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Self-intumescent polyelectrolyte for flame retardant poly (lactic acid) nonwovens

Xingguo Wang a, b, Wenjia Wang a, b, Shuheng Wang a, b, Yufan Yang a, b, Hongfei Li a, c, Jun Sun a, b, Xiaoyu Gu a, b, **, Sheng Zhang a, c, *

a State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing, 100029, China
b Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing, 100029, China
c Beijing Key Laboratory of Advanced Functional Polymer Composites, Beijing University of Chemical Technology, Beijing, 100029, China

** Corresponding author. State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing, 100029, China.
* Corresponding author. State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing, 100029, China.
E-mail addresses: guxy@mail.buct.edu.cn (X. Gu), zhangsheng@mail.buct.edu.cn (S. Zhang).

Abstract

The demand for eco-friendly poly (lactic acid) (PLA) nonwovens grows at a high rate in the past several decades, however, only a little attention has been received for flame retardant PLA nonwoven fabrics. In this work, a novel halogen-free self-intumescent polyelectrolyte tris (hydroxymethyl)-aminomethane polyphosphate (APTris) was synthesized by reacting ammonium polyphosphate with tris (hydroxymethyl) aminomethane, and was then used to improve the fire resistance of PLA nonwovens via a dip-nip process. The flammability characterization indicated the limiting oxygen index value was increased to 30.0% from 18.3%, and the damaged area in the vertical burning test was reduced by about 87.0% by the presence of APTris. The cone calorimeter test results revealed that the peak heat release rate and total heat release of the treated sample were decreased by 41.0% and 28.2% respectively compared with that of the control PLA nonwoven sample. The char residue was increased to 12.3 from 1.7 wt % at 800 °C. It is suggested that the dense char barrier formed at the presence of APTris prevents heat, smoke, and gas transfer, and hence enhance thermal dilatability and flame retardancy of PLA nonwovens. This simple sustainable halogen-free treatment has great potential to produce cleaner commercialized flame-retardant PLA nonwovens.

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1. Introduction

With the depletion of fossil resources and deterioration of the environment, bio-based and biodegradable materials have been drawn more and more attention. Poly (lactic acid) (PLA), which is derived from renewable resources (e.g., rice, corn, wheat, etc.), can be biodegradable to generate H2O and CO2 (Iwata, 2015; Murariu and Dubois, 2016), and has become one of the most widely used biodegradable materials. Compared with petroleum-based polymers, the production of PLA requires 25–55% less energy and consumes carbon dioxide, which doesn’t cause environmental damage and pollution (Farah et al., 2016). PLA fabrics are also considered as an ideal candidate to substitute petroleum-based chemical fabrics. PLA nonwovens grow at a high rate in the several decades (Wang et al., 2007), and it is widely applied in the textile industry, such as upholstery backings, needle punched carpets, agricultural textiles, furniture fabrics, linings, and geotextile products (Cheng et al., 2016a). Unfortunately, PLA nonwovens are unsuitable in many commercial cases for its intrinsic flammability (Parma et al., 2014). PLA is flammable with a very low limited oxygen index (LOI) of 18–19%, and the key challenge for flame retardant PLA is the severe molten dripping. Although intensive efforts have been made on the flame-retardant PLA thermoplastics, the research on flame-retardant PLA nonwovens are rarely reported so far. Therefore, it is necessary to develop high value-added biodegradable flame-retardant PLA nonwovens in the textile industry (Cheng et al., 2019; Shahid ul et al., 2013).

The halogen-containing flame retardants were widely applied in the textiles industry (Kemmlein et al., 2009; Qi et al., 2014), however, these halogenated compounds usually exist the harm of bio-accumulation in the environment and generate toxic gases during
combustion to cause serious environmental pollution and health problems (Liu et al., 2020). Therefore, halogen flame retardants are restricted more and more in many countries (Veen and Boer, 2012). It has been demonstrated that P/N containing flame retardants are efficient additives to reduce the fire hazard of PLA thermoplastics (Bourbigot and Fontaine, 2010; Wang, X. et al., 2019), and are more environmentally friendly than halogen-containing flame retardants. The introduction of phytic acid (PA) into PLA nonwovens by a pad-dry-cure process (Cheng et al., 2016b) increased the LOI value of PLA/45%PA sample by 37.3% in comparison with that of the control PLA nonwoven sample, but hardly reduced the damaged length in the vertical burning test. Other research reported (Cheng et al., 2016a) that cyclic phosphonate ester improved the flame retardancy of PLA nonwovens by gas-phase mechanism, and the LOI value was increased by 33.1%, but the performance of micro-scale combustion and vertical burning test was not satisfactory. A mixture of phosphonate esters was used to enhance the fire performance of PLA nonwovens (Avinc et al., 2012), after complex drying and curing procedure, the treated fabrics could pass the criteria of NFPA 701 after washing. The sheath/core configuration bicomponent PLA containing intumescent flame retardants were prepared by melt spinning to fabricate PLA nonwovens by thermal bonding (Magood and Seide, 2019). The obtained PLA/APPs/PES10/KL3 nonwovens showed a 46.0% reduction in pHRR and a 34.5% increase in residual mass compared pure PLA nonwovens, the LOI value of that increased to 30.4% from 19.3%. However, the preparation process which involves high temperature spinning and bonding, is complex and toilsome. In summary, the effective and feasible way for flame-retardant PLA nonwovens is still under seeking.

Polyelectrolytes are long chain compounds with ionizable groups in their repetitive molecular units, which have been widely used as porous materials on environmental remediation, tissue engineering, and catalyst (Zhang et al., 2018). Polyelectrolytes are prepared by ionic reaction in aqueous solution, which is convenient, efficient, and eco-friendly (Christophe et al., 2004). In recent years, polyelectrolytes have attracted extensive attention in the flame-retardant application. Some bio-based materials including phytic acid, chitosan, casein, and polyethyleneimine have been frequently selected to match each other as anionic or cationic (Holder et al., 2017). For examples, the chitosan/phytic acid (Zhang et al., 2014) was used to improve the flame retardancy of vinyl acetate copolymer (EVA), and showed excellent intumescent effect to promote the EVA composite to form a compact char layer. Polyethyleneimine and oxidized sodium alginate were alternately coated on polyester-cotton blend fabrics by the layer-by-layer assembly (Pan et al., 2018), which enabled the fabrics self-extinguish after being ignited. Guanidine sulfate (GSM) was added in intumescent polyelectrolyte to improve the flame retardancy of polyester fabrics by the LBL technique (Jordaan et al., 2019). In our previous work, phytic acid, casein, and ammonium polyphosphate were combined to form core-shell bio-polyelectrolyte PC@APP, and the presence of only 5% PC@APP significantly decreased the peak heat release rate of PLA composites (Jin et al., 2019). Overall, polyelectrolytes have been used to enhance the fire resistance of PLA plastic, so it is possible to improve the flame retardancy of PLA nonwoven fabrics by polyelectrolyte coating.

In this work, a novel polyelectrolyte of tris(hydroxymethyl)aminomethane polyphosphate (APTris) was designed and prepared based on the acid-base equilibrium theory. A high phosphorus-containing ammonium polyphosphate (APP) was chosen as anionic, and a polyhydroxy compound tris (hydroxymethyl)aminomethane was selected as a guest compound with opposite charge. APTris coating was then introduced onto the surface of PLA nonwovens by a convenient pressure leaching and heat cure process. The combustion behavior and thermal stability of treated PLA nonwovens were comprehensively evaluated, and the mechanism of APTris in improving the flame-retardancy of the fabrics was discussed. The strategy of coating single self-instrument polyelectrolyte provides an efficient, low cost way to enhance the fire safety of PLA nonwovens. The synthesis of water soluble APTris doesn’t involve any toxic solvents, and involved raw materials are readily available at reasonable prices, and the dip-nip technology for flame retardant finishing of PLA nonwovens is efficient, low cost, and suitable for commercialization. To the best of our knowledge, the application of polyelectrolytes to endow flame retardancy of PLA nonwovens has not been reported so far, this work should be one of the few to focus on the flame retardancy of bio-based PLA nonwovens.

2. Experimental

2.1. Materials

Hydrosoluble ammonium polyphosphate (APP, 10 < n < 20) was obtained from Shandong Shi An Chemical Industry Co. LTD. Tris (hydroxymethyl)-aminomethane (Tris) was purchased from Beijing Aoboxing Biotech Co., Ltd., Hexadecyl trimethyl ammonium bromide (CTAB) was received from Tianjin Jinke Fine Chemical Research Institute. PLA nonwovens were purchased from Chengdu Julong Non-woven Co., LTD. with an average filament diameter of 16.5 μm and a surface weight of 100 g/m².

2.2. Preparation of APTris solution

The preparation process of APTris was illustrated in Scheme 1(a). After dissolving 20 g APP in a 500 mL beaker with 300 mL DI water, 20 g Tris was added into the solution. The mixed solution was vigorously magnetic stirred at 70 °C, during which NH₃ was continuously released. The reaction was stopped when the pH value reached 7. The solvent was removed by using a rotary evaporator, and the obtained white sticky precipitate was washed with ethanol. Finally, the white viscous product was further dried under vacuum at 80 °C until constant weight. The yield of target product was around 87 wt%.

2.3. Flame retardant treatment of PLA nonwovens by APTris

The treatment process of PLA nonwovens was described in Scheme 1(b). Specifically, PLA nonwovens were pretreated with C₁₀H₂₂BrN to improve its hydrophilia and then was impregnated in APTris solution with a concentration of 150 g/L. The pretreated nonwovens were pressured through a two-roll laboratory padder (HB-BL, Huibao Dyeing and Finishing Machinery Factory). Different pressure between the two-rolls was used to obtain samples with different weigh gains, which was listed in Table 1. Finally, the impregnated nonwovens were dried at 80 °C for 2 h. PLA nonwovens impregnated with 150 g/L APP solution was selected as a control sample.

2.4. Characterization

2.4.1. Weight gain

The weight gain is calculated according to formula (1):

\[
\text{Weight gain (wt.%) } = \frac{W_1 - W_0}{W_0} \times 100\%
\]  

Where \( W_0 \) presents the original weight of PLA nonwovens before treatment, and \( W_1 \) is the weight after treatment.
2.4.2. Vertical burning (UL-94) and limiting oxygen index (LOI) test
The vertical burning test was carried out based on the standard ASTM D6413-13 using a JF-3 type instrument with the sample size of 30 × 8 cm², and the LOI value was measured based on the standard GB/T 5454-1997 with the sample size of 15 × 6 cm² using CFZ-2 type instrument. The results were averaged by five parallel specimens.

2.4.3. Cone calorimeter test (CCT)
Cone calorimeter tests were implemented according to ISO 5660 using a cone calorimeter (FTT, UK) under a heat flux of 35 kW/m². Five identical PLA nonwovens with a size of 100 × 100 × 1.8 mm³ were superimposed as one sample, and the test results were averaged by five measurements.

2.4.4. Microscale combustion calorimeter (MCC)
The pyrolysis of PLA nonwovens was analyzed at smaller-scale combustion by using an MCC. Samples of 4.0 ± 1 mg were heated from 25 °C to 750 °C at a heating rate of 1 °C/s under a mixing flow of N₂ (80 cc/min)/O₂ (20 cc/min), the final result was also obtained by averaging five measurements.

2.4.5. Spectroscopic analysis
Thermo Nicolet NEXUS 670 type spectrometers were used to collect the Fourier Transform Infrared Spectroscopy (FTIR) spectra by using a KBr pellet pressing method in a range of 4000–400 cm⁻¹.

The X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALAB 250 (ThermoFisher Scientific USA) spectrometer with a source of monochromated Al Kalph 150 W. The pass energy was 200 eV for a survey and 30 eV for high resolution scans.

2.4.6. Thermogravimetric analysis (TGA)
The thermal stability was evaluated using a TA-Q50 apparatus, an alumina crucible contained 6.0 ± 1.0 mg samples was heated from ambient temperature to 800 °C at a heat rate of 10 °C/min under N₂ atmosphere.

2.4.7. Microscopic observation
The microscope images were obtained from a scanning electron microscopy (SEM) instrument (HITACHI S-4700 at a 20 kV beam voltage).

2.4.8. Calcination
APTris and PLA nonwovens were calcined in a muffle (Thermo Scientific, FB-1310M) respectively according to a method reported elsewhere (Liu et al., 2017), and the calcined temperatures were determined according to the corresponding TG curves. 0.2 g APTris was calcined for 5 min at fixed temperatures (250, 275, 300, 350, 450, 550, and 650 °C, respectively), 1.0 g PLA and 1.0 g PLA/25% APTris nonwovens were calcined simultaneously for 5 min at fixed temperatures (200, 250, 350, 400, and 650 °C, respectively).

3. Results and discussion
3.1. Characterization of APTris
The FTIR spectra of APP, Tris, and APTris are shown in Fig. 1(a). The peaks at 3367 cm⁻¹ and 3203 cm⁻¹ in the APTris curve belong to the stretching vibrations of –OH and N–H, the peaks in the range 2970 to 2850 cm⁻¹ correspond to C–H of an aliphatic hydrocarbon, indicating the presence of Tris. Besides, the peaks at 1295 cm⁻¹, 1056 cm⁻¹, and 975 cm⁻¹ are the absorbance of P=O, P−O, and P–OH in APTris, respectively (Chen et al., 2020; Yuan et al., 2018), and the weakened relative intensity indicates that APP is
successfully combined with Tris (Zhang et al., 2019).

The elemental composition and chemical states of APTris and APP are investigated by XPS. The same element composition is found in the survey scanning spectra of APP and APTris in Fig. 1(b). The predominant peaks correspond to C1s (286.68 eV), N1s (401.72 eV), O1s (544.75 eV), P2s (191.0 eV) and P2p (133.66 eV) respectively. In the high resolution scanning of N1s in APP, it is fitted into two peaks (Fig. 1(c)), the first one at 401.6 eV is assigned to NH$_4^+$, the other at 399.6 eV is corresponding to -P NH -P- (Camino et al., 1985; Shao et al., 2014). However, N1s spectrum for APTris is fitted into two peaks at 400.5 and 401.8 eV (Fig. 1 (d)), which is assigned to N-C derived from the reaction of APP and Tris (Jin et al., 2017). Meanwhile, Table 2 also gives the changes of composition obtained from XPS results. The percentage of N, O, and P atomic in APTris decreases to 8.70\%, 42.74\%, and 7.69\% respectively, which is lower than that of APP. Besides, the C atomic percentage increases from 12.03\% to 39.87\% because of the reaction of APP and Tris. Similar results are obtained from organic elemental analysis (OEA) measurement, the C content increases from 4.36\% to 21.49\%, and the N content decreases from 25.07\% to 11.74\% for APTris.

As shown in Fig. 2, 200 mg APTris and 200 mg APP (as a control group) are simultaneously calcined in muffle for 5 min at a different temperature to evaluate the thermal dilatability. Fig. 2(a) shows that the color of APTris turns to brown and then to black from white with the increase of temperature, the volume of the APTris is gradually expanding observed from Fig. 2(b), which indicates that APTris has excellent quick thermal dilatability and carbonizing properties. The incorporated Tris acts as a blowing agent and a charing agent during combustion and plays an important role in achieving quick self-intumescence for APTris. Fig. 2(c) displays the inner structure of the intumescent char layer of APTris, one can see that a cavity structure is formed by the expansion process. Besides, the carbonized temperature of APTris is around 275°C, which is lower than the decomposition temperature of PLA nonwovens. Besides, the char layer maintains a compact intumescent structure from 350 to 550°C. Hence, the early char layer formed by APTris can well protect the underlying PLA nonwovens by slowing down the conduction of heat and the transfer of oxygen/volatile fuel.

### Table 2
The atomic percentage for APP and APTris.

| Sample | OEA (wt. %) | XPS (Atomic. %) |
|--------|-------------|-----------------|
|        | C   N   H   | C   N   O   P  |
| APP    | 4.36 | 25.07 | 6.36 | 12.03 | 14.96 | 53.37 | 19.64 |
| APTris | 21.49 | 11.74 | 7.17 | 39.87 | 8.70  | 43.74 | 7.69  |

3.2. The surface morphology

Table 1 listed PLA nonwoven samples with different weight gains obtained by controlling nip pressure. The variation of
appearances including color, flatness, and surface texture of non-wovens before and after treatment is minimal (Fig. S1). The surface microtopography of treated nonwovens and dispersion state of flame retardant can also observed in Fig. 3. The original PLA non-wovens show a multilayer overlap structure with quite smooth surface in Fig. 3(a, a1). For PLA/17%APP nonwoven sample in Fig. 3(b, b1), one can see most APP particles aggregate between fibers. The difference is that APTris affixed on fibers surface tightly and distributed evenly shown in Fig. 3(c, c1). It is supposed that it exist strong interfacial interaction between APTris and PLA, which is due to the polar polyhydroxy groups in APTris. Therefore, the compatibility of APTris is superior to that of APP in PLA.

3.3. Thermogravimetric analysis

TG and analysis curves of treated PLA nonwovens under N2 atmosphere are shown in Fig. 4 and Table 3. From Fig. 4(a), we can see that untreated PLA nonwoven decomposes in the range of 350–420 °C, with a 10% weight loss temperature (T10%) of 366.5 °C and a char residue value of only 1.7 wt% at 800 °C. After the introduction of APTris, the T10% value gradually decreases with the amount of APTris but the final char residue increases at high temperature range. The earlier pyrolysis of APTris leads to hydroxyl dehydration and inert gas release, which promotes the crosslink carbonization and reduce melt droplets of PLA nonwovens. In addition, APTris makes contribution to reducing the maximum weight loss rate (DTGmax) from 2.95 to 2.08%/°C in Fig. 4(b), and increasing char residues at 800 °C from 1.7 to 12.3 wt%. The experimental char residue value is 30% higher than that of calculated value. High char residue indicates uncomplete combustion of polymeric matrix, which usually reflects better flame retardancy. It can be found the PLA/17%APTris sample exhibits higher char residue and lower DTGmax value than the PLA/17%APP sample. TG analysis curves of treated PLA nonwovens under air atmosphere are also carried out and shown in Fig. S2 and Table S1. We can see similar result to that under nitrogen atmosphere.

![Fig. 2. Digital photographs of APP and APTris heated at a different temperature: top (a) and side (b) view of APP and APTris, cross-section (front) view of APTris (c).](image)

![Fig. 3. Microtopography of treated PLA nonwovens: PLA (a, a1), PLA/17%APP (b, b1), PLA/17%APTris (c, c1).](image)
3.4. The fire performance

3.4.1. LOI and vertical burning tests

The data obtained from LOI and vertical burning test is shown in Fig. 5. LOI, molten dripping, and damaged length are given in Fig. 5(a). One can see that the untreated PLA nonwoven sample has a LOI value of only 18.3% with a damaged length of 14.5 cm. The flame retardancy presents an upward tendency with the increase of APTris weight gain. The LOI value increases to 30.0%, and the damaged length decreases to 8.0 cm for the PLA/25%APTris sample. The severe melt droplets disappear in the vertical burning test for the PLA/17%APTris sample, while that is still observed for the PLA/17%APP sample, reflecting APTris is more effective in reducing melt dripping of PLA nonwovens. The polyhydroxy structure of Tris releases inert gases upon heating, which retards flame propagation. Meanwhile, the network structure formed by crosslinking between APP and Tris promotes charring formation, which increases the melt viscosity during combustion of PLA nonwovens. The combination effect of Tris and APP in both gas phase and condensed phase eliminates the melt dripping. In order to further characterize the flame retardancy of treated PLA samples, damaged area and after-flame time are recorded in Fig. 5(b), where the digital photographs (inset image) intuitively reflect fire damage state. The burning process of pure PLA nonwovens lasts 8 s accompanied with a damaged area of about 62.0 cm² with high fire hazards. The damaged area is significantly decreased by the presence of APTris, PLA/25%APTris shows only 8 cm² damaged area, and self-extinguishes immediately after the removal of the igniter. The after-flame time of PLA/17%APTris is decreased to 2 s, and the corresponding burning area is decreased by 43.7% in comparison with that of PLA/17%APP sample, indicating that APTris possesses higher flame-retardant efficiency than APP for PLA nonwoven

Table 3

The TG and DTG key data of PLA nonwoven samples in nitrogen atmosphere.

| Samples         | T10%/C | T50%/C | DTGmax%/°C⁻¹ | Tmax%/C | Char at 800 °C Exp/Cal (wt.%) |
|-----------------|--------|--------|---------------|---------|------------------------------|
| PLA             | 366.5  | 389.2  | 2.95          | 393.8   | 1.7/-                       |
| PLA/10%APTris   | 363.2  | 394.4  | 2.68          | 398.8   | 4.3/1.8                    |
| PLA/17%APTris   | 333.4  | 389.4  | 2.30          | 393.4   | 9.6/6.3                    |
| PLA/17%APP      | 364.6  | 390.6  | 2.86          | 394.0   | 4.4/4.9                    |
| PLA/25%APTris   | 289.8  | 387.3  | 2.08          | 391.6   | 12.3/8.7                   |

Fig. 4. The integrated data analysis obtained from LOI (a) and vertical burning test (b).
fabrics.

3.4.2. The calorimeter test

The mesoscale combustion behavior of PLA nonwoven samples is further investigated by cone calorimeter test (CCT) with a heat flux of 35 kW/m². Fig. 6 shows the combustion curves of the heat release rate (HRR), total heat release (THR), total smoking production (TSP), and charring residues rate. Table 4 collects some key data from the cone test. In Fig. 6(a and b), the PLA nonwovens release a mass of heat with an intense peak of heat release rate (pHRR) about 332.2 kW/m², while PLA/17%APTris and PLA/25% APTris has a decreased pHRR value of 232.5 and 196.2 kW/m², respectively. The THR values has also been decreased by the presence of APTris. Meanwhile, more char residue remains in the condensed phase shown in Fig. 6(d). It is proposed that the improvement of flame retardancy ascribes to the excellent carbonization performance of APTris. In terms of smoke release performance in Fig. 6(c), the control PLA decompose rapidly with the TSP of only 0.052 m². However, the TSP increases sharply to 0.207 m² for PLA/17%APP, the TSP values for PLA/17%APTris and PLA/25%APTris samples further drop to 0.164 m² and 0.089 m², indicating the smoke suppression effect of APTris is superior to that of APP because of its excellent thermal dilatability and carbonizing properties. This phenomenon can be explained according to the basic flame-retardant mechanism of phosphorus-containing compounds (Bauer et al., 2017; Jayaweera et al., 2005). PO$, P\text{O}_2$, etc. radicals are generated by APP pyrolysis, which can react with HO- and H- to block chain reaction of combustion, which leads to incomplete combustion of volatile compounds, hence the incorporation of phosphorus flame retardants into PLA generally cause an increase in smoke emission. Compared with APP, APTris is easier to form a crosslinking network structure in the condensed phase. On the one hand, that obstructs the release of combustible volatile and smoke (Tawiah et al., 2019); on the other hand, more phosphorus element is remained in the condensed phase rather than release to vapor phase, which demonstrates APTris acts in the condensed phase (Yang et al., 2010); on the other hand, APTris generates phosphorus containing radicals to capture hydroxyl radicals, and inhibits the combustion. The MCC data also demonstrates APTris also acts in the gas phase.

3.4.3. Char residue morphology

To analyze the morphology of char residues conduces to understand the flame retardation of the condensed phase (Wang, S. et al., 2019). The digital photographs and SEM images of the char residue after the cone calorimeter test are shown in Fig. 8. Compared with the macromorphology of char residues in From Fig. 8(a–c), we can see that the PLA nonwoven sample treated by APTris shows a more integrated morphology than that treated by APP. For PLA/17%APP sample, the residue displays serious breakage
3.5. Flame retardant mechanism

In order to investigate the flame retardant mechanism of PLA/APTris, the pyrolysis and carbonization process was simulated by calcining PLA and PLA/25%APTris nonwoven samples in a muffle furnace. Five calcined temperatures (200, 250, 350, 400, 650 °C) are selected according to the TG curves. As shown in Fig. 9(a), the untreated PLA is intensively pyrolyzed into combustible volatiles and leave more pyrolysis products in the condensed phase (Gong et al., 2020). Therefore, the flame retardancy of PLA nonwovens is improved.

3.6. Prospect forecast of PLA nonwovens

Eco-friendly nonwovens are a potential alternative for the current commercial petroleum-based nonwovens, such as polyethylene terephthalate (PET) and polypropylene (PP). PLA nonwovens have been regarded as a green and sustainable textile in industry, owning to energy saving of production (25%–55% than petro-based polymers) and biodegradability (Rasal et al., 2010). Therefore, PLA nonwovens have significant potential applications in garment industries, medical supplies, decoration, agricultural cultivation, and so on. For example, due to the coronavirus COVID-19, a mass of masks and protective personal equipment, made of polypropylene (PP) nonwoven material, have been used in the past several months (The Beijing News, 2020), but the post-treatment of medical waste will face a baptism because of the difficulty biodegradation for PP products. Therefore, biodegradable PLA nonwovens are a more ideal material to fabricate disposable protective equipment. The inherent flammability of PLA nonwovens is one of the limitations of its industrial application. PLA nonwovens can be fabricated via needle-punching, melt-blowing or spun-bonding. The functional additives are generally incorporated during melt spinning process, but the choice for flame retardants is limited by many factors, such as the thermal stability, compatibility, solubility, etc. Besides, the spinnability of PLA containing many factors, such as the thermal stability, compatibility, solubility, etc. Besides, the spinnability of PLA containing flame retardants is usually reduced. Table 5 lists the fire performance and cost of flame-retardant PLA nonwovens from the published literature.
this work. We can see APTris treated PLA nonwovens in this work is inexpensive, more feasible and higher efficiency than the chemical grafted (Cheng et al., 2016a), spun-bonded (Maqsood and Seide, 2019) and other flame retardant treated (Cheng et al., 2016b) PLA nonwovens. The synthesis of APTris doesn’t involve any toxic solvents, and the involved raw materials have reasonable price and rich source, which is suitable for industrial to produce cleaner flame retardant PLA nonwovens.
A novel polyelectrolyte APTris was successfully prepared through ion-exchange reactions between APP and tris(hydroxymethyl) aminomethane. The incorporation of polyhydroxy Tris significantly improved the presence of APTris. This research has provided a new strategy for preparing cleaner flame retardant PLA nonwovens in the textile industry. Further investigation on improving the durability of flame retardant PLA nonwovens are undertaken in our laboratory.

4. Conclusions

Annexure A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2020.124497.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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CRediT authorship contribution statement

Xingguo Wang: Data curation, Investigation, Visualization, Formal analysis, Writing - original draft. Wenjia Wang: Data curation, Software, Visualization. Shuheng Wang: Formal analysis, Visualization. Yufan Yang: Investigation, Software. Hongfei Li: Formal analysis, Resources. Jun Sun: Conceptualization, Funding acquisition, Supervision. Xiaoyu Gu: Conceptualization, Formal analysis, Methodology, Writing - review & editing. Sheng Zhang: Conceptualization, Funding acquisition, Supervision, Methodology, Writing - review & editing.

Table 5

The chemicals cost and fire performance of PLA nonwovens for the existing articles.

| Samples | Weight gain (%) | LOI (%) | THR (kJ/g) | pHRR (W/g) | Cost (\$) | Ref. |
|---------|-----------------|---------|------------|------------|-----------|-----|
| PLA     | 0               | 26.3    | 18.9       | 464.9      | –         | Cheng et al. (2016b) |
| PLA-100PA | 18.5           | +20.5%  | –23.8%     | −29.4%     | 2.6       | Cheng et al. (2016a) |
| PLA-250PA | 45.0           | +37.3%  | –38.6%     | −39.9%     | 6.3       | Cheng et al. (2016a) |
| PLA     | 0               | 26.3    | 18.4       | 462.0      | –         | Maqsood and Seide (2019) |
| PLA-100/DP-150 | 3.5        | +32.3%  | –7.6%      | −4.5%      | –         | Cheng et al. (2016b) |
| PLA-200/DP-150 | 4.4        | +35.0%  | –8.7%      | −7.1%      | –         | Cheng et al. (2016b) |

\* The cost was calculated according to the consumption of chemicals per treatment 100 g PLA nonwovens. The price of phytic acid (PA, 70% in H2O), APP, Tris and lignin (KL) were 14.0 $/100 g, 5.8 $/100 g, 10.2 $/100 g, and 42.4 $/100 g respectively, which obtained from Shanghai Aladdin Reagent Co., Ltd. (1 $ = 7.077 v).

\* According to the description of the 2.2 section, the calculated price of APTris is 9.2 $/100 g.
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