

Effects of Treatments With Alcohols and N-hydroxymethyl Compound on the Mechanical Properties of Wood

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Abstract

Both alcohols (ethylene glycol and 1,2-propylene glycol) were respectively incorporated with 1,3-dimethylol-4,5-dihydroxyethylene urea (DMDHEU) to treat poplar wood and the modifying effects on several mechanical properties of wood were investigated. Compared to the untreated controls, the treated wood obtained an increased weight percent gain (WPG) but reduced moisture content with increasing concentration of the treating solutions. Wood treated with the mixture of DMDHEU and MgCl₂ exhibited a reduction in impact strength and modulus of rupture in bending (MOR) up to 34.2 and 29.2%, respectively; at a comparable DMDHEU concentration, incorporation of the alcohols caused a reduction in impact strength and MOR of 14.4 and 14.9%. The less reduction due to addition of alcohols may be attributed to the extension of DMDHEU molecule chains thereby making the network established between DMDHEU and wood polymers more flexible. Modification of wood with DMDHEU and alcohols led to an increase in modulus of elasticity (MOE) in bending ranging from 6.0 to 32.7% compared to the untreated controls. In addition, the hardness and compression strengthen of wood in longitudinal, radial, and tangential directions were enhanced probably due to an increased density. This study demonstrates that incorporation of low molecular weight alcohols can inhibit the loss in impact strength caused from DMDHEU treatments.

Keywords: Wood chemical modification, N-hydroxymethyl, alcohols, ethylene glycol, mechanical properties.

Introduction

Wood as a nature material has been widely used by mankind for millennia because of its excellent material properties. However, there are some defects that such as dimensional instability, cracking and degradation by UV/sunlight or fungi, thus, both methods of heat treatment and chemical modification to modify wood are employed and developed. Heat-treatment is a type of techniques treating wood at high temperatures (typically 150-230°C) in the shield media such as steaming, nitrogen gas, and vegetable oils (Militz 2002). Chemical modification is that a kind of the methods impregnated reagent into wood, subsequently reacting with the cell wall caused permanent cell wall bulking (Hill 2006). Treatment of wood with DMDHEU, a kind of chemical modification wood, which had been reported about improving dimensional stability, decay resistance, surface coating, and mechanical properties. Xie (2007) showed that the zero and final span tensile strength of thin veneer lossed up to 40%. Bollums (2010) demonstrated that MOR and bending strength had same degree loss, especially the impact strength was significant reduced. Dieste (2008) pointed out DMDHEU treatment had slightly negative influence on the MOR of 5-layer plywood.

Polyethylene glycol (PEG) modification wood improved its dimensional stability, absorption vapor, and surface stability (Jeremic et al. 2007b, Wallström and Lindberg 1995). The low molecular weight of PEG (100 to 1000) easily made it to impregnate into cell wall (Jeremic et al. 2007a, Jeremic et al. 2007b), and to bulk the cell wall (Jeremic and Cooper 2009). However, large molecular weight (range from 1000 to 8000) filled in cell lumen (Jeremic et al. 2009).

Zeronian (2009) reported that tensile strength of DMDHEU treated cotton fiber was reduced. Kang (1998) and Yang (2003) demonstrated that increasing the brittleness of treated cellulose-based materials was increased might due to bulking and cross-linking with the cell walls. Combination ethylene glycol or 1,2-propylene glycol with DMDHEU to treat wood is very seldom. Only one literature reported about this, Simonsen (1998) showed that treated wood with polyglycol and DMDHEU had a lack of dimensional stability. Some mechanical properties of treated wood were increased, such as compression strength, hardness and MOE. However, to some degree, the compact strength and/or MOR were decreased.

The objective of this paper is that used both alcohols and DMDHEU to modify wood, and improved its mechanical properties compared to the traditional method of treatment wood with DMDHEU treated only.

Materials and Methods

Original materials: Poplar wood boards were purchased in China (Yicun, Harbin) measuring 1000mm×60mm×60mm (L×T×R), which cut into blocks according to China National Standard-Testing Methods. All chemicals (DMDHEU, ethylene glycol, 1,2-propylene glycol and MgCl₂) were purchased in China.

Impregnation and preparation of modified wood: The impregnation parameters of solution concentration are showed in Table 1. Prior to treatment all of the prepared samples were dried at 103±2°C for 24h before impregnation, then, with a vacuum of -0.1MPa for 6h and a subsequent at pressure of 0.6MPa for 6h, finally applying a vacuum of -0.05MPa for 30min to remove excrescent solution. After the impregnation processing, the treated samples were displayed at room temperature for 72h, then dried at the conditions of 40°C for 4h, 60°C for 4h and 80°C for 4h, finally at the curing temperature of 120°C for 24h.

Table 1 Solution concentration parameters of the untreated and treated samples used in this study.

Sample NO.	Solution concentration (w, %)	Mole ratio (DMDHEU/Ethylene glycol)	Mole ratio (DMDHEU/1,2-propylene glycol)	Magnesium chloride (w, %)
1	0	—	—	0
2	30	Only DMDHEU	—	0
3	10	Only DMDHEU	—	1.5
4	20	Only DMDHEU	—	1.5
5	30	Only DMDHEU	—	1.5
6	30	1:1	—	1.5
7	30	—	1:1	1.5

Note: — expression does not addition this reagent

Physical properties calculation: Weight percent gain (WPG) of treated samples was calculated using the following equation (1):

$$\text{WPG (\%)} = \frac{W_t - W_c}{W_c} \times 100\% \quad (1)$$

where W_t is the oven-dry weight of treated sample, and W_c is the oven-dry weight of untreated sample.

Leaching ratio evaluate the property of chemicals curing in wood after 3 repeat deionized water leaching test, which was calculated by the following equation (2):

$$\text{Leaching ratio (\%)} = \frac{W_t - W_l}{W_t - W_c} \times 100\% \quad (2)$$

where W_t is the oven-dry weight of treated sample, W_l is the oven-dry mass of after leaching test, and W_c is the oven-dry weight of untreated sample.

Moisture content (MC) is the moisture adsorption of treated sample, MC was calculated as (3):

$$\text{MC (\%)} = \frac{W_{ta} - W_t}{W_t} \times 100\% \quad (3)$$

where W_t is the oven-dry weight of treated sample, W_{ta} is the mass of treated sample at atmosphere ambient.

Mechanical properties test: The dimensions and mechanical properties of the samples size were prepared according to China National Standard-Testing Methods for Wood Physical and Mechanical properties.

Results and Discussion

Weight percent gain, leaching test and moisture content: The results of WPG were increased with solution concentration increasing, whether added alcohols into the DMDHEU solution or not (Fig. 1 a). The WPG of samples NO.5, 6 and 7 were higher than only 30% DMDHEU without catalyst treated sample (NO.2), and the WPG of both alcohols combination with DMDHEU samples (NO.6 and 7) were 67.15% and 68.48%, respectively. Leaching ratio of all the treated samples had slight changing, the ratio range from 6.21% to 9.94%. The moisture contents (MC) of treated sample were a little reduction compared to the untreated sample (Fig. 1 b). The MC of 30% solution concentration treated samples (NO.5, 6 and 7) were less than that of the untreated and low concentration samples (NO.3 and 4).

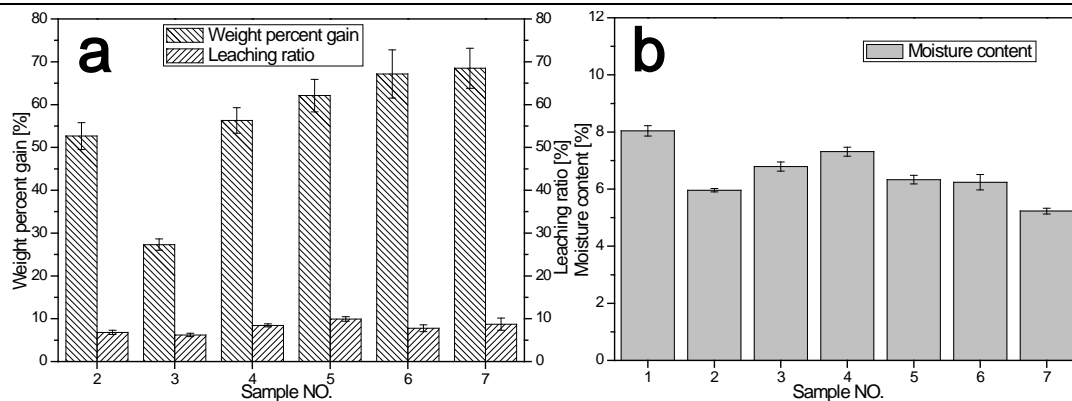


Figure 1 The weight percent gain, leaching ratio (a) and moisture content (b) of untreated (NO.1) and treated (NO.2~7) samples

Impact strength, MOE and MOR: The impact strength of all treated sample were declined (Fig. 2), this might be due to acid hydrolysis and cross-linking with the cellulose (Xie et al. 2007). Treated samples with alcohols and DMDHEU samples reduction 20.24% and 16.93% (Fig. 2 b) compared to the untreated sample, however, the impact strength was enhanced 14% and 17.31% compared to the NO.5 sample, respectively.

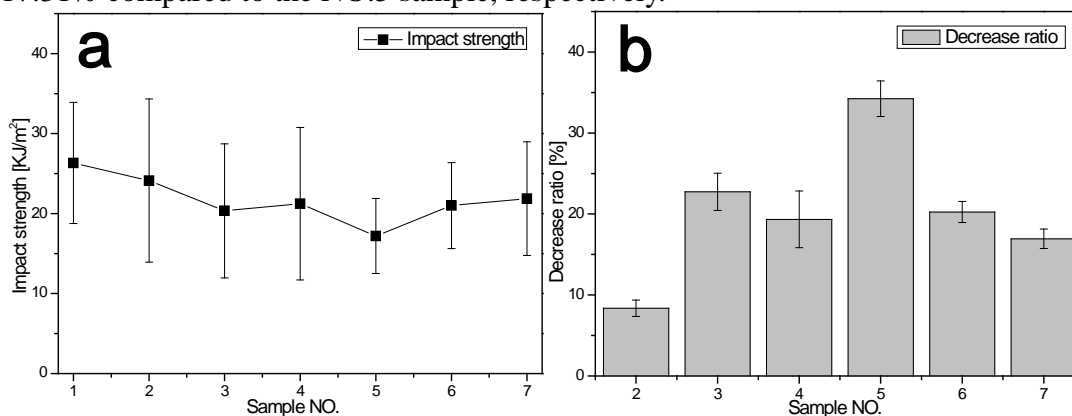


Figure 2 The impact strength of the untreated and treated samples (a), and decrease ration of the impact strength (b).

Several literatures had been reported that the alcohols (PEG, EG or PG) could soften nature cellulose-based materials (El-Sayed Mohamed et al. 2009, Yang and Chen 1999, Zeronian et al. 1989). Kang (1998) investigated the effects of mechanical properties of cotton fabrics on treated with DMDHEU, and the reduction tensile strength attributed to acid-catalyzed depolymerization and cross-linking cellulose molecules. Beside, the pre-curing cellulose treatment also caused a much higher loose than that of tensile strength (Yang et al. 2003).

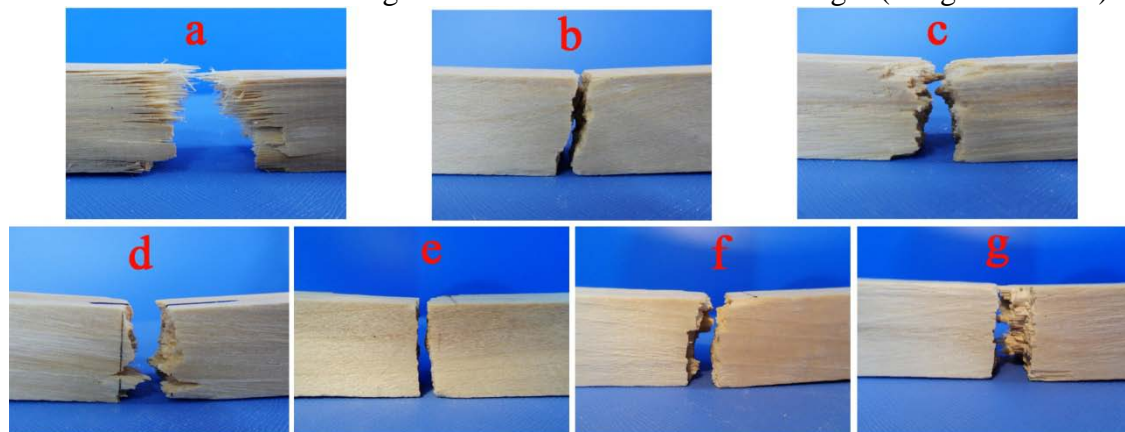


Figure 3 The impact fractures of (a) the untreated sample, and (b, c, d, e, f and g) treated Paper PS-75

samples NO. 2 to 7, respectively.

Treatment of wood veneer with DMDHEU and magnesium chloride caused a reduction of z- and f-span tensile strength due to Lewis acid depolymerization polysaccharide (Xie et al. 2007) which indicated that the treated samples were embrittlement. The Figure 3 illustrated that the fractures of treated samples were linear smoothing, while the untreated one was zigzag, the fractures samples of Figures 3 g and f were great more roughness than the without alcohols sample (Fig. 3 e). Bollums (2010) reported that the tensile and compact strength of Beech wood modified with DMDHEU reduction 38.8% and 79.3% compared to the control sample, respectively.

Both alcohols incorporated with DMDHEU samples loss impact strength, but enhancement the impact strength (Fig. 2) compared to the treated samples of treating with DMDHEU, which might due to be extension of DMDHEU molecule chains thereby making the network established between DMDHEU and wood polymers more flexible. When the treated wood subjected to a load could distribution power to the long molecule.

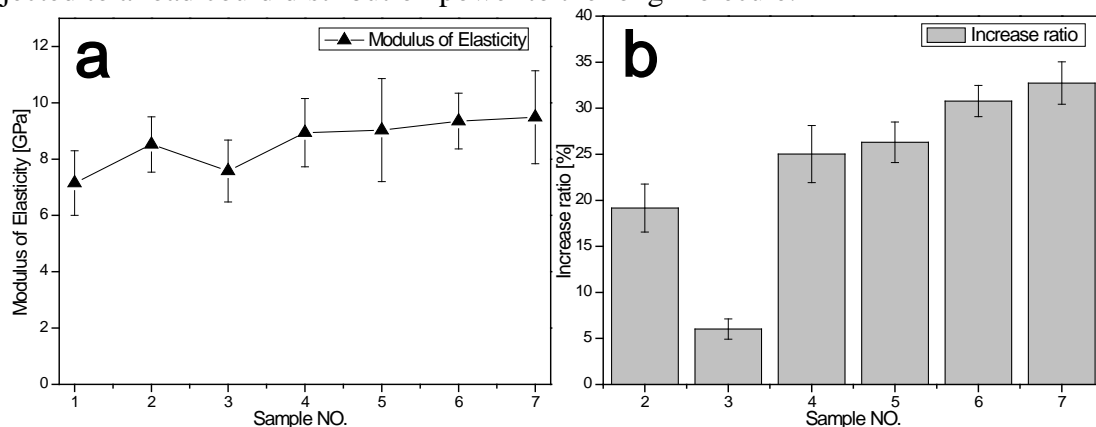


Figure 4 The MOE of the untreated and treated samples (a), and decrease ration of the MOE (b).

Modulus of elasticity (MOE) and modulus of rupture (MOR) datum were presented in Figures 4 and 5, the MOE increased with the concentration of alcohols and/or DMDHEU solution increased (Fig. 4 a). The MOE of treated samples ethylene glycol or 1,2-propylene glycol went up 30.78% and 32.73% (Fig. 4 b), respectively. Moreover, those two samples were higher 5% and 6.42% than the 30% DMDHEU concentration sample (NO.5). We found that the MOR reduced with the concentration of DMDHEU increasing (Fig. 5 a), however, the MOR of the samples treated with alcohols (ethylene glycol and 1,2-propylene glycol) and DMDHEU were enhanced 14.9% and 15.6% compared to sample NO.5 (Fig. 5 b), respectively.

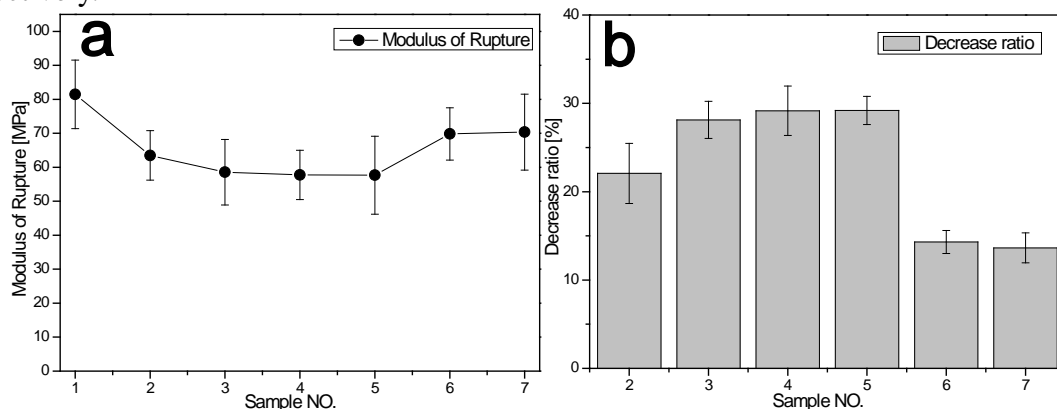


Figure 5 The MOR of the untreated and treated samples (a), and decrease ration of the MOR (b).

Bollums (2010) demonstrated that the bending strength reduced 19.3% for 1.3M DMDHEU concentration, while the MOE rosed 24.3%. Dieste (2008) founded that MOE and bending strength of 5-layer plywood were slightly effected by the treatment with DMDHEU, because the orientation of 5-layer plywood grain was significant. With N-methyl-melamine and aluminium salt as catalyst treated 5-layer beech veneers, the treated plywood sample exhibited increase in MOE and MOR (Trinh et al. 2012). DMDHEU modified wood caused acid-depolymerization cellulose, when every two orthogonal veneers fold up together and then manufacturing 5-layer plywood could enhancement the MOE and MOR, while the MOR was negatived influenced by using solid wood treatment. The MOE was enhanced, but the MOR was reduced, DMDHEU treatment samples decreased the compact strength and increased the brittleness. However, the alcohols addition exhibited some extent improving modified wood mechanical properties of the modified wood compared to without alcohols samples.

Hardness and compression strength: The hardness and compression strength increased with the solution concentration increasing (Fig. 6). Moreover, the value of hardness of longitudinal direction was twice as the other directions (Fig. 6 a), and the compression strength of longitudinal direction was dramatic more than the other directions (Fig. 6 b), which was connected with wood species and grain direction.

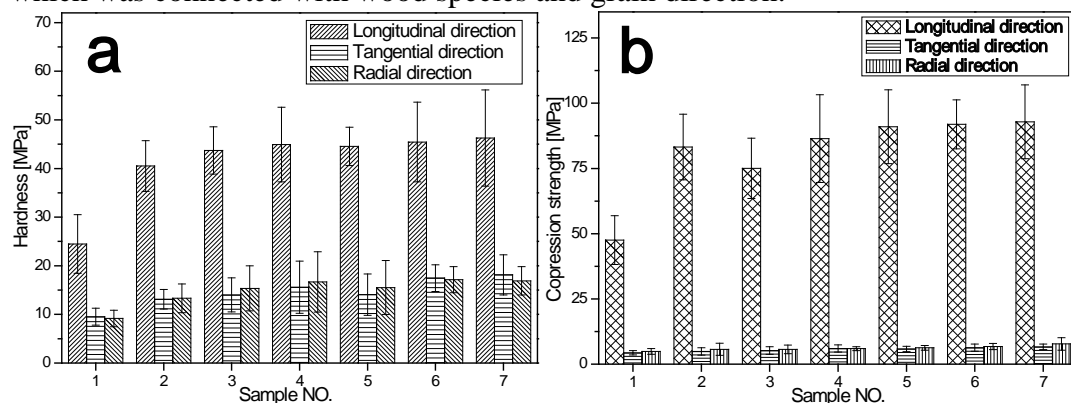


Figure 6 Three directions hardness (a) and compression strength (b) of untreated and treated samples.

The examination of hardness of Poplar wood at longitudinal direction was 24.5MPa (Fig. 6 a). Dieste (2008) reported the Brinell hardness of modified layer wood improving 46~108%, the higher DMHEUE concentration the higher hardness, which was the same to our research. Bollums (2010) demonstrated that hardness and compression strength increasing 82.1% and 65.1% treatment by 2.3M DMDHEU concentration, respectively. Table 2 shows the results of increase ratio hardness and compression strength of modified wood, we observed that the increasing ratio 37.78~90.24% for hardness, and 12.47~93.33% for compression strength. Moreover, the treated samples of addition alcohols were higher than other modified samples (Table 2).

Table 2 The increase ratio of hardness and compression strength of treated samples.

Sample NO.	Increase ratio of hardness (%)			Increase ratio of compression strength (%)		
	Longitudinal	Tangential	Radial	Longitudinal	Tangential	Radial
2	65.62	37.78	45.41	75.05	12.47	16.84
3	78.70	47.01	67.58	57.89	20.09	16.22
4	83.61	63.59	81.99	81.85	38.57	22.18
5	82.05	47.64	69.32	91.44	33.49	28.34
6	85.81	83.32	87.01	93.33	45.50	39.01

Conclusions

The results showed that the mechanical properties of hardness, compression and MOE were increase, but compact strength and MOR of treated wood decreased compared to the untreated wood. Mechanical properties of both two alcohols (ethylene glycol and 1,2-propylene glycol) respectively combination with DMDHEU treated wood were increased compared to the samples of DMDHEU treated only, especially the compact strength and MOR were enhanced, which might due to the addition of alcohols, and attributed to extension of DMDHEU molecule chains thereby making the network established between DMDHEU and wood polymers more flexible.

References

- Bollmus, S., P. Rademacher, Krause, A., and Militz, H. 2010. Material evaluation and product performances of Beech wood modified with 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU). European Conference on Wood Modification 2010.
- Dieste, A., Krause, A., Bollmus, S., and Militz, H. 2008. Physical and mechanical properties of plywood produced with 1.3-dimethylol-4.5-dihydroxyethyleneurea (DMDHEU)-modified veneers of *Betula* sp. and *Fagus sylvatica*. European Journal of Wood and Wood Products. 66:281-287.
- El-Sayed Mohamed, Z., Abo-Shosha, M., and Ibrahim, N. 2009. Preparation of polyethylene glycol/polyacrylamide adduct and utilization in cotton finishing. Carbohydrate Polymers. 75:479-483.
- Hill, C. 2006. Wood modification: chemical, thermal and other processes. Recherche 67:02.
- Jeremic, D., Cooper, P., and Brodersen, P. 2007a. Penetration of poly (ethylene glycol) into wood cell walls of red pine. *Holzforschung*. 61:272-278.
- Jeremic, D., Cooper, P., and Heyd, D. 2007b. PEG bulking of wood cell walls as affected by moisture content and nature of solvent. *Wood Science and Technology*. 41:597-606.
- Jeremic, D., Quijano-Solis, C., and Cooper, P. 2009. Diffusion rate of polyethylene glycol into cell walls of red pine following vacuum impregnation. *Cellulose*. 16:339-348.
- Kang, I.S., Yang, C.Q., Wei, W., and Lickfield, G.C. 1998. Mechanical strength of durable press finished cotton fabrics. *TextileResearch Journal*. 68:865-870.
- Militz, H. 2002. Thermal treatment of wood: European processes and their background. IRG/WP 40241.
- Simonsen, J. 1998. Lack of dimensional stability in cross-linked wood-polymer composites. *Holzforschung*. 52: 102-104.
- Trinh, H.M., Militz, H., and Mai, C. 2012. Modification of beech veneers with N-methylol-melamine compounds for the production of plywood. European Journal of Wood and Wood Products. 70:421-432.
- Xie, Y., Krause, A., Militz, H., Turkulin, H., Richter, K., and Mai, C. 2007. Effect of treatments with 1, 3-dimethylol-4, 5-dihydroxy-ethyleneurea (DMDHEU) on the tensile properties of wood. *Holzforschung* 61:43-50.
- Zeronian, S., Bertoniere, N., Alger, K., Duffin, J., Kim, M., Dubuque, L., Collins, M., and Xie, C. 1989. Effect of Dimethyloldihydroxyethyleneurea on the Properties of Cellulosic Fibers. *Textile Research Journal*. 59:484-492.
- Yang, C.Q., and W. Chen. 1999. Investigation of Flexible Crosslinking Systems for the

Retention of Mechanical Strength and Abrasion Resistance in Durable Press Cotton Fabrics. National Textile Center Annual Report. C 97:1.

Yang, C.Q., W. Zhou, G.C. Lickfield, and K. Parachura. 2003. Cellulase treatment of durable press finished cotton fabric: Effects on fabric strength, abrasion resistance, and handle. Textile Research Journal. 73:1062-1065.