Particuology 22 (2015) 82–88

Contents lists available at ScienceDirect

Particuology

journal homepage: www.elsevier.com/locate/partic

# Synthesis and surface modification of nanophosphorous-based flame retardant agent by continuous flow hydrothermal synthesis

Sherif Elbasuney*, Hosam E. Mostafa

*School of Chemical Engineering, Military Technical College, Kobry El-Koba, Cairo, Egypt*

ARTICLE INFO

*Article history:*
Received 27 July 2014
Received in revised form
28 September 2014
Accepted 2 October 2014

*Keywords:*
Flame retardancy
Phosphorous-based agent
Nanocomposites
Hydrothermal synthesis
Hydroxyapatite

ABSTRACT

Nanoparticles can provide flame retardance to hosting polymers and act as nano fire extinguishers. Hydroxyapatite ($Ca_5(OH)(PO_4)_3$) (HA) is not hygroscopic, and is thermally stable up to 800 °C, with 18.5 wt% phosphorous content. It is this high phosphorous content that can provide HA with flame retardant properties. In this paper, we report on the continuous synthesis of ultrafine HA using a hydrothermal synthesis technique. The HA surface properties were changed from hydrophilic to hydrophobic by post-synthesis surface modification. The ratio of the HA nanoparticles and an intumescent agent known as Exolit AP750 was investigated to yield a self-extinguishing multi-component epoxy nanocomposite for extended application under extreme fire conditions. The HA/AP750/epoxy nanocomposite was able to resist a flame at 1700 °C and self-extinguish after the flame had been removed. The nanocomposite showed an enhanced flammability performance in standard cone calorimetry testing and formed a compact and cohesive protective char layer with a 50% decrease in peak heat released compared with virgin epoxy. Our aim was to establish the use of HA as an effective nanofiller with phosphorous-based flame retardant properties. The surface of this nano fire extinguisher was modified effectively with different surfactants for enhanced compatibility with different polymeric matrices.

## Introduction

Hydrothermal synthesis offers a relatively simple, scalable route, which is chemically more benign than many other nanoproduction technologies (Adschiri, Hakuta, & Arai, 2000; Lester et al., 2006). It is characterized by excellent reproducibility and microstructure control (Lester et al., 2012; Wang, Tang, Lester, & O'Hare, 2013; Yoshimura & Byrappa, 2008). Nanoparticle surface properties can be altered from hydrophilic to hydrophobic and vice versa by the proper selection of surface-coating agents in hydrothermal synthesis (Yoshimura & Byrappa, 2008). Surface modification may enhance the dispersion characteristics of inorganic nanoparticles in an organic polymeric matrix (Elbasuney, 2014). Hydroxyapatite ($Ca_5(OH)(PO_4)_3$) (HA) is one of the most important bioceramic materials in medical applications. It has a much higher phosphorous content than most commercially available phosphorous-based flame retardant (FR) additives such as triphenyl phosphate and resorcinol bis-(diphenyl phosphate) (Horrocks & Price, 2008; Wilkie & Morgan, 2010). The efficiency of phosphorous-based FRs can be evaluated by their phosphorous content (Pinfa, 2010). HA can exhibit FR action in the gaseous phase because of the release of active flame scavenger species such as $PO_2^\bullet$, $PO^\bullet$, and $HPO^\bullet$ (Laoutid, Bonnaud, Alexandre, Lopez-Cuesta, & Dubois, 2009). These species are the most effective free radical scavengers; they are ten times more effective than chlorine, and five times more effective than bromine (Babushok & Tsang, 2000; Laoutid et al., 2009). HA may display a condensed phase FR action by promoting the formation of a protective char layer on a burning surface (Horrocks & Price, 2008). The HA nanoparticles could then fulfill a dual function as a nanofiller to improve polymer rheology in fire, and as a nanophosphorous-based FR agent (Green, 1996). A combination between selected nanoparticles and conventional FR systems is vital to achieve flammability standards at low solids loading by synergism between both components (Laoutid et al., 2009; Zammarano, Franceschi, Bellayer, Gilman, & Meriani, 2005).

In this paper, we report on the continuous hydrothermal synthesis of HA nanoparticles that could provide phosphorous-based FR action to a hosting polymer. The HA surface was modified using dodecenyl succinic anhydride (organic ligand) and poly(ethylene-co-acrylic acid) copolymer (polymeric surfactant). The surfactants

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* Corresponding author. Tel.: +20 1112630789.
*E-mail address:* sherif_basuney2000@yahoo.com (S. Elbasuney).

http://dx.doi.org/10.1016/j.partic.2014.10.005
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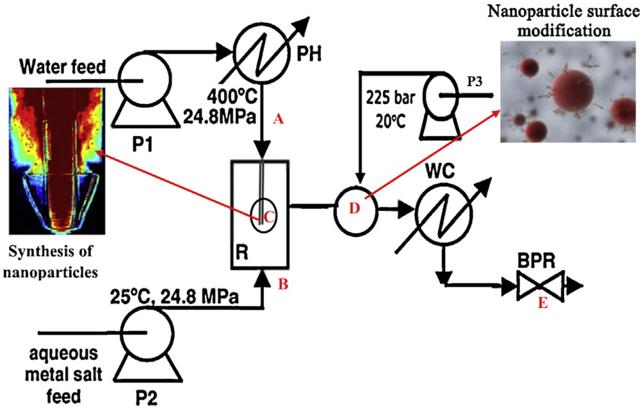

**Fig. 1.** Schematic of continuous hydrothermal synthesis.

could anchor to the HA surface and extract nanoparticles from the water to the organic phase. A proper combination of HA and intumescent agent (AP750) could be used to form a self-extinguishing epoxy nanocomposite at a total solids loading level of 10 wt%, with enhanced flammability performance in cone calorimetry testing. To the best of our knowledge, this is the first time that HA has been reported on as a FR agent and its flammability performance evaluated.

## Experimental

### *Materials*

Ammonium phosphate dibasic ($(NH_4)_2 \cdot HPO_4$) (Aldrich, 98%, Germany) and calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) (Aldrich, 99%) were used as precursors for HA synthesis. Dodecenyl succinic anhydride (DDSA) (Aldrich, 90%), and poly(ethylene-co-acrylic acid 15 wt%) (Aldrich) were used for HA surface modification. Ammonium polyphosphate with an aromatic ester of tris(2-hydroxy methyl)-isocyanurate, commercially known as Exolit AP750 (AP750) developed by Clariant (Germany), was used as an intumescent agent. The employed prepolymer was bisphenol-A (epichlorohydrin), with a molar mass $\leq$ 700 g/mol (Struers, UK) The hardener was triethylene tetramine (Struers).

### *Formulation and surface modification of HA nanoparticles*

HA was formulated using the continuous hydrothermal synthesis described in Fig. 1. Superheated fluid passes down an inner nozzle pipe (A) against the upflow of a cold precursor salt (B). Nanoparticles form at the fluid interface (C), and the buoyancy of the heated fluid causes the nanoparticle slurry to be carried upwards (downstream) for capping (D), where nanoparticle surface modification is achieved by injecting the surface coating agent dissolved in toluene at this point.

### *Synthesis of HA nanoparticles*

The superheated fluid (downflow) was a water solution of 0.015 M ammonium phosphate dibasic at 200 °C and 240 bar (20 mL/min). The metal salt feed (upflow) was an aqueous solution of 0.05 M calcium nitrate tetrahydrate (10 mL/min) at 25 °C and 240 bar. The nanoparticle stream was cooled prior to collection at (E).

### *HA surface modification with organic surfactants*

HA surface modification with DDSA was achieved by post-synthesis. DDSA in toluene (0.01 M) was injected at 5 mL/min at the capping point D (Fig. 1) under the same hydrothermal conditions as the HA synthesis. The HA surface was modified by injecting a solution of 0.06 g poly(ethylene-co-acrylic acid 15 wt%) in 100 mL toluene at the capping point at 5 mL/min. The DDSA and poly(ethylene-co-acrylic acid) could anchor the HA surface and extract HA nanoparticles into the organic toluene phase (Fig. 2(a)). The organic layer was separated and centrifuged (Fig. 2(b)). The organic-modified HA was collected as viscous colloidal nanoparticles dispersed in toluene (Fig. 2(c)). HA can therefore be integrated into a polymeric matrix as dry powder or colloidal nanoparticles dispersed in organic solvent (Fig. 2(c)). The integration of colloidal HA nanoparticles showed enhanced dispersion characteristics compared with dry particles (Elbasuney, 2013), but this is beyond the scope of this paper.

### *Characterization of HA nanoparticles*

The HA crystalline phase was investigated by X-ray diffractometry (XRD, D8 Advance, Bruker Corporation, Germany) for a $2\theta$ from 5° to 65° with a scan speed of 2°/min. The HA and organic-modified HA were studied using different techniques including: transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan) to investigate the nanoparticle size and shape, Fourier

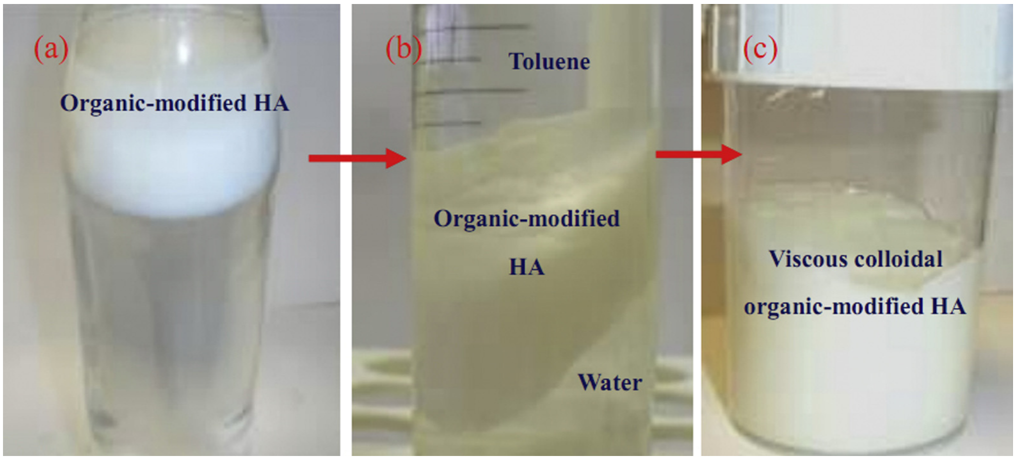

**Fig. 2.** Processing of organic-modified HA nanoparticles.