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Risk Points of Flame Retardant Textiles by Halogen and Halogen-Free Laminating Film

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Abstract

This study was to develop the flame retardant (FR) protective clothing which had multifunction such anti-bacterial, UV cut, FR function with water repellent and water vapor permeable laminating textiles for industrial workers. First of all, the FR yarn and FR textiles were developed for this purpose. Second, the comparison analysis between the halogen laminating textiles and halogen-free laminating textiles were tested to figure out the eco-friendly laminating method. Third, the flame retardant ability was compared the halogen laminated textiles to halogen-free laminated textiles. LOI, UV protection ratio, antibiosis after 50 laundry test, water proof pressure, and moisture permeability of developed textiles were tested. GC-HR-TOF-MS was used for analysis of laminating film (halogen and halogen-free). 4.1 wt% TiO_2 yarn showed antibacterial function (Pneumococcus & *Staphylococcus aureus*: 99.9%), UV Protection (UVA: 90.8, UVB: 92.1), and LOI (33.6). The chosen optimal compounding ratio for PU compound of HRF and HFFR were as followed: PU resin 58.3%, DMF (Dimethyl formamide, δ = 12.2) 8.3%, MEK (Methylethylketone) 8.3% and FR (flame retardants) 25.0%. Binder for laminating should not be included over 10% of FRs because of adhesion between textiles and FR laminating film. There were detected phosphorus compounds in the textiles treated by halogenated type flame retardants and halogenated-free type flame retardants. There were not any detected harmful compounds from all textile samples.

Keywords

Flame Retardant Yarn, Flame Retardant Textiles, GC-HR-TOF-MS, Halogen Laminating Textiles, Halogen-Free Laminating Textiles

1. Introduction

Firefighters, workers in the petro-chemical factory, drivers transporting toxic gases, and professionals handling

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toxic gases have been always potentially exposed to toxic pyrogenic thermal stress and impact of a fatalaccident, so that the risk factors for them are high. 36% of the total accidents caused in those types of work place [1]. The importance of the FR textiles management has been gradually increasing because the Act on safety management about installation and management of fire-fighting facilities, fire retardant requirement and standards for flame retardant products has been reinforced since 2008 [2] [3]. Special flame-retardant protective clothing for workers working in hazardous environment and fire-fighters were required [4].

Flame retardants (FRs) are incorporated into potentially flammable materials such as plastics, rubbers, and textiles to slow down and/or inhibit the initial phase of developing fire. Thus FRs performs an important service in our modern society by reducing the number of fires and limiting the consequences of fires that do develop. Common applications of FR chemicals include the plastic housings of electronic appliances and in printed circuit boards as well as in upholstery and construction materials [5] [6].

New fire retarding compounds have been developed including inorganic compounds as well as organ halogen chemicals, organophosphate esters and less common nitrogen containing compounds [7] [8]. Most present-day halogenated flame retardants are used in the area of electronics in the manufacturing of circuit boards, casings for home and office electronics, including mobile phone equipment. A smaller proportion of world production of flame retardants goes to the textile and the paper industries.

Major flame retardant were metal-hydrate inorganic flame retardants such as boron compounds, antimony oxides, aluminum hydroxide and so on, a halogenated compound containing chlorine or bromine, a nitrogen compound such as the melamine cyanurate, and a phosphorous compounds based on a phosphoric ester such as nitrogen [9].

Considering the using total FRs weight, inorganic FR compound was used the most, and then halogen compound and phosphorous compound. Ensuring adequate flame retardant and also keeping the quality of properties of the FR textiles, because the thermal or mechanical properties of FR film were decreased by the FRs compounds [10] [11]. Carcinogenicity of halogenated compounds has been the problem since 1980s. Environmental certification such as the Blue Angel of Germany and TCO of Sweden make to restrict using the Halogen FR [1]. Halogen-free flame retardants have been the focus of extensive research because of environmental problems.

There are few previous studies about flame retardant protective clothing in Korea. The chemical protective clothing with flame retardant function for fire-fighters was studied [4]. Others were about textiles such as compared the research trend of FR resin for FR textiles [1], the properties of FR textiles [11], and the properties of FR textiles using bicomponent yarn [3]. There was no study for developing the FR protective clothing and FR textiles. Other further research was reviewed the history and the new technology tend of flame retardant materials [12].

This study was to develop the flame retardant (FR) protective clothing which had multifunction such antibacterial, UV cut, FR function with water repellent and water vapor permeable coated textiles for industrial workers. First of all, the FR yarn and FR textiles were developed for this purpose. Second, the comparison analysis between the halogen laminating textiles and halogen-free laminating textiles were tested to figure out the eco-friendly laminating method. Third, the flame retardant ability was compared the halogen laminated textiles to halogen-free laminated textiles.

2. Materials and Methods

2.1. FR Yarn and FR Textiles

S/C type yarn were developed and used for this study. Sheath was encircled nano-TiO_2. Core was composed with FR PET (**Figure 1**). Strength, uniformity, denier and the TiO_2 contents were tested for this study. The strength of yarn was tested by KS K 0412: Test method for tensile strength and elongation of filament yarn. Uniformity was tested by KS K ISO 16549: Test Method for Unevenness of Textiles Strands. Denier of yarn was tested by KS K 0415: Textiles-Woven fabrics-Construction-Methods of analysis (Part 5): Determination of linear density of yarn removed from fabric. TiO_2 contents in yarn were tested by counting the weight of TiO_2 per 1 m^2 length.

Tested properties of textiles were LOI (Limiting Oxygen Index), UV protection ratio, Antibiosis after 50 laundry test, water proof pressure, and moisture permeability. LOI was tested by ISO 4589-2. UV protection was tested by KS K 0850: Test method for ultraviolet blocking and sun protection factor of textiles. Antibiosis after 50 laundry test was tested by KS K 0693: Test method for antibacterial activity of textile materials. Water

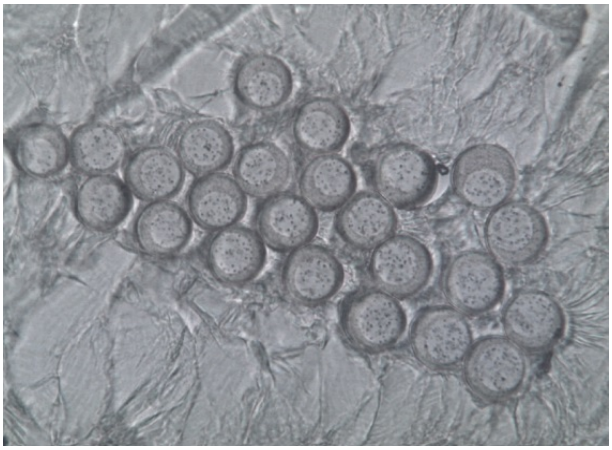

Figure 1. SEM of S/C type of developed FR yarn (S: nano-TiO_2, C: FR PET/original magnification 400×).

proof pressure was tested by ISO 0811. Moisture permeability was tested by KS K 0594: Testing methods for water vapor permeability of textile fabrics.

2.2. Laminating Film Type: Halogen and Halogen-Free

The properties of halogen FR (HFR) and halogen-free FR (HFFR) were presented in **Table 1**.

The chosen optimal compounding ratio for PU compound of HRF and HFFR were as followed: PU resin 58.3%, DMF (dimethyl formamide, δ = 12.2) 8.3%, MEK (Methylethylketone) 8.3% and FR (flame retardants) 25.0%. This optimal compounding ratio could get from the adhesion and LOI test results of 3 different rates. Three different ratio of PU resin:DMF:MEK:FR were 61.5:7.7:15.4:15.4 (Condition A) vs. 58.3:8.3:8.3: 25.0 (Condition B) vs. 50.0:8.3:8.3:33.3 (Condition C). LOI of condition A showed the lowest value (29.3) and others were similar with 33.1 (Condition B) and 33.3 (Condition C).

Laminating condition for multi-function film which had anti-bacterial, flame retardant, and water repellent function was as followers; coating gap from skin (0.12 mm), adhesion coating gap (0.15 mm), dry temperature (90˚C - 130˚C), dry times (100 - 150 sec), soaking temperature (60˚C - 80˚C), and soaking time (12 - 36 hours).

All organic solvents were of ultra-residue grade analysis (J.T Baker, Philipsburg, NJ, USA). Anhydrous sodium sulfate from E. Merck (Darmstadt, Germany) was used.

2.3. Analysis of Laminating Film Type with GC-HR-TOF-MS

Samples were the textiles of halogen and halogen-free flame retardant coating as four kind fiber weights per 10%, 30%, 50%, 70%. Samples were extracted using ultrasonification (SH-600) method with 20 ml of n-hexane on two times.

Gas chromatography coupled to high-resolution time-of flight mass spectrometry (GC-HR-TOF-MS) is a powerful analytical technique with excellent capabilities due to its high sensitivity in full-spectrum-acquisition mode together with its resolving power and accurate-mass measurements. These features make this technique very attractive in qualitative analysis, especially for wide-scope screening of a large number of organic contaminants and residues at trace levels (**Table 2**).

3. Results and Discussion

3.1. Properties of FR Yarn and FR Textiles

FR PET core and nano-TiO_2 surrounded as sheath of yarn was the first trial in Korea. This new developed yarn was important to make multifunctional textiles having anti-bacterial, UV cut and also FR function at the same time. The content of TiO_2 was very important to decide anti-bacterial function ability. Only over 3.75 wt% TiO_2 yarn showed antibacterial function even after 50 laundry test. The properties of FR yarn were suggested in **Table 3**.

Table 1. Properties of halogen flame retardant (HFR) and halogen-free flame retardant (HFFR).

Type	Product name	Color	Particle size (μm)	Solid content (%)	Viscosity (25˚C, cPs)
HFR	KU FR 1312	White	>10	65 ± 2	-
HFFR	KNF 1220HF	Pale white	>10	100	50,000 ± 20,000

Table 2. Analytical method and instrument of GC-HR-TOF-MS.

GC (Agilent 7890 A gas chromatograph)		MS (Waters GCT Premier TOF mass spectrometer)	
Column	DB-5MS (30 m × 0.25 mm × 0.25 μm)	Ionizing mode	Electron ionization (EI)
Oven temp	Start temp.: 60˚C, 3.0 min hold 10˚C/min to 320˚C, 10 min hold	Source temp.	250˚C
Interface temp	280˚C	Electron voltage	70 Ev
Injection mode	Splitless	Detector voltage	2300 V
Injector temp	280˚C		
Carrier gas	He (99.999%)		

Table 3. Properties of developed FR yarn.

Division	Measurement item	Unit	Results
Yarn	Strength	g/d	4.65
	TiO_2 content	wt%	4.1
	Uniformity ratio	U%	1.40
	Denier	upf (μm)	2

According to the results of HFR and HFFR, HFFR laminating was chosen as the film type. **Table 4** was suggested the results of developed FR textiles having multi-function such as FR, antibacterial, and water repellant function at the same time.

3.2. Optimal Compounding Ratio of HFR and HFFR

The chosen optimal compounding ratio for PU compound of HRF and HFFR were as followed: PU resin 58.3%, DMF (dimethyl formamide, δ = 12.2) 8.3%, MEK (Methylethylketone) 8.3% and FR (flame retardants) 25.0%. This optimal compounding ratio could get from the adhesion and LOI test results of 3 different rates. Three different ratio of PU resin:DMF:MEK:FR were 61.5:7.7:15.4:15.4 (Condition A) vs. 58.3:8.3:8.3:25.0 (Condition B) vs. 50.0:8.3:8.3:33.3 (Condition C). LOI of condition A showed the lowest value (29.3) and others were similar with 33.1 (Condition B) and 33.3 (Condition C).

Properties of HFR and HFFR by adhesive temperature were suggested in **Table 5**. At this time, HFR and HFFR compound ratio was followed in condition B and tested textiles were 2 layered. Five experts tested the touch of these final textiles. Considering from the results of the touch by experts, hydrostatic pressure, and water vapor permeability, adhesive temperature was more appropriate in 105˚C - 110˚C than 90˚C - 105˚C.

Laminating process was done under the condition of 90˚C - 130˚C dry temperature, 100 - 150 sec of dry time, and also aging room condition (40˚C, 40% RH), and 72 hours of aging time. However, all laminating coating was separated except 10% FR contents binder (**Table 6**). From this result, all binder was fixed the content as 10%. There was no relationship with film type such as Halogen FR or not. The higher flame retardant rate in textiles was the lower adhesion between the textiles and the FR film was [1]. These results were coincided with this study.

Table 4. Properties of developed FR textiles.

Division	Measurement item		Unit	Results
Textiles	LOI[1]		LOI	33.6
	UV protection ratio	UVA	%	90.8
		UVB		92.1
	Antibiosis after 50 laundry test	Pneumoccus	%	99.9
		Staphylococcus aureus		99.9
	Water proof pressure		mmH_2O	>10,000
	Moisture permeability		$g/m^2 \cdot 24$ hr	16,587

[1]LOI: Limiting Oxygen Index.

Table 5. Properties and touch of HFR and HFFR by adhesive temperature.

Adhesive Temperature	90˚C - 105˚C		105˚C - 110˚C	
Type of FR film	HFR	HFFR	HFR	HFFR
Hydrostatic pressure	9000	8800	Over 10,000	Over 10,000
Water vaper permeability	14,412	14,954	Over 15,000	Over 15,000
Touch	Bad (hard)	Bad (hard)	Good	Good

Table 6. Adhesiveness of laminating film by FR content in the binder.

Film type	Halogen FR film				Halogen-free FR film			
FR content in binder (%)	10	30	50	70	10	30	50	70
Adhesiveness	Pass	Fail	Fail	Fail	Pass	Fail	Fail	Fail

3.3. Analysis of Laminating Film Type with GC-HR-TOF-MS

Flame retardant effect was different by substituted by halogen sequence. Br had the highest degree of sequence retardant and then Cl and F because halogen-containing compounds of the Fbond energy were higher and also the flame retardant effect was lower than Br [1]. Char-forming polymers, flame-retarded using phosphorus containing flame retardants, consisted of the phenyl ring or oxygen linkage in their backbones, have widely used for the use of halogen-free housing applications [11]. In this study, DMF (dimethyl formamide, δ = 12.2) using a create PU compound was regulated substance for using but it was necessary material for making FR PU compound if halogen type or halogen-free type. There were detected phosphorus compounds in the textiles treated by halogenated type flame retardants and halogenated-free type flame retardants, However, there were not detected any harmful compounds in all textile samples (**Figure 2**, **Table 7** & **Table 8**).

4. Conclusion

In this study, 4.1 wt% TiO_2 yarn showed antibacterial function (Pneumococcus & *Staphylococcus aureus*: 99.9%), UV cut (UVA: 90.8. UVB: 92.1), and LOI (33.6). The chosen optimal compounding ratio for PU compound of HRF and HFFR were as followed: PU resin 58.3%, DMF (dimethyl formamide, δ = 12.2) 8.3%, MEK (Methylethylketone) 8.3% and FR (flame retardants) 25.0%. Binder for laminating should not be included over 10% of FRs because of adhesion between textiles and FR laminating film. There were detected phosphorus

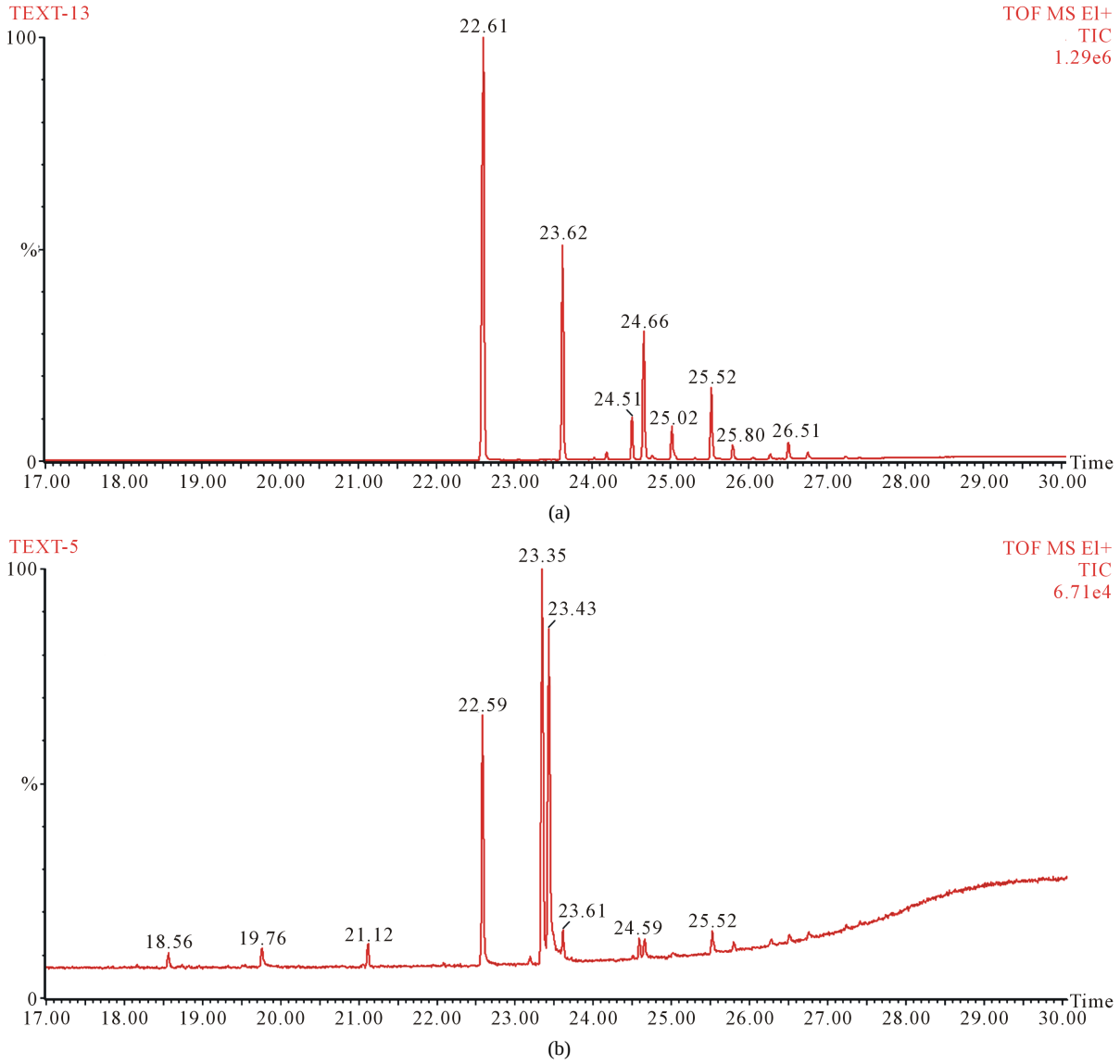

Figure 2. Chromatogram of textiles treated by halogen and halogen-free type flame retardants. (a) Halogen-free type; (b) Halogen type.

Table 7. Candidate of textiles Treated by halogen type flame retardants.

No	Ret. Time	Compound name	Match	Formula
1	17.86	4-Methyl-6-phenyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2H)-one	916	$C_{10}H_9N_3OS$
2	18.56	Dibutyl phthalate	818	$C_{16}H_{22}O_4$
3	22.58	Triphenyl phosphate	939	$C_{18}H_{15}O_4P$
4	23.34	2,4-Quinolinedicarboxylic acid	906	$C_{11}H_7NO_4$
5	23.43	Hexanedioic acid, bis(2-methoxyethyl) ester	982	$C_{12}H_{22}O_6$
6	23.61	Phosphoric acid, (1-methylethyl)phenyl diphenyl ester	739	$C_{21}H_{21}O_4P$
7	24.59	Phenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylpropyl)-	890	$C_{22}H_{29}N_3O$

Table 8. Candidate of textiles Treated by halogen-free type flame retardants.

No	Ret. Time	Compound name	Match	Formula
1	22.57	Biphenyl, 4-(4-diethylaminobenzylidenamino)-	624	$C_{23}H_{24}N_2$
2	22.58	Benzo[a]pentacene	683	$C_{26}H_{16}$
3	22.59	1-Hydroxy-3-methoxy-6-methylanthraquinone, TMS	709	$C_{19}H_{20}O_4Si$
4	22.60	Triphenyl phosphate	909	$C_{18}H_{15}O_4P$
5	23.62	Phosphoric acid, (1-methylethyl)phenyl diphenyl ester	872	$C_{21}H_{21}O_4P$
6	24.18	9H-Purine, 9-(trimethylsilyl)-2,6-bis[(trimethylsilyl)oxy]-	609	$C_{14}H_{28}N_4O_2Si_3$
7	24.66	4,8-Ditert-butyl-N,N-diethyl-2,10-dimethyl-12H-dibenzo[d,g][1,3,2] dioxaphosphocin-6-amine	633	$C_{27}H_{40}NO_2P$
8	25.05	Acetamide, N-[4-(4-methyl-1-phthalazinyloxy)phenyl]-	960	$C_{17}H_{15}N_3O_2$
9	25.54	1,5-Diacetyl-2,6-naphthalenediol dibenzoate	624	$C_{28}H_{20}O_6$
10	25.80	Phosphorhalogeic acid, tri(2-isopropylphenyl)ester	723	$C_{27}H_{33}O_4P$
11	26.06	Benzenamine, 4,4'-[(1-methylethylidene)bis(4,1-phenyleneoxy)]bis-	731	$C_{27}H_{26}N_2O_2$
12	26.28	Phosphoric acid, tri(2-isopropylphenyl)ester	779	$C_{27}H_{33}O_4P$

compounds in the textiles treated by halogenated type flame retardants and halogenated-free type flame retardants, however, there were not any detected harmful compounds from all textile samples. Therefore, developed textiles in this study were suitable for flame retardant protective clothing.

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