



# Influence of hybrid functionalized graphite nanoplatelets-tripolyphosphate on improvement in fire protection of intumescent fire resistive coating for steel structures



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## ABSTRACT

Functionalized graphite nanoplatelets (FGNP) were modified with tripolyphosphate (TPP) as a thermal oxidation inhibitor. The hybrid nano-particles (FGNP-TPP) effects on improvement of fire retardant properties of a traditional intumescent fire retardant (IFR) formulation were investigated. FT-IR results showed that TPP was linked to FGNP nano-particle by hydrogen bondings. TEM image showed homogenous dispersion of FGNP-TPP nano-particles in epoxy. Thermogravimetric analysis (TGA) in air showed the oxidation onset temperature of FGNP was increased by approximately 125 °C in the presence of TPP. Incorporation of 2 wt.% of FGNP-TPP into the traditional IFR coating increased the LOI value from 27.1 to 32. Also, a crack free char with high adhesion to the metal substrate was observed in bunsen burner test which increased the time of failure from 43 to 94 min. The results showed the hybrid nano-particles can improve the thermal oxidation stability of the IFR coating at higher temperatures (900–1000 °C) leading to improved char strength, char adhesion, char morphology, residual weight and fire protection properties.

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## 1. Introduction

Epoxy resins are extensively used as industrial surface coatings due to their exceptional characteristics like good adhesion to many substrates; moisture solvent and chemical resistance; low shrinkage on cure and outstanding mechanical properties [1]. However, having an organic matrix, their thermal and fire resistance need to be enhanced in many application areas [2]. Fire retardancy, as an outstanding element of safety, is one of the key challenges.

Steel does not burn but at temperatures above 550 °C, its load-bearing ability is reduced significantly. Protection of steel structures, using so-called intumescent fire retardant (IFR) coatings those swell to a thermally insulating char, is an efficient and space saving way to prolong the time before it collapses in the event of a fire [3,4]. Generally, the conventional IFR systems include three parts: a source of mineral acid catalyst (typically ammonium

polyphosphate (APP), a source of carbon (typically pentaerythritol (PER)) and a blowing agent (typically melamine (MEL)) [5].

However, the high loading requirements of the IFR ingredients in IFR coatings causing problems such as high density, lack of flexibility, low mechanical properties, low adhesion strength and difficulty in processing [6]. Thus, development of novel synergistic agents with IFR systems for high efficient fire retardancy is quite crucial [7].

The above mentioned disadvantages can be reduced by combination of nano-scale additives due to their high specific surfaces and nano-scale interactions with polymer matrix at very low filler concentrations [8].

So far, various kinds of nano-particles have been investigated as flame retardants differing in both their chemical compositions and morphologies [9].

In general, nano-particles with high aspect ratios have been regarded as good candidates for fire retardancy [10].

In recent years, graphene and derivatives such as graphite nanoplatelets (GNPs) have garnered the most interest for nano-materials [11]. Some reports regarding the combination of graphene with an intumescent agent as a flame retardant system are

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presented [12–15].

Previous researches of the flame retardant properties of polymer/graphene nano-composites demonstrated that the addition of graphene, usually less than 5%, into polymeric matrices could significantly decrease the heat release rate, change the char structure and decrease in time to ignition during combustion in a cone calorimeter [15,16].

The effect of particle sizes and morphologies of carbon materials on pyrolysis and burning behavior of polypropylene were compared by Dittrich et al. [9]. They compared spherical carbon black (CB), tubular multiwall carbon nano-tubes (MWNT), expanded graphite (EG) and semi-commercial thin multi-layer graphene (MLG). Results showed that MLG was favorable over spherical particles and tubes due to the increase in the onset temperature of PP decomposition and significant changes in the rheological behavior of polymer melt by a network of well dispersed nano-particles [9]. The flame retardancy of graphene for poly(vinyl alcohol) matrix surpassed both of montmorillonite and carbon nanotubes with the same addition contents [17].

These flame retardant properties of graphene compounds are attributed to the forming of a compact, dense and uniform char during combustion [17].

Beside the insolubility and reaggregation tendency of graphene compounds which limit their processing and result in their non-uniform dispersion in polymer matrices [14], one of the most important problems of graphene and graphitic compounds is their oxidation in ambient air at elevated temperatures [18,19].

It seriously limits the utility of graphite and carbon materials in applications such as brake linings and high temperature applications of coatings, by subsequent gasification and significant degradation in the structural properties of nano-composites [18,19]. Graphite starts to undergo gasification at temperatures as low as 700 °C in oxygen and the presence of catalytically active impurities such as metallic impurities can decrease this onset temperature and also increase the rate of oxidation [20].

Very few compounds are known to be oxidation inhibitors. Additives or adsorbates which have been reported to reduce the reactivity of carbon towards oxygen include: metal phosphates, halogen compounds, phosphorus oxychloride and organo-phosphorus compounds [18].

In this regard phosphorus compounds have been the most effective additives [20]. Corresponding to the literatures, three possible explanations have been offered for the role of phosphorus based inhibitors. The first is a physical blockage mechanism by formation of a protective glassy diffusion barrier. It results from the thermal decomposition of the phosphorus additives. The second one is active site poisoning mechanism and the third is that phosphorus scavenges otherwise catalytic impurities from the exposed surfaces of carbons, thus converts them to neutral phosphate salts [19,21]. Also the use of phosphorus compounds as flame retardants for polymeric materials has been reported for a long time [22,23].

Phosphorus was thought to block active sites by forming either C–O–P or C–P–O bonds at graphene edges to inhibit carbon oxidation [24].

Rakaszowski investigated the effect of group IIIA- VIA elements and their oxides on graphite oxidation at 700 °C and 800 °C. He showed P and P<sub>2</sub>O<sub>5</sub> inhibited the oxidation of graphite due to the high electron affinity and removal of free electrons from the active sites [25].

Organic phosphate and phosphite esters are strongly adsorbed on graphite surfaces at room temperature. Following heat treatment at temperatures generally in 600 °C, the adsorbates decompose to leave phosphate or phosphite groups on the surfaces which strongly inhibit the oxidation at elevated temperatures [18].

For a given adsorbate, the magnitude of the oxidation inhibition, depends on the amount of residual materials present and therefore on the heat treatment temperature after impregnation [18,21]. The low surface area and small numbers of surface functional groups in some carbonaceous compounds do not allow them to adsorb large amounts of phosphate compounds during impregnation [22]. Thus results in less oxidation inhibition effect [24]. To increase the final dopant concentration, Lee activated the carbon felt in nitric acid to increase its surface area, functional group content and fabric roughness [24].

Inorganic phosphorus precursors appear to be more beneficial than the organic ones result in a higher Phosphorus content [24].

The objective of this research work was to investigate the effect of tripolyphosphate (TPP) as a thermal oxidation inhibitor of functionalized graphite nano-platelets (FGNP). Its effects on fire retardant properties of the traditional IFR coating such as the char expansion, char strength, char morphology and residual weight were investigated in detail. FGNP is mild oxygenated graphite nano-platelets with high aspect ratio. The presence of some oxygen functionalities in FGNP, allow it to be used as a promising carbon nano-filler with ideal dispersion and less hydrophilic property in polar polymers such as epoxy.

On the other hand, oxygen functional groups decorated on the FGNP nano-sheets, including carboxylic acid, epoxy, and hydroxyl groups, can be utilized to modify its surface. FGNP comprises multiple stacks of graphene layers that is prepared using cost-effective method compared to mono-layers of graphene and graphene oxide (GO) [26,27].

Detail informations about Preparation and characterization of functionalized graphite nano-platelets (FGNP) in epoxy coating are presented in our previous paper [28].

The obtained hybrid nano-particles (FGNP-TPP) were capable of being thoroughly distributed in epoxy coating without requiring any dispersing and leveling agents.

In comparison with the other current methods of carbon compounds treatment with phosphate compounds (containing impregnating carbon with phosphorus compounds followed by thermal treatment [21]), TPP can be applied in high amounts in the form of aqueous solutions to impregnate FGNP at room temperature rather than thermal treatment at high temperatures.

## 2. Experimental

### 2.1. Materials

Graphite intercalated compounds (GIC), was an expandable sulfuric acid-intercalated graphite Spec: 9950250 (Boading Action Carbon Co.,Ltd). APP n > 1000 (soluble fraction in H<sub>2</sub>O, <1 wt.%) was supplied by Weidong Chemistry Co., Shandong, China. MEL was supplied by Luming Chemistry Co., Shandong, China. PER were supplied by Guoyao Chemical Reagent Co., Shanghai, China. Sodium tripolyphosphate (STPP) technical grade 85% was prepared from SIGMA-ALDRICH and ethanol 96% was prepared from merck.

Epoxy resin EPIRAN6 (EEW 185–196), H46 amine hardener (H active:100) and epoxy thinner T51 were prepared from Khuzestan petrochemical Co., Pars Gohar Co. and Rangin Zereh Co. respectively. Carbon steel (ST37) plates were used as base metal for the coatings.

### 2.2. Hybrid FGNP-TPP preparation

FGNP was fabricated as described in detail in our previous work [28]. In summary, expanded graphite (EG) was obtained by rapid thermal expansion of GIC at 900 °C under inert argon atmosphere. Then, EG was sonicated in water/ethanol (25/75 (% v/v)) solution in

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