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Effects from nano-titanium oxide on the thermal resistance of an intumescent fire retardant coating for structural applications

Hammad Aziz [a], Faiz Ahmad [b,*]

[a] Department of Mechatronics Engineering, College of Electrical and Mechanical Engineering, National University of Sciences and Technology, Pakistan
[b] Department of Mechanical Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak Darul Ridzuan, Malaysia

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ABSTRACT

Due to its effective performance, intumescent fire retardant coating (IFRC) is widely used by oil and gas industries as well as in processing and petrochemicals plants to protect metallic substrates from fire. The present work developed an epoxy based IFRC comprising phosphate, nitrogen, barium and boron containing flame-retardants. The product was reinforced with nano-titanium oxide and then examined for performance with a lab scale hydrocarbon fire test. Thermal analysis of the coating was evaluated using TGA and DTGA under nitrogen and oxygen environments. Further characterization studies included FESEM, EDS, FTIR, XRD and XRF to determine effects from nano titanium oxide on char's performance. Results indicated that a coating reinforced with 4.5 wt% of nano-TiO_2 added residual weight to the coating and provided longer thermal protection time compared to conventional fire retardant coatings.

1. Introduction

Structural steel is the building block of the construction sector due to its high strength-to-weight ratio, high ductility, short manufacturing process, less construction time, etc. [1], which have made it the most-desired component of the construction industry. Apart from skyscrapers and bridges; it is widely used in the oil and gas industry because it protects the transport of hydrocarbons that are vulnerable to low ignition temperatures [2,3]. On offshore sites, inadequate safety measures often result in the loss of lives and assets during a fire. While the strength of structural steel begins to decline at or above 450 °C, during accidental fires in hydrocarbon industries, flash fires can occur when temperatures abruptly rise above 900 °C.

Considering these matters and since large-scale fire tests are time consuming and costly, a hydrocarbon fire test was undertaken in a lab scale furnace. The heating rate of the flame approached the cited UL-1709 condition, i.e., a temperature reaching 1100 °C within 5 min. Over the years cellulosic fire tests have been conducted [4], but it is now apparent that certain types of materials such as petrochemicals, have higher burning rates compared to wood and timber. For example, the cellulosic fire curve described in BS-476 (Part 20), describes their heating-rate-of-flame as 'low' compared to the hydrocarbon fire curve.

Conventional fire retardant coatings comprise acid and carbon sources plus a blowing agent [5,6]. These coatings have poor fire performances and anti-oxidation properties [7], and cannot protect a substrate for long periods. Halogenated flame retardant additives are restricted by environmental regulations due to their release of toxic products during thermal degradation. Therefore, the cited limitations only provide sufficient time for worker evacuations as required by most countries. Nevertheless, researchers have still tried to improve fire protection time by exploiting different inorganic fillers [8,9], clays [10], and bio-fillers [11], etc. A Chinese research team studied the effects of ascending degrees of polymerization for APP and reported enhanced fire protection time due to the formation of a cross-linked char structure between APP and PER [12].

Nonetheless, recent advances in nano technology have made it possible to improve flame retardant coating efficiency due to a highly specific surface area and nano scale interaction with a polymer matrix composite, even with low filler loading [13]. Wang et al. [10] used nano sized organically modified montmorillonite and reported that a ceramic-like layer of aluminophosphate formed from reactions between OMMT and APP during combustion, which improved the foam structure of the char. Dong et al. [14] found that nano sized particles disperse better in an intumescent coating that improved fire resistance time. Recent studies by Beheshti et al. [15], improved the thermal performance of an intumescent coat-

* Correspondence to: Department of Mechanical Engineering, Universiti Teknologi PETRONAS, Malaysia.
E-mail address: faizahmad@petronas.com.my (F. Ahmad).

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Table 1
Raw materials and their sources.

Material	Function	Source
Ammonium polyphosphate-APP	Acid source	Clariant Malaysia Sdn Bhd
Expandable graphite-EG	Auxiliary foaming agent	Kaiyu Industrial HK Ltd, China
Melamine-M	Blowing agent	SABIC
Boric acid-BA	Flame retardant additive	Merck
Titanium oxide-TiO_2	Nano filler	Dong Tang (HK) Int'l Group Ltd
Barite-B	Inorganic filler	CNPC Powder Ltd, China
Bisphenol A BE-188 with polyamide polyamine	Epoxy resin and curing agent	ACR Tech Co. Ltd, Taiwan

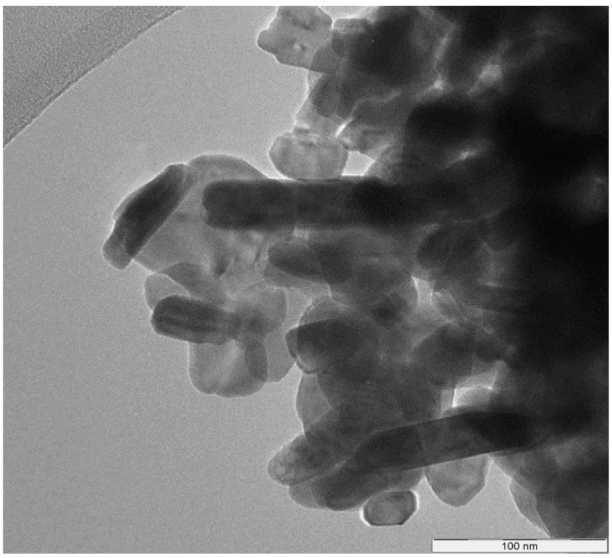

Fig. 1. Particle shape of Nano-TiO_2 examined by TEM.

ing by using nano-TiO_2 and chicken egg shell. They reported that by increasing the weight of nano particles (up to 20 wt%), improved fire performance and that after 1 h the final substrate temperature was >280 °C.

Barite is a barium-based mineral ($BaSO_4$), but unlike $BaCrO_4$, Barite is non-toxic [16] and has a wide range of industrial applications as a weighting element. It has a high specific gravity and is widely used as filler in paints, polymers and pharmaceutical products. Moreover, electrical-insulating composites have been made by incorporating it in polymers [17,18]. In light of its excellent properties, the author expected positive effects in an intumescent coating by studying effects from nano-titanium oxide and barite on char properties. Thermal properties were evaluated by a lab scale hydrocarbon fire test and thermogravimetric analysis. Char properties were further examined for microstructure, anti-oxidation characteristics, and the presence of functional groups and compounds.

2. Experimental procedure

2.1. Experimental materials

Raw materials used in developing formulations are given in Table 1.

2.2. Preparation of intumescent fire retardant coating (IFRC)

First of all, nano-TiO_2 was sonicated for 5 h for proper dispersion (see Fig. 1. of dispersed nano particles). IFRC preparation comprised three steps: grinding, mixing and curing. Initially, APP, M, BA, Barite and nano-TiO_2 were ground for 1 min to form a homogenous mix followed by 20 min of shearing the ground mixture with EG and an epoxy resin. A curing agent was then added to the composite and mixed for another 10 min. This resultant coating was then applied to single side of a sand blasted structural steel plate that was washed with ethanol to assure a better mechanical interlock with the coating-substrate (1.25 mm in thickness as per Positector measuring gauge). Five measurements were taken at different points ranging from 2.0 to 2.5 mm. Finally; the coated plates were left to cure for 1 d at ambient temperature.

Table 2
Wt.% of materials in preparing IFRC.

Intumescent formulations	APP/EG/M/BA	B/TiO_2	Epoxy binder
F-1	12.0/6.0/6.0/12.0	3.0/0.0	61.0
F-2	12.0/6.0/6.0/12.0	3.0/1.5	59.5
F-3	12.0/6.0/6.0/12.0	3.0/3.0	58.0
F-4	12.0/6.0/6.0/12.0	3.0/4.5	56.5

Table 2 lists wt% for each ingredient. The ratio of wt% for epoxy/hardener was 2:1. The ratio selected for APP/EG/M/BA was 2:1:1:2. Because the epoxy binder had no thermal insulating effect, increasing the content of nano-TiO_2 reduced the wt% of the epoxy binder. Indeed, the binder easily initiates or propagates fire and forms volatile components on decomposition. Furthermore, due to its organic nature, flame retardants were added [5].

3. Experimental methodology

3.1. Fire protection test

A fire protection test assessed the effects of nano-titanium oxide on the coating's thermal efficiency. We used a lab-scale hydrocarbon fire test in a portable cylinder filled with Butane gas at a flow rate of 105 g/h with three thermocouples affixed to the uncoated side of the substrate. Data Loggers were attached to thermocouples to digitally display temperatures minute-by-minute. Before and after burning, samples were weighed and any change in weight percent was calculated.

3.2. Thermogravimetric analysis (TGA)

A Q50 *Thermal Gravimetric Analyzer* verified the coating's residual weight (Perkin Elmer). Samples were run in both nitrogen and oxygen atmospheres at a heating rate of 10 °C/min within a temperature range of 30–800 °C. Final plot was obtained using Origin Pro 8 software.

3.3. X-Ray fluorescence (XRF)

The *S8 TIGER* high-end wavelength dispersive X-ray fluorescence (WDXRF, Bruker) verified the char's chemical composition using Helium.