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THE SYNERGISTIC EFFECT OF BORIC ACID AND AMMONIUM POLYPHOSPHATE ON THE THERMAL DEGRADATION AND FLAMMABILITY OF PINE-NEEDLES

The synergistic effect of ammonium polyphosphate (APP) and boric acid (BA) on the flame retardancy and thermal degradation of pine needles was investigated. Thermogravimetric analysis (TGA) showed that the presence of an ammonium polyphosphate and boric acid system increased the char residue and decreased the pyrolysis temperature of the pine needles. The derivative thermogravimetric analysis (DTG) showed that the ammonium polyphosphate and boric acid had shifted the degradation peaks of the pine needles to lower temperatures. The cone calorimetry test results showed that the values of HRR, THR, SPR, TSP and the mass loss (%) of the pine needles treated with ammonium polyphosphate and boric acid (APP/BA = 3/2) were significantly lower than the other samples. Therefore, the APP and BA system had a better effect on the pine needles overall than the APP alone.

Keywords: boric acid, ammonium polyphosphate, pine needles, flame retardancy, thermal degradation.

Introduction

Every year more than 2.2 million forest fires occur worldwide, burning areas of 300–400 million hectares and approx. 9 billion tons of plant biomass. Combinations of various techniques have been used to fight forest fires, the most important of which are those involving fire-fighting chemicals [Pappa et al. 1995; Liodakis et al. 2010]. Chemicals have been used in direct ways to attack fires; chemical additives have been widely used with water to fight forest fires in North America, Australia and countries in the Mediterranean basin [Águeda et al. 2008; Alvarez et al. 2012].

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The application of fire retardants has been a common method used to fight forest fires. Fire retardants have been applied ahead of a fire to reduce the spread rate or fire intensity. Several theories have attempted to explain the action of fire retardants on forest fuels [Pappa et al. 2006; Àgueda et al. 2011]. A fire retardant is seen as any substance that by chemical or physical action inhibits combustion in order to decrease the spread rate and the fire line intensity of a forest fire [Liodakis et al. 2006]. Such fire retardants include: (1) long-term retardants, which inhibit combustion even after the loss of water; (2) short-term retardants, which reduce the surface tension of water and increase its viscosity, their effectiveness disappearing with the evaporation of water; (3) fire-fighting foams, which form small bubbles when mixed with water; (4) wetting agents, which reduce the surface tension of water and increase its spreading ability [Kalabokidis 2000; Tan et al. 2011].

Long-term retardants consist of flame-inhibiting chemicals dissolved in water. They remain effective even after water has been removed by evaporation. The key ingredient in these retardants is an active fire retardant substance, usually referred as “active salt”, which is typically either an ammonium sulfate or ammonium phosphate. Retardant inorganic salts alter the pyrolysis mechanism, promoting the formation of char and water, decreasing the amount of heat and slowing fire progression [Liodakis et al. 2006]. The effects of fire retardants on the pyrolysis mechanism of cellulose have been extensively studied using various analytical techniques [Sekiguchi, Shafizadeh 1984; Faroq et al. 1991; Garba et al. 1994; Tata et al. 2011]. A common forest fuel has been studied in previous works using various analytical techniques, such as Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), desorption/ionization mass spectrometry (DI-MS), Pyrolysis-Gas Chromatography / Flame Ionization Detection (Py-GC-FID), Pyrolysis-Gas Chromatography / Mass Spectrometry Detection (Py-GC-MSD), optical microscopy and stereoscopy and cone calorimetry [Liodakis et al. 1996; Statheropoulos et al. 1997; Tzamtzis et al. 1999; Tzamtzis et al. 2002; Bakirtzis et al. 2003; Griffin 2011].

Among long-term forest fire retardants, monoammonium phosphate (MAP), diammonium phosphate (DAP), ammonium polyphosphate (APP) and ammonium sulphate (AS) have dominated use [Àgueda et al. 2010; Qu et al. 2011]. Ammonium polyphosphate (APP) is a fast developed non-halogen flame retardant in recent years [Riva et al. 2003; Castrovinci et al. 2005; Zhao et al. 2008].

APP contains N and P, two elements which are necessary for crop growth. The percentage content of N and P in the form of P_2O_5 is 14.6–22.8% and 57.7–73.2%, respectively. Therefore, APP is a kind of fertilizer with high concentrations of N and P. APP has a low degree of polymerization and is frequently made into solid and liquid agricultural fertilizers due to its excellent water solubility and ease of nutrient uptake by crops. Therefore, APP with its low degree of polymerization could be used not only as a flame-retardant, but also as a fertilizer when sprayed

on forests. However, APP can not produce the flame-retardant effect very well because of its low degree of polymerization, and it hydrolyses easily [Lin et al. 2011; Zhou et al. 2011]. Boric acid is an inorganic fire retardant which increases the dehydration reaction in the cellulose. This reaction increases the amount of char and reduces a large amount of the volatile compound. Boric acid reduces smoulder and the emission of smoke but has little effect on flame spread [Rowell, LeVan-Green 2005; Pedieu et al. 2012]. Both ammonium polyphosphate and boric acid are very cheap chemical reagents, therefore their use could reduce the huge losses with low cost.

The synergistic effect of flame retardants is an important field of research. Boric acid and APP are both cheap, highly efficient, and environmentally-friendly [Duquesne et al. 2002]. Research on the flammability of forest species is very important for forest fire management [Liodakis et al. 2009]. The research presented in this paper was conducted on Korean pine-needles. Korean pine is one of the most important forest species in the Northeast China Region and is often devastated by forest fires. It is very flammable, especially during the hot and dry summer season. This is mainly due to its low water and high resin content. The purpose of this article was to investigate the synergistic effect of ammonium polyphosphate and boric acid, and then to assess the effectiveness of the fire retardant on pine needle flammability and thermal degradation using TG analysis and cone calorimetry.

Methods

The pine-needles used in this study were collected in autumn from the ground from Lesser Khingan Range in north-eastern China. The ammonium polyphosphate (APP) used in the research was supplied by Changfeng Chemical Corporation (Sichuan China), while the boric acid (BA) was supplied by Tianjin Chemical Reagent Corporation. All the chemicals used in this study were analytical grade and used without further purification.

Sample preparation

The APP and BA were first dried at 60°C in a constant temperature oven for 24 h until the constant weight was within 1 mg. The APP and BA at 8% concentrations were dissolved in water in order to prepare aqueous solutions. The pine needles, which were dried at 105°C for 24 h to remove moisture, were immersed in the APP and BA aqueous solutions for 24 h and then oven-dried for 24 h at 60°C. The samples were then stored in desiccators before being tested. All the compositions are shown in table 1.

Table 1. Composition of APP and BA aqueous solutions

Samples	APP [g]	Boric acid [g]	Water [mL]
a (1:1)	4.0	4.0	92
b (2:1)	5.34	2.67	92
c (3:1)	6.0	2.0	92
d (3:2)	4.8	3.2	92
e (4:1)	6.4	1.6	92

APP/BA with a fixed ratio (3/2) was prepared in different concentrations (5%, 8%, 10%), and these were used to submerge the pine needles. All the samples are shown in table 2.

Table 2. Composition of samples in different concentrations

Samples	APP [g]	Boric acid [g]	Water [mL]
① (5%)	3.0	2.0	95
② (8%)	4.8	3.2	92
③ (10%)	6.0	4.0	90

The 8 wt% concentrated solution (APP/BA = 3/2) was chosen and used to submerge the pine needles and flame-retarded pine needles. The compositions are shown in table 3.

Table 3. Compositions of pure pine needles and flame-retarded pine needles

Samples	Water [mL]	APP [g]	Boric acid [g]
1 (pine needles)	100	0	0
2 (pine needles – APP)	92	8	0
3 (pine needles – APP-BA)	92	4.8	3.2

Thermogravimetric analysis

Thermal degradation behaviour tests were carried out using a PerkinElmer Pyris 1 Thermal Analyzer at a heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen. The range of temperature was from 30 to 800°C . The weight of each sample was kept within 3–5 mg. Two specimens of each formulation were tested, and the average values were reported.

Cone calorimetry study

The cone calorimeter (CONE) tests were performed according to the ASTM E 1354–2004 standard. Each specimen with the dimensions of $100 \times 100 \times 3 \text{ mm}^3$ was wrapped in aluminum foil and exposed horizontally to an external heat flux of 50 kW/m^2 [Babrauskas 1984]. Two samples of each formulation were tested for repeatability.

Results and discussion

Thermogravimetric analysis

The results of the TGA for the pine needles treated with different proportions of APP:BA (1:1, 2:1, 3:1, 3:2 and 4:1) at 8wt% concentration are shown in fig.1. From the TGA data, it was clearly seen that the char residue of the pine needles changed according to the different proportions of ammonium polyphosphate and boric acid at 800°C. The ratio of APP/BA affected the thermal behavior of the pine needles: the APP:BA (3:2) had a higher char residue than the others. It was observed that the char residue of sample b (APP:BA = 2:1) was the lowest at 800°C, while sample a (APP:BA = 1:1) increased slightly compared with that of sample b. Sample c (APP:BA = 3:1) and sample e (APP:BA = 4:1) also increased compared with that of sample b. However, a significant increase in the char residue was observed with the 3:2 proportion compared with the other samples. The reason for this may be that some synergistic effect occurred as the ratio of APP:BA changed.

It can be seen in fig 1 that the APP:BA = 3:2 system had poor thermal stability before 350°C compared with the other proportions, which due to the decomposition of APP, forming char layer and ester mixtures between-P-OH group in APP and -OH group in BA. But above 350°C, the APP:BA = 3:2 system had a much higher thermal stability and had approx. 50% char residue. This was due to the reaction between the boric acid and APP, when the boric acid in the char was converted into boron oxide and sassolite. In turn, the boron oxide reacted with the APP to form borophosphate, which formed the final protective layers on the substrate [Sami et al. 2013]. It can therefore be concluded that the APP/BA had a synergistic effect and the ratio of the APP/BA was also very important.

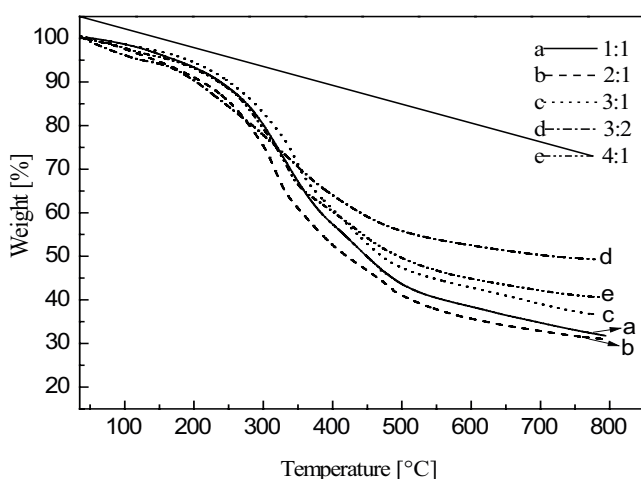


Fig. 1. TGA curves of pine needles treated with APP and BA in different proportions

The TGA curves of the APP:BA = 3:2 system in different concentrations (5%, 8% and 10%) (①, ② and ③) are shown in fig. 2. From the TGA data, it was clearly seen that the char residue of the pine needles treated with 5 wt% was approx. 33.3% at 800°C, while the highest char residue was obtained at 8 wt% concentration, which was 49.2% at 800°C, having significantly increased compared with that of the pine needles treated with 5 wt% and 10 wt% (40.3% char residue at 800°C).

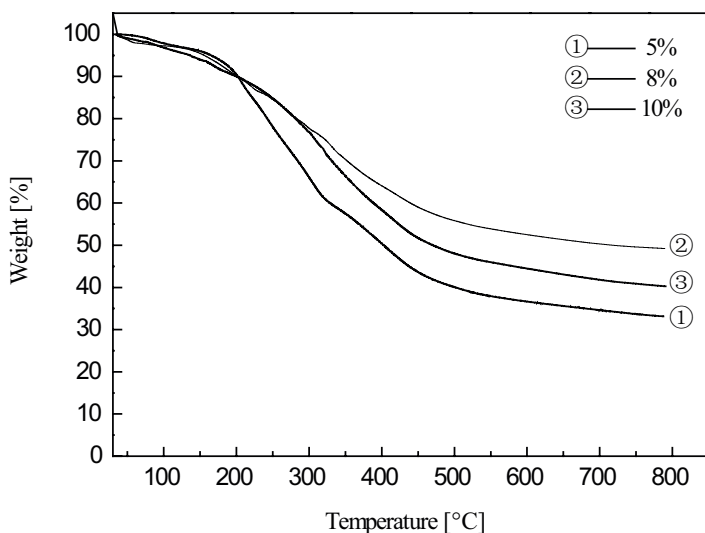


Fig. 2. TGA curves of pine needles treated with APP:BA = 3:2 in different concentrations

Fig. 3 shows the TGA curves of the samples. From the TGA data curves, the char residue of the pine needles which were treated with APP/BA = 3/2 was much higher than that of the pure pine needles. The char residue of the pine needles was approx. 18.8% at 800°C. An increase in the char residue was observed in those pine needles treated with APP (35.5% char residue at 800°C), while a more significant increase was observed in those pine needles treated with APP/BA = 3:2 (49.2% char residue at 800°C). This indicated that borophosphate was obtained as a product of the reaction between the degradation products of the boric acid and APP, which had better heat insulating performances.

Fig. 4 shows the DTG curves of the samples, as follows: (1) the first peak (I), there was a weight loss in each sample at below 100°C, which was attributed to the evaporation of moisture from the pine needles; (2) the second peak (II), the charring stage, from approx. 200°C to 420°C, mainly related to the decomposition of hemicellulose and cellulose into char residues and the production of CO₂, CO, NH₄; (3) the third peak (III), in the range of 370–550°C, mainly involved the lignin decomposition and the char residue oxidation.

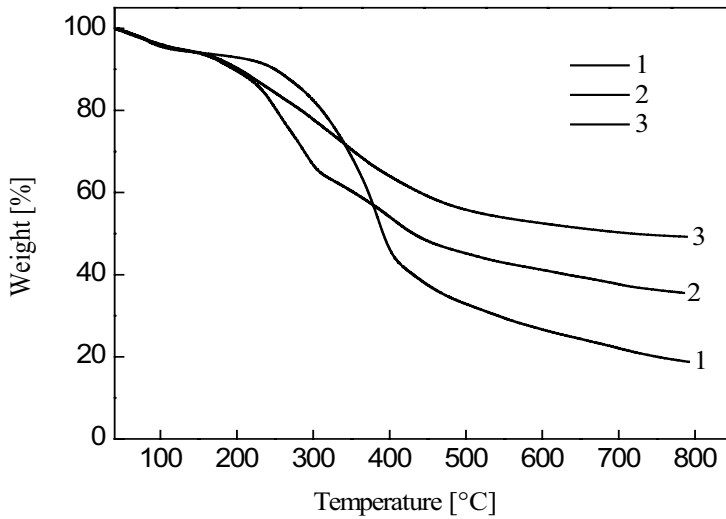


Fig. 3. TGA curves of pine needles and pine needles treated with flame retardant

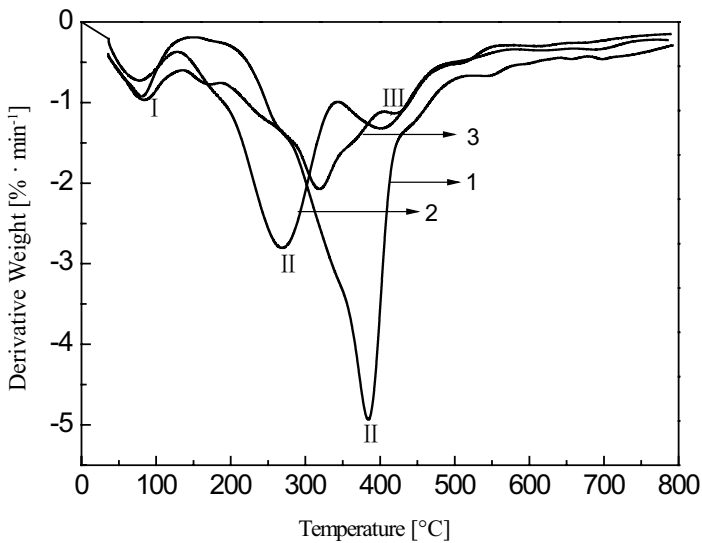


Fig. 4. DTG curves of pine needles and pine needles treated with flame retardant

It was obvious that the treated samples (2 and 3) started decomposing earlier, samples 2 and 3 shifted in both cases to a lower temperature compared with sample 1. The residual char at 800°C increased with the addition of flame retardants. The presence of the APP/BA = 3:2 decreased the decomposition temperature of the cellulose and lignin, and the maximum rate of decomposition was considerably lower. It seemed that the APP/BA = 3:2 could promote char formation and form a char layer in the pine needles, which endured the higher temperature to

protect the pine needles from decomposing. Thus, the APP/BA = 3:2 reduced the decomposition rate of the pine needles. It attributed to the thermal decomposition; the ammonium phosphate released non-flammable gases (such as N_2 , NH_3 , etc.) and in the meantime formed polyphosphoric acid or polymetaphosphate acid. These were strong dehydrating agents which could promote the dehydration of the pine needles and generate a char layer, which covered the surface of the pine needles, isolating the pine needles from the air; boron oxides were formed when the boric acid decomposed in the high temperature; the boron oxides had a glassy compact structure, therefore making the char layer more stable and protecting the substrate from fire.

Cone calorimetry study

Cone calorimetry is a small-scale test, but it has a good evaluation with real fire disaster and is used to predict the behavior of materials in real fires, and the method is used a great deal in the development of new materials [Schemel et al. 2008]. The results from the cone calorimeter tests are shown in figs. 4–8 and important data are summarized in table 4.

Table 4. Cone calorimeter test data of pine needles

Samples	HRR [kW/m ²]	THR [MJ/m ²]	SPR [m ² /s]	TSP [m ² /kg]	Mass Loss [%]
1 (pine needles)	164.1	27.9	0.016	0.739	78.1
2 (pine needles – APP)	130.1	22.5	0.017	1.000	70.0
3 (pine needles – APP-BA)	103.3	18.2	0.007	0.095	63.1

The heat release rate (HRR) is recognized as the most important factor in evaluating the development, spread, and intensity of fires. Fig. 5 shows the heat release rate (HRR) results. In the case of sample 2, its HRR peak value was a little lower (130.1 kW/m²) compared with sample 1 (164.1 kW/m²). The HRR peak value of sample 3 was the lowest (103.3 kW/m²). From fig. 5, it can be seen that the Time To Ignition (TTI) of sample 3 was 15 s, considerably higher compared with that of sample 1 (10 s) and sample 2 (10 s). It seemed that it took more time for sample 3 to ignite than the other two samples. The total heat release (THR) results are shown in fig. 6 and table 4. The THR dropped from 27.9 MJ/m² in sample 1 to 22.5 MJ/m² in sample 2 to 18.2 MJ/m² in sample 3 with the 3:2 ration of APP:BA. The incorporation of boric acid and APP enhanced the flame retardancy by promoting char formation and reduced the THR during the burning process. Clearly, the boric acid and APP system had some interesting effect on the combustion quality of the pine needles. This was due to the flame retardant decomposing and releasing free radicals and non-flammable gases, which catalyzed the pine needles into char, forming a cover layer on the surface of the pine needles to hinder combustion, and

so reducing the HRR; meanwhile, the boron compounds had a low melting point, they were heated to form a glassy coating which covered the surface of the pine needles, the char layers of the intumescent formulation acting as a fire-resistant layer providing heat insulation and, thus, shielding the needle substrate.

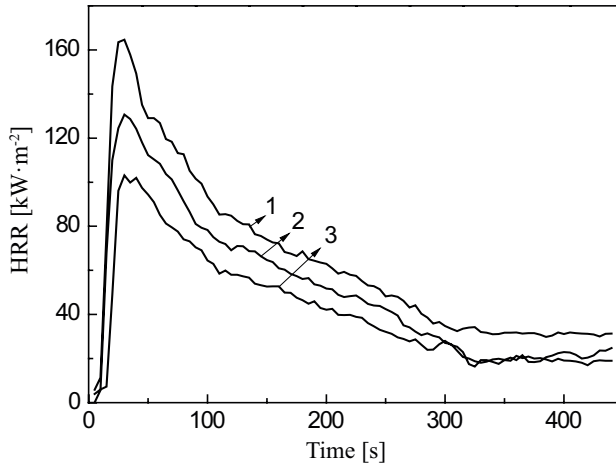


Fig. 5. HRR curves of pure pine needles and flame-retarded pine needles

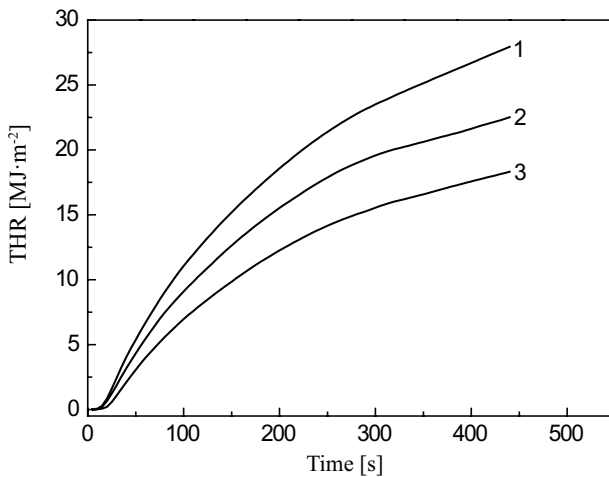


Fig. 6. THR curves of pure pine needles and flame-retarded pine needles

In addition, the smoke production rate (SPR) is another essential factor used to evaluate the development, spread, and intensity of fires. Fig. 7 and fig. 8 shows the SPR and TSP curves. It can be seen that when APP and BA were mixed in a 3:2 ratio, the SPR and TSP of the sample were significantly lower. The maximum value of the SPR for sample 1 was $0.016 \text{ m}^2/\text{s}$, however, the SPR of sample 3 ($0.007 \text{ m}^2/\text{s}$) was much lower than that of sample 1. In addition, it was clearly

seen that the Total Smoke Production (TSP) of sample 3 was much lower than the other samples from fig. 8. However, it was observed that sample 2 had much more SPR and TSP compared with samples 1 and 3. Clearly, APP had a fire retardancy effect on the pine needles, but it released more smoke during the burning process. The effect of smoke suppression was mainly due to the borax improving the quality of the char layer, which protected the internal organization, reducing the quantity of flammable gas and thereby reducing the production of smoke during burning. Hence, the boric acid and APP system had the remarkable effect of suppressing smoke during the burning process. Consequently, the boric acid and APP system was more effective in terms of the combustion quality of the pine needles.

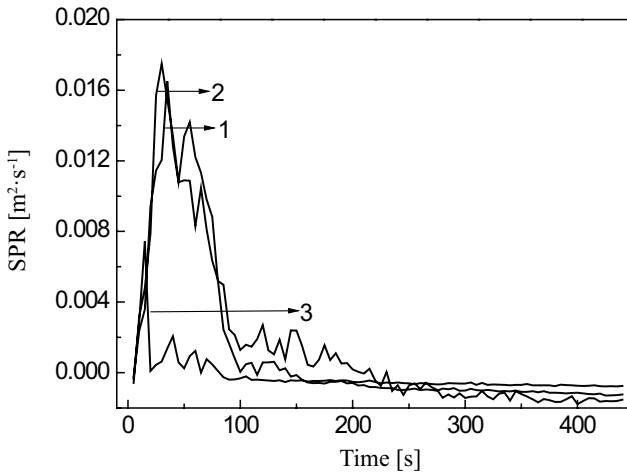


Fig. 7. SPR curves of pure pine needles and flame-retarded pine needles

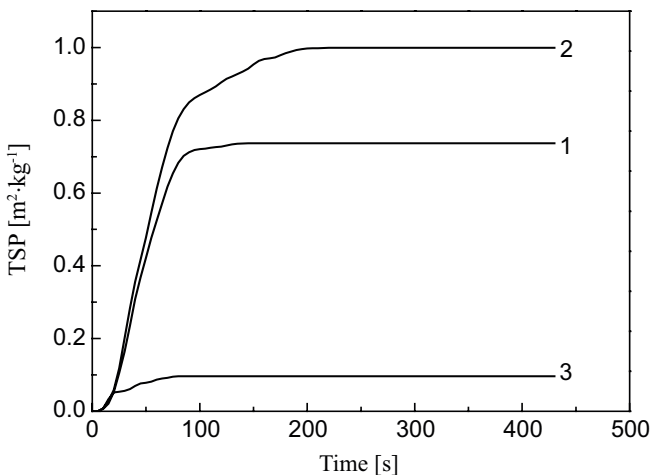


Fig. 8. TSP curves of pure pine needles and flame-retarded pine needles

The mass loss data are shown in table 4. It can be seen that the mass loss of sample 3 was lower than the other samples during the combustion process. As mentioned above, the compact char layer decreased the evolution of combustible gases during the combustion process, which lead to an increase in the residue char and a decrease in HRR, THR, SPR and TSP. This showed the synergistic effect of APP-BA.

Conclusions

The influence of forest fire retardants (APP and APP/BA system) was estimated by TG analysis and cone calorimetry tests. The APP and boric acid system affected the pyrolysis temperature of the pine needles by significantly increasing the char residue, shifting the degradation peaks of the pine needles to lower temperatures, reducing the maximum rate of decomposition considerably.

On the basis of the HRR, THR, SPR, TSP and the mass loss (%) of the pine needles treated with APP/BA = 3:2, the values were significantly lower than those of the pure pine needles and the pine needles treated with APP.

The APP and boric acid system prolonged the ignition time (TTI) compared with the pure pine needles and the pine needles treated with APP.

Therefore, the APP and boric acid system had an better effect on the pine needles overall than APP alone.

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