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THE CHITOSAN BASED FLAME RETARDANTS: A MINI REVIEW

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ARTICLE DETAILS

ABSTRACT

Article History:

Received 26 June 2018 Accepted 2 July 2018 Available online 1 August 2018 The based Chitosan flame retardant has the characteristics of green sustainable development and meets the future development direction of the flame retardant. Built on the study of the based chitosan flame retardants by scholars at home and abroad, the research progress of the based chitosan flame retardants is systematically introduced in recent years, namely single-component, composite and chemically modified chitosan flame retardants. The single-component chitosan flame retardant can improve the thermal stability of the polymer to a certain extent, but it cannot improve the flame-retardant grade of the material. The main research direction of chitosan composite flame retardant is the application of green compound phosphorus-containing substances, the exploration of different compounding technology, and the in-depth development of layer-by-layer self-assembly technology of fiber products. In the fields of fiber, plastic and other products, the molecular design is based on the requirements of the chitosan flame retardant and the adaptability of the materials, and the characteristics of high efficiency flame-retardant, blending compatibility, and finishing wash ability are obtained.

KEYWORDS

Chitosan, Bio-based, layer-by-layer self-assembly, Chemical modification.

1. INTRODUCTION

Greening of flame retardants has been achieved an inevitable trend in the development of flame retardant technology, and the use of natural biobased materials as flame retardants complies with the requirements of the green development strategy. Therefore, the flame retardants prepared with chitosan as raw materials have received extensive attention from researchers.

First of all, chitosan is a nitrogen-containing polysaccharide, biodegradable, biocompatible and environmentally nontoxic. Secondly, the molecular skeleton of chitosan is carbon-rich and contains a certain amount of hydroxyl and amino groups. During the process of thermal decomposition, carbonization prevents combustion and releases noncombustible gas such as CO₂, NH₃ and N₂, and thus is a flame-retardant effect. Finally, the amino and hydroxyl groups on the chitosan molecule make it get a good reactivity. It can be molecularly designed and introduce multiple flame-retardant elements, so as to amend its physical and chemical properties and improve the flame-retardant efficiency and applicability [1-3]. Chitosan can be used as an antibacterial agent in textiles, plastic, rubber and other products. Especially in the field of fiber products, it was fitted with antibacterial properties and could improve the dyeing, ironing, expansion and stamping resistance [4-6].

2. SINGLE-COMPONENT CHITOSAN FLAME RETARDANT

The single-component chitosan flame retardants are characterized by their unique flame-retardant components. Johns modified natural rubber by blending of chitosan. The mass loss after modification was reduced by 43%, and the thermal stability was greatly improved [7]. Don was doped with chitosan in the process of polymerization of methyl methacrylate, the glass conversion temperature was increased from 113°C to 127°C, the amount of carbon residue gradually increased with the increase of the amount of chitosan [8].

The theoretical C content of chitosan is 45.0%, and the N content is 8.7%. The modification of the material mainly increases the proportion of carbon in the material and improves the thermal performance. Since the nitrogen content was small, it could only play an auxiliary role in the gas phase flame retardant. Therefore, chitosan can improve the thermal

stability of the polymer to a certain extent and made flame retardant performance better, but it cannot improve the flame-retardant grade of the material.

3. BLENDED CHITOSAN FLAME RETARDANT

The blended chitosan flame retardant is the compound effect of chitosan and other flame-retardant substances to form multiple phosphorus-nitrogen, silicon-phosphorus-nitrogen and other flame-retardant elements. At present, there are mainly poly-phosphate, bio-based materials and inorganic nanoparticles for the blended flame retardants with chitosan.

3.1 Poly-phosphate

In the chitosan and poly-phosphate compounding system, chitosan provides carbon source and gas source. Poly-phosphate mainly provide acid source, the blended material can produce a synergistic effect of many flame-retardant elements such as P and N. Charuchinda used sodium polyphosphate to make cotton fabrics, and it had no flame-retardant effect after washing. On the other hand, the sodium poly-phosphate and chitosan were finished on cotton fabrics. After washing, the washing performance needed to be improved and the LOI was still 19% [9]. When chitosan and sodium poly-phosphate was used to flame retardant polyester cotton fabric, the system effectively promoted the carbonization of the fabric and self-extinguishing [10]. Carosio applied this technique to polyester cotton fabrics through layer-by-layer self-assembly. The carbon residue at 700°C after 20-layer finishing increasing from 14.7% to 20.9% and the total heat release rate decreased from 170 kw/m² to 128 kw/m² [11]. Srikulkit deposited poly-phosphoric acid and chitosan on silk fabrics by LbL, the silk was completely decomposed at 600°C, while 60 layers of silk were covered with coke, and the vein structure was intact [12]. Chen added 5% ammonium polyphosphate and 2% chitosan to polylactic acid by melt blending, and the heat release rate was reduced by 51.2% to UL-94 V-0 level [13]. Bai added 22.5% ammonium polyphosphate and 7.5% chitosan to polypropylene by melt blending. The LOI of composites increased from 18% to 28.1%, total flue gas release, CO and CO2 emissions obvious reduction [14].

Chitosan and poly-phosphoric acid (or phosphate) hold a good flame retardant synergistic effect on fibers, plastic and other products, and it could be applied to polymer materials with different processing forms through blending, adding and LbL techniques. The film forming properties of chitosan can improve the washability of polyphosphates, and high carbon content and nitrogen source favorably promote the formation of carbonized layers.

3.2 Bio-based materials

Bio-based materials have the advantages of wide source, low cost, recyclability and environmental protection, so it used to combine with other matrix of polyelectrolyte properties. At present, the flame retardant of bio-based blended with chitosan mainly include phytic acid, alginate and DNA.

3.2.1 Phytic acid

Phytic acid is called inositol six phosphoric acids, which contain six phosphate groups and easy to bind with positively charged molecules. Therefore, the chitosan and phytic acid blended flame retardant often used layer by layer self-assembly technology (LbL) for flame retardant finishing.

Zhang added chitosan and phytic acid to the ethylene-vinyl acetate copolymer, when the added amount was 20%, the flame retardancy of the composite reached UL-94 V-2 [15]. Laufer deposited chitosan and phytate acid onto cotton fabrics by LbL, after 30 layers were deposited, the peak heat release rate and total heat release decreased by 60% and 76%, and the fabric could be self-extinguished [16]. Xu used chitosan and sodium phytate to form a self-assembled layer on the silk fabric. When 20 layers were assembled, the LOI value of the silk fabric increased from 23.1% to 31.9%, and after washing 20 time. The LOI value remained at 27.8% [17].

3.2.2 Alginate

Alginate was primarily derived from the brown algae organisms in the ocean. Because alginate has abundant sources, environmental protection and biodegradable, decomposes and absorbs heat, it had certain flame-retardant properties.

Chen sorted chitosan and potassium alginate into cotton fabrics through layer by layer self-assembly technology. After 20 layers were deposited, the residual charcoal lines of the flame-retarded cotton fibers were evident, and the expanded char layer appeared on the surface, and there was no afterglow phenomenon [18]. Kumar assembled chitosan, oxidized sodium alginate and phytic acid onto polyamide 66 fabrics by LbL. After deposited 10 layers, the fabric would stop dripping and there would be an expansive char layer on the surface [19].

3.2.3 Cellulose

Cellulose is a macromolecular polysaccharide composed of glucose. It is the most widely distributed, most abundant polysaccharide in the natural world and rich in hydroxyl groups and used as a carbon source. Compared with other substances, cellulose is a non-food source and avoids waste. Cellulose can also be modified for different materials by different chemical or physical methods [20].

Mesquita obtained nanocomposites by layer-by-layer assembly (LBL) of highly deacetylated chitosan and cellulose nanowhiskers (CNW) of Eucalyptus. Hydrogen bonding and electrostatic interactions between negatively charged sulfates on the whisker surface and the ammonium groups of chitosan are driving forces for multilayer growth. Scanning electron microscopy showed high density and uniform distribution of CNW adsorbed on each chitosan layer [21]. Pan deposited polyelectrolyte multilayer films of chitosan and phosphorylated cellulose on the surface of cotton fabric by layer-by-layer self-assembly. When the polyelectrolyte multilayer film (PEM) was 20 layers, the peak HRR and THR decreased the most was 70.62% and 81.25% lower than that of the pure cotton fabric, and the self-extinguishment occurred. The residual coke at 700°C was 35% [22]. Li prepared polyvinyl alcohol/ nanowhisker cellulose /chitosan (PVA/CNWs/CH) nanocomposites using a water evaporation method. FTIR spectra show that there are hydrogen bonds between PVA and CNW, XRD shows that there are molecular interactions between chitosan and PVA molecules, the elongation at break of PVA/chitosan composites was lower than that of pure PVA. In general, the tensile strength and elongation at break of the PVA/CNWs nanocomposite films are significantly increased compared with the pure PVA films, the enhanced mechanical properties can be attributed to the increase in the interaction between the PVA chains and the CNW via hydrogen bonds. As well as the relatively high strength, stiffness and low density of the CNW, the flexibility of the PVA/CNWs/chitosan nanocomposites compared to the PVA/chitosan films is significantly improved [23].

3.2.4 DNA

DNA is a biological macromolecule consisting of a phosphate group, deoxyribose ring and a nitrogenous base. The molecule contains a large amount of nitrogen and phosphorous, which can serve as a synergistic flame retardant after being decomposed by heat. The unique double helix structure makes it form two single chains when heated, and consumes a lot of heat, so as to achieve a good flame-retardant effect [24,25]. Among chitosan-DNA composite flame retardants, chitosan mainly fixes DNA on the surface of the polymer to form chitosan membrane, so that DNA will not be lost too much in the washing process, thereby enhancing flame retardants and washing resistance.

Annalisa almost completely lost DNA in washing process when DNA was individually flame-retardant cotton fabric. But the flame-retardant effect was nice and showed better water resistance when the DNA and chitosan were finished on the cotton fabric by LbL [26]. Carosio found that selfextinguishing in the horizontal flammability test when the chitosan and DNA flame-retardant were used cotton fabrics, the LOI value increased to 24%, the peak heat release after the deposition of 20 layers decreased by about 41% and the residual carbon value increased from 2% to 13% [27]. At the present moment, the research on blended flame retardation of chitosan and bio-based materials was based on the fact that polyelectrolytes with opposite charges alternate at the liquid/solid interface to form a multilayer film on the surface of the fiber product through electrostatic interaction to achieve durable flame retardant. The layer by layer self-assembly technology (LbL) had the benefits of simple and convenient operation process, environmental protection and adjustable function, which was favorable to the application of the whole bio-based composite flame retardant in fiber products [28].

3.3 Inorganic nanoparticles

Nanoparticles have excellent resistance to oxidation and heat such as graphene, montmorillonite, silica, titanium dioxide and zinc oxide. On the basis of chitosan/poly-phosphate and chitosan/bio-based composite systems, the flame-retardant properties of polymer materials have been substantially improved.

3.3.1 Graphene

Graphene is an atomic-scale honeycomb lattice structure made up of carbon atoms. Due to its complete lattice structure, graphene has excellent physical barrier effect and higher thermal conductivity [29].

Zhang alternately immersed polyurethane foam in 0.5% chitosan solution, 0.1% graphene suspension and 0.3% alginate solution. After 10 layers were deposited, the peak heat release rate, peak smoke generation rate, total smoke release and carbon monoxide production decreased by 59.9%, 45.6%, 30.5%, 54.0%. Respectively, the amount of residual carbon increased dramatically [30]. Jin deposited chitosan, grapheme and ammonium polyphosphate onto cotton fabrics through LbL. When 15 layers were assembled, the fabric continued burning time was shortened to 1.5 s and the damaged length was reduced to 72mm. The dense carbon layer was formed after the coated fabric burned [31].

3.3.2 Montmorillonite

Montmorillonite is a layered silicate crystal consisted of two layers of Si-O tetrahedron and one layer of Al-O octahedron. The layer contains sodium, magnesium, calcium, potassium, lithium and other cations. The montmorillonite has good Dispersion and widely used in polymer materials industry, and it could improve impact resistance, fatigue resistance, dimensional stability and gas barrier properties [32].

Laufer applied chitosan and nano-montmorillonite onto polyurethane through layer-by-layer self-assembly technique. The peak heat release rate of the assembled 10-layer foam was decreased by 52%. In the vertical flame test, this coating completely prevented the flexible polyurethane foam from being ignited [33]. Holder assembled 20 layers of chitosan, ammonium polyphosphate and montmorillonite on polyurethane, the peak exothermic rate decreased by 66% [34]. Li found that when chitosan, montmorillonite and DNA were assembled onto polyurethane, the maximum heat release rate and average heat release rate decreased by 51% and 81% [35].

The tensile strength and thermal stability of polyvinyl alcohol nanometers were improved when chitosan and montmorillonite modified polyvinyl alcohol as electroplating [36]. Li used phytic acid-modified chitosan and melamine phosphate as the synergistic agent to prepare flame-retardant polylactic acid composites through melt blending. Then he found the LOI increased to 30.0%, residual carbon increased to 18.58%, UL-94 reached

V-0 and melt dripping disappeared [37]. In addition, nano-silica, nano-titanium dioxide and nano-zinc oxide have also been applied to chitosan composite flame retardant, and achieved a certain degree of flame retardant effect [38-41]. In the chitosan/inorganic nanoparticle flame retardant, the inorganic nanoparticle mainly serves as a heat-insulating material protecting matrix, so that the chitosan is not dehydrated in the early stage of the combustion process, water vapor is generated and the coke layer is formed, thereby insulating the air and achieving the goal of flame retardants.

At present, the composite of chitosan and inorganic nanoparticles is mainly through layer-by-layer self-assembly technology and the use of phosphorus-containing polyelectrolyte sandwich assembly to achieve flame-retardant applications in fiber products, polyurethane foam and other materials.

4. CHEMICALLY MODIFIED CHITOSAN FLAME RETARDANTS

In addition to the synergistic flame retardants of multi molecular compound, the chitosan based flame retardants have also modified the chitosan structure to form a variety of synergistic flame retardant effects. According to the way of modification, it can be divided into two categories: direct modification and degradation modification.

4.1 Direct modifications

The direct modification refers to direct activation of chitosan to enhance reactivity. At present, the main reagents used for direct modification is phosphoric acid and phosphorus pentoxide.

Abou-Okeil used chitosan phosphorylation products to prepare cotton fabrics, after finishing, the decomposition temperature decreased from 350°C to 325°C, the residual carbon value increased from 26.45% to 36.56%, and the washing resistance improved after finishing [42]. Eltahlawy grafted phosphorylated chitosan onto diammonium phosphate, also used in cotton fabrics. The residual carbon value of the finished fabric was 68% at 500°C, while the unfinished fabric left only a small amount of 0.45% [43].

Phosphorus pentoxide have a higher reactivity than phosphoric acid. Hu reacted chitosan activated with phosphorus pentoxide and urea, then applied it to polyvinyl alcohol fabrics. He found it accelerated the dehydration of the polyvinyl alcohol fabric and formed of a char layer at a low temperature, the residual carbon value of the ruined fabric increased from 0.7% to 14.3% at 500°C [44]. Subsequently, his research group reacted with chitosan activated with phosphorus pentoxide and melamine again and used in polyvinyl alcohol fabrics, the residual carbon value was increased to 18.5% and PHRR1 and THR were greatly reduced [45].

4.2 Degradation modifications

The degradation modification refers to the method of degrading chitosan into tiny molecules and grafting other flame retardant substances to modify. For the moment, the good flame retardant effects had been achieved on linen and polyurethane fabrics.

Wang reacted degraded chitosan with phosphonitrilic chloride trimer and applied it to linen fabrics. When the content of the flame retardant was 12%, the vertical burning performance of the flax fabric reached the B1 level standard and the B2 level could still be achieved after soaping 10 times [46]. Zhang polymerized carboxymethyl chitosan with sodium p-styrenesulfonate and applied it to the preparation of water-borne polyurethane emulsion. When the flame retardant used less, the mechanical strength of the composite film was changed very small. At the same time, the compatibility with the water-borne polyurethane was nice, so the problem of separating the flame retardant from the flame-retardant matrix material was solved [47].

Chitosan can be chemically modified depending on the requirements of the flame retardant and the adaptability of the material. Through molecular design, the flame retardants introduced a variety of flame retardant elements, which could effectively increase the material's applicability and washability. Through the finishing, blending and other ways to achieve flame retardant effect on fiber products and polyurethane plastic.

4.3 Problems and development direction of based chitosan flame retardants

4.3.1 Problems of based chitosan flame retardants

(1) The flame-retardant effect of chitosan monomer has a certain degree of flame retardant, but its flame-retardant effect cannot contented the all-

round demand of various materials:

- (2) The composite based chitosan flame retardant, the flame-retardant effect is better, but it will affect some of the properties of the fabric, such as color, breaking strength, feel.
- (3) The research on the application of bio-based the chitosan modification in the field of flame retardant is still in its infancy. There are still many problems that have not been solved, such as:

Bio-based materials mostly contain hydroxyl groups. Although they are good carbon sources, they are also poor in thermal stability and cannot meet the processing requirements of most polymer materials.

The flame-retardant effect of most of the chitosan bio-based flame retardants is not ideal, and it needs to be combined with the flame retardant elements such as phosphorus, nitrogen, and silicon. The modified grafting technology needs to be developed;

A few natural flame-retardant materials such as DNA and phytic acid are expensive and difficult to apply in large quantities;

The bio-based chitosan flame retardants are mostly incompatible with polymer materials and must be modified to improve the overall performance of the material.

4.3.2 Development direction of based chitosan flame retardants

- (1) Add some flame retardant monomers that have synergistic effect with chitosan and some compatibility with fiber macromolecules in the melt spinning process, so that the fiber macromolecular chains contain flame retardant groups, which is fundamentally method to improve the flame retardant of fabrics, so how to simplify the process and find new flame-retardant monomers is still the focus of future research;
- (2) The development of novel chitosan modified flame retardant monomers can achieve high flame retardant performance at a low grafting rate and reduce the drawbacks of fabrics with hard and poor feel due to high grafting rates;
- (3) Multi-functional modification, Simultaneously we can improve the flame retardant, while giving the fiber other features, such as antibacterial, hydrophilic, skin care and other properties.
- (4) The flame retardant finishing process of fabric should meet the requirements of simple process, convenient operation, energy saving and environmental protection;
- (5) Relying on bio-based raw materials, adopt reasonable and effective chemical modification technology to overcome the shortcomings of chitosan, while improving the flame-retardant efficiency;
- (6) New finishing techniques, such as layer self-assembly method, dualcuring method, nanoparticle adsorption and sol-gel method used to flameretard the polymer and enhance the washing fastness of the substrate.

5. SUMMARY

In this mini review, due to the characteristics of high carbon content and low nitrogen content, chitosan could improve the thermal stability of the polymer to a certain extent, and the flame-retardant performance became better. But it could not improve the flame-retardant grade of the material, which was limited as the use of the monocomponent flame retardant.

The blended chitosan flame retardant could be applied to the flame-retardant preparation of fibers and plastic products through blending, LbL and ordinary post finishing techniques. The application of green phosphorus-containing substances, the exploration of new compounding technologies and the development of LbL for layered fiber products were important research directions for blended chitosan-based flame retardants.

The chemically modified chitosan-based flame retardants could be molecularly designed based on the requirements of flame retardants and the adaptability of materials, so as to obtain highly effective in flame retardants, blending suitability and finishing wash ability, and it have a broad development space in the fields of fiber and plastic products.

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