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Toward halogen-free flame resistant polyethylene extrusion coated paper facings

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ABSTRACT

Extrusion coating experiments of flame retarded low density polyethylene (LDPE) onto a standard machine finished Kraft paper have been carried out. A pilot extrusion coating line was used in order to investigate the potential of halogen-free flame retardant system based on azoalkanes such as azocyclohexane (AZO) and 4′,4-bis(cyclohexylazocyclohexyl)methane (BISAZO) for fire resistant coating applications. In comparison, experiments were performed using FlameStab®NOR116, magnesium dihydroxide (MDH) and a brominated additive Luvogard MB81/PE as reference flame retardants. The concentration of azoalkane flame retardants was varied between 0.5 and 1 wt.%. The maximum extrusion temperature was varied between 260 and 290 °C and the coating layer weight from 12.9 to 25.0 g/m^2. The obtained multilayer facings containing azoalkanes exhibited significantly improved flame retardant properties, especially at the low coating weight of 12.9 g/m^2. Under all of the used experimental conditions the runnability on the pilot line was flawless for azoalkane formulations. In contrast, our pre-trials using MDH/LDPE (50:50) formulations failed due to poor film quality and visible white aggregates. Moreover, the multilayer facings containing the FlameStab®NOR116, Luvogard MB81/PE or mixtures thereof, showed inferior flame retardant properties compared to azoalkane based facings.

1. Introduction

Flame retardant additives are no different from any other plastic additives in terms of the need to know and understand their specific characteristics and mechanisms of action for optimal performance in various plastic products [1]. Fire safety is now taken extremely seriously in many sectors including building and construction, interior, consumer electronics and motor vehicles. Besides complying with stringent fire safety standards and legislation of finished goods [2] there has been an ongoing discussion about the environmental performance of various flame retardant families, especially halogenated flame retardants [3–5]. As a consequence of this, in recent years an increasing number of actions have been taken by companies as well as by politicians toward halogen free solutions [6]. Consequently, there is a strong need to carry out additional research efforts. Prompted by this, we have been developing new nitrogen based flame retardants such as azoalkanes of the general formula R′—N=N—R and related compounds such as azoxy, hydrazine, azine [7], triazene [8], triazinyl [9], tetrapotassium azodiphosponate (INAZO) [10] and bis(1-alkoxy-2,2,6,6-tetramethylpiperidyl)-4-diazene (AZONOR) compounds [11]. These nitrogen containing flame retardants exhibit self-extinguishing properties for polypropylene films or even in some cases for polypropylene moldings, polyurethane adhesives, polyethylene and high impact polystyrene already at very low concentrations of ca. 0.5 wt.% [12]. Apart from exhibiting a high intrinsic flame retardant efficacy, the selected flame retardant additives need to fulfill many parameters for optimal performance in various product types in which the polymer is incorporated and end-use application specifications [11,13]. In general, an important attribute of flame retardant additives used in extrusion coating

Abbreviations: APP, ammonium polyphosphate; AZO, azoalkane, azocyclohexane; BISAZO, 4′,4-Bis(cyclohexylazocyclohexyl)methane (BISAZO); BR, brominated flame retardant Luvogard MB81/PE; DTA, differential thermal analysis; INAZO, tetrapotassium azo diphosphonate; LDPE, low density polyethylene; MWD, molecular weight distribution; wt.%, weight percent; TGA, thermogravimetric analysis.

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Symbols

T_{feed}	feed temperature [°C]
T_{max}	maximum temperature [°C]
$T_{adapter}$	adapter temperature [°C]
T_{die}	die temperature [°C]

of paper or paperboard is a high decomposition temperature. The additive is required to survive even extreme processing temperatures used in an extrusion coating process of 260–320 °C without thermally induced breakdown. The optimal additive should not have any negative impact on polymer processability or its rheological properties in order to ensure flawless runnability. Other important factors are an adequate adhesion between polymer coating and the fiber-based paper substrate [14], as well as a pin-hole free coating without gel formation [15]. In addition, flame retardant additives should have high compatibility, be effective at low loadings and exhibit good dispersibility in the polymer matrix. They should also be non-toxic (preferentially compatible with food end contact products) and have a retained transparency (no discoloring) if required for the end-use. Multilayer polymer products are especially challenging to flame retard due to the very high processing temperatures used in extrusion coating, and because they are composed of different materials with different burning characteristics [16]. In the present work we report our findings of preparing flame retarded LDPE-coated paper by extruding low density polyethylene containing azoalkanes such as azocyclohexane (AZO) and 4′,4-bis(cyclohexylazocyclohexyl)methane (BISAZO) as flame retardant additive onto a high-density paper surface. In addition FlameStab®NOR116, Luvogard MB81/PE or mixtures thereof as commercially available flame retardants were also tested as the references. The fire retardant properties of the produced LDPE-coated papers were assessed by conducting a small-scale laboratory fire test, whereas the adhesion strength between LDPE and the paper sheet was evaluated visually and by manual peeling [17,18].

2. Experimental part

2.1. Materials

The chemical structures of halogen-free flame retardants used in this study are shown in Fig. 1.

The azocyclohexane (AZO) and 4′4-bis(cyclohexylazocyclohexyl)methane (BISAZO) were synthesized as earlier reported by us [19]. FlameStab®NOR116 was supplied by BASF, Germany, and it was used as received. Whereas, the brominated flame retardant Luvogard MB81/PE (82 percent bromine content) having a low density polyethylene as a carrier and a density of 2.35 g/cm^3 was available from Lehmann & Voss & Co, Germany. The low density polyethylene (LDPE) that was used for extrusion coating was of grade CA7230 (Mw = 155 000, Mn = 20 000 and MWD = 8.0) and it was supplied by Borealis Polymers, Finland. The magnesium dihydroxide (MDH) was supplied by Sigma–Aldrich. The used MF/60 paper was standard machine finished Kraft paper supplied by UPM Wisapaper, Finland.

2.1.1. Extrusion coating

The samples were extrusion coated at Walki Group's extrusion coating pilot line in Jakobstad, Finland. Extrusion conditions: LDPE coating weight on MF/60 paper = 12.9–25.0 g/m^2. Corona treatment = 0.7 KW, line speed = 15.3 m/min, chill roll temperature = 15 °C and press roll = 6 bar. Extruder settings: speed = 202 rpm, T_{feed} = 180 °C, T_{max} = 260–290 °C, $T_{adapter}$ = 260–290 °C, T_{die} = 260–280 °C.

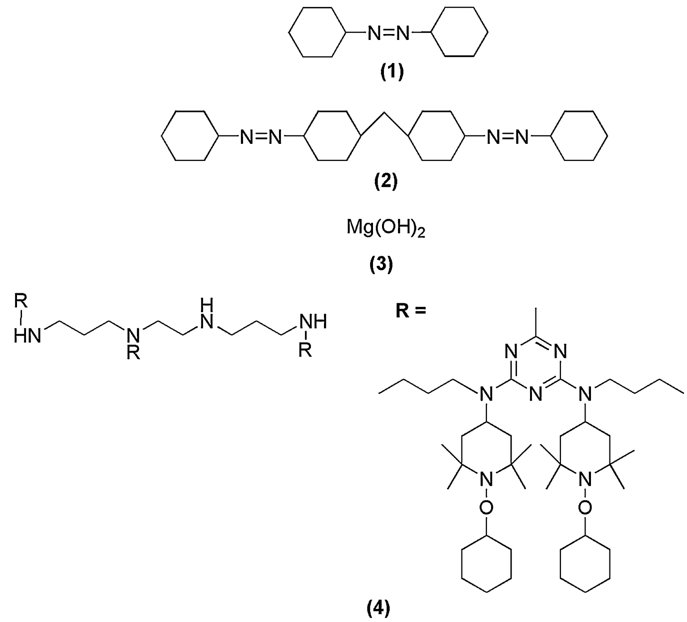

Fig. 1. Chemical structures of (1) Azocyclohexane (AZO), (2) 4′4-bis(cyclohexylazocyclohexyl)methane (BISAZO), (3) Magnesium dihydroxide (MDH) and (4) FlameStab® NOR116.

2.1.2. DIN 4102-1 B2 flammability test [20]

The additives were melt-compounded in mixing chamber at 190 °C together with a low density polyethylene (LDPE). The resulting polymer compounds were prepared by compression molding in a heated press into a film of 200 μm thicknesses and a size of 190 mm × 90 mm × 0.2 mm. The film was mounted vertically inside a test chamber. The samples were subjected to an edge exposure from a gas flame (45° angle, 16 mm away from the film, 40 mm flame length). Noteworthy is that a 40 mm flame length was used instead of the 20 mm flame length as described in the DIN 4102-1 B2 standard. In general, we have earlier noticed that 40 mm flame length allows a better differentiation of the flame retardant efficacy of the particular azoalkane candidates than using a 20 mm flame length. In total, three or five samples were ignited for each formulation. The damaged length and burning time were recorded from these flammability experiments.

2.1.3. Flammability test of multilayer facings

The sample of 190 mm × 90 mm was placed in a frame which was held in a vertical position. A gas burner flame was applied to the bottom edge of the sample for 15 s. After removal of the flame, the burning time was measured until the sample self-extinguishes or until the burning length reached 150 mm. Three parallel samples were burned and the average values were used for the classifications. The ranking was based on the burning time and length according to the standard of Walki Group:

Class I: Fast burning. Sample burns completely <5 s
Class II: Easy burning. Sample burns completely <20 s
Class III: Moderate burning. Sample burns completely >20 s
Class IV: Minor burning. Sample burns <20 s and self-extinguishes before the flame reaches the borderline at 150 mm
Class V: Non-flammable. Sample does not ignite nor char.

3. Results and discussion

Paper can be coated with a thin, single or multilayer of various polymer layers at its surface to impart specific properties to the final paper product [21–24]. When a thin layer (10–80 g/m^2) is coated onto a moving paper substrate, the process is known as "extrusion