



Weathering resistance of halogen-free flame retardance in thermoplastics

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ABSTRACT

The influence of weathering on the fire retardancy of polymers is investigated by means of a cone calorimeter test, before and after artificial weathering. The surface degradation was monitored using different techniques (ATR–FTIR, microscopy, colour measurement). Different kinds of polymeric materials were chosen, all as they are used in practice: polycarbonate (PC) blends, polyamide (PA) and polypropylene (PP) flame-retarded with arylphosphate, melamine cyanurate (MC) and intumescent formulation based on ammonium polyphosphate (APP), respectively.

All samples show material degradation at the surface due to weathering. No significant weathering influence occurs on the flame retardancy when it is a bulk property, as was observed for aryl phosphates in PC blends and MC in PA. When the fire retardancy is dominated by a surface mechanism, dependence on the duration of weathering is detected: for intumescent formulations based on ammonium APP in PP, a worsening in the formation of the intumescent network was observed.

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1. Introduction

Nowadays polymeric materials including thermoplastics, elastomers, thermosets, foams and composites are extremely successful and belong to the fastest growing markets, because of the wide range of properties available, accompanied by relatively low costs. Besides economic aspects, the major challenge for developing new polymeric materials is to realize a tailored or multifunctional material characteristic, like key physical, chemical or biological properties that are demanded by the different applications. Processability, mechanical properties, but also durability are general key properties of almost all polymeric products.

For a variety of polymeric applications, flame retardance is necessary, too, as for electronic facilities, building construction and in public transport. In outdoor use, where the materials are exposed to irradiation or weathering, they also need to show functional stability against weathering influences such as UV radiation, humidity, rain and variations in temperature. The necessary flame-retardant additives and UV stabilisers must not interact in an antagonistic way. Further, they should be stable over the lifetime of the polymer to guarantee public safety.

Various studies have investigated the oxidation and photo-oxidation durability of polymers, in particular in polyolefins, by

the presence of stabilisers and fire-retardant additives. In particular, it has been addressed whether the fire-retardant additives interfere with stabilisers against photo-oxidation. Brominated fire retardants act as photo-initiators of photo-oxidation and negatively affect the photo-protection by typical stabilisers [1,2]. A change in the oxidation behaviour of the polymer was also observed for materials containing nanocomposites as flame retardants [3,4]. In these materials, interactions between stabilisers and nanoparticles are believed to prevent the protection activity. Furthermore, the presence of ions in clay increases the oxidation rate of polymers. For flame retardants, containing phosphorus no significant change in photo-oxidation behaviour was proposed [5,6].

The influence of the weathering process on the fire retardancy with and without UV stabilisers is less studied and less clear. For polyolefin materials containing halogenated fire retardants, some studies have observed changes in flammability and others none at all [7–9]. This behaviour is caused by the different aging conditions and, consequently, the different migration behaviour of the flame retardants. For PP with intumescent formulations based on ammonium polyphosphate, a worsening of the fire-retardant effect was observed [10] due to migration of the additive and the hydrolysis of the polyphosphate chain.

The comprehensive and global understanding of the durability of flame retardance in dependency on the weathering process is still a matter of discussion. Therefore, in this work, the weathering resistance of various halogen-free fire-retarded

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polymers was investigated. Polymeric systems with different kinds of fire retardants were chosen, showing different fire-retardant mechanisms:

- Bisphenol A polycarbonate (PC) blends with bisphenol A bis (diphenyl phosphate) (BDP), which acts by flame inhibition and additional char formation [11,12],
- Polyamide 66 (PA) with melamine cyanurate (MC), which acts mainly by changed melt flow and dripping behaviour and fuel dilution [13,14] and
- Polypropylene (PP) with a fire retardant formulation mainly based on ammonium polyphosphate (APP), which acts mainly by intumescence [15,16].

The chosen polymeric materials are established solutions of halogen-free fire-retardant polymers, but not optimised for outdoor applications. They possess varying sensibilities to weathering. The aim of this work is not to assess the performance of the materials, but rather to discover the basic impact of weathering on the fire retardancy of realistic samples.

An artificial weathering test was used to imitate the outdoor use of the samples. The degradation effect on different properties was characterised by surface-sensitive measurements, such as microscopic and spectroscopic methods. The fire behaviour was tested in cone calorimeter under forced-flaming conditions.

2. Experimental

2.1. Materials

The compositions of all materials are summarised in Table 1. Different polymers with various fire-retardant systems were analysed: two PC blends with BDP, two PA-based materials with MC, and five PP-based materials with various intumescent formulations, based on APP. These materials were further modified in terms of their components, such as composition, flame retardant loading and the presence of stabilisation systems.

In the PC blends with BDP as flame retardant, the impact modifier was varied: in one PC blend an acrylonitrile–butadiene–styrene (copolymer of acrylonitrile and styrene grafted on polybutadiene rubber, ABS) was used and in the other blends an poly (methyl methacrylate) grafted acrylate silicone rubber (RB). Talc was added as a mineral filler to the latter material. Both PC blends did not contain additional UV stabiliser. In the PA-based materials with MC as flame retardant, a stabiliser mixture of HAS, phenolic and UV stabilisers was added and compared to a material without the stabilisers. All intumescent formulations in PP were based on APP. However, the synergists were varied, in particular the carbon source in the intumescent formulation. As a type-A intumescent formulation pentaerythritol was chosen, whereas an nitrogen containing polyester was used for the type-B intumescent formulation. Regarding the materials with the type-A intumescent formulation, the effect of encapsulation (A*) and the additive loading was analysed; regarding the type-B intumescent formulation, the presence of an HAS stabiliser was investigated.

2.2. Weathering

The materials were continuously exposed to UV in a fluorescent UV lamp device equipped with UVA-340 nm lamps. The temperature varied between $-20\text{ }^{\circ}\text{C}$ and $+70\text{ }^{\circ}\text{C}$ at humidity between dry conditions ($<5\%$ r.h.) and rain; see Table 2. The duration of exposure was 28 days (corresponding to 70 MJ/m^2 UV radiant exposure) or 84 days (corresponding to 210 MJ/m^2 UV radiant exposure), respectively. This artificial weathering was adapted from a German standardized test for traffic signs. For comparison, a horizontal surface outdoors in Berlin is subjected to UV radiant exposure of about 180 MJ/m^2 per year. The property changes were addressed in comparison to the unexposed material.

2.3. Surface characterisation

For microscopy, a Leica microscope with coaxial illumination was used. At $35\times$ magnification, the typical image sizes were about 3.4 mm by 2.6 mm .

For colour measurement, a Minolta CM 2600d was used which operates in an 8/d geometry. Specular gloss was included, D65 light was used, and the analysis was adapted to a 10° inspector angle. The colour values were expressed as CIE Lab values.

A Fourier transform infrared spectrometer (FTIR) Nexus 470 (Nicolet Instruments, Germany) was used with a smart orbit diamond ATR accessory. The infrared spectrometer equipped with a DTGS KBr detector operated at an optical resolution of 4 cm^{-1} . The detected spectra were calibrated on an invariant single band, marked by a double cross in the spectra. Spectra were taken of the top and the back of the samples.

2.4. Fire behaviour

Fire behaviour was characterised using a cone calorimeter (Fire Testing Technology, UK) according to ISO 5660. The heat release rate (HRR), the peak heat release rate (PHRR), the total heat release (THR), the mass loss rate (MLR) and total mass loss (TML) as well as the time to ignition (t_{ig}) were determined and interpreted [17]. An external heat flux of 50 or 70 kW m^{-2} was applied. The volatile products were ignited by spark ignition. All samples (specimen size: $100\text{ mm} \times 100\text{ mm}$, thickness $3\text{--}5\text{ mm}$) were measured in a horizontal position using an open aluminium tray (PP, PA materials) or a retainer frame (PC materials). The experiment was stopped when flames were extinguished and no further significant mass loss was observed. The rate of smoke release equalling zero was used as the flame-out criterion.

3. Results and discussion

3.1. Surface characterisation

Most materials in their original state already showed a rough surface except PC/ABS–BDP (Fig. 1), this surface roughness gradually gets smoother as weathering progresses. For the PC/RB–BDP/talc the image contrast decreased as the surface became covered

Table 1
Composition of the investigated materials (abbreviations are described in text).

Polymer	PC/ABS	PC/RB	PA66	PA66	PP	PP	PP	PP	PP
FR	BDP	BDP	MC	MC	APP A	APP A*	APP A*	APP B	APP B
Content wt.-%	12	12	10	10	25	25	20	30	30
Additive/Stabiliser	–	Talc	–	HAS	–	–	–	–	HAS
Sample	PC/ABS–BDP	PC/RB–BDP/talc	PA–MC	PA/st–MC	PP-A25	PP-A*25	PP-A*20	PP-B30	PP/st-B30

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