Electrophoretic deposition of a memory-type flame retardant material

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ABSTRACT

Al–Mg–Zr complex hydroxide (AMZH) showed promising behaviour for flame retardant applications due to a mass loss of 44.2% related to thermal dehydration. The original structure and properties of AMZH, fully dehydrated at 500 °C, can be reconstructed. The memory properties of AMZH pave the way for novel applications. Electrophoretic deposition (EPD) of AMZH coatings was performed using an advanced dispersing and charging agent, which exhibited binding and film forming properties. The deposition mechanism, advantages of AMZH and EPD method are discussed.

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1. Introduction

Flame retardant materials (FRM) are used in many applications, such as coatings in electrical, mining, transportation and wood industries and various products, containing polymer coatings, thermoplastics and thermosets [1]. The high demand for advanced FRM in car, aircraft and shipbuilding industries is related to the increasing use of plastics and replacement of metals with polymer based composites [1–4]. A new wave of interest in efficient FRM in automotive and aircraft industries is attributed to the use of lithium batteries [5]. FRM are widely used in insulation of communication cables and electrical cables, electronic products, fabrics, furniture and various building products [6,7].

There is an increasing interest in the use of various hydroxide materials as sustainable FRM due to concerns regarding the toxicity of other FRM, such as organophosphates and halogenated materials. The flame retardation mechanism of hydroxide type FRM involves energy consumption, related to the endothermic decomposition of the hydroxide phases and release of water vapour, which dilutes the fuel in the gas phase. The ratio (K) between the mass of released water and the mass of original hydroxide is an important characteristic of the hydroxide type FRM.

Aluminium hydroxide ($K=34.6$%) and magnesium hydroxides ($K=30.9$%) are important FRM for many applications, due to their low cost and relatively large K values. However, the application of such FRM as additives for polymer coatings requires relatively high FRM loadings. Moreover, the relatively low dehydration temperature of aluminium hydroxide and limited temperature range of flame retardant properties of magnesium hydroxide limit their practical applications [7–9]. Therefore, there is a need for the development of advanced materials with improved FRM properties. It is important to note that many applications of FRM materials are based on the use of coatings. Therefore, the advancement in the applications of FRM materials can be achieved by the development of coating deposition techniques. EPD is an important technique for the deposition of organic and inorganic coatings, laminates and composites [10]. Uniform coatings can be obtained by EPD on substrates of complex shape at high deposition rate. Therefore, EPD is a promising method for the fabrication of FRM coatings.

The goal of this investigation was the analysis of AMZH properties for flame retardant applications and EPD of AMZH coatings. The results presented below indicated that compared to aluminium and magnesium hydroxides, AMZH offers the advantages of a higher $K=44.2$%. AMZH exhibits unique memory properties, related to the possibility of complete reconstruction of this material after dehydration at 500 °C. EPD has been successfully applied for the deposition of AMZH coatings.

2. Experimental procedures

AMZH (Al:Mg:Zr atomic ratio of 0.78:3:0.14, MEL Chemicals) and aurintricarboxylic acid ammonium salt ($ATNH_4$, Aldrich) were used. The reconstructed AMZH was prepared by dehydrating of as-received AMZH at 500 °C for 2 h, followed by an addition of water with a mass ratio of powder:water =1:1 and drying in air for 24 h.

The EPD cell contained a stainless steel foil substrate, centred between two Pt counter electrodes. The distance between the

substrate and counter electrodes was 15 mm. EPD was performed from 10 gL^{-1} AMZH suspensions in water, containing 0–1.5 gL^{-1} ATNH$_4$ at a deposition voltage of 7 V. The coatings were dried in air for 48 h. As-received and reconstructed AMZH powders were studied by X-ray diffraction analysis (XRD) (diffractometer Bruker D8) using Cu-K$_\alpha$ radiation. Thermogravimetric (TGA) and differential thermal analysis (DTA) (thermoanalyzer NETZSCH STA-409) of the powders were performed in air at a heating rate 5 °C min^{-1}. Scanning electron microscopy (SEM) (JEOL, microscope JSM-7000 F), FTIR spectroscopy (Bio-Rad, spectrometer FTS-40) and UV–vis spectroscopy (Agilent Technologies, spectrometer Cary-50) studies were used for the characterization of the deposited material.

3. Results and discussion

Fig. 1 compares XRD, TGA and DTA data for as-received and reconstructed AMZH. The XRD pattern of as-received AMZH (Fig. 1A) showed peaks of hydrotalcite structure (JCPDS file 22-700), which disappeared after dehydration at 500 °C for 2 h, but appeared again in the X-ray diffraction pattern of the reconstructed material (Fig. 1B). The TGA data (Fig. 1C(a)) for the as-received material showed several steps in mass loss below 200 °C and in the range of 350–400 °C, attributed to dehydration. The DTA curve (Fig. 1C(b)) showed corresponding endothermic effects. The total mass loss at 1000 °C was 44.2 ± 0.1 mass %. Therefore, the molar ratio Al:Mg:Zr:O:H$_2$O in AMZH was 0.78:3:0.14:4.45:7.83. The analysis of TGA and DTA data for the reconstructed material (Fig. 1D(a) and (b)) showed a similar behaviour with total mass loss of 44.3 ± 0.1 mass% at 1000 °C. The use of AMZH offers the advantage of a higher K=44.2%, compared to aluminium and magnesium hydroxides. Moreover, in contrast to aluminium and magnesium hydroxides, AMZH exhibits a memory effect and can be reconstructed after dehydration at 500 °C.

EPD of AMZH was performed using ATNH$_4$ as a dispersing, charging, binding and film-forming agent. Previous investigations showed that aurintricarboxylic acid (ATH) films can be deposited from aqueous ATNH$_4$ solutions. The deposition mechanism was based on a pH decrease at the anode surface due to the electrochemical decomposition of water, protonation of COO$^-$ groups and formation of insoluble ATH films. Previous studies [11] showed a possibility of EPD of titanium dioxide using ATNH$_4$. As an extension of the previous investigations we found that hydroxide materials, such as AMZH, can be deposited from aqueous suspensions, containing ATNH$_4$. Due to the limitations of the concept of zeta-potential for analysis of electrokinetic behaviour of particles, containing adsorbed large organic molecules, the deposition process was analysed using the deposition yield data. Fig. 2A indicates that the deposition rate increased with increasing ATNH$_4$ concentration in the suspensions in the range of 0.4–1.5 gL^{-1}. The increase in the deposition time resulted in increasing coating mass, indicating continuous coating growth. Therefore, the amount of the deposited material can be controlled by the variation of ATNH$_4$ concentration and deposition time. It is suggested that anionic AT$^-$ adsorbed on the surface of AMZH and imparted a charge for EPD. Previous investigations showed that AT$^-$ adsorbed on titanium oxide surface via an inner sphere bonding mechanism, involving complexation of Ti atoms on the particle surface [11]. It was found [12] that undercoordinated defect sites on the surface of titanium dioxide are the source of enhanced and selective reactivity of the nanoparticles toward bidentate ligand bonding of phenolic molecules. For hydroxide materials, such as AMZH, we suggest outer sphere bonding mechanism [13], involving OH groups (Fig. 2C). The deposition mechanism involved the electrophoretic motion of AMZH, contained adsorbed anionic AT$^-$ species, toward the anode. The pH decrease at the anode surface resulted in the protonation of AT$^-$ and charge neutralization (Fig. 2C). The formation of electrically neutral and insoluble ATH, with excellent film forming and binding properties [11], promoted the formation of AMZH coatings. Fig. 3 shows typical SEM images of AMZH coatings, which adhered well to the substrates and exhibited relatively low porosity, mainly attributed to packing of the AMZH particles. The porosity can also be attributed to gas evolution at the electrode during EPD.

The AMZH coatings were scraped from the substrates and tested by UV–vis and FTIR methods (Fig. 4). The UV–vis spectrum of the deposited material showed broad absorptions at 300–320 nm and around 530 nm, attributed to ATH [14]. The FTIR spectrum showed broad absorptions centred at 1628 and 1488 cm^{-1}, attributed to C–C/C=C vibrations of the aromatic rings and a broad adsorption, centred at 1352 cm^{-1}, related to bending vibrations of C–OH groups and C–O vibrations of ATH [11,12]. Small peaks at 1133 and 1039 cm^{-1} were related to
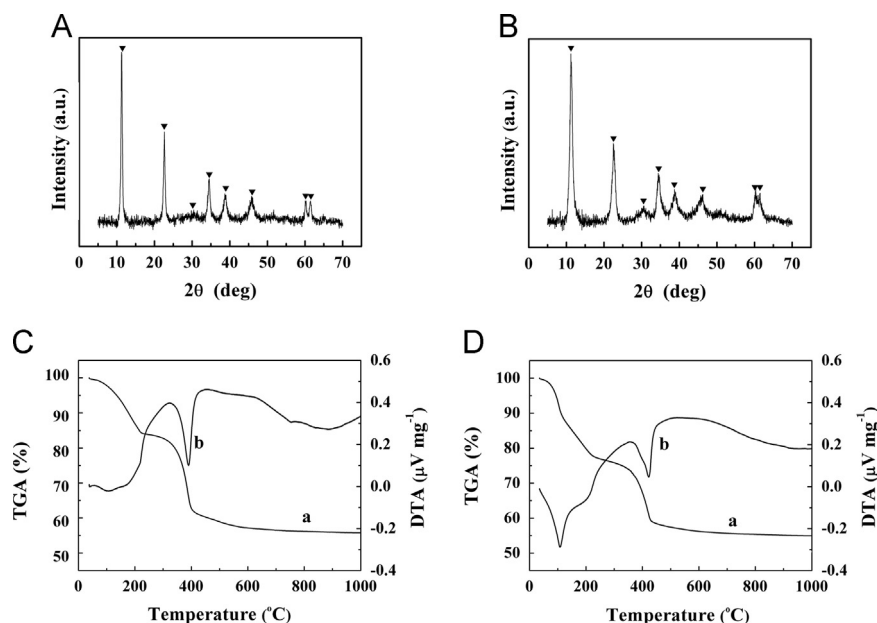

Fig. 1. (A,B) X-ray diffraction patterns (▾-peaks of hydrotalcite), and (C(a),D(a)) TGA and (C(b),D(b)) DTA data for (A,C) as received and (B,D) reconstructed AMZH.