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Decomposition mechanism of fire retarded ethylene vinyl acetate elastomer (EVA) containing aluminum trihydroxide and melamine

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A B S T R A C T

The objective of this study is to evaluate the influence of aluminum trihydroxide (ATH) and melamine (MEL) mixture on the flame retardant and smoke release properties of ethylene vinyl acetate (vinyl acetate content of 60 wt%, EVA). The fire retardant properties were evaluated by mass loss calorimetry (MLC), limiting oxygen index (LOI) and UL-94. A home-made smoke test was developed to evaluate the smoke release of the material in a given scenario. It was found that the addition of ATH to EVA leads to improved fire retardant properties and reduced smoke release. Partial substitution of ATH by MEL at different ratios resulted in better results in MLC for a ratio of ATH:MEL of 5:1 and 10:1. Moreover, a lower quantity of smoke was released for EVA–ATH–MEL materials during material decomposition.

A ratio of ATH:MEL of 5:1 was found to be the most promising. It was also shown that EVA–ATH–MEL ignited at shorter time in MLC test but longer ignition time in smoke test in comparison to EVA–ATH which is due to different test conditions. To understand the role of melamine on material properties, the degradation pathway of EVA–ATH–MEL was analyzed in details. The dispersion of the additives was examined by scanning electron microscopy (SEM) showing that all additives are homogenously dispersed in the matrix. In the next step the pyrolytic decomposition was investigated using thermogravimetric analysis (TGA) and pyrolysis-gas chromatography–mass spectrometry (py-GCMS). The decomposition of EVA–ATH–MEL was then analyzed in the gas phase using MLC coupled with a Fourier transform infrared spectrometer (MLC–FTIR) and in the condensed phase using solid state nuclear magnetic resonance (NMR) of ^{13}C and ^{27}Al. It was concluded that the additives protected the EVA both by a gas and condensed phase mechanism. The endothermic decomposition of ATH has a cooling effect and dilutes the fuel through release of water in the gas phase. Moreover, in the condensed phase, EVA–ATH–MEL is protected through formation of a char acting as barrier slowing down heat and mass transfer compared to EVA–ATH. Ignition at shorter times of EVA–ATH–MEL in comparison to EVA–ATH was found to be due to higher amount of flammable gases in the gas phase before ignition.

1. Introduction

Polymers are important products of the chemical industry. They are used worldwide in everyday live, for example in medicine, in textiles, for packaging, in building industry etc. One of the main drawbacks of polymeric materials is their high flammability. Therefore, it is necessary to flame retard materials for many of the previously cited applications. In the last decade, it was already possible to decrease the total number of fire deaths thanks to fire retardants incorporated in the polymers. The number of fire death was decreased in the USA from 4013 persons in 2001–3445 persons in 2010 [1]. Often development of fires is due to electrical problems, e.g. short-circuit occurring in electrical devices or discharge of static electricity [2].

In this paper, fire retardancy of ethylene vinyl acetate with a vinyl acetate content of 60% (EVA) is discussed. EVA has a huge range of applications: electronic devices, electrical engineering, wire and cables, buildings, transportation (aircraft, cars), photovoltaic etc. For many of these applications, it is required to fire retard EVA to meet the regulation. The most common method to enhance flammability properties of EVA based materials is the

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incorporation of mineral fillers, e.g. aluminum trihydroxide (ATH) or magnesium dihydroxide (MDH) [3]. However, high loadings of this type of filler (higher than 50 wt%) are required to enhance significantly fire retardancy of EVA leading to dramatically change of the mechanical properties of the material [4,5].

To overcome this disadvantage, mineral fillers can be incorporated in combination with other conventional flame retardants. In literature, mineral fillers are often combined with phosphorous compounds [6–8], nitrogen containing additives [9,10], silicone compounds [11,12] or nanoadditives [13–18] to improve fire retardant properties and also to decrease smoke release in some cases. Zilberman et al. [9] showed that the incorporation of ATH in combination with melamine enhances the fire retardant properties of ethylene vinyl acetate having 26 wt% vinyl acetate (VA) content, but also increases the smoke release in comparison to the pure polymer. This study was carried out on thermoplastic EVA and it is known that the fire retardant properties of EVA change drastically with increasing VA content [19,20]. The objective of this study is thus to investigate the fire retardant properties as well as smoke release of elastomeric EVA having a VA content of 60 wt%, so called EVA.

In the first part of this paper fire retardancy and smoke release of EVA-materials containing ATH and MEL will be investigated. Afterwards, the dispersion of the additives in the polymeric matrix will be analyzed via scanning electron microscopy (SEM). The decomposition mechanism of EVA-materials containing ATH in combination with MEL will be finally investigated using thermogravimetric analysis (TGA), solid state nuclear magnetic resonance (NMR) (^{13}C and ^{27}Al), pyrolysis-gas chromatography–mass spectrometry (py-GSMS) and mass loss calorimeter coupled with a Fourier transform infrared spectrometer (MLC–FTIR).

2. Experimental

2.1. Materials

Levapren®600 (hereafter called EVA), an ethylene-vinyl acetate with 60 wt% vinyl acetate, was supplied by LANXESS. Aluminum trihydroxide (hereafter called ATH) was supplied in powder from Nabaltec as Apyral 120E (BET = 11 m^2/g, D_{50} = 0.9 µm). The ATH grades used was not surface treated. PMN500, melamine (hereafter called MEL) was received in powder from Thor. The particle size of melamine particles lies between 3 and 15 µm. Rhenofit TAC/S (triallyl cyanurate) was supplied by LANXESS in powder. Perkadox 14-40B-PD (bis(tert-butyldioxyisopropyl)benzene) was received from Akzo Nobel in powder.

2.2. Processing of materials

Samples were prepared following an upside down process in an internal mixer GK 1.5L from Werner & Pfleiderer. Mixing was performed at 20 °C with a rotation speed of 40 rpm for 4 min. Additives were added into the mixing chamber before the polymer. Different ratios of ATH and melamine were tested: 5:1, 10:1 and 25:1 in order to investigate the influence of melamine on EVA materials. After mixing, materials were further dispersed on an open two roll mill at 20 °C. Vulcanization agents, Perkadox TAC/s (6 phr) and Rhenofit (1 phr), were added afterwards on the two roll mill. After batch off and 24 h relaxation time, materials were treated a second time on the two roll mill. Later the compounds were pressed into plates and vulcanized at 180 °C for 12 min at a pressure of 120 bar. Composition and name of the prepared formulations is gathered in Table 1.

Table 1
Composition and name of the formulations EVA/ATH/MEL.

Formulation name	EVA [phr]	FR [phr]	ATH [phr]	MEL [phr]
EVA	100	0	0	0
EVA–ATH	100	130	130	0
EVA–ATH–MEL (5:1)	100	130	108	22
EVA–ATH–MEL (10:1)	100	130	118	12
EVA–ATH–MEL (25:1)	100	130	125	5

2.3. Fire testing

Fire Testing Technology (FTT) Mass Loss Calorimeter was used to perform measurements on samples following the procedure defined in ASTM E 906. The equipment is identical to that used in oxygen consumption cone calorimetry (ASTM E-1354-90), except that a thermopile in the chimney is used to obtain heat release rate (HRR) rather than employing the oxygen consumption principle. Our procedure involved exposing plates (100 × 100 × 3 mm^3) in horizontal orientation. Samples are covered by a grid to prevent swelling. They were then wrapped in aluminum foil leaving the upper surface exposed to the heater (external heat flux = 35 kW/m^2) and placed on a ceramic backing board at a distance of 25 mm from cone base. The mass loss calorimeter is used to determine the following principal fire properties: heat release rate (HRR) as a function of time, peak of heat release rate (pHRR), time to ignition (TTI) and total heat release (THR). When measured at 35 kW/m^2, HRR, THR and TTI values are reproducible to within ±10%. Experiments were performed three times to ensure repeatability of results. Presented HRR curves and the corresponding values are the "worst case" results of the repeatable results.

To investigate the gases released during MLC experiment, MLC was connected to a Fourier transform infra-red spectrometer (MLC–FTIR). Using this device, released gases are analyzed online quantitatively and qualitatively. Gas picking pistol and transfer line were provided by M&C Tech Group; FTIR, Antaris™ Industrial Gas System, was provided by ThermoFisher. The transfer line between MLC and FTIR is 2 m long and was heated up to 200 °C. To assure constant temperature of the transfer line, two temperature controllers were installed. Before analyzing the gases by FTIR, soot particles were filtered off by two different heated filters (2 and 0.1 µm). Filters consist of glass fibers and ceramic respectively. The FTIR gas cell was set to 185 °C and 652 Torr. The optical pathway is 2 m long and the chamber of the spectrometer is filled with dry air. FTIR spectra obtained using (MLC–FTIR) were treated using OMNIC software. To quantify gases, spectra have to be recorded at different concentrations for targeted gases and a quantification method has to be created using TQ Analyst. To create a method, representative regions in the spectra of the selected gas have to be chosen and interactions with other gases have to be taken into account. Using (MLC–FTIR) the following gases can be quantified: water, carbon monoxide, carbon dioxide, acetic acid, ammonia, methane, nitrogen monoxide, nitrogen dioxide, hydrogen cyanide. Quantification is reproducible within ±10%. (MLC–FTIR) experiments were performed two times to ensure repeatability of the obtained results.

Limiting Oxygen Index (LOI = minimum oxygen concentration to support candle-like combustion of plastics) was measured using a Fire Testing Technology (FTT) instrument on sheets (100 × 10 × 3 mm^3) according to the standard 'oxygen index' test (ISO4589). It measures the minimum concentration of oxygen in a nitrogen/oxygen mixture required to just support combustion of a test sample under specified test conditions in a vertical position (the top of the test sample is ignited with a burner).

UL-94 tests were performed according to IEC 60695-11-10 on samples 127 × 13 × 1.5 mm^3. It describes the tendency of a material to extinguish or to spread the flame after ignition of the material. It classifies specimens from V-0, V-1 to V-2, where V-0 is the best rating.

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