

Central Lancashire Online Knowledge (CLOK)

Title	Ammonium polyphosphates: Correlating structure to application
Type	Article
URL	https://clock.uclan.ac.uk/id/eprint/54201/
DOI	https://doi.org/10.1016/j.eurpolymj.2024.113644
Date	2025
Citation	Hansen-Bruhn, Iben, Craig, Jessica, Hinge, Mogens and Hull, T Richard (2025) Ammonium polyphosphates: Correlating structure to application. European Polymer Journal, 223. ISSN 0014-3057
Creators	Hansen-Bruhn, Iben, Craig, Jessica, Hinge, Mogens and Hull, T Richard

It is advisable to refer to the publisher's version if you intend to cite from the work.
<https://doi.org/10.1016/j.eurpolymj.2024.113644>

For information about Research at UCLan please go to <http://www.uclan.ac.uk/research/>

All outputs in CLOK are protected by Intellectual Property Rights law, including Copyright law. Copyright, IPR and Moral Rights for the works on this site are retained by the individual authors and/or other copyright owners. Terms and conditions for use of this material are defined in the <http://clock.uclan.ac.uk/policies/>



Review

Ammonium polyphosphates: Correlating structure to application

Iben Hansen–Bruhn^{a,b,c,*}, Jessica Laura Craig^a, Mogens Hinge^{b,*}, Terence Richard Hull^a^a Centre for Fire and Hazard Science, University of Central Lancashire, Preston PR1 2HE, UK^b Plastic and Polymer Engineering, Department of Biological and Chemical Engineering, Aarhus University, Aabogade 40, 8200 Aarhus N, DK^c Fire Retardant Technology, R&D, Teknos A/S Industrivej 19, DK-6580 Vamdrup, Denmark

ARTICLE INFO

Keywords:

Fire retardant

Intumescent

Fertiliser

Ammonium polyphosphate

APP

Diammonium phosphate

Monoammonium phosphate

ABSTRACT

Ammonium polyphosphates (APP) are widely used as nontoxic, biodegradable additives for food, fire retardancy and fertilisers. APP has been shown to exist in six distinct phases, APP-I to APP-VI. Commercial products identified as APP may contain one or more of these phases. Direct synthesis routes to APP involve condensation of monoammonium phosphate or diammonium phosphate with urea or melamine as condensing agents, while indirect synthesis can be obtained by interconversion of one APP phase to another. The most important chemical properties for APP as a fertiliser are nitrogen and phosphorus content, water solubility, hydrolytic stability, and chelating properties (sequestering trace metals). For fire protection, chemical properties such as low water solubility or high hydrolytic stability, compatibility with polymers in plastics or coating formulations, thermal stability and promotion of crosslinking are beneficial. As food additive, low toxicity and water-binding ability are vital. This work found that few studies report on degree of polymerisation, particle size distribution, chain branching, phase, crystallinity or purity of APP, despite APP being the main functionalising additive in specific systems. It was found that some phases of APP (especially APP-III, IV, and VI) remained relatively uncharacterised, but development of new synthetic routes, and improved characterisation, opens new possibilities for commercial exploitation. The unsystematic terminology used to describe these phosphates is addressed in a glossary.

1. Introduction

Ammonium polyphosphate (APP) is an inorganic polymer with versatile applications from enhancing material fire safety to providing nutrients to support agricultural practices. Examples of common applications of APP include fertilisers, fire-safe electronics, frozen meat additives, water treatment, high-end materials for luxury boats and aviation, fire-resistant coatings for load-bearing steel structures, fireproofing textiles, and wood products. In 2023, the global market for APP was estimated at USD 1.9 billion with a potential to reach USD 2.7 billion by 2029 [1,2]. In 2021, 48 000 kt phosphorus pentoxide (P₂O₅) equivalents were consumed worldwide, of which 23 000 kt were ammonium phosphate [3]. Despite APP's importance, there is little consensus on nomenclature or characterisation, with morphology, crystallinity, particle size and its distribution, chemical purity, water solubility, chain length, or chain-branching often left unspecified. Hence, a systematic review on APP's chemical and physical properties is needed to bridge the gap in current literature. In contrast to earlier reviews in the field [4–9], the focus is on chemical and physical property

requirements for APP fertiliser and fire retardancy applications. A review is particularly relevant as the number of publications on APP has intensified. Using the Scopus® database (end of June 2024) showed 2494 publications when using the search criteria (“Ammonium polyphosphate” OR “APP”) AND ((fire OR flame) AND retardant*) in the title, abstract and keywords. Fig. 1 shows the number of publications divided into coatings and polymers over the preceding 50 years. It is apparent from Fig. 1 that around a fifth of the publications relate to coatings development (searching for (“Ammonium polyphosphate” OR “APP”) AND ((fire OR flame) AND retardant*) AND -coating*) found 465 documents) with the remainder assumed to cover solid polymers and textiles. 653 of the publications covered polypropylene; 376 epoxy resins; 314 polyurethanes; 172 polyesters; and 443 textiles, fibres or fabrics. In contrast, there were only 352 publications on APP and fertilisers. These numbers suggest that fire protection is the largest field of APP research, or possibly that APP compounds go by other names in different research fields.

Thus, this review starts with a clarification of APP nomenclature and structure, followed by a condensed historical overview of its discovery

* Corresponding authors at: Plastic and Polymer Engineering, Aarhus University, 8200 Aarhus N, Denmark.

E-mail addresses: ih@dbigroup.dk (I. Hansen–Bruhn), hinge@bce.au.dk (M. Hinge).<https://doi.org/10.1016/j.eurpolymj.2024.113644>

Received 21 September 2024; Received in revised form 3 December 2024; Accepted 9 December 2024

Available online 10 December 2024

0014-3057/© 2024 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

and development. Next, a brief overview of the synthetic routes to the various APP phases is presented. Having established the background, the main section on chemical properties of APP relevant to the industrial applications are described. Subsequently, tailoring APP to meet specific needs is described, alongside ongoing developments, with future challenges including limited phosphate rock reserves. Finally, a glossary has been compiled to aid the reader with the unsystematic nomenclature applied in this field.

2. Nomenclature and structure

Phosphates can be named according to their average degree of polymerisation ($\overline{DP}$). The repeating unit (monomer) is *orthophosphate* PO_4^{3-} (Fig. 2, 1). Linking two monomers linearly by joining corner O-atoms in the PO_4 tetrahedra forms the dimer *pyrophosphate* $\text{P}_2\text{O}_7^{4-}$ (sometimes *diphosphate*), and linking three monomers the trimer *triphosphate* $\text{P}_3\text{O}_{10}^{5-}$, is obtained (Fig. 2, 2 and 3, respectively). A generalized structure is given in Fig. 2, 5 that covers four to twenty monomer units ($n = [2 \dots 18]$) are termed *oligophosphates*, and chains above twenty monomer units ($n > 18$) are termed *polyphosphates*. The oligomer and polymer can have different structures: *metaphosphate* refers to cyclic phosphates (IUPAC: *cyclophosphates*) [4,5] of which *dimetaphosphate* $\text{P}_2\text{O}_6^{2-}$ (Fig. 2, 6) and *trimetaphosphate* $\text{P}_3\text{O}_9^{3-}$ (Fig. 2, 7) are the simplest cyclic phosphates [6]; *polyphosphates* are linear, flexible chains of PO_4 tetrahedra; *ultraphosphates* are branched or crosslinked polyphosphates (Fig. 2, 11 or 12, respectively) containing at least one tertiary phosphorus atom linked via oxygen atoms to three other phosphorus atoms [4,5].

Historically, both polyphosphate and ultraphosphate were termed metaphosphate as long-chain polyphosphates had approximately the same empirical formula as ring structures, $(\text{PO}_3)_n^{n-}$. The identity of the cation is added to the phosphate chain for inorganic salts, such as ammonium polyphosphate with NH_4^+ counter ions. The monosubstituted monomer $(\text{NH}_4)\text{H}_2\text{PO}_4$, IUPAC: ammonium dihydrogenphosphate) is named monoammonium phosphate (MAP). The disubstituted monomer $(\text{NH}_4)_2\text{HPO}_4$, IUPAC: diammonium hydrogen phosphate), is named diammonium phosphate (DAP), and the trisubstituted monomer $(\text{NH}_4)_3\text{PO}_4$, IUPAC: ammonium phosphate), is named triammonium phosphate (TAP). MAP, DAP, and TAP are illustrated in Fig. 3. The polyphosphates $(\text{NH}_4)_{n+2}\text{P}_n\text{O}_{3n+1}$ are collectively named *ammonium polyphosphate* (APP) [10].

However, different scientific fields have deviated from the systematic nomenclature and introduced field-specific nomenclature. In agri-

cultural research, MAP (sometimes ADP, for ammonium dihydrogen phosphate) and DAP are the established abbreviations, while polyphosphate covers all ammonium phosphates with $\overline{DP} > 3$. Further, superphosphate covers a specific commercial phosphate-based fertiliser consisting mainly of $\text{Ca}(\text{H}_2\text{PO}_4)_2$. In cell biology PolyP or P_i (i: inorganic) covers all linear polyphosphates, often as a general term without defining $\overline{DP}$, morphology etc. Within fire retardant chemistry a phase number (APP-I to APP-VI) is given to APP to indicate its identity, based on chain length, different unit cells, and parameters obtained from X-ray diffraction (i.e. crystal structure) [11–13]. APP-I consists of crystalline linear polyphosphate (Fig. 4, 16) with $\overline{DP} < 100$ [4]. For $\overline{DP} = 30$ to 50, reported orthorhombic unit cell parameters are $a = 14.500 \text{ \AA}$, $b = 24.590 \text{ \AA}$, and $c = 4.580 \text{ \AA}$ [13,14]. APP-II is a cross-linked ultraphosphate (Fig. 4, 17) with $\overline{DP} > 1000$ [15] that crystallises in the space group $\text{P}2_12_12_1$ with the orthorhombic unit cell dimensions of $a = 4.256 \text{ \AA}$, $b = 6.475 \text{ \AA}$, and $c = 12.04 \text{ \AA}$. For APP-III no pure phase has been isolated. APP-IV crystallises with the monoclinic unit cell parameters $a = 14.5 \text{ \AA}$, $b = 4.62 \text{ \AA}$, $c = 11.0 \text{ \AA}$, and $\beta = 100^\circ$. APP-V crystallises with the orthorhombic unit cell parameters $a = 4.346 \text{ \AA}$, $b = 6.135 \text{ \AA}$, and $c = 13.646 \text{ \AA}$ [11,16]. Finally, APP-VI has a triclinic unit cell with $a = 7.687 \text{ \AA}$, $b = 15.112 \text{ \AA}$, and $c = 4.845 \text{ \AA}$, but is difficult to produce in high purity [13]. GPC and NMR analysis show that APP-I is a rigid, linear polyphosphate with ammonium counter ions. The molecular structure of APP-II is hypothesised to be a chain spheroid with the ionic bonds wrapped inside the crystal structure (Fig. 4, 17 and 18). Chemically, APP-V is similar to APP-II (shown by similar FTIR spectra and solubility), but depending on synthesis route, with triazine rings from melamine in the APP backbone (suggested structure shown in Fig. 4, 18) [12,17].

Note that attention to the context often allows the APP phase to be identified. When APP is a commercial fertiliser or food additive [18] it is APP-I, but when it is an additive fire retardant for plastics or coatings, it is APP-II [8]. In general, these are the two commercially phases readily available. However, $\overline{DP}$, morphology, and crystal phase must in most cases be deduced from the application.

As shown, there are different naming conventions across different application fields and scientific disciplines. In this work the naming will be MAP, DAP, TAP, and APP. When APP is explicitly named, this refers to polyphosphates with $\overline{DP} > 20$. The reader is referred to the glossary provided at the end of this paper for a more complete overview of terminology.

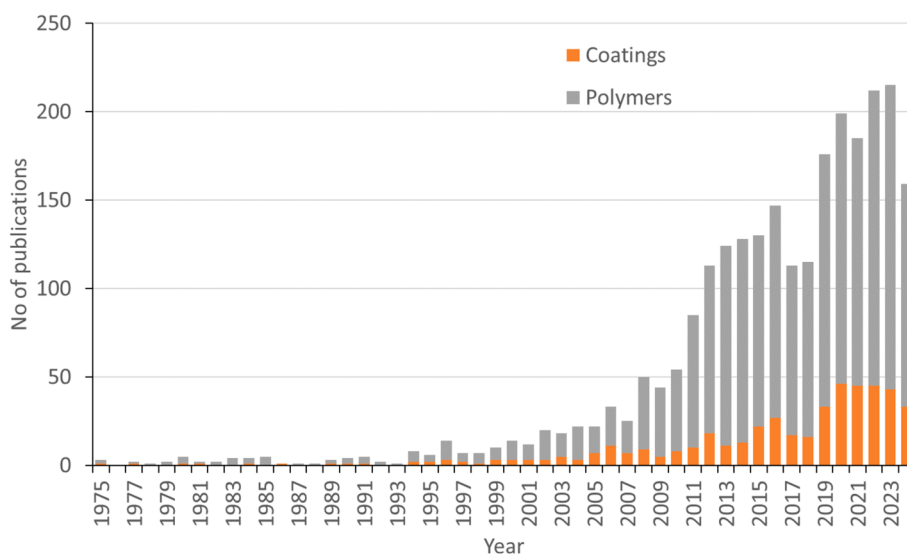


Fig. 1. Number of publications shown in Scopus® over the last 50 years on the applications of APP as a flame or fire retardant for polymers and coatings.

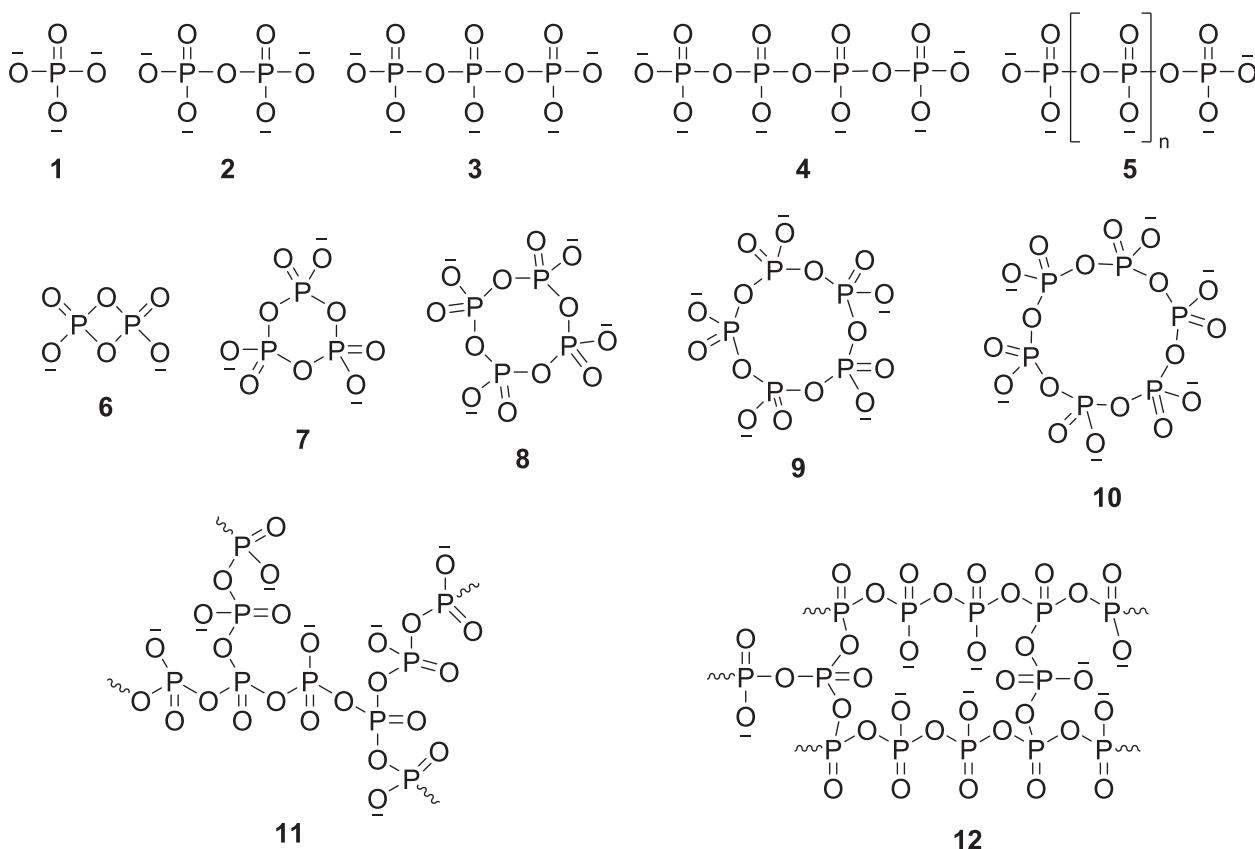


Fig. 2. Illustration of linear, cyclic, branched, and cross linked phosphate compounds. Counter ions are left out for clarity.

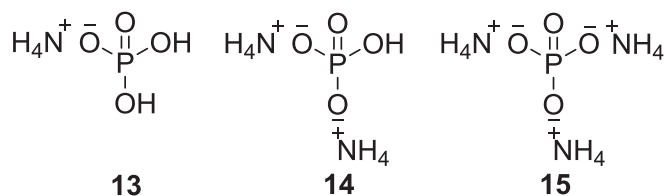


Fig. 3. Illustration of monoammonium phosphate (13, MAP), diammonium phosphate (14, DAP), and triammonium phosphate (15, TAP).

3. Discovery and development

The application of MAP as a fire retardant was first reported in 1821 by Gay-Lussac [19] with the discovery that a mixture of MAP, ammonium chloride, and borax provided flame inhibition when impregnated into fabrics of linen, jute, and hemp. It was concluded that the impregnation either decomposed into non-flammable vapours or formed a glassy layer [20]. However, condensation reactions using MAP as monomer proved challenging as MAP released its ammonia upon heating without polymerising. In 1892, the first successful condensation reaction resulted from heating DAP to give a water-insoluble ammonium oligophosphates with an empirical formula equivalent to $\overline{DP}$ around 10 [21]. It was further discovered that by immersing the product in lukewarm water, the structure hydrolyses to oligophosphates with $\overline{DP}$ around five. Even though no progress was made on APP synthesis routes until World War II, the application of MAP and DAP for fire protection continued. The research on fire retardant phosphorus salts from 1900 to 1968 is covered in detail in John Lyons' classic book on fire retardants [22]. By 1915, the US Department of Agriculture, Forest Products Laboratory (FPL) has tested various timber additives for their fire-retardant properties [23]. Until the 1930 s, FPL experimented systematically on wood treatment with inorganic salts. Of the 70 chemicals tested, they

reported four positive results for phosphoric acid, mono magnesium phosphate, MAP, and DAP [24–26], as described by Lyons [22]. Simultaneously, the development of synthetic ammonia (Haber–Bosch) and ammonium nitrate for munitions resulted in repurposing fertiliser production plants. This development resulted in a synthesis route for ammoniation of superphosphate, a process patented in 1930 [27], facilitating the first industrial production of a dual-nutrient fertiliser, providing both nitrogen and phosphorus [28]. In 1956, an industrial production process for superphosphoric acid was developed. This revolutionized the fertiliser industry as production of liquid fertilisers was introduced [29,30]. In 1962, oligophosphates were reported with unique potential as fertilisers [31,32] that also sequestered metal ions in soil [28]. In the 1960 s, with the growth of the plastics' industry and concomitant increase in the frequency and severity of unwanted fires, fertilisers of different types were studied as potential fire retardants [33]. The first ammonium polyphosphate fire retarding product *Phos-Chek 30/P* was introduced in 1962 [34,35] and approved by FPL for fire protection of wood in 1967 [36]. In 1965 the isolation from ammoniated superphosphoric acid of long-chain crystalline APP was reported and characterized with X-ray diffraction (XRD) [16]. Existence of six possible arrangements of polyphosphate chains of sodium and potassium polyphosphates had been established in the 1950's [4,13,37]. These different phases of APP (APP-I to APP-V) were experimentally verified with XRD in 1969 [11], followed by APP-VI in 1976 [13]. Around 1970, several methods of producing APP were patented, mainly in the US [31,38], and research activities accelerated. Starting from the 1980 s many publications focussed on understanding and exploiting the industrial applications of APP. These applications are grouped into agriculture, food and feed, and fire retardancy, described separately in Sections 5.1–5.3, respectively. These industries have collectively contributed considerable progress in new and more efficient synthetic routes to APP.

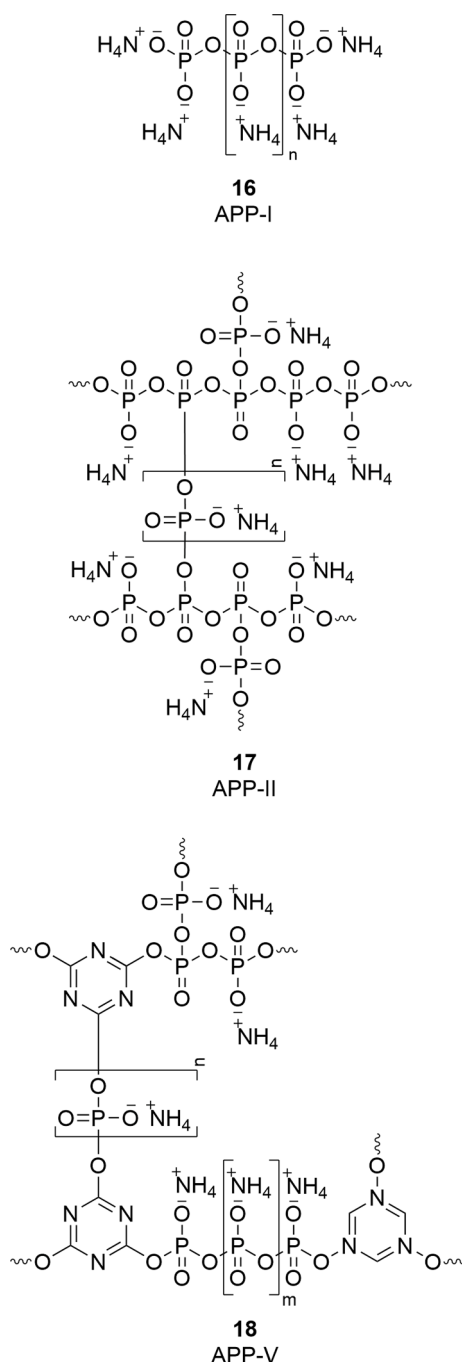


Fig. 4. Illustration of APP-I (13), APP-II (14) and APP-V (15). Note, that APP-V is a suggestion, as the ratio of melamine and phosphate cross links are unknown. For 14 and 15 $n \geq 1$ and $m \geq 1$.

4. Synthetic routes

The emphasis of this review is on applications of APP however, a brief overview of APP synthesis is given to explain the interrelationships between the phases and the starting material. In general, phosphate rock is the precursor for any APP production. Around 98 % of APP is made via a wet process yielding phosphoric acid (H_3PO_4) from phosphate rock, which can subsequently be neutralised with ammonia (NH_3) producing MAP, DAP, and TAP. For the 2 % APP, the phosphate rock undergoes a thermal process (Wöhler process), where it is converted into white phosphorus (P_4), which, by direct oxidation, gives phosphorus pentoxide (P_2O_5) [39,40]. To favour condensation polymerisation, avoiding

the release of ammonia, H_3PO_4 , P_2O_5 , MAP, DAP, and TAP are converted into APP using condensing agents such as urea ($\text{CO}(\text{NH}_2)_2$) or melamine ($\text{C}_3\text{H}_6\text{N}_6$). Careful control of condensing agent, reaction temperatures, reaction time, and flow conditions of wet/dry ammonia atmosphere yield the different APP phases. An overview on synthesis routes and phase transformations is presented in Fig. 5. The reader is referred to the scientific literature for further details.

Fig. 5 illustrates that crystalline forms of APP-I, APP-II, APP-V, and APP-VI [12,14,41–45], can be synthesised directly, whereas APP-III and APP-IV can only be obtained from phase transformations, as intermediates [11,13]. Synthesis of APP-VI is reported with P_2O_5 as the reagent. However, P_2O_5 is challenging to handle in commercial production as it reacts readily with water. When DAP is used as reagent, multiple condensing agents have been reported in literature (ψ in Fig. 5): urea, dicyandiamide [46], melamine [47], and melamine polyphosphate (MPP) [12]. Further, APP yields are higher when the reactant is DAP compared to MAP and TAP. Commercially, APP-I is prepared by heating an equimolar mixture of MAP and urea at 250 °C for 1 h [43]. Subsequent heating under alternating gas flow of dry air and wet ammonia, via an intermediate amorphous phase, results in APP-II formation [11,42,44]. Consequently, commercially available APP-II products commonly contain impurities of APP-I. Thus, commercial production of specific APP types at high purity is still challenging due to the phase transitions (dashed arrows in Fig. 5). This implies that proper chemical characterisation of APP (e.g. particle sizes, morphology, degree of crystallinity, $\overline{DP}$, and its distribution) is necessary when targeting specific applications. Only a few studies include molecular weight ($\overline{M}_w$ and $\overline{M}_n$), their distributions, polydispersity index ($\text{PDI} = \overline{M}_w/\overline{M}_n$), and/or the $\overline{DP}$ of the APP produced [48–52]. Henceforth, only APP-I, APP-II, and APP-V are discussed in detail as they are the most frequent APP phases [53].

5. Industrial applications

5.1. APP as fertiliser

The ability to provide both nitrogen (i.e. ammonium) and phosphorus (i.e. phosphoanhydride) makes APP a superior nutrient delivery system for crops. From the 1970 s, research focused on optimising fertiliser composition, thus driving continuous improvement of the industrial production methods [28,54,55]. As an example, addition of small amounts of APP to H_3PO_4 from the wet process (Fig. 5, upper left arrow) kept phosphate rock impurities from precipitating during liquid fertiliser production while remaining available to plants as micronutrients. However, plant roots can only absorb waterborne orthophosphate, so APP does not provide any nutrient value to plants until it is hydrolysed to orthophosphate. Thus, phosphorus uptake in the root zone depends on the hydrolysis kinetics of APP into orthophosphate and the degree of nutrient washout.

5.1.1. APP hydrolysis kinetics

Although the hydrolysis kinetics are of particular importance to APP's role as a fertiliser, it is also relevant when APP and water may both be present, from resilience to weathering of APP formulations to APP characterisation and analysis. Orthophosphate is released from APP by unzipping from the APP chain ends (Fig. 6, top), and the hydrolysis is a zero-order reaction with respect to oligophosphate (or APP) concentration [4,6,56].

The hydrolysis rate is influenced by soil i) temperature, ii) pH, iii) enzyme activity, and iv) metal ion content where increased temperature i) results in increased hydrolysis rate constant (k) [57], as described by the Arrhenius equation. ii) APP hydrolysis is acid catalysed and APP is thus stable in neutral and alkaline aqueous solutions. Hence, lowering the soil pH will increase the hydrolysis rate of APP into orthophosphate [32]. As the salt of a strong acid and a weak base, long-chain ammonium

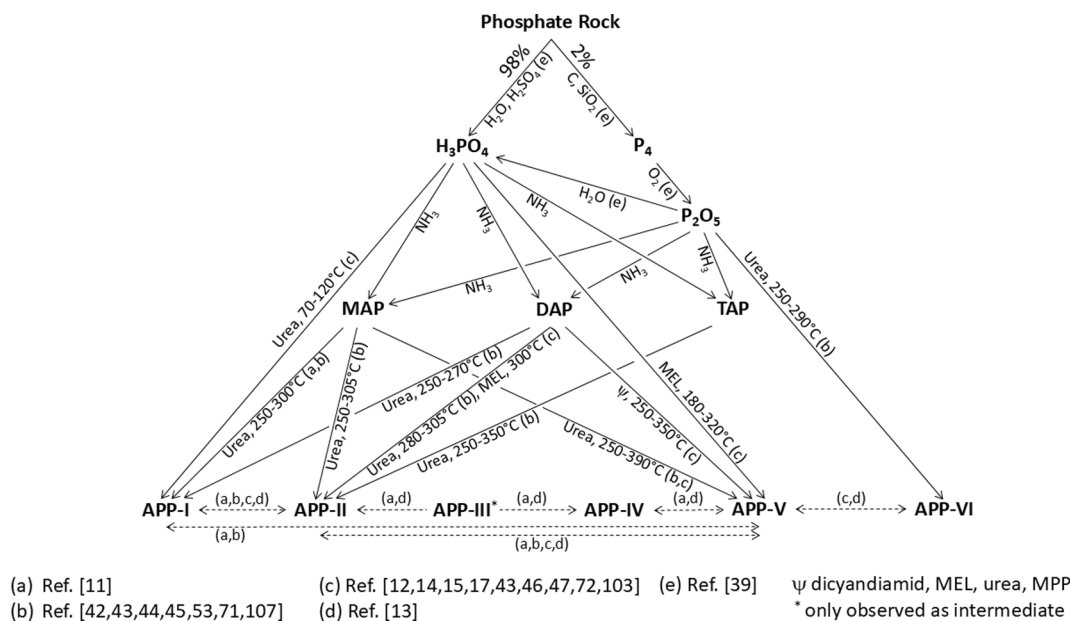


Fig. 5. Summarising the direct synthesis (solid arrow) and phase transformations (dashed arrow) of the six crystalline phases of APP from phosphate rock. Only APP-I, APP-II, and APP-V are thermodynamically stable at room temperature and can be prepared in high purity [41]. Note that processes using ammonia (NH_3) are protected by patents.

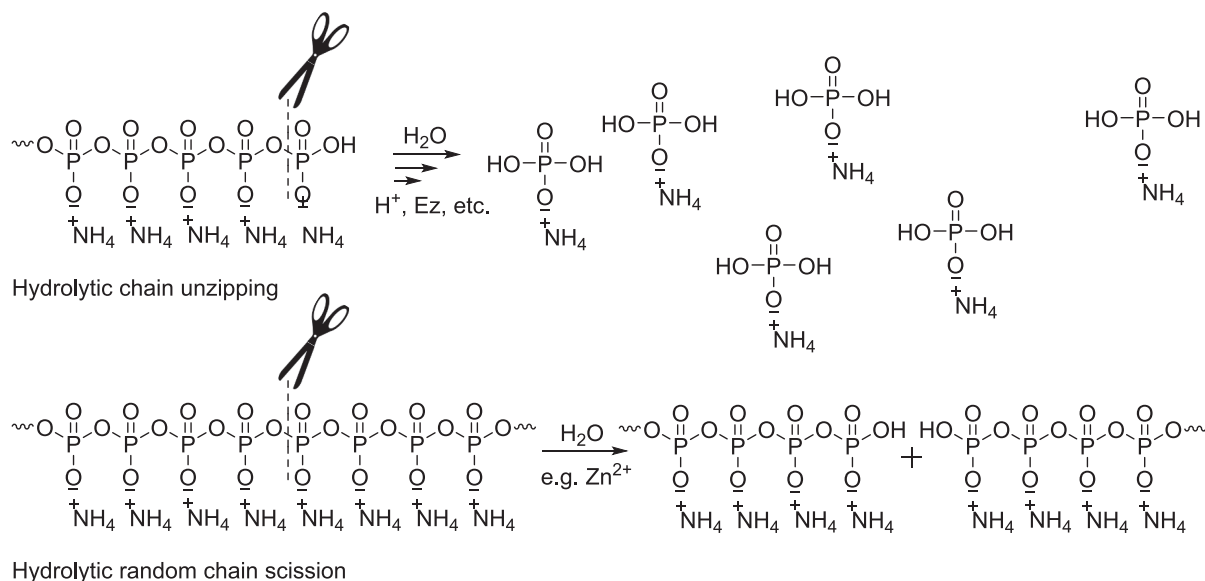


Fig. 6. Processes and products for hydrolysis of ammonium polyphosphate. Ez: Enzymes.

polyphosphates are slightly acidic, leading to suspensions of APP-II having a solution pH of 5 to 6 [6]. This is likely to promote some autocatalytic hydrolysis. iii) Hydrolytic stability is strongly dependent on the enzymatic activity of phosphatase from microorganisms present in the root zone of plants and the presence of phosphatase accelerates the hydrolysis by a factor of 106 [58–60]. When phosphatase-assisted, studies show that the hydrolysis rate of linear sodium polyphosphates is independent of chain length [59]. iv) Studies have shown that APP hydrolysis switches from unzipping to random chain scission when catalysed by Zn^{2+} , Fe^{2+} and/or Al^{3+} [61,62], promoting hydrolysis by generating more end-groups (Fig. 6). However, Ni^{2+} stabilises the P-O-P bond, retarding hydrolysis [63]. While MAP, DAP, and TAP in the soil predominantly ion-exchange to form insoluble precipitates with metal ions, APP chelates metal ions, sequestering micronutrients such as $\text{Fe}^{2+}/\text{Fe}^{3+}$ [64], Zn^{2+} [62,65], Ca^{2+} , and Mg^{2+} [66–68]. The metal ion

binding affinity depends on APP morphology, and only linear polyphosphates form stable complexes with all metal ions [6]. Hence, the affinity is strongest for linear polyphosphates, weaker for cyclic, and weakest for orthophosphates [69].

5.1.2. Nutrient water solubility and mobility

In general, the water solubility at 25 °C for APP-I [14,70], APP-II [41], and APP-V [45] is reported to range from 40–80, 0.03–3.1, and 0.05–3.2 g/L, respectively. Nevertheless, water solubility of APP decreases with higher $\overline{DP}$ [71], e.g. APP-I with a reported $\overline{DP}$ of 30 to 50 was reported to have a water solubility closer to 8.4 g/L [17,72] due to increased crystal lattice energy [41]. High water-solubility of APP-I allows it to be washed away from where it is needed, i.e. flowing away from the plant roots [73,74], resulting in nutrient run-off and potential eutrophication. An optimal fertilizer blend can be obtained by balancing

the faster uptake of MAP and DAP with the slow soil transport (e.g. due to metal ion complexation) and hydrolysis of APP-I with the even slower hydrolysis of APP-II (or APP-III to APP-V). Altogether, understanding and controlling transport and hydrolysis of APP in different environments has driven agricultural research to significantly improve nutrient uptake by designing fertilisers for specific soil and crop combinations [58,75]. Recent research includes doping APP [76–78] methodically mapping hydrolysis kinetics and storage stability [73,79,80] and hydrolysis control by encapsulation in bio-degradable polymers [81,82]. The aim of the research undertaken is to ensure that nutrients are available to the plants in the right amount at the right time.

5.2. APP in food, feeds, and other applications

Polyphosphates are registered as a food additive (E452, with E452v being ammonium polyphosphate) by the Joint FAO/WHO Expert Committee on Food Additives, with a maximum tolerable daily phosphate intake (including APP) of 70 mg kg⁻¹ per day [83–85]. APPs (mainly APP-I) are categorised as emulsifier and sequestrant. APPs are added to frozen prepacked meat preventing drip loss, minimising thaw drip, and cooked-out juices, mainly obtained due to APP's high water affinity via hydrogen bonding [7,86]. Further, agricultural studies show that long-chain polyphosphates act as a growth promoter for broilers and calves [87,88]. Polyphosphates are also employed in the medicinal industry to prevent coagulation of blood [89,90]. In water treatment, pentasodium triphosphates (Na₅P₃O₆) were historically added to laundry detergents as water softener to chelate mainly Ca²⁺ and Mg²⁺ ions, but now substituted by zeolites as the excess phosphorus in the wastewater promotes eutrophication. Finally, due to APP's ability to prevent formation of mineral scale, it is often utilized in closed water systems like heating/cooling systems for power engineering [7,91].

5.3. APP as a fire retardant

Fire retardants can be broadly classified into those which act predominantly in the gas phase, replacing highly reactive radicals in a flame with less reactive species; those which replace significant amounts

of polymer with material which decomposes endothermically to release inert volatiles (often loosely called “mineral fillers”) [92]; and those which promote barrier formation, such as char or ceramics on the surface of the condensed phase, of which a special case is the formation of a swollen, intumescent barrier which better insulates the underlying material. An overview of the fire retardant modes of action for APP is presented in Fig. 7.

Since many fire retardants are subject to criticism for their potential or proven toxicity, a fire retardant which has been approved as a food additive, such as APP, has clear advantages. APP has potential as an additive fire retardant because it releases ammonia when heated (Fig. 7, upper right corner), leaving a residue of polyphosphoric acid (Fig. 7, lower right corner). This combination is particularly valuable in intumescent formulations. With the possibility of obtaining long-chained and sparingly soluble APPs, the mechanism of thermal decomposition of APP in a multitude of material systems has been investigated to impart fire retardancy [93–100]. APP phases show distinct features in their thermal decomposition profiles [14], and the thermal decomposition temperature (T_d) of an APP is an important factor affecting its suitability in a particular polymer.

APP shows three stages of decomposition, starting around 300 °C with elimination of traces of water and ammonia (~2–5 %). Then, from 300 °C to 450 °C chain-stripping with release of ammonia occurs throughout the polymer, with ~ 18 % mass loss corresponding to complete loss of ammonia from the APP [41]. The resulting polyphosphoric acid undergoes dehydration and decomposition, leading to simpler compounds, such as P₂O₅ which are then progressively volatilised [101–103] from 450 °C to 700 °C (residue mass at 700 °C is around 31–39 % [72]). The released water, ammonia and volatile phosphorus compounds may dilute the fuel in the gas phase (Fig. 7, upper right corner). The volatile phosphorus species may decompose to form species such as HPO, which can replace highly reactive free radicals such as H·, ·OH, ·CH₃ and ·O· with less reactive radicals such as HPO₂· and PO· [104]. Both are processes that will inhibit flaming combustion [96,105].

$\overline{DP}$, crosslinking, and crystallinity influence the actual APP decomposition. For the different APP phases, onset T_d (at 1 % mass loss) is 176 °C, 255 °C, and 129 °C for APP-I ($\overline{DP}$ of 30–40), APP-II, and APP-V,

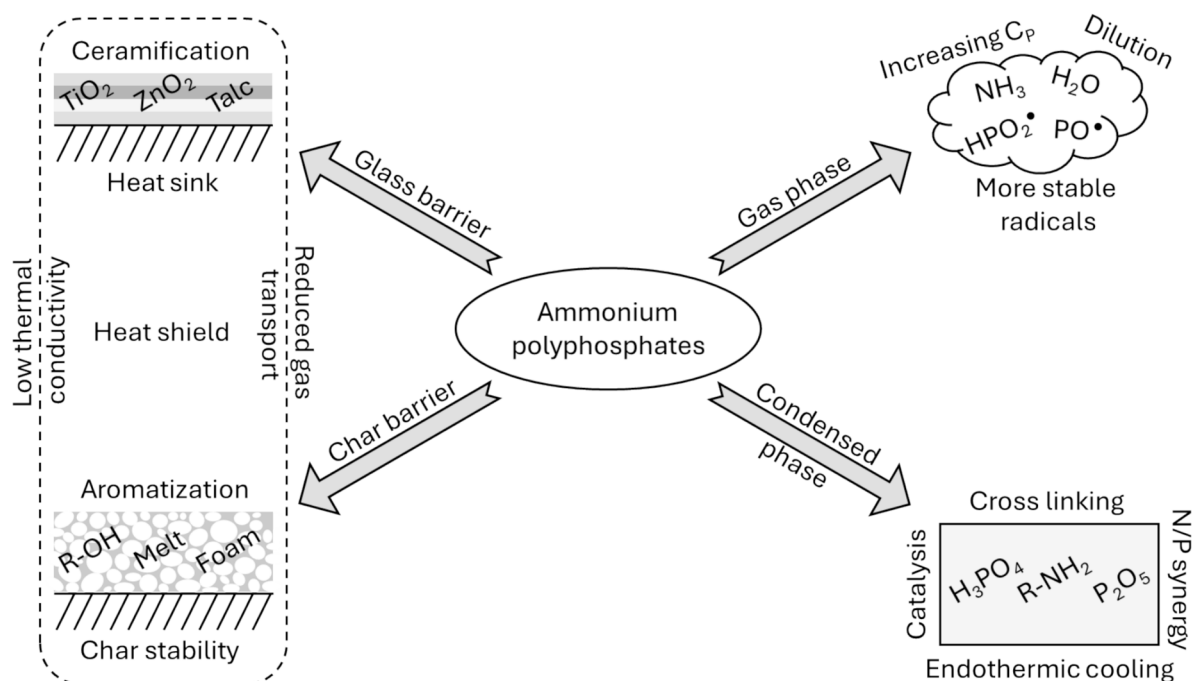


Fig. 7. The conceptual modes of action for ammonium polyphosphate (APP) as a fire retardant. Where ‘R-OH’ represents APP’s reactions with hydroxyl groups, ‘R-NH₂’ represents APP’s reaction with nitrogen-based functional groups, and C_p: Specific heat capacity.

respectively [14,72]. The low T_d for APP-I compared to APP-II has been ascribed to the presence of chelated metal ions [106]. In addition, the decomposition of polyphosphoric acid is reported to start at 324 °C, 356 °C, and 332 °C for APP-I, APP-II, and APP-V, respectively, at 10 % mass loss [14]. Literature shows that thermal decomposition behaviour of APP-V depends significantly on synthesis route: DAP/urea [14] and DAP/dicyandiamide [46] yield APP-V with higher thermal stability than APP-II in the range 300–580 °C, whereas MAP/urea [11] and DAP/MPP [72] yields lower thermal stability in entire temperature range (e.g. low residue mass at 700 °C (APP-V: 5 %, APP-I, APP-II: 31–39 %)). High thermal stability in the range 300–450 °C indicates greater trapping of ammonia within the lattice. High thermal stability above 450 °C indicates higher crosslinking/branching of the P-O-P structure, higher crystallinity, and thermodynamic stability of the crystal phase, resulting in less release of volatile phosphorus species due to polyphosphate degradation. Overall, it remains crucial to characterise the actual APP being used in that application field.

In addition to thermal decomposition, the particle size and compatibility with the host polymer are important. Particle sizes below 10 µm ensure faster release of ammonia and more homogenous dispersion in the polymer matrix but APP will only be adequately dispersed if the compatibility with the polymer is high. Since APP is a polar compound, compatibility with non-polar polymers such as polyolefins will require the use of compatibilisers etc. APP-II has been synthesized in research laboratories with particle size ~ 4–5 µm [107], whereas the mean diameter of APP-I is reported at ~15 µm [14]. In general, particle size of the different APP can be adjusted during production to match a specific application. The particle size is normally reported in the technical datasheets e.g. if 90 % of the particles measures a diameter of ≤ 7 µm (i.e. top size or D_{90} = 7 µm). Extensive research on compatibilization, microencapsulation, and surface modification of APP has resulted in improved fire retardant formulations and improved compatibility in organic matrices [108–112]. Even though APP-I has the lowest T_d and could be applied to polymers which decompose at low temperature, it has a high solubility in water (40–80 g/L), low hydrolytic stability and relatively large particle size. These drawbacks make APP-II the preferred choice in most fire retardant applications.

5.3.1. Intumescence

Intumescence essentially means “the process of expansion”. Within the field of fire science, the term covers the process in which several components react in a specific sequence, triggered by heat, to form an expanded and heat-resistant char to protect the underlying matrix from heat (Fig. 7, lower left corner). The reaction sequence ensuring intumescence is; gases from APP decomposition are released at temperatures above the melting temperature of the host polymer. This ensures that the released gases are captured to generate a porous cellular foam structure. Then, to solidify this porous structure, APP also acts as an *acid source* to catalyse β -elimination of the host polymer's substituents to generate cross links in the porous structure (i.e. a char). APP is the main functional component in many intumescent formulations. To boost char-building and cross-linking, a *carbon source* (i.e. a polyol) can be added to the formulation. To boost char expansion, an additional *spumific* (or *blowing agent*) can be added to the formulation [113]. Conventionally, most intumescent formulation consists of the polymeric matrix, APP as acid source, pentaerythritol (PER) as carbon source, and melamine as a secondary spumific source.

Prompted by a comprehensive review from Vandersall in 1971 [114] on intumescent systems, a significant part of fire retardant chemistry research in the 1980 s and 1990 s focused on understanding the role of APP in thermal degradation of various systems [115–117], especially carbonisation during intumescence [98,100,118–120]. In short, upon heating, the matrix undergoes viscoelastic softening which allows capturing of gases released by endothermic decomposition of APP and melamine to generate a foam. Simultaneously, phosphoric acid (released from APP) dehydrates the PER (and potentially also the polymeric

matrix) giving various phosphate ester products [121,122]. Subsequent phosphate ester scission results in unsaturated ring structures that react into polycyclic aromatic hydrocarbon structures, and via Diels–Alder or free radical reactions, to yield a cross-linked, foamed, cellular char [96,123,142]. The resulting foamed char provides thermal insulation and inhibits heat transfer to the matrix as well as reducing fuel transfer from the matrix to the flaming gas phase (Fig. 7, lower left corner). Reviews on intumescence and detailed studies of the mechanisms have been compiled in literature e.g. [118,124–126].

5.3.1.1. Fire retardant in thermoplastics. Thermoplastics offer cheap and easy manufacturing solutions as they can undergo plastic deformation at relatively low (< 300 °C) temperatures and can be formed into useful objects [127]. A critical property of an added fire retardant is that it must stay inactive during the polymer processing window (the temperature interval between melting and thermal decomposition). Secondly, when a fire retardant is incorporated into the plastic matrix and a fire triggers the intumescence process, the intumescent reaction sequence must take place when the plastic is molten and not yet decomposed. Lastly, for a fire retardant to be effective, it needs to suppress ignition, for example by the release of non-combustible volatiles, and/or promote char formation before polymer decomposition fuels the fire with combustible volatiles. In general, the plastic processing window is narrow (~20–40 °C [127]) and the fire retardant action must match the melting of the polymer with the onset temperature of the intumescent sequence. Hence, understanding the temperature sequence and the chemical decomposition of both matrix material and of the different steps in an intumescent process is crucial to component selection [8,128,129]. A drawback of APP usage is that both thermal stability and integrity of the thermoplastic is reduced through the physical disruptive forces from the ammonia release. The high crystallinity and resultant incompatibility with most fire retardant additives, has made polypropylene (PP) one of the most difficult plastics to formulate with a low flammability, halogen-free fire retardant. To increase the compatibility of APP with PP, either the polymer needs to be modified to reduce its crystallinity and increase its polarity (e.g. via grafting with maleic anhydride), the APP is to be compatibilized with non-polar moieties [130], or microencapsulation [131].

APP addition to polyesters has been shown to impart effective levels of fire retardancy with the formation of a fire protecting foamed cellular char [132]. However, a drawback is that poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) have accelerated thermal degradation via acid-catalysed ester hydrolysis (Fig. 7, lower right corner) [133]. In the absence of APP, polyamide 6 (PA6) decomposition occurs through competing mechanisms yielding e.g. caprolactam, volatile chain fragments containing nitrile, carbon–carbon unsaturated chain ends, and residue [134]. Addition of APP-II lowers T_d for PA6 by 50–70 °C due to acid catalysis amide depolymerisation. In PA6.6 APP-II catalyses char formation by scission of the alkyl amide bond resulting in formation of carbodiimide that subsequently trimerizes to form alkyl triazine [135,136]. The thermal degradation mechanisms of aliphatic polyamides blended with APP can be found in literature [137].

5.3.1.2. Fire retardant in thermosets. Thermosets are either liquids that can be pressurized and mixed upon entry into a mould or a pliable solid (e.g. rubber) that can be compression moulded into its final shape. After loading the thermoset into the mould, it is cured by heating at temperatures typically below 200 °C to produce the desired objects. As with thermoplastics, it is a prerequisite that incorporated fire retardant can withstand the heating during the curing process. For optimal fire retardancy a matching of the APP decomposition temperature with the thermoset decomposition temperature is required [138]. However, while thermoplastics soften when heated, the cross linking of thermosets lowers reactant interactions and the chemical mobility (Fig. 7, lower right corner). Consequently, APP's thermal release of phosphoric acid (H_3PO_4)

and catalysing the dehydration reactions in the condensed phase becomes AAP's predominant mechanism in fire protection of thermosets. In polyurethanes (PUR), APP-II lowers the decomposition temperature by promoting an acid-catalysed degradation of the urethane linkage. This changes the pyrolytic products that are formation of a thermostable phosphocarbonous char [116,139,140]. This phosphoric acid reactivity toward nitrogen containing groups is sometimes referred to as 'N/P synergy' [141,142]. In epoxy resins, the main hinderance for utilizing APP is the polarity difference between APP and the resin. Hence, a thermodynamical penalty (i.e. high ΔH_{mix}) in combination with low resin viscosity results in APP segregation. This is mitigated by either modifying the epoxy resin to obtain higher compatibility [143] or introduce surface modifications on the APP particles. APP surface modifications are obtained via cationic exchange of the ammonium ion with larger amines such as ethanolamine, ethylenediamine, diethyl triamine, and/or piperazine. An additional benefit is that APP obtains dual functionality as both cross linker and acid source [144–146]. Further, hydrophobic modification or multi-functionalization of APP is done to enhance the charring reactions with the cured epoxy matrix [147,148]. For rubbers a thiol functionalized APP can improve its fire retardancy and again function as a cross linker [149]. In general, multicomponent additive mixtures are required for sufficient fire protection of both epoxy and rubbers [150–152].

5.3.1.3. Fire retardant in cellulose based materials. Cellulose based materials (e.g. cotton, wood, etc.) are fire protected by addition of APP and has been extensively studied. In general, polysaccharides react with APP at elevated temperatures to promote dehydration and crosslinking, resulting in char formation. Above 300 °C, cellulose starts to decompose yielding CO, CO₂, and H₂O, and volatile tars (mainly laevoglucosan) [153,154]. During thermal decomposition an intermediate thermally stable aliphatic char (char I) is formed and upon further heating this leads to polycyclic aromatic structures (char II) [155,156]. In the presence of APP, phosphorylation of cellulosic hydroxyl groups and the subsequent phosphorus ester scission results in the formation of a stable conjugated aromatic char (Fig. 7, lower left corner) [157–161]. Hence, when APP decomposes with cellulose, an aromatic char is formed, which reduces the release of flammable volatiles and tars. Recently, APP has gained attention as an environmentally friendly fire retardant due to its low toxicity and compatibility with biopolymers, together with its biodegradability. Environment-friendly fire retardant formulations have been reported for APP in combination with polylactic acid (PLA), sugars, starch, chitin, lignin, etc., in multiple applications [162–164].

5.3.1.4. Intumescent coating formulations. Paint formulations are often stabilized dispersions i.e. wet formulations, and they normally consist of a polymeric binder, pigments, fillers, additives, solvent and potential cosolvents in either one- or two-component formulations. Post application, when the paint is dried or cured into a coating, the binder serves as the matrix embedding pigments, fillers and additives which together define the properties of the obtained coating [165–167]. The main purpose of a coating is to form a protective barrier whereby it separates the substrate from the environment. Intumescent coatings apply APP, PER and melamine as functional fillers to provide fire protection [124]. All pigments and fillers, including APP, are mechanically mixed into a paint dispersion together with multiple components with various chemical functionalities [168,169]. Hence, APP is exposed to both the solvent and all other paint ingredients that can potentially hamper APP's stability. The dispersion must remain stable during manufacturing, processing, storage, and application. Consequently, the utilized APP must be compatible with the solvent as well as the coating components and their chemistries. For thermoplastics, APP and other intumescent components are compounded directly into the matrix, while for coatings they precipitate together with the binder, pigments, fillers, and other additives during the drying process. When in the dried state, a coating

resembles a plastic with embedded intumescent reactants [170]. Thus, the reaction sequence and carbonisation process are equivalent to the process in thermoplastics.

Intumescent coatings are widely applied as passive fire protection, particularly to loadbearing steel structures [99,171,172]. The coating is activated by the increased temperatures during a fire, where the intumescence reaction sequence (Section 5.3.1) is initiated. As steel is non-combustible, the foamed char acts only as thermal insulation to delay temperature increase of the underlying steel substrate. To prevent weakening and potential collapse of a steel structure, the steel temperature should remain below 500 °C depending on the alloying elements [173]. To aid protective barrier formation during intumescence, coatings often contain inorganic fillers that react with APP. This is discussed in the following section.

5.3.2. Formation of ceramic barriers

Reactions at elevated temperatures between APP and inorganic compounds may form ceramic layers that limit heat and mass transport to and from the organic matrix (Fig. 7, upper left corner). Studies show that above 800 °C, APP's degradation products react with titanium dioxide (TiO₂) forming a stable titanium pyrophosphate (TiP₂O₇) [174–177]. Thermally stable products have also been found from reaction between APP and zinc borate (mainly as 2ZnO·3B₂O₃·3H₂O) which forms zinc pyrophosphate (Zn₂P₂O₇), zinc phosphate (Zn₃(PO₄)₂), and boron phosphates (BPO₄) [178,179], and in intumescent coating systems upon addition of boric acid [180,181] and zinc borate [182,183]. Aluminium hydroxide (Al(OH)₃) and APP are reported to form aluminium orthophosphate (AlPO₄) and cyclic aluminium metaphosphate ([Al(PO₃)₃]_n) [184]. Similar products are obtained from reaction between APP and magnesium oxide (MgO) or magnesium hydroxide (Mg(OH)₂) [185,186]. Mixtures of manganese dioxide (MnO₂) and APP form Mn₂P₄O₁₂ at around 600 °C [115]. Further, thermal reaction of APP with talc (3MgO·4SiO₂·H₂O) revealed a combination of Mg₂P₄O₁₂, Si₅O(PO₄)₆, and SiP₂O₇ at 800 °C while heating above 1000 °C resulted in formation of a magnesium silicon phosphate glass [187]. Other phosphate-based glasses have been obtained with silicon dioxide and silicates [188–190], zirconia [191,192], and calcium carbonate [193,194].

6. Ongoing developments

APP is a nontoxic, biodegradable additive for food, fire retardancy and fertilisers. However, for fertilisers, APP degradation via various biogeochemical pathways is still largely unknown [195]. This knowledge could provide better control of orthophosphate release in fertilisers to a matched uptake in specified crops to improve phosphorus utilisation [196]. Fertilisers with biobased coatings have been proposed to minimise accumulation of residual or undegraded synthetic polymers in nature [81]. Likewise in fire chemistry, functionalised APP with bio-based molecules have gained increased attention [197–200]. Other research ventures include APP based products tailored for specific systems (e.g. epoxy resins, [145,148,201–203], or PP [204–207]) and developed into single-component intumescent additives [208,209].

Lastly, inorganic polyphosphates hold medical potential for treatment of bone and blood diseases [90,210,211].

As an alternative to mining phosphate rock, recovery, recycling and re-manufacture of P-compounds must be considered. The increasing world population leads to increased fertiliser demand to secure agricultural productivity. As phosphate rock is a finite resource located unevenly in the world (predominantly in Morocco, Western Sahara, China, and US), recycling of phosphate is inevitable in the near future [39,212,213]. Human disruption of the biogeochemical P-cycle has caused increased nutrient content in surface water and wastewaters [214], leading to eutrophication. Hence, the feasibility of P-recovery from wastewater, sewage sludge, and alike have been extensively researched [215–217]. The mineral, struvite (magnesium ammonium

phosphate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) and calcium analogues are being investigated as fire retardants [218]; P-rich ash from incineration of meat and bonemeal have been proposed to obtain minerals like phosphate rock [219,220]; mechanical recycling of end-of-life FR plastics [221]; and in-line quantification of APP in plastic waste streams [222]; are just some of the ongoing initiatives in these fields.

7. Conclusions

As inorganic polymers, the different types of APP offer versatile solutions to a wide variety of problems. The range of APPs commercially available provides additional options for formulation. In scientific studies, it is necessary to identify the APP product used, and ideally to characterise its structure and composition. APP-I is ideally suited to fertiliser applications because of its high nitrogen and phosphorus content, its water solubility, its relative immobility and its slow rate of hydrolysis, maximising the chance that it will be released where it is needed. As a fire retardant additive in intumescent formulations, APP-II acts as both the blowing agent and as the acid source, promoting char formation. It is crucial to recognise that these two phases, APP-I and APP-II, have very different structures and properties. In both major applications, its polymeric nature and relatively low water solubility give it advantages over other additives. The prospect of tailoring these properties through different phases offers exciting possibilities for further development.

CRedit authorship contribution statement

Iben Hansen–Bruhn: Writing – review & editing, Writing – original draft, Visualization, Methodology, Formal analysis, Data curation, Conceptualization. **Jessica Laura Craig:** Writing – review & editing. **Mogens Hinge:** Writing – review & editing, Visualization, Supervision, Project administration, Methodology, Funding acquisition, Formal analysis. **Terence Richard Hull:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work is partly funded by Innovation Fund Denmark (grant no 9065–00233B). JLC would like to thank Tremco-CPG for provision of a PhD studentship.

Data availability

No data was used for the research described in the article.

References

- [1] Grand View Research Inc., US. Fire Retardant Market Analysis Report, ID: GVR-1-68038-281-5. Available online: <https://www.grandviewresearch.com/industry-analysis/flame-retardant-market> (accessed Aug 7, 2024).
- [2] Research Nester, US. *Global Ammonium Polyphosphate Market Research Report*, March 2024 (Status and Outlook), ID: 5768. Available online: <https://www.researchnester.com/reports/ammonium-polyphosphate-market/5768> (accessed Aug 7, 2024).
- [3] International Fertilizer Association, Data extract from IFASTAT on May 21, 2024, <https://www.ifastat.org/databases/plant-nutrition>.
- [4] E. Thilo, The structural chemistry of condensed inorganic phosphates, *Angew. Chem., Int. Ed. Engl.* 4 (12) (1965) 1061–1071.
- [5] L.V. Kubasova, Polyphosphoric acids and their ammonium salts, *Russ. Chem. Rev.* 40 (1971) 1–12.
- [6] F. Rashchi, J.A. Finch, Polyphosphates: A review of their chemistry and application with particular reference to mineral processing, *Miner. Eng.* 13 (10–11) (2000) 1019–1035.
- [7] T.V. Kulakovskaya, V.M. Vagabov, I.S. Kulaev, Inorganic polyphosphate in industry, agriculture and medicine: modern state and outlook, *Process Biochem.* 47 (1) (2012) 1–10.
- [8] K.S. Lim, S.T. Bee, L.T. Sin, T.T. Tee, C.T. Ratnam, D. Hui, A.R. Rahmat, A review of application of ammonium polyphosphate as intumescent flame retardant in thermoplastic composites, *Compos., Part B: Eng.* 84 (2016) 155–174.
- [9] A. Kornberg, N.N. Rao, D. Ault-Riche, Inorganic Polyphosphate: A Molecule of Many Functions, *Annu. Rev. Biochem.* 68 (1) (1999) 89–125.
- [10] J.K. Fink, Chapter 1 - Unsaturated Polyester Resins, in: J.K. Fink (Ed.), *Reactive Polymers: Fundamentals and Applications*, 2nd ed., William Andrew Publishing, Oxford, 2013, pp. 1–48, <https://doi.org/10.1016/B978-1-4557-3149-7.00001-2>.
- [11] C.Y. Shen, N.E. Stahlheber, D.R. Dyroff, Preparation and characterization of crystalline long-chain ammonium polyphosphates, *J. Am. Chem. Soc.* 91 (1969) 62–67.
- [12] G. Liu, W. Chen, J. Yu, A novel process to prepare ammonium polyphosphate with crystalline Form II and its comparison with melamine polyphosphate, *Ind. Eng. Chem. Res.* 49 (2010) 12148–12155.
- [13] K.R. Waerstad, G.H. McClellan, Preparation and characterization of some long-chain ammonium polyphosphates, *J. Agric. Food Chem.* 24 (1976) 412–415.
- [14] G. Liu, X. Liu, J. Yu, Ammonium polyphosphate with crystalline form V by ammonium dihydrogen phosphate process, *Ind. Eng. Chem. Res.* 49 (12) (2010) 5523–5529.
- [15] G. Liu, Ammonium polyphosphate—an overview with respect to its properties, environmental and toxicological aspects, in: *Proceedings of the 2010 4th International Conference on Bioinformatics and Biomedical Engineering (ICBBE)*, IEEE, 2010, pp. 1–4, <https://doi.org/10.1109/ICBBE.2010.5516557>.
- [16] A.W. Frazier, J.P. Smith, J.R. Lehr, Fertilizer materials: characterization of some ammonium polyphosphates, *J. Agric. Food Chem.* 13 (1965) 316–322.
- [17] G. Liu, W. Chen, X. Liu, J. Yu, Controllable synthesis and characterization of ammonium polyphosphate with crystalline form V by phosphoric acid process, *Polym. Degrad. Stab.* 95 (9) (2010) 1834–1841.
- [18] G.K. Ghosh, K.S. Mohan, A.K. Sarkar, Characterization of soil-fertilizer P reaction products and their evaluation as sources of P for Gram (*Cicer arietinum* L.), *Nutr. Cycl. Agroecosyst.* 46 (1996) 71–79.
- [19] J.L. Gay-Lussac, Note sur la propriété qu'ont les matières salines de rendre les tissus incombustibles, *Ann. Chim. Phys.* 18 (1821) 211–218.
- [20] A.R. Horrocks, Flame-retardant finishing of textiles, *Rev. Prog. Coloration Relat. Top.* 16 (1986) 62–101.
- [21] G. Tammann, Beiträge zur Kenntniss der Metaphosphate, *J. Prakt. Chem.* 45 (1892) 417–474.
- [22] J.W. Lyons, The chemistry and uses of fire retardants, Wiley-Interscience, New York, 1970.
- [23] H.F. Weiss, C.H. Teesdale, Tests of wood preservatives (No. 145), U.S. Department of Agriculture, 1915.
- [24] H.W. Eickner, E.L. Schaffer, Fire-retardant effects of individual chemicals on douglas fir plywood, *Fire Technol.* 3 (1967) 90–104.
- [25] R.B. Truax, Experiments in Fireproofing Wood, Fourth Progress Report, Forest Products Laboratory, in cooperation with the University of Wisconsin, Madison, Wisconsin, 1933.
- [26] T.R. Truax, The "Fireproofing" of wood, *Proc. National Fire Protect. Assoc.* 25 (1931) 212–220.
- [27] US Patent on Ammoniation of superphosphate by inventor E.W. Harvey from 1930, <https://patents.google.com/patent/US1948520A/en> (accessed on Aug 7, 2024).
- [28] D.A. Russel, G.G. Williams, History of chemical fertilizer development, *Soil Sci. Soc. Am. J.* 41 (1977) 260–265.
- [29] Walthall, J. H.; Striplin, M. Superphosphoric Acid by Absorption of Phosphorus Pentoxide Vapor; UTC: 1941; Vol. 33.
- [30] Parker, H. (1984). Tennessee Valley Authority National Fertilizer Development Center Progress 83 (No. TVA/OACD-84/4). Tennessee Valley Authority, Office of Agricultural and Chemical Development, Muscle Shoals, AL, USA.
- [31] J.G. Getsinger, M.R. Siegel, H.C. Mann Jr., High-analysis fertilizers: ammonium polyphosphates from superphosphoric acid and ammonia, *J. Agric. Food Chem.* 10 (1962) 341–344.
- [32] A.V. Slack, J.M. Potts, H.B. Shaffer Jr., Fertilizer solubility: Effect of polyphosphate content on properties and use of liquid fertilizers, *J. Agric. Food Chem.* 13 (1965) 165–171.
- [33] George, C. W. Evaluation of Liquid Ammonium Polyphosphate Fire Retardants; Department of Agriculture, Forest Service, Intermountain Forest and Range Experiment Station: 1977; Vol. 41.
- [34] Perimeter Solutions US, About us -History. Available online: <https://www.perimeter-solutions.com/en/about-history/> (accessed Aug 8, 2024).
- [35] C.E. Miles, J.W. Lyons, Properties of rigid urethane foams containing fire retardants based on phosphorus, *J. Cell. Plast.* 3 (1967) 539–546.
- [36] Brenden, J. J. Effect of Fire-Retardant and Other Inorganic Salts on Pyrolysis Products of Ponderosa Pine at 250 and 350 °C. Research Paper from Forest Products Laboratory, U.S. Forest Service, Department of Agriculture: 1967.
- [37] M.M. Markowitz, Defining the condensed phosphates, *J. Chem. Educ.* 33 (1956) 36.
- [38] J.F. McCullough, R.C. Sheridan, Ammonium polyphosphates, Defensive Publication, 1975.
- [39] A.R. Jupp, S. Beijer, G.C. Narain, W. Schipper, J.C. Slootweg, Phosphorus recovery and recycling – closing the loop, *Chem. Soc. Rev.* 50 (2021) 87–101.

- [40] L. Hermann, W. Schipper, K. Langeveld, A. Reller, Processing: What improvements for what products? in sustainable phosphorus management, Springer Netherlands, Dordrecht, 2014, pp. 183–206.
- [41] M. Watanabe, M. Sakurai, M. Takahashi, New preparation processes of phases II and V ammonium polyphosphate and their use as flame retardants, *Phosphorus Res. Bull.* 16 (2003) 39–46.
- [42] M. Watanabe, M. Watanabe, N. Narita, M. Sakurai, H. Suzuki, Preparation of ammonium polyphosphate form II from the system of ammonium orthophosphate-urea, *Bull. Chem. Soc. Jpn.* 73 (2000) 115–119.
- [43] G.S. Liu, Y.L. Liu, Selection of dehydration temperature to prepare ammonium polyphosphate with crystalline form V by phosphoric acid process, *Adv. Mater. Res.* 668 (2013) 203–206.
- [44] M. Watanabe, M. Sakurai, M. Maeda, Preparation of ammonium polyphosphate and its application to flame retardant, *Phosphorus Res. Bull.* 23 (2009) 35–44.
- [45] M. Watanabe, K. Yano, H. Suzuki, M. Sakurai, Dry synthetic process of ammonium polyphosphate form V from the system of ammonium orthophosphate-urea, *Phosphorus Res. Bull.* 10 (1999) 94–99.
- [46] D. Pan, Y. Wu, B. Wu, C. Kui, L. Ji, J. Zhu, A novel approach for water-insoluble ammonium polyphosphate crystal form II and V, *ChemistrySelect* 3 (2018) 10198–10204.
- [47] Y.L. Liu, W.Y. Chen, G.S. Liu, Preparation of ammonium polyphosphate by melamine as sole condensing agent, *Appl. Mech. Mater.* 275–277 (2013) 1710–1713.
- [48] J. Yang, X. Kong, D. Xu, W. Xie, X. Wang, Evolution of the polydispersity of ammonium polyphosphate in a reactive extrusion process: Polycondensation mechanism and kinetics, *Chem. Eng. J.* 359 (2019) 1453–1462.
- [49] J. Yang, W. Xie, X. Kong, D. Xu, X. Wang, Reactive extrusion of ammonium polyphosphate in a twin-screw extruder: polydispersity improvement, *Chem. Eng. Process.* 133 (2018) 58–65.
- [50] L. Miao, Z. Yan, X. Wang, Y. Zhong, J. Yang, D. Xu, A novel hierarchical structured calcium magnesium ammonium polyphosphate for high-performance slow-release fertilizer, *React. Funct. Polym.* 181 (2022) 105413.
- [51] F. Li, X. Yu, H. Fang, R. Zong, Influence of polymerization degree on the dynamic interfacial properties and foaming ability of ammonium polyphosphate (APP)-surfactant mixtures, *J. Mol. Liq.* 335 (2021) 116175.
- [52] G. Wang, Y. Wang, J. Yang, Influences of polymerization degree of ammonium polyphosphate on fire protection of waterborne intumescent fire resistive coating, *Surf. Coat. Technol.* 206 (8–9) (2012) 2275–2280.
- [53] M. Watanabe, Preparation of P-N compounds and their application to fireproofing substance, *Advances in Inorganic Phosphate Materials: Ceramic Transactions* 233 (2012) 27–38.
- [54] Tennessee Valley Authority, About TVA history. Available online: <https://www.tva.com/about-tva/our-history/tva-heritage/bringing-the-land-to-life> (accessed on Aug 8, 2024).
- [55] D. Xu, B. Zhong, X. Wang, X. Li, Y. Zhong, Z. Yan, X. Zhou, The development road of ammonium phosphate fertilizer in china, *Chin. J. Chem. Eng.* 41 (2022) 170–175.
- [56] H.J. De Jager, A.M. Heyns, Kinetics of acid-catalyzed hydrolysis of a polyphosphate in water, *J. Phys. Chem. A* 102 (17) (1998) 2838–2841.
- [57] N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Elsevier, 2012.
- [58] S.H. Chien, L.I. Prochnow, S. Tu, C.S. Snyder, Agronomic and environmental aspects of phosphate fertilizers varying in source and solubility: An update review, *Nutr. Cycl. Agroecosyst.* 89 (2011) 229–255.
- [59] R. Huang, B. Wan, M. Hult, J.M. Diaz, Y. Tang, Phosphatase-mediated hydrolysis of linear polyphosphates, *Environ. Sci. Technol.* 52 (2018) 1183–1190.
- [60] M.A. Tabatabai, W.A. Dick, *Enzymes in Soil: Research and Developments in Measuring Activities, in: Enzymes in the Environment: Activity, Ecology, and Applications*, 2002, pp. 567–596.
- [61] A.W. Frazier, E.F. Dillard, Ionic effects on the hydrolysis of polyphosphates in liquid fertilizers, *J. Agric. Food Chem.* 29 (4) (1981) 695–698.
- [62] Z. Yan, Y. Wang, D. Xu, J. Yang, X. Wang, T. Luo, Z. Zhang, Hydrolysis mechanism of water-soluble ammonium polyphosphate affected by zinc ions, *ACS Omega* 8 (20) (2023) 17573–17582.
- [63] J. Van Steveninck, The influence of metal ions on the hydrolysis of polyphosphates, *Biochemistry* 5 (6) (1966) 1998–2002.
- [64] B. Wan, P. Yang, H. Jung, M. Zhu, J.M. Diaz, Y. Tang, Iron oxides catalyze the hydrolysis of polyphosphate and precipitation of calcium phosphate minerals, *Geochim. Cosmochim. Acta* 305 (2021) 49–65.
- [65] L.R. Hergert, G.W. Rehm, R.A. Wiese, Field evaluations of zinc sources band applied in ammonium polyphosphate suspension, *Soil Sci. Soc. Am. J.* 48 (5) (1984) 1190–1193.
- [66] Y. Wang, D. Xu, J. Yang, Z. Yan, T. Luo, X. Li, X. Wang, Determination and correlation of the Ca^{2+} and Mg^{2+} solubility in ammonium polyphosphate solution from 278.2 to 323.2 K, *J. Chem. Eng. Data* 67 (1) (2021) 276–285.
- [67] J.A. Shah, G. Chu, Short-chain soluble polyphosphate fertilizers increased soil P availability and mobility by reducing P fixation in two contrasting calcareous soils, *PeerJ* 9 (2021) e11493.
- [68] L.R. Hergert, R.W. Blancher, An insoluble manganese ammonium pyrophosphate found in polyphosphate fertilizer residues, *Soil Sci. Soc. Am. J.* 32 (5) (1968) 731–733.
- [69] T. Miyajima, S. Ohashi, Gel chromatographic evaluation of the binding ability of linear phosphate anions to magnesium ions, *J. Liq. Chromatogr.* 5 (9) (1982) 1787–1799.
- [70] L. Gousheng, Ammonium polyphosphate—an overview with respect to its properties, environmental and toxicological aspects, in: *Proceedings of the 2010 4th International Conference on Bioinformatics and Biomedical Engineering (ICBBE 2010)*, 2010, pp. 1–4.
- [71] M. Watanabe, N. Yamazaki, M. Sakurai, H. Suzuki, M. Takahashi, M. Maeda, Measurement of polymerization degree of condensed phosphates by solid-state NMR, *Phosphorus Res. Bull.* 11 (2000) 47–52.
- [72] W. Chen, L. Wang, G. Liu, Synthesis of ammonium polyphosphate with crystalline form V (APP-V) from melamine polyphosphate (MPP), *Polym. Degrad. Stab.* 97 (12) (2012) 2567–2570.
- [73] T.M. McBeath, E. Lombi, M.J. McLaughlin, E.K. Bünemann, Polyphosphate-fertilizer solution stability with time, temperature, and pH, *J. Plant Nutr. Soil Sci.* 170 (3) (2007) 387–391.
- [74] F.E. Khasawneh, E.C. Sample, I. Hashimoto, Reactions of ammonium ortho- and polyphosphate fertilizers in soil: I. Mobility of phosphorus, *Soil Sci. Soc. Am. J.* 38 (1974) 446–451.
- [75] S.H. Chien, L.I. Prochnow, H. Cantarella, Recent developments of fertilizer production and use to improve nutrient efficiency and minimize environmental impacts, *Adv. Agron.* 102 (2009) 267–322.
- [76] K. Mikula, G. Izdorczyk, D. Skrzypczak, M. Mironiuk, K. Moustakas, A. Witek-Krowiak, et al., Controlled release micronutrient fertilizers for precision agriculture – A review, *Sci. Total Environ.* 712 (2020) 136365.
- [77] I. Bhattacharya, S. Bandyopadhyay, C. Varadachari, K. Ghosh, Development of a novel slow-releasing iron–manganese fertilizer compound, *Ind. Eng. Chem. Res.* 46 (9) (2007) 2870–2876.
- [78] C.L. Edwards, R.O. Maguire, G.B. Whitehurst, W.E. Thomason, M.M. Alley, Using synthetic chelating agents to decrease phosphorus binding in soils, *Soil Sci.* 181 (8) (2016) 377–385.
- [79] X. Wang, Y. Gao, B. Hu, G. Chu, Comparison of the hydrolysis characteristics of three polyphosphates and their effects on soil phosphorus and micronutrient availability, *Soil Use Manag.* 35 (4) (2019) 664–674.
- [80] T.M. McBeath, E. Lombi, M.J. McLaughlin, E.K. Bünemann, Polyphosphate speciation for soil and fertilizer analysis, *Commun. Soil Sci. Plant Anal.* 38 (2007) 2445–2460.
- [81] J. Chen, S. Lü, Z. Zhang, X. Zhao, X. Li, P. Ning, et al., Environmentally friendly fertilizers: A review of materials used and their effects on the environment, *Sci. Total Environ.* 613–614 (2018) 829–839.
- [82] Y. Xiang, X. Ru, J. Shi, J. Song, H. Zhao, Y. Liu, et al., Granular, slow-release fertilizer from urea-formaldehyde, ammonium polyphosphate, and amorphous silica gel: A new strategy using cold extrusion, *J. Agric. Food Chem.* 66 (2018) 7606–7615.
- [83] World Health Organisation. Data Extract from JECFA Database, Keyword “Ammonium Polyphosphate.” Available online: <https://apps.who.int/food-additives-contaminants-jecfa-database/Home/Chemical/2670> (accessed Aug 8, 2024).
- [84] *Toxicological Risks of Selected Flame-Retardant Chemicals*, National Academies Press, Washington, D.C., 2000. doi: 10.17226/9841.
- [85] E. Ritz, K. Hahn, M. Ketteler, M.K. Kuhlmann, J. Mann, Gesundheitsrisiko durch phosphatzusätze in nahrungsmitteln, *Dtsch. Arztebl.* 109 (2012) 49–55.
- [86] T. Yasui, T. Fukazawa, K. Takahashi, M. Sakanishi, Y. Hashimoto, Phosphate effects on meat, specific interaction of inorganic polyphosphates with Myosin B, *J. Agric. Food Chem.* 12 (1964) 399–404.
- [87] S.G. Moon, D. Kothari, W.L. Kim, W.D. Lee, K.I. Kim, J.I. Kim, et al., Feasibility of sodium long chain polyphosphate as a potential growth promoter in broilers, *J. Anim. Sci. Technol.* 63 (2021) 1286–1300.
- [88] B.L. Damron, L.K. Flunker, Supplementation of broiler drinking water with liquid ammonium polyphosphate, *Br. Poult. Sci.* 32 (1991) 377–382.
- [89] R.J. Travers, S.A. Smith, J.H. Morrissey, Polyphosphate, platelets, and coagulation, *Int. J. Lab. Hematol.* 37 (2015) 31–35.
- [90] J.H. Morrissey, S.H. Choi, S.A. Smith, Polyphosphate: An ancient molecule that links platelets, coagulation, and inflammation, *Blood* 119 (25) (2012) 5972–5979.
- [91] SPER Chemical Corporation, Dissolving Polyphosphate Beads, Available online: <https://www.sperchemical.com/portfolio/sper-polyphos-slowly-dissolving-polyphosphate-beads/> (accessed Aug 8, 2024).
- [92] T.R. Hull, A. Witkowski, L. Hollingbery, Fire retardant action of mineral fillers, *Polym. Degrad. Stab.* 96 (2011) 1462–1469.
- [93] Clariant Plastics and Coatings GmbH, The Flame Retardants Market 2020. Available online: <https://www.flameretardants-online.com/flame-retardants/market> (accessed Aug 8, 2024).
- [94] A.B. Morgan, J.W. Gilman, An overview of flame retardancy of polymeric materials: application, technology, and future directions, *Fire Mater.* 37 (2013) 259–279.
- [95] J.W. Mitchell, The history and future trends of non-halogenated flame retarded polymers, in: *Non-halogenated Flame Retardant Handbook*, 2014, pp. 1–16.
- [96] M.M. Velencoso, A. Battig, J.C. Markwart, B. Schartel, F.R. Wurm, Molekulare brandbekämpfung – wie moderne phosphorchemie zur lösung der flammenschutz aufgabe beitragen kann, *Angew. Chem.* 130 (2018) 10608–10626.
- [97] R. Delobel, M. Le Bras, N. Ouassou, R. Descressain, Fire retardance of polypropylene by diammonium pyrophosphate-pentaerythritol: Spectroscopic characterization of the protective coatings, *Polym. Degrad. Stab.* 30 (1) (1990) 41–56.
- [98] S. Bourbigot, M. Le Bras, R. Delobel, Carbonization mechanisms resulting from intumescence association with the ammonium polyphosphate-pentaerythritol fire retardant system, *Carbon* 31 (8) (1993) 1219–1230.
- [99] M. Jimenez, S. Duquesne, S. Bourbigot, Intumescent fire protective coating: toward a better understanding of their mechanism of action, *Thermochim. Acta* 449 (2006) 16–26.

- [100] G. Camino, L. Costa, L. Trossarelli, Study of the mechanism of intumescence in fire retardant polymers: Part I—Thermal degradation of ammonium polyphosphate-pentaerythritol mixtures, *Polym. Degrad. Stab.* 6 (1984) 243–252.
- [101] G. Camino, N. Grassie, I.C. McNeill, Influence of the fire retardant, ammonium polyphosphate, on the thermal degradation of poly(methyl methacrylate), *J. Polym. Sci.: Polym. Chem. Ed.* 16 (1978) 95–106.
- [102] G. Camino, L. Costa, L. Trossarelli, Study of the mechanism of intumescence in fire retardant polymers: Part V—Mechanism of formation of gaseous products in the thermal degradation of ammonium polyphosphate, *Polym. Degrad. Stab.* 12 (1985) 203–211.
- [103] D. Pan, J. Zhu, Y. Wu, K. Chen, B. Wu, L. Ji, Study on the crystal transformation of ammonium polyphosphate crystalline form V, *Phosphorus Sulfur Silicon Relat. Elem.* 191 (2016).
- [104] S. Tretsiakova-McNally, P. Joseph, Phosphorus-Containing Flame Retardants, Chapter 5, in: A.B. Morgan, C.A. Wilkie (Eds.), *Fire Retardancy of Polymeric Materials*, 3rd ed, CRC Press, Boca Raton, FL, 2024.
- [105] J. Green, A review of phosphorus-containing flame retardants, *J. Fire Sci.* 10 (1992) 470–487.
- [106] P.J. Davies, A.R. Horrocks, A. Alderson, The sensitisation of thermal decomposition of ammonium polyphosphate by selected metal ions and their potential for improved cotton fabric flame retardancy, *Polym. Degrad. Stab.* 88 (1) (2005) 114–122.
- [107] M. Watanabe, T. Onishi, A. Matsushita, Flammability characteristics of polymeric materials containing ammonium polyphosphate, *Fire Mater.* 28 (5) (2004) 307–317.
- [108] K. Wu, Z. Wang, H. Liang, Microencapsulation of ammonium polyphosphate: preparation, characterization, and its flame retardance in polypropylene, *Polym. Compos.* 29 (2008) 854–860.
- [109] C. Fukumura, M. Iwata, N. Narita, K. Inoue, R. Takahashi, U.S. Patent No. 5,599,626. U.S. Patent and Trademark Office, Washington, DC, 1997.
- [110] K. Zhao, W. Xu, L. Song, B. Wang, H. Feng, Y. Hu, Synergistic effects between boron phosphate and microencapsulated ammonium polyphosphate in flame-retardant thermoplastic polyurethane composites, *Polym. Adv. Technol.* 23 (2012) 894–900.
- [111] B. Wang, H. Sheng, Y. Shi, W. Hu, N. Hong, W. Zeng, et al., Recent advances for microencapsulation of flame retardant, *Polym. Degrad. Stab.* 113 (2015) 96–109.
- [112] Z. Zheng, H. Sun, W. Li, S. Zhong, J. Yan, X. Cui, et al., Co-microencapsulation of ammonium polyphosphate and aluminum hydroxide in halogen-free and intumescent flame retarding polypropylene, *Polym. Compos.* 35 (2014) 715–729.
- [113] R.G. Puri, A.S. Khanna, Intumescent coatings: A review on recent progress, *J. Coatings Technol. Res.* 14 (2017) 1–20.
- [114] H.L. Vandersall, Intumescent coating systems, their development and chemistry, *J. Fire Flamm.* 2 (1971) 97–140.
- [115] G.F. Levchik, S.V. Levchik, P.D. Sachok, A.F. Selevich, A.S. Lyakhov, A. I. Lesnikovich, Thermal behaviour of ammonium polyphosphate-inorganic compound mixtures. Part 2. manganese dioxide, *Thermochim. Acta* 257 (1995) 117–125.
- [116] G. Montaudo, E. Scamporrino, D. Vitalini, The effect of ammonium polyphosphate on the mechanism of thermal degradation of polyureas, *J. Polym. Sci. Part A: Polym. Chem.* 21 (1983) 3321–3331.
- [117] G. Montaudo, C. Puglisi, E. Scamporrino, D. Vitalini, Mechanism of thermal degradation of polyurethanes. Effect of Ammonium Polyphosphate, *Macromolecules* 17 (1984) 1605–1614.
- [118] G. Camino, L. Costa, L. Trossarelli, Study of the mechanism of intumescence in fire retardant polymers: Part II—mechanism of action in polypropylene-ammonium polyphosphate-pentaerythritol mixtures, *Polym. Degrad. Stab.* 7 (1984) 25–31.
- [119] R. Delobel, M. Le Bras, N. Ouassou, F. Alistiqa, Thermal behaviours of ammonium polyphosphate-pentaerythritol and ammonium pyrophosphate-pentaerythritol intumescent additives in polypropylene formulations, *J. Fire Sci.* 8 (1990) 85–108.
- [120] S. Bourbigot, M. Le Bras, L. Gengembre, R. Delobel, XPS study of an intumescent coating application to the ammonium polyphosphate/pentaerythritol fire-retardant system, *Appl. Surf. Sci.* 81 (3) (1994) 299–307.
- [121] A. Andersson, S. Lundmark, F.H.J. Maurer, Evaluation and characterization of ammonium polyphosphate-pentaerythritol-based systems for intumescent coatings, *J. Appl. Polym. Sci.* 104 (2007) 748–753.
- [122] Y. Xia, F. Jin, Z. Mao, Y. Guan, A. Zheng, Effects of ammonium polyphosphate to pentaerythritol ratio on composition and properties of carbonaceous foam deriving from intumescent flame-retardant polypropylene, *Polym. Degrad. Stab.* 107 (2014) 64–73.
- [123] G. Camino, G. Martinasso, L. Costa, R. Gobetto, Thermal Degradation of pentaerythritol diphosphate, model compound for fire retardant intumescent systems: Part II—Intumescence step, *Polym. Degrad. Stab.* 28 (1990) 17–38.
- [124] J. Alongi, Z. Han, S. Bourbigot, Intumescence: tradition versus novelty. A comprehensive review, *Prog. Polym. Sci.* 51 (2015) 28–73.
- [125] A. Coimbra, J. Sarazin, S. Bourbigot, G. Legros, J.-L. Consalvi, A Semi-Global Reaction Mechanism for the Thermal Decomposition of Low-Density Polyethylene Blended with Ammonium Polyphosphate and Pentaerythritol, *Fire Saf. J.* 133 (2022) 103649.
- [126] S. Bourbigot, Intumescence-Based Flame Retardant, Chapter 7, in: C.A. Wilkie, A. B. Morgan (Eds.), *Fire Retardancy of Polymeric Materials*, 3rd ed, CRC Press, Boca Raton, 2024, pp. 116–146.
- [127] A. Witkowski, A.A. Stec, T.R. Hull, Thermal decomposition of polymeric materials, in: M.J. Hurley (Ed.), *SFPE Handbook of Fire Protection Engineering*, 4th ed, Springer, New York, NY, 2016, pp. 367–382.
- [128] B. Scharrel, B. Perret, B. Ditttrich, M. Ciesielski, J. Krämer, P. Müller, et al., Flame retardancy of polymers: The role of specific reactions in the condensed phase, *Macromol. Mater. Eng.* 301 (2016) 9–35.
- [129] S. Bourbigot, M. Le Bras, S. Duquesne, M. Rochery, Recent advances for intumescent polymers, *Macromol. Mater. Eng.* 289 (2004) 499–511.
- [130] H. Xie, X. Lai, H. Li, X. Zeng, Fabrication of ZrP nanosheet decorated macromolecular charring agent and its efficient synergism with ammonium polyphosphate in flame-retarding polypropylene, *Compos. Part A: Appl. Sci. Manuf.* 105 (2018) 223–234.
- [131] M. Chen, M. Tang, F. Qi, X. Chen, W. He, Microencapsulated ammonium polyphosphate and its application in the flame retardant polypropylene composites, *J. Fire Sci.* 33 (5) (2015) 374–389.
- [132] T. Chu, Y. Lu, B. Hou, P. Jafari, Z. Zhou, H. Peng, et al., The application of ammonium polyphosphate in unsaturated polyester resins: A mini review, *Polym. Degrad. Stab.* (2024) 110796.
- [133] G. Montaudo, C. Puglisi, F. Samperi, Primary thermal degradation mechanisms of PET and PBT, *Polym. Degrad. Stab.* 42 (1993) 13–28.
- [134] S.V. Levchik, G. Camino, L. Costa, G.F. Levchik, Mechanism of action of phosphorus-based flame retardants in nylon 6. I. Ammonium Polyphosphate, *Fire Mater.* 19 (1995) 1–10.
- [135] H. Vahabi, J.-M. Lopez-Cuesta, C. Chivas-Joly, High-performance fire-retardant polyamide materials, in: *Novel Fire Retardant Polymers and Composite Materials*, Elsevier, 2017, pp. 147–170.
- [136] M.A. Schaffer, E.K. Marchildon, K.B. McAuley, M.F. Cunningham, Thermal nonoxidative degradation of nylon 6,6, *J. Macromol. Sci., Part C, Polym. Rev.* 40 (4) (2000) 233–272.
- [137] S.V. Levchik, E.D. Weil, M. Lewin, Thermal decomposition of aliphatic nylons, *Polym. Int.* 48 (1999) 532–557.
- [138] B. Scharrel, B. Perret, B. Ditttrich, M. Ciesielski, J. Krämer, P. Müller, M. Döring, Flame retardancy of polymers: The role of specific reactions in the condensed phase, *Macromol. Mater. Eng.* 301 (1) (2016) 9–35.
- [139] S. Duquesne, M. Le Bras, S. Bourbigot, R. Delobel, G. Camino, B. Eling, C. Lindsay, T. Roels, Mechanism of fire retardancy of polyurethanes using ammonium polyphosphate, *J. Appl. Polym. Sci.* 82 (13) (2001) 3262–3274.
- [140] C.C. Höhne, P. Blaess, S. Ilinzeer, P. Griesbaum, New approach for electric vehicle composite battery housings: Electromagnetic shielding and flame retardancy of PUR/UP-based sheet moulding compound, *Compos. Part A: Appl. Sci. Manuf.* 167 (2023) 107404.
- [141] G. Tang, H. Jiang, Y. Yang, D. Chen, C. Liu, P. Zhang, X. Liu, Preparation of melamine-formaldehyde resin-microencapsulated ammonium polyphosphate and its application in flame retardant rigid polyurethane foam composites, *J. Polym. Res.* 27 (1) (2020) 1–14.
- [142] S. Gaan, G. Sun, K. Hutches, M.H. Engelhard, Effect of nitrogen additives on flame retardant action of tributyl phosphate: phosphorus–nitrogen synergism, *Polym. Degrad. Stab.* 93 (1) (2008) 99–108.
- [143] G.J. Fleming, Prediction of heat shield performance in terms of epoxy resin structure, *J. Macromol. Sci., Chem.* 3 (3) (1969) 531–553.
- [144] M. Kim, H. Ko, S.M. Park, Synergistic effects of amine-modified ammonium polyphosphate on curing behaviors and flame retardation properties of epoxy composites, *Compos. Part B: Eng.* 170 (2019) 19–30.
- [145] Y. Tan, Z.B. Shao, L.X. Yu, Y.J. Xu, W.H. Rao, L. Chen, Y.Z. Wang, Polyethyleneimine modified ammonium polyphosphate toward polyamine-hardener for epoxy resin: Thermal stability, flame retardance and smoke suppression, *Polym. Degrad. Stab.* 131 (2016) 62–70.
- [146] Y. Tan, Z.B. Shao, L.X. Yu, J.W. Long, M. Qi, L. Chen, Y.Z. Wang, Piperazine-modified ammonium polyphosphate as monocomponent flame-retardant hardener for epoxy resin: flame retardance, curing behavior, and mechanical property, *Polym. Chem.* 7 (17) (2016) 3003–3012.
- [147] X. Zhang, F. Zhang, W. Zhang, X. Tang, H.J.S. Fan, Enhance the interaction between ammonium polyphosphate and epoxy resin matrix through hydrophobic modification with cationic latex, *Colloids Surf., A* 610 (2021) 125917.
- [148] Z.B. Shao, J. Zhang, R.K. Jian, C.C. Sun, X.L. Li, D.Y. Wang, A strategy to construct multifunctional ammonium polyphosphate for epoxy resin with simultaneously high fire safety and mechanical properties, *Compos. Part A Appl. Sci. Manuf.* 149 (2021) 106529.
- [149] C. Wu, X. Wang, J. Zhang, J. Cheng, L. Shi, Microencapsulation and surface functionalization of ammonium polyphosphate via in-situ polymerization and thiol–ene photogated reaction for application in flame-retardant natural rubber, *Ind. Eng. Chem. Res.* 58 (37) (2019) 17346–17358.
- [150] L.L. Ge, H.J. Duan, X.G. Zhang, C. Chen, J.H. Tang, Z.M. Li, Synergistic effect of ammonium polyphosphate and expandable graphite on flame-retardant properties of acrylonitrile-butadiene-styrene, *J. Appl. Polym. Sci.* 126 (4) (2012) 1337–1343.
- [151] B. Zirnstein, D. Schulze, B. Scharrel, Mechanical and fire properties of multicomponent flame retardant EPDM rubbers using aluminum trihydroxide, ammonium polyphosphate, and polyaniline, *Materials* 12 (12) (2019) 1932.
- [152] L. Wan, C. Deng, Z.Y. Zhao, H. Chen, Y.Z. Wang, Flame retardation of natural rubber: Strategy and recent progress, *Polymers* 12 (2) (2020) 429.
- [153] D. Drysdale, *An Introduction to fire dynamics*, John Wiley & Sons, 2011.
- [154] F. Shafizadeh, Y.L. Fu, Pyrolysis of cellulose, *Carbohydr Res* 29 (1973) 113–122, [https://doi.org/10.1016/S0008-6215\(00\)82074-1](https://doi.org/10.1016/S0008-6215(00)82074-1).
- [155] J. Alongi, G. Malucelli, Thermal degradation of cellulose and cellulosic substrates, *Reactions and Mechanisms in Thermal Analysis of Advanced Materials* 14 (2015) 301–332.

- [156] I. Milosavljevic, V. Oja, E.M. Suuberg, Thermal effects in cellulose pyrolysis: relationship to char formation processes, *Ind. Eng. Chem. Res.* 35 (1996) 653–662.
- [157] Y. Sekiguchi, F. Shafizadeh, The effect of inorganic additives on the formation, composition, and combustion of cellulosic char, *J. Appl. Polym. Sci.* 29 (1984) 1267–1286.
- [158] K. Matsumoto, T. Tanaka, M. Sasada, N. Sano, K. Masuyama, A mechanism for fire retardancy realized by a combination of biofillers and ammonium polyphosphate in various polymer systems, *Cellul.* 28 (2021) 3833–3846.
- [159] G. Camino, Fire retardant polymeric materials, *Atmospheric Oxidation and Antioxidants* 2 (1993) 461–494.
- [160] D. Price, A.R. Horrocks, M. Akalin, A.A. Farooq, Influence of flame retardants on the mechanism of pyrolysis of cotton (cellulose) fabrics in air, *J. Anal. Appl. Pyrolysis* 40–41 (1997) 511–524.
- [161] C.A. Holmes, Effect of fire-retardant treatments on performance properties of wood, in: I.S. Goldstein (Ed.), *Wood Technology: Chemical Aspects*, 1977, pp. 82–106.
- [162] Z.-B. Shao, J. Cui, X.-L. Li, J.L. Díaz Palencia, D.-Y. Wang, Chemically inorganic modified ammonium polyphosphate as eco-friendly flame retardant and its high fire safety for epoxy resin, *Composites Commun.* 28 (2021) 100959.
- [163] C. Réti, M. Casetta, S. Duquesne, S. Bourbigot, R. Delobel, Flammability properties of intumescent PLA including starch and lignin, *Polym. Adv. Technol.* 19 (2008) 628–635.
- [164] Z.-B. Shao, J. Cui, X.-B. Lin, X.-L. Li, R.-K. Jian, D.-Y. Wang, In-Situ coprecipitation formed Fe/Zn-layered double hydroxide/ammonium polyphosphate hybrid material for flame retardant epoxy resin via synergistic catalytic charring, *Compos. Part A Appl. Sci. Manuf.* 155 (2022) 106841.
- [165] T. Learner, Analysis of modern paints, Getty Publications, Los Angeles, 2004.
- [166] J.R. Costa, C. Correia, J.R. Gois, S.M. Silva, F.E. Antunes, J. Moniz, J.F. Coelho, Efficient dispersion of TiO₂ using tailor-made poly(acrylic acid)-based block copolymers, and its incorporation in water-based paint formulation, *Prog. Org. Coat.* 104 (2017) 34–42.
- [167] A.C. Hellgren, P. Weissenborn, K. Holmberg, Surfactants in water-borne paints, *Prog. Org. Coat.* 35 (1–4) (1999) 79–87.
- [168] F. Tiarks, T. Frechen, S. Kirsch, J. Leuninger, M. Melan, A. Pfau, C.L. Zhao, Formulation effects on the distribution of pigment particles in paints, *Prog. Org. Coat.* 48 (2–4) (2003) 140–152.
- [169] S. Farrokhpay, G.E. Morris, D. Fornasiero, P. Self, Titania pigment particles dispersion in water-based paint films, *J. Coat. Technol. Res.* 3 (4) (2006) 275–283.
- [170] S. Duquesne, S. Magnet, C. Jama, R. Delobel, Thermoplastic resins for thin film intumescent coatings—towards a better understanding of their effect on intumescence efficiency, *Polym. Degrad. Stab.* 88 (1) (2005) 63–69.
- [171] S. Duquesne, S. Magnet, C. Jama, R. Delobel, Intumescent paints: Fire protective coatings for metallic substrates, *Surf. Coat. Technol.* 180 (2004) 302–307.
- [172] M. Jimenez, S. Duquesne, S. Bourbigot, Characterization of the performance of an intumescent fire protective coating, *Surf. Coat. Technol.* 201 (3–4) (2006) 979–987.
- [173] V.H. Baltazar Hernandez, S.S. Nayak, Y. Zhou, Tempering of martensite in dual-phase steels and its effects on softening behavior, *Metallurg. Mater. Trans. A* 42 (2011) 3115–3129.
- [174] E.D. Weil, Fire-protective and flame-retardant coatings - A state-of-the-art review, *J. Fire Sci.* 29 (2011) 259–296.
- [175] J. Gu, G. Zhang, S. Dong, Q. Zhang, J. Kong, Study on preparation and fire-retardant mechanism analysis of intumescent flame-retardant coatings, *Surf. Coat. Technol.* 201 (2007) 7835–7841.
- [176] S. Duquesne, P. Bachelet, S. Bellayer, S. Bourbigot, W. Mertens, Influence of Inorganic Fillers on the Fire Protection of Intumescent Coatings, *J. Fire Sci.* 31 (3) (2013) 258–275.
- [177] T. Mariappan, A. Agarwal, S. Ray, Influence of titanium dioxide on the thermal insulation of waterborne intumescent fire protective paints to structural steel, *Prog. Org. Coat.* 111 (2017) 67–74.
- [178] F. Samyn, S. Bourbigot, S. Duquesne, R. Delobel, Effect of zinc borate on the thermal degradation of ammonium polyphosphate, *Thermochim. Acta* 456 (2007) 134–144.
- [179] G. Walter, U. Hoppe, J. Vogel, G. Carl, P. Hartmann, The structure of zinc polyphosphate glass studied by diffraction methods and ³¹P NMR, *J. Non-Cryst. Solids* 333 (2004) 252–262.
- [180] S. Ullah, F. Ahmad, P.S.M.M. Yusoff, Effect of boric acid and melamine on the intumescent fire-retardant coating composition for the fire protection of structural steel substrates, *J. Appl. Polym. Sci.* 128 (2013) 2983–2993.
- [181] S. Ullah, F. Ahmad, A.M. Shariff, M.A. Bustam, G. Gonfa, Q.F. Gillani, Effects of ammonium polyphosphate and boric acid on the thermal degradation of an intumescent fire retardant coating, *Prog. Org. Coat.* 109 (2017) 70–82.
- [182] Y. Zeng, C.E. Weinell, K. Dam-Johansen, L. Ring, S. Kiil, Exposure of hydrocarbon intumescent coatings to the ULI709 heating curve and furnace rheology: effects of zinc borate on char properties, *Prog. Org. Coat.* 135 (2019) 321–330.
- [183] Y. Zeng, C.E. Weinell, K. Dam-Johansen, L. Ring, S. Kiil, Effects of coating ingredients on the thermal properties and morphological structures of hydrocarbon intumescent coating chars, *Prog. Org. Coat.* 143 (2020) 105626.
- [184] A. Castrovinci, G. Camino, C. Drevelle, S. Duquesne, C. Magniez, M. Vouters, Ammonium polyphosphate–aluminum trihydroxide antagonism in fire retarded butadiene–styrene block copolymer, *Eur. Polym. J.* 41 (2005) 2023–2033.
- [185] T. Sugama, L.E. Kukacka, Characteristics of magnesium polyphosphate cements derived from ammonium polyphosphate solutions, *Cem. Concr. Res.* 13 (1983) 499–506.
- [186] U. Braun, B. Schartel, Flame retardant mechanisms of red phosphorus and magnesium hydroxide in high impact polystyrene, *Macromol. Chem. Phys.* 205 (2004) 2185–2196.
- [187] G.F. Levchik, A.F. Selevich, S.V. Levchik, A.I. Lesnikovich, Thermal behaviour of ammonium polyphosphate–inorganic compound mixtures. Part 1. Talc, *Thermochim. Acta* 239 (1994) 41–49.
- [188] B. Yuan, H. Zhao, S. Wang, Surface modification of ammonium polyphosphate by kaolinite and the study on thermal decomposition behavior and flame-retardant performance, *J. Therm. Anal. Calorim.* 147 (2022) 7311–7321.
- [189] M. Pan, C. Mei, J. Du, G. Li, Synergistic effect of nano silicon dioxide and ammonium polyphosphate on flame retardancy of wood fiber–polyethylene composites, *Compos. Part A Appl. Sci. Manuf.* 66 (2014) 128–134.
- [190] M. Le Bras, S. Bourbigot, Mineral fillers in intumescent fire retardant formulations—criteria for the choice of a natural clay filler for the ammonium polyphosphate/pentaerythritol/polypropylene system, *Fire Mater.* 20 (1996) 39–49.
- [191] W. Xing, P. Zhang, L. Song, X. Wang, Y. Hu, Effects of alpha-zirconium phosphate on thermal degradation and flame retardancy of transparent intumescent fire protective coating, *Mater. Res. Bull.* 49 (2014) 1–6.
- [192] Z. Wang, S. Jiang, H. Sun, Expanded polystyrene foams containing ammonium polyphosphate and nano-zirconia with improved flame retardancy and mechanical properties, *Iran. Poly. J.* 26 (2017) 71–79.
- [193] F. Laoutid, H. Vahabi, E. Movahedifar, P. Laheurte, C. Vagner, M. Cochez, et al., Calcium carbonate and ammonium polyphosphate flame retardant additives formulated to protect ethylene vinyl acetate copolymer against fire: hydrated or carbonated calcium? *J. Vinyl Addit. Technol.* 27 (2021) 264–274.
- [194] S. Deodhar, K. Shanmuganathan, Q. Fan, C.A. Wilkie, M.C. Costache, N. A. Dembsy, et al., Calcium carbonate and ammonium polyphosphate-based flame retardant composition for polypropylene, *J. Appl. Polym. Sci.* 120 (2011) 1866–1873.
- [195] I. Kulaev, V. Vagabov, T. Kulakovskaya, New aspects of inorganic polyphosphate metabolism and function, *J. Biosci. Bioeng.* 88 (2) (1999) 111–129.
- [196] S. Heuer, R. Gaxiola, R. Schilling, L. Herrera-Estrella, D. López-Arredondo, M. Wissuwa, et al., Improving phosphorus use efficiency: A complex trait with emerging opportunities, *Plant J.* 90 (2017) 868–885.
- [197] M.N. Prabhakar, G.M. Raghavendra, B.V.D. Vijaykumar, K. Patil, J. Seo, S. Jung-il, Synthesis of a novel compound based on chitosan and ammonium polyphosphate for flame retardancy applications, *Cellul.* 26 (2019) 8801–8812.
- [198] S. Peil, R. Mouhoubi, R. Streekstra, H. Ridard, L. Veith, W. Ali, F.R. Wurm, Encapsulation of ammonium polyphosphate in lignin nanocontainers enhances dispersion and flame retardancy in polylactic acid foams, *ACS Appl. Polym. Mater.* 6 (10) (2024) 6096–6107.
- [199] Q. Fang, Y. Zhan, X. Chen, R. Wu, W. Zhang, Y. Wang, B. Yuan, A bio-based intumescent flame retardant with biomolecules functionalized ammonium polyphosphate enables polylactic acid with excellent flame retardancy, *Eur. Polym. J.* 177 (2022) 111479.
- [200] Y. Sui, X. Dai, P. Li, C. Zhang, Superior radical scavenging and catalytic carbonization capacities of bioderived assembly modified ammonium polyphosphate as a mono-component intumescent flame retardant for epoxy resin, *Eur. Polym. J.* 156 (2021) 110601.
- [201] P. Zheng, H. Zhao, J. Li, Q. Liu, H. Ai, R. Yang, W. Xing, Recent advances in constructing new type of epoxy resin flame retardant system using ammonium polyphosphate, *J. Saf. Sci. Resilience* (2024).
- [202] H. Qu, J. Hao, W. Wu, X. Zhao, S. Jiang, Optimization of Sol–Gel coatings on the surface of ammonium polyphosphate and its application in epoxy resin, *J. Fire Sci.* 30 (4) (2012) 357–371.
- [203] W. Yang, W. Chang, J. Zhang, G.H. Yeoh, C. Boyer, C.H. Wang, A novel strategy for high flame retardancy and structural strength of epoxy composites by functionalizing ammonium polyphosphate (app) using an amine-based hardener, *Compos. Struct.* 327 (2024) 117710.
- [204] Z.B. Shao, C. Deng, Y. Tan, L. Yu, M.J. Chen, L. Chen, Y.Z. Wang, Ammonium polyphosphate chemically-modified with ethanolamine as an efficient intumescent flame retardant for polypropylene, *J. Mater. Chem. A* 2 (34) (2014) 13955–13965.
- [205] Y. Sun, B. Yuan, S. Shang, H. Zhang, Y. Shi, B. Yu, X. Yang, Surface modification of ammonium polyphosphate by supramolecular assembly for enhancing fire safety properties of polypropylene, *Compos. Part B Eng.* 181 (2020) 107588.
- [206] Z. Lei, Y. Cao, F. Xie, H. Ren, Study on surface modification and flame retardant properties of ammonium polyphosphate for polypropylene, *J. Appl. Polym. Sci.* 124 (1) (2012) 781–788.
- [207] J.C. Liu, M.J. Xu, T. Lai, B. Li, Effect of surface-modified ammonium polyphosphate with KH550 and silicon resin on the flame retardancy, water resistance, mechanical and thermal properties of intumescent flame retardant polypropylene, *Ind. Eng. Chem. Res.* 54 (40) (2015) 9733–9741.
- [208] Z. Chen, Y. Yu, Q. Zhang, Z. Chen, T. Chen, C. Li, J. Jiang, Surface-modified ammonium polyphosphate with (3-Aminopropyl) triethoxysilane, pentaerythritol and melamine dramatically improve flame retardancy and thermal stability of unsaturated polyester resin, *J. Therm. Anal. Calorim.* 143 (2021) 3479–3488.
- [209] C. Zhu, M. He, Y. Liu, J. Cui, Q. Tai, L. Song, Y. Hu, Synthesis and application of a mono-component intumescent flame retardant for polypropylene, *Polym. Degrad. Stab.* 151 (2018) 144–151.
- [210] S.N. Moreno, R. Docampo, Polyphosphate and its diverse functions in host cells and pathogens, *PLoS Pathog.* 9 (5) (2013) e1003230.
- [211] N.N. Rao, M.R. Gómez-García, A. Kornberg, Inorganic polyphosphate: Essential for growth and survival, *Annu. Rev. Biochem.* 78 (2009) 605–647.

- [212] Y. Liu, S. Kumar, J.-H. Kwag, C. Ra, Magnesium ammonium phosphate formation, recovery and its application as valuable resources: A review, *J. Chem. Technol. Biotechnol.* 88 (2013) 181–189.
- [213] J. Cooper, R. Lombardi, D. Boardman, C. Carliell-Marquet, The future distribution and production of global phosphate rock reserves, *Resour. Conserv. Recycl.* 57 (2011) 78–86, <https://doi.org/10.1016/j.resconrec.2011.09.009>.
- [214] S. Gao, T.H. DeLuca, Influence of fire retardant and pyrogenic carbon on microscale changes in soil nitrogen and phosphorus, *Biogeochem.* 152 (2021) 117–126, <https://doi.org/10.1007/s10533-020-00746-8>.
- [215] B. Tansel, G. Lunn, O. Monje, Struvite formation and decomposition characteristics for ammonia and phosphorus recovery: A review of magnesium-ammonia-phosphate interactions, *Chemosphere* 194 (2018) 504–514.
- [216] Y. Ye, H.H. Ngo, W. Guo, Y. Liu, J. Li, Y. Liu, et al., Insight into chemical phosphate recovery from municipal wastewater, *Sci. Total Environ.* 576 (2017) 159–171.
- [217] A.L. Forrest, K.P. Fattah, D.S. Mavinic, F.A. Koch, Optimizing struvite production for phosphate recovery in WWTP, *J. Environ. Eng.* 134 (2008) 395–402.
- [218] A.H. Kim, A.C. Yu, S.H. el Abbadi, K. Lu, D. Chan, E.A. Appel, et al., More than a fertilizer: wastewater-derived struvite as a high value, Sustain. Fire Retardant. *Green Chem.* 23 (2021) 4510–4523.
- [219] Z. Kowalski, M. Banach, A. Makara, Optimisation of the co-combustion of meat–bone meal and sewage sludge in terms of the quality produced ashes used as substitute of phosphorites, *Environ. Sci. Pollut. Res.* 28 (2021) 8205–8214.
- [220] L. Leng, J. Zhang, S. Xu, Q. Xiong, X. Xu, J. Li, et al., Meat & bone meal (MBM) incineration ash for phosphate removal from wastewater and afterward phosphorus recovery, *J. Clean. Prod.* 238 (2019) 117960.
- [221] L. Delva, S. Hubo, L. Cardon, K. Ragaert, On the role of flame retardants in mechanical recycling of solid plastic waste, *Waste Manage.* 82 (2018) 198–206.
- [222] G. Amariei, M.L. Henriksen, P. Klarskov, M. Hinge, In-Line quantitative estimation of ammonium polyphosphate flame retardant in polyolefins via industrial hyperspectral imaging system and machine learning, *Waste Manage.* 170 (2023) 1–7.
- [223] T.E. Robinson, L.A. Arkinstall, S.C. Cox, L.M. Grover, Determining the structure of hexametaphosphate by titration and ^{31}P -NMR spectroscopy, *Comments Inorg. Chem.* 42 (1) (2022) 47–59.

Glossary: Normal typography: An overview of what has become a convoluted terminology across different application fields

Ammonium phosphate: IUPAC name for *triammonium phosphate*. Conventionally, any of the following: $(\text{NH}_4)\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, $(\text{NH}_4)_3\text{PO}_4$.

Ammonium dihydrogen phosphate: IUPAC name for the *monoammonium hydrogen phosphate* (MAP). Sometimes also abbreviated ADP in agriculture.

Ammonium polyphosphate (APP): $(\text{NH}_4)_{n+2}\text{P}_n\text{O}_{3n+1}$, where n is larger than 18. More than 20

phosphate monomers linked with oxygen atoms and with ammonium ions as counter ions. Confusingly, in some scientific fields also ammonium phosphates with more than 3 monomers.

Condensed phosphates: Compounds containing phosphates linked together with shared oxygen atoms.

Diammonium hydrogen phosphate: IUPAC name for *diammonium phosphate*.

Diammonium phosphate (DAP): $(\text{NH}_4)_2\text{HPO}_4$, disubstituted phosphate monomer. IUPAC name is *diammonium hydrogen phosphate*.

Dimetaphosphate: $\text{P}_2\text{O}_6^{2-}$, cyclic anion. IUPAC name is *cyclodiphosphate*.

Cyclodiphosphate: IUPAC name for *dimetaphosphate*.

Cyclotriphosphate: IUPAC name for *trimetaphosphate*.

Cyclophosphate: $(\text{PO}_3)_n^{\frac{n}{2}}$, all phosphates with ring structure regardless counter ion.

Diphosphate: IUPAC name for *pyrophosphate*.

Gramham's salt: A water-soluble glass mainly consisting of chains with molecular weight 12 000–18 000 Da and with up to 10 % ring *metaphosphates* and some crosslinked material.

Hexametaphosphate: $\text{P}_6\text{O}_{18}^{6-}$, a cyclic phosphate with six phosphate monomers. Commercially, the name often covers linear chains of variable chain length [223].

Linear polyphosphate: All chain phosphates containing more than 20 phosphate monomers. $(\text{NH}_4)_{n+2}\text{P}_n\text{O}_{3n+1}$

Monoammonium phosphate (MAP): $(\text{NH}_4)\text{H}_2\text{PO}_4$, salt between the phosphate monomer and a single ammonium as counter ion.

Oligophosphate: Compounds containing from 4 to 20 phosphate monomers.

Orthophosphate: PO_4^{3-} , the simplest phosphate anion, thus the monomer unit in polyphosphates. In cell biology, traditionally abbreviated P_i (i: inorganic).

Phosphate: IUPAC name for *orthophosphate*.

Polyphosphate: Polymers containing more than 20 phosphate monomers linked with shared oxygen atoms. Conventionally, only *linear polyphosphates*.

Pyrophosphate: $\text{P}_2\text{O}_7^{4-}$, linear anion consisting of two monomers, thus *diphosphate*. In cell biology, traditionally abbreviated PP_i

Tetraphosphate: $\text{P}_4\text{O}_{13}^{6-}$, linear anion consisting of four monomers, sometimes named tetrapolyphosphate.

Trimetaphosphate: $\text{P}_3\text{O}_9^{3-}$, cyclic anion. IUPAC name is *cyclotriphosphate*

Triphosphate: $\text{P}_3\text{O}_{10}^{5-}$, linear anion consisting of three monomers, sometimes named tripolyphosphate

Triammonium phosphate (TAP): $(\text{NH}_4)_3\text{PO}_4$, trisubstituted phosphate monomer. IUPAC name is *ammonium phosphate*.

Superphosphate: $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ or $\text{Ca}(\text{H}_2\text{PO}_4)_2$, also known as single or triple superphosphate, respectively. Commercial phosphate fertilizer also used in backing powder and as mineral supplement for food and feeds

Ultraphosphate: Condensed phosphate with a least one PO_4 tetrahedra sharing three corner atoms to obtain crosslinking.

Vitreous phosphates: Glasses of long-chain sodium polyphosphates or *ultraphosphates*, depending on Na_2O to P_2O_5 ratio.