



Electrophoretic deposition of flame retardant polymer–huntite coatings



Tianshi Zhang¹, Dan Luo¹, Patrick Wojtal, Igor Zhitomirsky*

Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada L8S4L7

ARTICLE INFO

Article history:

Received 19 January 2015

Received in revised form

30 May 2015

Accepted 28 June 2015

Available online 30 June 2015

Keywords:

Electrophoretic deposition

Polymer

Flame retardant

Huntite

Composite

Coating

ABSTRACT

Electrophoretic deposition (EPD) method has been developed for the deposition of composite coatings, containing huntite as a flame retardant additive (FRA) in a polymer matrix. Alginate and hyaluronate were used as model anionic polymers for EPD. The adsorbed polymers allowed dispersion of plate-like huntite particles and imparted a charge for EPD. The deposition yield, microstructure, composition, and corrosion protective properties of the coatings were investigated. The results indicated that EPD is a promising technique for the fabrication of protective coatings, containing flame retardant additives.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

EPD is important technique for the deposition of thin films and coatings [1]. Comprehensive reviews describe the present state of knowledge in the EPD of various materials and advanced applications [2–5]. Of particular interest are applications of EPD in nanotechnology [2,4,6,7]. EPD offers many processing advantages for the deposition of polymers for biomedical devices, corrosion protection and energy storage devices [8,9]. Various strategies for EPD of polymers and polymer matrix composites have been exemplified [9].

An important requirement for many applications of polymer coatings is their flame retardancy [10]. There is a strong need to incorporate FRA in various polymer products [10–12]. It was recognised that mineral huntite ($\text{Mg}_3\text{Ca}(\text{CO}_3)_4$) is a promising FRA for many applications. The flame retardant properties of huntite [13,14] are related to its endothermic decomposition and release of CO_2 gas, which reduces the oxygen access to the flammable polymer material. Huntite offers advantage of lower cost, compared to other FRA, such as aluminium hydroxide and magnesium hydroxide [14]. Moreover, the production of aluminium and magnesium hydroxides generates a problem related to the disposal of toxic chemical waste [14]. It is expected that huntite can

replace toxic [11,12] halogenated FRA, in many polymer products. Polymer–huntite composites showed improved mechanical properties compared to pure polymers [13,14].

The goal of this investigation was the development of the EPD method for the deposition of polymer coatings, containing huntite as an FRA. The approach was based on anodic EPD using alginate and hyaluronate as model anionic polymers. For the first time we demonstrate the possibility of EPD of polymer–huntite composites.

2. Experimental procedures

Huntite (Sibelco), sodium alginate (MW=250,000–300,000) and sodium hyaluronate (MW=150,000–250,000) (Aldrich) were used as starting materials. According to the manufacturer, the particle size of huntite was in the range of 0.41–0.90 μm , average particle size was 0.56 μm , specific surface area was 18 $\text{m}^2 \text{g}^{-1}$. EPD was performed from 4 g L^{-1} huntite suspensions, containing 1 g L^{-1} sodium alginate or sodium hyaluronate in a mixed water–ethanol (60% ethanol) solvent at a deposition voltage of 30 V. The distance between a stainless steel anodic substrate (grade 304) and a Pt counter electrode was 15 mm. The size of the substrate and counter electrodes was 50 × 50 × 1 mm, both electrodes had edge insulating protection, only one side of the electrodes was in contact with a suspension. The suspensions were ultrasonically agitated for 30 min before EPD using an ultrasonic bath (Branson,

* Corresponding author.

E-mail address: zhitom@mcmaster.ca (I. Zhitomirsky).

¹ Authors contributed equally to this work.

model 5510). The measurements of electrophoretic mobility were performed according to the method, described in the literature [15], the suspension compositions and electric field were the same as in the EPD experiments.

The coatings were studied using X-ray diffraction analysis (XRD) (diffractometer Bruker D8, Cu-K α radiation), scanning electron microscopy (SEM) (JEOL, microscope JSM-7000F), and FTIR spectroscopy (Bio-Rad, spectrometer FTS-40). Thermogravimetric (TGA) and differential thermal analysis (DTA) (thermo-analyzer NETZSCH STA-409) were performed in air at a heating rate 5 °C min⁻¹. The coatings were removed from the substrates for the fabrication of powder samples for XRD, TGA, DTA and FTIR studies.

The corrosion studies (potentiostat PARSTAT2273, Princeton Applied Research) were performed using saturated calomel reference electrode and 3% NaCl electrolyte at a potential change rate of 1 mV s⁻¹.

3. Results and discussion

Alginate or hyaluronic acid coatings can be deposited by anodic EPD from sodium alginate or sodium hyaluronate solutions, respectively [16]. In this method, electrophoresis of the anionic alginate or hyaluronate molecules, results in their accumulation at the anode surface. The deposition mechanism involved local pH decrease at the anode surface, protonation of COO⁻ groups of the polymers and precipitation of insoluble alginate or hyaluronic acid at the electrode [16].

The major difficulties in the fabrication of composite coatings were related to the dispersion, charging and deposition of huntite. Sedimentation tests showed that alginate and hyaluronate improved dispersion and stability of the huntite suspensions. The huntite suspensions, containing alginate and hyaluronate were stable for more than 3 days. Anodic deposits were obtained from huntite suspensions, containing alginate or hyaluronate. The deposit mass increased with increasing deposition time, indicating the possibility of EPD of coatings of controlled mass (Fig. 1). The deposition yield, achieved from huntite suspensions, containing alginate or hyaluronate was significantly higher, compared to that achieved from pure polymer solutions [16]. The electrophoretic mobilities of the huntite particles in the 4 g L⁻¹ huntite suspensions without additives, containing 1 g L⁻¹ sodium alginate and 1 g L⁻¹ sodium hyaluronate were found to be $-0.32 \cdot 10^{-9}$, $-1.12 \cdot 10^{-7}$ and $-1.65 \cdot 10^{-7}$ m² s⁻¹V⁻¹, respectively.

The comparison of X-ray diffraction patterns of huntite and composite coatings showed that huntite was incorporated into the polymer coatings (Fig. 2A). The XRD patterns of coatings showed peaks of huntite, similar to the peaks of as-received huntite material. The formation of composite coatings was also confirmed by FTIR. The FTIR spectrum of as-received huntite showed characteristic absorptions [17] at 870 and 891 cm⁻¹, attributed to carbonate ligands (Fig. 2B). Similar absorptions observed in the spectra of the coatings.

The SEM studies (Fig. 3) at low magnifications showed the formation of continuous coatings, containing platy huntite particles. The SEM images at higher magnifications showed that the typical size of the plate-like particles is on the submicrometre scale. The shape of the huntite particles is of special interest for flame retardant applications. It is known [14] that platy morphology helps to reduce the rates of heat transfer and gas transfer. It is also beneficial for the polymer reinforcement [14]. The adhesion test (ASTM standard D3359) showed that coating adhesion corresponded to 5B classification.

The TGA studies of as-received huntite showed two major steps in mass loss (Fig. 4A). The total mass loss of 48.9% at 1000 °C is

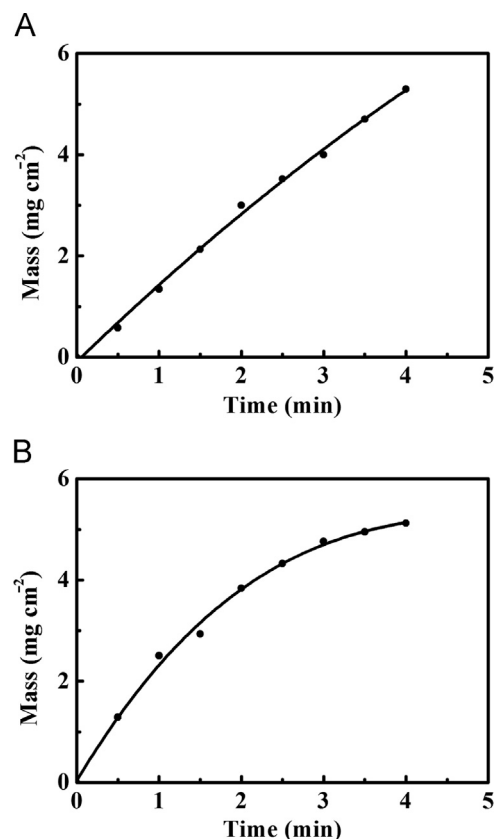
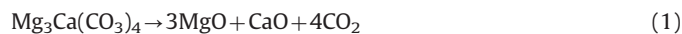


Fig. 1. Deposit mass versus time for deposits prepared from 4 g L⁻¹ huntite suspension, containing (A) 1 g L⁻¹ sodium alginate and (B) 1 g L⁻¹ sodium hyaluronate.

related to release of four CO₂ molecules:



The first step in the mass loss (36.7%) below ~600 °C corresponds to release of three CO₂ molecules [18] (theoretical mass loss 37.4%) bonded to Mg atoms. A step in the mass loss at higher temperatures is related to release of additional CO₂ molecule, bonded to Ca atoms. No mass loss was observed at temperatures above 800 °C. The DTA data showed two endothermic peaks, corresponding to observed steps in the mass loss. The TGA data for the composite materials (Fig. 4B and C) showed several steps in mass loss. The total mass loss for alginate–huntite and hyaluronic acid–huntite composites at 1000 °C was found to be 57.1% and 58.0%, respectively. The additional mass loss for deposits (Fig. 4B and C), compared to that of pure huntite (Fig. 4A), can be attributed to burning out of the polymers. Therefore, the results of TGA analysis confirmed the formation of composite coatings. The compositions of the coatings, estimated from the results of the TGA analysis, were found to be 84.0 mass% huntite and 16.0 mass% alginate or 82.2 mass% huntite and 17.8 mass% hyaluronic acid. The corresponding DTA data showed endothermic peaks related to decomposition of huntite and small exotherms below 500 °C, related to burning out of the polymers.

The results of this investigations indicated that composite coatings with relatively large huntite content can be obtained. Moreover, we found that the amount of huntite in the coatings can be varied by the variation of the huntite concentration in the polymer solutions. It is suggested that alginate and hyaluronate adsorbed on huntite particles and imparted a negative charge for anodic EPD. The adsorption mechanism can result from interactions of carboxylic groups of the polymers with Mg and Ca atoms

Download English Version:

<https://daneshyari.com/en/article/1642257>

Download Persian Version:

<https://daneshyari.com/article/1642257>

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