Available online at www.sciencedirect.com
ScienceDirect
Carbohydrate Polymers 73 (2008) 223–230
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Crosslinking of rayon fibers with co-oligomer of maleic acid and methylacrylate and their responses to water

Wenbin Li [a], Xuchen Zhao [a], Siyao Chen [a], Xingping Zhou [b], Dajun Chen [a], Xiaqin Wang [a,*]

[a] College of Materials Science and Engineering, Donghua University, 2999 North Renmin Road, Shanghai 201620, China
[b] Institute of Biosciences and Biotechnology, Donghua University, 2999 North Renmin Road, Shanghai 201620, China

Received 31 March 2007; received in revised form 8 October 2007; accepted 14 November 2007
Available online 22 November 2007

Abstract

A co-oligomer of maleic acid and methylacrylate (COMM) was used to crosslink rayon fibers. It was shown to be a more effective polycarboxylic crosslinking agent than 1,2,3,4-butanetetracarboxylic acid (BTCA) as judged by the enhancement of mechanical properties. Similar to BTCA, COMM formed a five-membered cyclic anhydride intermediate by anhydridisation of a carboxyl group pair, and subsequently the anhydride intermediate reacted with cellulose in the amorphous regions to form an ester linkage. Apparent crosslinking degree (ACD) of the crosslinked rayon fibers was proposed to quantify the crosslinking efficiency of COMM. The water sorption isotherm was not strongly affected by crosslinking whereas water retention after swelling in excess water decreased with the degree of crosslinking.

Keywords: Cellulose; Co-oligomer of maleic acid and methylacrylate; Crosslinking; Structure–property relationship; Responses to water

1. Introduction

Crosslinking of cotton cellulose with polycarboxylic acids has provided an alternative route to formaldehyde-free durable press cotton fabrics. Polycarboxylic acids containing a pair of adjacent carboxyl groups can be used to crosslink cellulose. Examples are 1,2,3,4-butanetetracarboxylic acid (BTCA) (Morris, Morris, & Trask-Morrell, 1996; Yang, 1991; Yang & Bakshi, 1996; Yang, Wei, & Lickfield, 2000), poly(maleic acid) (Chen, Yang, & Qiu, 2005), maleic acid and itaconic acid copolymer (Yang & Lu, 1999), maleic acid (MA) (Yang & Wang, 1996), itaconic acid (ITA) (Yang & Wang, 1996), succinic acid (SUA) (Yang & Wang, 1996), tricarballylic acid (TCA) (Yang & Wang, 1996), citric acid (CA) (Ibrahim, Abo-Shosha, Elnagdy, & Gaffar, 2002; Yang & Wang, 1996), 1,2,3-benzenetricarboxylic acid (Yang & Wang, 1996), 1,2,4-benzenetricarboxylic acid (Yang & Wang, 1996), 1,2,3,4-cyclobutanetetracarboxylic acid (CBTCA) (Yang & Wang, 1996), 1,2,3,4-cyclopentanetetracarboxylic acid (CPTA) (Yang & Wang, 1996), tetrahydrofuran-2,3,4,5-tetracarboxylic acid (HFTA) (Yang & Wang, 1996), 1,2,4,5-benzenetetracarboxylic acid (BZTA) (Yang & Wang, 1996), 1,2,3,4,5,6-cyclohexacarboxylic acid (CHHA) (Yang & Wang, 1996), and mellitic acid (Yang & Wang, 1996). Cellulose esterification by all these polycarboxylic acids proceeds in two steps, formation of a five-membered cyclic anhydride intermediate by anhydridisation of a carboxyl group couple, and esterification of cellulose by the anhydride intermediate to create an ester linkage. The second carboxyl group in the pair is less effective that the first one for esterification for cellulose (Yang & Wang, 1996). Among these polycarboxylic acids, BTCA has attracted most attention because it is generally acknowledged as the most efficient crosslinking agent for cellulose. Crosslinking of cellulose fabrics with these polycarboxylic acids significantly improved resiliency or wrinkle-resistance, but caused severe loss of tensile strength of cellulose fabrics due to the molecular rigidity of the crosslinkers.

* Corresponding author. Tel./fax: +86 21 67792836.
E-mail address: xqwang@dhu.edu.cn (X. Wang).

0144-8617/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2007.11.016

Polysaccharide fibers, such as cellulose and chitosan fibers, are generally low in strength, especially in wet strength, which limits their application. Some efforts have been reported to crosslink chitosan fibers in order to enhance its mechanical properties with glutaraldehyde or glyoxal (Knaul, Hudson, & Creber, 1999; Yang, Dou, Liang, & Shen, 2005). Glutaraldehyde was also used in durable press finishing of cotton fabrics. However, these crosslinking agents are toxic, which is an obstacle to industrial application.

Design of aldehyde-free, more flexible polycarboxylic acids with higher crosslinking efficiency to enhance both resiliency and mechanical properties of polysaccharide fibers and fabrics still remains a challenge (Chen, Lickfield, & Yang, 2004). These polycarboxylic acids should be co-oligomers comprising segments with at least two carboxyl groups and flexible segments to improve the accessibility of the carboxyl groups and distribution homogeneity of the crosslinks. Copolymers of high molecular weights are not desirable as their penetration into the amorphous regions of cellulose is difficult. Moreover, redundant carboxyl group pairs on the copolymers result in overcrosslinking, which has an adverse effect on mechanical properties because of internal stress concentration. Here we describe the use of a co-oligomer of maleic acid as a flexible crosslinking agent for cellulose fibers to form intrafiber crosslinked structures in order to optimize the mechanical properties of cellulose fibers. The molecular structure of the co-oligomer of maleic acid and methylacrylate (COMM) is shown in Chart 1. The crosslinking behavior of COMM was compared with BTCA to illustrate the advantages of COMM. Cellulose fibers in their completely dry state have the consistency of a brittle resin and are completely inflexible. The cohesive forces in the micellar system are so powerful that the whole molecule becomes rigid. Water is an indispensable softener for cellulose, no other substance having this property to such a marked degree. In particular, macroscopic properties, such as mechanical properties and resiliency, rely strongly on molecular-level swellability of cellulose fibers. Therefore, responses of the COMM-crosslinked cellulose fibers to both liquid water and water vapor are also investigated to understand the mechanical properties and resiliency of the crosslinked fibers.

2. Experimental

2.1. Materials

Never-dried cotton-type rayon staple fibers with an average length of 38 mm and linear density of 1.67 dtex were kindly supplied by the Nanjing Chemical Fiber Co., Ltd., China. COMM ($Mn = 500$–1200) was purchased from Changmao Biochemical Engineering Co., Ltd., China. The molar fraction of methylacrylate segments in COMM is 0.759, and that of maleic acid is 0.241. Sodium hypophosphite monohydrate ($NaH_2PO_2{\cdot}H_2O$) with purity of 98.0%, sodium hydroxide (NaOH) with purity of $\geqslant$96.0%, potassium acetate (KAc) with purity of $\geqslant$92.0%, potassium carbonate (K_2CO_3) with purity of $\geqslant$99.0%, and magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$) with purity of $\geqslant$99.0% were purchased from Shanghai Chemical Reagent Co., Ltd. Phosphorus(V) oxide (P_2O_5) with purity of $\geqslant$98.0%, and potassium hydrogen phthalate with purity of $\geqslant$99.8% were obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. Magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$) with purity of $\geqslant$98.0% was from Shanghai Jingxi Chemicals Co., Ltd., and sodium chloride (NaCl) with purity of $\geqslant$99.5% was from Shanghai Wenhao Boichemical Co., Ltd.

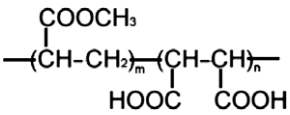


Chart 1. Molecular structure of COMM, $n \geqslant 2$, $m + n < 14$.

2.2. Determination of crystallinity of cellulose fibers

Crystallinity of the cellulose fibers was derived from wide angle X-ray diffraction (WAXD). WAXD was measured at a scanning rate of $0.02°\ S^{-1}$ in 2θ ranging from 5° to 60° on a Rigaku X-ray diffraction D/MAX 2580VB with high intensity Cu Kα radiation ($\lambda = 0.154056$ nm).

2.3. Crosslinking of rayon fibers

Never-dried cotton type rayon fibers corresponding to 5.0 g dry weight were treated with an aqueous solution containing 8.0 wt% of COMM as the crosslinking agent and 5.0 wt% sodium hypophosphite (SHP) as the catalyst for crosslinking via padding through two dips and two nips to reach an average wet pickup of 120%. After drying at 40 °C in a vacuum, the treated fibers were cured at a specified temperature ranging from 150 to 210 °C for 5 min in a curing oven. Finally, the cured fibers were washed with a large amount of distilled water three times to remove excessive COMM and SHP, and then dried completely at 40 °C under vacuum.

2.4. Fourier transform infrared (FTIR) measurement

FTIR absorption spectra were recorded with a Nicolet 670 spectrometer. A total of 10 scans for each sample were taken with a resolution of $2\ cm^{-1}$. The sample for FTIR analysis was prepared as follows. Cellulose fibers were cut into powder with a fiber microtome (Hardy's thin cross-section sampling device). Potassium bromide (KBr) powder was used as a reference to produce a background spectrum. Prior to measurement the cured fibers were treated with 0.1 M NaOH solution for 3 min with vigorous stirring to convert carboxyl groups into carboxylate anions so as to separate absorption band of the ester carbonyl from that of the overlapping carboxyl carbonyl.

2.5. Titration of free carboxyl groups and ester linkages in crosslinked fibers

The concentration of carboxyl groups in 1 g of the dry COMM-treated rayon fibers before curing (C_0) was determined by first grinding them into a powder to improve sample uniformity. The powder sample was dispersed into distilled water and then titrated with a 0.0188 M NaOH solution as a titrant in the presence of phenolphthalein as an indicator. The NaOH solution had been standardized with potassium hydrogen phthalate prior to titration. Concentrations of free carboxyl groups in 1 g of the crosslinked fibers before washing (C_1) and after washing (C_2) were determined in the same way as described above. So the concentration of the generated ester linkages in 1 g of the crosslinked fibers could be determined indirectly, and was equal to the difference between C_0 and C_1. It should be noted that ester linkages in the methylacrylate segments of COMM were not incorporated into the concentration of the titrated ester linkages, which was based on the concentration of carboxyl groups. Concentration of carboxyl groups arising from ageing or oxidation (C_3) was obtained by titration of the virgin cellulose fibers. Consequently, the concentration of free carboxyl groups in the bound COMM could be estimated from the difference between C_2 and C_3.

2.6. Measurement of tensile properties

Dry and wet tensile strength of the uncrosslinked and crosslinked rayon fibers was measured on a universal tensile tester (XQ-1, China Textile University) according to the standard method ASTM D3822-01. The fiber samples were preconditioned for 1 day so that they would reach the standard atmospheric equilibrium of 65% relative humidity (RH) at 20 °C. A gauge length of 20 mm was employed at a constant drawing rate of strain at 100% min, or 20 mm/min. Fifty tests were completed for each result.

2.7. Water retention value (WRV)

WRV was measured by dispersing 0.5 g of the cured fibers in deionized water, soaking for 12 h, and then centrifuging the fibers in a tube at 1000*g* for 20 min with a porous screen at the bottom to separate initially surplus water from the fiber masses. The centrifuged fibers were weighed to get the wet weight W_W. After a thorough drying of the centrifuged fibers in a vacuum at 40 °C, the dry weight W_D was reweighed. WRV was calculated as

$$\mathrm{WRV} = \frac{W_W - W_D}{W_D} \quad (1)$$

2.8. Sorption and desorption cycles

An absolutely dry system with relative humidity (RH) 0% was created by adding P_2O_5 into a desiccator with a diameter of 180 mm. In a similar way, closed systems with RH of 23%, 33%, 43%, 52%, 75%, and 100% at 25 °C were generated by substituting P_2O_5 with saturated salt solutions of KAc, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, NaCl, and deionized water, respectively. After the rayon fibers were deposited into a weighing bottle and then placed in the desiccator with P_2O_5, the moisture sorption cycle was started by rising RH from 0% to 100% successively. The rayon fibers were conditioned in each desiccator for 24 h and weighed in a closed weighing bottle. One hour was sufficient for each system to reach its equilibrium RH after opening and adding the rayon fibers as checked by a hygrometer, and 15 h was long enough for the rayon fibers to attain equilibrium weight (Okubayashi, Griesser, & Bechtold, 2004; Okubayashi, Griesser, & Bechtold, 2005). Desorption cycle was measured in the same way by stepwise decrease in RH.

3. Results and discussion

3.1. Crosslinking of cellulose fibers via esterification

Cellulose structures in never-dried rayon fibers (corresponding to dry weight 5.0 g) were fully open and had a much greater tendency to adsorb 6.0 g of the mixed solution containing COMM (0.48 g) and SHP (3.0 g, 0.0283 mol) than a fiber which had been collapsed by drying and then rewetted. The WAXD pattern of the rayon fibers was shown in Fig. 1. There was a small peak at $2\theta = 12.4°$ and double peaks at $2\theta = 20.4°$ and 21.5°, corresponding to lattice planes of $(1\bar{1}0)$, (110), and (200) of cellulose II, or hydrate cellulose, respectively (Cai et al., 2004; Kaplan, 1998). The crystallinity of the rayon fibers determined from the WAXD pattern was 50.2%, indicating that only 49.8% amorphous cellulose regions were accessible to esterification by COMM (Rowell & Young, 1978). Accordingly, the accessible hydroxyl in the never-

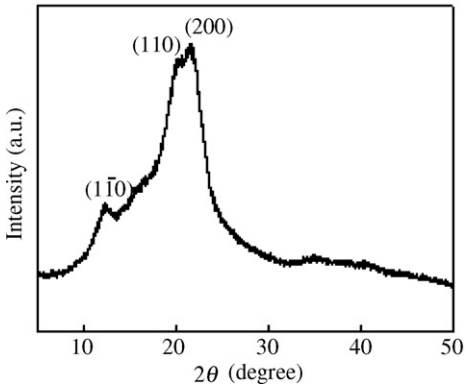


Fig. 1. XRD pattern for virgin rayon fibers.

dried rayon fibers (dry weight 5.0 g) was estimated to be 0.0461 mol. The relative reactivity of the hydroxyl groups of cellulose was in the order C-6 > C-2 > C-3 during the heterogeneous esterification, in which cellulose remained insoluble in the reaction mixture (Zhou, Qin, Liu, & Zhang, 2006). However, a homogeneous reaction ensured a more uniform accessibility of these hydroxyl groups (Hirrien, Desbrières, & Rinando, 1996). It was determined by titration that 4.083×10^{-3} mol of carboxyl groups located on COMM had penetrated into the amorphous regions of the never-dried rayon fibers, and esterified the hydroxyl groups of cellulose molecules (Scheme 1). So the feed molar ratio of the accessible hydroxyl groups to carboxyl acid groups was 11.3. This ratio was kept constant for all the crosslinking reactions of the rayon fibers in this research.

When the esterification occurred between COMM and cellulose, the carbonyl originated from the maleic acid segments of COMM bound to cellulose macromolecules existed in two forms, intermolecular ester linkages and free carboxyl groups. Both the forms could be present in one COMM molecule. Because the absorption band of the carboxyl carbonyl overlapped with that of the ester carbonyl in FTIR spectra (Yang, 1991), the carboxyl carbonyl was converted into carboxylate carbonyl by treating the crosslinked fibers with an aqueous NaOH solution of 0.1 M at room temperature. In Fig. 2, the absorption bands at 1716 and 1574 cm^{-1} were assigned to the ester and carboxylate carbonyl, respectively (Yang, 1991). There was no absorption corresponding to the ester or carboxylate carbonyl for the uncrosslinked rayon fibers. The esterification between cellulose and COMM was still difficult to identify although the relative absorption intensity at 1716 cm^{-1} increased with the curing temperature, because both the generated ester linkages and methylacrylate segments of COMM contributed to the increase of the absorption intensity at 1716 cm^{-1}. The amount of the bound COMM increased with the curing temperature as discerned from the absorption intensity at 1574 cm^{-1}. Therefore, the generated ester linkages were further quantified by direct titration as shown below.

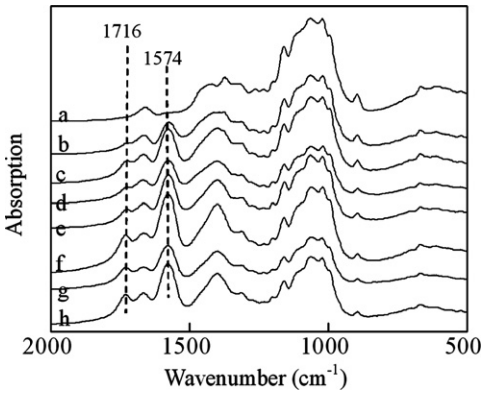


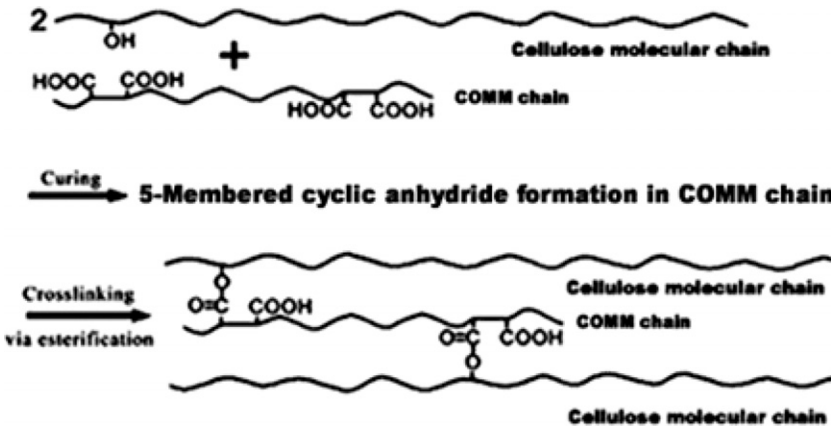
Fig. 2. FTIR absorption spectra of (a) virgin rayon fibers, and crosslinked rayon fibers at curing temperatures of (b) 150 °C, (c) 160 °C, (d) 170 °C, (e) 180 °C, (f) 190 °C, (g) 200 °C, and (h) 210 °C.

3.2. Carboxyl conversion rate and apparent crosslinking degree

Conversion rate of carboxyl groups into ester linkages for COMM was defined as the number ratio of the generated ester linkages to total esterifiable carboxyl groups on bound COMM according to the following equation:

$$\text{Conversion rate} = \frac{N_e}{0.5N_{e\&f}} \times 100\% = \frac{C_0 - C_1}{0.5(C_0 - C_1 + C_2 - C_3)} \times 100\% \quad (2)$$

where N_e is the number of the ester linkages derived from the esterification in the crosslinked cellulose fibers. $N_{e\&f}$ is the total number of carbonyl from the maleic acid segments of the bound COMM, which is the sum of the generated ester linkages and free carboxyl groups in the bound COMM. After an ester linkage was formed from an anhydride intermediate, the generated carboxyl group was less effective than the first one for further esterification, because formation of a five-membered cyclic anhydride intermediate was necessary for a polycarboxylic acid to esterify cellulose, and hence only one of two neighbouring carboxyl groups was able to esterify cellulose (Mao & Yang,



Scheme 1. Schematic diagram of esterification crosslinking between cellulose and COMM.

2001). So on average only half of the total carboxyl groups in the bound COMM were esterifiable. Fig. 3 revealed the dependence of the total concentration of carbonyl from the maleic acid segments of COMM and conversion rate of the carboxyl groups into the ester linkages on curing temperature. The total concentration of carbonyl groups in Fig. 3 was exactly the sum of the concentrations of both the generated ester linkages and the free carboxyl groups on COMM molecules covalently bound to the fibers via at least one ester linkage. The amount of esterified COMM increased with curing temperature, that is, more COMM was esterified at the higher curing temperature. The conversion rate increased by approximately 10% for each 10 °C interval of the curing temperature in the range from 150 to 200 °C, and approached its equilibrium value of 68.68% at curing temperatures of 200 and 210 °C, which is more than five times that at 150 °C. In particular, as many as 50% of esterifiable carboxyl groups in COMM were esterified at a curing temperature of 180 °C. The total carboxyl concentration in Fig. 3 was divided into the concentrations of the generated ester linkages and free carboxyl groups in Fig. 4. The concentration of the generated ester linkages increased rapidly with curing temperature and the maximal value was obtained at 200 °C. The concentration of the free carboxyl groups that were attached to the rayon fibers but not involved in esterification increased from 0.31 mmol/g fiber (150 °C) to 0.48 mmol/g fiber (190 °C), and then decreased slightly.

Apparent crosslinking degree (ACD) is defined as the number ratio of bridgeable crosslinkages formed from pairs of the generated ester linkages in the amorphous regions of a cellulose fiber sample to the total accessible hydroxyl groups for the crosslinking agent located in the amorphous regions of the same cellulose fiber sample.

$$\mathrm{ACD} = \frac{0.5N_e}{\frac{W \cdot f_a}{162} \times 3 \times 1000} = \frac{0.5(C_0 - C_1)}{\frac{f_a}{162} \times 3 \times 1000} \quad (3)$$

where W is the weight of the cellulose fiber sample in g. $0.5N_e$ means the number of the bridgeable crosslinkages in mmol formed from pairs of the generated ester linkages in the cellulose fiber sample. f_a is the weight fraction of the amorphous regions of the cellulose fibers obtained from WAXD. One hundred and sixty two is the molecular weight of a glucopyranose ring, and there are three hydroxyl groups in each glucopyranose ring. C_0 and C_1 are in mmol/g fiber. Because some of the generated ester linkages were not in the form of the bridgeable crosslinkages, i.e., pendant ester linkages, apparent crosslinking degree was adopted here to evaluate the crosslinking efficiency. In Fig. 5, ACD increased from 1.13×10^{-3} at the curing temperature of 150 °C to 1.34×10^{-2} at 200 and 210 °C. Actually, ACD of 7.88×10^{-3} at 180 °C afforded optimal tensile strength of the crosslinked fibers with the optimal dry tensile strength 2.78 ± 0.17 cN/dtex and wet tensile strength 1.43 ± 0.19 cN/dtex, increased 30.5% and 28.8%, respectively, based on the tensile strength of the virgin rayon fibers. However, ACD of 1.01×10^{-2} at 190 °C reduced the mechanical properties of the COMM-crosslinked fibers probably due to excessive crosslinking and thus internal stress concentration. That is to say a medium optimal crosslinking extent was desired from the viewpoint of the mechanical properties of the crosslinked rayon fibers. So far as BTCA-crosslinked rayon fibers are concerned, the mechanical performance of the same rayon fibers was opti-

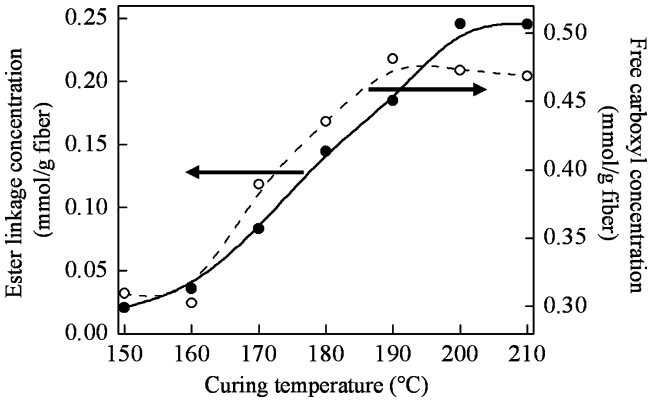


Fig. 4. Concentration of generated ester linkages and free carboxyl groups in the crosslinked fibers cured at various temperature.

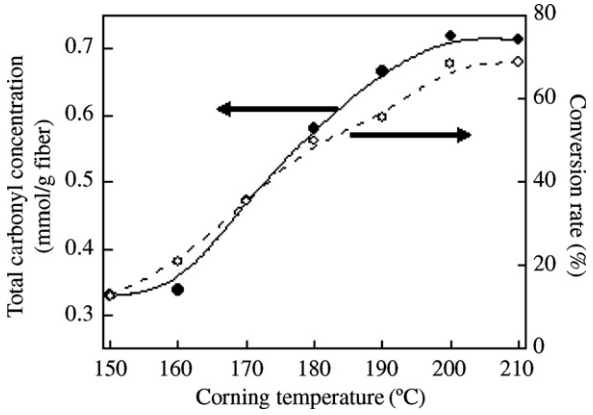


Fig. 3. Dependence of total carbonyl concentration from maleic acid segments of esterified COMM and conversion rate on curing temperature.

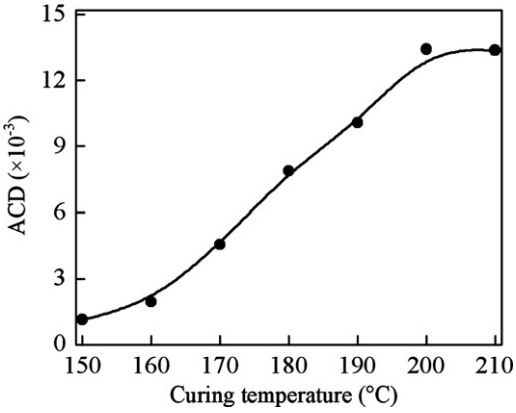


Fig. 5. Dependence of apparent crosslinking degree on curing temperature.

mized under the curing temperature of 180 °C with dry and wet tensile strength of 2.51 ± 0.06 and 1.42 ± 0.10 cN/dtex. However, a higher crosslinking degree of the BTCA-crosslinked rayon fibers was necessary than that of the COMM-crosslinked fibers to attain their respective optimal dry and wet tensile strength. It seemed that there was some relationship between the distribution homogeneity of the crosslinkages and the optimal tensile strength. The comparative rigidity of BTCA might account for the lower optimal dry tensile strength at the higher crosslinking degree required to attain the most homogeneous distribution of the crosslinkages at the curing temperature of 180 °C.

3.3. Liquid water response

Water retention of the crosslinked fibers was closely related to swellability of cellulose molecules, which was influenced dramatically by ACD. Swelling of the crosslinked fibers occurred in the amorphous regions when the fiber molecules were pushed apart by the absorbed water molecules. Mechanically held water was removed from capillaries and interfiber areas via centrifugation during the WRV tests to obtain the true water content (Xu, Yang, & Den, 2006). So the WRV tests provided an indication of the capacity of the crosslinked fibers to take up liquid water and swell. Fig. 6a and b shows that the WRV reduced with curing temperature and apparent crosslinking degree of the crosslinked fibers from the WRV value of 0.972 g/g for the virgin rayon fibers. The higher crosslinking degree caused a denser macromolecular network with less capillary spaces in the amorphous regions. The crosslinked network structures effectively screened the interior of the fibers from the flux of incoming water, preventing swelling of cellulose molecules by water. A decreased number of the hydroxyl groups available for bonding with water as a result of the generation of the numerous ester linkages in the crosslinked fibers might be a minor reason for the reduction of WRV. It was the densely packed structures and less swelling of the crosslinked fiber that accounted for the enhanced wet tensile strength.

3.4. Gaseous water vapor response

The affinity of cellulose fibers for water has been known for more than a century. The moisture absorption capacity, regarded as a function of the amorphous regions, is of paramount importance in the processing. Furthermore, it is an important indicator to evaluate the wearing comfort of textile materials. The sorption and desorption data for cellulose together formed a sorption loop, i.e., a pair of BET Type II multilayer isotherms, as shown in Fig. 7. Adamson explained the first section of the Type II isotherm up to the 'knee' corresponded to a single layer of water molecules adsorption over the surface of the cellulose (monolayer formation) (Adamson, 1982). The intermediate region indicated multilayer build-up, and the apparent infinite film thickness at high relative humidity (asymptotic section) indicated interparticle, or capillary, condensation. The difference between the sorption and desorption isothermals occurred due to hysteresis which was not explained by BET theory. Hysteresis arose from two competitive possibilities. Considering a hydroxyl group on a glucopyranose ring in a cellulose molecule, either a water molecule was absorbed on it or a hydrogen bonding was formed with another hydroxyl group in the neighbouring cellulose molecules. The chance of hydrogen bonding formation with water depended on the number and velocity of the water molecules present in the atmosphere. But the chance of hydrogen bonding formation with another hydroxyl group relied on the proximity of another hydroxyl group, which was more likely to occur during the sorption process as the other hydrogen bonding held the cellulose molecules close together than during the desorption process as the cellulose molecules were far apart. Consequently, the net chance of water absorption was greater in the desorption process, resulting into hysteresis in the moisture absorption. In Fig. 7, the equilibrium moisture regain of the crosslinked fibers under the curing temperature of 180 °C was slightly lower than that of the uncrosslinked fibers during the second and third sections, whereas difference could be scarcely observed for the first section. Since moisture was

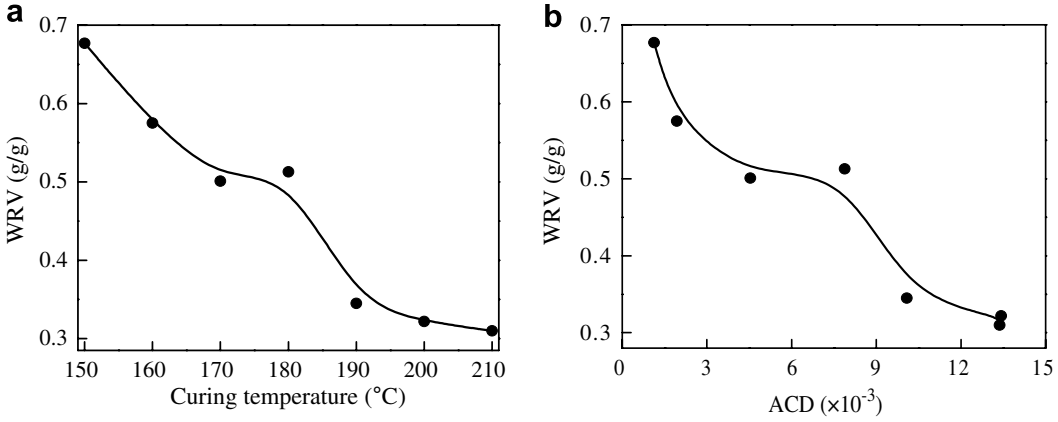


Fig. 6. Dependence of water retention value on (a) curing temperature, and (b) apparent crosslinking degree.

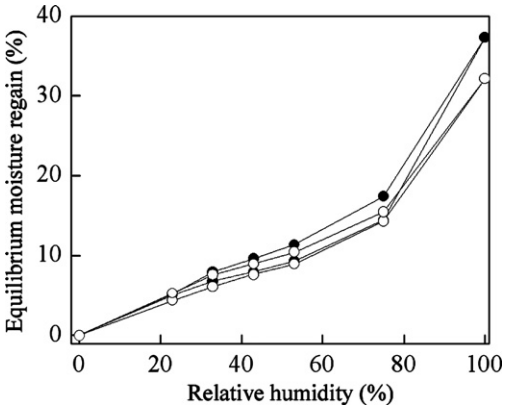


Fig. 7. Equilibrium moisture sorption and desorption isothermals at 25 °C for the uncrosslinked rayon fibers (●), and crosslinked rayon fibers at 180 °C (○).

attached only to the fiber surfaces as well as multilayer stacking on fiber surfaces, the network structures of the crosslinked fibers slightly mitigated multilayer stacking and interparticle, or capillary, condensation of water molecules as mesopore size did not vary much due to the low ACD of 7.88×10^{-3} at the curing temperature 180 °C in Fig. 5. The sorption–desorption cycles and concomitant hysteresis were hardly affected by the still low crosslinking degree of 1.01×10^{-2} at 190 °C curing (not shown), indicating the fiber surfaces and spacers of the cellulose molecules were not obviously affected by the low crosslinking degree, and thus the interaction between moisture and the crosslinked fibers was not as distinct as the differences in swelling in excess water.

The moisture absorption was related to the behavior of fibers exposed to atmospheric humidity, which occurred chiefly on the internal surfaces of the hygroscopic cellulose. Fortunately, water regain decreased little after crosslinking, indicating fabrics from the crosslinked fibers may be as comfortable as uncrosslinked fibers to wear because of its maintenance of moisture balance with respect to human skin. However, the liquid water retention of the crosslinked fibers was due to the penetration of liquid water into the amorphous regions and swelling of the cellulose molecules. The cellulose molecules moved apart and gave room for the water to enter, but the ingress of liquid water was strongly restricted by the crosslinks in the amorphous regions, which anchored cellulose molecules and prevented their breaking away completely. The removal of liquid water from masses of fibers has practical application in the drying of textiles, where the initial surplus water may be removed by squeezing, centrifuging, or merely by gravity. Reduction of wet weight of the crosslinked fibers is of great significance to economize on energy in the process of drying from the viewpoints of both rayon industry and the daily use of rayon fabrics. Moreover, diminished swelling in liquid water of the crosslinked fibers has technical consequences in wet tensile strength and dimensional stability of cellulose fabrics.

4. Conclusions

The co-oligomer of maleic acid and methylacrylate (COMM) was utilized to crosslink the viscose rayon fibers via intermediate anhydridisation followed by the esterification crosslinking. For the first time the chemical structure of the obtained polymer complex has been characterized through the carboxyl esterification rate of COMM and ACD. The crosslinking reaction was conducted under a series of curing temperature in the presence of SHP as the catalyst. Both the carboxyl esterification rate of COMM and ACD increased with curing temperature up to 200 °C.

It was found that the crosslinking reaction had a notable impact on the response of the crosslinked fiber to liquid water as shown by the WRV results, but very little influence on the moisture sorption–desorption isotherms. It is believed that the WRV is correlated with the swelling behavior of the crosslinked cellulose fibers, while the sorption–desorption isotherms are correlated with the total accessible water to absorption sites over their internal surfaces. These interesting phenomena may have valuable utility for the COMM-crosslinked rayon fibers as a new kind of textile fibers.

In comparison with the low molecular weight crosslinkers, e.g., BTCA, the oligomeric crosslinker with the flexible molecular chains is a more efficient way to improve the mechanical properties of cellulose fibers. Detailed mechanical and resiliency properties of the COMM-crosslinked fibers will be published in a successive paper.

More flexible crosslinkers containing various co-monomers with controlled chain sequences and length are being considered to tailor special structures and properties of the crosslinked cellulose fibers and fabrics. This idea can also be applied to other polymer materials, which are crosslinkable through flexible oligomeric molecules.

Acknowledgements

This work was supported by Program for Changjiang Scholars and Innovative Research Team in University (No. IRT0526), Shanghai Rising-Star Program (04QMX1449), Specialized Research Fund for the Doctoral Program of Higher Education (No. 20060255008), and Program for New Century Excellent Talents in University.

References

Adamson, A. W. (1982). *Physical chemistry of surfaces* (4th ed.). New York: Wiley, p. 534.

Cai, J., Zhang, L., Zhou, J., Li, H., Chen, H., & Jin, H. (2004). Novel fibers prepared from cellulose in NaOH/urea aqueous solution. *Macromolecular Rapid Communications, 25*(17), 1558–1562.

Chen, W., Lickfield, G. C., & Yang, C. Q. (2004). Molecular modeling of cellulose in amorphous state part II: effects of rigid and flexible crosslinks on cellulose. *Polymer, 45*(21), 7357–7365.

Chen, D., Yang, C. Q., & Qiu, X. (2005). Aqueous polymerization of maleic acid and cross-linking of cotton cellulose by poly(maleic acid). *Industrial & Engineering Chemistry Research, 44*(21), 7921–7927.

Hirrien, M., Desbrières, J., & Rinando, M. (1996). Physical properties of methylcelluloses in relation with the conditions for cellulose modification. *Carbohydrate Polymers, 31*(4), 243–252.

Ibrahim, N. A., Abo-Shosha, M. H., Elnagdy, E. I., & Gaffar, M. A. (2002). ECO-friendly durable press finishing of cellulose-containing fabrics. *Journal of Applied Polymer Science, 84*(12), 2243–2253.

Kaplan, D. L (1998). *Biopolymers from renewable resources*. Berlin Heidelberg: Springer, p. 55.

Knaul, J. Z., Hudson, S. M., & Creber, K. A. M. (1999). Crosslinking of chitosan fibers with dialdehydes: proposal of a new reaction mechanism. *Journal of Polymer Science B: Polymer Physics, 37*(11), 1079–1094.

Mao, Z., & Yang, C. Q. (2001). Polymeric multifunctional carboxylic acids as crosslinking agents for cotton cellulose: poly(itaconic acid) and *in situ* polymerization of itaconic acid. *Journal of Applied Polymer Science, 79*(2), 319–326.

Morris, C. E., Morris, N. M., & Trask-Morrell, B. J. (1996). Interaction of meso-1,2,3,4-butanetetracarboxylic acid with phosphorus-containing catalysts for esterification cross-linking of cellulose. *Industrial & Engineering Chemistry Research, 35*(3), 950–953.

Okubayashi, S., Griesser, U. J., & Bechtold, T. (2004). A kinetic study of moisture sorption and desorption on lyocell fibers. *Carbohydrate Polymer, 58*(3), 293–299.

Okubayashi, S., Griesser, U. J., & Bechtold, T. (2005). Moisture sorption/desorption behavior of various manmade cellulosic fibers. *Journal of Applied Polymer Science, 97*(4), 1621–1625.

Rowell, R. M, & Young, R. A (1978). *Modified cellulosics*. New York: Academic Press, Inc..

Xu, G. G., Yang, C. Q., & Den, Y. (2006). Mechanism of paper wet strength development by polycarboxylic acids with different molecular weight and glutaraldehyde/poly(vinyl alcohol). *Journal of Applied Polymer Science, 101*(1), 277–284.

Yang, C. Q. (1991). Characterizing ester crosslinkages in cotton cellulose with FT-IR photoacoustic spectroscopy. *Textile Research Journal, 61*(5), 298–305.

Yang, C. Q., & Bakshi, G. D. (1996). Quantitative analysis of the nonformaldehyde durable press finish on cotton fabric: acid–base titration and infrared spectroscopy. *Textile Research Journal, 66*(6), 377–384.

Yang, Q., Dou, F., Liang, B., & Shen, Q. (2005). Studies of crosslinking reaction on chitosan fiber with glyoxal. *Carbohydrate Polymer, 59*(2), 205–210.

Yang, C. Q., & Lu, Y. (1999). In-situ polymerization of maleic acid and itaconic acid and crosslinking of cotton fabric. *Textile Research Journal, 69*(10), 782–789.

Yang, C. Q., & Wang, X. (1996). Formation of cyclic anhydride intermediates and esterification of cotton cellulose by multifunctional carboxylic acids: an infrared spectroscopy study. *Textile Research Journal, 66*(9), 595–603.

Yang, C. Q., Wei, W., & Lickfield, G. C. (2000). Mechanical strength of durable press finished cotton fabric. Part II: comparison of crosslinking agents with different molecular structures and reactivity. *Textile Research Journal, 70*(2), 143–147.

Zhou, J., Qin, Y., Liu, S., & Zhang, L. (2006). Homogenous synthesis of hydroxyethylcellulose in NaOH/urea aqueous solution. *Macromolecular Bioscience, 6*(1), 84–89.