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Progress in Natural Science: Materials International 25 (2015) 503–511

Progress in Natural Science Materials International

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Original Research

Preparation and performance of lipophilic α-zirconium phosphate with high thermal stability and its application in thermal-plastic polymers

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Received 2 July 2015; accepted 1 August 2015
Available online 21 November 2015

Abstract

To prepare lipophilic α-zirconium phosphate with high grafting ratio and thermal stability (OZrP-HT) and explore its potential application in thermal-plastic polymers, a novel method was developed by surface lipophilicity enhancement strategy. The commercial α-zirconium phosphate (α-ZrP) was pre-intercalated by n-propylamine (PA) and grafted by silane coupling agents. Then the pre-intercalated PA was removed by heat-treatment, and the obtained OZrP-HT was utilized to fabricate the phosphorous-containing polyester (P-*co*-PET)/OZrP-HT nanocomposites by melt-blending method. The prepared OZrP-HT and P-*co*-PET/OZrP-HT nanocomposites were characterized by Wide Angle X-ray Diffraction (WAXD), Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Transmission Electron Microscope (TEM), etc. The results show that OZrP-HT with high grafting ratio (13.78 wt%) and thermal stability (T_{onset}=368 °C) was successfully prepared via this novel method and was uniformly intercalated by P-*co*-PET molecular chains. OZrP-HT had no significant effect on the fiber processability of P-*co*-PET polymer, and flame retardant properties of (P-*co*-PET)/OZrP-HT nanocomposites were improved. This method may be suitable for organic modification of general inorganic layered compounds and could extend the potential applications in thermo-plastic polymers.

Keywords: α-zirconium phosphate; Lipophilic; Thermal stability; Thermal-plastic polymers

1. Introduction

Increasing attentions have been devoted to the usage of inorganic layered compounds, such as montmorillonite (MMT), hydrotalcite (LDHs), and zirconium phosphate (ZrP), as inorganic fillers in thermo-plastic polymers [1,2]. The introduction of inorganic layered compounds results in the improvement of thermal stability, mechanical properties [3], gas barrier property [4] and anti-flammability of polymers due to the baffle effect of inorganic layered compounds in the polymeric matrix [5,6]. However, two main subjects have to be addressed for their further developments and applications: inherent agglomeration of nano-sized inorganic compounds [7,8] and their incompatibility with polymers [9].

Different strategies have been explored to solve the aggregation problem of inorganic layer compounds and improve their miscibility with polymers. Among them, surface organic modification has been proved to be an effective step to prevent the aggregation of inorganic layered compounds and endow them sufficiently strong miscibility with polymers, which can effectively enhance properties of resultant nanocomposites [10]. This method mainly strives to induce thin layer of organic molecules on the surface of inorganic layered compounds by different strong interactions to improve their miscibility with polymers. Meanwhile, the

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Peer review under responsibility of Chinese Materials Research Society.

http://dx.doi.org/10.1016/j.pnsc.2015.10.007

intercalation of organic molecules into layer region of inorganic layered compounds increases the distance between every layer and favors the further penetration of other molecules.

The surface organic modification was generally realized by non-covalent or covalent bonding interactions between inorganic layered compounds with polymers. The former is a simple and effective way, which needs modifiers possessing the opposite charge to the inorganic layered compound surface, but the interaction is usually very weak and easy to be broken [10,11]. Covalent bonding method may endow them with strong binding ability by reacting with functional groups, however, it is generally hard to intercalate directly into the internal layer of inorganic compounds, which prefers to attach onto the surface exclusively [12,13]. Mosby [12] attached epoxides to the surface of ZrP nanoplatelets, however only the top and bottom layers were modified while the interlayer structure remained unchanged, thus the prepared organic layered compound has weak interaction with polymers as its lipophilicity is very poor. And it has also been found that, the small interlayer distance is adverse to the intercalation of polymer molecular chains. Therefore, exploring a suitable surface organic modification method for inorganic compounds is crucial and important to realize the well dispersion and better compatibility with polymers by a facile way.

Most of the previous reports were focused on the investigation of novel categories and preparations of organic layered compounds, while their thermal stability and applications in thermo-plastic polymers were almost ignored. At present, only a few qualified lipophilic organic layered compounds are stable enough to be used in modification of general thermal-plastic polymers, such as polyethylene terephthalate (PET) processed at about 300 °C, which limits their application scope greatly. Therefore, apart from the improvement of lipophilicity, the enhancement of thermal stability is also crucial. Compared to these classical modification routes which aim at obtaining a compatibilization effect toward the polymer matrix [10], the goal of this work is to propose a novel method to prepare lipophilic layered compounds with qualified thermal stability for general thermal-plastic polymers modification.

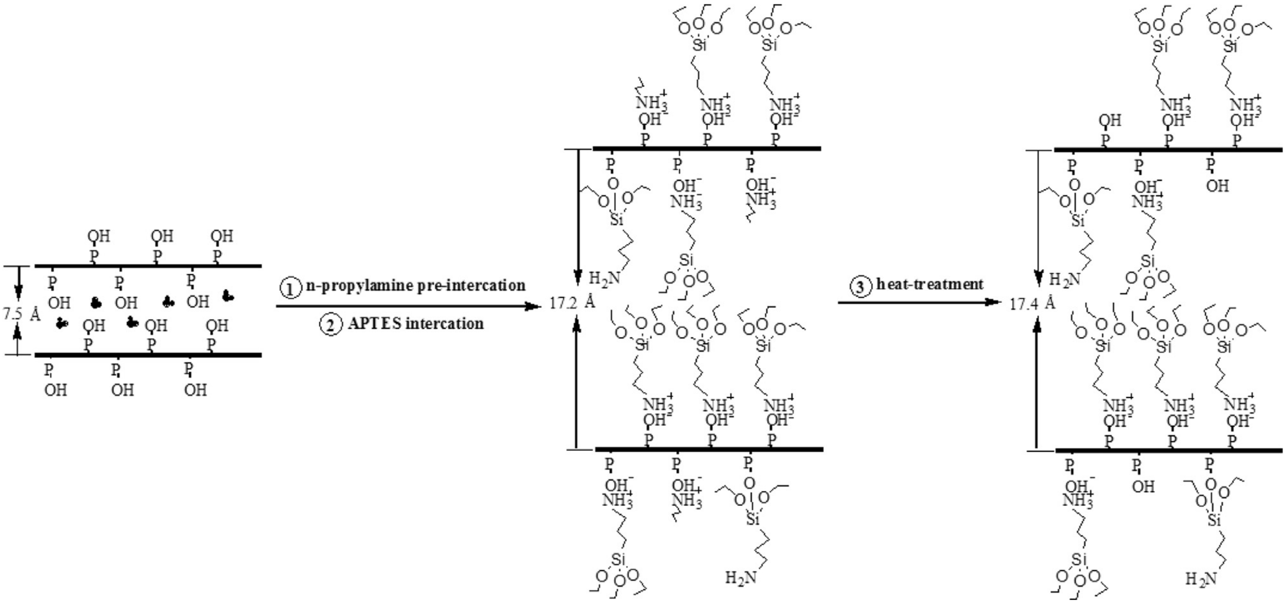
In the present investigation, lipophilic α-zirconium phosphate with enhanced thermal stability (ZrP-HT) was prepared by a novel method, and its application in thermal-plastic polymers was studied.

2. Materials and experimental procedure

The synthetic route for preparation of lipophilic α-ZrP with improved lipophilicity and thermal stability (OZrP-HT) is illustrated in Scheme 1, α-ZrP was pre-intercalated by n-propylamine (PA) to increase the interlayer distance, and then intercalated by 3-Aminopropyl triethoxysilane (APTES) (as an example of silane coupling agents), finally it was heat-treated to remove the thermolabile PA, the specific experimental operation will be explained later. The obtained OZrP-HT was melt-blended with phosphorous-containing polyester (P-*co*-PET) to preliminarily evaluate its applicability in thermo-plastic polymers. The modification process of α-ZrP was investigated by Wide Angle X-ray Diffraction (WAXD), Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA) and Transmission Electron Microscope (TEM), and the performances of P-*co*-PET/OZrP-HT nanocomposites were investigated by the hydrophilic/lipophilic experiment, WAXD, TEM, TGA, Limiting Oxygen Index (LOI), Underwriter Laboratories-94 (UL-94), etc.

2.1. Materials supply

Alpha-zirconium phosphate (α-ZrP) was supplied by Shanghai Runhe Nanotechnology Company (China). Ethanol,



Scheme 1. Synthetic route for preparation of lipophilic α-ZrP with improved lipophilicity and thermal stability.