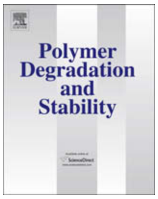
Polymer Degradation and Stability 94 (2009) 544–549

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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



Preparation and characterisation of a novel fire retardant PET/α-zirconium phosphate nanocomposite

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ARTICLE INFO

Article history:
Received 7 January 2009
Accepted 29 January 2009
Available online 5 February 2009

Keywords:
Fire retardant
Flame retarded
Poly(ethylene terephthalate)
PET
In situ polymerisation
Nanocomposite

ABSTRACT

The preparation of a novel fire retardant nanocomposite of poly(ethylene terephthalate) (PET) using nanoscopic α-zirconium phosphate (α-ZrP), by *in situ* polymerisation was investigated. The novel fire retarded PET nanocomposite, PET-*co*-DDP/α-ZrP, was synthesized by the direct condensation of terephthalic acid, ethylene glycol, 9,10-dihydro-10[2,3-di(hydroxycarbonyl)propyl]-10-phosphaphenanthrene-10-oxide (DDP) and nano α-ZrP. The morphology, thermal stability and burning behaviour of the nanocomposite with 1 wt% α-ZrP loading was investigated. The extent of dispersion of the nanofillers was quantified by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Significant improvements in fire retardant performance were observed for the nanocomposite from limiting oxygen index (increased from 21.2 to 32.6), UL-94 (achieving V-0), and cone calorimetry (reducing both the heat release rate and the total heat released, without reducing the time to ignition).

1. Introduction

Poly(ethylene terephthalate) (PET) is a semicrystalline polymer possessing excellent chemical resistance, thermal stability, high strength, and spinnability. PET fibre is the textile industry's most widely used synthetic polymer [1–3]. However, its flammability and severe dripping during combustion greatly limits its applications. As a result of recent studies of fire retardant PET, phosphorus-containing copolyesters have been recognised as one of the most efficient ways of imparting fire retardance to PET, because they have excellent fire retardancy, and compared to halogenated flame retardants, lower toxic gas evolution during burning. Asrar and Mo [4] studied the synthesis of a copolyester, PET-*co*-CEPP, from terephthalic acid (TPA), ethylene glycol (EG) and 2-carboyethyl (phenylphosphinic) acid (CEPP). Wang et al. [5–8] have also synthesized some novel phosphorus-containing fire retardants in polyester copolymers. Recently our laboratory in Chengdu has successfully synthesized a series of phosphorus-containing fire retardant polyester copolymers including those with phosphorus linked as pendent groups and incorporated into the main chain [9–16]. Furthermore, it has also been recognised that the formation of nanocomposites can improve the fire retardant performance at relatively low nanoparticle loadings [17–19].

Polymer nanocomposites containing layered silicates have been studied extensively as a new generation of advanced composites that exhibit greatly improved mechanical properties [20], enhanced gas barrier properties [21], and fire retardancy [17]. Among the layered nanofillers, montmorillonite clay is one of the most widely used nanofillers for preparing polymer nanocomposites, due to its high ion-exchange capacity for attachment of surfactant molecules, and high aspect ratio for better barrier properties [20]. Zirconium bis(monohydrogen orthophosphate) monohydrate, (α-$Zr(HPO_4)_2 \cdot H_2O$) (α-ZrP), has a layered structure with many interesting properties, such as high ion-exchange capacity, thermal and chemical stability [22], catalytic activity, ionic conductivity, and the potential to delaminate and become intercalated within the polymer [23]. Many of these properties are common to natural layered nanofillers such as montmorillonite, but α-ZrP has a higher ion-exchange capacity [24], and has different elements in its structure. However, only a few studies have been reported on layered zirconium phosphate polymer nanocomposites, such as the preparation of epoxy-α-ZrP [24–27] nanocomposites, polyethyleneimine-γ-ZrP nanocomposites [28] and poly(ethylene terephthalate)/lamellar zirconium phosphate nanocomposites [23]. Furthermore, the foci of these studies was the synthesis and the improvement of thermal or mechanical

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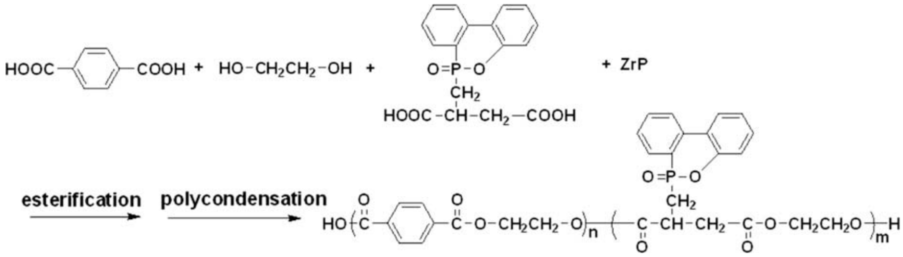
doi:10.1016/j.polymdegradstab.2009.01.018



Scheme 1. Reaction route of PET-*co*-DDP/ZrP nanocomposite.

properties. To the best of our knowledge, no studies of fire retardant property enhancement by ZrP have been reported, although its structure contains elements (zirconium and phosphorus) with potential to impart fire retardant behaviour.

In this work, we describe the preparation of a novel fire retarded PET nanocomposite with α-ZrP by *in situ* polymerisation. The α-ZrP was synthesized by direct precipitation. The PET nanocomposite, PET-*co*-DDP/zirconium phosphate (α-ZrP) nanocomposite, was synthesized by condensation of terephthalic acid (TPA), ethylene glycol (EG), 9,10-dihydro-10[2,3-di(hydroxycarbonyl)propyl]-10-phosphaphenen-threne-10-oxide (DDP) and nano-ZrP, as shown in Scheme 1. The thermal stability and burning behaviour of the nanocomposite have been investigated and are presented here.

2. Experimental

2.1. Materials

TPA and EG were supplied by Zhenghao New Materials Company (Jinan, China). α-ZrP was synthesized in our laboratory in Chengdu from zirconium oxychloride ($ZrOCl_2$) and phosphoric acid (H_3PO_4) both from the Shanghai Chemical Agent Company, and modified using diethanolamine ($(HOCH_2CH_2)_2NH$) and octadecyltrimethylammonium chloride (1831) through cation exchange. DDP was provided by Weili Flame Retardant Chemicals Industry Co. Ltd. (Chengdu, China).

2.2. Preparation and modification of α-ZrP

α-ZrP was synthesized from $ZrOCl_2$ and H_3PO_4, having established that the optimum synthesis condition was achieved when the mole ratio of $ZrOCl_2$ to H_3PO_4 was 1:2 and the mixture reacted for 8 h at 40 °C. The precipitate was filtered and washed using de-ionised water until the rinsing water was neutral (pH 7). The results from XRD concur with those of Ref. [27]. The layered structure of α-ZrP was modified by two routes using $(HOCH_2CH_2)_2NH$ and 1831, by cation exchange under various conditions. For the first modification, the optimum conditions were obtained when the mole ratio of $(HOCH_2CH_2)_2NH$ and α-ZrP was 2.5 and the exchange time was 10 h at 40 °C with stirring. The product was washed with de-ionised water until the washing water was neutral. This was further modified with 1831 and the $(HOCH_2CH_2)_2NH$-modified α-ZrP in a 2.5 mole ratio using an exchange time of 12 h at 60 °C with stirring. This modified ZrP was centrifuged and washed with de-ionised water until neutral.

2.3. Preparation of PET-co-DDP/α-ZrP nanocomposites

PET-*co*-DDP/α-ZrP nanocomposite was prepared from TPA, EG, DDP and modified α-ZrP by direct condensation polymerisation. The synthetic route was as follows: initially, the modified α-ZrP (1 wt%) was added to EG (200 ml) and stirred in an ultrasonic bath for 0.5 h as pretreatment. After this, TPA, EG, DDP and the pretreated α-ZrP solutions were introduced into a reactor equipped with a nitrogen inlet, a condenser and a mechanical stirrer. The reactor was heated to 240 °C under high pressure (0.4–0.5 MPa) and maintained for 3.5 h. After this, the pressure of the reactor was reduced to less than 100 Pa and maintained for 2 h. A comparison material, PET-*co*-DDP with 1 wt% phosphorus was prepared from TPA, EG and DDP according to the procedure reported by Chang and Chang [29]. The intrinsic viscosities (η) of the copolyesters were determined with an Ubbelohde viscometer at 30 °C in phenol/1,1,2,2-tetrachloroethane (60/40, w/w) solution; the results are given in Table 1.

2.4. Characterisation

2.4.1. X-ray diffraction (XRD)

X-ray diffraction (XRD) was performed using a Rigaku X-ray powder diffractometer with a copper target. The generator power was 40 kV and 150 mA, the scan mode was continuous with a scan rate of 0.8°/min, and the 2θ scan range was from 2° to 45°.

2.4.2. Scanning electron microscopy (SEM)

PET-*co*-DDP/α-ZrP nanocomposite was made into films and then cracked in liquid N_2. The fresh face of the sample was gold coated for SEM observation. The sample was examined in a JEOL JSM-5410 scanning electron microscope (Tokyo, Japan) using a working voltage of 10 kV.

2.4.3. Transmission electronic microscopy (TEM)

TEM images of nanocomposite specimens without staining were taken at room temperature. The TEM grids were mounted in a liquid nitrogen cooled sample holder. The ultrathin sectioning (50–70 nm) was performed by ultramicrotomy at low temperature using a Reichert Ultracut E low temperature sectioning system. A transmission electron microscope (JEM-100CX, JEOL) operated at 80 kV was used to obtain images of the nanocomposite specimens.

2.4.4. LOI and UL-94 test

The LOI values were measured on a JF-3 oxygen index meter (Jiangning, China) with sheet dimensions of $130 \times 6.5 \times 3\ mm^3$ according to ASTM D2863-97. Vertical burning tests (UL-94) were conducted on a vertical burning test instrument (CZF-2-type)

Table 1
Summary of polyester copolymer characterisation.

Sample	P % (w/w)	ZrP % (w/w)	[η] (dl /g)	LOI	UL-94	Drip
PET	0	0	0.67	21.2	No rating	Severe
PET-*co*-DDP	1	0	0.65	30.8	V-2	Moderate
PET-*co*-DDP/ZrP nanocomposite	1	1	0.64	32.6	V-0	slow