Polymer Degradation and Stability 105 (2014) 1–11

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

On flame retardancy in polycaprolactam composites by aluminium diethylphosphinate and melamine polyphosphate in conjunction with organically modified montmorillonite nanoclay

A. Ramani*, A.E. Dahoe

Faculty of Art, Design and the Built Environment, University of Ulster, Northern-Ireland, United Kingdom

ARTICLE INFO

Article history:
Received 11 December 2013
Received in revised form
24 February 2014
Accepted 20 March 2014
Available online 4 April 2014

Keywords:
Polycaprolactam
Aluminium diethylphosphinate
Melamine polyphosphate
Natural montmorillonite

ABSTRACT

The effect on flame retardancy in polycaprolactam composites with the combination of aluminium diethylphosphinate and melamine polyphosphate, and, organically modified montmorillonite nanoclay was investigated. TGA, DSC, TGA-FTIR and FTIR-ATR were applied to assess the condensed phase action of the flame retardants. A mechanism for the decomposition of polycaprolactam and its interaction with the flame retardants is deduced. The outcome of this study implies that combining both flame retardants results in an enhanced effect when compared with their application on a separate basis.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Polycaprolactam or polyamide 6 (PA6) is a semi-crystalline polymer with desirable physical properties such as a high fatigue strength, low friction coefficient, enhanced toughness, and, material compatibility with a broad spectrum of fuels, oils and chemicals [1]. Its susceptibility to fire hazards, however, poses a major drawback. The LOI-value is 23 and the UL-94 fire test rates merely V2. While its heat of combustion of 29.8 MJ kg^{-1} [2] is less than that of other commercial polymers like polyethylene (44.60 MJ kg^{-1} [3]), polypropylene (42.66 MJ kg^{-1} [3]) and polystyrene (41.96 MJ kg^{-1} [3]), it supersedes that of poly(1,4-butanediolterephtalate) (26.71 MJ kg^{-1} [3]). The fire spread of PA6 is also exacerbated by melt drips that result from exposure to heat. For these reasons considerable research efforts are being devoted to the development of flame retardants for PA6.

Brominated flame retardants such as hexabromobenzene, brominated polystyrene, and octabromodiphenyloxide are used as flame retardants in nylons because of their effectiveness, small dosage, reasonable cost and minor effect on the physical properties of the polymer. But in real fire scenarios the combustion products of brominated flame retardants pose severe toxicity hazards. The formation of polybrominated dioxins and polybrominated dibenzofurans by pyrolytic and thermo-oxidative processes during combustion has prompted the implementation of the Restriction of Hazardous Substances Directive (Directive 2002/95/EC) to limit the use of brominated flame retardants and apply halogen free flame retardants instead. Entirely in line with this development, the present study is focused on the application of two halogen free flame retardants to PA6: Cloisite 30B and Exolit OP1311. Cloisite 30B is a nanoclay made from Cloisite Na^+ (which is a natural montmorillonite) by the ion exchange of alkaline cations with methyl, octadecyl, bis-2-hydroxyethyl quaternary ammonium chloride (Fig. 1). Exolit OP1311 consists of aluminium diethylphosphinate ($Al[(C_2H_5)_2PO_2]_3$, Fig. 1) and melamine polyphosphate (Fig. 1) in the ratio of 2:1. In some composite systems aluminium diethylphosphinate acts mainly as an intumescent flame retardant, but in other systems flame inhibition or the formation of an inorganic layer may be the main flame retardancy mechanism. Melamine polyphosphate acts mainly via intumescence, and to a lesser extent via char formation. Details of their compositions are given in Table 1.

Samples of four different PA6 formulations were made by melt compounding:

- F0: Pristine PA6
- F1: PA6 + Exolit OP1311

---

* Corresponding author.
E-mail address: alwar.ramani@gmail.com (A. Ramani).

http://dx.doi.org/10.1016/j.polymdegradstab.2014.03.020
0141-3910/© 2014 Elsevier Ltd. All rights reserved.

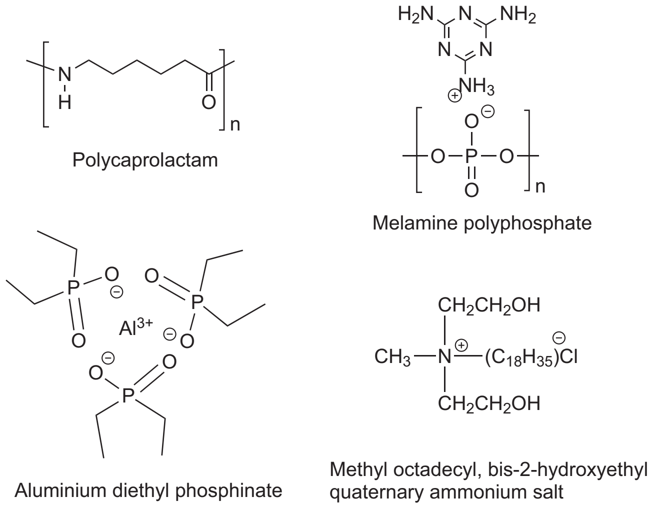

Fig. 1. Chemical structure of polycaprolactam; melamine polyphosphate; aluminium diethylphosphinate; and methyl, octadecyl, bis-2-hydroxyethyl quaternary ammonium chloride.

- F2: PA6 + Cloisite 30B
- F3: PA6 + Exolit OP1311 + Cloisite 30B

The samples were subjected to thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in a nitrogen atmosphere. Solid residues obtained at different temperatures (25, 250, 350, 450 and 550 °C) from TGA were examined using FTIR-ATR. TGA measured the mass loss, the amount of residue, the steps of degradation, and the pyrolysis temperature. Depending upon the nature of the additives present in the polymer matrix, thermal degradation can be either exothermic or endothermic, thereby accompanied by changes in enthalpy. But TGA does not reveal whether a particular step in the thermal decomposition of the polymer matrix is exothermic or endothermic. Only the change in the mass with respect to either time or temperature is measured. DSC, on the other hand, does reveal information about enthalpy changes. While the literature [4–7] only deals with phase changes such as glass transition and heat of melting of PA6 using DSC, the present study addresses the pyrolysis and condensed phase action of the additives in the polymer matrix. Enthalpy changes were measured by means of DSC. The chemical composition of the residue was investigated by means of FTIR-ATR [8]. From the present observations, coupled with earlier results on evolved-gas analysis [9], a mechanism is deduced for the decomposition of PA6 and its interaction with the additives, both in the gaseous and condensed phase (Figs. 5 and 6).

2. Experimental techniques and procedures

2.1. Materials and sample preparation

Polyamide 6 was obtained from Rhodia Technyl. Cloisite 30B was purchased from Southern Clay. Exolit OP1311 was purchased from Clariant. The formulations (Table 1), made by melt compounding, were first ground in a cryogenic grinder and subsequently dried for 72 h at 60 °C in vacuum and stored in sealed desiccators prior to testing.

Table 1
The formulations and their composition.

Formulation	PA6 (wt%)	Cloisite 30B (wt%)	Exolit OP1311 (wt%)
F0	100	–	–
F1	95	5	–
F2	82	–	18
F3	77	5	18

2.2. Experimental techniques

2.2.1. Thermogravimetric analysis

A Mettler-Toledo TGA/SDTA 851^e measuring module was deployed for thermogravimetric analyses. The inaccuracy in the temperature measurements was ±0.5 °C. The samples were heated in a 70 μl alumina (Al_2O_3) crucible (without lid). The crucible was annealed before each experiment. The buoyancy effect in TGA was taken into account by performing empty crucible runs and subtracting these data from the subsequent sample mass loss data. The measurements were carried out at a heating rate of 10 °C min^{-1} in nitrogen, with a 50 cm^3 min^{-1} flow rate of nitrogen between 30 °C and 700 °C. Mettler-Toledo STAR^e software (version 10.0) was used to record the data digitally. DTG curves (middle-part of Fig. 2) were computed by applying a least-squares filter based on Ref. [10] (3rd-order polynomial, window size: 7 points, 3 left, 3 right) to the TGA curves (upper-part of Fig. 2).

2.2.2. Differential scanning calorimetry

A Mettler-Toledo STAR^e system equipped with a DSC calorimetric cell was deployed for this work. STAR^e software, version 10.0, was used for data acquisition. Indium was applied as a reference material to calibrate the instrument. The temperature scale was calibrated using the onset of the melting of indium (156.6 °C). The heat flow rate was calibrated on the basis of the heat of fusion of indium and then corrected at the temperature of measurement with a heat capacity determination of sapphire. The indium samples were heated from 30 to 600 °C at a heating rate of 10 °C min^{-1} in nitrogen. The DSC curves of PA6 and its composites are shown in the lower part of Fig. 2.

2.2.3. Attenuated total reflection infrared analysis of solid residues

The samples were heated at a rate of 10 °C min^{-1} in a nitrogen atmosphere using the aforementioned TGA instrument to temperatures of 25, 250, 350, 450 and 550 °C. After attaining these temperatures they were subsequently cooled down to room temperature under a nitrogen atmosphere and homogenised through careful grinding with a pestle in a mortar. The ATR experiments were carried out at ambient temperature. FTIR-ATR spectra were recorded using a Golden Gate™ single reflection ATR accessory coupled to a Thermo Nicolet Nexus FTIR spectrometer model 470, equipped with a deuterated triglycine sulphate (DTGS) detector, a horizontal ATR cell and a zinc selenide trapezoidal internal reflection crystal (refractive index 2.4). FTIR data were recorded (baseline corrected) using OMNIC v6.1a software provided by Thermo Nicolet. The data (Fig. 4) were obtained in the spectral range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}.

3. Results and discussion

Based on the characteristics of the thermal decomposition process during the TGA experiments (mass loss rate, Fig. 2), DSC thermograms (Fig. 2), TGA-FTIR analysis of evolved gases [9] and FTIR-ATR analysis of solid residues collected from TGA experiments (Fig. 4), a decomposition model is proposed. The postulated decomposition model considers only the major pathways and is given in Figs. 5 and 6.

Download English Version:

https://daneshyari.com/en/article/5201873

Download Persian Version:

https://daneshyari.com/article/5201873

Daneshyari.com