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Preparation and characterization of Ammonium Polyphosphate/Diatomite Composite flame-retardant fillers

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ABSTRACT

Ammonium Polyphosphate (APP) has been known as an effective flame retardant, but its dispersion in some materials is very poor so it is necessary to incoporate APP with some suitable additives. This study refers to the preparation of APP/Diatomite (DIA) composite flame-retardant fillers. The materials were prepared by two methods: by adding diatomie powder to the mixture during the preparation of APP or by adding diatomite powder to the suspension of very fine solid APP particals in water. The samples were put into separate porcelain bowls and dried at 210°C for 3 hours. The structure and morphology of the material was identified using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) techniques. Thermogravimetric (TG) analysis was performed to evaluate the thermal degradation behaviors of the material.

Introduction

Ammonium polyphosphate, $NH_4(PO_4)n$, is an inorganic flame retardant because it built mainly from phosphorous and nitrogen, it decomposed by heat into phosphoric acid and ammonia. Phosphoric acid acts an acid catalyst in the dehydration of carbon bond of poly alcoholic materials, such as cellulose in wood or paper and the hydrocarbons chain in the polymeric materials and finally released CO_2 gas which helps to dilute the oxygen and inhibit the spread of flame. While nitrogen is an inert gas works as inhibitor to spread the flame. Several trials (3-5) were done to improve the flame retardant of APP. In previous works (1,2), the authors synthesized ammonium polyphosphate (APP) and used it as flame retardant for paper. In order to increase the flame retardant effect of APP, many studies have focused on increasing the surface area of the material by reducing particle size or dispersing APP particles on suitable fillers.

In general, the modification of APP includes the methods of preparation to produce a high surface area particles or adding some modifier materials, organic or inorganic. Recently a system of ammonium polyphosphate/ Diatomite composite fillers was used as flame retardant for paper by Sha et al (3).

Experimental

Materials

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This work used following chemicals: Laboratory reagent-grade phosphoric acid (Bioreagent, 85%), granular urea 46.3%N (industrial grade) and diatomite (DE) containing 80.26% SiO_2, 5.64% Al_2O_3, 1.57% Fe_2O_3, 6.65% CaO, and others 5.88%.

Methods of preparation

Preparation of APP

The desired amount of phosphoric acid was poured into a reaction vessel and heated to 130°C in an oil bath. The required amount of urea was added slowly into the flask while the mixture was stirred continuosly and the temperature was kepted at 130°C. After finishing the addition of urea to the reaction vessel, the temperature was raised up to 140°C with the rate of 2-3°C/min and kept at 140°C for 15 minutes. After that the product was poured onto a ceramic cup and dried at 200°C for 2 hours in an electric dryer in air environment to solidify. The solid product was ground and sieved into a fine powder (sized at around 80µm) and was stored in sealed plastic bags for later uses.

Preparation of APP/Diatomite

I - Type APP/DIA: 5g APP powder and 100 mL distilled water were added to a 250-mL beaker. The mixture was heated to boiling and became a clarified solution under magnetic stirring for 2 h to obtain APP-1. Datomite powder (2.5 g) was then added to the beaker under magnetic stirring and the mixture was heated to boiling and was held for 1 h to obtain mud mixture. The mixture was then poured into a ceramic cup and dried in 105°C in 24h. Solid products are pulverized to obtain an additive mixture 1.

II - Type APP/DIA: During APP synthesis from phosphoric and urea acid solutions, 2.50g of powder diatomite was added after urea was completely filled with phosphoric acid solution at 130°C. Then the mixture was stirred at 130°C for 1 h to obtain mud mixture. At the end of the process, the product is poured into a ceramic bowl and dried at 200°C for 24 hours. Solid products are pulverized to obtain an additive mixture 2.

Characterization of the samples

The prepared APP was characterized previously by using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis, (TG/DTA) scanning electron microscope (SEM). The results of the characterization show that the prepared APP is crystalline in form I and have particle sizes of 5-65 nm. The same techniques were used to characterize the APP/diatomite mixture.

All materials and methods used should be clearly mentioned .

Results and discussion

Ammonium Polyphosphate was synthesized from phosphoric acid and urea as following reaction:

$$nH_3PO_4 + (n-1)CO(NH_2)_2 \rightarrow (NH_4)_{n+2}P_nO_{3n+1} + (n-4)NH_3 + (n-1)CO_2$$

The optimum condition for the reaction has been set up (1-2).

- The mol ratio H_3PO_4/urea = 1/1.8
- Reaction temperature: 140°C
- Reaction time: 15 minute
- Drying temperature: 200°C
- Drying time: 3 hours

Characterization and linking in APP

To specify the crystalline form of the prepared ammonium polyphosphate, the x-ray patterns was performed. Also, to study the crystalline changes by adding diatomite, x-ray spectra were recorded in Fig 1. From the x-ray patterns of pure APP an appearance of a maximum intensity at 2Θ = 14-18 was recorded. The appearance of this peak indicates that the prepared APP is in form I. The special APP structure was determined by X-ray diffraction method on XRD - D8 ADVANCE - BRUKER AXS using CuKa radiation (λCuKa = 1.5148 Å, 40 kV, 30 mA) with 2θ interval 5° to 60°. The results are shown in figure 1.

The IR curve for APP shows different absorption peaks at 760, 682, 597, 3200 and 1256 cm^{-1} corrosponding to the formation of APP-I. Results from figure 1 also shown that the absorption peak at 3179.6 cm^{-1} is thought to be characteristic of the NH_4^+ group, the absorption peak at 1400.1 cm^{-1} is the absorption of NH^+. The peaks in the range of 1100 - 850 cm^{-1} are said to be fluctuating in the P-O group, the peaks in the range of 1350 - 1100 cm^{-1} are considered to be oscillations of the group P = O, all of these peaks are typical bands of polyphosphate chains and is not related to the crystal form (2). Composite APP with peaks at 760 cm^{-1}, 682 cm^{-1} and 600 cm^{-1}. The absorption peak at 760 cm^{-1} is thought to be the oscillation of O = P-O, the peaks at 682 cm^{-1} and 600 cm^{-1} are the oscillations of the O-H and O-P-O groups. These absorption peaks represent the absorption peaks of APP-I (2), from which we can confirm that the composite APP product is APP-I. The IR chart of APP is shown figure 1.

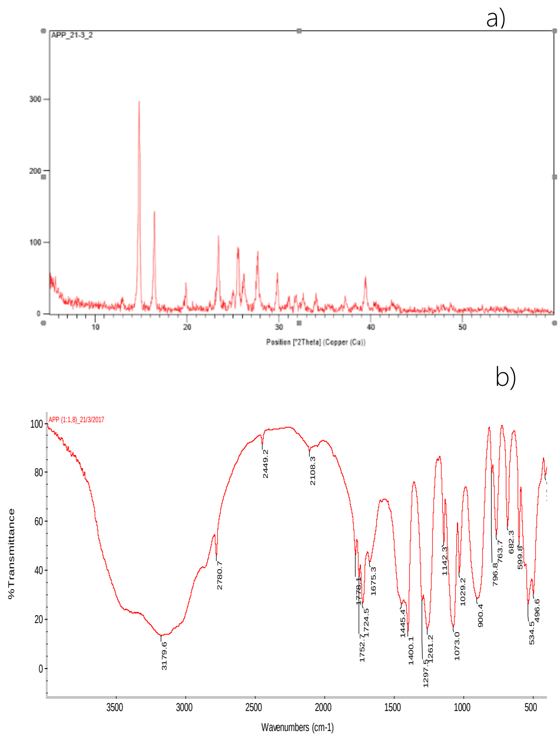


Figure 1: XRD (a) and FTIR spectra (b) of APP

Structure and characterization of APP/Diatomite admixture

Figures 2 and 3 show the spectrum of diatomite, I-Type APP/DIA and II-Type APP/DIA. Diatomite has absorption peaks at 3452.1 cm^{-1}, 1099.3 cm^{-1} and 466.7 cm^{-1}. The absorption peak at 3452.1 cm^{-1} is assumed to be the absorption of –OH, while the absorption peaks at 1099.3 cm^{-1} and 466.7 cm^{-1} correspond to asymmetric stretching and asymmetric bending vibrations, respectively, worthy of Si-O. The absorption peak at 796.6 cm^{-1} is thought to be the symmetric stretching oscillation of Si-O-Si. All characteristic peaks show that diatomite is mainly composed of SiO_2. The FTIR spectrum of I-Type APP/DIA is similar to that of II-Type APP/DIA. Peaks at 1082.8 cm^{-1} and 536.2 cm^{-1} of I-Type APP/DIA and peaks at 1073.3 cm^{-1} and 496.8 cm^{-1} of I-Type APP/DIA. II-Type APP/DIA is the absorption peak of Si-O, indicating the corresponding presence of diatomite. The sharp absorption peaks at 760 cm^{-1}, 680 cm^{-1} and 600 cm^{-1} in I-Type APP/DIA and II-Type APP/DIA are the absorptions of O=P-O, -OH and O-P-O. Therefore, I-Type APP/DIA and II both contain a certain amount of APP.

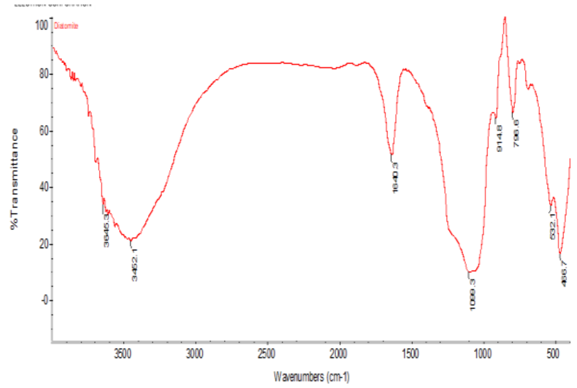


Figure 2: FTIR spectrum of diatomite

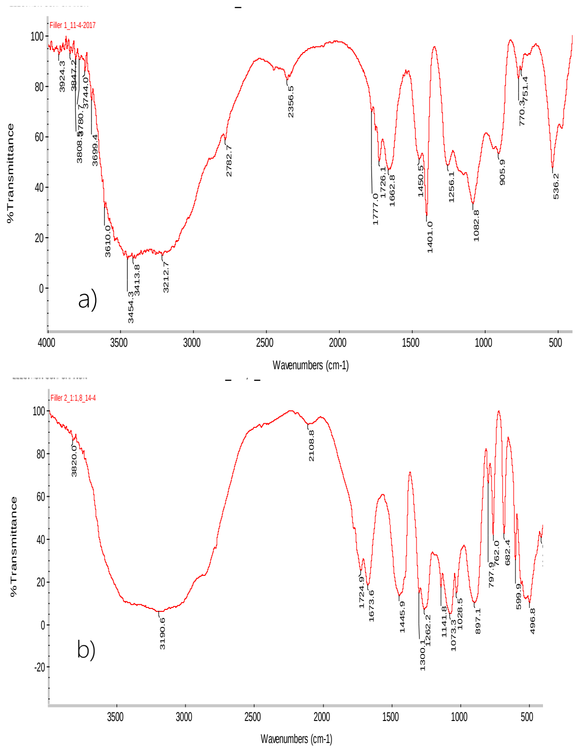


Figure 3: FTIR spectra of I-Type APP/DIA (a) and II-Type APP/DIA (b)

The TG curves of additive mixture 1 and 2 (Fig.5) are quite similar as they both contain APP. Additive mixture 1 has about 1.43% weight loss before 160°C and additive mixture 2 has 1.79% weight loss before 160°C. The weight loss of both additive blends increased in the range of 200-500°C (first weight loss phase) and reached about 25% at 500°C in sample 2, about 30% at 400°C in sample 1.

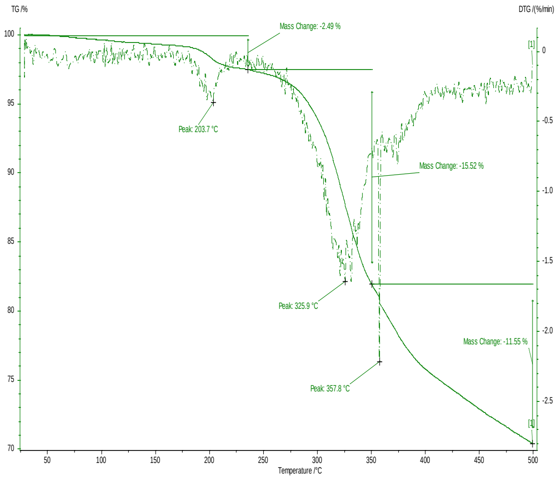
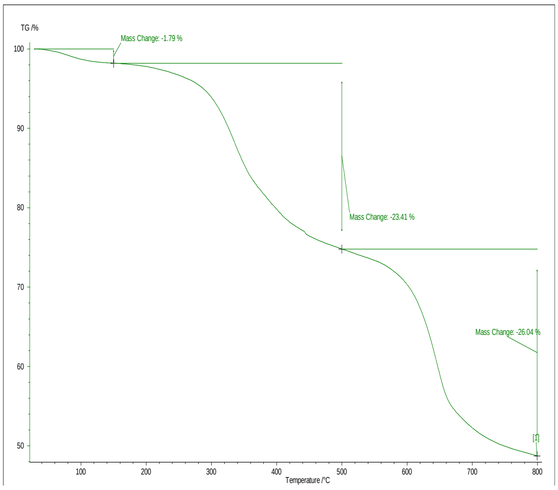
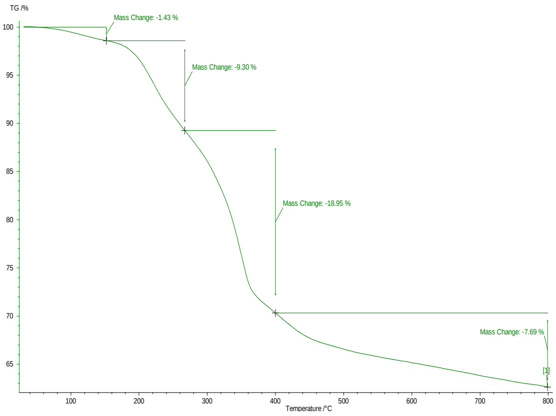


Figure 4: The TG curve of APP



a) II - Type APP/DIA



b) I - Type APP/DIA

Figure 5: TG curves for II - Type APP/DIA and I - Type APP/DIA

In this temperature range, the weight of the additive decreases sharply due to the decomposition of APP in the mixture. This weight loss can be attributed to the release of a limited amounts of NH_3 and H_2O, mainly from thermally unstable structural groups or terminals of APP. However, this thermal decomposition results in a more thermally stable O-P-O cross-linked structure, which has (3). During the second stage of thermal decomposition, the additive weight was reduced by approximately 48% for sample 2 and 37% for sample 1 between 500°C and 700°C, and the weight loss at both stages is due to the decomposition of the APP. This wieght loss at this stage is contributed to the released of phosphoric acid, polyphosphoric acid and metaphosphoric acid with APP decomposition. Compared with the additive blend, the weight loss in the case of pure APP (Fig.4) at both stages was higher because the APP content in the additive mixture was lower than that of pure APP. However, both pure APP and the 2 additive mixtures have similar flame retardancy mechanisms.

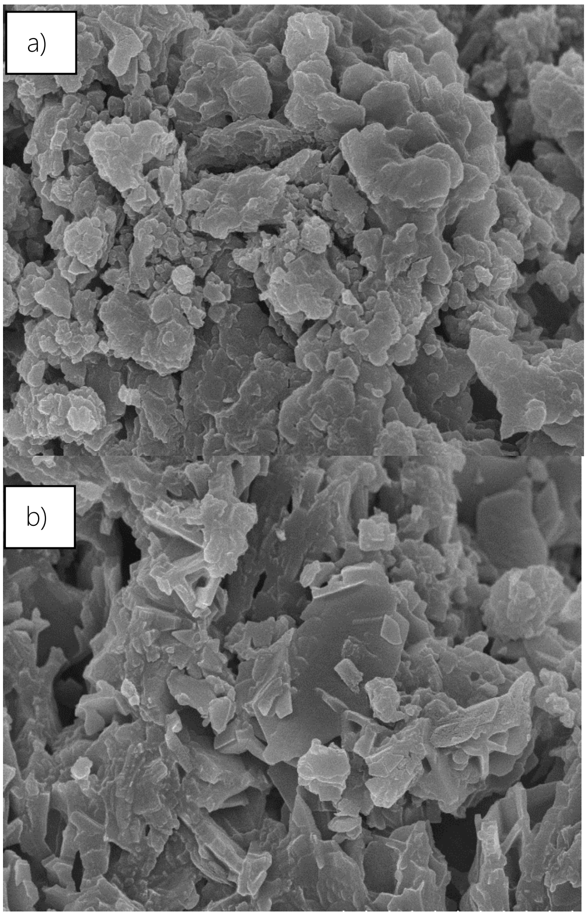


Fig 6: SEM images of the II - Type APP/DIA(a) and APP (b)

Figure 6 shows the APP particles distributed on the surface of the diatomite and also in the voids of the diatomite. During the fabrication of sample 2, diatomite was added before the formation of APP from

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phosphoric acid and urea. In this way, the two reactants can be adsorbed and reacted right on the surface and inside the pores of the diatomite, thus creating strong bonds between APP and diatomite.

Conclusion

The APP/Diatomite additive mixture was synthesized by two methods.
Analytical methods FTIR, XRD, TG and SEM show the composition and properties of APP, diatomite, and additive mixture.

The weight loss in pure APP was higher than that of APP/DIA because the APP content in the additive mixture was lower than that of pure APP.

The thermal decomposition of the flame retardant admixtures was slower than that of the APP powder.

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