[Technical Paper]

Influence of Eco-Friendly Surface Pretreatment of Cotton Fabric on $\text{Mg}(\text{OH})_2$ Immobilization for Flame Retardancy

Yan Hao^{*1}, Xiao Wang^{*1,#}, Jing Li^{*2}, Bing Du^{*1}, and Chunyan Wei^{*1}

^{*1} School of Textile and Material Engineering, Dalian Polytechnic University, Dalian 116034, China

^{*2} Argus (Shanghai) Enterprise Group, Shanghai 201800, China

Abstract: $\text{Mg}(\text{OH})_2$ particles are immobilized onto the surface of cotton fiber by simple physical heat pressing method with the aid of swelling in ionic liquid and shrinkage in water. The effect of eco-friendly surface pretreatment of cellulase, UV and plasma on $\text{Mg}(\text{OH})_2$ immobilization for thermal stability and flammability of cotton fabric is discussed. Improved swelling effect of cellulose after surface treatment is beneficial to contact of $\text{Mg}(\text{OH})_2$ particles with cotton fiber. Due to good adhesion of $\text{Mg}(\text{OH})_2$ particles to fiber surface after partial dissolution and resolidification of fragmented fibril, the flame retardancy of cotton fabric is significantly enhanced under plasma pretreatment with the afterflame time of 1.0 s and afterglow time of 2.0 s. It is found that cellulase treatment is a mild treating method while plasma pretreatment improves flame retardancy at a cost of damaging fiber in a reasonable range.

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1. Introduction

Cotton fiber products are widely used in clothing, home decoration and other fields by virtue of their excellent moisture absorption, air permeability and natural skin-friendly characteristics. But cotton fabric (CF) is easily ignited, which can cause fires [1–2]. Thus, flame retardant finishing of cotton textiles has great practical significance for protecting the safety of human life and avoiding the harm caused by fire [3]. Due to non-toxicity and environmentally friendliness, there is growing interest in the use of $\text{Mg}(\text{OH})_2$ (MH) powder as a flame retardant agent to impart cotton fiber for flame retardancy [4]. MH is relatively stable when it is less than 340 °C. When the temperature exceeds 340 °C, it begins to decompose. When the temperature exceeds 490 °C, it is completely decomposed into MgO and H_2O . When MH is burning, it absorbs the heat of CF, reduces the surface temperature and reduces the burning rate. At the same time, after MH burns, a protective film of MgO is formed on the surface of CF to block the contact of the fabric with heat and oxygen, thereby achieving a flame retardant effect. Mao et al. [5] treated the mercerized cotton fabric with citric acid to impart

carboxyl groups to fiber surface. MH seeds were first adsorbed on the citric acid-treated CF and then MH thin films grew on the fabric through secondary growth method, thereby enhancing the flame retardancy and thermal insulation properties of CF. Wang et al. [6] used MH hybrid pigment bearing vinyl groups after surface silane modification, which is grafted onto the surface of bromo end-functional cellulose fiber by ATRP. The cellulose fiber grafted with modified MH hybrid and afterglow time. However, MH inorganic particles are usually introduced onto cellulose fiber to obtain flame retardancy involving a chemical reaction. Zheng et al. used IL as solvent and MH nanoparticle aqueous solution as coagulation bath via electrospinning [7]. However, due to the presence of MH, physical voids inside the fibers impaired the fiber strength. Generally, inorganic particle is rarely reported to be immobilized onto the surface of cellulose fiber by simple physical heat pressing method with the aid of swelling in ionic liquid (IL) and shrinkage in water for improvement of thermal stability.

Cotton fiber has a unique multi-stage high crystalline fibril structure. The Cotton fiber structure includes the cuticle, primary wall, secondary all and

corresponding author: Xiao Wang (E-mail: wangxiao@dlpu.edu.cn)

lumen. The reticular fibril layer on the upper surface of cotton fiber is difficult to be swelled and for MH to be adhered and entrapped. It has been found that surface reticular fibril can be damaged to a certain extent by surface pretreatment [8–10], which can be beneficial to cellulose swelling in IL. Lam et al. [11] applied atmospheric plasma pretreatment to achieve effective and lasting flame retardant performance of CF. It is found that the surface morphology of the treated CF showed high deposition of flame retardant finishing agent of organophosphorous compounds. Li et al. [12] investigated the effect of UV radiation on the structure and properties of cellulose macromolecules. UV radiation can break the C-C and C-O bond in the supramolecular chain of cellulose and cause some damage to the fiber. Plasma treatment and UV treatment are physical treatments, which have the advantages of fast reaction rate, water saving and energy saving. Moreover, these two treatment methods do not involve the use of hazardous chemicals, and there is no problem of waste gas and wastewater treatment. Lee et al. [13] discovered that cellobiohydrolase CBH I is able to penetrate through the cellulose surface and pry apart the microfibrils, while endoglucanase EG II removed loose outer portions to increase fiber accessibility. There are no toxic substances in the production process due to the non-toxic nature of cellulase.

In this work, MH particles are immobilized onto the surface of cotton fiber by simple physical heat pressing method with the aid of swelling in IL and shrinkage in water. The objective of this work is to investigate the effect of surface pretreatment of cellulase, UV and plasma on MH immobilization for thermal stability and flammability of CF. After many experiments, it has been shown that simple mixing causes MH to agglomerate more easily than in-situ synthesis of MH/IL suspension. The in-situ synthetic dispersion is more uniform and has a better flame retardant effect. Therefore, the method of in-situ synthesis of MH/IL suspension for flame retardant finishing is selected in this article. The flame retardant prepared by in situ synthesis of IL with MH is sprayed on the cotton fiber, and MH particles are fixed onto swelled fiber under heating and pressure. The morphology and structure of surface treated cotton fabric(T-CF), T-CF after swelling by IL and T-CF immobilized with MH (T-CF/MH) are analyzed.

2. Experimental

2.1 Materials

CF was commercially available plain-weave CF, which was extracted to a constant weight with ether. MH was obtained from Beijing Dekedao Gold Technology Co., Ltd. Allyl chloride and cellulase were supplied by Sigma Aldrich Co., Ltd. 1-Methylimidazole was purchased from Beijing Bailingwei Technology Co., Ltd.

2.2 Preparation of T-CF

CF was dipped in an cellulase solution with a mass fraction of 2% at 45 °C, pH value of 5 and bath ratio of 1:20 in a oscillation tank (DKZ-450 A, Shanghai Senxin Experimental Instrument Co., Ltd.) to prepare T-CF via cellulase treatment. T-CF via cellulase treatment with washing. The T-CF via cellulase treatment was dipped in 45 °C water with a bath ratio of 1:20 and shaken for 10 min in a oscillation tank. Then it was placed in a precision blast drying oven (BAO-80 A, Shidukai Instrument Equipment Co., Ltd.) at 105 °C and dried to a constant weight. CF was placed in UV radiation device (GZJ 100 F-XF-2, Shanghai Dart Special Light Source Co., Ltd.) and plasma radiation device (CTP-2000 K, Nanjing Suman Plasma Technology Co., Ltd.) to obtain T-CF via UV treatment and T-CF via plasma treatment.

2.3 Preparation of MH/IL suspension

Sieved MH powder was slowly added to 1-methylimidazole. The suspension was stirred at room temperature for 30 min and then ultrasonically dispersed(FS-600, Probe type ultrasonic disperser, Shanghai Senxin Experimental Instrument Co., Ltd.) for 9 min. Allyl chloride was added at a ratio of 1.2:1 to 1-methylimidazole and the mixture was magnetically stirred for about 7 h at 60 °C under N₂ atmosphere [14]. The above suspension was purified to obtain a product of in-situ MH/IL suspension via in-situ synthesis of IL with MH.

2.4 Preparation of T-CF/MH

The preliminary experiments were performed to obtain the following preparation conditions for MH immobilization. The ends of CF was attached to a needle holder and placed on a conveyor running at a speed of 0.5 m/s. Using a spray gun, the MH/IL suspension was evenly sprayed onto the front and back of the fabric under the conditions of spraying temperature of 39 °C and spraying times of 3. Vacuum drying was carried out for 2h at room temperature using a electric vacuum (VD-216, Done-E Industry Co.,

Ltd.). Finally, the fabric was pressed on an ironing machine for MH immobilization under swelling of cellulose fibrils on the fiber surface (HF 3805, Jinan Huafei Information Technology Co., Ltd.). The effect of heat pressing parameters of temperature and time on MH immobilization ratio and flame retardancy was discussed. MH particles were adhered to fiber surface after washing. The immobilization ratio of MH onto CF after washing was calculated by the following formula:

$$\text{MH immobilization ratio} = \frac{m - m_0}{m_0} \times 100\%$$

m_0 and m represent the mass of CF before and after MH immobilization.

2.5 Characterization and measurement

The surface morphology of the prepared samples was analyzed by scanning electron microscope (JSM-6460 LV, JEOL). Thermogravimetric analysis (TGA) of the samples under N_2 atmosphere was examined on a STA PT 1600 apparatus (Germany Lineis) from 20 to 500 °C at a heating rate of 10 °C/min. The burning behavior of the fabric in the vertical direction was tested using a vertical burner (YG815, Shandong Anqiu Jingwei Textile Instrument Co., Ltd.). The average particle size and surface potential of MH/IL suspension was tested using a Zeta potential, particle size analyzer (Delsa Nano C, Beckman Coulter, Inc.). The tensile strength was tested on the electronic fabric strength meter (YG065HC, Laizhou Electron Instrument Co., Ltd.) according to FZ/T 80007. The

fabric style instrument (YG821L, Laizhou Electron Instrument Co., Ltd.) was used for the friction performance test.

3. Results and discussion

3.1 Effect of particle size and heat pressing parameters on flame retardancy of CF/MH

The surface potential and particle size of the MH/IL suspension are shown in Table 1. The surface potential of MH in the suspension is positive potential (422.73 mV), so that MH nanoparticles are not easily agglomerated due to the electrostatic repulsion of IL. In addition, the surface of the CF has a negative potential. The electrostatic attraction between the MH in the suspension and the CF helps more MH to be immobilized on the CF. The effect of heating temperature and time on the ratio of MH fixation MH immobilization ratio and flame effect retardancy of CF/MH are discussed, as listed in Table 2. The increment of heating temperature and time leads to higher immobilization ratio of MH and the resultant lower afterflame time and afterglow time of CF. It can be explained that heat helps to increase the swelling effect of cellulose fibril by IL on the surface of the cotton fiber, thereby facilitating more MH fixation. Swelling effect of IL on cotton fibers at different temperatures is shown in Fig. 1. As can be seen from Fig. 1(a), there is no significant change in cotton fiber when heated at 70 °C for 90 min. Under heating at 80 °C for 1 min in IL, cotton fibers become thicker and

Table 1 The data of particle size and surface potential of MH/IL suspension

sample	surface potential/mV	particle size ($\geq 90\%$)/nm
MH/IL suspension	422.73	98.1

Fig. 1 Swelling of cotton fibers at different temperatures by IL with time varying

Table 2 The data of flame retardancy of CF/MH under different heat pressing conditions

Samples ¹	MH immobilization ratio/wt/%	Afterflame time/s	Afterglow time/s
CF	0	4.2	40.8
Heart pressing time of 60s ²	70℃	5.1	7.6
	80℃	3.2	4.0
	90℃	2.0	3.0
	95℃	2.5	4.6
	100℃	2.5	4.4
Heat pressing temperature of 90℃	30 s	1.4	13.0
	60 s	2.0	3.0
	180 s	2.8	4.0
	300 s	3.0	3.8

¹ Pretreatment conditions :spraying temperature of 39℃ and spraying times of 3

² Heat pressing time of 60 s: heat pressing time was 60 s at different temperatures

³ Heat pressing temperature of 90 °C: heat pressing temperature was 90 °C at different time

Table 3 The data of flame retardancy of T-CF/MH under different pretreatment

Samples	Treating time/min	MH immobilization ratio/wt/%	Afterflame time/s	Afterglow time/s
CF	0	0	4.2	40.8
CF/MH	0	7.36	2.0	3.0
T-CF/MH via cellulase treatment	30	8.34	1.7	2.9
T-CF/MH via UV treatment	15	6.80	1.7	4.0
T-CF/MH via plasma treatment	30	8.06	1.0	2.0

¹ Surface treatment on flame retardancy of T-CF/MH :Heat pressing temperature of 90 °C and time of 60 s

the number of natural convolutions decreased, indicating a significant swelling effect on cotton fibers. Since swelling of cellulose can occur above 80 °C, heating time of 60 s and heating temperature of 80 °C are required for MH to be immobilized on the fiber surface to obtain the afterflame time and afterglow time of CF shorter than 5 s at a MH immobilization ratio of 6.28/wt%, respectively, meeting the GB 17591-1998 flame retardant materials standard. Under the heat pressing condition of 90 °C, the swelling effect of IL on CF is limited. Prolonged heating time slightly influences MH fixation. A further increase in heating temperature results in higher immobilization ratio of MH. Nevertheless, the afterflame time and afterglow time is not reduced accordingly, which indicates that MH distribution on fiber surface is an important factor for flame retardancy of CF. The lowest afterflame time and afterglow time was obtained under heat pressing at 90 °C for 60s.

3.2 Effect of surface treatment on flame retardancy of T-CF/MH

The flame retardancy of T-CF/MH under cellulase, UV and plasma pretreatment are shown in Table 3. It is found that cellulase and plasma pretreatment have positive effects on improving MH immobilization ratio and flame retardancy other than

UV pretreatment. Despite of similar MH immobilization ratio with that of cellulase treatment, the lowest afterflame time of 1.0 s and afterglow time of 2.0 s of T-CF/MH is obtained under plasma treatment.

3.3 Surface morphology

The SEM image of CF, T-CF, T-CF/MH and swelled T-CF by IL without washing are displayed in Fig. 2. It can be seen from the Fig. 2a that the surface of CF is relatively smooth with only a small amount of impurities. Due to microfibrils pried apart by cellulase [14], fuzzy fiber is noticed on the surface of T-CF via cellulase treatment in Fig. 2d. In contrast with slight damage under UV pretreatment (Fig. 2g), heavy etching of cotton fiber is found under plasma treatment in Fig. 2j. The plasma active species destroy cellulosic molecular chains, resulting in fibril fragmentation [15–18]. More wrinkles and thicker fibers are seen in the SEM images of CF and T-CF swelled by IL without washing (Fig. 2(b, e, h, k)), which is caused by fibril swelling. Reticular topology distinctly appears in a swelling state of cotton fiber in Fig. 2b, proving the existence of reticular fibril on fiber surface. The extent of adhesion of MH particles to cotton fiber is improved after surface pretreatment (Fig. 2(c, f, i, l)). It can be seen in Fig. 2k that the mesh

Fig. 2 SEM images of CF, T-CF, swelled CF and T-CF without washing and T-CF/MH: (a) CF, (b) swelled CF without washing, (c) CF/MH, (d) T-CF via cellulase treatment, (e) swelled T-CF via cellulase treatment without washing, (f) T-CF/MH via cellulase treatment, (g) T-CF via UV treatment, (h) swelled T-CF via UV treatment without washing, (i) T-CF/MH via UV treatment, (j) T-CF via plasma treatment, (k) swelled T-CF via plasma treatment without washing, (l) T-CF/MH via plasma treatment

structure disappears, which is due to the plasma treatment destroying the mesh structure on the surface of the cotton fiber, thereby increasing the chance of contact between the cotton fiber and MH. Partial dissolution and resolidification of fragmented reticular fibril [19, 20] together with swelling occurs (Fig. 2k), which leads to intimate contact of MH particles with cotton fiber via plasma treatment (Fig. 2 l), in comparing with cellulase and UV methods (Fig. 2 (f, i)).

3.4 Thermal stability and flammability

Fig. 3 displays TGA and DTG curves of MH, CF, CF/MH and T-CF/MH under N_2 atmosphere. The maximum thermal decomposition temperature and weight loss of MH, CF, CF/MH, T-CF/MH are listed in Table 4. The maximum decomposition temperature of T-CF is increased by the introduction of MH except plasma treatment. Therefore, IL and MH will not produce side reactions. There is a certain degree of

weight loss around 100 °C for CF/MH and T-CF/MH. It is caused by dehydration of CF at 100 °C. The char residue of T-CF/MH at 500 °C are 12.3%, 16.4% and 18.1% under cellulase, UV and plasma treatment, respectively, which are 0.8%, 4.9%, 6.6% higher than that of the CF/MH, indicating that MH promotes char formation of CF. The photographs of combustion residue of CF, CF/MH and T-CF/MH are showed in Fig. 4. In comparison with CF and CF/MH, more combustion residue is remained for T-CF/MH. The most complete shape of combustion residue is observed for T-CF/MH via plasma pretreatment. The highest ratio and complete shape of combustion residue are attributed to intimate contact between MH and cellulose fibril on fiber surface shown in SEM images.

3.5 Physical and mechanical performance

Table 5. shows the test results of activity ratio and tensile properties of CF, CF/MH and T-CF/MH.

Fig. 3 TGA(a) and DTG(b) curves of MH, CF, CF/MH and T-CF/MH

Table 4 The thermal decomposition temperature and weight loss of MH, CF, CF/MH and T-CF/MH

Sample	Tm/°C	Weight loss/%
MH	411.3	35.4
CF	359.5	91.4
CF/MH	367.2	88.5
T-CF/MH via cellulase treatment	361.3	87.7
T-CF/MH via UV treatment	366.0	83.6
T-CF/MH via plasma treatment	358.7	81.9

Fig. 4 Char photograph of CF, CF/MH and T-CF/MH after vertical burning test (from left to right: CF, CF/MH, T-CF/MH via cellulase treatment, T-CF/MH via UV treatment, T-CF/MH via plasma treatment)

Activity ratio is an indication of fabric drapability. The higher activity ratio, the higher fabric drapability and the looser the fabric. The reason for reduced activity ratio is that surface damage due to pretreatment and the immobilized MH particles increase the surface roughness of the fiber. At the same time, the introduction of MH also reduces the pores between the cotton fibers, making the cotton fabric structure more compact, thereby reducing the slip between the yarns and fabric drapability. Higher breaking strength of CF/MH than CF means reinforcing effect from MH. Nevertheless, after cellulase, UV and plasma treatment, the breaking

strength of T-CF/MH is decreased by 2.8%, 7.9% and 26.4% in contrast with CF, respectively. It clearly indicates that all three surface treatments have caused different degrees of damage to surface fibers, which is consistent with the results of SEM analysis.

4. Conclusion

MH is successfully immobilized onto CF via heat pressing using a in situ synthesized of MH/IL suspension. When the MH loading ratio exceeds 6.28/wt%, the afterflame time and the afterglow time of CF can be kept within 5s, respectively. The

Table 5 Physical and mechanical performance of CF, CF/MH, T-CF/MH

Samples	Activity ratio/%	Breaking strength/N	Breaking elongation ratio/%
CF	71.13	470	7.1
CF/MH	70.75	493	7.7
T-CF/MH via cellulase treatment	66.72	457	5.9
T-CF/MH via UV treatment	67.46	433	6.5
T-CF/MH via plasma treatment	65.73	346	5.2

immobilization of MH onto CF leads to increased maximum decomposition temperature and combustion residue. The extent of damage to fiber is in the descending sequence of plasma, UV and cellulase pretreatment. The flame retardancy of CF is significantly enhanced under plasma pretreatment. Intimate contact of MH with fiber surface due to partial dissolution and resolidification of fragmented reticular fibril results in the afterflame time, afterglow time and combustion residue of 1.0 s, 2.0 s and 18.1% at a cost of breaking strength reduced by 26.4% which can be accepted in practical application.

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