PREPARATION OF AMMONIUM POLYPHOSPHATE AND ITS APPLICATION TO FLAME RETARDANT

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Abstract: Ammonium polyphosphate forms II, V, and VI have been prepared by new preparation processes using ammonium orthophosphate, urea and/or phosphorus pentoxide as starting materials. The preparation processes are very useful for a large scale preparation in a factory. These crystal phases of APP showed flame retardant effect to organic polymer materials. The order of flame retardation effect among the phases was $V > II > VI \geq I$.

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1. INTRODUCTION

Many kinds of organic polymer materials have been used in various fields of construction, home furnishing, electric and electronic materials, vehicles, and other industrial applications, because of their excellent characteristics. One of the weak points of them is flammability. Growing use of organic polymer materials is requiring retardation of flammability. There are several ways to give retardation of flammability to organic polymer materials. One of the good ways is to add flame retardants to polymer materials. There are many kinds of flame retardants. P-N compounds are useful flame retardants to polymer materials.^{1, 2, 3, 4, 5)} Among many kinds of P-N compounds, ammonium polyphosphate (APP) is a useful compound for flame retardation of organic polymer materials when it is added to organic materials and the compound is environmentally friendly and a low cost substance.

APP has six crystal forms^{6, 7)} and form I has been prepared very easily, but other crystal forms are difficult to produce and sophisticated preparation processes are required to produce them. In this study, preparation processes of APP forms II, V, VI and flame retardation effect of the APP phases will be described.

2. EXPERIMENTAL PROCEDURES

2.1. Preparation of APP form I

APP form I was prepared by heating an equimolar mixture of ammonium dihydrogenorthophosphate and urea at 250 to 300 °C.

2.2. Preparation of APP form II

Preparation of form II APP was carried out by heating form I APP under alternate gas flow of wet ammonia and dry air at 270 to 290 °C, and also by heating a mixture of ammonium orthophosphate and

urea at 250 to 305 °C under wet ammonia. The wet ammonia was prepared by passing air through aqueous ammonia having various concentrations at flow rate of 40 dm³/h. Aqueous ammonia was changed every 20 min to prevent lowering of concentration of aqueous ammonia.

2.3. Preparation of APP form V

Preparation of form V APP was examined by heating the same mixture as that of the preparation of form II APP at 320 to 350 °C under wet ammonia which was prepared by passing purchased ammonia gas through 29% of aqueous ammonia.

2.4. Preparation of APP form VI

Form VI APP was tried to prepare by heating a mixture of phosphorus pentoxide and urea at 250 to 290 °C under air and wet ammonia which was obtained by passing air through aqueous ammonia having various concentrations.

2.5. Analytical methods

An X-ray diffraction analysis of a powder sample was employed to examine the production of APP forms I, II, V, and VI. The content (%) of APP phase in a product was calculated automatically by the calculation program installed in a computer that is attached to the XRD instrument. The standard XRD diagrams of APP forms I to VI are shown in Fig. 1. Scanning electron microscopic (SEM) observation of an APP sample was made to check particle size and shape of the sample. Particle size distribution was measured by a centrifugal sedimentation technique, using isobutyl alcohol as a sedimentation medium. Determination of phosphorus and nitrogen was achieved by the Molybdenum Blue method and Kjeldahl technique, respectively. Flame retardation effect of APP was tested with a sample which was

prepared by adding APP to organic polymer materials by using a mixing roller. The oxygen-index technique was employed to study flame retardation effect of APP.

3. RESULTS AND DISCUSSION

3.1. Preparation of form II APP

3.1.1. Transformation of APP form I to II ^{8, 9, 10)}

Shen and his coworkers showed that the transformation of APP form I to II was accelerated by the presence of an amorphous phase and the amorphous phase was produced by removing a small amount of ammonia of APP or by introducing a small amount of water vapor into the reaction system.⁶⁾ Accordingly, the phase transition of form I to II is thought to be progressed by the following process:

Stage 1 is accelerated by removing a small amount of ammonia or by introducing a small amount of water vapor as they wrote. Accordingly, amorphous APP produced by the process would be ammonium-deficient APP. When the amorphous APP is crystallized to APP form II, ammonia would be required to produce a well crystallized form II APP. From the basic consideration, the preparation of form II APP according to the phase transition of APP form I was examined under several atmospheric conditions. Heating temperature is also very important factor for the phase transition.

The results of phase transition of APP form I to II in dry air, dry ammonia, and wet ammonia are listed in Table 1. From the results, it was impossible to achieve 100% of phase transition of APP form I to II. Among the reaction conditions, dry air and wet ammonia gave a fairly good result.

FIGURE 1 XRD diagrams of APP forms I to VI

TABLE 1 Phase transition of APP form I to II

Atmosphere	Reaction temp. (°C)	Content (%) of APP form II
Dry air	250	62
	260	65
Dry ammonia	250	11
	260	11
	270	11
	280	12
	290	12
	300	15
Wet ammonia (5% aqueous ammonia)	250	13
	260	16
	270	18
	280	32
	290	50
	300	86

Therefore, alternate gas flow of dry air and wet ammonia was examined and the condition of alternate-exchanging gas flow of wet ammonia and dry air is indicated in Table 2. XRD diagrams of the products which were obtained according to the reaction condition in Table 2 and at 270 °C using 3% of aqueous ammonia are indicated in Fig. 2. The phase transition of APP form I to II under the reaction

conditions listed in Table 2 was examined and the results shown in Table 3 were obtained.

The results in Table 3 show that the 100% of phase transition of APP form I to II was achieved under alternate gas-flow condition of No. 2 to 4, reaction temperature of 270 to 290 °C and concentration of aqueous ammonia of 3 to 5%. Concentration of aqueous ammonia less than 3% did

TABLE 2 Condition of alternate gas flow

Condition No.	Exchanging condition of flow gas (min)		Total reaction time (min)
	Wet NH ₃	Dry air	
1	3	7	33
2	6	14	66
3	9	21	99
4	12	28	132

FIGURE 2 XRD diagrams of the products of the phase transition of APP form I to II at 270 °C using 3% aqueous ammonia

FIGURE 3 SEM photographs of APP forms I and II

TABLE 3 Phase transition of APP form I to II under various reaction conditions

Concentration of aqueous ammonia (%)	Reaction temp. (°C)	Content (%) of APP form II			
		Condition No.			
		1	2	3	4
8	270	71	93	94	88
	280	59	77	87	94
	290	64	91	96	98
	300	54	86	95	melt
	310	80	98	89	melt
5	270	28	65	84	66
	280	71	71	96	89
	290	78	90	100	95
	300	71	92	97	melt
	310	89	98	88	melt
3	270	77	83	89	100
	280	92	100	100	100
	290	80	100	100	melt
	300	74	melt	melt	melt
	310	86	melt	melt	melt

not give a good phase transition of APP form I to II at any reaction temperature. SEM photographs of APP forms I and II are shown in Fig. 3. APP form I showed a small particle size and form II exhibited a large crystal shape. The all products showed P/N ratio of 0.93 to 1.06 and the ratios are almost equal to the standard ratio (1.0) of APP.

3.1.2. Preparation of APP form II from the system of ammonium orthophosphate-urea^{9, 10)}

Preparation of form II APP has usually been done by using phosphorus pentaoxide in factory scale, but phosphorus pentaoxide is very reactive with

moisture in the air and, therefore, treatment in large scale is not easy in a production field, and the substance is also harmful to human body. Accordingly, the direct preparation of form II APP from an easy reaction system to human body and also easy to a large scale production in a factory was examined by using the system of ammonium orthophosphate-urea. The reaction system is environmentally friendly. The direct preparation of form II APP from the system was successfully achieved in this experiment. A part of the results is indicated in Table 4.

TABLE 4 Content of form II APP in the thermal products of the reaction system of ammonium orthophosphate-urea

Mixing molar ratio [(NH ₄) ₂ HPO ₄ :CO(NH ₂) ₂]							
		1:3		1:2		1:1	
Reaction time (min)		30	60	30	60	30	60
Reaction temp. (°C)							
270		△	○	△	△	×	△
280		◎	◎	△	◎	×	×
290		◎	◎	◎	◎	△	○
300		◎	◎	◎	◎	△	◎
305		◎	◎	◎	◎	△	◎

APP content: ×;0~50%, △;50~70%,○;70~90%, ◎;higher than 90%.

There are three kinds of ammonium orthophosphates of triammonium orthophosphate, diammonium hydrogenorthophosphate and ammonium dihydrogenorthophosphate. Among them, diammonium hydrogenorthophosphate gave the best result. Mixing molar ratio of diammonium hydrogenorthophosphate and urea, reaction

temperature, atmospheric condition were examined to find a good preparation result of APP form II. As for atmospheric condition, wet ammonia which was obtained by passing air through 3 to 5% of aqueous ammonia gave the best result. According to the results in Table 4, reaction temperature of 280 to 305 °C and mixing molar ratio of 1:3 to 1:2 seemed to be

the best reaction condition to prepare form II APP from the reaction system. Under the reaction condition, form II APP can be prepared in 30 to 60 min.

P/N molar ratios of the products were 0.97 to 1.04 and the values were close to the standard P/N ratio (1.0) of APP.

3.2. Preparation of form V APP ^{11, 12, 13)}

Direct preparation of form V APP from the system of ammonium orthophosphate and urea was examined. Among the three ammonium

orthophosphates, diammonium hydrogenorthophosphate gave the best result. Reaction conditions of mixing molar ratio of the ammonium orthophosphate and urea, atmosphere, heating temperature, and heating time were tested to obtain the best reaction condition of the preparation of form V APP. The results are given in Table 5. Particle size and shape of APP form V were almost the same as those of APP form I. As it can be seen from the results in Table 5, mixing molar ratio of 1:4 to 1:5, reaction temperature of 340 to 350 °C, and reaction time of 105 to 120 min gave an excellent result to prepare APP form V from

TABLE 5 Content of form V APP in the product

Mixing molar ratio [(NH ₄) ₂ PO ₄ :CO(NH ₂) ₂]	1:3		1:4		1:5	
Reaction temp. (°C)	340	350	340	350	340	350
Reaction time (min)						
30	×	△	×	△	×	○
60	×	○	△	○	○	◎
75	×	○	○	○	○	◎
90	△	○	○	◎	○	◎
105	△	○	◎	◎	◎	◎
120	△	○	◎	◎	◎	◎

The same marks as those in Table 4 are used.

the reaction system of (NH₄)₂HPO₄-CO(NH₂)₂. Atmospheric condition under wet ammonia which was prepared by passing ammonia gas through 29% of aqueous ammonia gave the best result.

P/N ratios of the products having an APP form-V content higher than 90% were 0.96 to 1.03 and the ratios were very close to the standard P/N

molar ratio (1.0) of APP.

3.3. Preparation of APP form VI

Direct preparation of form VI APP was tried with the system of P₂O₅-CO(NH₂)₂. Reaction conditions of mixing molar ratio of phosphorus pentoxide to urea, reaction temperature, and

atmospheric condition were studied and the results are listed in Table 6. Particle size and shape of form VI APP were almost the same as those of APP form I. According to the results in Table 6, preferable reaction condition to prepare form VI APP from the system seems to be the molar ratio of 1.0 to 1.5, reaction temperature of 250 °C, atmosphere under wet ammonia that is prepared by passing air through

29% of aqueous ammonia, and reaction time of 60 min. In the air, mixing molar ratio of 1:3.0 and reaction temperature of 270 to 290 °C gave an excellent result.

P/N molar ratios of the products having an APP form-VI content higher than 90% were 0.94 to 0.99 and were very close to the standard ratio (1.0) of APP.

TABLE 6 Content of form VI APP in thermal product

Reaction temp.(°C)		210	230	250	270	290
Conc. (%) of aqueous ammonia	Mixing molar ratio [P ₂ O ₅ :CO(NH ₂) ₂]					
10	1:0.5	melt	melt	melt	melt	melt
	1:1.0	△	△	melt	melt	melt
	1:1.5	△	△	△	△	△
20	1:0.5	△	△	melt	melt	melt
	1:1.0	△	△	○	melt	melt
	1:1.5	×	×	⊙	△	△
29	1:0.5	△	△	melt	melt	melt
	1:1.0	△	△	○	△	melt
	1:1.5	×	×	⊙	△	△
In the air	1:3.0	△	△	○	⊙	⊙

The same marks as those in Table 4 are used.

4. FLAME RETARDATION EFFECT OF APP

Oxygen indices of organic polymer materials of polyethylene (PE) and polypropylene (PP) containing APP are shown in Table 7. From the results in Table 7, all kinds of APP having forms I, II, V, and VI are effective to the flame retardation on organic polymer materials. The flame retardation

effect of APP to organic polymer materials seemed to be dependent on the sort of organic polymer materials and the flame retardation effect of APP was larger to PP than PE. The order of the effectiveness looks like V>II>VI≥I. It is very important factor to have a high dispersibility for flame retardants to obtain a high retardation effect. Dispersibility of flame retardants is very dependent on particle size of them.

Average particle size of APP used in this experiment was 3.6 μm of APP-I, 12.6 μm of APP-II, 3.0 μm of APP-V, and 3.4 μm of APP-VI. APP phases II and V have a higher thermal stability than APP phases I and VI. Accordingly, APP phases II and V show a higher flame retardation effect than APP phases I and VI, because APP phases I and VI decompose at a

temperature lower than thermal decomposition temperature of PE and PP. The flame retardation effect of APP phase V is larger than II, because the particle size of APP phase V is smaller than that of APP phase II and therefore, APP phase V has a higher dispersibility than phase II.

TABLE 7 Oxygen indices of organic polymer materials containing APP

	Oxygen index							
	PE				PP			
	APP form							
APP amount (%)	I	II	V	VI	I	II	V	VI
0	17	17	17	17	17	17	17	17
5	18	20	20	19	19	20	25	20
10	20	21	21	20	21	22	27	21
15	20	21	21	21	22	25	28	23

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