Composites Part A 112 (2018) 558–571

Contents lists available at ScienceDirect

Composites Part A

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

Fabrication of zeolitic imidazolate frameworks on layered double hydroxide nanosheets to improve the fire safety of epoxy resin

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ARTICLE INFO

Keywords:
Hybrid
Polymer-matrix composites (PMCs)
Flame/fire retardancy
Thermal properties

ABSTRACT

ZIF@MgAl-LDH hybrids were synthesized by zeolitic imidazolate frameworks (ZIF) and MgAl-layered double hydroxide (MgAl-LDH) via electrostatic interactions. Their structure and morphology were systematically characterized. Then, ZIF@MgAl-LDH hybrids were added to epoxy resin (EP) to study their effects on the thermal properties and fire resistance of the material. The results of TGA showed that ZIF@MgAl-LDH could improve the char yield of the EP composites. The cone calorimetry, smoke density tests, limiting oxygen index (LOI) and UL94 vertical burning test showed that ZIF@MgAl-LDH effectively improved the flame retardancy and smoke suppression of EP. Furthermore, the laser Raman spectroscopy (LRS) and X-ray photoelectron spectroscopy (XPS) results of the char residue showed that ZIF@MgAl-LDH promoted the formation of a char layer with high graphitization and thermal oxidation resistance, which was conducive to the reduction of the fire hazards. This simple treatment of EP may expand its fire safety applications.

1. Introduction

Epoxy resin (EP) is one of the most important thermosetting polymers. At present, it is widely used in many fields, such as printed circuit boards, adhesives, laminates and coatings, because of its good dielectric properties, electrical insulation and dimensional stability [1–3]. Unfortunately, EP is extremely flammable, and it tends to produce a large amount of toxic fumes during the process of combustion [4,5]. Therefore, it is crucial to improve the flame retardancy and smoke suppression performance of EP for its application.

Layered double hydroxide (LDH) is the most important part of halogen-free flame retardants, as it is non-toxic, non-volatile, and secondary pollution-free [6–8]. However, many studies have shown that LDH is accompanied by a problem of high addition of inorganic flame retardants while improving the flame retardancy of the polymers [9,10]. Therefore, it is usually necessary to be modified or used in combination with other flame retardants to provide better flame retardancy with fewer additives. There have been many reports about improving the flame retardancy via the addition of modified LDH. For example, 2 wt% PWA-LDH (MgAl-LDH intercalated by phosphotungstic acid) and 18 wt% intumescent flame retardant decreased the peak heat release rate (PHRR) of poly (lactic acid) from 306.3 to 40.1 kW/m^2 [11]. RGO-LDH (a hybrid composed of MgAl-LDH loaded on a reduced graphene nanosheet) intercalated by $Mo_7O_{24}^{6-}$, and P-LDH (LDH was intercalated by tripolyphosphate) grafted by aminopropyltriethoxysilane showed good flame retardancy and smoke suppression performance in PUE (polyurethane elastomer) composites [12,13]. DT-M (an intumescent flame retardant consisting of diethylenetriamine penta-(methylenephosphonic) acid and melamine) and LDH intercalated by phytic acid increased the LOI of polylactic acid to 38.9%, and upgraded the UL94 rating to V-0 [14]. In addition, the application of modified LDH in EP has also been studied in recent years. It has been reported that LDH/MoS_2 hybrid, LDH-β-FeOOH hybrid and m-SiO_2@Co-Al LDH hybrid (Co-Al LDH coated mesoporous SiO_2) had a significant effect on improving the flame retardancy of EP [15–17]. Moreover, Wang et al. found that the addition of 8 wt% Fe_3O_4@Ph-CDBS-LDH (Fe_3O_4 loaded on the surface of MgAl-LDH which is modified by phytic acid and CDBS (hydroxypropyl-sulfobutyl-β-cyclodextrin)) increased the limit oxygen index (LOI) by 16%, and decreased the total smoke output by 34%, compared with pure EP [18]. Wang et al. found that cardanol as a surfactant to modify LDH effectively improved EP's flame retardancy and smoke suppression properties [19]. Modified LDH significantly improved the flame retardancy and smoke suppression properties of EP.

As a new type of porous nanomaterial, metal-organic framework materials (MOFs) are widely used in various fields, such as gas storage and separation, chromatographic separation and catalysis, due to their high specific surface area and adjustable pore size [20–23]. Recently, there have been some studies showing that MOFs can improve the flame

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https://doi.org/10.1016/j.compositesa.2018.07.001
Received 23 April 2018; Received in revised form 16 June 2018; Accepted 1 July 2018
Available online 02 July 2018
1359-835X/

retardancy of polymers. Hou et al. found that Fe-MOF and Co-MOF improved the flame retardancy of PS (polystyrene). Compared with pure PS, the PHRR of PS/Fe-MOF and PS/Co-MOF decreased by 14% and 28%, respectively [24]. Hou et al. also synthesized Ni-MOF and graphene hybrid (GOFs), and added GOFs to PS to study its effect on the flame retardancy of PS. Their results showed that the PHRR of the PS composites decreased by more than 33% with only 1.0 wt% addition of GOFs. GOFs showed excellent flame retardancy [25]. Furthermore, zeolite imidazole framework material (ZIF), as a subset of MOFs, has better thermal properties and chemical stability, compared with regular MOFs. This is because the interaction of metal cations with nitrogen atoms in imidazole is stronger than the interaction with carboxybenzene [26–28]. Therefore, it is of extraordinary significance to use ZIF to improve the flame retardancy of polymers. Shi et al. added ZIF-8 to polylactic acid (PLA) to study its effect on PLA. As a result, they found that 1 wt% of ZIF-8 increased the LOI of PLA from 20.5% to 26.0%, and ZIF-8 exhibited an extremely superior flame retarding effect. This was mainly because that: (a) ZIF8 contained N element that generated N_2 and NH_3 during the combustion process, and N_2 and NH_3 could dilute combustible gas; and (b) Zn element in ZIF8 produced metal oxides during the combustion process that demonstrated a catalytic charring effect. The char layer had the function of protecting the underlying matrix from further combustion [29].

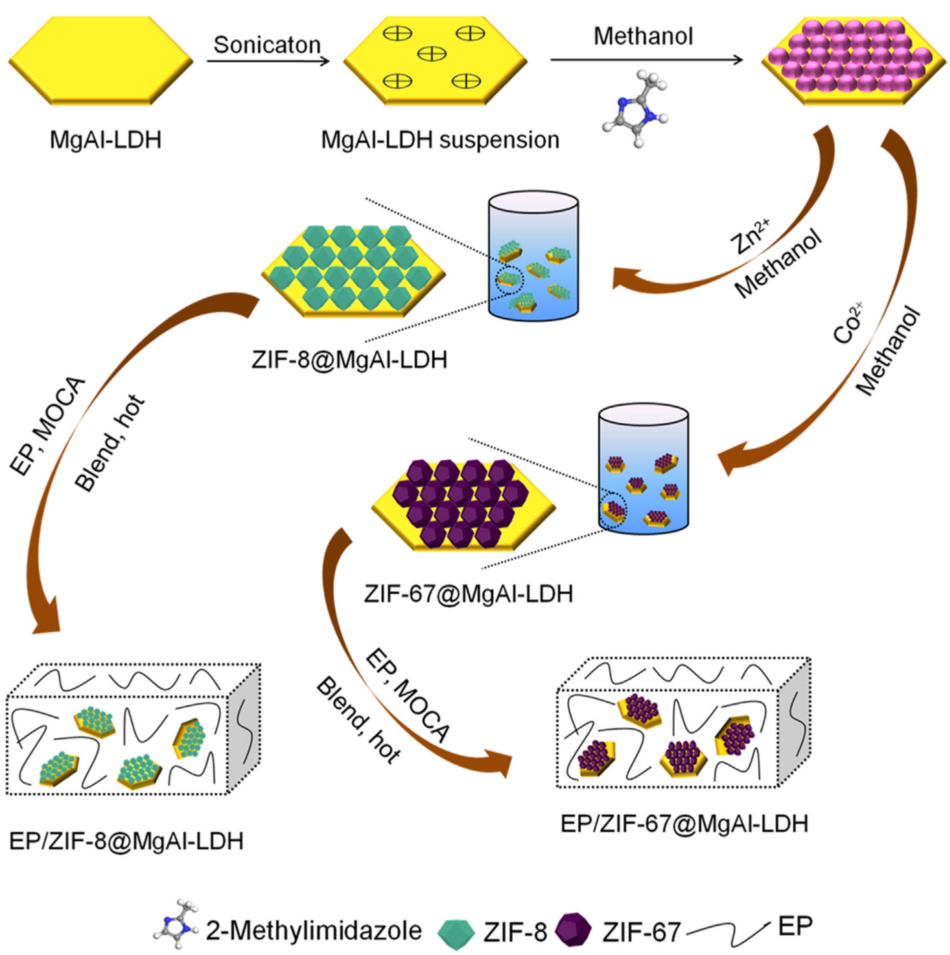
In this work, MgAl-LDH was designed through the structural features of MgAl-LDH surface with strong positive charge. ZIF-8 and ZIF-67 were loaded on the surface of MgAl-LDH by electrostatic interaction, respectively, to obtain ZIF-8@MgAl-LDH and ZIF-67@MgAl-LDH hybrids. It was hoped that modified MgAl-LDH would not only fully reflect the original flame retardancy of MgAl-LDH, but also achieve a better flame-retardant effect with the combination effect of various elements (due to the introduction of N, Zn or Co elements). To the best of our knowledge, there has been no similar work reported on the surface modification of MgAl-LDH with ZIF-8 and ZIF-67 in relation to their flame retardancy.

In this study, MgAl-LDH modified by ZIF-8 and ZIF-67 respectively were successfully synthesized (ZIF-8@MgAl-LDH, ZIF-67@MgAl-LDH), as shown in Scheme 1. Then, they were each added to EP, and their effects of thermal stability, flame retardancy and smoke suppression properties on EP were investigated by means of thermogravimetric analysis, cone calorimeter, smoke density meter, and so on. In addition, the possible mechanism of ZIF@MgAl-LDH to reduce the fire risk of EP was explored by further analysis of the char residue after the cone calorimeter test.

2. Experimental section

2.1. Materials

$Al(NO_3)_3 \cdot 9H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, NaOH, 2-Methylimidazole, $Zn(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). EP was purchased from Wuxi Pinhua Chemical Co., Ltd. (China). 3,3′-Dichloro-4,4′-diaminodiphenyl methane (MOCA) was purchased from Jinan Haiwu Chemical Co., Ltd. (China).



Scheme 1. Illustration for the modification of LDH and preparation of EP composites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)