



## Property modelling

## Modeling of surfactant release from polymer-clay nanocomposites into ethanol



Yining Xia, Maria Rubino\*, Rafael Auras

School of Packaging, Michigan State University, East Lansing, MI 48824, USA

## ARTICLE INFO

## Article history:

Received 29 October 2015

Accepted 10 December 2015

Available online 17 December 2015

## Keywords:

Nanocomposite

Surfactant release

Migration modeling

Solubility parameter

## ABSTRACT

A kinetic study was carried out of the release of surfactants from two types of nanocomposites: polypropylene (PP) and nylon 6 compounded with nanoclay. The migration experiment was performed in accordance with ASTM 4754-11 with the nanocomposite films exposed to ethanol as a fatty-food simulant at 22, 40, and 70 °C. The surfactant release from the nanocomposite films followed a migration behavior as described by Fick's second law of diffusion. Diffusion coefficients derived from the model were in the range of  $10^{-13}$  to  $10^{-12}$   $\text{cm}^2 \text{s}^{-1}$  for the surfactant release from the PP-clay film and  $10^{-13}$  to  $10^{-11}$   $\text{cm}^2 \text{s}^{-1}$  for the surfactant release from the nylon-clay film between 22 and 70 °C. The rate of surfactant release was greater from both nanocomposite films at the higher temperatures. At the same temperature, the rate of surfactant release was greater from the nylon-clay film than from the PP-clay film. Moreover, the surfactant was more likely to be released from the nylon-clay film, as indicated by the smaller partition coefficients (*i.e.*, the ratio of surfactant in the polymer vs in ethanol). The difference in surfactant release between the two nanocomposites was explained by considering the affinity among the surfactant, polymer, and solvent.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Nanocomposites with nanoclay as the nanofiller account for over half of total global nanocomposite consumption (estimated at 225,000 metric tons in 2014), and most are used as packaging materials [1,2]. The extensive use of polymer-clay nanocomposites in consumer goods, especially in food packaging, has raised concern about the potential release of nanocomponents that may impact the environment and human health [3–5]. The most common type of nanoclay used in nanocomposites is montmorillonite, obtained from layered silicate minerals. The hydrophilic nature of montmorillonite makes it unfavorable for dispersion in most engineered polymers, which are hydrophobic. Therefore, montmorillonite is usually modified with organic surfactants (*e.g.*, alkylammonium salt) through ion exchange, both to improve compatibility with the polymer and to achieve homogeneous dispersion in the polymer matrix [6].

For nanocomposites that will be in contact with food, the release of nanoclay, as well as other components (*e.g.*, organic surfactants),

should be assessed to ensure food safety. Although a few studies have addressed the release of nanoclay from polymer nanocomposites [7–9], little attention has been placed on the surfactant release. Some surfactants and their degradation products have been demonstrated to be harmful to ecosystems, animals and humans [10–12]. Evaluation of the release of surfactant from polymer nanocomposites under different environmental conditions is crucial to develop safe nanocomposites.

The authors previously showed a substantial release of surfactant from polymer-clay nanocomposites, and the level of release ranged from 0.14  $\text{mg dm}^{-2}$  to 0.65  $\text{mg dm}^{-2}$  for different types of polymer-clay nanocomposites [13]. The release of surfactant from nanocomposites can be considered a migration process involving diffusion toward the polymer surface and desorption from the polymer surface into the surrounding environment. Fick's diffusion equations are usually applied to model the migration and/or release of molecules with low molecular weight from polymeric materials and to determine the parameters associated with the migration process of these molecules [14,15]. Understanding the release behavior of surfactants and their mass transfer parameters should enable the prediction of surfactant release from nanocomposites in contact with food or food simulants and the environment.

The aim of this work was to perform a kinetic study on the

\* Corresponding author. School of Packaging, Michigan State University, East Lansing, MI 48824-1226, USA.

E-mail address: [maria@msu.edu](mailto:maria@msu.edu) (M. Rubino).

release of surfactant from polymer-clay nanocomposites into a widely used food simulant. Two types of polymer-clay nanocomposites, polypropylene (PP) and nylon 6 compounded with nanoclay, were selected as model systems due to the different characteristics of the two polymers (*i.e.*, polarity, chemical composition, and hygroscopicity). A liquid chromatography tandem mass spectrometry (LC-MS/MS) method was used to quantify the release of surfactant into the food simulant. Fick's second law of diffusion was applied to describe the release of surfactant by solving for the parameters associated with the migration process. The amount of surfactant released from the two polymer nanocomposites was compared and correlated with the affinity among surfactant, polymer and solvent.

## 2. Materials and methods

### 2.1. Materials

Polypropylene (PP or Profax 6523; LyondellBasell Industries, TX, USA), maleic anhydride-graft-polypropylene (MAPP or Bondyram<sup>®</sup> 1001, 1 wt% bound maleic anhydride; Polyram Co., MI, USA), and nylon 6 (Ultramid<sup>®</sup> B40 01; BASF, NJ, USA) were commercially procured and used as received. MAPP was used as a compatibilizer to improve the dispersion of nanoclay into PP.

The nanoclay Nanomer<sup>®</sup> I.44P was used with PP, and was obtained from Nanocor (Aberdeen, MS, USA) containing 65 wt% montmorillonite and 35 wt% surfactant (dimethyl dihydrogenated tallow amine or Arquad<sup>®</sup> 2HT-75; AkzoNobel, IL, USA). Cloisite<sup>®</sup> 93A was used with nylon 6, and was obtained from Southern Clay Products (Gonzales, TX, USA) containing 60 wt% montmorillonite and 40% surfactant (methyl dihydrogenated tallow amine or Armeer<sup>®</sup> M2HT; AkzoNobel). The selection of nanoclay for each polymer was based on the nature of surfactant and the compatibility between the nanoclay and the polymer. Nanomer<sup>®</sup> I.44P is usually added to non-polar polymers like PP [16] while Cloisite<sup>®</sup> 93A is usually added to polar polymers like nylon 6 [17].

### 2.2. Preparation of polymer-clay films

Polymer-clay films were produced as described in our previous study [13]. Briefly, the film processing techniques used were melt-mixing followed by blow-extrusion for PP-clay film or cast-extrusion for nylon-clay film. The final composition of the PP-clay film ( $22.5 \pm 1.1 \mu\text{m}$  thickness) was 85 wt% PP, 12 wt% MAPP and 3 wt% nanoclay, while the nylon-clay film ( $21.1 \pm 1.2 \mu\text{m}$  thickness) was composed of 95 wt% nylon 6 and 5 wt% nanoclay.

### 2.3. Extraction of surfactant from the nanocomposite films

Due to the strong affinity between surfactant and polymer in the prepared films, extraction of the surfactant by a solvent without dissolving the polymer would be time consuming and impractical. Therefore, both PP-clay and nylon-clay films were dissolved in a solvent to fully extract the surfactant in the polymer matrix that was not bonded to the clay surface through ion exchange. PP-clay film (0.1 g) was placed in a 20-mL glass vial with 10 mL xylene (98.5%, Jade Scientific Inc., MI, USA) and stirred at 100 °C until the film sample was dissolved; triplicate samples were prepared. The solution was then transferred to a 200-mL beaker containing 190 mL ethanol to precipitate the polymer. The precipitate was collected by vacuum filtration and used for a second cycle of dissolution. No third cycle was adopted since most of the surfactant (>99%) was extracted from the polymer in the first two cycles. The solution from each cycle was filtered with a Waters GHP filter (13 mm, 0.2  $\mu\text{m}$ ; Waters Co., MA, USA) and transferred to a 2-mL

glass vial for LC-MS/MS analysis. The same procedures were applied to 0.05 g samples of nylon-clay film (in triplicate) with formic acid (94.5%, Mallinckrodt Baker Inc., NJ, USA) although the solvent was stirred at room temperature to dissolve the film samples.

### 2.4. Migration experiment

Migration testing of the surfactant was performed in accordance with ASTM D4754-11. For each test, 16 round disks (2-cm diameter) were cut from the nanocomposite films. The disks for each film type (100 cm<sup>2</sup> total surface area, approximately 0.10 g for PP-clay film and 0.12 g for nylon-clay film) were threaded on a stainless steel wire and separated by Teflon beads, and then placed into a separate amber glass vial (2.5 × 9.5 cm). Each vial was filled with 40 mL ethanol (200 proof) for use as a fatty-food simulant, and vials were held at 22, 40 or 70 °C until the steady state of surfactant release was achieved. Multiple sample solutions were removed from the vials at various time intervals, and each was filtered with a Waters GHP filter and then analyzed by LC-MS/MS.

### 2.5. LC-MS/MS analysis

Quantification of surfactant in ethanol was performed by using a previously developed LC-MS/MS method [18]. The instrument used was a Shimadzu LC-20AD high performance liquid chromatograph (HPLC) (Shimadzu Scientific Instruments, MO, USA) coupled with a Quattro API Tandem micro mass spectrometer (Waters Co.). Briefly, the sample solution from each sampling time of the migration test (diluted appropriately with ethanol) as well as from each cycle of dissolution was injected into the HPLC and measured in multiple reaction monitoring (MRM) mode. The use of MRM enabled the detection of surfactant by selecting both its molecular ion and fragments, thereby avoiding the interference of other substances or contaminants.

### 2.6. Fick's diffusion model

The migration of low molecular weight molecules from a polymer into a food or food simulant in contact with the polymer can be described by Crank's mathematical model derived from Fick's second law [14]:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2q_n^2} \exp\left(-\frac{Dq_n^2 t}{L^2}\right) \quad (1)$$

with

$$\alpha = \frac{1}{K_{p,f}} \frac{V_f}{V_p} = \frac{W_{f,\infty}}{W_{p,\infty}} = \frac{W_{f,\infty}}{W_0 - W_{f,\infty}} \quad (2)$$

where  $D$  is the diffusion coefficient of migrant in the polymer;  $M_t$  is the migrant concentration in food at time  $t$ ;  $M_\infty$  is the migrant concentration in food at the steady state of migration;  $L$  is the film thickness for one-sided migration, and half film thickness for two-sided migration;  $V_p$  and  $V_f$  are the volume of the polymer and food, respectively;  $W_{p,\infty}$  and  $W_{f,\infty}$  are the mass of migrant in the polymer and food at the steady state of migration, respectively;  $W_0$  is the initial mass of migrant in the polymer;  $q_n$  is the positive root of the equation  $\tan q_n = -\alpha q_n$ ; and  $K_{p,f}$  is the partition coefficient of the migrant in the polymer/food system.

Eq. (1) is used to describe a migration process within a finite polymer – finite food system controlled by both partition ( $\alpha < 1$ ) and diffusion [19]. To enable the application of the diffusion model,

Download English Version:

<https://daneshyari.com/en/article/5205830>

Download Persian Version:

<https://daneshyari.com/article/5205830>

[Daneshyari.com](https://daneshyari.com)