

Effects of APP/SiO₂ polyelectrolyte composites on wood-plastic composite

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Abstract. This paper was aimed to evaluate process of APP/SiO₂, which used Nano-crystalline cellulose (NCC) modified ammonium polyphosphate (APP) as anionic polyelectrolyte (a-APP), and cationic polyethyleneimine (PEI) modified Nano-SiO₂ as cationic polyelectrolyte (c-SiO₂). The flame retardant system was built due to the reaction of a-APP and c-SiO₂. Polyelectrolyte composite of a-APP/c-SiO₂ were then assembled on the surface of wood powder and HDPE composites. The effect of polyelectrolytes on wood-plastic composites (WPC) were investigated and the results showed that the flame-retardant property of WPC treated by polyelectrolyte was the best. The average heat release rate was 152.8kW/m², the peak heat release rate was 352.2kW/m², the total heat release was 108.5kW/m², the limit oxygen index reached the maximum was 27.5%, compared with the WPC treated by APP, the elongation at break increased by 60.4%. After anionic and cationic polyelectrolyte treatment, making anionized a-APP and cationized c-SiO₂ due to the charge interaction, in the WPC combustion process to form a dense, uniform WPC carbon layer, thereby reducing the heat transfer to the material inside, and increasing the flame retardancy of WPC composites.

Keywords. Polyelectrolytes; Ammonium polyphosphate; Nano-SiO₂; Wood-plastic composite; properties

1 Introduction

Wood-plastic composite (WPC) was a new type of general-purpose composite material composed of renewable and inexpensive wood fiber or wood powder and resin polymer. WPC was widely used in outdoor decking, building materials, ship materials and automotive materials due to their excellent corrosion and water resistance, and recyclability [1-3]. With the application of WPC gradually expanding into the field of interior decoration, researches on flame retardant properties of WPC became increasingly important. Flame-retardant treatment of WPC was usually carried out by adding a flame retardant (such as a halogen-based flame retardant, a phosphorus-nitrogen flame retardant, a silicon-based flame retardant) [4-6], these flame retardants were often added to the WPC system by direct addition [7, 8]. Compared with the traditional flame retardant method, the flame retardant system was constructed between the matrix material and the external environment. By directly interfered with the combustion process and adjusted the conditions and processes, the flame retardant properties of the material can be effectively regulated [9, 10]. The suitable cationic polyelectrolyte and anionic polyelectrolyte were

constructed into a polyelectrolyte flame retardant system, and the flame retardant treatment of the material was one of the methods for effectively improving the flame retardant effect [10].

Ammonium polyphosphate (APP) was a commonly halogen-free flame retardant, its existence is easy to outflow, the amount of addition was large etc. APP has a low solubility and it was a weak polyelectrolyte. In aqueous solution, it can ionize cationic ammonium and anionic polyphosphate and exhibit the characteristics of polyanion [11]. Surface modified nano-SiO₂ could exhibit polycationic properties in aqueous solution [12]. In this paper, Nano-crystalline cellulose (NCC) modified APP was used as an anionic polyelectrolyte, and polyethyleneimine (PEI) modified Nano-SiO₂ was used as a cationic polyelectrolyte to build APP/SiO₂ flame retardant colloid system on WPC matrix, which providing useful experience for polyelectrolyte in the application of WPC.

2 Materials and methods

2.1 Materials

Poplar powder was obtained from Suqian, Jiangsu (china), and the water content was 12.8%. Samples were prepared with a screen system equipped with a 60- to 80-

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mesh screen, and were dried at 103 °C to constant weight. HDPE was a homopolymer pellet; grade 5000S; $\rho=0.95\text{g/cm}^3$; melt-flow index (MFI) of 0.8–1.2g/10min (190 °C/2.16kg) and was supplied by Sinopec Yangzi Petrochemical Company Ltd. (China). APP powders (Phase II, the polymerization degree > 1000) was supplied from Shifang Changfeng Chemical Co., Ltd. (China). Nano-SiO₂ has a purity of 99.5% and the particle size of 30nm was supplied by Shanghai Aladdin Biochemical Technology Co., Ltd. Polyethyleneimine (PEI) has a molecular weight of 1800 and the purity of 99% was supplied by Shanghai Maclean Biochemical Technology Co., Ltd.

2.2 Preparation of polyelectrolytes

2.2.1 Preparation of anionic polyelectrolyte APP

13g APP and 20g NCC suspension (NCC concentration of 0.65 wt%) were added in a 250 mL three-neck round bottom flask, then added 45mL distilled water, stirred for 120min at 60 °C, the rotation speed was 200 rpm, then cooling to room temperature, an anionized APP was obtained, which was designated as a-APP, and the Zeta potential was -0.6mV.

2.2.2 Preparation of cationic polyelectrolyte Nano-SiO₂

1g Nano-SiO₂ and 100 mL distilled water were added in a 250 mL three-neck round bottom flask, stirred for 30min, then 0.5g 50% PEI was added, mechanically stirred at 40 °C for 100min, and cooled. The PEI modified Nano-SiO₂ solution was ultrasonicated for 15min, and the ultrasonic power was 900 W, the cationized Nano-SiO₂ was obtained, which was recorded as c-SiO₂, and the Zeta potential was 15.3 mV.

2.3 Preparation of WPC

The poplar powder and HDPE powder were pre-mixed uniformly, and then the poplar powder/HDPE mixture was dipped into the anionic polyelectrolyte a-APP system prepared above, immersed for 1h, and dried at 70 °C until the water content was about 2.0%. Then, the anionic polyelectrolyte a-APP flame retardant treated poplar powder/HDPE mixture was impregnated into the cationic polyelectrolyte c-SiO₂, and dried at 70 °C until the water content was about 2.0%, thereby obtaining a polyelectrolyte a-APP/c-SiO₂ treated poplar powder/HDPE mixture. The polyelectrolyte treated poplar powder/HDPE mixture were well-mixed in an open mill (ZG-160, Dongguan ZhengXin Electromechanical Science and Technology Ltd.) at 175 °C for 5–10 min. Afterwards, the blends were molded for test specimens by using hot pressing, firstly at 175 °C and 5 MPa for 3 min, and then by cold pressing for 20min. The formulation of WPC was present in Table 1. WPC were incorporated with 70 wt% HDPE and 30 wt% wood powders. For the comparative

test, the WPC was not treated by anionized APP was prepared in the same manner.

Table 1 Components of WPC treated with polyelectrolyte composites (%)

Samples	Wood	HDPE	APP	a-APP	c-SiO ₂
WPC	30	70	-	-	-
WPC/APP ^a	30	70	20 ^b	-	-
WPC/a-APP	30	70	-	20 ^c	-
WPC/a-APP/c-SiO ₂	30	70	-	20	10 ^d

a: APP was solid powder;

b, c, d: The weight ratio of flame retardant was solid weight based on the whole weight of WPC.

2.4 Characterizations

2.4.1 Fourier transform infrared (FTIR) spectra analysis

FTIR were recorded by a VERTEX 80 infrared spectrum instrument (Bruker, Germany). Samples and KBr powder were uniformly ground and pressed to form pellet. The spectra of samples were recorded within a range of 4000–400cm⁻¹ with a resolution of 0.5cm⁻¹.

2.4.2 Transmission electron microscope (TEM)

Both APP, a-APP, Nano-SiO₂ and c-SiO₂ suspension were diluted to 0.1wt% and deposited onto carbon-coated grids (300-mesh copper) and then observed with transmission electron microscopy (TEM, JEM-1400, JEOL) at 100kV.

2.4.3 Scanning electron microscope (SEM)

The char residues after the combustion from cone calorimeter testing were observed with a QUANTA 200 scanning electric microscopy (SEM) (FEI Company, USA). All samples were coated with gold before examination.

2.4.4 Cone calorimetry and LOI testing

Flammability of WPCs was measured with a cone calorimeter (CC, Fire Testing Technology, UK) in accordance with ISO 5660. An external heat flux of 50 kW/m² was applied. The specimen size was 100×100×4 mm. All measurements were performed in duplicate. Limited oxygen index (LOI) test was also performed on an HC-2C oxygen index meter (Jiangning, China) with a dimension of 100×10×4 mm according to ISO 4589, and each test was performed six times for all samples.

2.5.5 Mechanical testing

Tensile tests of WPC were carried out with a universal material-testing machine equipped with a 1kn load cell (CMT 4202, SANS, Shenzhen, China) at a crosshead speed of 1mm/min according to National Standards of the People's Republic of China GB/T 1040-1992, which is technically equivalent to ISO527-1. Tensile specimen size was 100mm×10mm×4mm. The bending properties tests by the electronic universal testing machine. The test method refers to GB/T 1449-2005, and the sample size is 80mm×10mm×4mm. The unnotched charpy impact tests of 80mm×10mm×4mm test pieces were performed with a SANS ZBC 1251-1 tester. The impact properties were determined according to the National Standards of the People's Republic of China GB/T 1043-92. Six specimens were tested in each run.

2.5.6 X-ray photoelectron spectroscopy (XPS) analysis

X-ray photoelectron spectroscopy (XPS) was conducted to determine chemical compositions of char residues. A small quantity of sample was mounted on double-sided adhesive tape and the XPS spectra were recorded by AXIS UltraDLD (Kratos Co, Japan), using a monochromatic Al K α source (14866eV).

3 Results and discussion

3.1 FTIR analysis of polyelectrolyte

Polyelectrolyte were analyzed with FTIR to investigate their chemical structures, and their spectra were shown in Fig 1. The spectra of APP show that the absorption at 3400cm⁻¹, 1687cm⁻¹ were N—H telescopic vibration peak and N—H bending vibration peak, respectively. The absorption at 1256cm⁻¹ and 1075cm⁻¹ were P = O telescopic vibration peak and P — O symmetrical stretching vibrational peak. For PO₂ and PO₃, the absorption at 1020cm⁻¹ was P—O stretching vibrational peak. The peak locating at 880 cm⁻¹ corresponds to the asymmetric stretching vibration peak of P—O—P [13]. When the APP was anionized, N—H stretching vibration peak and N-H bending vibration peak were enhanced by the action of O—H stretching vibration peak in NCC. The spectra of Nano-SiO₂ show that the absorption peak at 1095cm⁻¹ was attributed to Si—O—Si asymmetric stretching vibration peak. The peak locating at 798cm⁻¹,

955cm⁻¹, 1687cm⁻¹ and 3400cm⁻¹ corresponds to the Si—O Symmetrical stretching vibrational peak, Si—OH bending vibration absorption peak, H—O—H bending vibration peak and —OH antisymmetric stretching vibration peak, respectively. When the Nano-SiO₂ was cationized, the stretching vibration absorption peak at 3400 cm⁻¹ becomes wider and stronger, because of partial overlap of the —OH and N—H stretching vibration absorption peaks. Due to the small size of Nano-SiO₂, the basic characteristic peak of Nano-SiO₂ was still present in c-SiO₂.

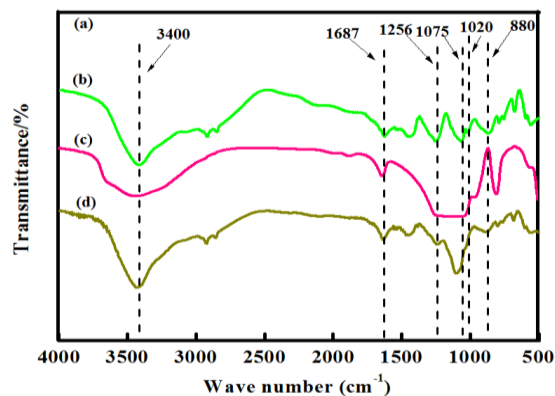


Fig.1 FTIR spectra of (a) APP, (b) a-APP, (c) SiO₂, (d) c-SiO₂

3.2 Morphology analysis

A transmission electron microscope was used to study the structure of polyelectrolyte particles. Fig 2(a) shows images of diluted APP suspension. The neat APP exhibits an irregular distribution in the water phase. Fig 2(b) shows anionic APP, when APP was anionized, which uniformly distributed in the aqueous phase. Due to the sulfuric acid reacts with the surface hydroxyl groups of cellulose to yield charged surface sulfate esters that promote dispersion of the individual NCC. At the same time, the NCC surface was rich in O—H and forms a new hydrogen bond between N—H in APP, which promotes the uniform dispersion of APP in the aqueous phase system. The surface of Nano-SiO₂ contains a large amount of active silanol groups, so it was easy to agglomerate when used in Nano-SiO₂, as shown in Fig 2(c). The cationization of Nano-SiO₂ improves the agglomeration phenomenon, as shown in Fig 2(d). This was because the dispersibility of the c-SiO₂ in the aqueous phase was improved.

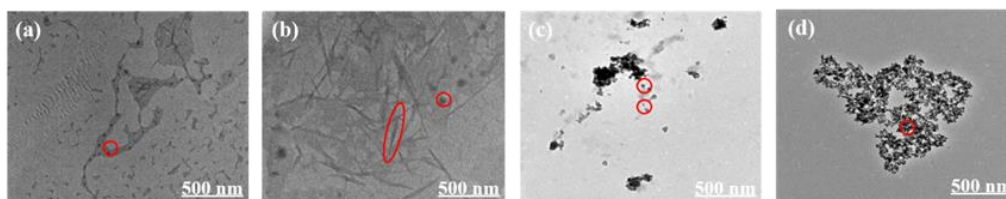


Fig.2 TEM image of (a) APP, (b) a-APP, (c) SiO₂, (d) c-SiO₂

In order to further characterize the dispersion of the polyelectrolyte on the surface of the wood powder, the polyelectrolyte was sprayed on the surface of the wood powder and observed by scanning electron microscopy (SEM). Fig 3(a) shows the APP was added to wood flour, which can evenly has dispersed on the surface. However, with the added of APP, some APP will peel off the surface of the wood flour, which lead to the flame retardant performance of the material not being guaranteed during the use and subsequent process. Fig 3(b) shows the anionic APP was added to wood flour, which can closely disperse on the surface. This was mainly due to the dehydration reaction between NCC and APP, at the same time which combined with the hydroxyl groups in poplar powder, so the APP adsorbed

on the surface of the poplar powder, which solved the problem of easy outflow of APP. It can be seen from Fig. 3(c) that, the Nano-SiO₂ particles were uniformly distributed on the surface of wood powder. Due to the action of PEI, the c-SiO₂ were more evenly distributed on the surface of the wood powder. On the surface of wood flour, the c-SiO₂ completely covers the a-APP. Between the a-APP and the c-SiO₂, the positively and negatively charged attract each other, so the cationic SiO₂ were closely adsorbed on the surface of the a-APP. In addition, the c-SiO₂ were uniformly dispersed on the surface of the wood powder, which can effectively prevent the APP migration phenomenon as the using time prolongs [14, 15].

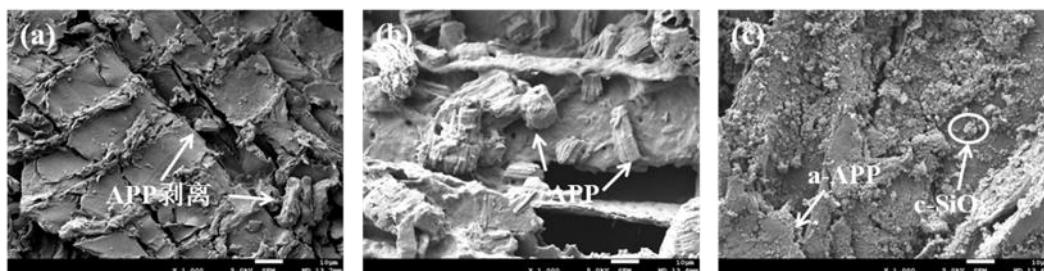


Fig.3 SEM of image of (a) APP, (b) a-APP, (c) a-APP/c-SiO₂

3.3 Flammability analysis

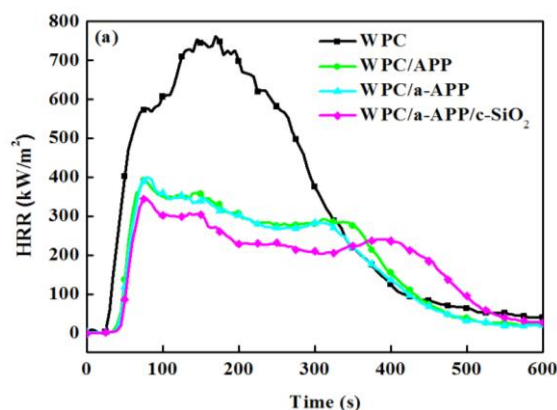
Flammability properties of WPC were analyzed by LOI and CC testing. The results of LOI, average and peak heat release rates (HRR), total heat release (THR), time to ignition (TTI), mass loss rate (MLR) and total smoke release (TSR) from CC testing are summarized in Table 2.

From Table 2, WPC was an easily flammable polymeric material with a lower LOI of 19.8%. By incorporating 20 wt% APP to WPC, LOI of WPC/APP reached to 26.0%, which increased by 31.3%. When the a-APP was added to WPC, LOI of WPC/a-APP reached to 26.6%. The polyelectrolyte complex a-APP/c-SiO₂ were added to WPC, LOI of WPC/a-APP/c-SiO₂ reached to 27.5%. This means a-APP/c-SiO₂ can improve the flame retardant of WPC. This was mainly due to the interaction of positive and negative charges, so the c-SiO₂ were closely adsorbed on the surface of a-APP. In the burning process of WPC, a continuous dense and uniform of WPC carbon layer was formed.

At the same time, the presence of Nano-SiO₂ can keep the carbon layer skeleton stable of WPC, which form a protective barrier, delay the burning rate of WPC and enhance the flame retardant effect.

Combined with Figure 4 and Table 2. The peak HRR and THR for neat WPC were 744.8kW/m² and 198.3 kW/m², respectively. When the APP was added to WPC, the peak HRR and THR decreased by 48.0% and 40.0%,

respectively. TTI for WPC reached to 34s. When the a-APP was added to WPC, which HRR THR and TSR has decline, compared with WPC/APP decreased by 4.1%, 4.4% and 2.04%, respectively. This indicate that NCC has stable effect on the carbon layer, which improving the flame retardant of the WPC. When the a-APP/c-SiO₂ was added to WPC, which TSR and THR were the lowest decreased to 1694.7m²/m², 108.5 MJ/m², compared with WPC/APP decreased by 13.9% and 8.8%, respectively. TTI for WPC/a-APP/c-SiO₂ reached to 37s. The main reason was that PEI has a large number of NH₄⁺. During the combustion process, a large amount of NH₃ was generated, and the combustible gas was diluted to achieve flame retardant effect.



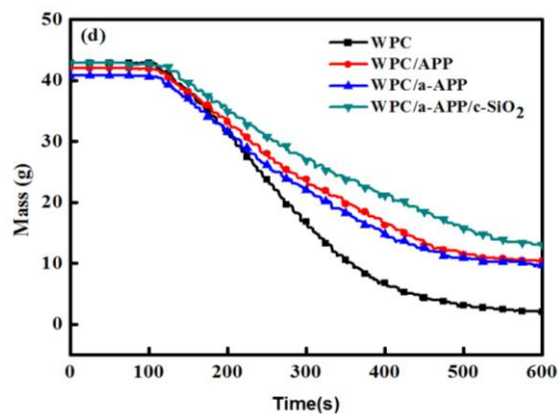
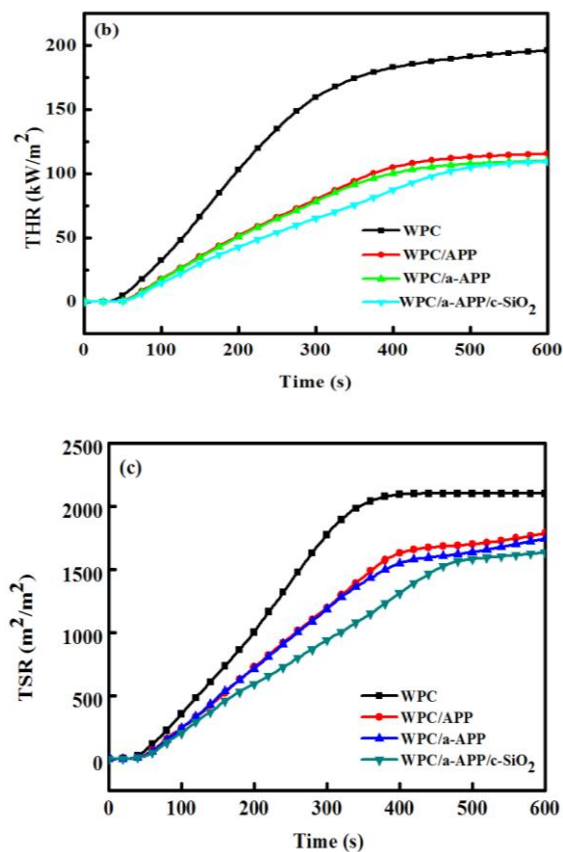


Fig 4 Influences of a-APP/c-sSiO₂ on WPC by cone calorimetry analysis (a) HRR, (b) THR, (c) TSR, (d) Mass

Table 2 Flame retardant properties of WPC

Samples	LOI (%)	Average HRR (kW/m ²)	Peak HRR (kW/m ²)	THR (MJ/m ²)	TSR (m ² /m ²)	TTI (s)	MLR (mg/s)
WPC	19.8	259.6	744.8	198.3	1922.9	23	55.1
WPC/APP	26.0	166.5	387.1	119.0	1968.8	34	47.2
WPC/a-APP	26.6	159.6	405.4	113.8	1929.4	35	46.5
WPC/a-APP/c-SiO ₂	27.5	152.8	352.2	108.5	1694.7	37	43.0

3.4 Mechanical properties analysis

The mechanical properties of WPC are summarized in Table 3. The tensile strength and tensile elongation at break of WPC/APP decreased compared to the neat WPC. When the a-APP was added to WPC, which tensile strength, tensile elongation at break and flexural strength were reached the maximum of 19.53 MPa, 2.43%, and 40.00 MPa, respectively. This indicate that NCC has good compatibility and contains large amount of hydroxyl groups and high specific surface area, which can generate a large number of hydrogen bonds with APP, and improving the mechanical properties of WPC [16]. Compared with the neat WPC, the impact strength of WPC/APP significant decreased. When the a-APP was added to WPC, the impact strength increased, compared with the results of WPC/APP, which increased

7.1%. This can be explained by that the NCC undergoes acid hydrolysis and mechanical treatment to obtain uniform and stable nanostructure, and the phenomenon of mutual cross-linking between the fibers through hydrogen bonding and electrostatic adsorption lays foundation for excellent mechanical properties. When the a-APP/c-SiO₂ was added to WPC, the tensile elongation at break increased by 60.4%, compared with WPC/APP. This indicate that PEI can improve the dispersion of Nano-SiO₂. At the same time, PEI contains polar group amino group and hydrophobic group vinyl group, which can be combined with NCC, wood fiber and improve the interfacial properties of the WPC, and improving its toughness.

Table 3 The data of mechanical property of WPC

Sample	Tensile strength (MPa)	Tensile elongation at break (%)	Flexural strength (MPa)	Impact strength (KJ/m ²)
WPC	17.94	2.3	30.83	13.93
WPC/APP	17.16	1.59	34.26	6.76
WPC/a-APP	19.53	2.43	40.00	7.24
WPC/a-APP/c-SiO ₂	16.11	2.55	31.38	6.92

3.5 Morphology analysis of WPC char residues

Fig 5 shows the morphology of char layer of WPC after Cone testing. Fig 5(a) shows the char layer of neat WPC after Cone testing, which has discontinuous carbon residue and has large number of cracks. When the APP was added to WPC can obtain WPC char layer which was continuous, uniform and has small amount of cracks [Fig 5(b)]. Fig 5(c) shows the char layer of WPC/a-APP after cone calorimeter testing, which has continuous, dense, and hard char layer. When the a-APP/c-SiO₂ was added to WPC can obtain WPC/a-APP/c-SiO₂ char layer, which has physical integrity and compactness [Fig 5(d)].

To further investigate the microscopic structure of char layer further, char residues of WPC after Cone testing were examined by SEM. Fig 5(a') shows the char layer framework of neat WPC still exists, and presents a lamellar structure, but the structure was not continuous and compact, and has many gaps. After burning, the original morphology structure of poplar cells can be preserved. When the APP was added to WPC, it was

denser than neat WPC [Fig 5(b')]. This indicate that during the combustion process of WPC, APP as an acid source, the polyphosphate acid was produced by thermal decomposition can effectively bond the char layer to form a continuous, uniform and dense char layer, the flammable gas and the release of heat were delayed [17]. For WPC with a-APP, the char layers were tightly connected and almost seamless [Fig 5(c')]. This was due to the fact that APP promotes dehydration and esterification of NCC at high temperatures and bonds the char layers together [18]. For WPC with a-APP/c-SiO₂, the surface of the char residue of the WPC was covered with uniform particle. This was due to the interaction of positive and negative charges, the c-SiO₂ was closely adsorbed on the a-APP and covering the surface of the WPC, which reducing the transfer of heat to the interior of the WPC during combustion.

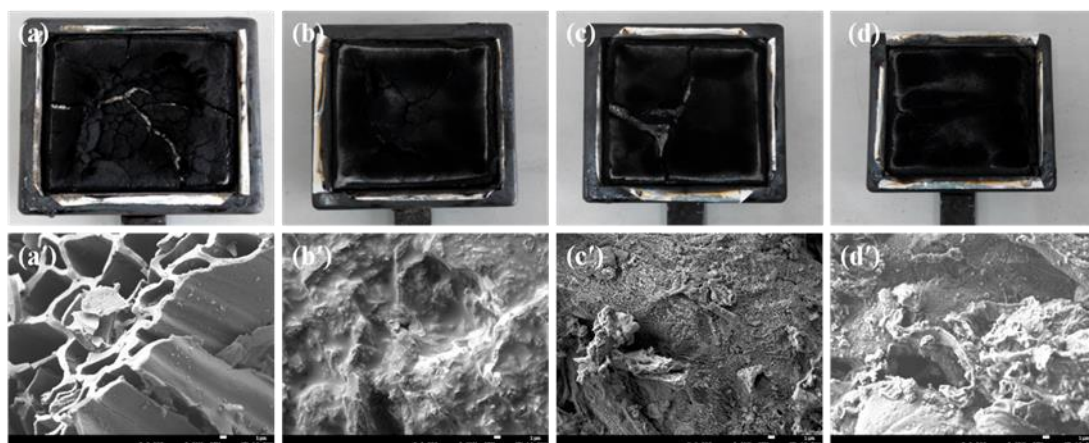


Fig.5 The morphological structure of the residues from CC test: (a) WPC, (b) WPC/APP, (c) WPC/a-APP, (d) WPC/a-APP/c-SiO₂. Top row is digital photographs and bottom row is SEM image.

3.6 Composition analysis of WPC char residues

Fig 6 shows XPS spectra of char residues after Cone testing, and the atomic composition results are also summarized in Table 4. The peaks at 133eV, 191eV, 284eV, 400eV, 531eV represent P2p, P2s, C1s, N1s, O1s in the char layer, respectively. The main chemical

constituents of carbon residue after combustion of neat WPC are C and O elements. When APP was added to WPC, a new peak spectrum appeared at 133eV and 191eV, representing P2p and P2s in the char layer. This indicate that P element was introduced when the APP powder was added to WPC. For WPC with a-APP, the N element increased significantly, compared with the results of WPC/APP, which increased by 140%. For

WPC with a-APP/c-SiO₂, the C and Si element increased significantly, compared with the results of WPC/a-APP, which increased by 2% and 266%, respectively.

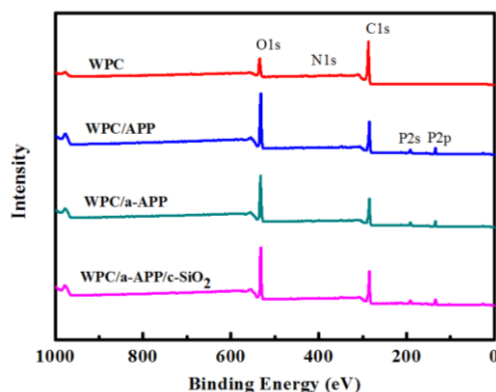


Fig.6 XPS spectra of char residues after cone calorimeter tests of WPC

Table 4 Atomic composition of char residues after cone calorimeter tests of WPC

Sample	C(%)	O(%)	N(%)	P(%)	Si(%)	O/C(%)	P/C(%)
WPC	82.2	16.5	0.5	0.2	0.6	0.2	0.0
WPC/APP	61.1	33.0	0.7	4.9	0.3	0.5	0.1
WPC/a-APP	60.0	33.3	1.2	5.3	0.3	0.6	0.1
WPC/a-APP/c-SiO ₂	61.2	32.2	1.1	4.5	1.1	0.5	0.1

3.7 Flame retardant mechanism of composite polyelectrolyte

Fig 7 shows flame retardant mechanism diagram of polyelectrolyte WPC/a-APP/c-SiO₂. According to above-mentioned analysis, in an initial burning stage, the products polyphosphate acid, HPO and PO radicals generated from a decomposition of APP polyelectrolyte can trap the active H radicals and HO radicals produced by wood fibers. On the other hand, it can promote the esterification and dehydration reaction of NCC and promote the formation an intumescent, stable, and compact char layer [Fig 7(1)]. Fig 7(3) shows the interaction of positive and negative charges, c-SiO₂ was

closely adsorbed on the surface of a-APP, when the temperature reached about 300 °C, in the c-SiO₂, —OH and the a-APP undergo dehydration and cross-linking reaction to form P—O—C, P—O—Si and Si—O—C [6, 19]. And finally formed crystalline phase of silicon metaphosphate (SiP₂O₇), the crystalline phase of SiP₂O₇ can form protective barrier and contribute to the carbonization of WPC, lead to the C content was increased [20]. Fig 5(d) and Fig 5(d') shows the Nano-SiO₂ enhances the physical integrity of the char layer structure, the flame retardant efficiency of WPC was improved.

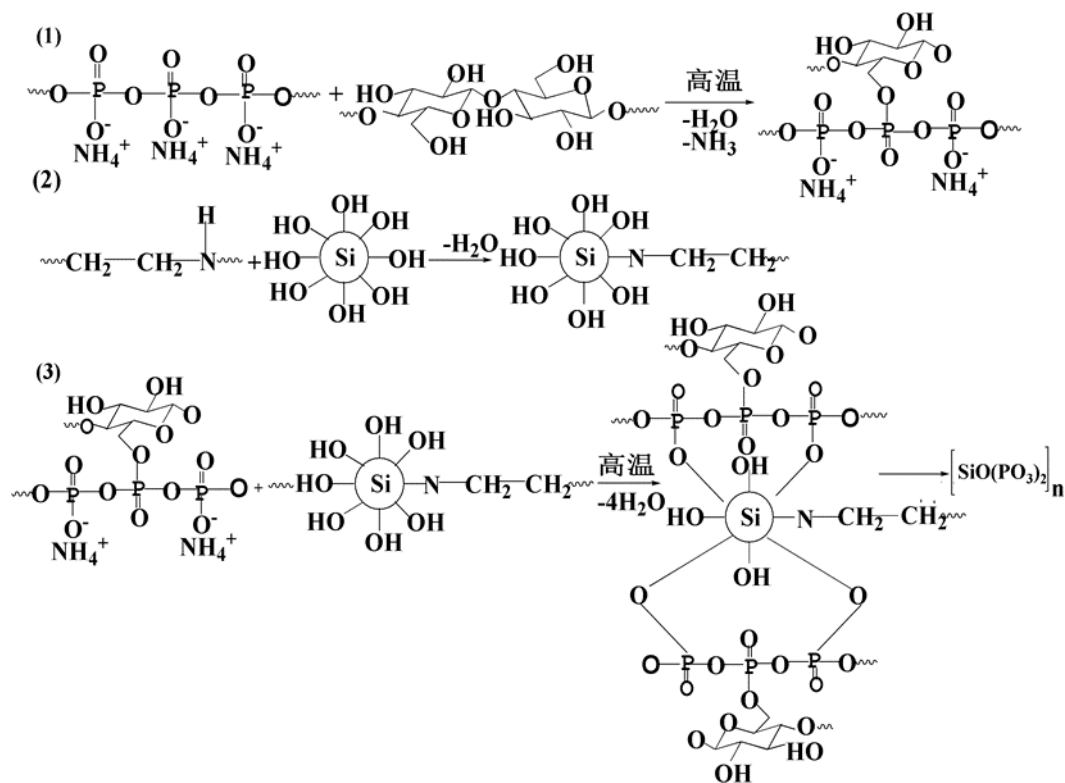


Fig 7 Possible mechanism for charring during the combustion process of WPC/a-APP/c-SiO₂

4. Conclusion

This paper used Nano-crystalline cellulose (NCC) modified ammonium polyphosphate (APP) as anionic polyelectrolyte (a-APP), and cationic polyethyleneimine (PEI) modified Nano-SiO₂ as cationic polyelectrolyte (c-SiO₂). The flame retardant system was built due to the reaction of a-APP and c-SiO₂. Polyelectrolyte composite of a-APP/c-SiO₂ were then assembled on the surface of wood powder and HDPE composites. The effect of polyelectrolytes of WPC were investigated.

The positive and negative charges were attracted to each other between the a-APP and the c-SiO₂, so the cationized Nano-SiO₂ was closely adsorbed on the surface of the a-APP. In addition, the c-SiO₂ were uniformly dispersed on the surface of the wood powder, which can effectively prevent the APP migration phenomenon as the using time prolongs. When the a-APP/c-SiO₂ was added to WPC, which TSR and THR were the lowest decreased to 1694.7m²/m², 108.5MJ/m², compared with WPC/APP decreased by 13.9% and 8.8%, respectively. LOI and TTI for WPC/a-APP/c-SiO₂ reached to maximum were 27.5% and 37s, respectively. For WPC with a-APP/c-SiO₂, the C and Si element increased significantly. At high temperatures, APP was thermally decomposed to release polyphosphate acid and

ammonia. These products undergo esterification and dehydration reactions with NCC to promote the formation of char layers, lead to the C content was increased. When the a-APP was added to WPC, which tensile strength, tensile elongation at break and flexural strength were reached the maximum of 19.53MPa, 2.43%, and 40.00MPa, respectively. When the a-APP/c-SiO₂ was added to WPC, the impact strength and tensile elongation at break were increased by 9.4% and 60.4%, compared with WPC/APP.

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