

# Preparation of Non-flammable Wiper Paper by Simple $H_3PO_3$ Treatment

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## 아인산 처리에 의한 불연성 와이퍼 용지의 제조

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**Abstract** A thin and porous non-flammable wiper was prepared by phosphorus acid solution treatment and subsequent oven annealing. The  $H_3PO_3$  treatment improved flame retardancy of wiper paper to nonflammable level. Thermogravimetric analyses showed that residues increased to 50% at 700°C, which means this treatment helps dehydration of the cellulose chain and promotes the formation of char-like structures during the burning. FT-IR and X-ray photoelectron spectroscopy showed that some of the added  $H_3PO_3$  could react with the functional groups of the cellulose chain. The reacted  $H_3PO_3$  components promote dehydration of the cellulose components and the formation of a char-like structure and improve the flame retardancy of the wiper paper.

**Key Words** : Wiper Paper, Cellulose, Fiber, Flame Retardancy, Phosphorous Acid, Char

**요약** 매우 얇고 다공성 비인화성 와이퍼 용지를 아인산 수용액 처리에 의해 준비되었다.  $H_3PO_3$  처리는 와이퍼 용지의 난연성을 불연성 수준으로 개선시켰다. 열중량 분석 결과 700°C에서 잔량이 50%까지 증가했다. 이것은 본 실험과 같은 아인산 처리가 셀룰로오스 사슬의 탈수를 돕고, 연소중에 차르(char)와 유사한 구조의 형성을 촉진한다는 것을 의미한다. FT-IR과 X선 광전자 분광학에서는  $H_3PO_3$ 의 일부는 셀룰로오스 사슬의 작용기와 반응하는 것으로 보였다. 반응한 아인산은 셀룰로오스의 체인의 탈수를 촉진하고, 차르와 같은 구조의 형성을 도와 와이퍼 용지의 난연성을 향상시킨다.

**주제어** : 와이퍼 용지, 셀룰로오스, 섬유, 난연성, 인산, 숯

## 1. Introduction

Cotton fabrics and cellulose paper with flame retardancy are useful for certain applications. Conventional halogen and phosphorus flame retardants have been widely used for that purpose, but the use of halogen compounds is limited due to toxic effects on ecosystems [1-4].

Some phosphorus compounds are currently being applied as halogen-free flame retardants in cellulose materials. Many studies have been conducted to improve the flame retardancy of cellulose materials using red phosphorus, phosphates and phosphoric acid compounds [2-5].

These phosphorus flame retardants promote the dehydration reaction of the cellulose chains

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and the formation of char-like residues, and these flame retardants tend to lower the decomposition temperature of the polymer [6-8]. Char-like components are known to be formed through several steps including formation of conjugated double bonds and polycyclic aromatic rings [1-9]. These char-like structures act as barriers to the movement of mass, heat, fire and oxygen. Another important factor is that when the char-like structure is made of fire, it has to be expanded and thick enough to be a protective layer [10-14].

In general, more than 20% phosphorus compounds are considered necessary to achieve flame retardancy of UL 94V0 [7,10,15]. However, adding large amounts of phosphorus compounds can cause ecological and cost efficiency problems. Some phosphorus compounds have been banned due to toxicological hazards. Phosphorus flame retardants are commonly used with other additives to improve char formation performance [1-7]. These char forming agents (CFAs) are generally added to catalyze the char forming ability [16,17]. For example, combining phosphorous compounds with amine compounds such as ammonia, urea, and melamine compounds enhances char formation and has a synergistic effect on flame retardancy [18-20]. However, products with thinner parts require higher amounts of flame retardant to have the same level of flame retardancy as thicker parts.

In this work, we studied how to improve flame retardancy by treating thin wiper paper made of cellulose material with phosphorous acid solution. The goal of this study is to produce non-combustible wiper paper material with simple  $H_3PO_3$  treatment. Since thin porous wiper paper is known to be difficult to inflammable, it is considered a good test case to study how to improve the flame retardancy of cellulosic materials.

We measured the amount of char-like structure produced by the treatment, and investigated the reaction with phosphorus and cellulose, and the effect of the treatment on the flame retardancy of wiped paper.

## 2. Materials and Methods

### 2.1 Chemicals and Materials

The paper used in this experiment is a porous wiper (Kimwipe, Yuhan Kimbley Klacke Co. Korea) thinner than A4 size paper. Phosphorous acid ( $H_3PO_3$ ) was obtained from Samchun Chemicals.

### 2.2 $H_3PO_3$ Treatment

The wiper paper was thoroughly soaked in 20% aqueous  $H_3PO_3$  solution for 20 min. The remaining solution on the wiper paper was squeezed out. The  $H_3PO_3$  solution-treated paper was oven-annealed at 120 °C for 3 h. After oven annealing, the paper was rinsed with de-ionized water at least 5 times to remove residual unreacted  $H_3PO_3$  and any water-soluble low molecular compounds. The samples were then dried in an oven at 80 °C before analysis. No further treatments or additives were used.

### 2.3 Flammability Testing

The specimen used for the flammability test were 20 mm wide and 150 mm long. The flame retardancy was evaluated according to UL94 vertical burning test method [1]. It was burned for 10 seconds at a height of 10 mm from the tip of the vertically erected sample. Checked the time until the flame went out. Immediately after the first flame was turned off, a second ignition test was performed for 10 seconds and the time until the fire was turned off was measured.

### 2.4 Thermogravimetric Analysis (TGA)

Weight loss according to temperature was

measured using TGA2950 of TA Instruments. The analysis was performed at a heating rate of 20°C./min and a nitrogen flow rate of 100 mL/ min.

### 2.5 Scanning Electron Microscopy (SEM)

We observed neat wiper paper, H<sub>3</sub>PO<sub>3</sub> treated paper and TGA scan samples (TGA test to 180 °C) using a scanning electron microscope (JSM-6380, Jeol Co.). SEM was observed at 20 kV.

### 2.6 Fourier Transform Infrared Radiation Spectroscopy (FT-IR)

FT-IR was used to investigate the change of functional groups by the H<sub>3</sub>PO<sub>3</sub> treatment. Nicolet IR-200 FT-IR (ThermoFisher Scientific, UK) was used with 4 cm<sup>-1</sup> resolution and 16 total scans.

### 2.7 X-ray Photoelectron Spectroscopy (XPS)

XPS wide spectra were collected using K-Alpha+ (ThermoFisher Scientific, UK) with AlK $\alpha$  radiation with a step of 1 eV and a pass energy of 200 eV. The C1s spectrum was collected from 298 to 279 eV with a step width of 0.05 eV. The C1s standard binding energy of C-C species was set at 284.8 eV. Deconvolutions for O1s and P2p were performed using a Shirley background method and a ratio of Gaussian to Lorentzian characters of 30%.

## 3. Results and Discussion

### 3.1 Flame Retardancy

The neat wiper paper remained white after the oven annealing (Fig. 1a). When treated with the H<sub>3</sub>PO<sub>3</sub> solution and oven annealing, the treated paper turned gray and black. Fig. 1a shows that as soon as the neat wiper paper was ignited, it burned completely within 2 seconds without delay.

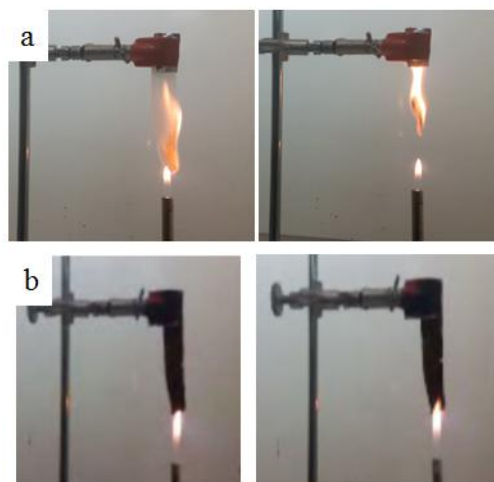


Fig. 1. Photographs during flammability tests for a) neat wiper paper, at 0 sec (left) and 2 sec (right), b) treated paper, at 0 sec (left) and 20 sec (right).

The treated paper neither ignites nor burns for 10 seconds exposure to flame sources as appeared in Fig. 1b. No burning occurred even after 20 seconds exposure to the second ignition. These results indicate that this simple H<sub>3</sub>PO<sub>3</sub> treatment improves the flame retardancy of wiper paper to non-flammable level.

Although the flame retardancy of cellulose materials is known to be based on char formation and intumescent mechanism, it is difficult to develop thin non-flammable paper materials. It is understood that char structure of cellulose occurs through several chemical steps and this process can be triggered by a dehydration of cellulose [10-14]. Dehydration subsequently produces double bonds and polycyclic hydrocarbon compounds, which proceed to the production of compounds with aromaticity similar to the char structure [1,10-14]. From this experiment, it is believed that this improvement in the flame retardancy of the wiper paper is due to the formation of a carbon double bond and a polycyclic structure on the paper surface by H<sub>3</sub>PO<sub>3</sub> treatment,

which are combined to quickly form a char-like structure.

### 3.2 TGA

Fig. 2a shows the weight loss according to the temperature of the treated paper. A large weight loss of 30% was observed at about 277°C. However, at temperatures above 370°C, the slope of weight loss gradually decreases.

To compare the changes occurring in cellulose by the  $H_3PO_3$  treatment, TGA analysis of  $H_3PO_3$  itself and the neat paper was performed. The weight of the neat paper remained unchanged to 320°C, and the weight loss suddenly appeared at about 350°C as seen in Fig. 2b. This sudden weight loss corresponds to the decomposition of cellulose components [18,21]. The  $H_3PO_3$  compound lost 18.2% by weight at 227°C due to evaporation of  $H_3PO_3$  itself as seen in Fig. 2b. The large weight loss at about 600°C can be explained by the decomposition of  $H_3PO_3$ . Therefore, it is believed that the weight loss of about 277°C. seen in the treated paper is due to the decomposition of the cellulose components modified by the treatment with  $H_3PO_3$ .

As shown in Fig. 2c, several control experiments were performed to investigate the change of cellulose paper by the  $H_3PO_3$  treatment. Any heat treatment was not performed to avoid reaction with cellulose due to treatment.

After the wipe paper was immersed in 20%  $H_3PO_3$  aqueous solution for 20 minutes, the preparation of the as-dipped paper was prepared as follows. The excess solution was squeezed off, wiped with a clean wiper, air dried for 30 seconds, and then a TGA scan was performed. Weight loss at about 70°C is due to adsorption water. Another control samples were prepared by further drying of the as-dipped paper in the hood for 12h (12h-dried) and 24h (24h-dried). By the way, they showed less

weight loss in this range because most of adsorption water was volatilized as seen in Fig. 2c. The weight loss at 227°C for the as-dipped paper is less than 5%. The weight loss ratios of the 12h and 24h-dried samples in this temperature range are 10.7% and 14.3%, respectively. This is because the control samples contain not only  $H_3PO_3$  compounds but also water, the longer the drying time, the greater the proportion of  $H_3PO_3$  evaporated at that temperature. Evaporation of  $H_3PO_3$  itself appears to occur at 227°C, and in all controlled experiments, this temperature did not change even with long drying times.

A plateau curve appeared until extensive weight loss occurred at approximately 530°C in all control samples (Fig. 2c). This weight loss is believed that  $H_3PO_3$  component remaining in the cellulose matrix or some low molecular weight compounds formed by reaction of  $H_3PO_3$  with cellulose is decomposed. For the treated paper, no apparent weight loss occurred at this temperature range, which means that some of the components are dissolved by the washing procedure. This weight loss can be attributed to the loss of volatile material in the degraded cellulose and stagnated  $H_3PO_3$  [18]. During the TGA experiments, changes in the shape of the sample were observed at specific temperatures (see Fig. 2d). Control specimens tested to 180°C are slightly yellowish in color, but seems to retain mechanical strength. The sample at the top right of Fig. 2d, taken at 300°C, turned black and began to crumble. This temperature is higher than the vaporization temperature of  $H_3PO_3$ . This observation indicates that the dehydration reaction occurs at a temperature of more than 227°C under nitrogen atmosphere, and above the temperatures the carbon double bond and bond cleavage occurs to make color change and it degrade the mechanical properties of the sample.

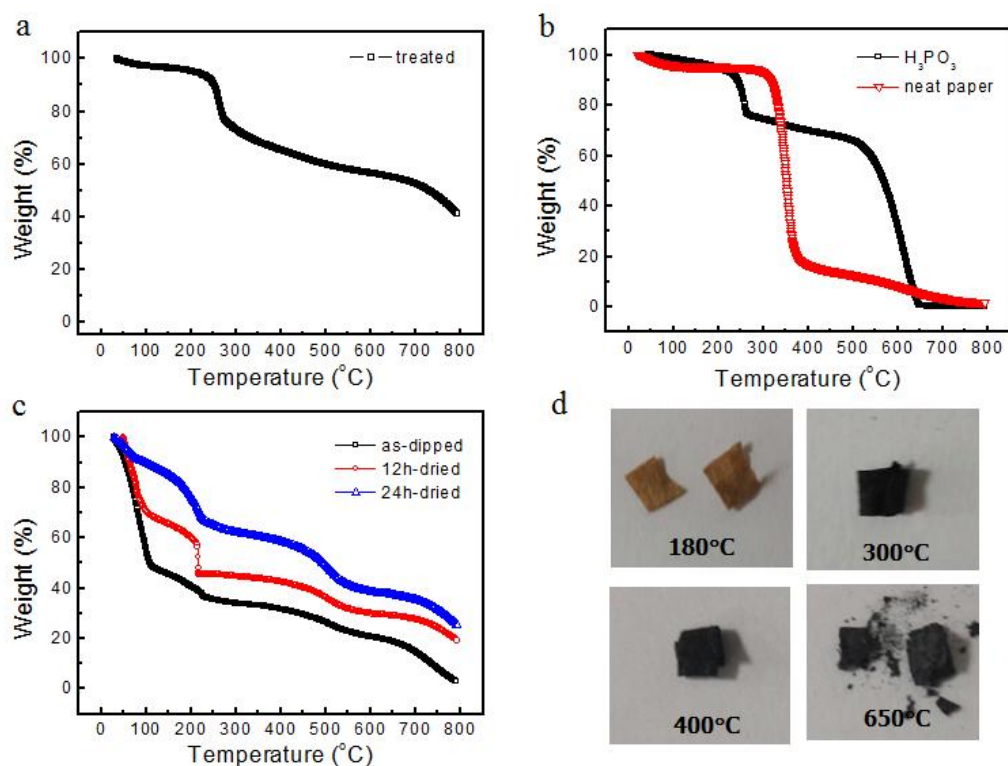


Fig. 2. TGA measurements showing a) weight loss in treated; b) weight loss in neat wiper paper and  $\text{H}_3\text{PO}_3$ ; c) weight loss in as-dipped, 12h-dried and 24h-dried samples after  $\text{H}_3\text{PO}_3$  dipping. d) Digital camera images of samples taken out after heated up to pre-determined temperatures under the environment of TGA experiment after  $\text{H}_3\text{PO}_3$  dipping.

The treated sample showed a decomposition temperature at 277 $^{\circ}\text{C}$ , which is lower than the decomposition temperature of the neat wiper paper decomposed at a temperature of 320 $^{\circ}\text{C}$ . However, as shown in Fig. 2b, this is higher than the evaporation temperature of  $\text{H}_3\text{PO}_3$ , 227 $^{\circ}\text{C}$ .

As can be seen in the control experiment of Fig. 2c, the evaporation temperature of  $\text{H}_3\text{PO}_3$  remaining unreacted was not changed compared to the evaporation temperature of  $\text{H}_3\text{PO}_3$  itself. The shift of the decomposition temperature for the treated paper imply that heat treatment in the presence of  $\text{H}_3\text{PO}_3$  would induce the modification of cellulose.

It is known that the phosphorylation of cellulose chain increases the rate of dehydration of the cellulose chains and reduce the degradation temperature of cellulose [18].

The residues of the treated paper reached more than 50% at 700 $^{\circ}\text{C}$  by the  $\text{H}_3\text{PO}_3$  treatment (Fig. 2a). However, untreated cellulose (the neat paper) did not exceed 3% at that temperature (Fig. 2b). This pattern has been observed previously in the decomposition of plastics and cellulose materials with phosphorus flame retardants [22,23]. These results suggest that the heat treatment has made  $\text{H}_3\text{PO}_3$  compound react with the cellulose, and the addition of  $\text{H}_3\text{PO}_3$  onto the cellulose chains can promote the formation of char structure during the combustion of the cellulose components.

### 3.3 FT-IR Analysis

Fig. 3a shows the FT-IR spectra of the neat paper, the treated non-washed and the treated samples. A broad absorbance peak near 3500

$\text{cm}^{-1}$  is assigned to the stretching of OH bonds and remains strong after treatment (peak 1 in Fig. 3a). However, the peaks generated at  $2900 \text{ cm}^{-1}$  are relatively weak for C-H<sub>2</sub> symmetry and anti-symmetric bending for the treated samples (peak 2 in Fig. 3a). The peak at  $1710 \text{ cm}^{-1}$  (peak 3 in Fig. 3b) is noticeable only for the treated and the treated non-washed samples, indicating the formation of C=O bonds [8,9,22,24].

The peak around  $1630 \text{ cm}^{-1}$  corresponds to the O-H bending (Peak 4 in Fig. 3b) and this is as large as the peak of the neat wiper (Fig. 3b, neat paper). These observations suggest that the H<sub>3</sub>PO<sub>3</sub> treatment can induce oxidation reactions as well as the dehydration, leading to the production of carbonyl groups.

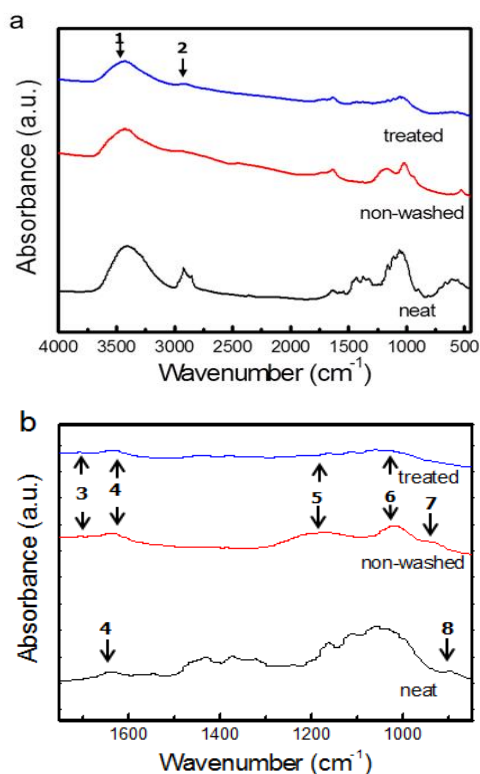


Fig. 3. FT-IR spectra of a) and b) treated (upper), treated non-washed (middle) and neat paper

As can be seen in Fig. 3b, most absorbance peaks of cellulose in the  $1500\text{-}1250 \text{ cm}^{-1}$  region

were blunted by the H<sub>3</sub>PO<sub>3</sub> treatment. These bands correspond to the bending vibrations of the C-H<sub>2</sub>, O-CH, C-CH and C-OH bonds of the cellulose chain and the stretching vibrations of the pyranose ring [24-27]. This bluntness is mainly due to the dehydration of the cellulose rings. The treated non-washed samples after H<sub>3</sub>PO<sub>3</sub> treatment revealed new broad and large bands at  $1170 \text{ cm}^{-1}$  (peak 5),  $1030 \text{ cm}^{-1}$  (peak 6) and  $990 \text{ cm}^{-1}$  (peak 7). This is assigned to the P=O, P-O and P-OH bonds, respectively, which are attributable to the H<sub>3</sub>PO<sub>3</sub> treatment [28]. However, after washing, these peaks were not clear as shown in Fig. 3b.

This information does not imply that the added H<sub>3</sub>PO<sub>3</sub> reacts with the cellulose component to form a grafted group. We have found that it is difficult to investigate the presence of such reactions using FT-IR observations, as can be seen in Fig. 3b.

Peak 8 in Fig. 3b corresponds to the vibration of the glycosidic bond of cellulose. it is reduced for both non-washed and treated paper. This means that the bond breakage is severe and the mechanical properties may be deteriorated.

### 3.4 XPS Characterization

Fig. 4 shows wide-scan XPS spectrum for each sample. P2p peaks appeared only in the treated samples. As seen in Table 1, only C, O and P elements were considered. The treated sample has a notable P content of about 3%, while the treated non-washed sample has a high P content as high as 12%.

Table 1. Atomic ratios of neat paper and treated non-washed and treated papers measured from XPS spectra.

Sample	C1s	O1s (%)	P2p
neat paper	59.5	38.9	0.4
treated non-washed	42.9	43.7	12.4
treated	55.7	39.7	3.1

The O1s band can be divided into two peaks, one of the O double bonds of O=C, O=P and the other of the O single bonds of the O-C and O-P bonds [30,31].

Table 2. Shift in O1s and P2p XPS spectra for neat wiper and treated paper.

Sample	O1s				P2p
	O=C- O=P-		C-O-C P-O-P C-O-P		P-O-C O=P-O
Functional groups	Binding energy (eV)	Atomic ratio (%)	Binding energy (eV)	Atomic ratio (%)	Binding energy (eV)
neat paper	531.4	11.7	533.0	82.3	-
treated non-washed	531.6	26.4	533.0	74.6	134.1
treated	532.0	23.5	533.5	76.5	134.5

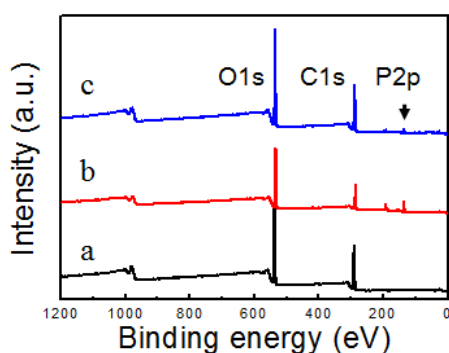


Fig. 4. XPS wide scan spectra of a) neat wiper paper, b) treated non-washed, c) treated.

For the neat paper, these peaks are centered at 531.4 and 533 eV, respectively as seen in Fig. 5a. However, as seen in Fig. 5c, the peaks of the treated samples were shifted up to 532 and 533.5 eV. For comparison, the treated non-washed tends to slightly rise at 531.6 and 533 eV as seen in Fig. 5b and Table 2, mainly due to the phosphate groups of H<sub>3</sub>PO<sub>3</sub> added.

Atomic ratios for O double bonds (O=) increased from 11% for the neat paper to 26.4% and 23.5% of the non-washed and the treated samples, respectively as seen in Table 2. For the non-washed paper, this increase was attributed to the addition of H<sub>3</sub>PO<sub>3</sub> to cellulose. For treated samples, the ratio of O double bonds reduced, but the O single bond increased over that of the non-washed sample as seen in Table 2. It is explained that the increase in atomic ratio corresponding to the O single bond in the treated sample is due to the formation of the C-O-P bond,

[32] which implies chemical reaction between cellulose and H<sub>3</sub>PO<sub>3</sub>.

The P2p XPS spectra in Fig. 6 show that the treated non-washed sample has a relatively large peak centered at 134.1 eV, which is attributed to the P=O and P-OH groups of the added H<sub>3</sub>PO<sub>3</sub>. The P2p peak of the treated sample as seen in Fig. 6c is centered at 134.5 eV and the intensity around 134.1 is lowered.

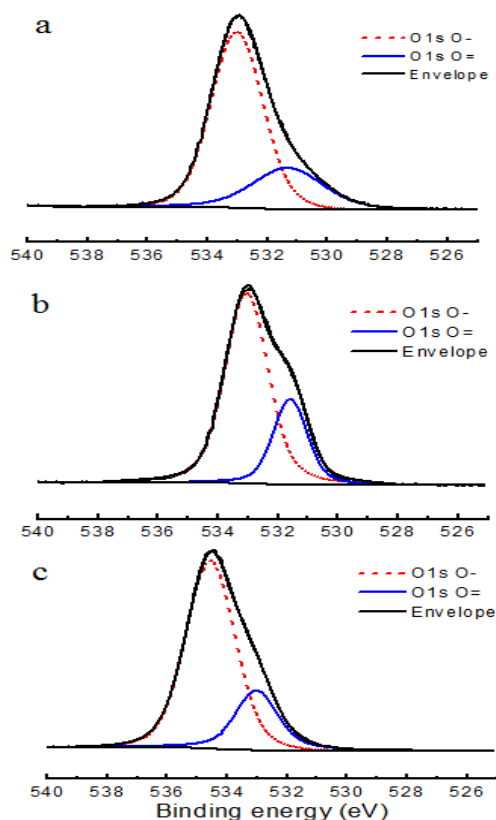


Fig. 5. O1s XPS spectra for a) neat wiper paper, b) treated non-washed, c) treated.

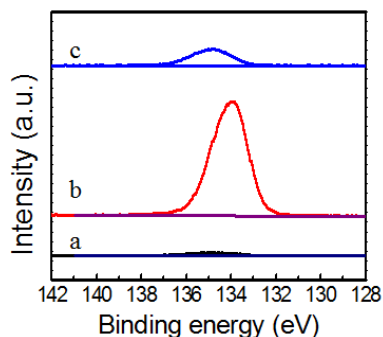


Fig. 6. P2p XPS spectra for a) neat wiper paper, b) treated non-washed, c) treated

The difference is attributable that most of the unreacted stagnant  $H_3PO_3$  is removed by the cleaning process, but some newly formed phosphorus bonds generate peaks around 134.5 eV, indicating peak shift. New bonds can be formed by the reaction of  $H_3PO_3$  with the -OH and -O- components of cellulose. This reaction would form O=P-O-C bonds and reacting  $H_3PO_3$  is grafted onto the cellulose chain [8,30,31].

### 3.5 Scanning Electron Microscopy

Fig. 7a and 7b show SEM images of neat wiper paper and treated paper. There are many broken fibers in treated paper. For comparison, the morphology of the sample scanned by TGA up to 180°C was observed. As can be seen in Fig. 7c, the fibers remained in their original morphological form. Indeed, the strength of the fabric is not easily tearable by hand and was similar to the original wiper paper. The dehydration of glycosidic bonds and pyranose rings in the cellulose ring make cellulose chains decomposed and changed into a char-like structure. However cleavage of the glycosidic bond results in a severe attenuation of the fiber strength. Therefore, glycosidic bond breakage can be seen not to occur for the sample for the TGA scanned up to 180°C. However the  $H_3PO_3$

treatment for long time would cause not only the dehydration but also decomposition of the glycosidic bond of cellulose. This observation is consistent with the results of FT-IR and TGA analyses [12].

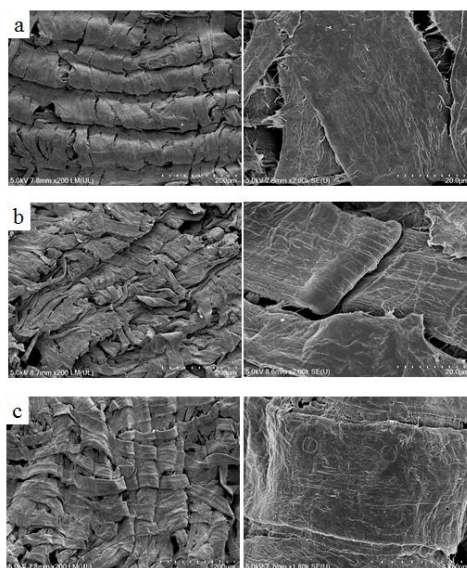


Fig. 7. SEM photographs for a) neat wiper paper, b) treated, and c) TGA scanned up to 180°C

## 4. Conclusions

This study has shown that a simple treatment with  $H_3PO_3$  without addition of flame retardant compounds can improve flame retardancy of wiper paper. We made a thin paper non-flammable by the  $H_3PO_3$  treatment. The treatment helped the residue ratio increased to 50% in the TGA test up to 700°C, which promote the formation of char-like structures.

As a result of TGA, FT-IR XPS and SEM analyses showed some  $H_3PO_3$  would react with cellulose component. The grafted phosphorus component by this reaction can increase the dehydration of cellulose of wiper paper to increase the formation of char component and lead to non-flammability characteristics and cellulose fibers to be brittle.



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