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Synthesis and Characterization of Melamine Polyphosphate and its Flame Retardance

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ABSTRACT

The halogen free flame retardant additives always attract scientists for the research and applications due to its superior characteristics compared to the halogen based ones. Melamine polyphosphate (MPP) which contain both nitrogen and phosphorus can be prepared by two step method, the precipitation of melamine phosphate (MP) in aqueous mother liquor at room temperature, and the heat treatment of the intermediates into MPP at 340°C for 8 to 10 h. The MPP can be used as the flame retardant additives for various types of flammable materials such as paper, both as coatings and the blends or the epoxy composite. The flammable tests of the show that the prepared specimens suppresses the flame when the content of MPP is higher than 5%, and the grades of HB and V-1 to V-0, the limiting oxygen indices of 32% to 35% are obtained.

Introduction

In recent years, the number of the fire, and the damage caused by the fire tends to increase sharply and the fire protection for people and properties from fire becomes imperative in the design and preparation of materials together with the personal fire protection equipments for citizens or the fire extinguishers in the buildings. Another way to deal with the fire is the use of flame retardants added to the materials to help the fire difficult to start or to spread at the rate much slower, so that, someone may have enough time to escape the fire and save their lives. This approach is useful and can be applied for the previously established materials as well as the new ones [1].

Several kinds of flame retardants have been studied and applied in many types of materials. The study on halogen-free flame retardants, or toxic-free ingredients is the subject of intensive investigations and gets a great deal of intention in both research and applications [1-2].

Among these types of flame retardants, melamine polyphosphates are widely applied in preparation of flame-retarded materials because of high content of nitrogen and phosphorus, both of which contribute to the effective parts of flame retardants [1]. MPP has 6 nitrogen unit on each basic formula unit so the when decomposed, MPPs can form a lot of nonflammable gases, while the phosphorus play the role of the dehydrating agent for the materials that may accelerate the formation of char and insulate the condensed phases, or materials inside from burning media [3].

MPP is compatible to various types of materials such as paper, epoxy resin composite, polyamide, and synthetic polymers. The solubility of MPP is rather low,

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so it can be applied widely as the additive in these materials [4].

MPP are mainly prepared by the interaction of melamine and phosphoric acid, and then the intermediates are condensened at elevated temperature. In most researches, the slurry of intermediates from the interaction of melamine and phosphoric acid is dried out directly, so that lot of water are required to be evaporated, that will consume lot of energy and time for the preparation of MPP. In this work we present the synthesis and characterization of the melamine polyphosphate by two step method, in which, the preparation of melamine phosphate is carried our in recycling aqueous mother liquor, and the polycondensation of MP is done at elevated temperature. The prepared MPP can be used as the flame retardant additive for coatings on paper, paper blend or epoxy resin composite.

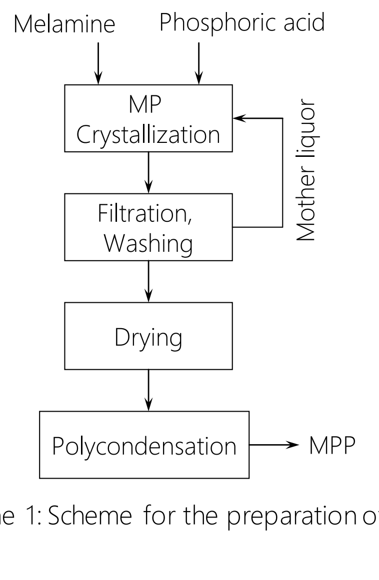
State the background and mention clearly the objective of the present work, avoiding a detailed literature survey or a summary of the results (Segoe UI Light 10p, single line spacing, before spacing 0pt, after spacing 6pt).

Experimental

Reagents

Phosphoric acid technical grade (85.44% H_3PO_4, Duc Giang Chemicals Group) and melamine (99.5% $C_3H_6N_6$, Xilong, China) are used as received without any further purification.

Preparation procedure



Scheme 1: Scheme for the preparation of MPP

The preparation of melamine polyphosphate (MPP) is illustrated in scheme 1.

Phosphoric acid (100 g) is added with mother liquor from previous experiment (~200 g) at room temperature, melamine (110 g, the molar ratio of melamine to phosphoric acid is 1:1) is added to the formed solution in small portions, and the slurry is stirred vigorously to favor the crystallization of melamine phosphate (MP). After aging in the solution for about 4 h, the solid is filtered and washed with water, then dry at 100 °C to constant weight (~195 g). The yield of MP is almost quantitative. The dry solid is calcined for the polycondensation of phosphate species to form melamine polyphosphate (MPP), at various temperature profiles. The mother liquor is recycled for the next experiments. The yield of MPP ranges from 85 to 95% based on phosphoric acid, depending on the temperature and heating duration.

Analytical and characterization methods

The nitrogen content in the MPP is determined by Kjeldahl method; and the P_2O_5 content is determined by the vanadomolybdophosphoric acid colorimetric method on a Thermo Scientific SPECTRONIC 20D+ spectrophotometer at the wavelength of 470 nm.

The thermogravimetric analysis of the synthesis is measured on Setaram Labsys Evo S60/58988 thermal analyzer. The MPP sample is put on an alumina crucible and heated from room temperature to 700 °C at the heating rate of 10 °C/ min, under flow of air, with the flow-rate of 20 mL/ min. The weight and heat flow of sample of sample is recorded during heat treatment.

A small amount of the product is mixed with KBr, pelletized, and measured in transmission mode with the blank sample of pure KBr, on a Jasco FTIR-4200 series spectrophotometer over the range 4000–400 cm^{-1} with the spectral resolution of 4 cm^{-1}.

Crystal structure of the phases formed has been measured with powder X-ray diffraction on a D8 Advance Bruker diffractometer Cu anode, λ(CuKα) = 1.54059 Å, at room temperature with the two theta angle from 5° to 80° on continuous mode with scanning speed of 5 °/ min, recorded at interval of each 0.02°.

The flame retardant effect of the melamine polyphosphate has been done by mixing a certain amount of the MPP and commercial alkyd paint (Dai Bang paint) then coats on paper. The standards UL94:2010 has been used for evaluation of flammability of the materials on both vertical and horizontal positions [5].

The Limiting Oxygen Index (LOI) values were measured according to the ASTM D2863 on an ATLAS LOI instrument. The MPP is added to the paint and coated on a sheet of paper. The size of the sheet was 130 × 13 × 1.2 mm^3 aligned vertically in the center of the tube of the LOI equipment.

For determination of MPP solubility in water, a small amount (~ 1 g) of the prepared MPP is dispersed in 100 mL of water at 25 °C. After stirring for about 15 min, the suspension is centrifuged at 4000 v/ min, then 20 mL of supernatant is withdrawn and evaporated at 105 °C, to constant weight. The weight of soluble product is assigned for the one of MPP.

Results and discussion

Composition of the synthesized product

The chemical composition of the synthesized melamine polyphosphate has been examined by determination of phosphorus and ammonium nitrogen content in the sample by chemical analysis. The results show that the contents of 34.1 and 37.2.0% by weight, for P_2O_5 and nitrogen, respectively. The molar ratio of nitrogen to phosphorus is 5.51:1 which is very close to the one of 6:1 for MPP.

The dispersion of 0.1 g of MPP in 100 mL is stirred for 30 min then centrifuged at 4000 rpm; the supernatant has the pH value of 6.22 at 25 °C, which is typical value for the solution of MPP. The pH value of the solution indicates that the solubility of the MPP is very low and the free acid content in the synthesis product is also small.

Influence of calcining duration and temperature to the formation of MPP and its LOI index

The preparation of MPP in this work is done with two steps. The precipitation of MP is performed by the interaction of melamine and phosphoric acid in aqueous mother liquor. This process is quite straightforward and fast whereas the polycondensation of MP to form MPP at elevated temperature is rather complicated.

The heating duration at certain temperatures will have great impact on the MPP features such as polymerization degree or its LOI index. When the degree of polymerization is increased the solubility is normally degreased. Hence, the results of MPP solubility in water will give some information on the condensation of the product. The water solubility of MPP and LOI of the coat on paper sheet is given in Figure 1a, and the influence of temperature on the LOI index is shown in Figure 1b.

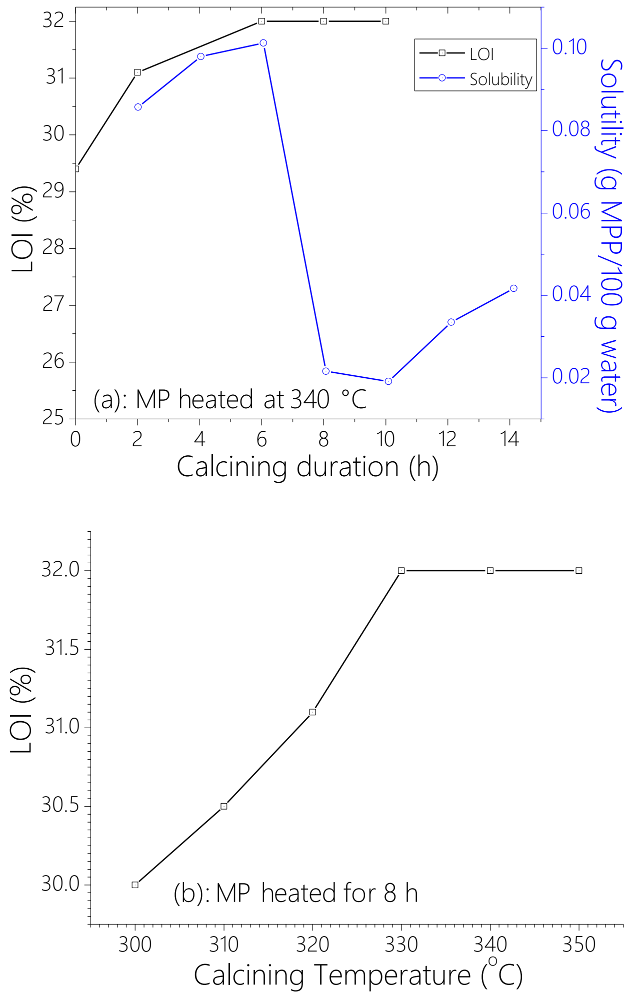


Figure 1: The influence calcination duration (a); and the calcining temperature (b), on the solubility of MPP in water and the LOI index of the MPP-alkyd paint coated paper

The data from Figure 1a show that when samples are held for long time from 2 to 6 h, the solubility of the products tend to increase from 0.0857 to 0.1013 g/ 100 g of water and the LOI from 29.4 to 32%. However, when the samples are held for 8 to 10 h, the solubility decrease sharply, the values of 0.0216 and 0.0191 g/100 g of water are obtained. The low solubility is probably due to the condensation of MP into MPP as indicated by the steady value of LOI as 32%. For 12 to 14 hours of heating, the solubility of MPP products seems to increase, that may be ascribed to the decomposition of the MPP. So that, when the samples are heated at 340

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°C, the suitable heating duration will be from 8 to 10 hours.

The heating temperature also influence to the condensation of MPP, when the temperature form 300 to 320 °C in 8 h, the LOI increased from 30 to 31%, and when the temperature is heated to 330 to 350 °C, the LOI is stable at 32 %.

The crystal phase of the prepared MPP

The phase of the prepared MPP can be studied by the X-ray diffraction measurement. The XRD pattern of the prepared MPP (polycondensation at 340 °C, for 8h) is given in Figure 2

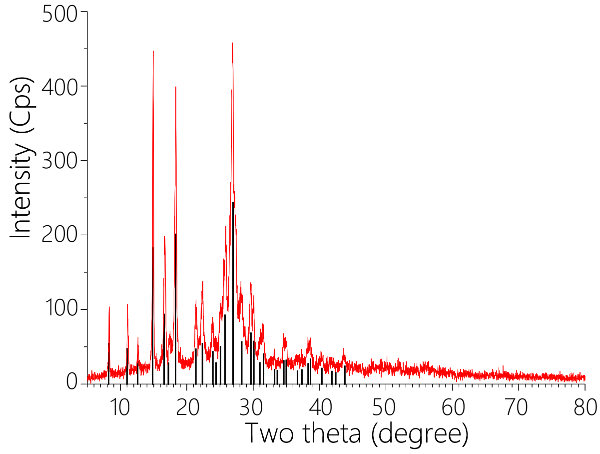

Figure 2: The powder pattern of the prepared MPP (red curve) and the adapted data from Zhow (represented as black bars) [6]

The results of the XRD in the Figure 2 confirmed that the phase of the synthesized product is similar to the one of MPP. The observed peaks of the sample (red curve) are in good agreement with the ones in literature (represented as black bars) [6].

The Figure 2 also shows that there are no additional peaks detected from XRD data (from 5 to 45°). It means that the synthesized product does not contain any raw materials such as melamine or any intermediates like melamine phosphate or melamine pyrophosphate. It is probably that most melamine phosphate has been transformed into expected MPP in the heat treatment step.

Themogravimetric analysis of the synthesized product

One of the most important properties of a flame retardant is its thermal decomposition at high temperature because it relates to the endothermic reactions and gases evolved (if any) will play the role of diluents for radicals, oxygen or the barrier for the diffusion of gases to surface of materials. The decomposition temperature is critical for the effectiveness of a flame retardant. The thermogravimetric patterns (TG/DTA) of the synthesized product (polycondensation at 340 °C, for 8h) recorded from room temperature to 700 °C under a flow of air, is given in Figure 3.

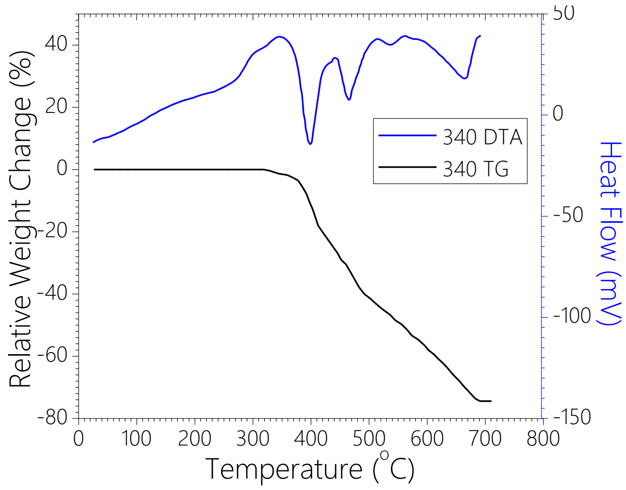

Figure 3: Thermogravimetric analysis (TG, lower curve) and differential thermal analysis (DTA, upper curve) of the as-synthesized sample

Figure 3 shows that the sample is stable when heated from room temperature to about 300 °C. The weight loss from 300 to 700 °C can be divided into different steps which related to the thermal degradation of MPP in the specimen. The thermal decomposition of 27.71% form room temperature to 448 °C corresponding to the thermal decomposition of MPP into melam ultraphosphate, melem or melon polyphosphate, ammonium polyphosphate, melamine, ammonia, water. On further heating to 700 °C, the weight loss about 74% is ascribed to the elimination of water, P_4O_{10}, and the intermediates.

The infra-red analysis of the synthesized product

The presence of certain functional groups in the product can be further studied with infrared spectroscopy (IR). The IR spectrum of the product is shown in Figure 4.

Figure 4 shows that the IR results are very similar to those of MPP observed previously, and the assignment of the bands can be summarized as: [4]

The band at 3360 cm^{-1} is the stretching vibration of N-H bonds, the band at 3154 and 2852 cm^{-1} are the

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vibration absorption of NH_3^+ and NH_3 group respectively. The band at 1682 and 1512 cm^{-1} are the deformation vibration of N-H bond and the triazine ring in the MPP.

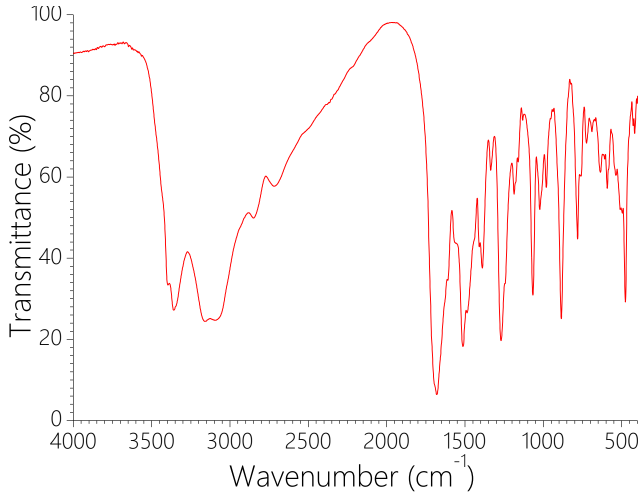

Figure 4: The Fourier transformation infrared spectrum of the synthesized MPP

Phosphate group bands are at 1271 cm^{-1} for free P=O group. The vibration of P–O–P group broad band is at 884 cm^{-1} and the absorption is at 781 cm^{-1}. Hence, the FTIR data of the prepare sample confirm the presence of functional groups in melamine and the polyphosphate parts in the MPP.

The flame retardation effect of the synthesized MPP

The influence of MPP content on the flammability of an alkyd paint coated on paper and its LOI index is shown in Table 1.

Table 1: The influence of MPP content in an alkyd paint on the flame retardation of the coating

MPP content, % bw	Vertical	Horizontal	LOI (%)
0	F[(a)]	F	29.4
5	F	HB	30.0
10	V-1	HB	31.5
15	V-1	HB	32.0
20	V-0	HB	32.0
25	V-0	HB	35.0

[(a)] F: Fail to UL-94 test.

The flammability results show that, when MPP is not added to the alkyd paint – paper system, the specimens are failed to the UL94. When MPP is added the flame retardant effects is increased.

With the specimens contain 5 to 25% MPP, test specimens do not maintain the flame or spread of the flame when burned on the horizontal position and all get the HB grade even at low content of MPP e.g. 5%. The HB grade indicates that burning rate is less than 76 mm/min for the horizontal specimens. When the torch is turned off, the flame is also been extinguished.

On the vertical position tests, the flame retardant effects of MPP are increased with its content in the system. At 5% of MPP in the paint, the flame retardant of coating is still not effective, but the LOI is 30%, somewhat higher than the bare samples. When MPP content increased from 10 to 15%, the grade of V-1 is obtained, the specimens are not burned for longer 30 seconds in each test, and the LOI is 31.5 and 32%, respectively.

When the MPP content is 20 to 25%, all specimens get the V-0 grade and the burning stops within 10 seconds on a vertical specimen test. The corresponding LOI indices are 32 and 35%. The materials with high value of LOI will be protected effectively from fire because it is difficult to be burned out.

When the content of MPP exceeds 25 %, the paint slurry becomes highly viscous that make the preparation of sample somewhat difficult. Thus, the suitable content of MPP in the paint in the range from 20 to 25 % will give the good results.

In addition to use as the protective layer of the flammable materials, the MPP is also a very effective flame retardant additive when it is added directly to the materials such as paper, sawdust, wood powder… The addition of 5% MPP in paper power before shelling gives the HB grade on horizontal tests and V-0 grade on the vertical test position. It means that when the MPP is mixed with the paper, its flame retardancy becomes more effective than the coating on the surface of samples.

The preliminary survey on using MPP in epoxy composite also obtains good results, with 5% MPP in epoxy, the composite gets the HB and V-1 grade on the tests. This may open the great possibility in applications of MPP as the flame retardant additive for the widely used coating materials.

Conclusion

The synthesis and characterization of the melamine polyphosphate by two step method, the precipitation of melamine phosphate at room temperature in aqueous mother liquor, and then polycondensation of the intermediate into melamine polyphosphate at elevated temperature have been successfully investigated. The heat treatment of at 330 – 340 °C, for 8 – 10 h will give the MPP with low solubility and good flame retardant behaviors. The applications of the as synthesized MPP as additive for an alkyd paint coating give HB and V-1 to V-0 grade when MPP content is higher than 10%. The addition of MPP into paper powder before shelling also gives the grade of HB and V-0 even at 5% of MPP in the mixture. On the epoxy composite, the MPP also give the HB and V-1 grade in the flammability tests.

The chemical composition analysis results, XRD data, IR spectrum confirm that the synthesized product is melamine polyphosphate, $H(C_3H_6N_6HPO_3)_nOH$ as expected phase.

Acknowledgments

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