.

In 2008, AgNP migration rates and their equilibrium distribution were mathematically predicted from several packaging materials [6]. Scientists considered polymer physiochemical and viscosity properties and assumed a spherical 10nm diameter NP. Computations predicted diffusivity values ranging from  $2.18 \times 10^{-23} \text{ m}^2/\text{s}$  to  $6.62 \times 10^{-19} \text{ m}^2/\text{s}$  at 25°C for LDPE, HDPE, and PP materials. NPs are much larger than typical small molecular weight additives historically found to migrate into waters and foods [17]. Based on mathematical computations, diffusion may not be a likely release mechanism, but more data are needed.

Interestingly, some researchers have reported that NPs interact with antioxidants (AOX) also present in the polymer, and it is possible these interactions influence NP as well as additive release. Nanoclay incorporation into LDPE sheets resulted in a reduction of AOX loss during oven aging [24] and a reduction in AOX diffusivity through PA films [25]. These phenomena may be due to both nanoclay's ability to act as a physical barrier and the NP adsorption of additives. Nanoencapsulation of an AOX with  $\beta$ -cyclodextrin resulted in a large reduction in the AOX diffusion coefficient from LLDPE into an unsaturated food oil [26]. In this case, nanoencapsulation is believed to have greatly slowed the molecular diffusion process.

A few studies were found that reported NP release from nanocomposite fabrics into water. AgNP release from an unidentified sock fabric was detected by collecting and microscopically analyzing NPs in wash water [27]. While sock material was not identified, it is possible that NPs initially coating the surface detached during washing. A subsequent study determined that certain oxidizing agents, surfactants, and pH conditions can influence Ag ion release from AgNPs fabrics [28].

### 3.2 Mechanical Abrasion

Mechanical-induced release is a likely release route for NPs in both water pipe and food packaging. These materials may encounter abrasion and chipping during storage, transport, and use. NP release for ZnO, Fe<sub>2</sub>O<sub>3</sub>, CNT, alumina, and uncharacterized NPs [29–35] have been detected from nanocomposites. Major questions that have received little study are: In what form is the NP present after mechanical abrasion? Will released NPs be present as individual NPs, agglomerates, or NPs embedded in the surrounding polymer? Does abrasion enable increased NP migration?

### 3.3 Matrix Degradation

Questions remain regarding long-term nanocomposite stability due to externally- and internally-caused matrix degradation. UV exposure is common for polymer water pipe during storage and transport, and there is the potential for UV radiation to facilitate polymer decomposition and enable NP release. TiO<sub>2</sub> NP release was detected from recently painted buildings in runoff water [36,37], and results confirmed NPs were embedded in an organic coating (e.g., not present as virgin NPs). Under UV radiation similar to that of the sun light, spherical silica NPs have been observed to release from epoxy nanocomposite to the environment, but the fiber-like multi-walled CNTs form a dense, entangled network on the composite surface with no evidence of release even after prolonged exposure to UV radiation [38]. Photodegradation of the matrix, which removes the surface polymer layer on the nanocomposite, is suggested to be responsible for this observation. Long-term stability of polymers that contain MONPs is a concern because UV light can efficiently photocatalyze the generation of potent oxidants, and these photoactive compounds can facilitate polymer degradation [39]. This review underscores the urgent need for complete lifecycle analysis of food packaging and water contact materials that contain nanomaterials.

#### 4 FUTURE RESEARCH NEEDS

Several research needs were identified from the literature review and our collective research experience.

1. Existing literature primarily describes how NPs affect nanocomposite mechanical performance. NP release from food packaging and potable water materials has not been adequately characterized, quantified, and modeled. Basic and applied research is needed to quantify and predict NP release rate under different exposure conditions during polymer nanocomposite life cycle.
2. At present, metrologies for precisely and reliably quantifying NP release from polymers to water and foods are not widely available.
3. Past investigators have implied NP release into water/food, but many lacked quantitative data, statistical comparisons, appropriate NP detection methods, and differentiation between metal ions and NPs.

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