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Flame retardant high density polyethylene optimized by on-line ultrasound extrusion

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ABSTRACT

The effect of on-line ultrasound application by a special static mixer die which promotes extensional flow simultaneously during the single screw extrusion process was thoroughly studied. The proportion of aluminum trihydroxide (ATH) used as flame retardant on high density polyethylene (HDPE) was optimized. The morphological, thermal, flammability, combustion, mechanical and rheological properties of the materials were investigated. The morphological study pointed out that this process is able to strongly reduce the size of ATH particles and improve their dispersion and distribution within the polymer matrix. The addition of zinc borate (ZB) at low concentration (namely 3 phr) showed its well-known synergistic effect in the thermal, oxygen index and fire combustion behavior. According to the UL94 standard, the rating for all materials tested changed from HB to V2, with respect to materials prepared without ultrasound; furthermore a rating V0 was achieved only with the addition of 2 phr organo-clay. Rheological results under simple and small amplitude oscillatory shear flow confirmed the enhanced particle dispersion and finer particle morphology evidenced by larger values of the moduli and by deviations from the semicircular shape observed in the Cole–Cole diagram. Mechanical properties such as Izod impact resistance, tensile strength, strain at break and tenacity were also improved by the on-line ultrasound process. In this work, the appropriate on-line ultrasound extrusion conditions to use the lowest ATH content (30 phr or 21.5 in wt%) were found, rendering HDPE optimized flame retardant materials with improved processability and mechanical properties.

1. Introduction

Additives for flame retardant polymers include metal hydroxides, which are some of the most used non-halogen flame retardant additives due to their low cost and toxicity, easy of handling and minimal corrosion effects. Furthermore, during polymer combustion they can also reduce smoke emission. In particular, aluminum trihydroxide (ATH) is the most commonly used metal hydroxide, specially in elastomers, thermoplastic, and thermosetting resins [1]. The main disadvantage in the use of ATH is the large content (40-65 wt%) necessary to produce flame retardant polymers suitable for demanding applications, V0 classification according to UL94 standards. This high load has negative effects on the mechanical properties of the polymer matrix [2]. On the other hand, it is well known that zinc borate (ZB) has an important synergistic effect in combination with ATH, resulting in an important reduction on ATH content [3]. Bourbigot et al. [4] thoroughly investigated the synergistic effect of ZB and ATH on EVA. The authors proposed that ATH decomposes by an endothermic reaction in Al_2O_3 as a first event, and then the polymer forms a cross-linked network and a carbonaceous char, which limits the degradation of the polymer. At the same time, ZB forms a vitreous phase providing a more effective char. The authors reported a significant increase in thermal stability in air, oxygen index and ignition time as well as an important reduction on EVA combustion rate, substituting partially ATH with ZB (total content 65%). Hull et al. [5] investigated the combustion

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toxicity of EVA using ATH/ZB additives at 70% as total amount; this system presented a significant reduction of CO yield with respect to the pure copolymer. The authors attributed the result to the effectiveness of the fillers which reduce the oxidation of the residual organic material under fuel rich conditions.

In another context, on-line ultrasound extrusion is a processing method that has been reported to enhance particles dispersion at nanometric level [6,7]. Swain and Isayev [8] studied the effect of continuous ultrasonic treatment during the melt intercalation of HDPE into montmorillonite clay on their structural, mechanical, rheological and oxygen barrier properties. The authors evaluated the effect of the clay at different content (namely, 2.5, 5.0 and 10.0 wt%); the nanocomposites were prepared using a single screw extruder attached with an ultrasonic slit die, operating at a frequency of 20 KHz and amplitudes of 5, 7.5 and 10 μm. High dispersion of clay in the HDPE matrix and higher complex viscosity due to the ultrasonic treatment were reported. Mechanical properties were improved and oxygen permeability was substantially decreased after ultrasonic treatment.

In this work, the effect of the on-line ultrasound application during the extrusion process of HDPE with flame-retardant additives (ATH, ZB and OBEN) is studied in detail. The ultrasonic transducers are attached to a special mixer die. This experimental arrangement is intended to improve additive particle dispersion and distribution in the HDPE matrix. It is expected that the processing of these materials would be largely improved and hence the flame retardant properties, avoiding the use of high additive loads that have a negative effect on the mechanical properties of the compounds.

2. Experimental part

2.1. Materials

High density polyethylene (referred from here on as PE) from PEMEX, México, sodium bentonite clay (BEN) Actisil 220FF, with 55 meq/100 g ionic interchange capacity from Süd-Chemie, L-lysine mono-chlorohydrated aminoacid (Lys), industrial grade aluminum trihydroxide ($Al(OH)_3$) with 99.5% purity and surface area of 12 m^2/g, zinc borate ($2ZnO.3B_2O_3.3.5H_2O$), maleic anhydride (MAH) and benzoyl peroxide (BOP) were used as received.

2.2. Equipment

The PE, flame retardant additives and clay were processed in a twin screw counter-rotating extruder, Leistritz Micro 27 with L/D = 32 and diameter of 27 mm; alternatively, a single screw extruder with L/D = 24 and diameter of 25.4 mm was coupled to a static mixer die which promotes extensional flow assisted by ultrasonic elements to generate ultrasonic waves. Details of this device and application conditions of ultrasonic waves have been reported elsewhere [9]. Injection molding process was carried out in a Milacron M50 injection molding machine.

2.3. Procedure

Preparation of materials included the bentonite clay modification via ionic interchange reaction using L-lysine amino-acid as intercalate agent to produce organoclay (OBEN) [10–12]. In order to improve PE and OBEN affinity, a compatibilizer based on PE and MHA (PE_{-g-MAH}) was produced by reactive extrusion. The grafting reaction was carried out in a twin screw extruder at 195 °C (mixer zone) and 50 rpm screw speed using BOP as initiator [13].

Table 1
Materials composition based on PE.

Sample code	Extrusion process	ATH [phr]	ZB [phr]	OBEN [phr]	PE_{-g-MAH} [phr]
PE	–	–	–	–	–
$PE-ATH_{50}$	TS	50	0	0	0
$PE-ATH_{30}/ZB_5$	TS	30	5	0	0
$PE-ATH_{30}/ZB_5$/US	SS-US	30	5	0	0
$PE-ATH_{30}/ZB_3$	TS	30	3	0	0
$PE-ATH_{30}/ZB_3$/US	SS-US	30	3	0	0
$PE-ATH_{30}/ZB_3/OBEN_1$	TS	30	3	1	2
$PE-ATH_{30}/ZB_3/OBEN_1$/US	SS-US	30	3	1	2
$PE-ATH_{30}/ZB_3/OBEN_2$	TS	30	3	2	4
$PE-ATH_{30}/ZB_3/OBEN_2$/US	SS-US	30	3	2	4

2.4. Processing

1. Twin screw extrusion (TS): materials were compounding according to Table 1, using the twin-screw extruder. The temperature at the mixer zone was set to 195 °C and the rotation speed at 200 rpm.
2. Single screw-ultrasound assisted extrusion (SS-US): materials extruded by on-line ultrasound were compounding according to stage 1, afterwards they were extruded in the single screw extruder/static mixer die assisted with the ultrasound system. The temperature at mixer zone and the rotation speed were set to 200 °C and 30 rpm, respectively.
3. Suitable samples for UL94, LOI, cone calorimetric and mechanical tests of the materials compounding in stages 1–2, were obtained by injection molding at a temperature of 210 °C and injection speed of 70 mm/s.

2.5. Characterization

Flame retardant properties were evaluated by the UL94 classification, according to ASTM D635 (IEC60695-11) in horizontal position and ASTM D3801 (IEC 707-9 e ISO 1210) in vertical position. Sample dimensions were 125 × 13 × 3 mm, maintained at 23 °C and 50% humidity during 48 h prior to analysis. Limiting Oxygen Index (LOI) tests were performed with a FIRE oxygen index apparatus according to ISO 4589. The combustion behavior was studied by cone calorimetric (Fire Testing Technology, FTT) according to the ISO 5660 standard. The measurements were carried out under a 35 kW/m^2 irradiative heat flux, in horizontal configuration, sample dimensions: 100 × 100 × 3 mm. All measurements were performed in triplicate in order to have reproducible data and the results were averaged. Thermogravimetric analysis (TGA) was carried out in a TA-Instruments Q500 calorimeter with heating rate of 10 °C/min under argon atmosphere. Micrographs were taken in a field-emission scanning electron microscope (SEM) Jeol JSM-7600F. Rheological measurements were carried out in a stress-controlled TA-G2 rheometer using the parallel-plates fixture with 25 mm diameter and a heating chamber (TA-Extended Temperature System). The rheological tests were performed at 190 °C, using 0.75 mm gap, particularly, the oscillatory tests were carried out in the linear viscoelastic regime, i.e. under small amplitude oscillatory shear (SAOS) flow.

3. Results and discussion

3.1. Morphology

The morphology of the investigated materials was studied by Scanning Electron Microscopy (SEM). Fig. 1 shows SEM micrograph of the fractured surface of the neat polymer matrix and some investigated materials (namely: (a) PE, (b) $PE-ATH_{50}$, (c) $PE-ATH_{30}$/