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Nonformaldehyde durable press finishing of cotton fabrics using the combination of maleic acid and sodium hypophosphite

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ABSTRACT

Polycarboxylic acids have been used as nonformaldehyde crosslinking agents for cotton with sodium hypophosphite (NaH_2PO_2) as the catalyst to replace the formaldehyde-based dimethyloldihydroxyethleneurea (DMDHEU). Maleic acid (MA), an α, β-unsaturated bifunctional carboxylic acid, can esterify cotton but is not able to form crosslinking between two cellulose molecules by itself. In this research, we discovered that the wrinkle resistance of the cotton fabric treated with MA and NaH_2PO_2 was significantly increased and phosphorus was bound to cotton when the treated fabric was exposed to temperatures higher than that required for esterification of cotton by MA. Elevation of the fabric wrinkle resistance and increase in quantity of the phosphorus bound to cotton had similar dependency on curing temperature, on MA concentration, and on NaH_2PO_2 concentration. All the data support the hypothesis that H–P–(residual of NaH_2PO_2) added to >C=C< of the MA already bound to cotton by esterification, thus forming a new crosslink between two cotton cellulose molecules. The cotton fabrics treated by MA/NaH_2PO_2 showed fabric wrinkle resistance similar to that treated with DMDHEU, but the breaking strength and tearing strength of the MA-treated cotton fabrics were significantly improved.

1. Introduction

Dimethyloldihydroxyethleneurea (DMDHEU) is a formaldehyde-based crosslinker for cotton and other cellulosic fibers. DMDHEU and its modified "low formaldehyde" versions form ether linkages with cellulose in the presence of a catalyst, such as magnesium chloride ($MgCl_2$). Those reagents have been widely used in textile industry to produce wrinkle resistant and easy-care cotton fabrics and garments since 1980s (Petersen, 1983). DMDHEU is a highly effective durable press finishing agent with excellent laundering durability, little fabric yellowing effects and good fabric hand properties. However, those reagents have fundamental disadvantages due to formaldehyde-release and severe decrease in fabric mechanical strength.

The effectiveness of DMDHEU is based on its two methylol groups, which releases free formaldehyde vapor from treated cotton fabrics during industrial production and home treatments such as laundering and ironing. When the cotton fabric crosslinked by DMDHEU is subjected to multiple laundering cycles, the ether linkages of DMDHEU gradually hydrolyze to become N-methylol groups. Consequently free formaldehyde is released continuously during the entire life of the finished garment (Scheme 1). Both textile workers and consumers are subjected to the health risk caused by formaldehyde vapor released during industrial production and consumer use of durable press finished cotton garments.

In 1987, the U.S. Environmental Protection Agency classified formaldehyde as "a probable human carcinogen" (Environmental Protection Agency, 1989). The risk of formaldehyde exposure was upgraded to "carcinogenic to humans" by the working group of WHO International Agency for Research on Cancer in 2004 (Cogliano et al., 2004). Five of seven most recent case-control studies showed increased risk for people exposed to formaldehyde. Epidemiology studies showed that individuals exposed to formaldehyde in their workplaces are at increased risk of leukemia and brain cancer compared with general public (Beane Freeman et al., 2009; Hauptmann et al., 2009). More specifically, a cohort study observed "an excess in leukaemia mortality among a cohort of formaldeyde exposed garment workers" and the mortality from leukaemia was greatest among workers first exposed in the earliest years and workers with 10 or more years of exposure (Pinkerton, Hein, & Stayner, 2004). Other epidemiology studies also indicated the increased cancer risk and mortality rate as a result of industrial formaldehyde exposure (Coggon, Harris, Poole, & Palmer, 2003; Hauptmann, Lubin, Stewart, Hayes, & Blair, 2003, 2004). The proven link between cancer and exposure to formaldehyde

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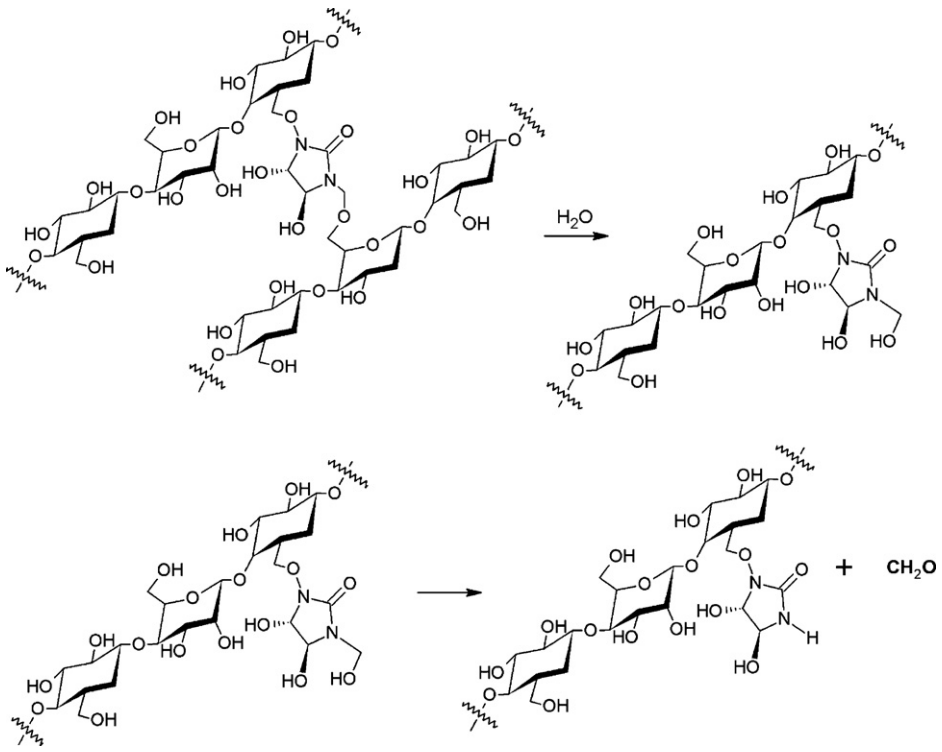

Scheme 1. Hydrolysis and formaldehyde release of cotton fabric crosslinked by DMDHEU.

for textile workers also makes it necessary to consider the health risk presented by formaldehyde-containing garments to the vast consumers since consumers are exposed to the low concentration formaldehyde vapor in their entire lives.

In our previous research, we found that magnesium chloride, the most commonly used catalyst for DMDHEU on cotton, caused significant degradation of cotton cellulose and significantly diminished the strength of cotton fabrics (Yang, Wei, & Lickfield, 2000). We found that the cotton fabrics treated with DMDHEU or its modified low formaldehyde versions lost 50–70% of their original breaking strength in order to achieve reasonably high levels of durable press performance (Wei & Yang, 1999, 2000). Severely decreased mechanical strength of the durable press finished cotton fabrics is a major limitation for the current durable press finishing technology based on DMDHEU.

Since the late 1980s, extensive efforts have been made to develop formaldehyde-free crosslinking agents for cotton to replace the traditional formaldehyde-based reagents as durable press finishing agents for cotton (Welch, 1992, 2001). Among those agents investigated, multifunctional carboxylic acids have attracted most attention when Welch discovered sodium hypophosphite as the most effective catalyst (Welch, 1988; Welch & Andrews, 1989). In our previous research, we studied the mechanism of ester crosslinking of cellulose by polycarboxylic acids and found that a polycarboxylic acid esterifies cellulose through the formation of a 5-membered cyclic anhydride intermediate by the dehydration of two carboxylic groups bound to the adjacent carbons in their molecular backbone as shown in Scheme 2 (Yang, 1993; Yang & Wang, 1996a,b, 1997).

In our previous research, we found that oligomers of MA were able to impart high levels of wrinkle resistance to cotton fabrics (Chen, Yang, & Qiu, 2005). MA, an α, β-unsaturated dicarboxylic acid, can only form a single ester linkage with cellulose, and it is not able to form the second cyclic anhydride intermediate for crosslinking cotton cellulose. However, we also discovered that the wrinkle resistance of the cotton fabric treated with MA was significantly improved when NaH_2PO_2 was used as a catalyst. Such phenomenon was not observed when the cotton fabric was treated with combinations of succinic acid/NaH_2PO_2 or MA/Na_2HPO_3 (Yang, Chen, Guan, & He, 2010). Thus, the experimental evidence suggested that the reaction between NaH_2PO_2 and two MA molecules already esterified with cotton forms a crosslinkage between two cellulose molecules as shown in Scheme 3. The objective of this research was to evaluate the effectiveness of combination of MA and NaH_2PO_2 as a crosslinking system for cotton. We also compared the performance of MA/NaH_2PO_2 with that of DMDHEU as durable press finishing agents for cotton fabrics.

2. Experimental

2.1. Materials

Two cotton fabrics were used in this study: (a) a desized, scoured and bleached plain weave cotton printcloth weighing 109 g/m^2 (Testfabrics style 400) produced by Testfabrics, West Pittston, PA; and (b) a 3/1 twill weave Khaki cotton fabric weighing 264 g/m^2 produced by Milliken, Blacksburg, SC. MA and NaH_2PO_2 were reagent grade chemicals supplied by Aldrich, Milwaukee, WI. The modified low-formaldehyde DMDHEU with the trade name of "Freerez 845", which was 45% modified DMDHEU pre-mixed with the catalyst ($MgCl_2$), was supplied by Emerald Carolina Chemical, Charlotte, NC. The non-ionic wetting agent with commercial name of "Triton X-100" was supplied by Bio-Rad Laboratories, Hercules, CA. The aminofunctional silicon softener with the commercial name of "DM-3362" was supplied by Dymatic Chemicals, Shunde, China. The concentrations (w/w) of MA and NaH_2PO_2 were based on 100% active ingredient, whereas those of DMDHEU, the silicon softener and the wetting agent were based on the weight of commercial products.