Materials and Design 122 (2017) 247–254

Contents lists available at ScienceDirect

Materials and Design

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

Exfoliation of layered zirconium phosphate nanoplatelets by melt compounding

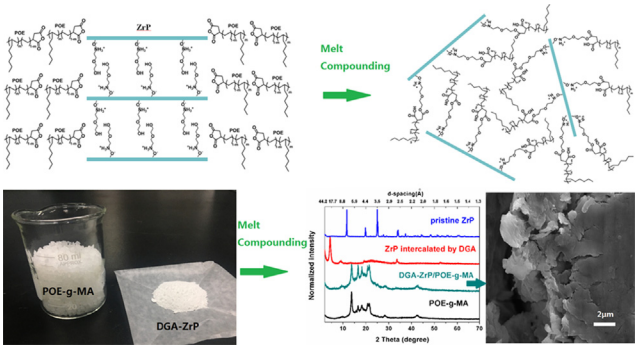
Lei Chen [a,b], Dazhi Sun [a,*], Jin Li [b], Guangdao Zhu [c]

[a] Shenzhen Key Laboratory of Nanoimprint Technology, Department of Materials Science and Engineering, Southern University of Science and Technology, Shenzhen, Guangdong 518055, People's Republic of China
[b] Department of Materials Science, Fudan University, Shanghai 200433, People's Republic of China
[c] Huaian Nylon Chemical Fibre Co., Ltd., Huaian, Jiangshu 223400, People's Republic of China

HIGHLIGHTS

- ZrP nanoplatelets with various sizes were successfully exfoliated by the presented melt compounding method.
- This fabrication method could be used to prepare polymer nanocomposites with exfoliated ZrP nanoplatelets in a large scale.
- The improvement of modulus of elasticity of ZrP/POE-g-MA was attributed to the well-exfoliated nanoplatelets.
- The ductility of ZrP/POE-g-MA compounds also became better, if ZrP nanoplatelets were first intercalated by diglycolamine.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 January 2017
Received in revised form 6 March 2017
Accepted 7 March 2017
Available online 07 March 2017

Keywords:
Zirconium phosphate nanoplatelets
Exfoliation
Melt compounding method
Polymer nanocomposite
Maleic anhydride grafted polymer

ABSTRACT

A melt compounding method to achieve the exfoliation of layered zirconium phosphate (ZrP) nanoplatelets was presented in this work. ZrP nanoplatelets were first intercalated by diglycolamine (DGA) to increase the interlayer distance and functionality. In the next melt compounding process, the cyclic anhydrides of maleic anhydride grafted polyolefin elastomers (POE-g-MA) reacted with the hydroxyls in DGA-ZrP. Subsequently, the long polyolefin chains of POE-g-MA intercalated into the interlayer of ZrP smoothly and exfoliated the nanoplatelets successfully. ZrP nanoplatelets with various sizes were fully exfoliated in POE-g-MA matrices. The modulus of elasticity of POE-g-MA was improved by the incorporation of ZrP nanoplatelets and further increased if the nanoplatelets are exfoliated. The ductility of ZrP/POE-g-MA compounds also became better, if ZrP nanoplatelets were first intercalated by DGA and then exfoliated, especially for the smaller nanoplatelets. Our work provides a general method to prepare polymer nanocomposites containing exfoliated ZrP nanoplatelets in a large scale.

1. Introduction

Adding synthetic or natural nanoscale inorganic compounds into polymeric materials is a well-known technique to improve various properties of the organic matrices, such as mechanical strength [1–11], flame retardancy [12–18], barrier properties [18–24],

* Corresponding author.
E-mail address: sundz@sustc.edu.cn (D. Sun).

http://dx.doi.org/10.1016/j.matdes.2017.03.026
0264-1275/

dimensional stability [25–28], and so on. Such prepared polymer nanocomposites can be distinguished into three types, depending on the dimension of the incorporated nanoparticles, i.e. 0-dimensional (0D) spherical/quasi-spherical nanoparticles, 1-dimensional (1D) nanorods/nanotubes/nanowires and 2-dimensional (2D) nanoplatelets/nanosheets [29,30]. Among all the potential nanocomposite additives, clay and layered silicates have been widely investigated probably because they are easily available and their intercalation chemistry has been studied for a long time [29–32]. Clays have several advantages, such as high ion exchange capacity, high aspect ratio and inexpensiveness, thereby resulting in high potential for large-scale commercial uses. But the main drawback of clays is that they are produced via purification and modification of the mined clay. It is extremely difficult to achieve 100% purity, narrow particle size distribution and controlled aspect ratio for clays, which affect the mechanical properties of polymer nanocomposites directly [11,33,34]. Compared with clay, synthetic zirconium phosphate ($Zr(HPO_4)_2 \cdot H_2O$, ZrP) nanoplatelets have a much higher ion exchange capacity (6 times higher than clay), and their size and aspect ratio can be controlled by varying reaction time and reactant concentrations [35–38]. Furthermore, the size distribution of ZrP nanoplatelets has been found to be quite narrow, thus suitable for fundamental study of nanofiller effect on the properties of the host polymers. Moreover, ZrP nanoplatelets have also been found to improve the flame retardancy of the polymer matrices mainly through catalytic carbonization effect, rather than physical effects, by forming a high-performance carbonaceous char on the sample surface [13].

In preparing polymer nanocomposites containing layered nanoplatelets, intercalation and exfoliation have always been the two most critical steps. In general, inorganic nanoplatelets cannot be easily dispersed in most polymers due to their preferred face-to-face stacking in agglomerated tactoids. Dispersion of the tactoids into discrete monolayers is further hindered by the intrinsic incompatibility of hydrophilic layered inorganic compounds and hydrophobic engineering plastics. Effective intercalation has been shown to be essential for the preparation of fully exfoliated polymer nanocomposites with greatly improved modulus and barrier properties [39–43]. In the past two decades, the most traditional and popular approach is to intercalate the nanoplatelets by organic amines to produce polymer–compatible nanoplatelets. There are three methods to prepare polymer nanocomposites, i.e. intercalation of a suitable monomer followed by polymerization, polymer intercalation from solution, and direct polymer melt compounding [3]. Among them, direct polymer melt compounding is the most attractive because of its low cost, high productivity and compatibility with current polymer processing techniques. It uses widespread and conventional equipments in the plastic industry with high producing rates. Up till now, a few exfoliated nanocomposites with clay were successfully prepared by melt compounding method, such as PP/clay [4], PA6/clay [44,45], and EVA/clay [46] composites. The intercalated-exfoliated type of PA6/ZrP nanocomposites have also been prepared whereas PET/ZrP, PP/ZrP and EVA/ZrP compounds appear to be micro-composites [12]. To the best of our knowledge, no exfoliated nanocomposites with ZrP nanoplatelets have been successfully prepared by melt compounding method.

Hence, the objective of this study is to develop a viable melt compounding method for achieving full exfoliation of layered zirconium phosphate nanoplatelets. This was done using a two-step process: in the first, ZrP nanoplatelets were intercalated by diglycolamine. Secondly, the intercalated ZrP nanoplatelets were mixed with maleic anhydride grafted polymer (polymer-g-MA) matrices using a mixer rheometer. To demonstrate the validity of this method, ZrP nanoplatelets with different sizes were prepared. The usefulness of polymer-g-MA to exfoliate layered ZrP nanoplatelets was monitored using X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscope. To study the effect of ZrP nanoplatelets on the mechanical property of polymer-g-MA matrices, the tensile properties of the ZrP/polymer-g-MA nanocomposites were also tested and discussed.

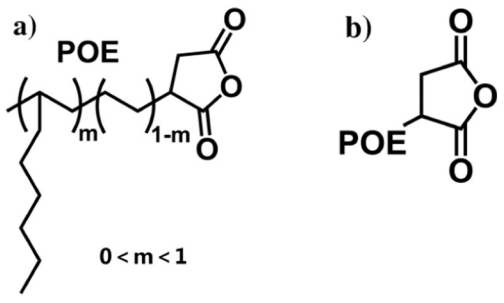


Fig. 1. The chemical structure of POE-g-MA: a) the details of the structure of POE-g-MA, b) the simplified version of POE-g-MA.

2. Experimental section

2.1. Materials

Zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$, 98%, Aladdin Industrial Co., Ltd), phosphoric acid (85%, Tianjin Yongda Chemical Reagent Co., Ltd), and diglycolamine (DGA, Aladdin Industrial Co., Ltd) were used as received. Maleic anhydride grafted polyolefin elastomer (POE-g-MA, 1801B, Guangzhou Haosu Chemical Co., Ltd) was chosen as the polymer-g-MA to exfoliate ZrP nanoplatelets. The chemical structure of POE-g-MA was shown in Fig. 1.

Table 1
The abbreviations of all the samples in this work.

The abbreviation of sample	The description of sample
ZrP	Zirconium phosphate nanoplatelets
Refl3MZrP	ZrP synthesized by refluxing method in the condition of 3.0 mol/L H_3PO_4
3MZrP	ZrP synthesized by hydrothermal method in the condition of 3.0 mol/L H_3PO_4
6MZrP	ZrP synthesized by hydrothermal method in the condition of 6.0 mol/L H_3PO_4
9MZrP	ZrP synthesized by hydrothermal method in the condition of 9.0 mol/L H_3PO_4
DGA-ZrP	Zirconium phosphate intercalated by diglycolamine (DGA)
DGA-Refl3MZrP	Refl3MZrP intercalated by diglycolamine
DGA-3MZrP	3MZrP intercalated by diglycolamine
DGA-6MZrP	6MZrP intercalated by diglycolamine
DGA-9MZrP	9MZrP intercalated by diglycolamine
POE-g-MA	Maleic anhydride grafted polyolefin elastomer
ZrP/POE-g-MA	The compounds of ZrP with POE-g-MA
Refl3MZrP/POE-g-MA or R3M/MA	The compounds of Refl3MZrP with POE-g-MA
DGA-Refl3MZrP/POE-g-MA or DGA-R3M/MA	The compounds of DGA-Refl3MZrP with POE-g-MA
3MZrP/POE-g-MA or 3M/MA	The compounds of 3MZrP with POE-g-MA
DGA-3MZrP/POE-g-MA or DGA-3M/MA	The compounds of DGA-3MZrP with POE-g-MA
6MZrP/POE-g-MA or 6M/MA	The compounds of 6MZrP with POE-g-MA
DGA-6MZrP/POE-g-MA or DGA-6M/MA	The compounds of DGA-6MZrP with POE-g-MA
9MZrP/POE-g-MA or 9M/MA	The compounds of 9MZrP with POE-g-MA
DGA-9MZrP/POE-g-MA or DGA-9M/MA	The compounds of DGA-9MZrP with POE-g-MA
POE-g-MA-1	POE-g-MA prepared in the same melt compounding conditions with the samples of Refl3MZrP series
POE-g-MA-2	POE-g-MA prepared in the same melt compounding conditions with the samples of 3MZrP series
POE-g-MA-3	POE-g-MA prepared in the same melt compounding conditions with the samples of 6MZrP series
POE-g-MA-4	POE-g-MA prepared in the same melt compounding conditions with the samples of 9MZrP series