



Reactive extrusion of ammonium polyphosphate in a twin-screw extruder: polydispersity improvement

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ABSTRACT

Reactive extrusion has been widely applied to polymerization processes with high-viscosity materials. In this work, the co-extrusion of monoammonium phosphate (MAP) and urea for the synthesis of ammonium polyphosphate (APP) was performed in a co-rotation twin-screw extruder (TSE). APP with a maximal polymerization degree less than 10, was obtained for the potential application as fertilizers where the polydispersity index (PDI, defined as the ratio of weight-average molecular weight to number-average molecular weight M_w/M_n) is a key parameter for controlled release of the phosphorus in soil. The properties of samples along the screws, such as molecular weight distributions (MWD), were characterized via ion chromatography (IC), Fourier-transformed infrared spectrum (FT-IR), X-ray diffractometer (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). A pyrophosphate-controlled growth mechanism of PDI is revealed, and viscous dissipation in TSE could extend the urea-assisted polycondensation stage. The resulting PDI value is increased to 1.272 at a screw rotation speed of 150 rpm. This reactive extrusion for inorganic polymers is highly efficient and is flexible in controlling the polymer PDI.

1. Introduction

Nitrogen (N), phosphorus (P), and potassium (K) are the three main nutrient elements essential for plants. However, the uptake of P by plants is challenging because artificial P fertilizers suffer the most serious fixation by soil [1–3]. Therefore, it has received great attention no how to improve the efficiency of phosphorus supply into plants in recent years [4–6]. The use of ammonium polyphosphate (APP), an oligomer of traditional fertilizer monoammonium phosphate (MAP), is the most direct approach to prevent fixation. The APP has six known crystalline forms [7], among which the most common forms are Form I and Form II. Form I has a short linear structure. Most of its ion bonds ($-O^- - NH_4^+$) are exposed outside and can easily be ionized by water, leading to its water solubility; Form II shows smaller water solubility for most of its ion bonds ($-O^- - NH_4^+$) are inside the crystal spheroid and are difficult to be ionized by water [8,9]. APP with a high polymerization degree (more than 20) is mainly used in flame retardant [10–14]. When the polymerization degree is less than 10, APP becomes water-soluble and is an effective phosphatic fertilizer for controlled release and is also resistant to precipitation with metal ions in soil. Such

water-soluble APP has been applied in agriculture since 1960s [15–18]. Tennessee Valley Authority (TVA) developed a process for water-soluble APP in 1967, by ammonifying the hot-process phosphoric acid in a tubular reactor [19]. While the introduction of water inhibited the polymerization. To prevent the water interference, MAP was then condensed in a stirring kneader or tank reactor with a dehydration agent like urea.

Nowadays, the researches on the synthesis of APP focuses on the average molecular weight, while the molecular weight distribution (MWD) has not attracted much attention. The MWD of oligomers/polymers can be characterized by the polydispersity index (PDI, defined as the ratio of weight-average molecular weight to number-average molecular weight ratio M_w/M_n). In fact, lots of studies from the agriculture field have reported that the release profile of APP with a large PDI can be more synchronous with the phosphorus demand of plants in their whole growth cycle [20]. Indeed, in soil only orthophosphate is plant-absorbable. For APP with wider MWD, the end groups of the long-chain portion can be swiftly hydrolyzed to orthophosphate, which serves in the seedling stage. Meanwhile the short-chain portion of APP releases phosphorus controllably, because pyrophosphate dimer

Abbreviations: MAP, ammonium phosphate; TSE, twin-screw extruder; APP, ammonium polyphosphate; PDI, polydispersity; MWD, molecular weight distributions; IC, ion chromatography; FT-IR, fourier transform infrared spectrum; XPS, X-ray photoelectron spectroscopy; SEM, scanning electron microscopy; AN, acyl-nitrogen content; R, reactive extent; LAPP, low-polydispersity ammonium polyphosphate; HAPP, high-polydispersity ammonium polyphosphate

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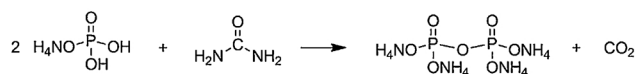
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Table 1
Composition of used monoammonium phosphate (MAP).

	Elementary components [wt%]									
	Total N	P ₂ O ₅	Fe ₂ O ₃	Al ₂ O ₃	MgO	CaO	MnO ₂	ZnO	F	SO ₄
MAP	11.52	51.66	0.01	0.01	1.18	0.49	0.13	Trace	0.31	8.58

Ammonium pyrophosphate formation



Further polycondensation

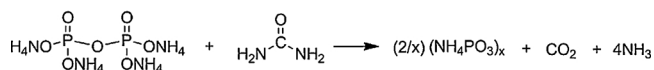


Fig. 1. Schemes showing the polycondensation of ammonium polyphosphate (APP) in the monoammonium phosphate (MAP)/Urea fusant.

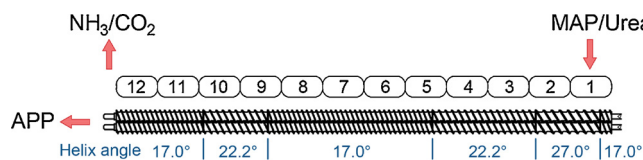


Fig. 2. Schematic screw configuration of the co-rotating twin-screw extruder which also shows the helix angles and the materials flow.

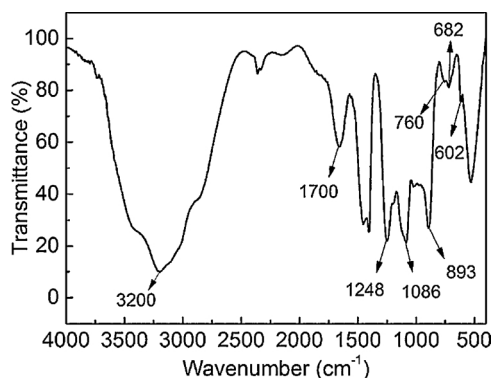


Fig. 3. FT-IR spectrum of the APP extrudate synthesized at a screw rotation speed of 150 rpm.

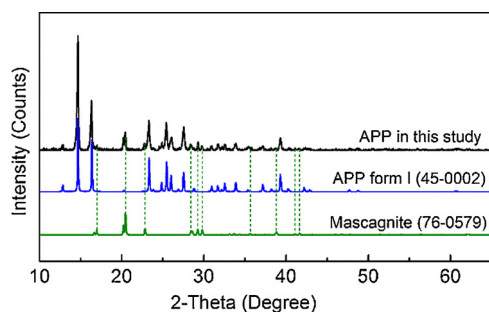


Fig. 4. XRD pattern of the APP extrudate synthesized at a screw rotation speed of 150 rpm, together with reference XRD patterns.

hydrolyzes slowly, to serve in the ripe period [1,21]. Therefore, future research about APP should focus on PDI control and the polymerization intensification. However, batch reactors can scarcely regulate PDI. Therefore, research on the MWD-controllable technology is of both

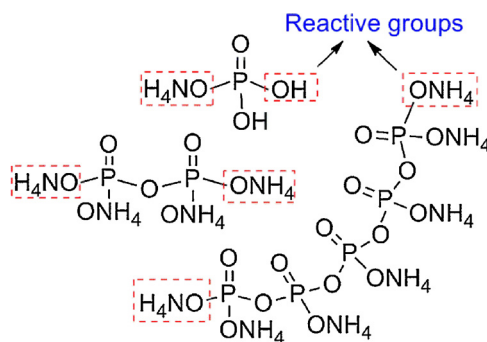


Fig. 5. Schemes that show the possible molecular structure of the synthesized APP, and the reactive groups are indicated by the dashed rectangles.

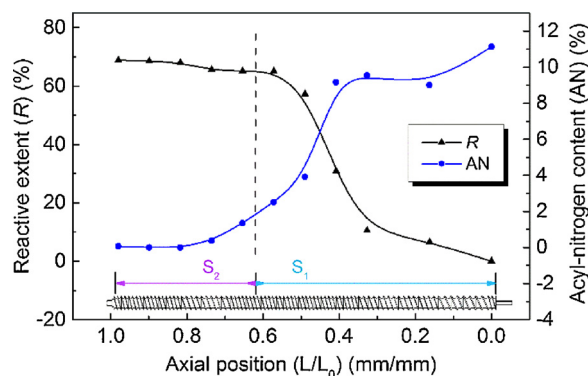


Fig. 6. Profile of the reactive extent (R) and the acyl-nitrogen content (AN) at a screw rotation speed of 150 rpm.

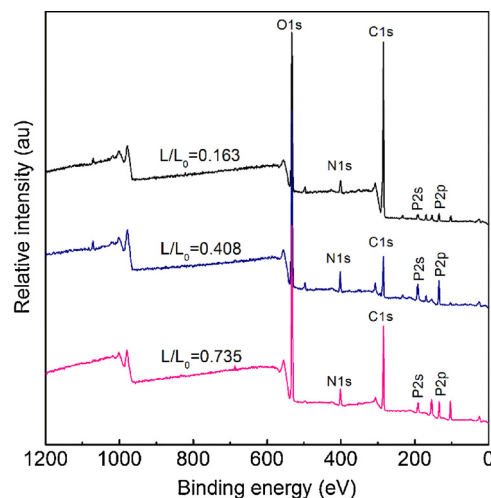


Fig. 7. Wide-scan XPS spectra of APP sampled along the screws (results produced at 150 rpm).

scientific and practical significance.

The twin-screw extruder (TSE) can satisfy the reactive extrusion of viscous melt formed by phosphate. As a continuous process, the TSE provides considerable mixing performance and heat transfer capacity [22–25], both of which make it possible to obtain APP in a limited polycondensation time [26,27]. The PDI can be controlled by adjusting the material rheology and reaction kinetics, and the TSE process enables flexibility of the temperature control and the screw design to achieve this controllable PDI [28,29].

In this work, a TSE was employed to shorten the polymerization time to several minutes. The polycondensation process of phosphate along the screws was investigated in detail. The possible reactive

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