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Ignitability and thermal stability of asphalt binders and mastics for flexible pavements in highway tunnels

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HIGHLIGHTS

- TG analysis and LOI test were performed on asphalt binders and FR-mastics.
- A specific test method was developed to perform LOI test on asphaltic materials.
- Asphalt binders ignitability and smoke emissions are related with SARA composition.
- Aluminium hydroxide strongly improves flame resistance and reduces smoke emission.
- FR-fillers effectiveness is mainly related with their decomposition temperature and physical properties.

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ABSTRACT

Due to their chemical composition, asphalt binders and mixtures are quite flammable and tend to produce smoke and poisonous gases while burning. Therefore, fire reaction of asphalt pavements is a topic of increasingly interest to improve fire safety in highway tunnels. Different asphalt binders and mastics containing aluminium hydroxide and magnesium hydroxide as inorganic flame retardants (FRs) were analysed through Thermo-Gravimetric Analysis (TGA) and Limiting Oxygen Index (LOI) test. Due to the lack of technical specifications for LOI measurements of asphaltic materials, a specific sample geometry and preparation as well as a testing procedure were developed and applied. The comparison between the two techniques indicated that both thermal stability and flammability are strictly related to asphalt composition. Moreover, the Thermo-Gravimetric test can be preventively used to select the most appropriate FR filler, whose decomposition temperature (together with particle size) is a factor of primary importance. Among the different flame retardants tested, the aluminium hydroxide showed the most important increase in LOI with respect to the unmodified binders. On the contrary, the SBS-modified binder, probably due to the unsaturated nature of the polymeric modifier, showed an increased flammability when compared with the base asphalt binders.

1. Introduction

It is well known that fire events in tunnels may involve the road pavement and lead to the development of high quantities of heat, smoke and toxic gases which can impede escape and rescue. Recent studies have been conducted to investigate the behaviour in case of fire events of the two possible technical solutions for highway pavements: asphalt mixtures flexible pavements or Portland cement concrete (PCC) rigid pavements. Noumowe [1] carried out comparative fire tests by heating several samples in a furnace programmed according to the ISO 834 temperature curve; this experience showed that asphalt mixtures ignite between 428 °C and 530 °C and that smoke and gases produced before ignition are toxic, suffocating and carcinogenic (they contain carbon monoxide and dioxide, aldehydes, methanol, propanol, acetone, benzene, toluene, sulphur dioxide and acetic acid, among others). Carvel and Torero [2] subjected Stone Mastic Asphalt samples to different radiant levels through the cone calorimeter test and found that the critical radiant flux was always smaller than 40 kW/m^2; on the other hand, during fire tests in Runehamar Tunnel, Norway 2003 [3,4], heat fluxes above this critical limit were recorded 5 m upstream of the fire location. Under the remit of the SAMARIS (Sustainable and Advanced Materials for Road Infrastructure) research project, Colwell [5] compared the radiant panel flooring test (ISO 9239) and the cone calorimeter test (ISO 5660) by using three mixtures characterised by different asphalt content and air voids. The former test is required by EN 13501-1

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for the fire classification of construction products and building elements, but resulted inappropriate for the characterisation of road pavements fire behaviour. On the contrary, cone calorimeter seems to be the most fitting laboratory test to describe the actual fire response of asphalt mixture road pavement [5]. Moreover, the results assessed a relation between asphalt mixture composition and critical heat flux. Once again, the critical heat fluxes are smaller than those recorded in large scale fire tests [3,4].

The asphalt flammability and consequent evolution of smoke and poisonous gases aggravate fire burning effects in confined environments such as road tunnels. Therefore, in highway tunnels PCC pavements may be preferable since they are intrinsically fireproof; however, they are subjected to severe damages due to spalling when high temperatures are reached. Moreover, PCC pavements involve difficulties and drawbacks in laying and maintenance and show inadequate performances in terms of functional characteristics. Finally, their costs of realisation and subsequent maintenance are considerably higher compared to the asphalt mixtures' ones. Thus, the development of fire resistant asphalt mixtures could fill the gap with PCC rigid pavements and provides a preferable solution for flexible pavements in highway tunnels. Since asphalt binder may be considered as a natural polymer of low molecular weight, this goal can be approached starting from the flame retardants (FRs) developed for polymers, whose flammability has been extensively studied in the last decades (see e.g. [6]). The first products that captured the market were mainly the halogen-based FR, which operate in the gas phase, by replacing the free radicals responsible for flame propagation with more stable species, such as chlorine and bromine anions, able to stop the combustion reaction. First studies on asphalt binder modification concerned the use of these halogenated FR [7–9] which showed to have good flame-retarding effects but also some important drawbacks, like, i.e. the formation of very smoky, highly toxic and corrosive fire effluents rich in products of incomplete combustion. Moreover, they can be expensive and the technology used to mix flame retardants may be quite complex and inappropriate for the production of an asphalt binder. Thus, despite of their effectiveness in improving fire reaction of asphalt, halogenated FR are nowadays abandoned because of the risks associated to their chemical composition. These problems addressed the research to alternative "halogen-free" FR, such as metal hydroxides, carbonates, and phosphorus compounds. Some of these FR work in a similar manner of halogens, while the majority of them basically act directly on the condensed phase, i.e. by forming a barrier made of char or inorganic residue or by swelling to create an insulating layer (intumescence) [6]. Mineral fillers, especially magnesium hydroxide (MH) and aluminium hydroxide (also referred to as alumina trihydrate, ATH), thus became of increasingly interest for asphalt binders [10–14]. Thanks to their endothermic decomposition (which cools the solid or condensed phase), char forming ability and production of inert diluent gases, they represent an effective and environmentally sustainable solution. At the same time, mineral fillers are an essential component of all asphalt mixtures and influence their mechanical performance through physical and chemical effects [15–18]. Among these, water reaction deserves particular attention because it is one of the most important factors affecting asphalt mixture durability, even if in tunnels its presence should be limited only to the entry/exit zones. Therefore, mineral fillers must be qualified not only in terms of capability to improve asphalt mastics fire reaction, but also considering their influence on mechanical performance. As an example, the filler fractional void is an effective indicator of the interactive effect of the geometric characteristics on stiffening asphalt binders and can be measured through a specific test method, first introduced by Rigden in 1947 [19].

Based on these preliminary remarks, we studied the thermal stability and flammability of asphalt binders and mastics containing inorganic flame retardants. The Thermo-Gravimetric Analysis and the Limiting Oxygen Index (LOI) test were used in order to correlate the flammability of an asphalt binder with its composition and to evaluate the flame retardant efficiency of some commercial ATH and MH fillers. Hence, the evaluation of performance-related criteria for technical specification of flame-retardant asphalt mastics could be achieved and, consequently, a specific mix design of asphalt mixtures for flexible pavements with improved fire reaction can be outlined.

2. Experimental program

2.1. Materials

Three different unmodified asphalt binders were investigated and subsequently referred to as B50, B70, B170, where the number identifies the penetration grade. Basic characterisation of the three asphalt binders is reported in Table 1. The ring and ball softening point was measured according to ASTM D36-95 and the penetration was assessed according to ASTM D5-06e1. Penetration Index is a measure of temperature susceptibility and was evaluated according to the equation developed by Pfeiffer and Van Doormaal [20] considering the penetration corresponding to the Softening Point equal to a conventional value of 800 dmm. Basic rheological properties were determined through a Dynamic Shear Rheometer (DSR Physica MCR 101) with a parallel-plate testing system consisting of 8 mm diameter plates with 2 mm gap. The general testing procedure was referred to the standard ASTM D7175-08.

Conventional and rheological properties of unmodified asphalt binders are integrated by a preliminary analysis of Saturates, Aromatics, Resins and Asphaltenes (SARA) fractions carried out through the Thin Layer Chromatography–Flame Ionisation Detection (TLC–FID) technique by using a IATROSCAN MK-5. This information is extremely relevant because asphalt binders contain chemical components significantly different in terms of molecular weight and structure which may have different influence on the fire reaction, as already observed by Jimenez-Mateos et al. [21]. The obtained results are reported in Table 2, where I_C is the Gaestel Index [20] and represents a measure of the dispersing capability of maltenes to asphaltenes.

In order to outline the possible influence of polymeric modification of asphalt binders on ignitability and thermal stability, styrene–butadiene–styrene (SBS) block copolymer modified asphalt, subsequently referred to as B50-SBS, was prepared by adding 5 wt.% of SBS to B50. The SBS was EUROPRENE® SOL T 161B, a radial block copolymer with 30 wt.% of styrene, kindly provided by Versalis S.p.A.

Asphalt binder B50 was subsequently used to prepare several asphalt mastics obtained using three classes of fillers: (i) aluminium hydroxide (ATH), (ii) magnesium hydroxide (MH) and (iii) conventional limestone filler. ATH is by far the largest-selling inorganic hydroxide used as a fire retardant for polymeric materials and it is produced through two main processes which lead to different particle size gradations and flame-retardant effectiveness. In order to evaluate the influence of particle size, three different commercial ATH, subsequently referred to as ATH-1, ATH-2 and ATH-3, were tested. All these ATH are characterised by minimum $Al(OH)_3$ content equal to 99.0%. The same purity degree characterises the MH and the conventional limestone filler, referred in the text to as C. The main physical and chemical properties of the fillers are summarised in Table 3. The "Rigden Voids" test outlines the main factor defining the consistency of filled systems. Currently, this

Table 1
Main conventional and basic rheological properties of unmodified asphalt binders.

Asphalt binder	Penetration (dmm)	Softening point (°C)	Penetration index (–)	Complex modulus (10 rad/s, 20 °C) (MPa)	Phase angle (10 rad/s, 20 °C) (°)
B50	44	52.0	−1.0	6.45	60.8
B70	68	50.7	−0.3	4.19	65.3
B170	150	44.5	+0.5	1.42	71.3

Table 2
SARA fractions of unmodified asphalt binders.

Asphalt binder	Saturates (%)	Aromatics (%)	Resins (%)	Asphaltenes (%)	I_C (–)
B50	3.1	70.1	16.9	9.9	0.149
B70	3.0	68.6	17.6	10.8	0.160
B170	4.7	71.0	14.9	9.4	0.164