CELLULOSE CHEMISTRY AND TECHNOLOGY

OPTIMIZATION OF WRINKLE RESISTANT FINISHING WITH DIMETHYLOLDIHYDROXYETHYLENEUREA (DMDHEU) USING TITANIUM DIOXIDE AS CO-CATALYST

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Cotton cellulose is an essential textile material. A finishing treatment is always done on cotton fabrics to impart functional properties. In this research, wrinkle resistant finishing using DMDHEU in the presence of titanium dioxide as co-catalyst is applied to cotton cellulose. Different curing temperature and curing time combinations have been studied to investigate the performance of wrinkle recovery properties and tear strength. It has been found that the addition of titanium dioxide could improve the wrinkle recovery properties with less reduction in tear strength at a temperature of 150 ºC for 2 minutes, which is lower than the conventional curing temperature.

Keywords: co-catalyst, cotton, DMDHEU, titanium dioxide, wrinkle resistant finishing

INTRODUCTION

Cotton fiber is widely used in apparel, home furnishings and industrial products. The large usage of cotton fiber is due to its numerous advantages: it is a good absorbent, inexpensive and breathable. Applying functional finishing to cotton fabrics is a common practice. Textile finishing refers to the final step carried out after coloration and before the materials are made up into garments. The purposes of finishing are to enhance the materials' end uses and to meet customers' expectations.[1-3] Although cotton cellulose fabrics have numerous advantages, their main problem is easy wrinkling after being washed or immersed into water. Cotton fiber absorbs moisture and moisture facilitates the movements of internal polymer chains in the amorphous areas and intermediate regions with non-crystalline arrangement. Moisture absorption will disrupt the internal hydrogen bonding between the polymer chains. Once the moisture laden cellulose fiber is stressed, the internal polymer chains are rearranged, followed by the reformation of hydrogen bonds inside the chains. The bonds form in their new positions and lock in the new configuration, inhibiting the movement of cellulose chains. Therefore, a newly formed wrinkle or crease remains on the fabric unless any additional processes, such as ironing, are applied.[2]

In order to overcome the problems, crosslinking is carried out in order to link cellulose chains by chemical bonds and thus provide dimensional stabilization, wrinkle resistance and crease retention for cellulose.[2-4]

A commonly used crosslinker in the textile industry nowadays is a formaldehyde-based compound called dimethyloldihydroxyethyleneurea (DMDHEU). It is widely used due to its low cost and superior results.[2-4] Recently, using TiO_2 as a catalyst or co-catalyst in wrinkle-resistant finishing to improve the crease recovery property has been found to be feasible.[5-8] Moreover, the use of TiO_2 can impart additional functionality to the fabrics, by improving their UV protection properties.[9-13] In the present study, the effect of curing temperature and curing time on the wrinkle-resistant finishing using DMDHEU in the presence or absence of TiO_2 will be investigated and the reaction conditions will be optimized in order to minimize side effects. The wrinkle recovery properties and mechanical properties will be evaluated after the finishing treatment.

EXPERIMENTAL

Materials

Semi-bleached plain-weave 100% cotton fabric (67 ends/cm, yarn count 34 tex, in warp; 55 picks/cm, yarn count 40 tex, in weft; fabric weight 169 g/m^2) specimens of size 30 x 30 cm^2 were used. Modified DMDHEU containing an integrated catalyst magnesium chloride was supplied by DyStar Limited and used as crosslinking agent. Titanium dioxide (TiO_2 with an effective diameter of about 0.4 µm) with purity of ≥99.8% was supplied by Accuchem. Tween 80, a dispersing agent, was supplied by Shanghai Lingfeng Chemical Reagent Co. Ltd. All other chemicals used in the study were reagent grade.

Methods

The compositions of the finishing agents are listed in Table 1. In the study, the one-bath pad-dry-cure method was used in the finishing treatment. The fabrics were impregnated and padded with the prepared wrinkle-resistant finishing agents until a wet pick up of 75-80% was reached at room temperature. Then, the samples were dried in an oven at 85 °C for 5 minutes, followed by curing at four different curing temperatures, which were 110 °C, 130 °C, 150 °C and 170 °C, for 1, 2 or 3 minutes (170 °C and 3 minutes are the conventional curing temperature and time, respectively). Finally, the specimens were conditioned at 21±1 °C and 65±5% for 24 hours before performing any tests.

Table 1
Composition of DMDHEU finishing agent with different concentrations of TiO_2 used

Treatment	DMDHEU	Acetic acid	Tween 80	TiO_2
Conventional	5%	0.1%	10%	0
With TiO_2	5%	0.1%	10%	0.1%

Wrinkle recovery test

The wrinkle recovery angle (WRA) test was performed according to AATCC Test Method 66-2008. The test method is used to determine the wrinkle recovery performance of fabrics. The WRA presented is the average of all the values obtained in both warp and weft directions.

Elmendorf test

The tearing properties of the fabrics were assessed by the Elmendorf test, following BS EN ISO 13937 – Part 1 (2000). An Elmatear Digital Tear Tester, manufactured by James H. Heal & Co. Ltd., Halifax England, and a standard weight of 1600 g were used to this end. The average value of tearing force was calculated from all warp and weft measurements.

Scanning electron microscopy (SEM)

SEM was used to investigate the surface morphology of the cotton specimens before and after the treatment. The specimens were observed by a JEOL JSM-6490 Scanning Electron Microscope, with 20 kV accelerating voltage and 10 µA current, under a magnification of 2000.

RESULTS AND DISCUSSION

Wrinkle recovery test

After the wrinkle recovery test, the wrinkle recovery angle (WRA) values obtained for both warp and weft directions were summed up and the average was calculated. Figures 1 and 2 show the WRAs of the specimens treated in the absence and in presence of TiO_2 finishing solutions, respectively, at different curing temperatures and curing times. The solid line stands for the control specimen, for which a 78^o WRA was recorded. It is obvious that the WRAs increase with the curing temperature from 130 °C to 170 °C (Figs. 1 and 2). At the highest studied temperature – 170 °C – the best WRAs were recorded. Thus, the wrinkle recovery performance is related to the curing temperature. At the reaction temperature, DMDHEU reacts with the hydroxyl groups of cellulose chains, crosslinking the cellulose chains together by chemical bonds through etherification. The crosslinking restricts the movement of the cellulose chains when stress is applied, thus preventing wrinkle formation and leading to a better WRA.[2]

However, there is only a slight change between 110 °C and 130 °C. At a low curing temperature, crosslink formation is not satisfactory, resulting in low WRAs. The WRAs of the specimens obtained after curing at 110 °C and 130 °C are lower than that of the control sample. A possible reason is that the heat energy is not enough to activate the reaction for crosslink formation. Meanwhile, the chemicals used and the slightly acidic conditions damage the fiber, resulting in low WRAs.

Moreover, the WRAs are affected by the curing time. It is observed that when the curing time is prolonged, a higher WRA of the fabric can be obtained. The test specimens subjected to 3-min curing time have the largest WRAs, because there is much more time for the crosslink formation compared with that for the samples cured for 1 min. Therefore, the specimens that are cured at a conventional temperature of 170 ºC and the longest curing time of 3 minutes present a significant increase in WRAs, compared with the control specimens (Figs. 1 and 2).

As noted in Figure 2, the fabrics treated in the presence of TiO_2 have slightly higher WRAs than those treated in the absence of TiO_2. This shows that TiO_2 can improve the wrinkle recovery performance. Metal oxides can restrict the interfibillar movement within the yarn structure, so that the wrinkle recovery property is improved.[6] Another possible reason is that titanium dioxide acts as a Lewis acid catalyst to boost and enhance the reaction efficiency. The specimen cured at 150 ºC for 2 minutes shows a 5.6% improvement in WRA. Hence, the fabrics treated in the presence of TiO_2 and cured at 150 ºC for 2 minutes are found to be an alternative for the wrinkle-resistant treatment. As noted above, higher temperature and longer curing time resulted in a better wrinkle recovery property. This property could be further improved by the addition of 0.1% TiO_2. Moreover, the curing temperature can be lower when the fabrics are treated in the presence of 0.1% TiO_2.

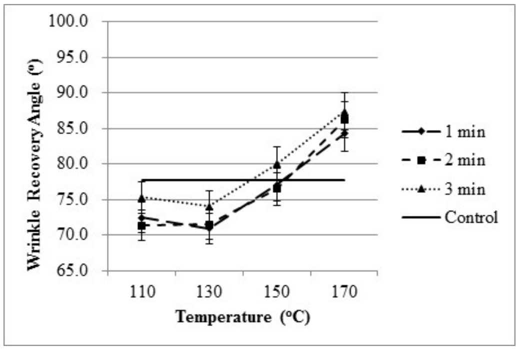

Figure 1: Wrinkle recovery angle of fabrics treated in the absence of TiO_2 at different curing temperature and time

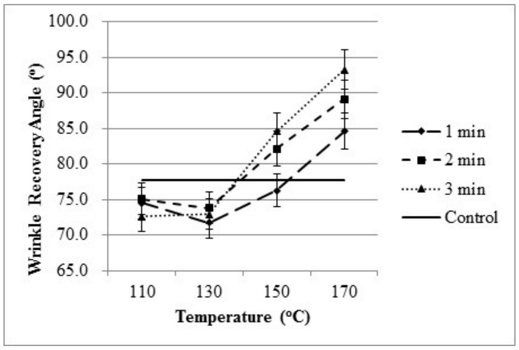

Figure 2: Wrinkle recovery angle of fabrics treated in the presence of 0.1% TiO_2 at different curing temperature and time

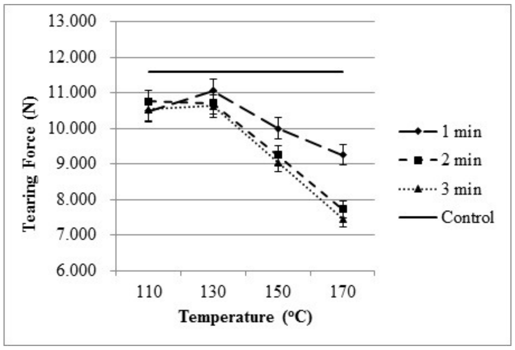

Figure 3: Tearing force applied to fabrics treated in the absence of TiO_2 at different curing temperature and time

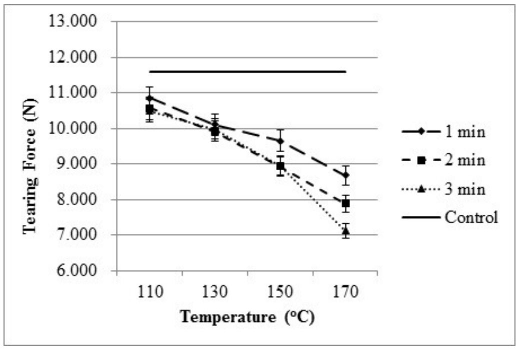

Figure 4: Tearing force applied to fabrics treated in the presence of 0.1% TiO_2 at different curing temperature and time

Elmendorf test

Figures 3 and 4 show the tearing force (in Newton, N) of the specimens treated in the absence and in the presence of TiO_2 finishing solutions, respectively, with different curing temperatures and curing times. In both figures, the solid line represents the control specimen (which did not undergo any pre-treatment). Among all tested specimens, the control fabric has the highest tear strength – of 11.6 N. A great drop in tear strength is remarked after the application of the DMDHEU wrinkle-resistant finishing (Figs. 3 and 4). The drop in tear strength is the result of crosslink formation. The crosslinks restrict the movement of cellulose chains and lock the molecules. The external tear stress can no longer be slightly shared by many neighbor molecules in crosslinked cellulose chains. Therefore, a decrease in tear strength results.[2,3] Another reason for this decrease could be the slightly acidic wrinkle-resistant treatment conditions. Cotton fibers are tendered and slightly damaged by acids.

Moreover, there is a decreasing trend of the tearing force for increasing curing temperature from 110 ºC to 170 ºC. The loss of tear strength at a curing temperature of 170 ºC for 2-3 minutes is significant, exceeding 30%. The loss of tear strength becomes moderate at a lower temperature. In addition, when the curing time is increased, lower tear strength is obtained, as indicated by the dash lines representing different curing times (Figs. 3 and 4). In this case, longer curing time results in higher loss of tear strength. The number of crosslinks formed is expected to be greater at higher curing temperature and longer curing time. Thus, under such conditions, the loss of tear strength was significant. However, the difference between the fabrics treated in the presence and the absence of TiO_2 was not significant.

Combination of tearing test and wrinkle recovery test

Figures 5 and 6 plot the results of the tearing force test and wrinkle recovery test of the specimens treated in the absence and in presence of TiO_2 finishing solutions, respectively. The left y axis indicates the wrinkle recovery angle and the right y axis shows the tearing force in Newton.

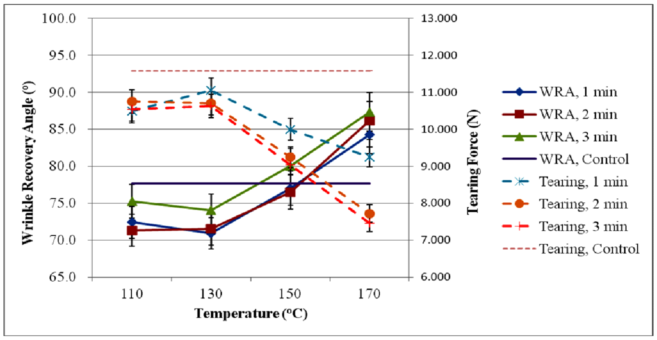

Figure 5: WRA and tearing force of fabrics cured at 150 ºC for 3 minutes in the absence of TiO_2

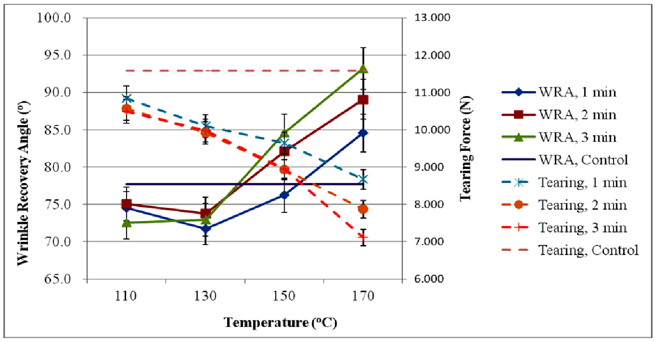

Figure 6: WRA and tearing force of fabrics cured at 150 ºC for 3 minutes in the presence of 0.1% TiO_2

The dash lines are the results of tear strength, whereas the solid lines are the results of WRAs. The horizontal dash line and solid line represent the tear strength and the WRA of the control sample, respectively. The decrease in tear strength after the heat curing process was unavoidable. The cross point of the solid lines and dash lines lay around 150 ºC. This is the balance point between the WRA and tearing force, and represents the optimum conditions for the wrinkle resistant finishing treatment. Under optimum conditions, there is an improvement in WRA with minimum loss of tear strength. Hence, the optimum conditions concerning the WRA and tear strength have been determined. As shown in Figure 5, the fabrics treated in the absence of TiO_2, and curing conditions set to 150 ºC and 3 minutes, gave acceptable results: 3% WRA improvement and 21.9% loss in tear strength. Meanwhile, the fabrics treated in the presence of TiO_2, and curing conditions set to 150 ºC and 2 minutes, were found to afford even better values: 5.6% WRA improvement and 22.9% loss in tear strength (Fig. 6). Lower curing temperature and time consumption means that less energy is consumed when the fabrics are treated in the absence of TiO_2, *i.e.* conventional treatment.

Scanning electron microscopy (SEM)

Figure 7 shows the SEM image of the control sample at a magnification of 2000X. The characteristic spiral structure is clearly defined and can be easily observed. The surface of the control cotton fiber is flat with a twisted ribbon-like structure caused by spiraling of cellulose fibrils. The control cotton fabrics have a smooth fiber surface.

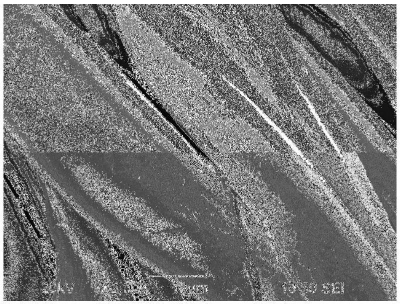

Figure 7: SEM image of control sample at 2000X

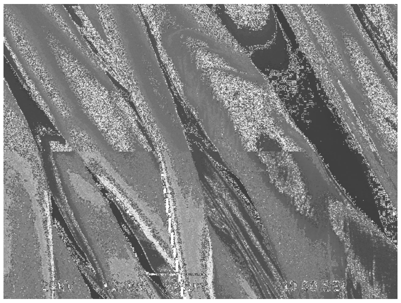

Figure 8: SEM image of DMDHEU treated sample in the absence of TiO_2 at 2000X

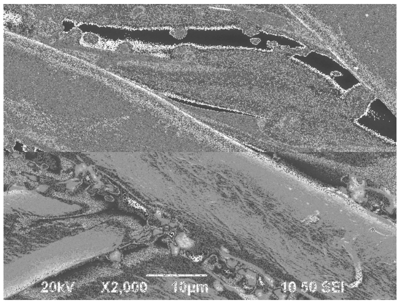

Figure 9: SEM image of DMDHEU treated sample in the presence of 0.1% TiO_2 at 2000X

Figure 8 shows the SEM image of the DMDHEU treated cotton sample in the absence of TiO_2 at the same magnification. After the wrinkle resistant treatment with DMDHEU, the characteristic spiral structure is still clearly defined. The surface of the cotton fiber is not changed by the crosslinking agent. The extent of smoothness is similar to that of the untreated control sample. There is no significant change in fiber appearance.

Figure 9 shows the SEM image of the DMDHEU treated cotton sample in the presence of 0.1% TiO_2. Some particles are found to be attached to the fiber surface. The TiO_2 agglomerates to form a TiO_2 cluster. Clustered TiO_2 particles deposit on the fiber surface irregularly and in different sizes. The particle size of TiO_2 ranges between 1-6 µm.

CONCLUSION

The results of wrinkle recovery angle, tear strength and morphology of cotton fabrics treated with DMDHEU crosslinking agent in the absence or presence of TiO_2 as co-catalyst at different curing temperature and time were examined. It was found that the wrinkle recovery angles increased and the tearing force decreased with increasing curing temperature and time. The tear strength was lost significantly after the finishing treatment. Also, better WRA performance was found after the treatment in the presence of 0.1% TiO_2. Regarding surface morphology, the fibers were not damaged after the DMDHEU treatment and clustered TiO_2 particles deposited on the fiber surface irregularly. Based on the present study, the optimum conditions for the fabrics treated in the presence of TiO_2 would be the curing temperature of 150 ºC and time of 2 minutes. These conditions are lower than conventional curing treatment conditions (170 ºC and 3 minutes). It can be concluded that the addition of TiO_2 can improve the effectiveness of conventional wrinkle recovery treatment.

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