Eggshells: A novel bio-filler for intumescent flame-retardant coatings

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ABSTRACT

The aim of this study was to develop intumescent flame-retardant coatings that incorporate chicken eggshell (CES) waste as a novel eco-friendly bio-filler. Three flame-retardant additives, namely, ammonium polyphosphate phase II, pentaerythritol and melamine were mixed with flame-retardant fillers and acrylic binder to synthesize the intumescent coatings. The fire performance of the coatings was evaluated in accordance with 'BS 476: Part 6-Fire Propagation' and 'BS 476: Part 7-Surface Spread of Flame' test standards. It was found that 4 out of 5 of the coated specimens (B, C, D and E) neither showed surface spread of flame nor any afterglow combustion upon fire exposure. The addition of 5.0 wt% and 2.5 wt% eggshell bio-filler into formulations B and E, respectively, improved fire protection due to char formation, with better morphology, height and structure of the protecting shield. The filler compositions of samples D (3.4 wt% TiO_2/3.3 wt% $Al(OH)_3$/3.3 wt% $Mg(OH)_2$) and E (2.5 wt% TiO_2/2.5 wt% $Al(OH)_3$/2.5 wt% $Mg(OH)_2$/2.5 wt% CES) applied at a thickness of 1.5 ± 0.2 mm achieved the lowest fire propagation index with a value of 4.5 and 5.0, respectively (BS 476 Part 6, Class 0 materials) which indicates excellent fire-stopping properties. The results showed that the coatings were effective in fire protection, with good qualities of water resistance, thermal stability, and adhesion strength. Significantly, coating E (with CES) has proved to be efficient in the protection of plywood against fire.

1. Introduction

Intumescent flame-retardant coatings have been widely used for passive fire protection (PFP) in buildings, offshore constructions, ships and aircraft. Intumescent coatings are fire-retardant and fire-resistant materials which have gained wide acceptance for fire protection throughout the world. These coatings are used for PFP in fire-stopping and fire-proofing applications, in order to reduce the devastating cost of fires in terms of life hazard and property damage [1].

Structural steel loses its load carrying capacity in a fire when its temperature exceeds 500 °C. The loss is mainly attributed to its high thermal conductivity, low specific heat, as well as rapid degradation of strength and elastic modulus of steel [2]. Studies on intumescent coatings have flourished since the collapse of the World Trade Center in 2001 [3]. Intumescent coatings are designed to perform under severe conditions and to preserve the integrity of steel in the event of a fire [4–6]. Many researchers have extensively studied the performance of intumescent coatings in terms of fire protection, mechanical properties and water resistance [7–17]. The formulation of the coating needs to be optimized with regards to its physical and chemical properties in order to effectively retard heat transfer and ignition on steel. Intumescent coatings play a significant role to insulate structural steel by reducing heat transfer and thus prolong the evacuation time for occupants before the critical temperature of steel is reached.

The intumescent coatings are composed of three halogen-free flame-retardant additives: an acid source (e.g. phase II ammonium polyphosphate, APP), a carbon source (e.g. pentaerythritol, PER) and a blowing agent (e.g. melamine, MEL) mixed with flame-retardant fillers and polymer binders. Intumescent coatings expand when exposed to a sufficiently high temperature such as in the event of a fire. The heated coating forms a porous char and produces residues that are swelled by escaping non-combustible gases to establish a protective barrier against oxygen. Combustion residue can be efficiently puffed up in order to produce a tough foam over the surface, which will protect the substrate [18]. More importantly, the use of aluminium hydroxide ($Al(OH)_3$) or magnesium hydroxide ($Mg(OH)_2$) in a polymer matrix at 60% filler loading in place of a conventional flame-retardant filler (e.g. clay) is a realistic and promising way to reduce fire propagation and surface

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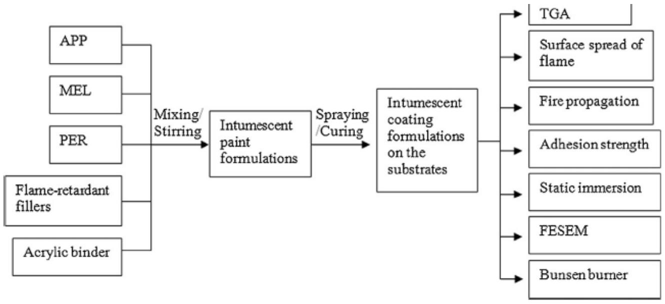

Fig. 1. Flowchart of experimental procedure.

Table 1
Compositions of intumescent flame-retardant coatings.

Ingredients	Parts by weight for formulations				
	A	B	C	D	E
APP	18.5	18.5	18.5	18.5	18.5
MEL	9.25	9.25	9.25	9.25	9.25
PER	9.25	9.25	9.25	9.25	9.25
TiO_2	5.0	5.0	5.0	3.4	2. 5
$Al(OH)_3$	–	5.0	–	3.3	2. 5
$Mg(OH)_2$	5.0	–	–	3.3	2. 5
CES	–	–	5.0	–	2. 5
Binder					
Acrylic resin	53.0	53.0	53.0	53.0	53.0

spread of flame as conventional flame-retardant fillers have low flame-retarding efficiency [19–22]. The performance of intumescent systems is generally dependent on the selection of ingredients and their appropriate combinations.

This study highlights a useful bio-filler derived from CES waste and its potential role in the fire protective coating industry. CES waste is an industrial by-product, and its disposal constitutes a serious environmental hazard. It is known that CES waste consists of about 95% calcium carbonate in the form of calcite and 5% organic materials such as type X collagen, sulphated polysaccharides, and other proteins [23,24]. CES has garnered attention recently because of its reclamation potential. Due to its high thermal stability and mechanical properties, new value can be created in CES waste by incorporating it into commercial products. Although there have been several attempts to use CES components for various applications [25–29], its chemical composition and availability makes CES a potential source for bio-filler reinforced bio-polymer composites, improving their mechanical properties [30]. CES offers other benefits as it is lightweight, inexpensive, eco-friendly, available in bulk quantities and has high thermal stability.

In this experimental work, the efficiency of intumescent coatings on steel was investigated according to the 'BS 476: Part 7-Surface Spread of Flame' and 'BS 476: Part 6-Fire Propagation' test standards. The development and evaluation of intumescent coatings form the primary focus of this paper, particularly with respect to the water resistance, thermal stability, bonding strength, and small scale fire test of the coatings.

2. Experimental

2.1. Materials and method

Intumescent flame-retardant coatings were formulated using acrylic resin binder, fillers and flame-retardant additives. The acrylic resin binder was supplied by Shinko Chemical Sdn Bhd. The compositions of the intumescent flame-retardant coatings are presented in Table 1.

The formulations were prepared by mixing the flame-retardant ingredients using a high-speed disperse mixer. The coating was then deposited onto a steel plate using a gun sprayer. The thickness of the intumescent coating was kept constant in order to attain effective fire retardancy. The coated substrates were cured at ambient temperature for 1 week. The fully cured coating samples were considered ready for characterization (see Fig. 1).

2.2. Surface spread of flame test

The surface spread of flame test was performed according to the procedure specified in the 'BS 476: Part 7' standard in order to determine the classification of the specimens [31]. The test involves measuring the lateral spread of flame over the surface of a specimen oriented in a vertical position and classifying the system based on the rate and extent of flame spread. The steel plate (dimension: 225 mm × 225 mm × 2.3 mm) coated with intumescent coating (thickness: 1.5 ± 0.2 mm) was exposed to specific heating conditions during the test. The test specimen was mounted vertically and placed at a 90° angle from the radiation panel, and was exposed to a radiant panel over a duration of 10 min. Pilot flame was applied to the bottom corner of the specimen during the first minute of the test. The time required for the flame front to reach the reference marks on the specimen and the extent of flame spread were recorded over a period of 1 min 30 s as well as at the end of

Table 2
Flame spread classification.

Classification of spread of flame				
Classification	Spread of flame at 1.5 min		Final spread of flame (10 min)	
	Limit (mm)	Limit for one specimen in the sample (mm)	Limit (mm)	Limit for one specimen in sample (mm)
Class 1	165	165 + 25	165	165 + 25
Class 2	215	215 + 25	455	455 + 45
Class 3	265	265 + 25	710	710 + 75
Class 4	Exceeding the limits for class 3			

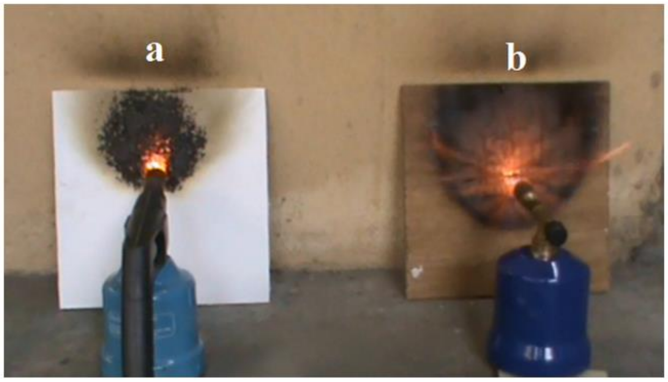

Fig. 2. The Bunsen burner test: (a) coated plywood and (b) bare plywood.

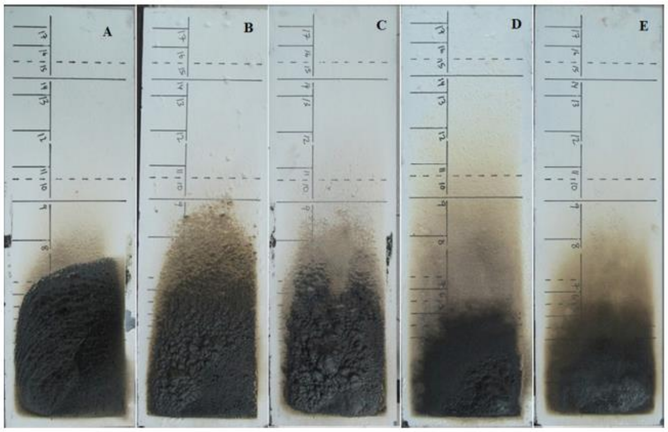

Fig. 3. Samples A, B, C, D and E tested according to BS 476: Part 7-Surface spread of flame.

Table 3
Results of large-scale surface spread of flame test.

Specimen No.	A	B	C	D	E
Spread of flame at 1½ minutes (mm)	165 mm	0 mm	0 mm	0 mm	0 mm
Distance (mm)	Time of spread of flame to indicated distance (min.s)				
75	1.11				
165	1.32				
190	1.44				
215	1.54				
240	2.12				
265	2.26				
290	2.39				
375					
455					
500					
525					
600					
675					
710					
750					
785					
825					
865					
Time of maximum spread of flame (min.s)	2.39				
Distance of maximum spread of flame (mm)	290 mm	0 mm	0 mm	0 mm	0 mm
Classification	Between class 1 and 2	Class-1	Class-1	Class-1	Class-1

Table 4
Results of fire propagation test.

Time (min)	Calibration	Specimen A AR + T + M	Specimen B AR + T + A	Specimen C AR + T + CES	Specimen D AR + T + M + A	Specimen E AR + T + M + A + CES
0.5	14	18	12	14	12	11
1	18	21	15	18	16	15
1.5	23	26	19	23	19	19
2	27	30	22	27	23	22
2.5	30	34	25	31	26	26
3	34	38	30	34	30	29
4	72	122	87	55	54	60
5	108	212	149	133	129	150
6	129	274	179	169	181	179
7	148	321	223	243	202	208
8	166	364	312	327	219	226
9	182	378	336	372	234	236
10	192	405	372	360	244	241
12	214	417	391	355	249	246
14	230	418	370	349	253	250
16	238	416	326	310	258	253
18	246	403	298	299	260	253
20	257	384	281	290	263	259
Subindex 1		1.8	0	0.2	0	0
Subindex 2		15	8.4	8.3	3.8	4.4
Subindex 3		5.7	3.4	2.9	0.7	0.6
Index of performance		22.5	11.8	11.4	4.5	5

the test. The burning behaviour of the coating was also observed. The materials were classified according to the test performance, as shown in Table 2. Class 1 is the best classification while Class 4 is the worst classification and is considered high risk.

2.3. Fire propagation test

The fire propagation test was performed in accordance to the procedure outlined in the 'BS 476: Part 6: 1989 + A1′ standard [32]. The test involves exposing the product to a row of small flames for 20 min and an additional impressed irradiance of 2 kW from the third minute to the end of the test. The temperature of the evolved combustion products was recorded and compared to the temperature generated from a bare steel specimen. The result is expressed as a fire propagation index, which provides a comparative measure of the contribution to the growth of fire made by an essentially flat material, composite or assembly. The coated face of the specimens was exposed to the heating conditions of the test. The fire propagation index (I) must be ≤12 and the subindex (i) must be ≤6 in order to be certified as Class 0. A lower numerical index indicates a better material. The test procedure used to determine the index of performance of the specimens and calculation of the results are detailed as follows.

In the fire propagation test, the rate and amount of heat evolved by the specimen was taken into account while it was heated in an enclosed space under prescribed conditions. Specimens of steel plate (dimension: 885 mm × 270 mm × 2.3 mm) were coated with intumescent coatings (thickness: 1.5 ± 0.2 mm) and the index of performance was determined from the following equations:

$$i_1 = \sum_{t=0.5}^{t=3} \frac{\theta m - \theta c}{10t} \qquad (1)$$

$$i_2 = \sum_{t=0.5}^{t=10} \frac{\theta m - \theta c}{10t} \qquad (2)$$

$$i_3 = \sum_{t=12}^{t=20} \frac{\theta m - \theta c}{10t} \qquad (3)$$

$$I = i_1 + i_2 + i_3$$

where I is the index of performance, t is the time (min) from the origin at which readings were taken, θ_m is the temperature (°C) of the material at time t, θ_c is the temperature (°C) of the calibration curve at time t.

2.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out at 20 °C/min under air flow within a range of 30–1000 °C using a thermogravimetric analyzer (Model: TGA/SDTA851e) in order to examine the thermal degradation and determine the residual weight of the coatings.

2.5. Field emission scanning electron microscopy

Field emission scanning electron microscope (FESEM) was used to examine the surface morphology of the intumescent char layers. For FESEM observation, a low beam energy of 1 kV was operated to reduce the possibility of any thermal damage to the char layers.

2.6. Static immersion test

Static immersion test is a standard method used to evaluate the water resistance of thin films using the gravimetric method. Specimens of films (dimension: 20 mm × 10 mm × 0.5 ± 0.1 mm) were immersed in distilled water at 25 °C. The specimens were removed at specific time intervals and blotted with a piece of paper towel to absorb excess water on the surfaces. The weight change was calculated using Eq. (4) and expressed as a function of time [30].

$$E_{sw} = \frac{W_e - W_o}{W_o} \times 100\%. \qquad (4)$$

where E_{sw} is the water uptake ratio of film, W_e denotes the weight of the film at different times and W_o is the dry weight of the sample.

2.7. Adhesion strength

The adhesion strength of each coated specimen was determined using Instron Micro Tester equipment. The coating was sprayed on one side of a 50 mm × 50 mm × 2.6 mm steel plate to obtain a film thickness of 0.5 ± 0.05 mm. The side with the

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