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Towards advanced flame retardant organic coatings: Expecting a new function from polyaniline

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Abstract

The necessity of research on flame retardancy has directed attentions toward development of advanced coating systems in order to meet requirements of competitive markets. As a result, a wide range of organic coating materials were developed in the quest of higher flame retardancy performance. Polyaniline (PANI) as a promising conductive polymer has been widely considered for various applications, and it quite frequently took credit for the success. This article deals with the benefits expecting from PANI in advanced flame retardant systems in view of its extraordinary fire retardancy performance. The necessity of study on potentially high thermal stability and flame retardancy of advanced coating systems containing PANI was also discussed. There is a belief that identifying the worth of PANI as the most famous member of conductive polymers may help determine the locus of PANI in an inevitable shift from general-purpose to advanced flame retardant (FR) systems in which PANI plays a dual role. Harmoniously, ongoing progress in the knowledge and technology of FR coating systems would enliven emerging technologies for utilizing organic materials in response to increasing demand for PANI-based systems with an additional flame retardancy mission in the near future.

Keywords: Flame retardancy; polyaniline; conductive polymers; multifunctional flame retardants

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Fire retardancy school of thought

The dilemma of choosing polyaniline (PANI) for advanced coating systems

A new horizon has opened to the investigators in both academia and industry by exploring polyacetylene as a conductive polymer since 1977. In the last decades, conductive polymers such as polyaniline (PANI), polypyrrole, and polythiophene have attracted significant attentions because of their unique properties. PANI has become a most commonly considered conductive polymer because of its affordable cost, easy synthesis, proper chemical stability, adjustable electrical conductivity and good processability. Imine and amine groups are the repeating segments in chemical structure of PANI that can fluctuate among three redox states including leucoemeraldine base (LEB) (colorless or light yellow), emeraldine base (EB) (blue) and pernigraniline base (PB) (violet or black). PANI in PB and LEB states acts as an insulator, while in the form of EB after doping process it changes into emeraldine salt (ES) (green) state with superior electrical conductivity. Thanks to the mentioned advantages, PANI has been utilized in various applications such as anti-corrosion coatings [1], conductive textiles [2], conductive inks [3, 4], energy storage [5], dye-sensitized solar cells [6, 7], and biomedical usages [8, 9]. Unsurprisingly, however, some aspects of PANI such as flame retardancy has attracted less attention among researchers until now-what necessitate further survey [10, 11].

Thermal degradation of PANI should be firstly taken into attention before its flame retardancy character. Regardless of the surrounding atmosphere, two weight loss steps have been frequently observed in thermograms obtained by thermogravimetric analysis (TGA) on PANI [12, 13]. The onset temperature of thermal degradation of PANI is below 100 °C, where adsorbed water and some small dopant molecules are vaporized. Under air atmosphere, the second weight loss takes place below 400°C until 600-700°C beyond which weight loss is approximately 100% implying complete degradation of PANI to gaseous products. In nitrogen atmosphere, however, the second step shifts to higher temperatures of ca. 500 °C, whereas mass loss is usually less than 50% until 600-700 °C. Weight loss of PANI under N₂ atmosphere continue beyond 700 °C with a slower rate, where even at 1000 °C there are some residue [14]. When a dopant is added to the PANI, polaron structures are created which are responsible for significant electrical conductivity enhancement [15, 16]. However, dopant molecules are anchored to PANI chains through poor physical interactions that can be removed even at slightly higher temperatures resulting in a

considerable conductivity loss [17]. Thus, there might be a correlation between degradation behavior and conductivity performance of PANI, which has been rarely addressed. Dopant weight loss usually occurs somewhere in between the first and the second steps that sometimes results in a detectable fall in the TGA thermogram [18, 19]. Thermal degradation of PANI in air atmosphere can produce gaseous products such as CO_x, NO_x, and H₂O, along with vaporized dopant molecules or the degraded products of dopants. Thus, selection of a proper dopant, when necessary, is of prime importance for flame retardancy applications.

In addition to intrinsic thermal stability, PANI shows anticorrosive properties and superior photostability as well. Besides, because of electrical conductivity, it is also used in electrostatic discharge and electromagnetic wave absorption coatings [20, 21]. Such properties indicate the potential of PANI as a multifunctional precursor for advanced coating applications where it can combine the properties of several additives such that more economical, thinner, and low-weight coatings can be applied on different substrates. Furthermore, it can be potentially used in electrically-heated coatings and textiles such as electrically heated gloves, clothes, blanket, and rugs. Incorporation of PANI into the textiles not merely produces electric warming textiles, but can also significantly reduce serious safety issues related to fiber flammability [22]. More interestingly, PANI-based sensors/electrodes can also be embedded into smart fire retardant fabrics for online monitoring of vital functions of human body [23]. The redox transition and color switching characteristics of PANI make it an appealing candidate for smart window applications. As an emerging era, organic electronics uses small organic molecules and polymers instead of inorganic semiconductors/metals [24]. Low density, inexpensiveness and mechanical flexibility are some of the advantageous features of organic electronics which has led to development of organic light-emitting diode (OLED), organic field-effect transistor (OFET) and organic solar cells. Unsurprisingly, however, organic-based materials are potentially more flammable than the conventional inorganic-based materials that underline serious safety concerns. PANI, simultaneously benefited from electrical conductivity properties and flame retardancy characteristics, could potentially resolve the safety issues in organic electronics.

Along with rapid developments in design, manufacture, and commercialization of smart materials for the future coating systems, electronic, clothing, house appliances, and automotive industries on one hand, and the critical safety issues related to flammability of advanced

materials on the other hand, PANI should be viewed as a lost ring that could combine electroactive properties with flame retardancy, while preserving its own organic nature as illustrated in **Fig. 1** [25].

Figure 1. Flame retardants based on PANI as lost piece in advanced system's puzzle

PANI as an element of advanced systems with flame retardancy mission

The majority of flame retardant (FR) molecules contain halogens, phosphorus and nitrogen elements. Each element exhibits its own action in condensed and/or vapor phase when subjected to flame [26, 27] Halogen-rich FRs release halogen radicals and form the stable hydrogen halide in the presence of H[°] and OH[°] radicals. In this way, halogenous FR precursors are very efficient. However, some of the halogenous flame retardants are currently considered harmful in terms of health and environment [28] Thus, organo-phosphorus and/or nitrogen compounds, as halogen

free FR, have been emerged [29-31]. Materialized FRs containing phosphorous functional groups allow formation of a char layer during decomposition of polymer that can act as thermal insulator, inhibiting the heat flux to diffuse inward and decelerate combustion reaction. It has been demonstrated that the performance of phosphorous-based FRs enhances *via* synergistic effects in the presence of nitrogen-based FRs. On the other hand, nitrogen-rich systems can act in vapor phase by releasing nonflammable gases including NH_3 and N_2 to make diluted combustion gases [32-34].

Among polymer additives, FRs have the most consumption and demand on their usage takes ascending order not only because of increasing demand on polymers globally, but also due to the emerging of more strict fire regulations [35, 36]. It goes without emphasizing that market trend is gradually moving to utilization of safer, greener and polymeric based FRs which has stimulated the development of many newly emerged FRs [27]. Bearing market trends in mind while scrutinizing the PANI structure as nitrogen-containing aromatic chain, one may imagine PANI as a potential polymeric FR with fascinating electroactive properties. Chemical modification of PANI with nitrogen/phosphorous agents (as side chains for instance) may result in more efficient PANI-based FR precursors. This idea has been attracted significant attentions toward PANI as a FR agent. To the best of our knowledge, some of recent works related to flame retardancy of PANI are reviewed. Even if exhaustive reviews are rare, some reports give pattern about the importance of the use of PANI in flame retardant systems. The effect of PANI deposition on the surface of several materials such as cellulosic paper [37], cellulose fibers [38-40], and wood [41] and its effects on flame retardancy of these materials has been reported.

Mao et al. [39] utilized two types of organic sulfonic acid, p-toluenesulfonic acid (PTSA) and sulfosalicylic acid (SSA), to dope the PANI deposited cellulosic paper. It was concluded that the doping agent had a significant effect on flame retardancy features of system. It was also reported that the limiting oxygen index (LOI) value enhanced with acid content augmentation. Thus, LOI value of deposited paper increased to 34.9 %, against 20 % measured for blank sample. SSA had more influence on flame retardancy than the PTSA because of formation of more compact and finer PANI [39]. There are also reports that underline the fact that dopants suffer from several disadvantages such as dedoping and low level of doping [42].

Stejskal et al. [32] deposited PANI on cellulose fiber. In-situ polymerization of aniline in the presence of cellulose fiber resulted in hollow carbonaceous microtubes in which PANI was polymerized around cellulose. In the course of burning, cellulose was disintegrated and the PANI shell carbonized such that microtubes were formed. Depending on its thickness, the restrictive feature of PANI shell against oxygen delivery and heat conduction were observed so that wood block turned to charcoal instead of ash [32, 43]. PANI doped with sulfuric acid (H_2SO_4), hydrochloric acid (HCl) and phosphoric acid (H_3PO_4) were also applied as a coating on paper where phosphoric acid exhibited the highest LOI value, but the highest conductivity was attained with H_2SO_4 as dopant. Furthermore, co-doping using H_3PO_4 and H_2SO_4 resulted in more appropriate flame retardancy and conductivity [44, 45]. Naturally occurring phytic acid was also utilized as dopant in order to enhance the flame retardancy of PANI. Moreover, it was observed that polymerization temperature had a significant role in flame retardancy of PANI. In fact, polymerization at low temperatures could result in high-molecular-weight polymers with less side reactions and less oligomer/side products formation, which finally led to an enhanced flame retardancy and conductivity of PANI [46]. Bhat et al. reported that PANI usage in cotton enhanced the time to ignition of the modified cotton [47].

Yu et al. [48] synthesized co-doped PANI with phosphoric acid and hydrochloric acid in the presence of ammonium persulfate (APS) as oxidant to boost conductivity and flame retardancy of PET fabrics. Thermal analyses revealed that PANI coating enhances the thermal stability of PET fabric. The onset of thermal decomposition (T_{onset}) for pristine PET fabric was higher than that of PANI-treated PET. The fall observed in T_{onset} value was related to degradation of PANI layer decomposed before PET, which produced non-flammable diluting gases such as N_2 , CO_2 , NH_3 , and NO_2 in addition to active component like PO° radicals in gas phase that decelerated PET decomposition rate. Simultaneously, the presences of phosphorous and nitrogen containing compounds contributed from dopants in PANI structure enhanced the remaining residue during pyrolysis in the condensed phase up to 9%, instead of 0% observed for pristine PET fabric. The results disclosed that a special threshold in the ratio of APS/aniline monomer (1:2, molar) permitted to obtain a high value in LOI test (42 vol%). The authors concluded that at such ratio a higher molecular weight for PANI was responsible for a stronger Van der Waals interaction between PANI and PET fabrics. Using high-molecular-weight PANI with a higher amount of P and N was the reason behind improved flame retardancy. A similar study on PET fabrics has

been reported by Salgaonkar, where LOI value increased from 19 for PET to 28.7 % for PANI-grafted PET [49].

Zhang et al. [50] introduced the PANI nanostructures (both fibril and spherical structures) to epoxy resin in order to produce a conductive FR nanocomposite. It was observed that the incorporation of PANI nanostructures into epoxy reduced the heat-release rate and enhanced char formation. It has also been shown that PANI nanofiber particles exhibited better thermal stability and lower peak of heat release rate compared to PANI nanospherical particles. Authors explained such observations in terms of the larger specific surface area of PANI nanofibers, which meant a higher amount of amine groups leading to more reaction with epoxy resin. Their conclusion on flame retardancy was principally based on condensed phase action by formation of char, but it was solely supported by TGA and microcalorimetry analyses.

Zhao et al. [51] synthesized a polymer aerogel using PANI and pectin via polymerization-coagulation process in order to use it for thermal insulation application. Cone calorimetry test showed that PANI/pectin aerogel has a higher flame retardancy potential compared to conventional polyurethane foam in terms of peak of heat release rate, total heat release, and total smoke release. PANI nanocomposites containing nanoclay or carbon nanomaterials can potentially create more efficient FRs. The idea has led to investigation of FR properties of PANI nanocomposites [52]. PANI/montmorillonite (MMT) nanocomposite was obtained in-situ in the presence of sodium dodecyl benzene sulphonate (DPM) and 1,5-naphthalene disulfonic acid (NPM) to enhance thermal stability and flame retardancy of polystyrene. The association of MMT and PANI revealed efficient for improving the onset thermal degradation temperature as well as flame retardancy properties. The peak of heat release rate decreased from 862 kW/m² for pristine polystyrene to 349 kW/m² for polystyrene/PANI/MMT nanocomposite. The presence of PANI helps formation of carbonaceous components during the combustion and its association with MMT would be responsible for efficient flame retardancy, as reflected in a more reinforced and compact residue structure [53]. Guo et al. [26] investigated both flame retardant and coupling agent action of PANI doped with phosphoric acid and then applied it as a coating on silica nanoparticles in epoxy resin. Zhang et al. [54] utilized PANI coated-barium titanate nanoparticles (BaTiO₃) in the epoxy matrix and reported improvement of network formation in epoxy together with flame retardancy.

Zhaou et al. [55] synthesized PANI in the presence of molybdenum disulfide (MoS_2) nanosheets and then added PANI-coated MoS_2 to the epoxy matrix upon which reduction in heat release rate and total heat release values were observed. Moreover, the release of CO and toxic gases was inhibited. Results due to differential scanning calorimetry revealed that glass transition temperature (T_g) was enhanced because of active amine groups in chemical structure of PANI acting as a crosslinker in epoxy matrix. It was mentioned that FR properties of PANI- MoS_2 /epoxy composites are attributed to appropriate dispersion of nanoparticle originating from strong interfacial interaction between hybrid nanoparticles and epoxy matrix. The hybrid nanoparticles acted as a barrier to reactive species, oxygen, and heat. Furthermore, oxidation to MoO_3 species during combustion suppressed smoke formation. It was lastly declared that graphitization degree of catalytic carbonization through degradation process resulted in char formation; along with MoS_2 enhanced the thermal stability of the formed char. PANI formed the carbonaceous layer and released nonflammable gases. All in all, a new era was noticed (Fig. 2).

Fig. 2. The mission of PANI in advanced flame retardant coating systems

Concluding remarks and future perspective

At high temperatures, PANI can be carbonized and act as an insulator char layer; in addition, it can hinder the combustion through releasing nonflammable gases which dilute reactive species in the gas phase. PANI due to its nitrogen-rich structure along with diverse phosphorus containing dopants such as phytic acid and phosphoric acid can be considered as a FR agent. Moreover, polymeric structure of PANI could assist in more compatibility with other polymeric systems. Physical/chemical interaction of amine/imine groups with functional groups present in other materials and π - π interaction of aromatic rings with surfaces containing benzene rings can result in development of high performance PANI-based FR coatings with enhanced adhesion. Self-doped PANI structures containing phosphor/nitrogen side chains can act as an inherent FR which can significantly reduce the dedoping concerns while generating extra FR performance will also stimulate future investigations on PANI FRs [56, 57]. On the other hand, fast developments in emerging technologies, such as smart textiles, organic electronics, and smart windows, which are mainly based on organic materials has created safety issues. Thus, it seems that organic electroactive FR agents are essential for developing safe materials for such advanced applications. Thanks to its superior electrical properties and flame retardancy nature, PANI is expected to take a portion of market as multifunctional polymer in the near future. The hope message comes from the angle that the conductivity of PANI can be controlled through adjusting various parameters during the polymerization of aniline such as dopant type, concentration of monomer, oxidant agent, temperature and reaction time. Moreover, hybrid nanostructures based on PANI and other nanomaterials such as graphene, carbon nanotube, and metal oxides, can further improve the overall FR performance of PANI.

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Diluting action by
releasing NH_3 , N_2 , NO_2

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