

Flame-retarding effects depending on the number of phosphonate groups attached to phosphorus flame-retarding compounds and coating binder resins

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인계 난연화합물 및 코팅 바인더 수지에 부착된 phosphonate group에 따른 난연효과

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Abstract : In this study, we prepared phosphorous flame-retarding coating solutions by mixing triphosphate (3 phosphonate), phytic acid (6 phosphonate), or ammonium polyphosphate (10 phosphonate) with boric acid as a crosslinking agent and acryl resin binder. Prepared phosphorous flame-retarding coating solutions were coated onto non-woven fabrics, respectively, to obtain high flame-retarding effects. These prepared flame-retardant non-woven fabrics were evaluated using smoke density standard test (ASTM E662), limit oxygen index standard test (ISO E622), and vertical burning standard test (UL 94). Their flame-retarding effects were affected by the number of phosphonate groups. Regardless of natural or synthetic binder resins, their effects showed the following order: ammonium polyphosphate > phytic acid > triphosphate. Natural hydrocarbon compounds were also examined to determine the possible retardancy of binder resins. Results showed that natural hydrocarbon binder resins could be used for preparing fire-retardant nonwoven fabrics.

Keywords : Flame-retardant effects, natural and synthetic binders, triphosphate, phytic acid, ammonium polyphosphate, cyclodextrin, oligosaccharide, acryl resin binder

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요약 : 본 연구에서는 가교제인 붕산과 아크릴 수지 바인더에 삼인산(3 인산), 피트산(6 인산) 또는 폴리인산암모늄(10 인산)을 혼합하여 인계 난연 코팅액을 제조하였다. 제조된 인계 난연 코팅액을 부직포에 각각 코팅하여 높은 난연 효과를 얻었다. 이렇게 제조된 난연성 부직포를 연기밀도기준시험(ASTM E662), 산소한계지수기준시험(ISO E622), 수직연소기준시험(UL 94)을 이용하여 평가하였다. 그들의 난연 효과는 phosphate 그룹의 수에 의해 영향을 받았으며, 천연 또는 합성 바인더 수지에 관계없이 그 효과는 ammonium polyphosphate > phytic acid > triphosphate의 순서로 나타났다. 천연 탄화수소 화합물도 바인더 수지의 난연성을 결정하기 위해 조사되었다. 그 결과 천연 탄화수소 바인더 수지가 난연성 부직포 제조에 사용될 수 있음을 보여주었다.

주제어 : 난연 효과, 천연 및 합성 바인더, 피트산, 폴리인산암모늄, 아크릴 수지 바인더

1. Introduction

Phosphorus flame-retardants (PFRs) have already been used for over 150 years [1]. They are considered as suitable alternatives of brominated flame-retardants. Because of the need for vapor-phase activity, a number of volatile PFRs such as tributyl phosphate, triphenyl phosphate, and triphenylphosphine oxide have been studied as possible substitutes for bromine-containing formulations used in textile back-coatings [2]. Some PFRs can facilitate the recyclability of printed circuit boards as it is more feasible and cost effective to recover copper from halogen free circuit boards [3]. Not only several brominated flame-retardants need to be replaced by PFRs, but also halogen-containing PFRs need to be substituted by non-halogenated PFRs. However, studies about flame-retarding effects of PFRs and coating binders according to the number of phosphonate groups are insufficient.

On the other hand, nonwovens are used in a multitude of household applications ranging from cleaning and filtering to adding an aesthetic touch to a home. Used in bedrooms, kitchens, dining rooms, and living rooms, high-performance nonwovens can create comfortable, practical, hygienic, safe, beautiful, and smart solutions for modern living. However, few studies have reported about the preparation of nonwoven fabrics for fire prevention in household application materials

to the best of our knowledge.

Acrylic binder resin is usually used to coat woven or nonwoven fabrics to modify their physical properties (such as hydrophobicity and impermeability) and to improve their mechanical properties including the chosen of the fibers, softness, and resilience. Coating can also use fire-retarding chemicals to modify the fire performance of nonwoven fabrics. A major requirement of any flame-retardant coating treatment is its ability to transfer flame-retardant properties from the surface to the inside of nonwoven fabrics. During the past 10 years, many flame-retardant systems have been developed and used in textile and nonwoven fabric coating [4]. Antimony-bromine systems have been used as the most successful flame-retardant systems for textiles [5]. Horrocks et al. [6,7] have tried to replace such hazardous flame-retardant system with phosphorous-containing materials. Acrylic binder resin and ammonium polyphosphate (APP) composite are widely used to provide flame-retardant of diverse textiles with different polymer main chains [8-10]. Natural hydrocarbon compounds such as cyclodextrin, oligosaccharide, starch, and so on are widely used as coating binder resin in food and polymer chemistry fields [11-13]. However, few studies have reported about applications of coating binder resin to make flame-retardant coating solution.

In this study, we prepared PFRs coating

solution by mixing triphosphate, phytic acid, ammonium polyphosphate, and acrylic binder resin in aqueous solution to determine their flame-retarding effects according to different numbers of phosphonate group in PFRs. To search for the best flame-retarding effects of coating binder resins, we also prepared coating solutions by mixing ammonium polyphosphate as PFRs, cyclodextrin, oligosaccharide, and starch as natural coating binder resin on behalf of acryl binder resin in an aqueous solution, respectively. After that, we coated the surface of nonwoven fabrics with PFRs coating solution to obtain the best flame-retarding effects based on smoke density test, oxygen index test, and smoke generation test. We also performed thermal analysis and scanning electron microscopy (SEM) analysis before and after combustion.

2. Experiments

2.1. Reagents

Ammonium polyphosphate (APP, $n = 10$) was obtained from RS Tech Co. (Seoul,

Korea). Sodium triphosphate, phytic acid, β -cyclodextrin (CD), starch, boric acid, and oligosaccharide were purchased from Samjeon Co. (Seoul, Korea). Acrylic resin binder was bought from Daeyang Chemical (Seoul, Korea). Nonwoven fabrics for heating, ventilation, & air conditioning (HVAC) were obtained from Korea Vilene Co., Ltd. (Gyeonggi-do, Korea).

2.2. Instruments

Surface properties of samples were characterized by scanning electron microscopy (FE-SEM, S 4800, Hitachi, Tokyo, Japan) and thermal analysis (TGA, TA Instruments, Waters, 10 °C/min to 1000 °C, Air).

2.3. Preparation of samples

Fig. 1 shows chemical structures of three types of phosphorus flame-retardants synthesized by dehydrogenation of boric acid and phosphorous flame-retardants. In detail, triphosphoric acid was first synthesized by exchange reaction of sodium phosphate (22.1 g) and hydrogen chloride (26.1 mL, 35 %). It was then separated using a separation funnel with a work up process. Triphosphate (FR-1),

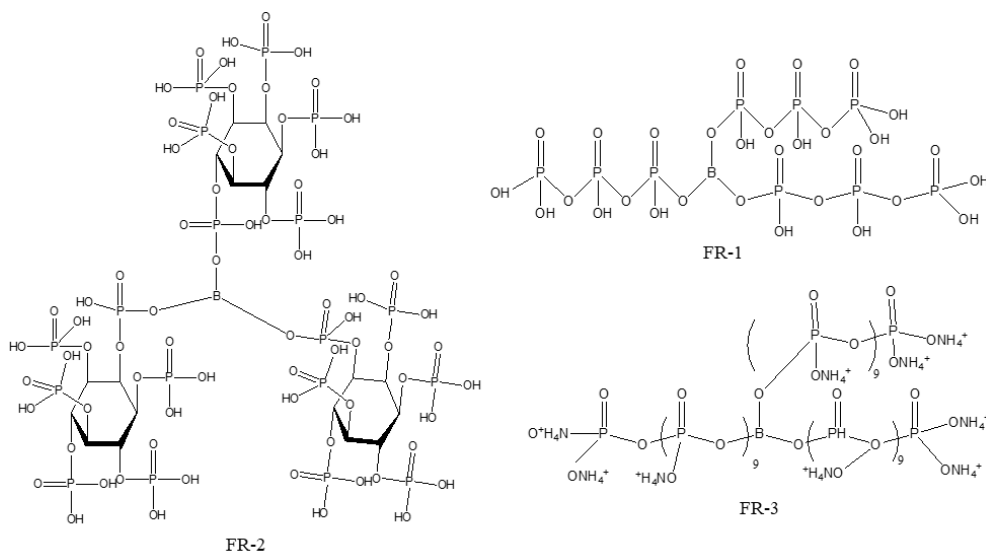


Fig. 1. The suggested chemical structure of the prepared flame-retardants.

phytic acid (FR-2), and ammonium polyphosphate (FR-3) solutions were firstly synthesized by dehydration reaction of triphosphoric acid (0.06 mol), phytic acid (0.06 mol), and ammonium polyphosphate (0.06 mol) with boric acid (0.06 mol) in 100 mL distilled water, respectively. Suggested chemical structures of synthesized flame-retardants are described in Fig. 1.

Subsequently, samples were deep coated with the phosphorus flame-retardant coating solution synthesized by mixing synthesized phosphorus flame-retardants (FR-1, FR-2, and FR-3) with acryl binders, respectively, as shown in Table 1.

2.4. Flammability of samples

Flammability of each prepared sample was tested using smoke density standard test (ASTM E662), limit oxygen index standard test (ISO E622), and smoke generation standard test (UL 94) at Energy Prevention Support Center of Gangwon Techno Park (Korea).

3. Results and Discussion

3.1. Flame-retarding effects of the number of phosphonate groups attached to phosphorus flame-retardant compounds

Thermal stabilities of FR-1, FR-2, and FR-3 were studied by TGA analysis. Results

are shown in Fig. 2. In FR-1, the 1st weight loss in the temperature range of 50 °C~100 °C due to removal of water and the 2nd weight loss in the temperature range of 100 °C~200 °C due to dehydration of water from FR-1 chemicals were obtained. The 3rd and 4th weight losses at temperature range from 450 °C to 1,000 °C were also observed.

This might be that oxygen was removed to recombined P₂O₅ or P₂O₃ compound. In FR-2, three weight losses were observed via TGA analysis. The 1st weight loss at temperature up to 200 °C was due to dehydration of water. The 2nd weight loss in the temperature range of 200 °C~400 °C was due to decomposition of carbon framework with cyclohexane. The 3rd weight loss in the temperature range from 400 °C to 1,000 °C was due to formation of P₂O₅, P₂O₃, and B₂O₃.

In FR-3, an explosive 1st weight loss in the temperature range of 100 °C~400 °C was observed. From these results, we could prepare cross-linked flame-retardants with thermal stable properties by dehydration reaction of boric acid and phosphorus flame-retardants.

Fig. 3 shows scanning electron microscope (SEM) images of samples (No. 1 in Table 1). The upper panel shows pictures after coating nonwoven fabrics. The bottom panel shows pictures after burning by torch fire with butane gas. Before burning samples (upper), FR-1 was partially coated on the surface of fiber strands by deep coating process because of acryl binder resins. After burning (bottom),

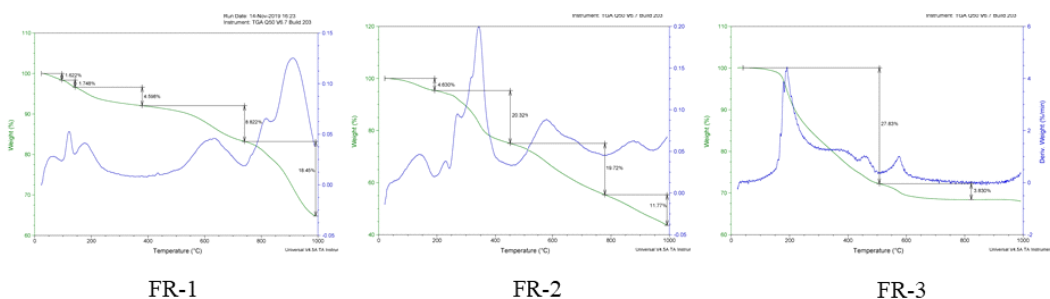


Fig. 2. TGA curves of the prepared flame-retardants.

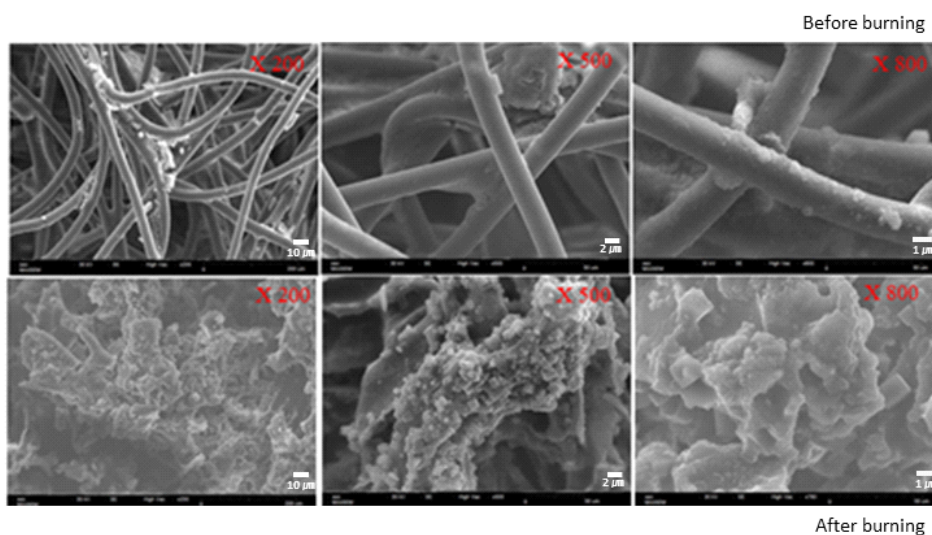


Fig. 3. SEM images of the sample (No. 1 in Table 1).

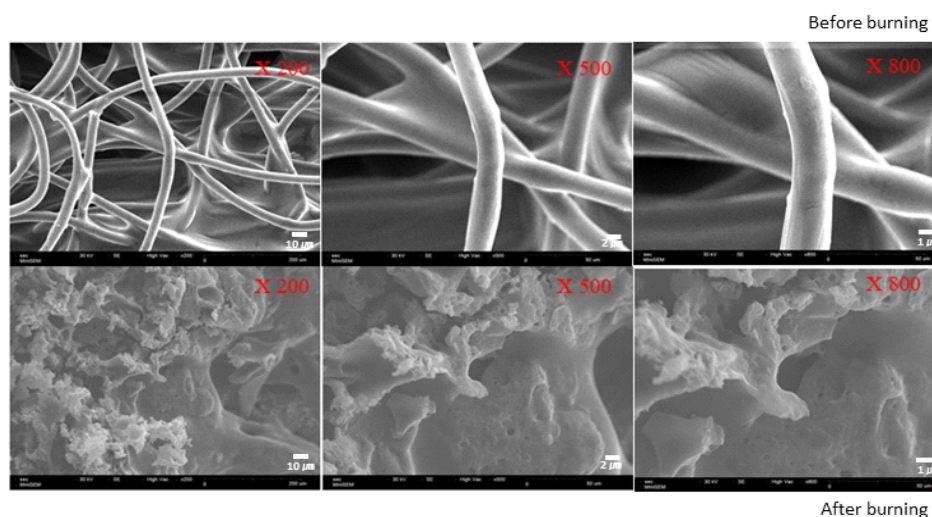


Fig. 4. SEM images of the sample (No. 2 in Table 1).

pictures were obtained for black color char with a tetrahedral structure due to FR-1 and acrylic binder resin.

Fig. 4 exhibits SEM images of samples (No. 2 in Table 1). The upper panel shows photos before burning and the bottom panel shows photos after burning by torch fire with butane gas. Morphologies of samples showed an amorphous structure of FR-2 and acrylic binder resins after a deep coating process.

After samples were burned using torch fire with butane gas, a black color char with an amorphous structure was obtained as shown in Fig. 4. The hole in the char was due to gas out, which was generated by thermal decomposition of nonwoven fabric.

Fig. 5 exhibits SEM images of samples (No. 3 in Table 1). The upper panel shows samples before burning and the bottom panel shows images after burning using torch burner with

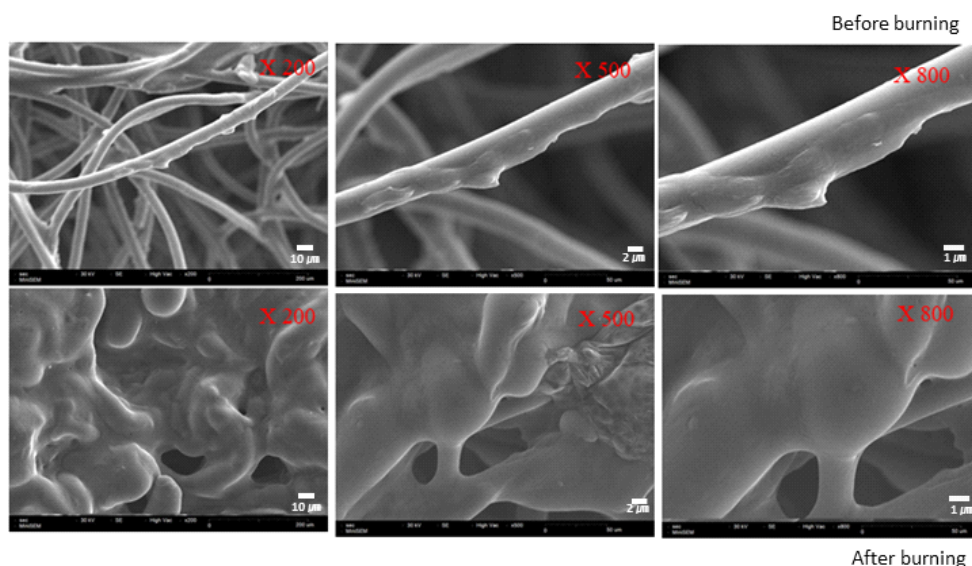


Fig. 5. SEM images of the sample (No. 3 in Table 1).

Table 1. Preparation of the fire retardant coating solution by mixing of the synthesized phosphorus flame-retardant solution (FR-1, FR-2 and FR-3) and acrylic binders and flammability test

Coating solution No.	Flame-retardant solution	Acryl Binder solution	Ds (ASTM E622) ^{a)}	Limit oxygen test (ISO E622) ^{b)}	Verical buring test (UL 94) ^{c)}
No.1	FR-1 (5 g)	50 g	15	54.8	V-0
No.2	FR-2 (5 g)	50 g	18	47.1	V-0
No.3	FR-3 (5 g)	50 g	17	54.4	V-0

^{a)}Specific optical density of smoke generation by sample. ^{b)}at ambient temperature at 4min. ^{c)}for 20mm at 250sec.

butane gas. Morphology of the coating by a deep coating process using FR-3 and acrylic binder resin mixture solution showed an amorphous structure. After burning of the sample, the morphology also exhibited an amorphous structure as shown in the bottom of Fig. 5.

We also analyzed flammability properties of prepared samples using smoke density standard test (ASTM E662), limit oxygen index standard test (ISO E622), and smoke generation standard test (UL 94). Results are shown in Table 1. Specific optical densities of

smoke generation (Ds) for samples were in the range of 15~18 at 4.0 min. Limit oxygen values were in the range of 47~55. Results of the vertical burning test were at V-0 level. These results indicate that prepared flame-retardant nonwoven fabrics could be applied as fire-retarding materials in vehicles.

3.2. Flame-retardant effects of coating binder resin

To know flame-retardant effects of coating binder resin, we selected three types of natural hydrocarbon compounds, starch, β

-cyclodextrin, and oligosaccharide, as shown in Table 2. We prepared coating solutions (No.4, No. 5, and No. 6) using phosphorus flame-retardant solution (FR-3, 35.0 g) and natural hydrocarbon compounds. Flame-retardant samples were also prepared by deep coating in the synthesized phosphorus flame-retardant solution as shown in Table 2. We evaluated the flammability of each prepared sample by performing smoke density standard test (ASTM E662), limit oxygen index standard test (ISO E622), and smoke generation standard test (UL 94). Results are shown in Table 2. Specific optical densities of smoke generation (Ds) for samples were in the range of 34~44 at 4.0 min. Limit oxygen values were in the range of 50~90. Results of vertical burning test were at V-0 level. These results indicate that the prepared flame-retardant nonwoven fabric could be applied as fire-retarding materials in vehicles.

Fig. 5 exhibits prepared flame retardant nonwoven fabrics using natural hydrocarbon binder resins. The flame retardant coating solution used to coat fibers of nonwoven fabrics was found to have an amorphous structure. A small amount of crystal formed in sample No. 5 prepared with β -cyclodextrin.

Fig. 6 displays TGA curves of prepared flame retardant samples. The base nonwoven fabric showed three weight losses (Fig. 6). The first weight loss at temperature below 200 °C appeared due to vaporization of water present

on the surface of nonwoven fabrics. The 2nd weight loss at temperature range from 200 °C to 400 °C occurred due to decomposition of polymeric backbone in nonwoven fabrics. The 3rd weight loss was found at temperature above 400 °C. This occurred because of gas formation from fragments caused by thermal decomposition.

On the other hand, fire-retarding samples had residue weights of 30~60 % due to char formation. The char formation occurred by reaction between phosphorous radical and polymeric binder resin. The residue due to char formation was found for flame retardant sample No. 5. These results indicate that a natural hydrocarbon binder resin could be used for preparing fire-retarding nonwoven fabrics.

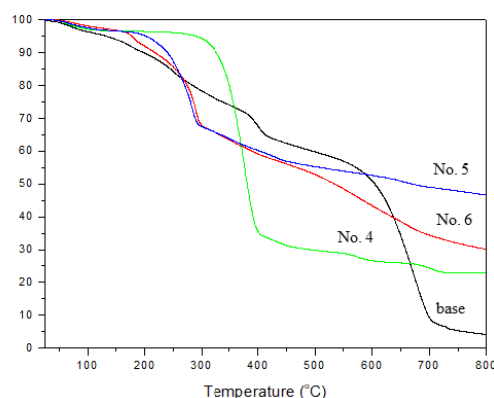


Fig. 6. TGA curves of the samples in Table 2.

Table 2. Preparation of the fire retardant coating solution by mixing of the synthesized phosphorus flame-retardant solution (FR-3, 3.50 g) and natural binders and flammability test

Coating solution No.	Natural binders (3.50 g)	Ds (ASTM E622) ^{a)}	Limit oxygen test (ISO E622) ^{b)}	Verical buring test (UL 94) ^{c)}
No.4	Starch	41	86.4	V-0
No.5	β -Cyclodextrin	34	47.9	V-0
No.6	Oligosaccharide	44	57.7	V-0

^{a)}Specific optical density of smoke generation by sample. ^{b)}at ambient temperature at 4min. ^{c)}for 20mm at 250sec.

4. Conclusion

Fire-retarding coating solutions were prepared by mixing phosphorous chemicals and acrylic binder resins or natural hydrocarbon binder resins. Flame-retarding nonwoven fabric samples were then prepared by deep coating with prepared fire retardant coating solutions. Fire-retarding effects were then determined with smoke density standard test (ASTM E662), limit oxygen index standard test (ISO E622), and vertical burning standard test (UL 94). From obtained results, we had the following conclusions:

(1) Flame-retarding effects were affected by the number of phosphonate groups. Regardless of natural or synthetic binder resins, the following order of flame-retarding effect was found: ammonium polyphosphate > phytic acid > triphosphate.

(2) Natural hydrocarbon binder resin (starch, β -cyclodextrin, and oligosaccharide) could be used as a flame-retarding binder resin.

(3) Flame-retarding effects using acryl binder resins were higher than those using natural hydrocarbon binder resins.

Acknowledgments

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