

Preparation of Ammonium Polyphosphate Forms II and V and their Use as Flame-Retardants

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Abstract

Preparation of ammonium polyphosphate form II was made by heating a mixture of ammonium orthophosphate and urea at 280 to 300 °C under wet ammonia which was prepared by passing air through 3 to 5% ammonia water. Simple dry process of the preparation of ammonium polyphosphate form V was studied and the ammonium polyphosphate was prepared by heating a mixture of ammonium orthophosphate and urea at 330 to 340 °C under wet ammonia which was made by passing air through 15 to 29% aqueous ammonia. The ammonium polyphosphates had flame retardation effect to organic polymer materials and the materials containing the ammonium polyphosphates showed an oxygen index higher than 20.

INTRODUCTION

There are many kinds of ammonium ortho- and condensed phosphates. The phosphates are used as chemical fertilizers, food additives, flame retardants, dye-leveling agents etc.¹⁻³ The growing use of plastics and other flammable synthetic organic materials in construction, home furnishing, and various industrial applications is requiring polymer compatible, thermally stable, environmentally friendly, and cost-efficient flame retardants. There are many kinds of organic and inorganic flame retardants. Phosphorus-nitrogen compounds are thought to be effective flame retardants. Ammonium phosphates are well known compounds and are used as flame retardants. Water-soluble ammonium phosphates bleed easily when they are used as flame retardants for synthetic organic materials and the materials are exposed to humid air at a moderately high temperature. Bleeding of flame retardants drops down a material power. For example, electric resistance is lowered by bleeding. Accordingly, water-insoluble ammonium phosphates are required for organic materials to prevent bleeding. Among many ammonium phosphates, it is found that only ammonium polyphosphate (APP) forms II and V are hardly soluble in water. Therefore, the APPs are thought to be a good flame-retardant containing phosphorus and nitrogen. The preparation of APP forms II and V is not easy and requires a sophisticated process.⁴ It is very important to develop a new and simple process to prepare APP forms II and V from an easy reaction system. This paper describes simple and direct preparation processes of APP forms II and V from the system of ammonium orthophosphate-urea.

EXPERIMENTAL PROCEDURE

Preparation of APP Forms II and V

Preparation of APP forms II and V was made by heating a mixture of ammonium orthophosphate and urea at 250 to 300 °C and 330 to 340 °C, respectively, under wet ammonia which was made by passing air with a flow rate of 40 dm³/h through ammonia water. Ammonia water was exchanged to new one every 20 min to prevent a lowering of the concentration of ammonia water. Dry ammonia was also used for the preparation of APP form V. Dry ammonia was prepared by passing the wet ammonia through a column filled with tablets of potassium hydroxide. Experimental conditions of a mixing molar ratio of ammonium orthophosphate to urea, heating temperature, heating time, and a concentration of ammonia water to prepare wet ammonia were examined. The reaction was run in a glass tube placed in an electric furnace.

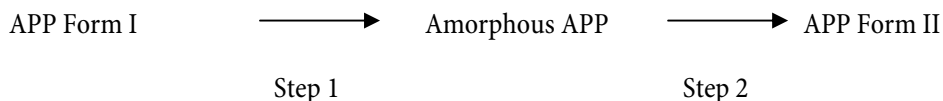
Analytical Methods

Determination of APP forms II and V in a product was made automatically using software installed in an XRD machine, Rigaku RAD-1B diffractometer. Scanning electron microscopic (SEM) observation of a sample was made using an Akashi DS-180 instrument. Particle size distribution was measured by the centrifugal sedimentation technique, with isobutyl alcohol as a sedimentation medium, using a Shimadzu SA-CP3 instrument. The determination of phosphorus and nitrogen was made by the molybdenum Blue method and the Kjeldahl technique, respectively. To examine flame-retardation effect of APP, an oxygen index of polyethylene and polypropylene blending with APP was measured.

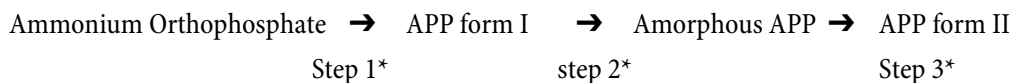
RESULTS AND DISCUSSION

Preparation of APP Form II

A previous paper pointed out that the transformation of APP form I to II was accelerated by the presence of amorphous APP. Formation of the amorphous APP from form I APP was able to be made by introducing a small amount of water vapor or by removing a small amount of ammonia.⁴ Accordingly, the amorphous APP is ammonium-deficient APP. From the result, present authors proposed the following transformation mechanism and established a simple and easy transformation reaction process of form I APP to form II on the basis of the consideration⁵:



An XRD study on the products prepared in this experiment gave a result that APP form I was formed at the initial step and the APP converted to form II as progress of the reaction. This phenomenon was observed in every reaction in this experiment and the following formation mechanism of APP form II can be given to this reaction system,



On the above basic consideration of the formation mechanism of APP form II, favorable reaction conditions of direct preparation of APP form II from the system of $(\text{NH}_4)_{3-n} \text{H}_n\text{PO}_4 \cdot \text{CO}(\text{NH}_2)_2$ ($n=0, 1, \text{ or } 2$) were examined.

Mixing Molar ratio

Diammonium hydrogenorthophosphate gave good results in preliminary experiments of the preparation of APP form II and a favorable mixing molar ratio of Diammonium hydrogenorthophosphate to urea was mainly examined under constant other reaction conditions (reaction temperature: 280°C, heating time: 3h, concentration of ammonia water to prepare wet ammonia: 3%) and the result is indicated in table 1. These reaction conditions except for the molar ratio gave a very good result for the conversion of form I APP to Form II. As shown in table 1, favorable mixing molar ratios of the orthophosphate to urea were 1/3 to 1/4.

Table 1: Dependence of Formation of APP Form II on Molar Ratio
(Heating temperature: 280°C, heating time: 3 h, concentration of ammonia water: 3%)

Molar ratio [(NH ₄) ₂ HPO ₄ :CO(NH ₂) ₂]	Content % of Form II APP
1:1	11
1:2	21
1:3	80
1:4	70
1:5	49

Heating Temperature and Time

Heating temperature and time to give a good result for the preparation of APP form II were tested under constant other reaction conditions. Mixing molar ratios of 1/3 and 1/4 were adopted according to the result obtained above. It was found that reaction temperatures of 280 to 300°C and reaction time longer than 3 h were favorable.

Concentration of Ammonia Water

The formation of APP form II from the system of $(\text{NH}_4)_2\text{HPO}_4 \cdot \text{CO}(\text{NH}_2)_2$ was very dependent on the concentration of ammonia water which was used to prepare wet ammonia. Ammonia water with the concentration of 3 to 5% gave a favorable result. This result is the same as that obtained in the transformation of form I APP to form II and this seems to support the reaction mechanism proposed above for this reaction system. Water vapor in wet ammonia is useful to form amorphous APP (step 2*). As mentioned above, the amorphous APP_s seem to be ammonium-deficient APP. As mentioned above, the amorphous APP seems to be ammonium-deficient APP and ammonia in the atmosphere is effective to form well crystallized form II APP from the amorphous APP (step 3*).

Preparation of APP Form V

Preparation of form V APP did not progress well under dry ammonia and form I APP was a main product. A reaction under wet ammonia which was obtained by passing air through ammonia water with a concentration lower than 15% did not give a good result and a product

containing a large amount of APP form I and/or amorphous APP was prepared. Under any reaction condition, a reaction temperature lower than 330°C did not give a favorable result and a product containing a large amount of APP form I was obtained, and a sample melted at a reaction temperature higher than 340°C. Accordingly, reaction temperatures of 330 and 340°C were adopted. Ammonium dihydrogenorthophosphate and diammonium hydrogenorthophosphate were used as a starting material, a mixture with a molar ratio (ammonium orthophosphate/urea) larger than 1/0.7 melted at 330 °C. Triammonium orthophosphate was employed as a starting material, a mixture with a molar ratio (ammonium orthophosphate/urea) larger than 1/0.8 melted at 330 °C. Therefore, mixtures with molar ratios smaller than these ratios were used for the preparation of APP form V. Under these reaction conditions, APP form V exhibiting two different XRD patterns was obtained. One of the XRD diagrams was a usual pattern of APP form V and the other one was found to be given by incomplete form V APP with N/P molar ratio smaller than unity, that is, ammonium deficient form V APP. In any reaction condition, the product containing usual or incomplete APP form V and/or form I was prepared.

Table 2: Content of APP form V in the products of $(\text{NH}_4)_3\text{PO}_4:\text{CO}(\text{NH}_2)_2$ system

Heating temp./°C		330		340	
Heating time/min.		30	45	30	45
Mixing molar ratio [$(\text{NH}_4)_3\text{PO}_4:\text{CO}(\text{NH}_2)_2$]	Concentration of NH_3 Water/%				
1:2.0	29	A	B	A	A
	15	B	A	A	A
1:1.5	29	B	B	A	A
	15	A	A	A	A
1:1.0	29	B	A	A	A
	15	A	A	A	A
1:0.9	29	A	A	A	A
	15	A	A	A	A

A: product with form V APP content higher than 90%, B: product with incomplete form V APP content higher than 90%.

The result of the reaction system of $(\text{NH}_4)_3\text{PO}_4:\text{CO}(\text{NH}_2)_2$ is given in Table 2. When ammonium dihydrogenorthophosphate was used as a starting material, form V APP was prepared well at 340 °C for 45 min under any other reaction conditions. Mixtures with the molar ratios of 1/1.0 to 1/0.8 gave a good result under any other reaction conditions. In case of a starting material of diammonium hydrogenorthophosphate, APP form V was prepared well with 15% of ammonia water. The molar ratios of 1/1.0 to 1/0.8 gave a good result even with 29% of ammonia water.

The preparation of APP form V under air was examined because the atmosphere of the above reaction system seemed to contain enough ammonia, but the reaction under air did not give a good result in any reaction condition.

Flame retardation effect of APP forms II and V

Flame retardation effect of APP forms II and V was examined by measuring an oxygen index of polymer materials containing APP and the result is listed in Table 3.

Table 3: Flame retardation effect of APP forms II and V

APP amount (%)	Oxygen index			
	PE		PP	
	APP form			
	II	V	II	V
0	17	17	17	17
5	20	20	20	25
10	21	21	22	27
15	21	21	23	28

PE and PP stand for polyethylene and polypropylene, respectively.

According to the result given in Table 3, APP forms II and V have flame retardation effect for PE and PP. Especially, form V APP has high flame retardation effect for PP and content of the APP of 10% gave enough effect. The effect of form II APP is not so high as form V APP, but the APP can be used as a flame retardant for PP when content of the APP is higher than 15%. APP indicated a better flame retardation effect to PP than PE. Particle size of a flame retardant affects on the effect and in this experiment, average particle sizes of 12.6 μm of form II APP and 3.0 μm of form V APP were used.

Furthermore, in a recent study, we found that these ammonium polyphosphates show a high electric conduction due probably to the high proton mobility. These results will be published elsewhere.

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