

# Ethylene Oxide for the Mass Deacidification of Paper Relics

**Yunpeng Qi**

Shaanxi Normal University <https://orcid.org/0000-0003-4417-7943>

**Zhihui Jia**

Shaanxi Normal University

**Yong Wang**

Shaanxi Normal University

**Guangtao Zhao**

Shaanxi Normal University

**Xiaolian Chao**

Shaanxi Normal University

**Yajun Zhou**

Shaanxi Normal University

**Yuhu Li** (✉ [liyuhu@snnu.edu.cn](mailto:liyuhu@snnu.edu.cn))

School of Materials Science and Engineering, Engineering Research Center of Historical Cultural Heritage conservation, Ministry of Education, Shaanxi Normal University, Xi'an, Shaanxi, 710119, China

<https://orcid.org/0000-0002-7425-5140>

---

## Research article

**Keywords:** Ethylene oxide, Mass deacidification, Paper relics, Preservation

**Posted Date:** August 27th, 2020

**DOI:** <https://doi.org/10.21203/rs.3.rs-58063/v1>

**License:**   This work is licensed under a Creative Commons Attribution 4.0 International License. [Read Full License](#)

---

# Abstract

In order to solve the international problem of deacidification protection at scale for the whole book and archives, this paper designs the equipment and technology of bulk deacidification treatment with ethylene oxide gas phase. the procedure is simple and the investment is small. In this process, a mixture of ethylene oxide and argon gas is added with the aid of medium vacuum, and the large-scale deacidification of acidification books and archives can be realized by controlling temperature and humidity. This technology does not need to screen acidic and alkaline paper. After the overall treatment, the paper pH value remains at 7.0 to 9.5, which has no effect on handwriting, no discoloration, and has a certain strengthening effect on the paper. The accelerated aging test shows that the pH value remains stable after deacidification and the durability is enhanced. It is a new deacidification technology of paper cultural relics with high efficiency, safety, good compatibility and scale.

## 1. Introduction

Paper is the witness and carrier of human civilization and social progress, recording the rise and fall of human civilization and development, and has a crucial role in the memory of the past few centuries. Paper-based cultural relics are an important part of cultural heritage, such as manuscripts, books, periodicals, calligraphy, paintings, letters and photos, which have extremely important historical, cultural and artistic values.

However, affected by the composition of paper materials and the preservation environment<sup>[1-3]</sup>, the natural degradation of paper cultural relics has become a widespread social problem, resulting in the loss of paper heritage. The natural degradation of paper involves the complex internal and external factors of biophysics and chemistry<sup>[4-6]</sup>, which is the first difficult problem in the field of archival culture.

The results show that the natural aging of paper mainly consists of acid catalyzed cellulose hydrolysis<sup>[7]</sup> and oxidation degradation<sup>[8]</sup>. Acid catalyzed cellulose hydrolysis is to destroy cellulose chain by randomly cutting hemiacetal chain<sup>[9-11]</sup>. Therefore, deacidification is an important means of paper preservation<sup>[12]</sup>, which has been proved to greatly reduce the degradation rate.

In recent years, countries around the world have been carrying out deacidification treatment of cultural relics. According to relevant information, deacidification in some developed countries, such as the United States, Germany, France, Britain, Canada and Italy, has been going on for 30 or 40 years<sup>[13]</sup>. The most widely used deacidification methods in the market mainly include Wei T'o method Bookkeeper (USA PTLP, 1985)<sup>[14]</sup>, ZFB:2 (ZFB, 1994)<sup>[15]</sup>, BookSaver(CSC, 1999) <sup>[16]</sup>and solution deacidification method (Bückerger, Neschen, 2003) <sup>[16, 17]</sup>, which are liquid phase deacidification.

The above liquid phase deacidification method USES magnesium methoxide magnesium oxide or magnesium bicarbonate dispersed into organic solvent or aqueous solution, and then by brush painting, spraying or soaking, the deacidification agent penetrates into the paper fiber as alkali storage, used to neutralize the acid in the paper<sup>[8]</sup>. The advantages are obvious deacidification effect and strong operability. However, in the process of deacidification, cultural relics need to be separated from the original binding or open the scroll, which causes more interference and greater damage to cultural relics. Besides, after deacidification, paper

folds and deforms, books expand and thicken, and archival handwriting, calligraphy and painting fade. As the most widely used method for deacidification of paper cultural relics in the world, Bookkeeper also has some defects. When the paper porosity is low, MgO particles can not fully penetrate into the fiber interior and may cause the paper white. On the other hand, the acid removal solution adds surfactants whose long-term effects on the paper are unclear.<sup>[18]</sup>

Some methods, such as Paper save, Bookkeeper, also provide methods for deacidification of the whole Book, but they need the assistance of high vacuum and large equipment size<sup>[16]</sup>. Books need to be soaked in the acid solution, and with a brush to spread out each page to achieve uniform immersion. This requires books to have a certain strength, ancient books and other serious acidification of cultural relics, calligraphy and painting, and other scroll cultural relics without re-mounted can't be deacidified.

For a long time, many countries have carried out a lot of work on the batch deacidification protection of the whole book and the whole volume of archives. The traditional solution deacidification method the formation of powdery depositions and the bleeding of inks and colours in some occasions<sup>[16]</sup>. Gas phase deacidification requires the cooperation of high vacuum environment, and the equipment requirements are very demanding<sup>[19]</sup>. Therefore, it is urgent to study the new efficient and practical theory and technology of deacidification which can be processed on a large scale.

The gas phase batch deacidification equipment of ethylene oxide is designed in this paper. The mechanical strength, FT-IR, high resolution X-ray diffraction was used to characterize the simulated samples of untreated and EO-Ar treated paper samples before and after artificial accelerated aging. It was found that the degree of polymerization of treated samples was higher than that of untreated samples. The characterization of by GC-MS, FT-IR, SEM shows that epoxy ethane has esterification reaction with acid substances in the paper, produces ester substances, which plays a certain role in strengthening the paper.

## **2. Materials And Methods**

### **2.1. Paper samples**

In this paper, acidified books from the 1950s to the 1980s were selected as the simulation samples of the whole book, and Ingrain paper from the 1940s (provided by the archives bureau of shaanxi province), Xuan paper made with traditional Chinese techniques (provided by the archives bureau of shaanxi province) were selected as paper simulation samples (Table 1).

Table 1  
Paper samples

Samples	Name	Years	pH	Manufacturer or publisher
Sample 1	Groundwood printing papers	1980	3.82	Shaanxi provincial archives bureau
Sample 2	Ingrain paper	1950	5.57	Shaanxi provincial archives bureau
Sample 3	Xuan paper	2017	8.85	China xuan paper co. LTD
Sample 4	Forensic identification of bodily secretions	1980	3.80	Qunzhong Press.
Sample 5	Small dictionary of modern Chinese	1980	3.54	People's Education Press
Sample 6	Licheng county annals		3.25	Yellow River Archives

## 2.2. Deacidification treatment equipment and deacidification process

The equipment consists of deacidification box, inflation system, control system, vacuum system, exhaust degradation system, safety system and other parts. The schematic diagram of EO-Ar deacidification equipment is shown in Fig. 1. Ethylene oxide gas needs to be gasified in the gasification chamber and then filled into the chamber. The argon inlet system is divided into dry argon and humidified argon. The purpose of filling water vapor with argon as carrier gas is to control the relative humidity of the chamber and achieve better deacidification effect. Deacidification temperature was controlled at  $40^{\circ}\text{C} \pm 1^{\circ}\text{C}$ .

## 2.3. Artificial accelerated aging

According to ISO 5630-1 (Part 1: Dry heat treatment at  $105^{\circ}\text{C}$ ), the specific method of artificial accelerated aging of samples is to place samples under constant temperature and humidity cabinet ( $105^{\circ}\text{C}$ ) for artificial accelerated aging ( $72 \pm 0.75$ )h to simulate the condition of 25 years' preservation under natural conditions<sup>[20, 21]</sup>.

## 2.4. Analytical methods

### 2.4.1. pH tests

According to International Standard ISO 6588-1:2012, the pH value of paper simulated sample was measured by cold water extraction method. Cut the sample into pieces (The area is less than  $5\text{mm}^2$ ). Accurately weigh 2 g sample in 250 mL beaker, Add 100 mL distilled water and soak for 1 h. Shake the flask at least once during this time. Mettler Toledo Seven Compact S210-K pH meter was used to measure the extraction solution pH of simulated paper samples as the pH of paper samples. The pH value of the entire book sample was determined nondestructive with a Mettler Toledo S210-K pH meter with a InLab® Surface electrode.

## 2.4.2. Mechanical strength test

The tensile test was conducted according to ISO 1924-2. Cut the sample into 15 mm wide and 180 mm long, and stretch at a uniform rate of 20 mm/min until fracture. At least 10 valid data for Machine direction and Cross-direction measurement.

The folding resistance was tested by referring to BS-ISO-5626-1993. Cut the sample into  $(15 \pm 0.1)$  mm wide  $\times$  150 mm long. At least 10 valid data for Machine direction and Cross-direction measurement.

## 2.4.3. X-Ray diffraction

Smart Lab(9) high resolution X-ray diffraction system (Nippon science co., LTD.) was used for the test. The instrument used Cu\_K-beta to generate X-rays, 45 kV, 200 mA, step Angle 0.01, reflection Angle 2 theta, range  $10^{\circ}$ - $50^{\circ}$ .

## 2.4.4. FE-SEM

During fiber section observation, the paper samples were first soaked with water and then frozen in liquid nitrogen for 1 min. The frozen paper sample is broken along the length perpendicular to the paper. The frozen paper was broken along the longitudinal direction perpendicular to the paper and dried in a vacuum drying oven ( $60^{\circ}\text{C}$ ) for 2 h.

The sample to be tested is pasted on the special sample table with conductive adhesive, and the surface of the sample is not damaged. An ion sputtering instrument was used to spray gold 60 s uniformly on the surface of the sample to increase the conductivity of the sample. SU-8020 field emission scanning electron microscope (Hitachi hi-tech co., LTD.) was used for the test, and the test condition was: acceleration voltage 1 kV.

## 2.5. Analysis of deacidification treatment products

### 2.5.1. Sample preparation

Take treated and untreated Samp.4 edge without text part, cut it up (fragment area less than  $5\text{mm}^2$ ). Weighing take 2 g in 100 mL fine mouth bottle with glass plug, add 20 mL chromatographic methanol solution, ultrasonic oscillation (40KHz) 1 h. The extracted liquid was filtered with a  $0.45\ \mu\text{m}$  needle filter and rotary evaporation to 2 mL, and then filtered with a  $0.22\ \mu\text{m}$  needle filter.

### 2.5.2. FT-IR spectral analysis of paper

Infrared spectra are measured by Bruker Vertex 70 FT-IR Spectrometer in the range of  $4000\ \text{cm}^{-1}$ - $400\text{cm}^{-1}$ . The spectrometer is equipped with a microscope and an ATR lens containing germanium crystals.

### 2.5.3. FT-IR analysis of paper extract

Weigh 300 mg of dried KBr, put them in agate mortar, mix well and grind in one direction for 2 min. Pour the ground KBr into the tablet mold, and pressurize it under 20 MPa pressure for 3 min to obtain the fully transparent potassium bromide tablet. Drop a drop of methanol extract from paper on the pressed potassium bromide tablet, and the infrared absorption spectrum of methanol was measured after volatilization.

## 2.5.4. GC-MS

Chromatographic column: hp-5 ms capillary column (30.0 m, 0.32 mm, 0.25 ms); The temperature of the column box is 80°C, the temperature of the injection port is 250°C, and the heating procedure is maintained at 80°C for 2 min and 5°C/min for 230°C and 3 min. With the carrier gas He, the purge flow rate is 3.0 mL/min, and the column flow rate is 1.97 mL/min.

Electron bombardment (EI) ion source, ion source temperature :230°C, interface temperature :250°C, 30 m/z ~ 600 m/z.

## 3. Results And Discussion

### 3.1. Deacidification process

In this paper, simulated paper samples and discarded acidification books were deacidified with ethylene oxide for reinforcement. The EO-Ar treated and untreated blank control samples were tested and analyzed to demonstrate the beneficial effects of ethylene oxide on paper archives and cultural relics.

The deacidification process is carried out in the deacidification equipment independently developed and designed (Fig. 1). Place the samples to be processed in the deacidification vehicle neatly and push them into the box, close the door and seal them. After the first vacuumization reaches below 10 mmHg, stop the vacuumization and fill argon gas to normal pressure. Control certain temperature and humidity conditions for 24 h pretreatment. After the pretreatment, vacuumize below 10 mmHg and fill with ethylene oxide and argon at a certain proportion and speed. Control a certain temperature and appropriate time for static treatment. Finally, the water ring vacuum pump and light medium are opened to degrade the exhaust gas. After the pressure drops to 100 mmHg, nitrogen is charged to the normal pressure to degrade the exhaust gas again. After reciprocating for three times, open the air valve to return the pressure inside the box to normal pressure, and open the box to take out the sample.

There are four main factors that affect the deacidification effect of epoxy ethane - argon system on paper, namely the processing temperature, processing time, pretreatment humidity and gas ratio. The optimum process conditions for deacidification of epoxy ethane - argon gas system were found by orthogonal test. The pH value of sample 1 after deacidification was taken as the test index. In this experiment, the interaction between factors is not considered. Let's use the  $L_9(3^4)$  orthogonal table. Factor levels are shown in Table 2. The range analysis process of the test results is shown in Table 3. The pH value of acidified wood pulp paper with pH 3.8 was taken as the test index.

Table 2  
Factor level table

<b>Factors</b>	<b>Pre-treatment humidity</b>	<b>Gas ratio</b>	<b>Processing temperature</b>	<b>Processing time</b>
<b>Levels</b>	<b>(%)</b>	<b>(EO:Ar)</b>	<b>(°C)</b>	<b>(h)</b>
	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>
1	30	9:1	30	2
2	55	7:3	40	10
3	80	5:5	50	24

Table 3  
Test plan and result analysis

Test No.	Factors				Test results pH
	A	B	C	D	
1	1(30%)	1(9:1)	1(30°C)	1(2h)	4.34
2	1(30%)	2(7:3)	2(40°C)	2(10h)	5.12
3	1(30%)	3(5:5)	3(50°C)	3(24h)	3.97
4	2(55%)	1(9:1)	2(40°C)	3(24h)	6.78
5	2(55%)	2(7:3)	3(50°C)	1(2h)	6.23
6	2(55%)	3(5:5)	1(30°C)	2(10h)	5.45
7	3(80%)	1(9:1)	3(50°C)	2(10h)	7.89
8	3(80%)	2(7:3)	1(30°C)	3(24h)	8.03
9	3(80%)	3(5:5)	2(40°C)	1(2h)	6.38
K <sub>1</sub>	13.43	19.01	17.82	16.95	
K <sub>2</sub>	18.46	19.38	18.28	18.46	
K <sub>3</sub>	22.3	15.8	18.09	18.78	
`K <sub>1</sub>	4.47	6.34	5.94	5.65	
`K <sub>2</sub>	6.15	6.46	6.09	6.15	
`K <sub>3</sub>	7.43	5.27	6.03	6.26	
Optimal levels	A <sub>3</sub>	B <sub>2</sub>	C <sub>2</sub>	D <sub>3</sub>	
R <sub>j</sub>	2.96	1.19	0.15	0.61	
Primary and secondary order	A□B□D□C				
Note: All pH values in the table are averages of the 10 valid tests.					

According to the direct comparison of Table 3, among the 9 experimental results, the deacidification effect of experiment 8 is the best, and it can be seen that the optimal combination of all factors in this experiment is A<sub>3</sub>, B<sub>2</sub>, C<sub>2</sub> and D<sub>3</sub>. The value of R indicates that there is a significant order of factors in this experiment, and the primary and secondary relationship is A□B□D□C. In other words, the pretreatment humidity and the ratio of ethylene oxide to argon are the main factors affecting the deacidification effect. The second is the processing time and temperature. Therefore, it is concluded by orthogonal test that the pretreatment relative humidity and gas ratio are the most influential factors in deacidification of ethylene oxide - argon gas system. The best condition for deacidification is that the deacidification item is pretreated for 24 h under the condition of 80%RH and 40°C, vacuumed to less than 10 mmHg. The ethylene oxide and argon (volume ratio 7:3) were

filled into the tank at a rate of 2 mmHg/min to atmospheric pressure. Keep the temperature at 40 for 10 h. In addition, in the three levels of factor D in the table,  $D_2$  and  $D_3$  are very little different. Considering the deacidification efficiency,  $D_2$  is selected in the actual deacidification to improve the mass deacidification efficiency.

## 3.2. Evaluation on the effect of EO-Ar deacidification reinforcement EO-Ar

### 3.2.1. pH variation

In order to prove the effect of EO-Ar mass deacidification process on the deacidification effect of paper. In this paper, the pH values of EO-Ar treated and untreated paper samples were tested.

After epoxy ethane treatment, the pH value of the samples can reach 7–9<sup>[22]</sup>, which is the safe pH range for the durable preservation of paper cultural relics.

Sample 1 is Ground-wood printing paper, produced in the 1980s, which is the representative of acid paper archives. Before treatment, the pH value was about 5.57, and after treatment, the safe pH value was 8.74. Sample 2 is an ancient bamboo fiber paper sample, which is the representative of weak acid paper archives. Before treatment, the pH value was about 5.57, and after treatment, the safe pH value was 8.74. Sample 3 is handmade rice paper, a representative of alkaline paper cultural relics. You can see that there's not much change in pH after treatment, only a slight increase. It indicates that epoxy ethane treatment will not cause too high pH of alkaline paper as traditional acid-base neutralization reaction deacidification, and prevent alkaline degradation of alkaline paper due to deacidification. To sum up, the pH of paper cultural relics treated with ethylene oxide can reach the optimal range of 7–9, no matter it is acidic paper or alkaline paper, and it will not cause too high pH of alkaline paper in the same volume or book.

Samp. 4, Samp. 5 is the book sample from the 1940s to the 1990s. The acidification is extremely serious. Before treatment, the pH is between 3–4, and after treatment, the pH can reach between 7–8, which is the most suitable range for paper durable preservation. Sample 6 is an ancient book. It is representative of the severely acidic Ancient books. The pH value was about 3.25 before deacidification, and increased to 7.12 after EO-Ar treatment.

Sample 5 is a sample of a thick book, 4.5 cm thick, with 765 pages in total. This book is a small dictionary of modern Chinese published by People's Education Press in 1980. We did a pH test every 100 pages from the first page of the book to study the effect of the book's thickness on deacidification. As can be seen from Fig. 2(b), the pH value of both the middle page and the first page of the book reaches a neutral alkalinity range of more than 7. The deacidification method is not affected by the thickness of the book, and each page can be effectively deacidified.

### 3.2.2. Effect on thermal stability of paper

Studies show that the natural degradation of paper is divided into acid catalytic degradation<sup>[7]</sup> and thermal oxidative decomposition<sup>[23]</sup>. It can be seen from pH values the EO-Ar treated and untreated of Samp.1, Samp.2, and Samp.3 that the EO-Ar treatment can effectively remove the acid in the paper and eliminate the hidden

danger of catalytic hydrolysis of paper acid. However, whether EO-Ar treatment can effectively alleviate the thermal decomposition and aging of paper fibers, we conducted thermogravimetric curve analysis of EO-Ar treated and untreated Sample.

Figure 3 shows the TG and DTG curves of EO-Ar treated and untreated Sample. This curve was obtained at room temperature to 600°C, 20°C/min. It can be seen that there are three peaks on the DTG curve, indicating that thermal decomposition can be divided into three steps.

The first step corresponds to the loss of adsorbed water weight within the paper fiber. The second step corresponds to the mass loss of small molecules such as lignin and hemicellulose in paper. The third step corresponds to the thermal decomposition of cellulose in paper.

TG curves and DTG curves of untreated and EO-Ar treated acid paper are shown in Fig. 3a and Fig. 3b. It is obvious that the thermal decomposition of acid paper is divided into three stages. But different from alkaline and weak acid paper, it has the greatest loss of mass for the second stage. This is because sample 1 has been seriously acidified degradation, the paper fiber crystal area has been destroyed. Due to the  $\beta$ -(1,4)-glycosidic bonds fracture in cellulose molecules, most of the cellulose has been broken down into small molecular fibers. The thermal decomposition of small molecular cellulose coincides with that of lignin and hemicellulose. In the TG curve, the mass loss in the second step is the largest, the initial decomposition temperature decreases, and the thermal stability of the paper decreases. However, after EO-Ar treatment, the paper thermal decomposition temperature increased to 256.3°C. It shows that EO-Ar treatment can effectively improve the thermal decomposition temperature and thermal stability of paper.

The TG curves of sample 2 and sample 3 are basically the same. The only difference is that the TG curve of sample 2 has a significant mass loss around 269°C. This is because sample 2 is slightly acidic Ingrain paper, containing a small amount of lignin pectin and other small molecules not removed during the papermaking process. The initial extrapolation decomposition temperature of the untreated sample 2 was 297.49°C, reached the peak at 337.25°C, and the thermal decomposition ended at about 353.75°C in Fig. 3c. The initial extrapolation decomposition temperature of the EO-Ar treated sample 2 was 296.96°C, reached the peak at 344.71°C, and the thermal decomposition ended at about 358.69°C in Fig. 3d. It is speculated that ethylene oxide and paper carboxylic acid esterification reaction or it is condensed with its hydroxyl group to form esterified oligo - glycol. The paper fiber thermal stability is improved to prevent paper thermal degradation.

Figure 3e and Fig. 3f show alkaline handmade rice paper. In the papermaking process, lignin and pectin are removed thoroughly, so there are only two stages of mass loss in the TG curve. The initial extrapolation decomposition temperature of the untreated sample 3 was 323.43°C, reached the peak at 354.66°C, and the thermal decomposition ended at about 371.85°C in Fig. 3e. The initial extrapolation decomposition temperature of the EO-Ar treated sample 3 was 331.75°C, reached the peak at 357.73°C, and the thermal decomposition ended at about 372.88°C in Fig. 3d. It can be seen that the decomposition temperature of sample 3 also increased to a certain extent after EO-Ar treatment. It shows that EO-Ar treatment can also improve the thermal stability of alkaline paper. In addition, the weightlessness composition of alkaline paper treated with EO-Ar is slightly higher than that of untreated control samples, indicating that EO has a protective effect on inorganic materials such as calcium carbonate in alkaline paper.

### 3.2.3. Effect on mechanical strength of paper

The mechanical strength of paper is the basis for the use of books, archives and other paper cultural relics<sup>[24]</sup>. In order to analyze the influence of EO-Ar treatment on paper strength, the tensile force, folding endurance and tearing resistance of raw and EO-Ar paper samples were tested.

As can be seen from Fig. 4, the mechanical strength of the paper samples after EO-Ar treatment has been improved to a certain extent. Although the increase in strength is extremely small, it also indicates that the EO-Ar deacidification process will not adversely affect the mechanical properties of paper. As can be seen from Fig. 4a and Fig. 4b, the tensile force of sample 1 is very high, but its folding resistance and tearing resistance are low. In particular, the tearing resistance is the smallest of the three samples. Although sample 1 has a certain tensile strength, but the folding and tearing resistance is very low, indicating that the paper is very fragile, breaking at a touch.

Sample 2 is Bamboo paper, the basic weight of the paper is very small, the thickness of the paper is very uneven. The paper has the place of shade grain fiber is less, resulting in folding endurance can not be tested, the error is very large. However, it can also be seen from Fig. 4c and Fig. 4d that the tensile force and tearing resistance are slightly increased both machine direction and cross-direction.

Sample 3 is handmade Xuan paper with alkaline pH. It can be seen from Fig. 3 that the machine direction and cross-direction tensile force, folding endurance and tearing resistance are relatively high. Rice paper fiber is relatively long, paper is very soft. After EO-Ar treatment, the mechanical properties of the paper are improved, which makes the paper more durable. It shows that EO-Ar mass deacidification process will not cause damage to alkaline paper.

Whether the EO-Ar mass deacidification process is really conducive to long-term paper preservation requires further accelerated aging tests<sup>[4]</sup>.

## 3.3. Effect on the aging resistance of paper

It can be seen that EO-Ar treatment has obvious deacidification effect on acidified paper, and on the macro level, EO-Ar treatment does not cause direct loss of mechanical strength of paper, but increases to some extent. Whether EO-Ar treatment is beneficial to the durable preservation of paper, the following experiment is done in this paper. EO-Ar treated and untreated acidified paper samples and acidified books were put into the aging box at the same time for manual accelerated aging test, aging  $240 \text{ h} \pm 1 \text{ h}$  under  $105^\circ\text{C}$  conditions. Mechanical strength conservation rate and crystallinity index test was carried out on the samples after aging.

### 3.3.1. Mechanical strength retention rate

The tensile strength, flexural strength and tear strength of the untreated paper samples and the EO-Ar mass deacidification paper samples were tested before and after aging. The mechanical strength retention rate after aging was calculated, and the influence of EO-Ar treatment on paper durability was further analyzed.

As can be seen from Fig. 5, the mechanical strength retention rate of the paper after EO-Ar deacidification reinforcement treatment is higher than that of the untreated samples, indicating that the EO-Ar treatment slows

down the aging of the paper to a certain extent. Figure 5a and 5b show the retention rates of longitudinal and transverse tensile strength of paper samples, respectively. It can be seen that the strength retention rate of EO-Ar treated paper after aging is much higher than that of untreated samples, indicating that EO-Ar treatment can significantly improve the aging resistance of paper. Figure 5c is the longitudinal folding endurance retention rate, and Fig. 5d is the lateral folding endurance retention rate. It can be seen that, whether the paper longitudinal or transverse, after the EO-Ar deacidification treatment, the paper folding endurance retention rate is much higher than the untreated samples, and even some of the untreated samples are extremely fragile after aging, folding endurance cannot be measured at all, while the EO-Ar treated samples still maintain 40–50% folding endurance. It is speculated that the reaction products attached to the paper fiber network structure, on the one hand directly increased the strength of the paper fiber and the binding force between the fiber bundles, on the other hand to reduce the loss of the paper binding water, so that the paper still maintain a certain degree of toughness.

### 3.3.2. Crystallinity index Cr.I based on XRD

In order to prove the beneficial effect of EO-Ar mass deacidification on paper durability, this paper conducted dry heat treatment artificial ageing for both the EO-Ar treated and untreated samples conducted XRD test for the samples before and after aging. The XRD crystallinity index Cr.I of the fiber is calculated according to the diffraction intensity<sup>[25, 26]</sup>.

$$\text{Cr. I} = \frac{I_{002} - I_{\text{am}}}{I_{002}} \times 100\%$$

Where,  $I_{002}$  is the XRD peak strength of cellulose crystallization zone, with  $2\theta$  between  $22^\circ$  and  $23^\circ$ .  $I_{\text{am}}$  is the amorphous region of cellulose with an XRD peak intensity  $2\theta$  of about  $18^\circ$ .

It can be seen from Fig. 6 that after artificial accelerated aging, the crystallinity index of paper treated by EO-Ar is higher than that of the untreated blank control group. It indicates that EO-Ar treatment has a certain protective effect on the crystallization area of paper, which is conducive to the durability of paper.

It is worth noting that several sharp strong peaks in FIG. 6a correspond to X-ray diffraction peaks of talc powder packed in the paper. For printing paper, talc powder and calcium carbonate will be added to improve the paper's printability.

## 3.4. Mechanism of deacidification reaction

There are two main reasons for acidification degradation of paper cultural relics. On the one hand, acidic and oxidizing gases ( $\text{CO}_2$ ,  $\text{SO}_2$ , HS, NO,  $\text{NO}_2$ , etc.)<sup>[3]</sup> in the external environment are enriched in paper. These acidic and oxidizing gases lead to paper cellulose acid catalytic degradation and oxidative decomposition<sup>[27]</sup>.

Especially lignin and hemicelluloses<sup>[28]</sup>, chemical properties are not stable, easy to be oxidized to form acid. On the other hand is the papermaking process, due to bleaching, sizing and other introduced acid substances. Such as chlorine bleach, alum ( $\text{KAl}(\text{SO}_4)_2$ ), gelatin, rosin, etc.

### 3.4.1. FT-IR spectral analysis

In order to study the deacidification mechanism of EO-Ar mass deacidification process, this paper tested the Untreated and EO-Ar treated paper by ATR-FTIR spectroscopy<sup>[29, 30]</sup>. This method can be used to study whether the fiber structure changes caused by the EO-Ar treated of paper, as shown in Fig. 7. The FT-IR spectra of the EO-Ar treated and untreated samples were compared and some changes were found.

In the infrared spectrum of paper samples, the wide and strong absorption peak of about  $3330\text{ cm}^{-1}$  is the associative hydroxyl O-H stretching vibration peak<sup>[31]</sup>. Because the hydroxyl group is a strong polar group, the paper cellulose molecules adsorbed water formed hydrogen bonds between each other, so only wide and strong associated hydroxyl absorption peak can be observed. The peak around  $2900\text{ cm}^{-1}$  is C-H and  $\text{CH}_2$  stretching vibration<sup>[32]</sup>. The peak around  $1640\text{ cm}^{-1}$  is attributed to the bending vibration peak of O-H<sup>[33]</sup>. The peak around  $1429\text{ cm}^{-1}$  is the bending vibration peak of C-H<sup>[34]</sup>. The plane bending vibration of O-H is at  $1370\text{ cm}^{-1}$ . The peak at  $1160\text{ cm}^{-1}$  was attributed to the stretching vibration peak of C-O-C, which was related to the cellulose  $\beta$ -(1-4) glycoside bond. About  $1105\text{ cm}^{-1}$  is the asymmetric tensile vibration of glucosidecyclic ring. The stretching vibration peak of primary alcohol C-O is at  $1028\text{ cm}^{-1}$ , and the stretching vibration peak of secondary alcohol C-O is around  $1055\text{ cm}^{-1}$ <sup>[35]</sup>.

The characteristic peak of cellulose is located in the spectral range of  $850\text{-}1500\text{ cm}^{-1}$ <sup>[36]</sup>. Among them, the  $1650\text{ cm}^{-1}$ - $1450\text{ cm}^{-1}$  region is the framework vibration of aromatic ring in lignin. In the infrared spectra of Fig. 7a,  $1509\text{ cm}^{-1}$  and  $1602\text{ cm}^{-1}$  represent the p-phenyl ring vibration, and  $811\text{ cm}^{-1}$  or so represents the vibration absorption peak outside the benzene ring surface. This indicates that the acid paper contains more lignin. In Fig. 7b and 7c, there was no absorption of  $1509\text{ cm}^{-1}$ ,  $1602\text{ cm}^{-1}$ , and  $811\text{ cm}^{-1}$ , indicating that lignin content in basic Xuan paper and Weak acid bamboo paper was very low. This is also the rice paper is not easy to acidify yellow, one of the reasons for the long preservation life.

Different from rice paper (Fig. 7c) and bamboo paper (Fig. 7b), acid paper (Fig. 7a) has absorption peaks around  $1733\text{ cm}^{-1}$ ,  $1718\text{ cm}^{-1}$  and  $1647\text{ cm}^{-1}$ . The literature suggests that  $1718\text{ cm}^{-1}$  is the stretching vibration absorption peak of ketone and carboxylic acid carbonyl C = O, and  $1647\text{ cm}^{-1}$  is the stretching vibration absorption peak of aldehyde carbonyl<sup>[37, 38]</sup>. Therefore, Fig. 7a  $1718\text{ cm}^{-1}$  is attributed to the stretching vibration absorption peak of carboxylic acid carbonyl C = O. After EO-Ar treatment, the peak position shifted slightly to the high wave number, and it was speculated that the carbonyl group of aldehyde<sup>[39]</sup>, ketone and carboxylic acid<sup>[40]</sup> reacted with ethylene oxide to form ester carbonyl group. The formation of the carbonyl ester can be verified by the absorption peak of C-O-C asymmetric stretching vibration of the  $1200\text{ cm}^{-1}$  ester. However, this peak is associated with asymmetric stretching vibration of C-O-C of cellulose  $\beta$ -(1,4) glycoside bond. It is impossible to determine whether EO-Ar treated acid paper actually has esters, which needs further study.

As can be seen from Fig. 7d, after the EO-Ar deacidification treatment, ester group-related peaks at  $1730\text{ cm}^{-1}$  were significantly enhanced, while peaks related to carboxyl and aldehyde groups at  $1666\text{ cm}^{-1}$  were significantly weakened. This indicates that ester substances are indeed formed after EO-Ar treatment. It is speculated that with the participation of water, ethylene oxide after ring opening reacts with carboxyaldehyde

group produced after paper fiber degradation and ester is formed. In Fig. 7d, the -OH peak at  $3379\text{ cm}^{-1}$  is strong, because the paper extraction agent is methanol solution, which is not considered.

What happens to ethylene oxide during the deacidification process that increases the pH value of the paper and makes it more flexible and mechanically stronger. In this paper, the methanol extract of paper treated with ethylene oxide was analyzed by GC-MS to determine the reaction product, and then the mechanism of ethylene oxide acting on the acidified paper was speculated.

Table 3  
Untreated sample 4 methanol extract

Number	Retention time	Componentsname	Peak area%	Peak height/%	Mass peak	Similarity/%
1	2.517	Acetic acid	0.76	0.68	327	76
2	3.508	Propanoic acid	1.45	0.71	139	87
3	7.776	Octanoic Acid	0.31	0.27	260	88
4	9.227	Nonanoic acid	0.51	0.45	319	94

Table 4  
EO deacidification Sample 4 methanol extract

Number	Retention time	Componentsname	Peak area/%	Peak height/%	Mass peak	Similarity/%
1	1.560	Ethylene glycol, monoacetate	6.77	9.06	273	98
2	3.470	2-(2-Hydroxyethoxy)ethyl acetate	5.98	6.72	339	97
3	4.795	Triethylene glycol	12.92	7.60	349	98
4	5.515	Diethylene glycol, diacetate	0.15	0.29	282	95
5	6.930	2-[2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy]ethyl acetate	0.96	0.65	257	90
6	12.175	Tetradecanoic acid, 2-hydroxyethyl ester	0.83	0.41	303	87
7	16.240	Palmitic acid, 2-hydroxyethyl ester	1.98	0.95	347	93
8	17.801	Tetraethylene glycol	0.44	0.46	367	92

The results showed that the severely aged paper contained a large number of acidic substances in Table 3. The structure of cellulose was a long linear polymer based on the repeated dimer anhydrous fiber disaccharide unit. The hydroxyl groups on the anhydrous glucose unit form carbonyl and carboxyl groups during oxidation or photooxidation<sup>[41]</sup>. The formation of aldehydes and ketones on carbon atoms C-2 and C-3 in anhydrous glucose unit is the cause of yellowing of cellulose during the aging process<sup>[42]</sup>. Acid catalyzed cellulose hydrolysis, resulting in cellulose  $\beta$ -1, 4-glycoside bond fracture, and then the formation of more acidic substances, which is the main reason for the loss of mechanical strength of the paper.

A large number of polyethylene glycol and esters with different molecular weights were detected in the paper treated with ethylene oxide. From the point of view of the structure of ester substances, it is produced by the esterification reaction between polyethylene glycol with different molecular weight and acid. During the treatment, the gas ethylene oxide was ring-opening polymerized into polyethylene glycol with different molecular weights. The main reaction of ethylene oxide deacidification is polyethylene glycol with acid dehydration condensation to form ester. Ester substances are formed on the surface of cellulose containing a certain amount of free water and acid substances, which is the main reaction of ethylene oxide deacidification (Fig. 10). The presence of polyethylene glycol (PEG) formed by ring-opening polymerization of ethylene oxide increases the toughness of paper fibers.

### **3.4.3. Macroscopic feature**

Figure 8 shows the forensic identification of bodily secretions published by People's Publishing House in 1979(Sample 4). The cover is color printing on offset paper, and the inside page is printed on ordinary mechanical offset paper. The book is cut into two parts, the lower part is strengthened by EO-Ar deacidification, and the upper part is not treated. After the treatment, EO-Ar treatment and untreated parts were put into moist heat aging box for artificial accelerated aging for 240 h.

As can be seen from Fig. 8, the color printed pages such as the cover and back cover of the untreated samples and the inner pages are seriously yellowed and brittle after aging, breaking at a touch. The EO-Ar treated book paper retains its original color and strength after accelerated aging. The contrast between the untreated paper samples and the EO-Ar treated paper samples is very obvious, indicating that the EO-Ar treatment has a strong protective effect on coated paper. EO-Ar mass deacidification can increase the paper toughness, so that the paper has a better aging resistance.

Book covers and other color printing paper generally for coated paper. This is to get better color when printing, the paper added talc kaolin and other fillers to improve the whiteness of the paper and printability. Compared with the untreated samples, the coated paper after EO-Ar treatment has a higher whiteness and physical strength after aging, which indicates that EO-Ar treatment not only has a certain protection effect on the paper fiber itself, but also on the paper fillers.

After the accelerated aging of the untreated samples, in addition to the yellowing and fragility of the paper, the color printing ink has also changed color to a certain extent, with a dark color, as shown in Fig. 8a. This in addition to paper yellowing and darkening affect the ink color, the ink itself has changed the color. However, EO-Ar processing of the bottom half of the book in the aging ink color is still bright. It shows that EO-Ar treatment can protect the paper and increase the durability of color printing inks.

### **3.4.4. SEM analyses**

The fiber and porous structure from nano-to micrometer range can be observed by scanning electron microscopy (SEM). In order to study the effect of EO-Ar treatment on the microstructure of paper fibers, field emission scanning electron microscopy tests were carried out for Sample 4(Acidic paper), which were EO-Ar treatment and untreated treatment.

The paper after dry and aging, EO- Ar processing paper fiber sections a full, round texture Fig. 9a, And untreated paper fiber dry shrinkage. Fold, crisp, fracture, powder, peeling Fig. 9b. Look at Fig. 9b can be found that the fiber surface with a layer of thin film, analyzes its possible the formation of ethylene oxide polymerization by polyethylene glycol (PEG) deposited on the fiber surface (Fig. 9b), retained the fiber moisture content. hence EO-Ar fiber by dry heat aging does not appear shrink after processing, it also from microstructure proved that EO-Ar aging after processing paper high mechanical strength retention than untreated samples. In conclusion, EO-Ar treatment has a certain strengthening effect on alkaline paper.

As can be seen from Fig. 9, after Sample 4 is aged by dry heat, the EO-Ar treated paper fiber is smooth and mellow, while the untreated paper fiber is crisp,breakage-peeling.

It indicates that EO-Ar treatment consumes free acid in paper and prevents autocatalytic acid hydrolysis and oxidation  $\beta$ -elimination decomposition of paper fiber. However, the presence of free acid and high temperature conditions in untreated paper, acid hydrolysis and  $\beta$ -elimination decomposition of the combined effect of the paper fiber degradation. EO-Ar treatment forms a film on the surface of acidic mechanical paper fiber, protecting the paper fiber and preventing the oxidation  $\beta$ -elimination decomposition of the fiber, which is also the microscopic performance of the increase in mechanical strength of paper after EO-Ar deacidification. In conclusion, EO-Ar treatment has the effect of deacidifying and strengthening acid paper.

As can be seen from the paper fiber section in Fig. 9c and 9d, there are significant differences in the inner wall of the fiber cavity after accelerated aging. The inner wall of the untreated paper fiber is cracked and tilted with flake shedding, while the inner wall of the paper fiber strengthened by EO-Ar treated is smooth and round. In addition, the fiber wall thickness of the EO-Ar treated paper was about 2.4  $\mu\text{m}$ , and the fiber wall thickness of the untreated paper was about 1.5  $\mu\text{m}$ . This indicates that in the aging process, the untreated paper loses water, and the glucose chain recombines due to water loss, making the paper brittle. However, the EO-Ar treated paper retains some water, while the glucose chain is not recombined, thus maintaining better softness. It further shows that EO-Ar deacidification reinforcement can thoroughly and effectively remove the acid inside the paper fiber, improve the aging resistance of the paper fiber, and extend the life of paper cultural relics.

Based on this, we speculated that EO-Ar scale deacidification mechanism is shown in Fig. 10. In the whole deacidification system, argon plays a role in promoting the penetration of ethylene oxide in paper, adjusting humidity and ensuring the safety of deacidification system<sup>[43]</sup>. Ethylene oxide as a deacidification agent can produce nucleophilic substitution reaction with free acid organic acid in acidified paper and eliminate a large number of acidic substances<sup>[44]</sup>. Part of ethylene oxide self-ring-opening polymerization to form polyethylene glycol, increase the toughness of paper. Ethylene oxide can also nucleophilic substitution reaction with alkaline substances, will not lead to non-acidic paper alkaline too strong. Some small molecular weight polyethylene glycol can be condensed with hydroxyl group in cellulose to form branched oligopolyeglycol and enhance the antioxidant function of paper.

## 4. Conclusions

Using the mixture of argon and ethylene oxide as deacidification agent, the paper cultural relic mass deacidification research was carried out by using independently developed deacidification equipment and

technology. There is no need to sort out the deacidification items, only need to be put into the box, vacuum pumping, gas distribution, aeration, static reaction and other simple operations, making the large-scale deacidification and reinforcement process extremely simple. At the same time, the environmental protection and safety facilities, such as zero emission of photomedia degradation, have been developed. Argon has fast diffusibility and no specific adsorption, which makes ethylene oxide diffuses quickly and the microscopic reaction is uniform and deep. It overcomes the disadvantages of mechanical dispersion and liquid immersion in the international existing technology, such as low efficiency and damage to the paper of deterioration, and lays a foundation for the efficient operation of the whole mass deacidification and reinforcement.

The study revealed that ethylene oxide gas could nucleophilic substitution reaction with free acids in acidified waste paper and esterification reaction with organic acids in situ, and established a stable system for removing free acids and organic acids. At the same time, with alkaline paper in the free alkali, organic alkali can also occur nucleophilic substitution reaction, so that its pH basically unchanged, keep appropriate. Ethylene oxide in aging paper after the reaction to open loop self-polymerization to form polyethylene glycol, or cellulose hydroxyl condensation to form branched oligopoly glycol, enhanced the anti-oxidation function of paper, protect the fiber crystal area, improve the durability of paper. It overcomes the weakness of alkaline materials in international technology, such as incomplete reaction to organic acids, easy acid reflux and lack of reinforcement. Discard it will make alkaline paper alkali retention excessive lead to corrosion, degradation of the fatal weakness. In particular, the above functions and advantages accord with the fact that archives, books and ancient books are mixed with acid and alkali, which lays a theoretical foundation for the mass deacidification and reinforcement.

## **Declarations**

### **Availability of data and material**

The datasets analysed during the current study are not publicly available but are available from the corresponding author on reasonable request.

### **Funding**

This work was supported by the Fundamental Research Funds For the Central Universities (No. 2017TS050) and Xi 'an Science and Technology Planning Project: Research and Development of key Technologies of removable Integral deacidification (2020KJRC0014).

### **Acknowledgements**

Not applicable.

### **Authors' contributions**

All authors contributed to the research. Yunpneg Qi performed all experiments and measurements, interpreted the data and wrote the manuscript. Zhihui Jia helped writing the manuscript. Yong Wang performed accelerated aging and analyses. Guangtao Zhao completed part of the experiment and performed FE-SEM

microscopy analyses. Xiaolian Chao and Yajun Zhou performed part of the analytical work. Yuhu Li was responsible for design of experiments. All authors read and approved the final manuscript.

### Competing interests

The authors declare that they have no competing interests.

## References

- [1] Zhang C, Huang Y, Zhang H, et al. Selectively Functionalized Zeolite NaY Composite Materials for High-Efficiency Multiple Protection of Paper Relics. *Ind Eng Chem Res*, 2020, **59**(24): 11196-11205.
- [2] Bukovský V. The Influence of Light on Ageing of Newsprint Paper. *Restaurator*, 2000, **21**(2): 55-76.
- [3] Havermans J. Effects of Air Pollutants on the Accelerated Ageing of Cellulose-based Materials. *Restaurator International Journal for the Preservation of Library & Archival Material*, **16**(4): 209-233.
- [4] Area M C, Cheradame H. PAPER AGING AND DEGRADATION: RECENT FINDINGS AND RESEARCH METHODS. *Bioresources*, 2011, **6**(4): 5307-5337.
- [5] Bukovsky V, Trnková M. The Influence of Secondary Chromophores on the Light Induced Oxidation of Paper Part II: The Influence of Light on Groundwood Paper. *Restaurator*, 2003, **24**(2):
- [6] Chamberlain D. Anion mediation of aluminium-catalysed degradation of paper. *Polymer Degradation & Stability*, 2007, **92**(7): 1417-1420.
- [7] Gehlen M H. Approximate solution of the autocatalytic hydrolysis of cellulose. *Cellulose*, 2009, **16**(6): 1069-1073.
- [8] Carter H A. The Chemistry of Paper Preservation: Part 1. The Aging of Paper and Conservation Techniques. *Journal of Chemical Education*, 1996, **73**(5): 417.
- [9] Ahn K, Henniges U, Banik G, et al. Is cellulose degradation due to  $\beta$ -elimination processes a threat in mass deacidification of library books? *Cellulose*, 2012, **19**(4): 1149-1159.
- [10] Carter H A. The Chemistry of Paper Preservation: Part 2. The Yellowing of Paper and Conservation Bleaching. *Journal of Chemical Education*, 1996, **73**(11): 1068.
- [11] Calvini P. Comments on the article "On the degradation evolution equations of cellulose" by Hongzhi Ding and Zhongdong Wang. *Cellulose*, 2007, **15**(2): 225-228.
- [12] Mihram, Danielle. Paper deacidification: a bibliographic survey. Part II. *Restaurator*, 1986, **7**(2):
- [13] Holik D I H. Chapter 13. Book and Paper Preservation [M]. Wiley-VCH Verlag GmbH & Co. KGaA, 2006.
- [14] Bookkeeper® Deacidification [M]. Preservation Technologies <http://preservationtechnologieslp.com/deacid.html>.

- [15] ZFB:2 Massenentsäuerung [M]. Zentrum für Bucherhaltung GmbH in Leipzig: <https://zfb.com/unsere-leistungen/service/massenentsaeuerung>.
- [16] Zervos S, Alexopoulou I. Paper Conservation Methods: A Literature Review. *Cellulose*, 2015, **22**(5): 2859-2897.
- [17] Banik, Gerhard. Mass Deacidification Technology in Germany and its Quality Control. *Restaurator*, 2005, **26**(1):
- [18] Poggi G, Giorgi R, Toccafondi N, et al. Hydroxide Nanoparticles for Deacidification and Concomitant Inhibition of Iron-Gall Ink Corrosion of Paper. *Langmuir*, 2010, **26**(24): 19084-19090.
- [19] Baty J W, Maitland C L, Minter W, et al. Deacidification for the conservation and preservation of paper-based works: A review. *Bioresources*, 2010, **5**(3): 1955-2023.
- [20] Havlíková B, Katuňák S, Petrovičová M, et al. A study of mechanical properties of papers exposed to various methods of accelerated ageing. Part I. The effect of heat and humidity on original wood-pulp papers. *J Cult Herit*, 2009, **10**(2): 222-231.
- [21] Batterham I, Rai R. A comparison of artificial ageing with 27 years of natural ageing The paper samples. *Agiftnaagovau*, 2008,
- [22] Standards B. [Information and documentation. Paper for documents. Requirements for permanence]. *Norme Internationale Iso*, 1994,
- [23] Li Q, Xi S, Zhang X. Conservation of paper relics by electrospun PVDF fiber membranes. *J Cult Herit*, 2014, **15**(4): 359-364.
- [24] Gurnagul N, Howard R C, Zou X, et al. The mechanical permanence of paper: a literature review. *Journal of Pulp & Paper Science*, **19**(4): J160.
- [25] Causin V, Marega C, Marigo A, et al. Forensic differentiation of paper by X-ray diffraction and infrared spectroscopy. *Forensic Ence International*, 2010, **197**(1-3): 70-74.
- [26] Duran A, Perez-Rodriguez J L, Espejo T, et al. Characterization of illuminated manuscripts by laboratory-made portable XRD and micro-XRD systems. *Analytical & Bioanalytical Chemistry*, 2009, **395**(7): 1997-2004.
- [27] Lojewski T, Miskowiec P, Molenda M, et al. Artificial versus natural ageing of paper. Water role in degradation mechanisms. *Applied Physics A*, 2010, **100**(3): 625-633.
- [28] Matisová-Rychlá L, Rychlý J, Ebringerová A, et al. Chemiluminescence accompanying the oxidation of hemicelluloses. *Polym Degrad Stabil*, 2008, **93**(9): 1674-1680.
- [29] Łojewski T, Miśkowiec P, Missori M, et al. FTIR and UV/vis as methods for evaluation of oxidative degradation of model paper: DFT approach for carbonyl vibrations. *Carbohyd Polym*, 2010, **82**(2): 370-375.

- [30] M., Manso, And, et al. Application of spectroscopic techniques for the study of paper documents: A survey. *Spectrochimica Acta Part B Atomic Spectroscopy*, 2009,
- [31] Maréchal Y, Chanzy H. The hydrogen bond network in I [beta] cellulose as observed by infrared spectrometry. *J Mol Struct*, 2000, **523**(523):
- [32] Xiao S, Gao R, Lu Y, et al. Fabrication and characterization of nanofibrillated cellulose and its aerogels from natural pine needles. *Carbohyd Polym*, 2015, **119**(202-209).
- [33] Polovka M, Polovková J, Vizárová K, et al. The application of FTIR spectroscopy on characterization of paper samples, modified by Bookkeeper process. *Vibrational Spectroscopy*, 2006, **41**(2006): 112-117.
- [34] Ciolacu D, Kovac J, Kokol V. The effect of the cellulose-binding domain from *Clostridium cellulovorans* on the supramolecular structure of cellulose fibers. *Carbohydrate Research*, 2010, **345**(5): 621-630.
- [35] Garside P, Wyeth P. Identification of Cellulosic Fibres by FTIR Spectroscopy: Thread and Single Fibre Analysis by Attenuated Total Reflectance. *Studies in Conservation*, 2003, **48**(4): 269-275.
- [36] Calvini P, Silveira M. FTIR analysis of naturally aged FeCl<sub>3</sub> and CuCl<sub>2</sub>-doped cellulose papers. *E-Preservation Science*, 2008, **5**(
- [37] Righini G, Calvini P, Mattogno G, et al. Derivative infrared spectroscopy and electron spectroscopy for chemical analysis of ancient paper documents. *Cellulose Chemistry & Technology*, 1990, **24**(2): 263.
- [38] Calvini P, Gorassini A. FTIR – Deconvolution Spectra of Paper Documents. *Restaurator International Journal for the Preservation of Library & Archival Material*, 2002, **23**(1):
- [39] Ann, Fenech, And, et al. Volatile aldehydes in libraries and archives. *Atmospheric Environment*, 2010,
- [40] Gaspar E M, Santana J C, Lopes J O F, et al. Volatile organic compounds in paper—an approach for identification of markers in aged books. *Analytical & Bioanalytical Chemistry*, 2010, **397**(1): 369-380.
- [41] Lattuati-Derieux A, Bonnassies-Termes S, Lavédrine B. Characterisation of compounds emitted during natural and artificial ageing of a book. Use of headspace-solid-phase microextraction/gas chromatography/mass spectrometry. *J Cult Herit*, 2006, **7**(2): 123-133.
- [42] Carter H A. The Chemistry of Paper Preservation: Part 2. The Yellowing of Paper and Conservation Bleaching. *J Chem Educ*, 1996, **73**(11): págs. 1068-1073.
- [43] Ballard M W, Baer N S. Ethylene Oxide Fumigation: Results and Risk. Assessment. *Restaurator International Journal for the Preservation of Library and Archival Material*, 1986, **7**(4): 143.
- [44] Dupont A L, Egasse C, Morin A, et al. Comprehensive characterisation of cellulose- and lignocellulose-degradation products in aged papers: Capillary zone electrophoresis of low-molar mass organic acids, carbohydrates, and aromatic lignin derivatives. *Carbohyd Polym*, 2007, **68**(1): 1-16.

# Figures

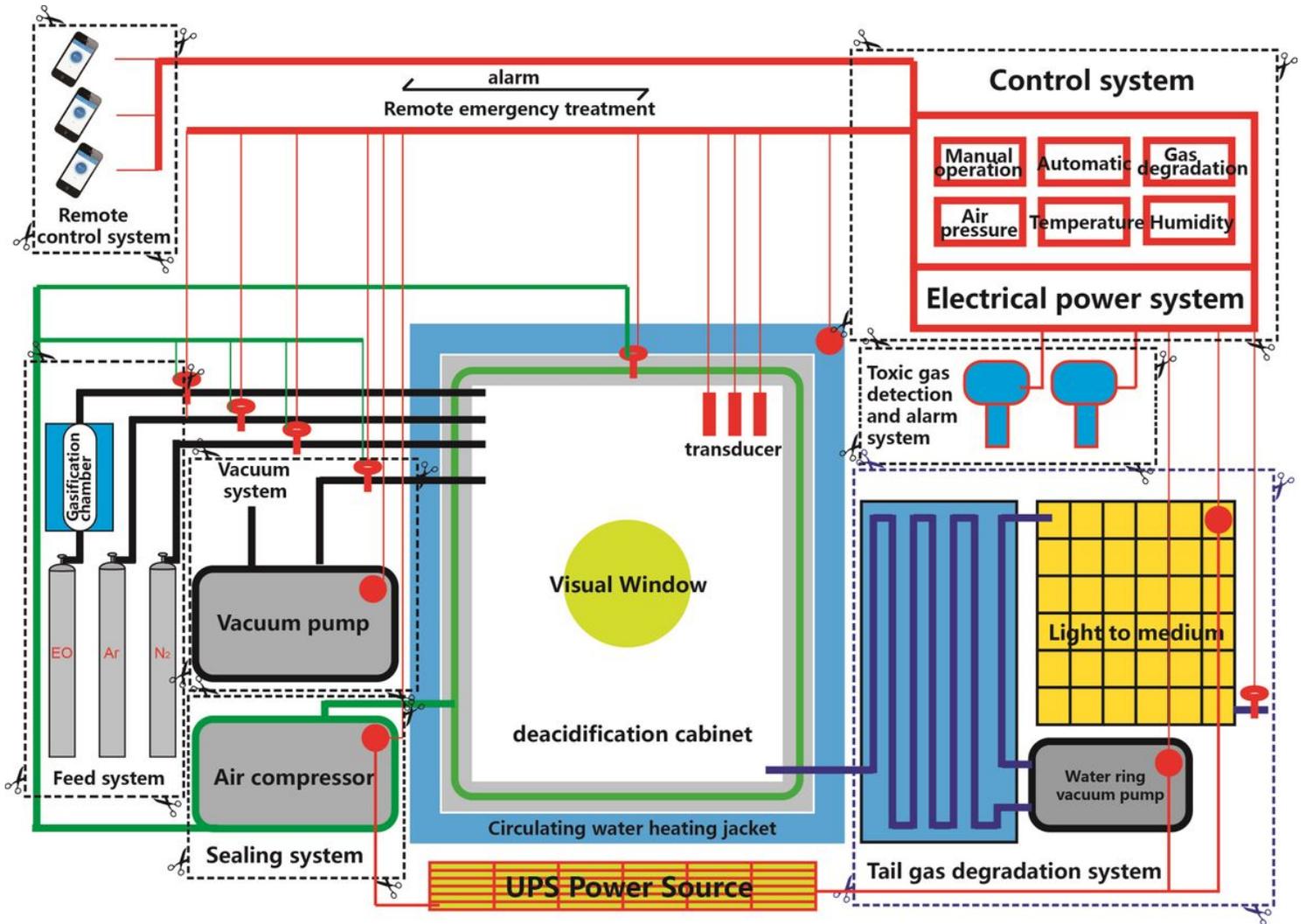
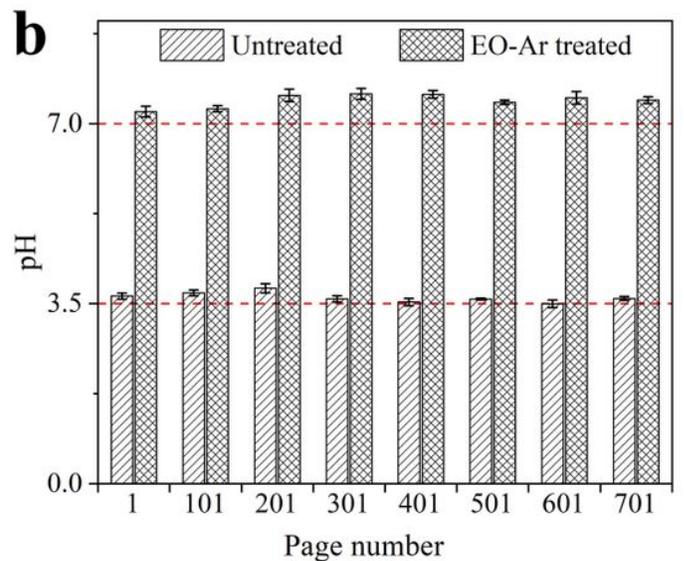
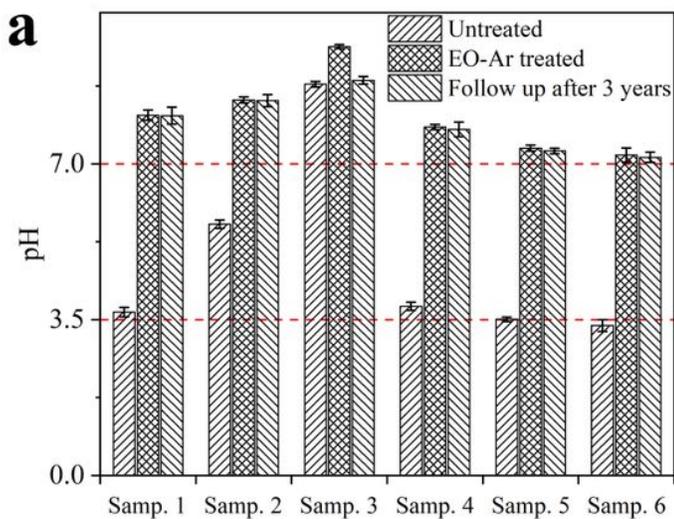


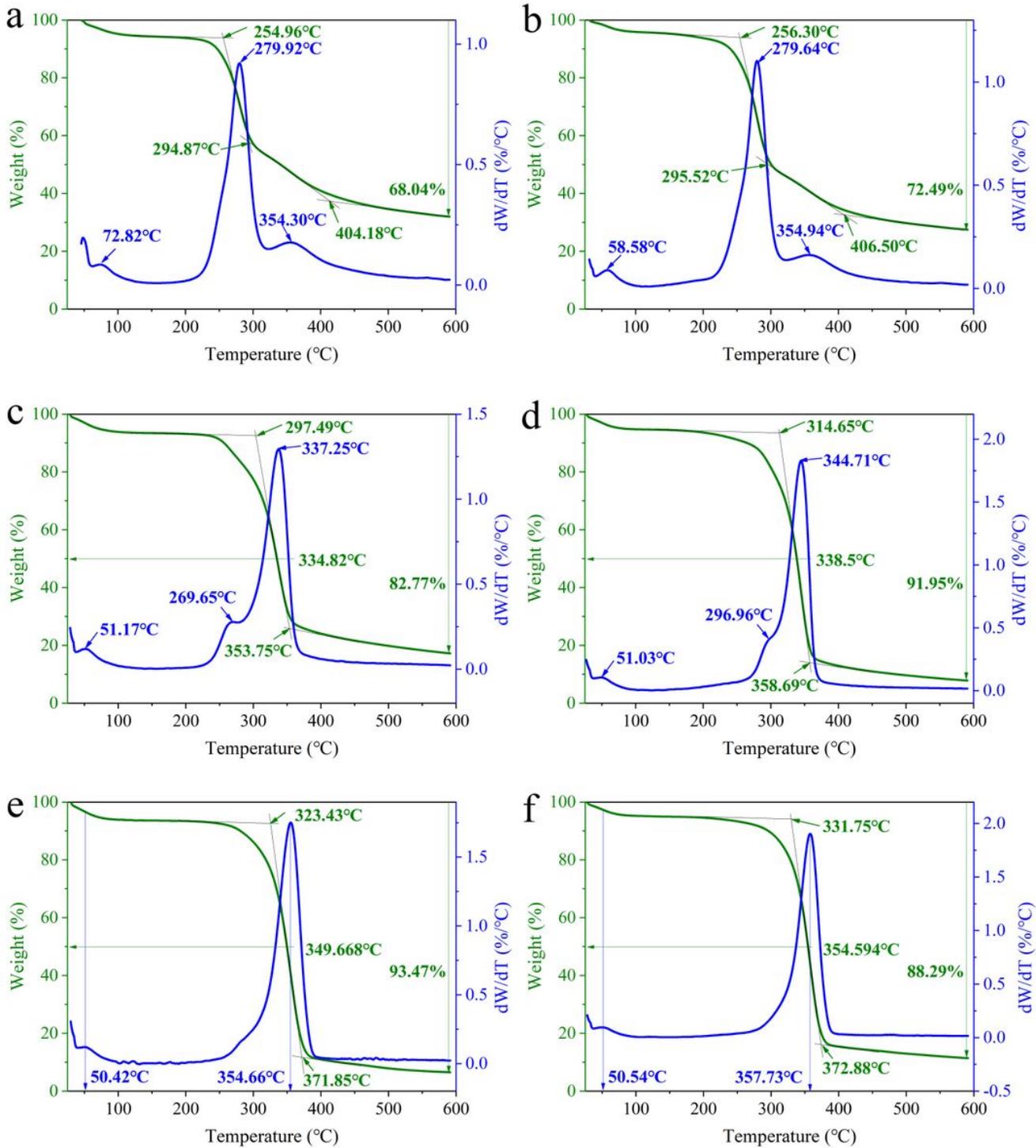
Figure 1

Schematic diagram of deacidification equipment



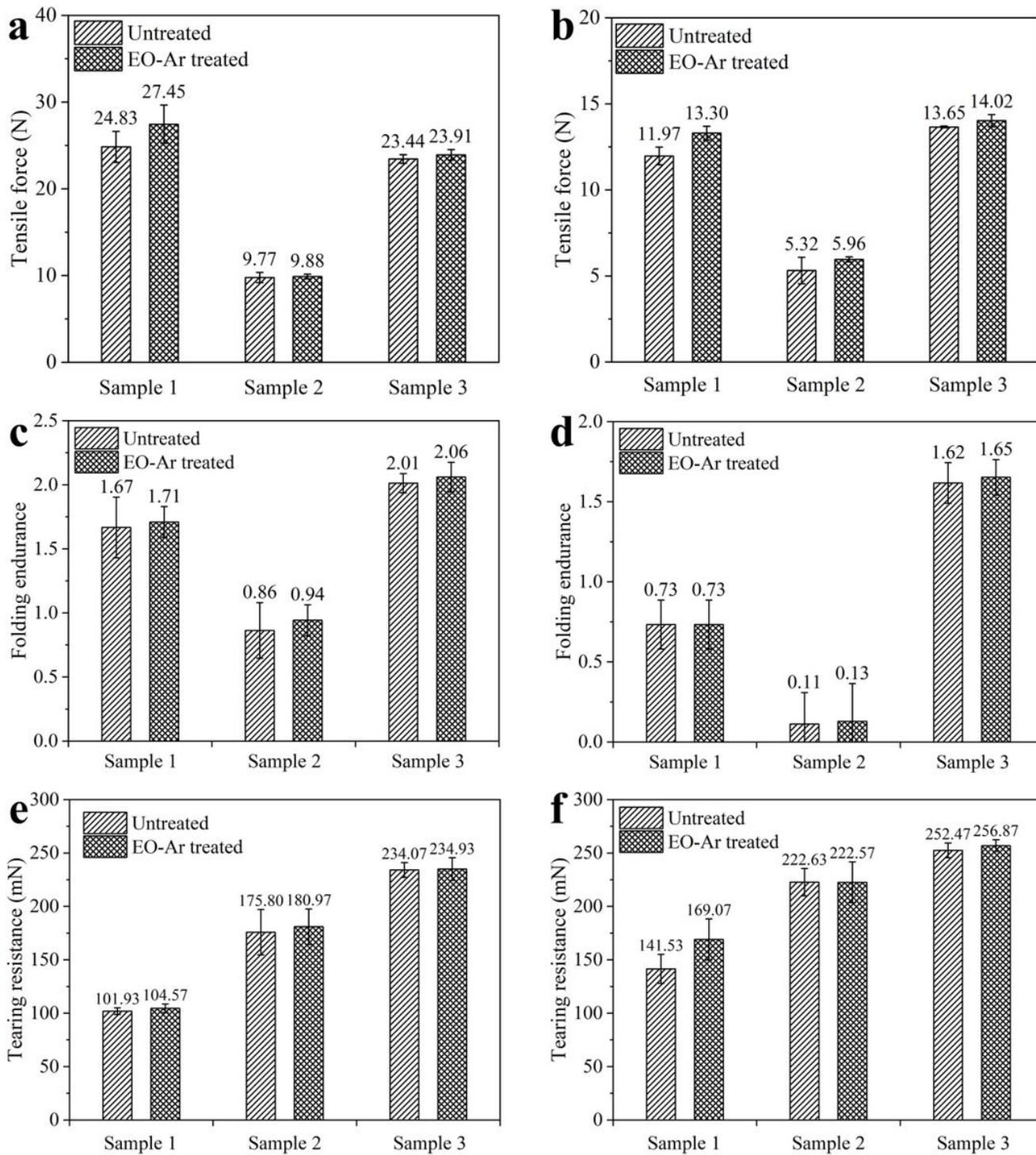
**Figure 2**

pH, The pH values of paper samples were tracked before and after treatment and after 3 years of treatment(a), Sample 2 pH of different pages before and after treatment(b).



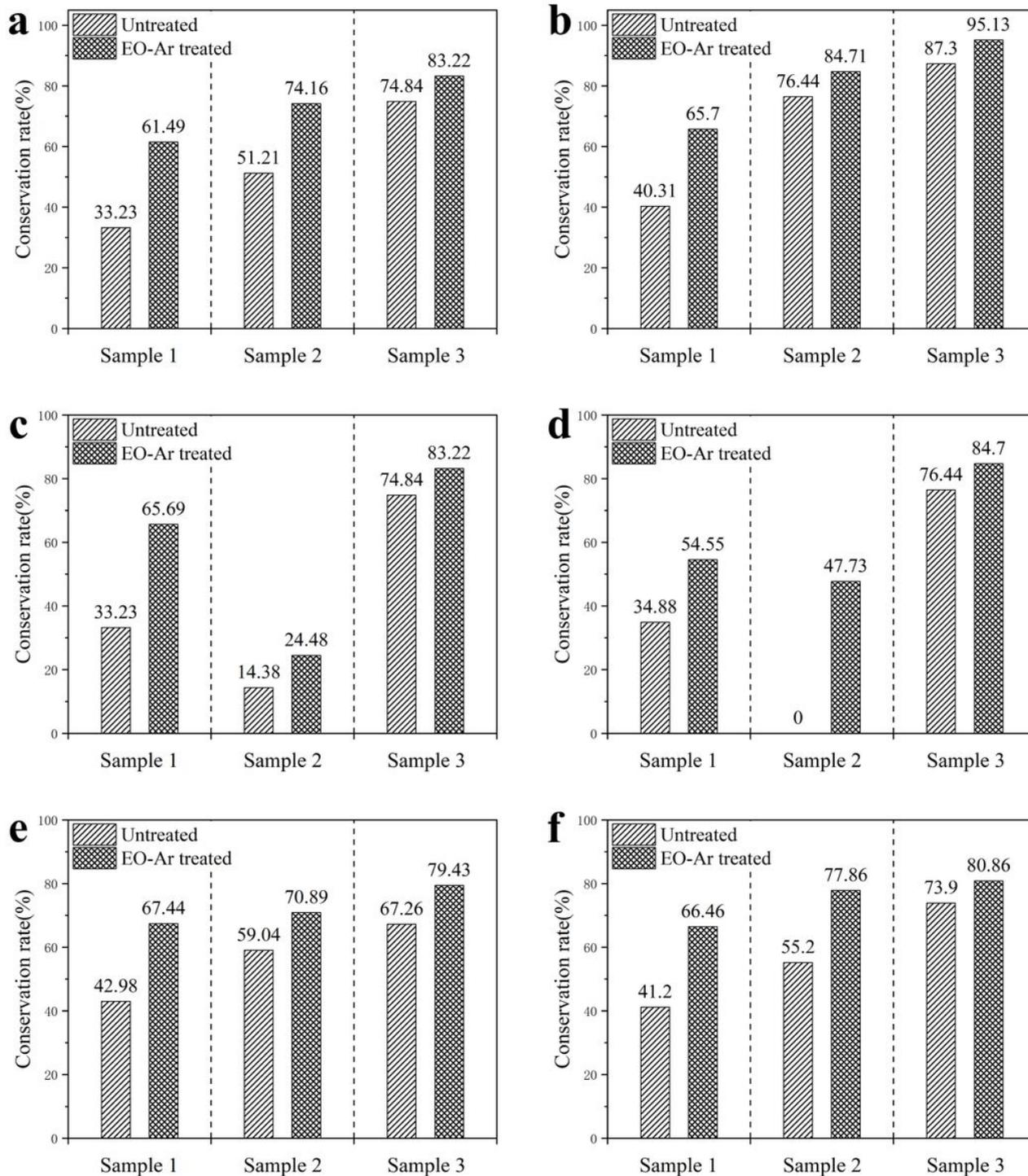
**Figure 3**

TG of paper samples untreated and EO-Ar treated: (a) Untreated sample 1, (b) EO-Ar treated Sample 1, (c) Untreated sample 2, (d) EO-Ar treated Sample 2, (e) Untreated Sample 3, (f) EO-Ar treated Sample 3.



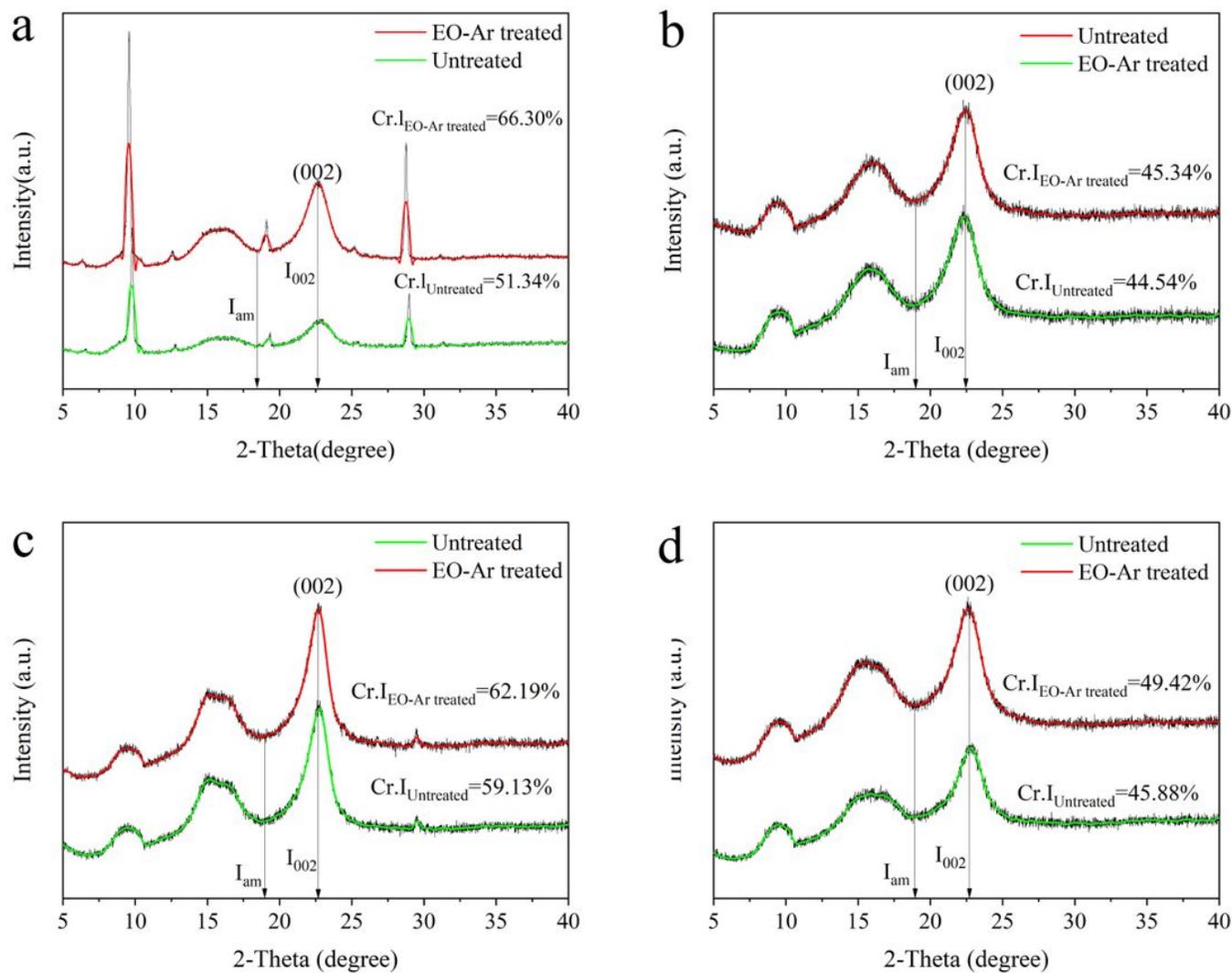
**Figure 4**

Mechanical strength of treated and untreated paper samples—Machine direction tensile strength(a), Cross-direction tensile strength(b), Machine direction folding endurance(c), Cross-direction folding endurance(d), Machine direction tearing resistance(e), Cross-direction tearing resistance (f)



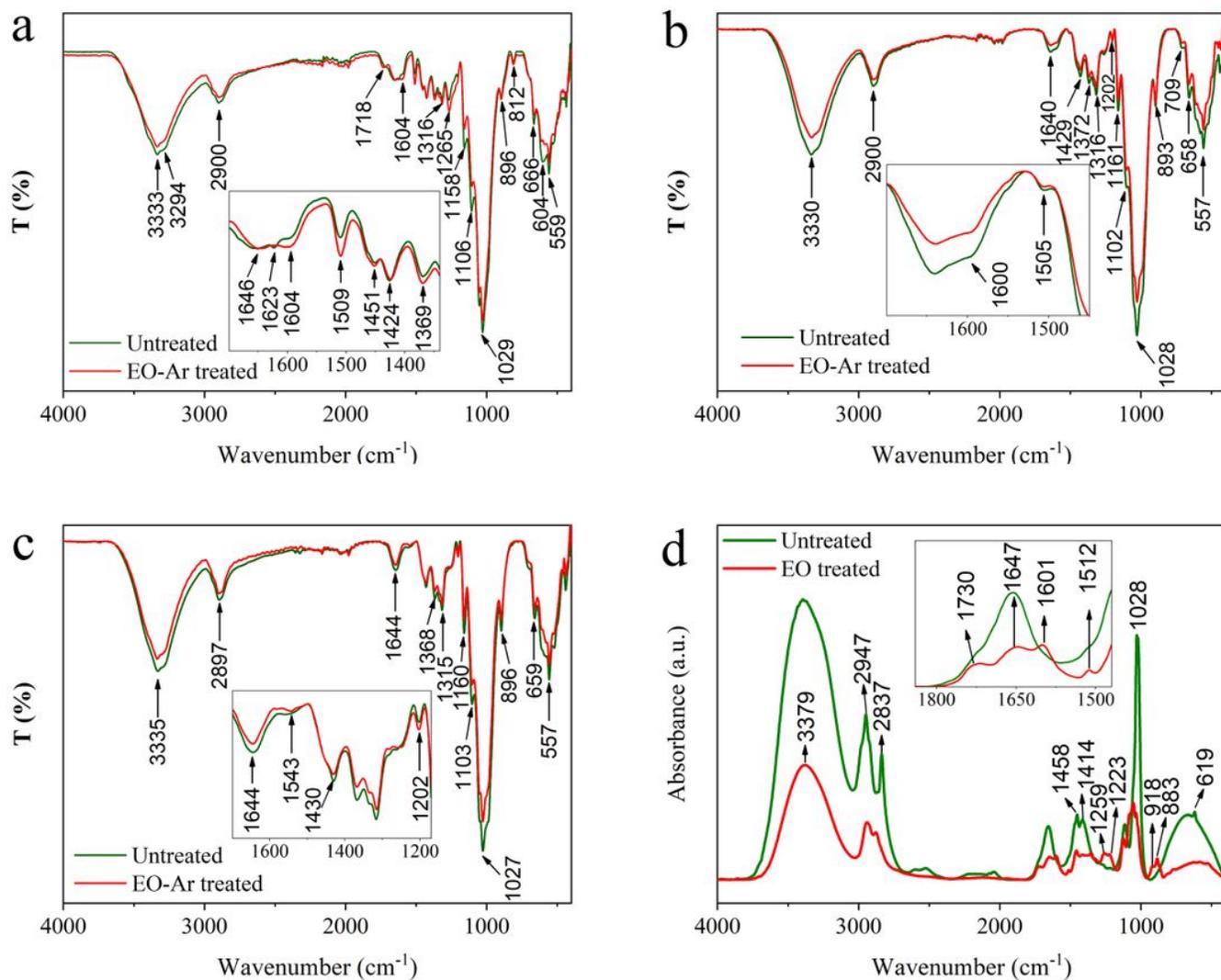
**Figure 5**

Mechanical strength retention rate before and after aging, machine direction tensile strength retention rate (a), cross-direction tensile strength retention rate (b), machine direction folding endurance retention rate (c), cross-direction folding endurance retention rate (d), machine direction tearing resistance retention rate (e), cross-direction tearing resistance retention rate (f)



**Figure 6**

XRD of paper samples untreated and EO-Ar treated, (a) Samp.1, (b) Samp.2, (c) Samp.3, (d) Samp.4



**Figure 7**

FT-IR spectra: (a) Samp.1, (b) Samp.2, (c) Samp.3, (d) Infrared absorption spectra of methanol extract of Sample 4.

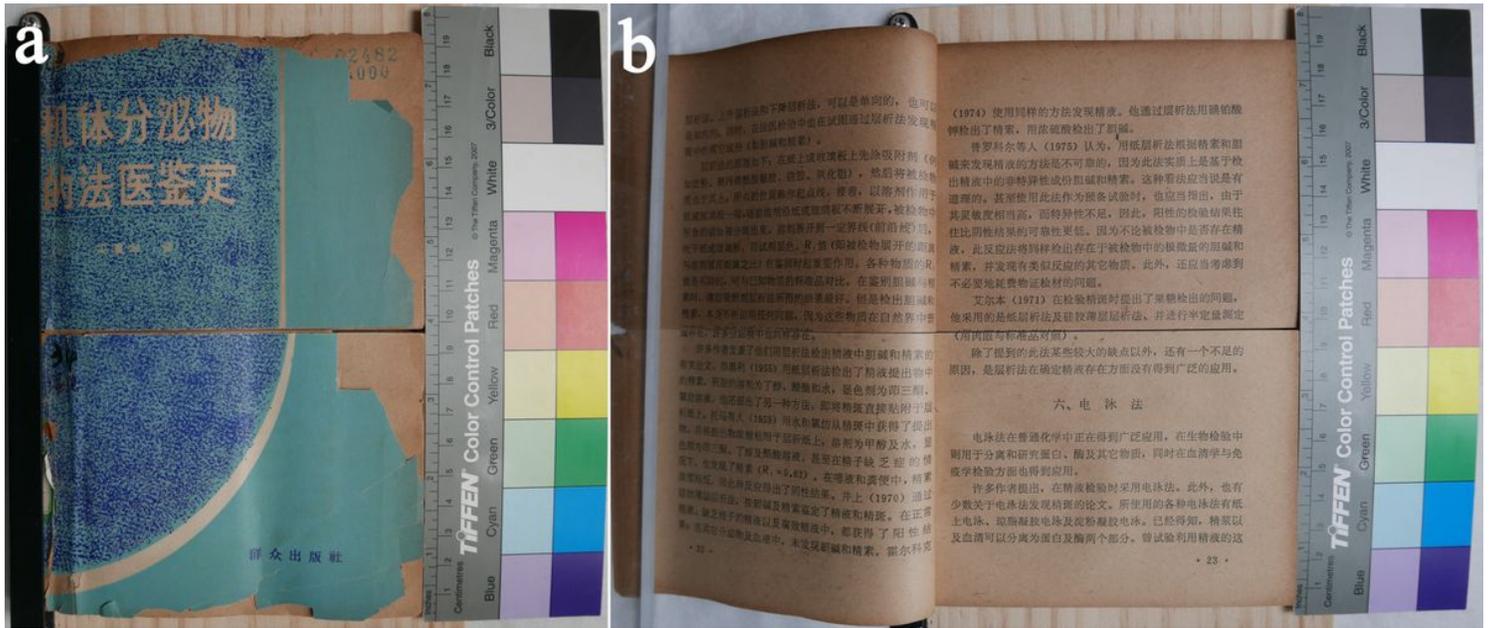
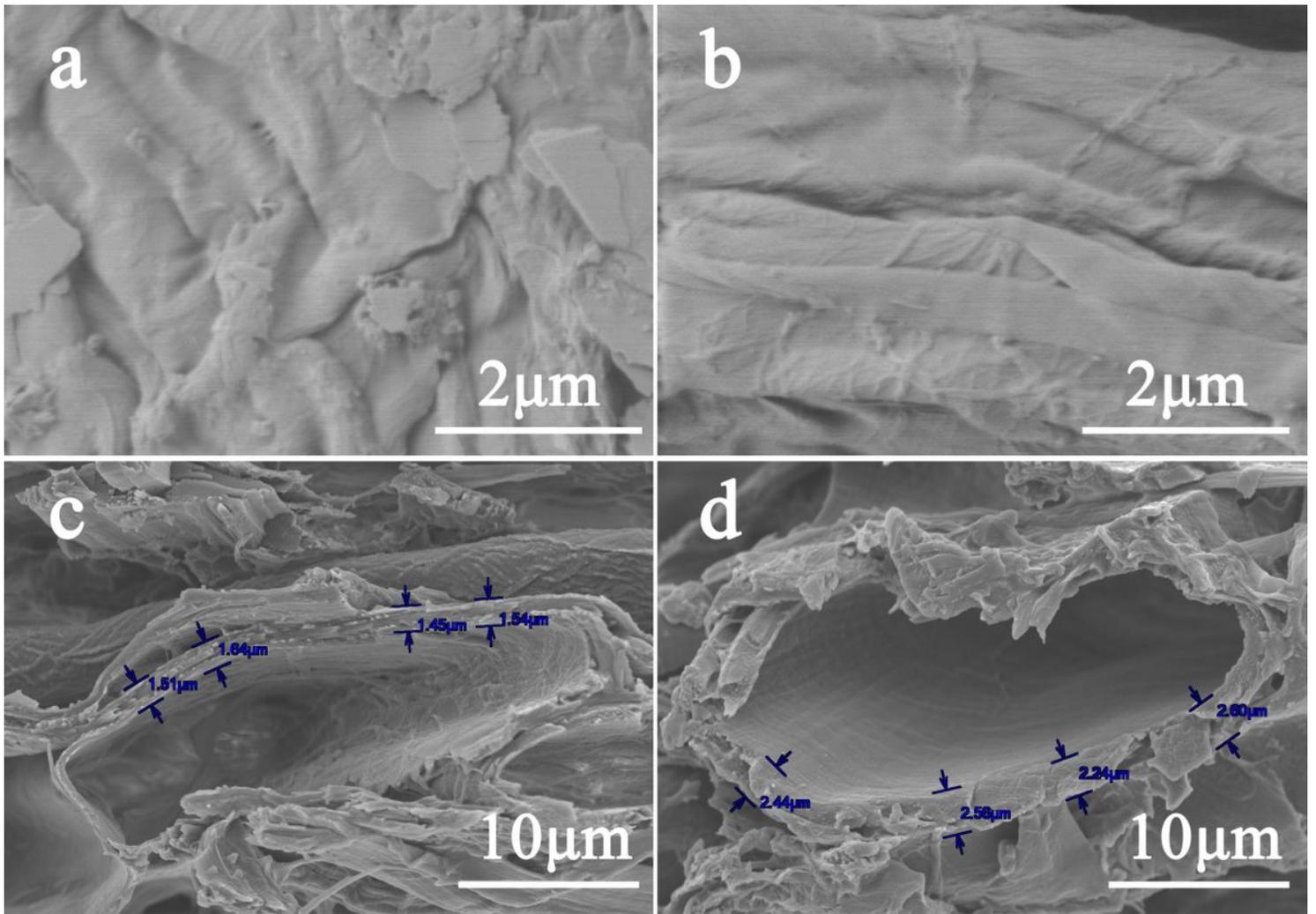


Figure 8

Sample 4 contrast effect after artificial accelerated aging. The upper part is untreated, while the lower part is EO-Ar deacidification and reinforcement sample. Color offset printing cover (a), The inside page of offset printing (b)



**Figure 9**

SEM images of Sample 4 after aging. The fiber surface Untreated  $\times 20k$  (a). The fiber surface EO-Ar treated  $\times 20k$  (b). The inner wall of the untreated fibroblast cavity  $\times 3.5k$  (c). The inner wall of the EO-Ar treated fibroblast cavity  $\times 3.5k$  (d).

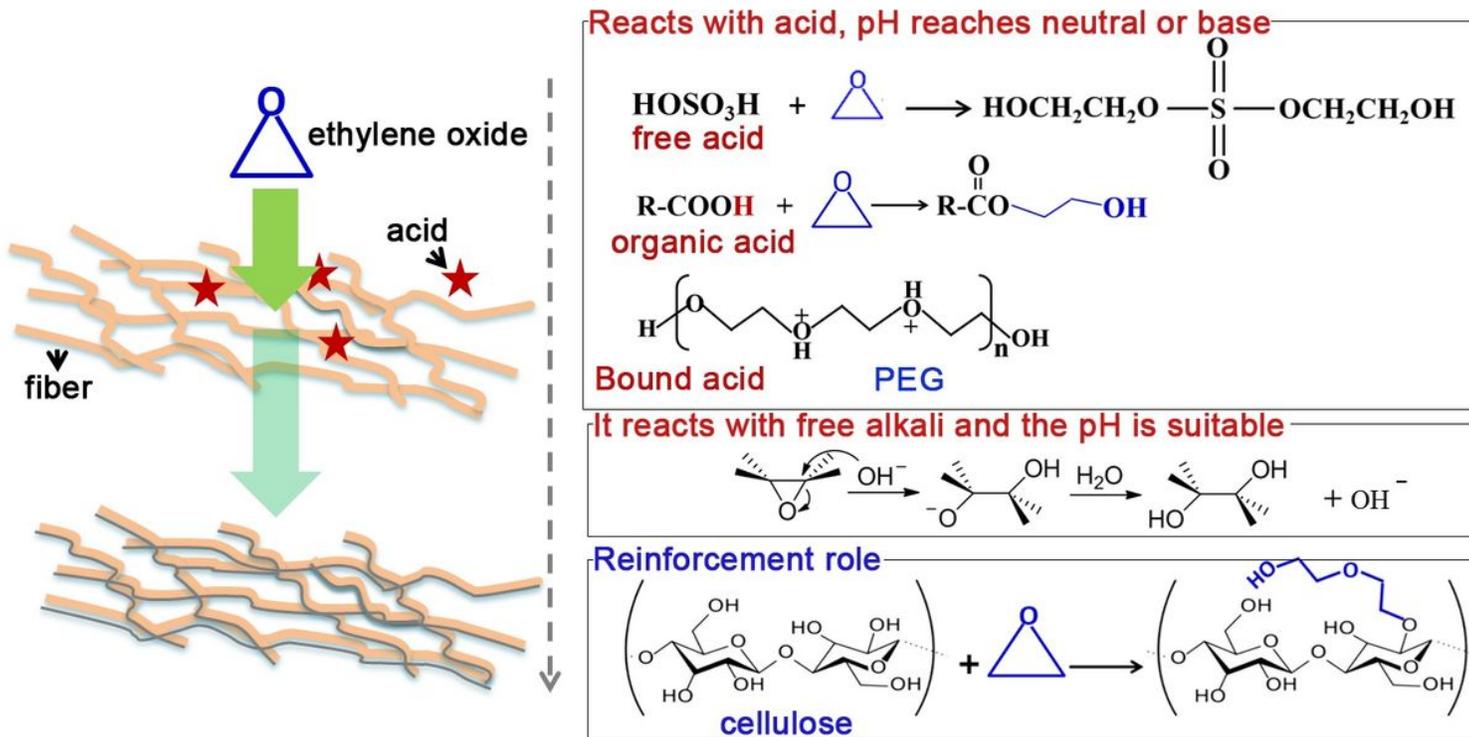


Figure 10

Protective effect of EO-Ar treatment on paper fibers

## Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [GraphicalAbstract.png](#)