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Bulk or surface treatments of ethylene vinyl acetate copolymers with DNA: Investigation on the flame retardant properties

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ABSTRACT

Deoxyribose nucleic acid (DNA) has recently proven to be an efficient flame retardant for ethylene vinyl acetate (EVA) copolymers, when added in bulk via melt-blending. Indeed, thanks to its char-former features, DNA was able to quite efficiently protect an EVA copolymer (containing 18 wt.% of vinyl acetate) against an irradiative heat flux of 35 kW/m^2, strongly reducing the combustion kinetics and favouring a remarkable decrease of CO and CO_2 yields. In the present work, the evolution of the DNA flame retardant concept is presented: in spite of bulk compounding, DNA has been confined as a coating on EVA surface. Thus, a comparative study on the flame retardant properties of EVA loaded or coated with DNA has been thoroughly carried out. The collected results have shown that the DNA coating blocks the ignition of the copolymer when tested by cone calorimeter under a heat flux of 35 kW/m^2, increasing the time to ignition by 228s (+380%, with respect to pure EVA), while it greatly postpones (102s, +625% with respect to pure EVA) and reduces the combustion kinetics under a heat flux of 50 kW/m^2. Finally, unlike melt-compounded DNA, the bio-macromolecule coating is able to protect the underlying material from a butane/propane torch applied three times consecutively to the specimen for 5s.

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1. Introduction

Generally speaking, a polymer combustion is fuelled by pyrolysis products escaping from its surface due to the heat transferred from the flame to the polymer surface and also radiated from the flame itself, as schematised in Fig. 1. This process can be modelled at the laboratory scale by cone calorimeter [1,2]. The oxygen required for sustaining the flaming combustion diffuses in and from the surrounding air environment. Solid particles escape from the flame as smoke, which is accompanied by gaseous species, some of which can be toxic [3]. As already documented [1], the most significant polymer degradation reactions usually occur in the condensed phase, as they take place mainly within 1 mm of the interphase between the flame and polymer, where the temperature raise is high enough. These reactions involve the polymer and any additives (in particular flame retardants) included in the formulations or applied as surface treatments. Experimental studies of this region have been published by Price and co-workers [4] and by Marosi and coworkers [5,6]. The volatile species formed during combustion escape into the flame zone, whilst heavier species undergo further reactions and may eventually turn into *char*: this multi-lamellar carbonaceous structure acting as a thermal insulator protects the surrounded polymer. It is common consensus that the flame retardants operating in the condensed phase may be considered the unique and worthy alternative to halogen-based flame retardants (that are currently under scrutiny by governments because of environmental and human safety issues) [1], although their action mechanism is significantly different. Indeed, these systems are able to facilitate the char formation and to reduce the evolution of the flammable volatile species. In this scenario, DNA has proven to exhibit the same

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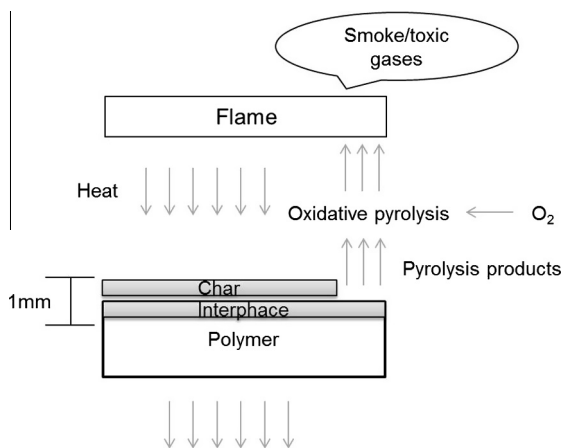*E-mail address:* jenny.alongi@polito.it (J. Alongi).

Fig. 1. Schematic representation of a polymer combustion.

behaviour: indeed, due its chemical structure, it is an all-in-one intumescent bio-macromolecule able to promote the char formation either when deposited on cotton fabrics through simple impregnation [7,8], Layer-by-Layer deposition [9], or when added in bulk to ethylene vinyl acetate (EVA) copolymers [10]. In particular, as far as these latter are considered, compounds with different DNA amounts (namely, 10, 15 and 19 wt.%) have been recently prepared via melt-blending and the resulting thermal and fire properties have been thoroughly investigated. The collected results by cone calorimetry have shown that DNA is able to promote a significant reduction of the heat release rate peak (−40%) as well as of CO and CO_2 yields (approximately −50% and −40%, respectively). Pursuing this research, further improvements can be foreseen when DNA is deposited on EVA surface, instead of being added to the bulk. Indeed, as depicted in Fig. 1, the surface plays a key role during the combustion of a polymer; as a consequence, a flame retardant loaded in the bulk has to diffuse toward the surface in order to perform its action. On the other hand, if confined on the surface, the same flame retardant can provide the full potential flame retardant feature even from the beginning of combustion. Thus, in the present manuscript, a comparative study on the flame retardant properties of EVA loaded or coated with DNA (being equal the bio-macromolecule content) has been thoroughly performed. The resulting flame retardant properties have been assessed by cone calorimeter and burning-through tests.

2. Experimental part

2.1. Materials

An EVA copolymer containing 18 wt.% vinyl acetate (El-vax®470 from DuPontTM; melt flow index: 0.7 g/10 min) was used. DNA from herring sperm was supplied as a high purity grade reagent by Sigma Aldrich, Inc. and used as received.

2.2. Deposition of DNA on EVA

1 g of DNA was deposited on EVA square plates (6.7 g) and subsequently compressed, using a hot compression moulding press at 120 °C for 1.5 min (applied pressure: 5 MPa). DNA:EVA weight ratio was set at 15 wt.%, that corresponds to the bio-macromolecule content already added to EVA in bulk [10]. Hereafter, we will refer to EVA added with DNA (EVA_DNA in bulk) and EVA coated by DNA (EVA_DNA on surface).

2.3. Characterization techniques

The surface morphology of EVA treated with DNA was assessed by using an optical microscope (Nikon Eclipse LV100D instrument) in transmission mode and a LEO-1450VP Scanning Electron Microscope (beam voltage: 20 kV). An X-ray probe (INCA Energy Oxford, Cu Kα X-ray source, $k = 1.540562$ Å) was used to perform elemental analysis. Fragments of the compounds obtained by a fragile fracture in liquid nitrogen (5×5 mm^2) were fixed to conductive adhesive tapes and gold-metallized.

Cone calorimeter tests (Fire Testing Technology, FTT) were performed according to the ISO 5660 standard [2]. The samples ($50 \times 50 \times 3$ mm^3) were placed on a sample holder and irradiated at a heat flux of 35 or 50 kW/m^2 in horizontal configuration. For each formulation, the test was repeated three times and an experimental error of 2% has been calculated as standard deviation for all the measured parameters. The calculated value was significantly lower than that usually quoted for these tests (±10%); this finding can be ascribed to the controlled conditions adopted during these measurements: indeed, all the samples were run on 1 day at 23 °C and 50% R.H.

Time To Ignition (TTI, s), Total Heat Release (THR, MJ/m^2), and Heat Release Rate peak (PHRR, kW/m^2). Total Smoke Release (TSR, m^2/m^2), Rate of Smoke Release (RSR, 1/s), peaks of carbon monoxide and dioxide ([CO] and [CO_2], ppm and %, respectively) were evaluated, as well.

The temperature profile of square samples ($50 \times 50 \times 3$ mm^3) as a function of time upon heating was monitored by using the cone calorimeter and following the procedure described elsewhere [11,12]. In particular, the specimens were placed on a ceramic pad holed in the centre and kept 25 mm far from the irradiating source. Two separated thermocouples (stainless steel sheathed K-type thermocouples with 0.5 and 1 mm outer diameter for the thermocouple located at the top and bottom of the sample, respectively) connected with the heating source were used for monitoring the temperature profile as a function of time (heat flux: 35 kW/m^2).

Burning-through tests were carried out placing the specimen ($50 \times 50 \times 3$ mm^3) in vertical configuration, and applying a 50 mm butane–propane flame (65:35 vol./vol.) to its centre. The flame was applied for 5s at 100 mm distance from the surface for three times. The temperature on the back site of the specimen (the surface not exposed to the flame) was measured by using a thermocouple (stainless steel sheathed K-type thermocouples with 0.5 mm diameter). The test was duplicated and the experimental error on temperature peak was ±5 °C.