Thermoanalytical Characteristics of Durable Press Treated Cotton Fabrics

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SYNOPSIS

Thermoanalytical characteristics of chemically treated cotton fabric often appear similar to those of untreated cotton. The overwhelming amount of cotton cellulose versus the small quantities of finishing chemicals present can mask many features contributed by reactant. The current work is an initial attempt to detect and differentiate among a variety of durable press finishes. They include three *N*-methylol reactants, and four polycarboxylic acids with two alkali metal salts of phosphorus-containing acids used to catalyze their reaction with cellulose. Differential scanning calorimetric and thermogravimetric techniques were employed under dynamic nitrogen conditions. Changes in residue, rate of weight loss, peak intensity, and peak temperature were observed and varied with reactant, catalyst used, and washing. The ability to distinguish among polycarboxylic acids, catalysts, and/or other formaldehyde-based reactants is of value to the textile chemist. With these preliminary results, we may soon offer a new means of finish identification. © 1993 John Wiley & Sons, Inc.†

INTRODUCTION

Thermoanalysis (TA) of treated cotton fiber and fabrics is difficult mainly because of the overwhelming quantity of cellulose present vs. the amount of added chemicals. Thermal studies have been carried out at the Southern Regional Research Center. Beginning with Perkins et al.,[1] differential thermal analyses (DTA) and thermogravimetric (TG) analyses were conducted on flame retardant (FR) cotton fabrics. A series of studies carried out by Neumeyer et al.[2] using TG analyses and Hobart et al.[3] using DTA examined cotton/polyester blends treated with an FR finish. Perkins et al.[4] combined TG and differential scanning calorimetric (DSC) analyses and compared two FR finishes on fabric blends of cotton/polyester. Another study of FR cotton was carried out by Muniswamy and Kumarbadami[5] using DTA and TG analyses.

Early thermal studies involving durable press (DP)/FR fabrics also involved cotton blends. Holme and Patel[6] performed some TG analyses of DP/FR treated polyester/cotton blend fabrics in air. Using computer controlled instrumentation and an inert atmosphere, we studied cotton/polyester/wool fabric blends treated for DP/FR using DSC and TG analyses.[7] In that research we recognized the presence of the different fibers and finish with TA; however the finish itself was visualized by phosphorus mapping techniques using EDAX. Some early thermal research on fibers under similar test conditions was successful with cellulose derivatives.[8]

A thorough study of DP reactants, both formaldehyde-based (*N*-methylol compounds)[9] and nonformaldehyde-based (polycarboxylic acids),[10] gave a better understanding of these reactants. With this information as a reference, an investigation of a large variety of treated fabrics was initiated. This article presents some preliminary results, which are first

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steps toward a goal of thermoanalytical characterization and identification of unknown DP finishes on cotton fabrics.

EXPERIMENTAL

Materials and Methods

The fabric was 80 × 80 cotton printcloth that had been desized, scoured, and bleached. The fabric weighed 3.2 oz/yd^2 (0.109 kg/m^2). Fabric treatments were carried out on a laboratory scale. Samples were padded to approximately 85–95% wet pickup using two dips and two nips. After padding, fabrics were dried on pin frames at 60°C for 7 min and cured at 160°C for 3 min for the *N*-methylol treatments or dried at 85°C for 5 min and cured at 180°C for 30 or 90 s for the polycarboxylic acids. The cured fabrics labeled washed were given a home-type laundering with a nonionic detergent in an automatic washer and tumble dried before testing.

Reactants and catalysts were all commercially available reagent grade chemicals. Formaldehyde-based agents are coded with letters and polycarboxylic acids (PCAs) are coded with numbers for some figures or abbreviated when space allows.

N-methylol compounds were applied from pad baths containing 9% solids reactant + 2.7% $MgCl_2 \cdot 6H_2O$/citric acid catalyst in a 20:1 ratio. PCA concentrations (shown in parentheses below) were slightly different; as listed, they each produced a carboxyl content equivalent to that of 1,2,3,4-butanetetracarboxylic acid. Two catalysts were used to produce DP finishes with PCAs: Na_2HPO_4 (Na_2) and $NaH_2PO_2 \cdot H_2O$ (HYPO). Catalyst concentrations were approximately equimolar to the acid concentrations. The crosslinking reactants are listed below:

(A) DMDHEU: 1,3-dimethylol-4,5-dihydroxyethyleneurea;
(B) PTMeDMDHEU: partially methylated DMDHEU;
(C) 4Me-DMDHEU: tetramethylated DMDHEU;

(1) TRICARB: 1,2,3-propanetricarboxylic acid (6.3%);
(2) CA: citric acid (6.9%);
(3) BTCA: 1,2,3,4-butanetetracarboxylic acid (6.3%);
(4) CP-TCA: all-cis cyclopentanetetracarboxylic acid (6.6%).

Thermoanalytical data were acquired on a Dupont (TA Instruments) 1090 Thermoanalyzer using a DSC module 910 and TG module 951. Samples were analyzed under flowing nitrogen at 15°C/min to the maximum 600°C.

DSC samples were normalized to 5 mg for comparability. These analyses were performed with standard aluminum DSC pans that were sealed and pricked with a pin hole just prior to analysis to allow gases to escape. As a precaution, we now perform DSC procedures involving magnesium chloride catalyst in hermetically sealed pans with high nitrogen flow to minimize damage to the DSC cell from corrosive decomposition products.

TG samples were in the range of 10–12 mg. Percent residues were measured at 575°C. The derivative (DTG) thermograms measure the rates of weight loss; the maximum rate of weight loss for each sample was recorded as percent weight loss/min. Residue and rate data are averages of duplicate analyses unless otherwise noted in the text. Thermograms shown are of individual samples.

RESULTS AND DISCUSSION

In Figure 1 are shown the DSC (top) and TG (bottom) thermograms of the fabrics that were treated with *N*-methylol reactants based on DMDHEU and washed. For comparison, the curves of untreated printcloth, with and without a wash, are overlaid at the top. The DSC thermograms are all plotted on the same mW scale; those for the three treated fabrics are separated for clarity. The major feature produced by cotton cellulose is an endotherm that peaks between 350 and 380°C and produces a heat flow of approximately −13 mW.

Well crosslinked DMDHEU/cotton (A) produced the DSC thermogram that most differs from the one for untreated cotton. There was a small exothermic peak that preceded the main decomposition endotherm. The endothermic peak intensity is < 4 mW for the treated fabric vs. > 10 mW for the controls. The DSC endothermic peaks increased for the PTMeDMDHEU (B) and the 4Me-DMDHEU (C) treated fabrics. The crosslink reactant for the latter is the least reactive toward cotton[11] and the fabric crosslinked with it has a DSC thermogram that is most like untreated cotton.

The bottom of Figure 1 shows overlaid TG weight loss curves. Well crosslinked DMDHEU/cotton (A) produced the earliest onset of weight loss and the highest residue in TGA. All three treated fabrics

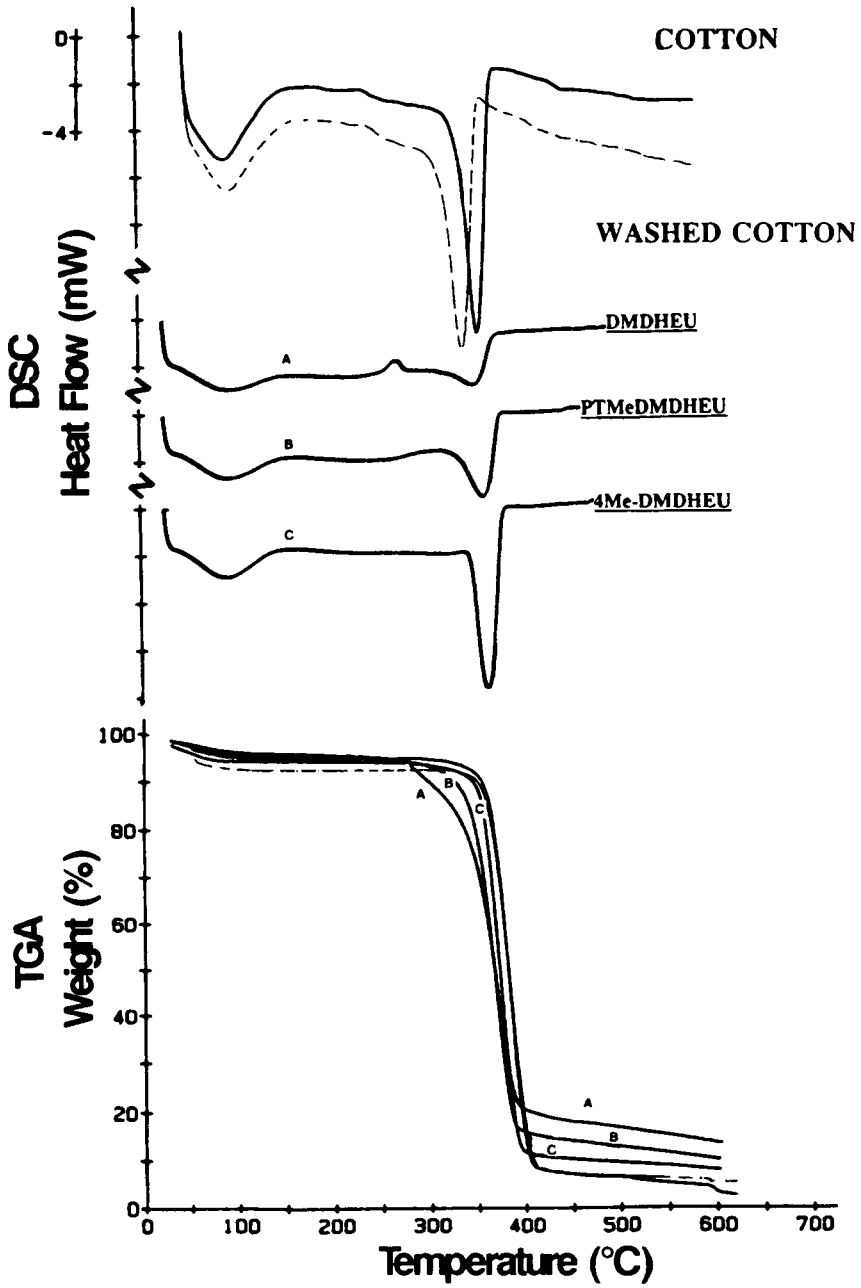

Figure 1 Differential scanning calorimetric (DSC) and thermogravimetric (TG) thermograms of five cotton fabrics: cotton control and washed cotton control (dashed line) and three HCHO based finished fabrics that were washed. DSC curves are at the top of the figure; TGA curves are overlaid at the bottom.

produced measurably higher residues and the period of rapid weight loss occurred at slightly lower temperatures for each sample than were observed for untreated cotton fabrics. Both unwashed and washed specimens of the untreated cotton controls thermally decomposed at higher temperatures and produced lower percent residue values than did the treated fabrics. DMDHEU-crosslinked cotton had the best DP properties of the three finished fabrics, and its thermograms were the most different from those for untreated cotton. As methylation of DMDHEU increased, the thermograms more closely approached those of unfinished cotton printcloth.

A comparison of DSC thermograms of untreated

cotton, DMDHEU and BTCA, and the corresponding DP fabric after laundering is shown in Figure 2. Figure 2(a) contains the DMDHEU thermograms. We found an exotherm near 250°C in the DSC thermogram of DMDHEU solid. DSC thermograms of methylated DMDHEU revealed that the exotherm disappears as the agent is methylated (not shown).[5] The cotton fabric treated with DMDHEU still showed evidence of that exotherm.

In contrast, Figure 2(b) shows comparable data for solid BTCA. The BTCA thermogram is one of the most distinctive of those for the PCAs and yet it is simpler than that of DMDHEU. Correspondingly, no distinctive features are visible in the DSC thermogram of the washed fabric treated with this polycarboxylic acid finish. Both DMDHEU and BTCA treatments reduced DSC peak height for cotton fabrics by more than half. Crosslinking the cellulose changed this thermal characteristic.

In Figure 3 are the DSC thermograms of samples that were washed (dashed line) and not washed (solid line) after crosslinking with BTCA and sodium hypophosphite (HYPO) catalyst. Unique exothermic DSC features of the treated fabric are visible when samples are cured only. This is probably due to the presence of unreacted finishing agent. Samples given a wash have more "cotton character" (Fig. 1). Since this additional washing step in the industry is rarely carried out, fabric samples that will be more readily available should exhibit more identifiable thermoanalytical features.

The DSC and TG thermograms of fabrics treated with the four PCAs catalyzed by HYPO and given no afterwash are presented in Figure 4. DSC ther-

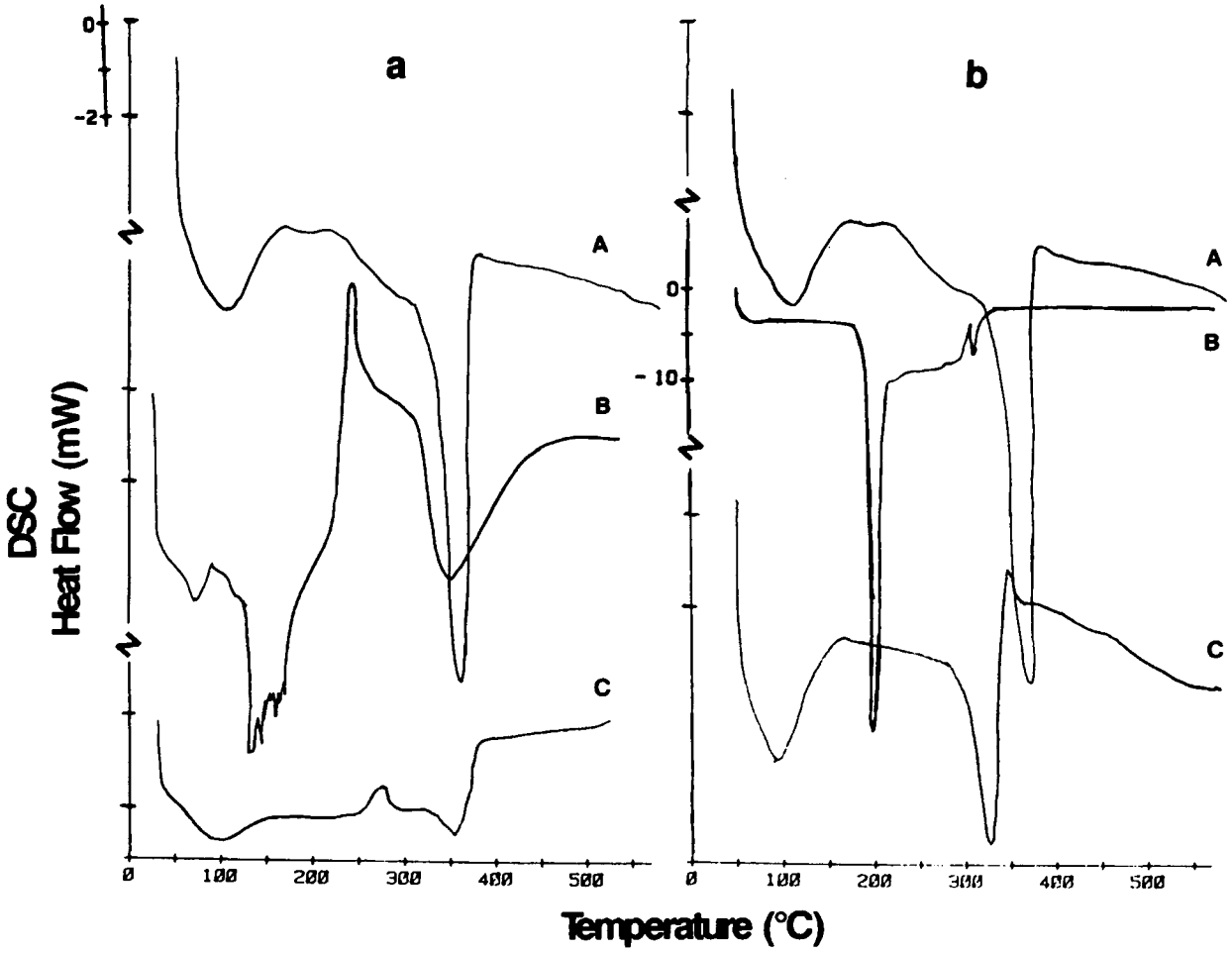

Figure 2 Two sets of differential scanning calorimetric (DSC) thermograms comparing (A) untreated cotton fabric, (B) a durable press (DP) reactant, and (C) the corresponding DP finished fabric after a wash. For the (a) left set the reactant was DMDHEU and for the (b) right set it was BTCA (note larger mW scale for the BTCA reactant thermogram).

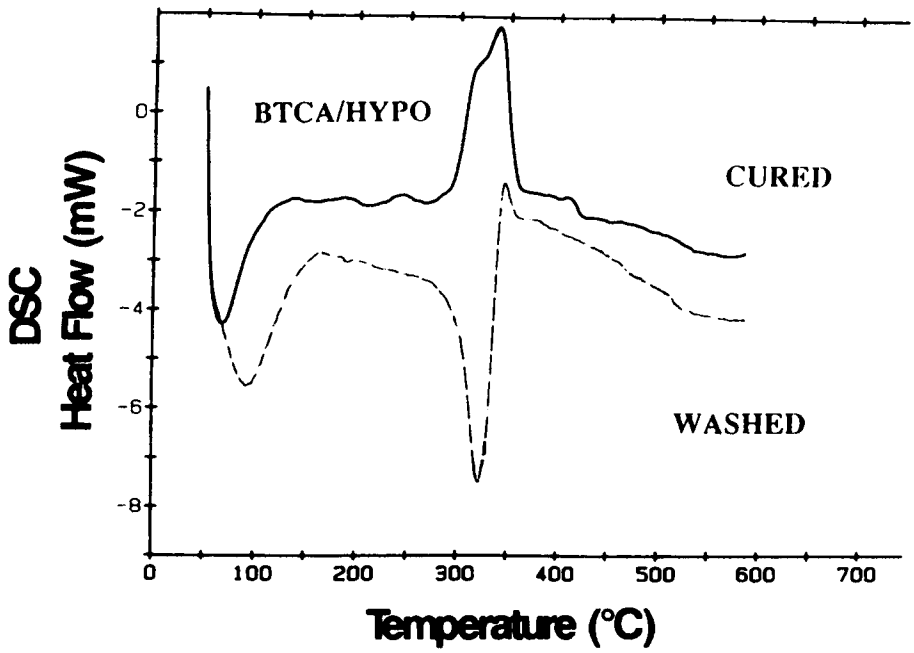

Figure 3 Differential scanning calorimetric (DSC) thermograms comparing durable press finished fabrics that were unwashed (——) and washed (- - -) after crosslinking with BTCA and sodium hypophosphite catalyst.

mograms (A) for the treated fabrics have common distinctive exothermic regions. These thermograms are easily distinguishable from those for untreated cotton fabric (Fig. 1). In addition, these treated fabrics have very high TG residues of 30–40% (B).

Figure 5 shows comparable thermograms of fabrics treated with PCAs catalyzed with disodium monohydrogen phosphate (Na_2). Each of these fabrics also exhibits an exotherm in DSC analysis and high residue production in TGA that distinguish them from untreated cotton fabric. Differences between HYPO and Na_2 catalysts that may allow identification of those finishes will be addressed in a future study.

TG data have proven valuable in the characterization of DP reactants. The amount of residue produced and the maximum rate of weight loss are the two parameters that we have found most useful. In general, high residue values and low rates of weight loss are indicative of a good DP finish with PCAs.[10] Figure 6 shows TG results of a limited series of fabrics treated with polycarboxylic acids that were tested after drying. Results are compared for the same finishes after curing and after curing and washing.

After fabrics were padded and dried, the physical presence of DP finishing agents was reflected by changes in TG parameters. Untreated cotton leaves approximately 5% residue and has a maximum rate of weight loss of 35–40%/min (not shown). Most finishes, when simply dried on the fabric, increased the amount of residue (top) and lowered the rate of weight loss (bottom).

After being heat cured to crosslink cotton cellulose with the reactant, most fabrics exhibited an increase in the amount of residue and varying decreases in maximum rate of weight loss. The thermal characteristics of fabrics treated with CA/Na_2 and BTCA/HYPO changed the least. Physically there should be almost the same amount of reactant material on the cured fabrics as there was on the dried specimens (less the mass of water that is formed during all crosslinking reactions). Curing caused the crosslinking reactions that changed the thermal characteristics. High percent residue values may be a better indicator of the degree of crosslinking than low rates of weight loss.

A portion of the thermal activity of unwashed fabric is attributable to the presence of unreacted/uncrosslinked chemicals in it. When excess, unreacted materials are removed by washing, we observed a drop in percent residue; all treated fabrics took on more cotton character. Those fabrics treated with HYPO catalyst (dashed lines) generally produced higher residues than those treated with Na_2 catalyst. Rates of weight loss correspondingly in-

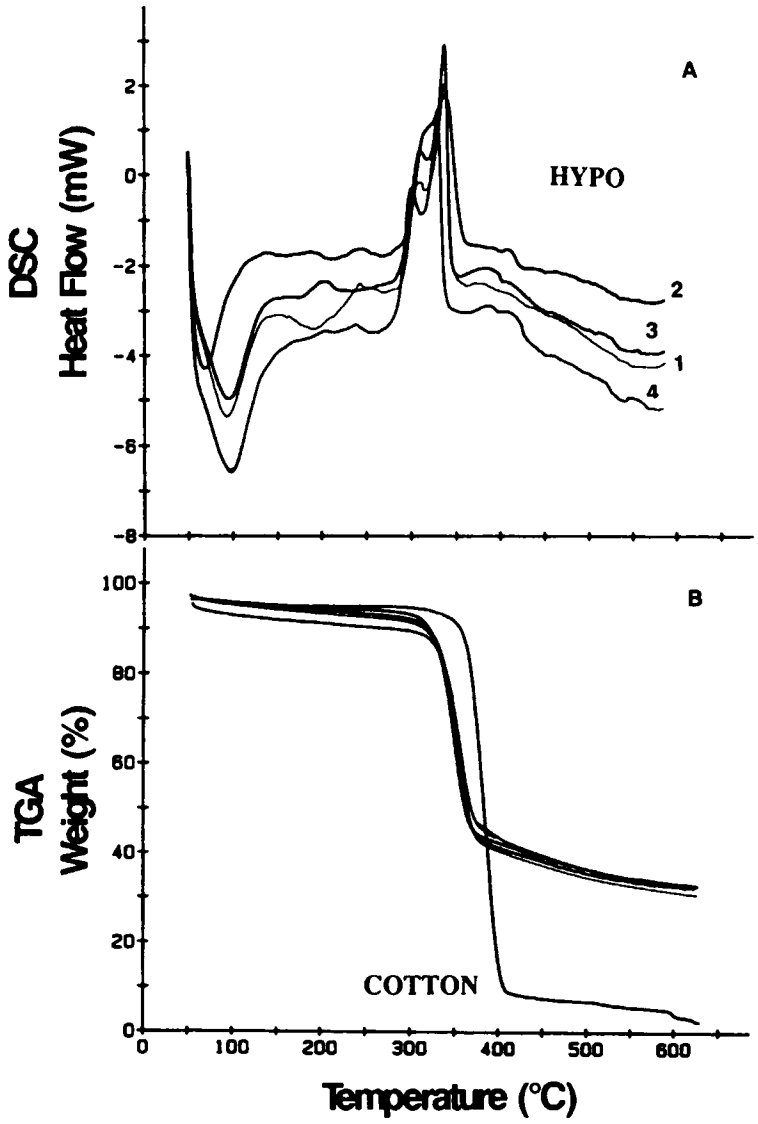

Figure 4 Thermograms of cotton fabrics treated with PCA reactants catalyzed by sodium hypophosphite. Thermograms shown are (A) DSC and (B) TG. PCAs are: (1) 1,2,3-propanetricarboxylic acid; (2) citric acid; (3) 1,2,3,4-butanetetracarboxylic acid; and (4) all-cis cyclopentanetetracarboxylic acid.

creased after washing; HYPO catalyzed fabrics had the lowest rates. Using these indicators, HYPO is a better catalyst.

Thermoanalytical parameters have been used to rank catalyst effectiveness with PCAs. A predictor factor was developed to study PCA interaction with three inorganic salts of phosphorus acids.[12] In that study, samples were heated to 300°C with an isothermal portion at the beginning and end of each thermogram. For each acid/catalyst combination in that study, percent residue was divided by maximum rate of weight loss and multiplied by a DSC parameter entitled total heat of reaction. This latter value was essentially the integration of the entire thermogram. Total heat of reaction data were not as accurately measurable under the analysis conditions used in this study. Therefore, we examined the data from this study for treated fabrics and calculated a partial predictor factor using the two available TG parameters. We define the residue/rate factor as the percent residue divided by the maximum percent weight loss/min. Residue is in the numerator because good DP properties correlate with high residue. Conversely, the rate is in the denominator because

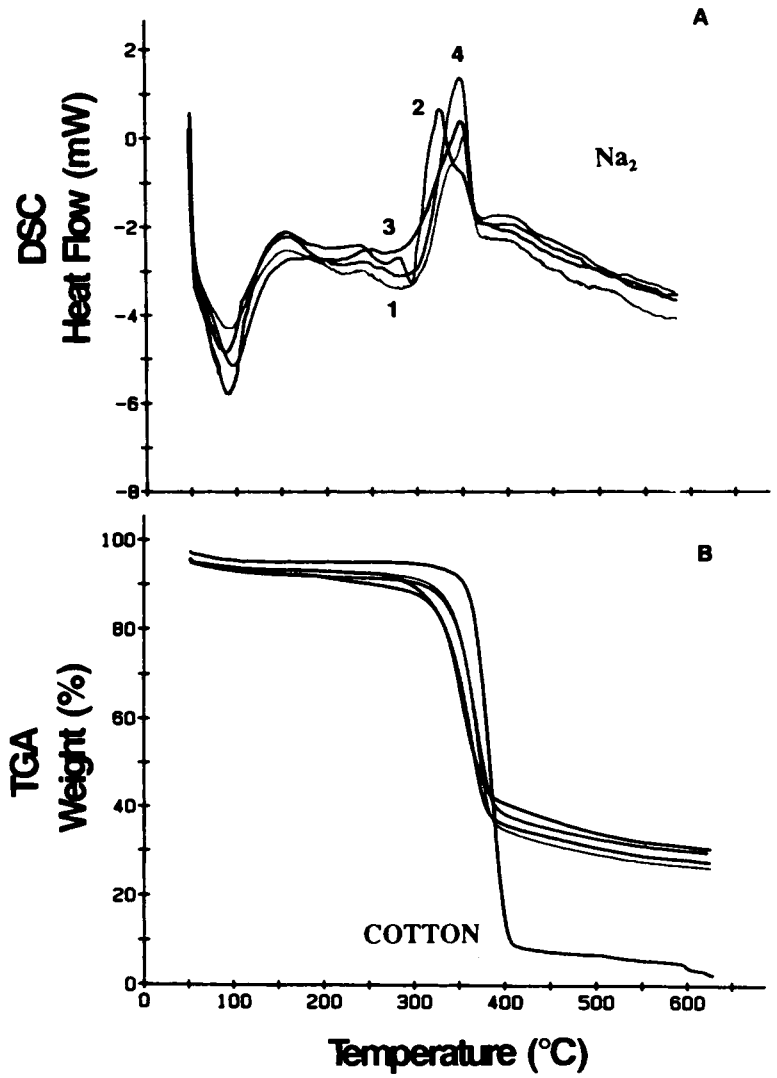

Figure 5 Thermograms of cotton fabrics treated with PCA reactants catalyzed by disodium hydrogen phosphate. Thermograms shown are (A) DSC and (B) TG. PCAs are: (1) 1,2,3-propanetricarboxylic acid; (2) citric acid; (3) 1,2,3,4-butanetetracarboxylic acid; and (4) all-cis cyclopentanetetracarboxylic acid.

low rates indicated better DP performance. A higher factor should indicate a better DP finish. These factors are presented in Figure 7. Grouped at the left of the graph are two sets of bars for PCA finished fabrics with catalysis by Na_2 and HYPO, respectively. These samples were dried and cured. They are clearly different from the corresponding fabrics on the right that were washed. All of the PCA treated fabrics are different from the untreated cotton control bar (C). Using the residue/rate factor, we see that HYPO-catalyzed PCA fabrics produce higher residue/rate factors more often than fabrics made with the other catalyst; generally HYPO is a better catalyst for PCAs than Na_2. The side of the figure for washed fabrics contains bars for single analysis specimens of fabrics finished with DMDHEU-based agents (HCHO). On the basis of the residue/rate factor, DMDHEU ranks best among them. In addition, the factor for the DMDHEU-finished sample is similar to those for citric acid and BTCA fabrics finished with HYPO as catalyst. This may indicate a similar level of crosslinking.

The residue/rate factor alone does not identify individual finishes. To achieve finish identification through the use of TA data, additional information must be incorporated. Because DSC total heat values

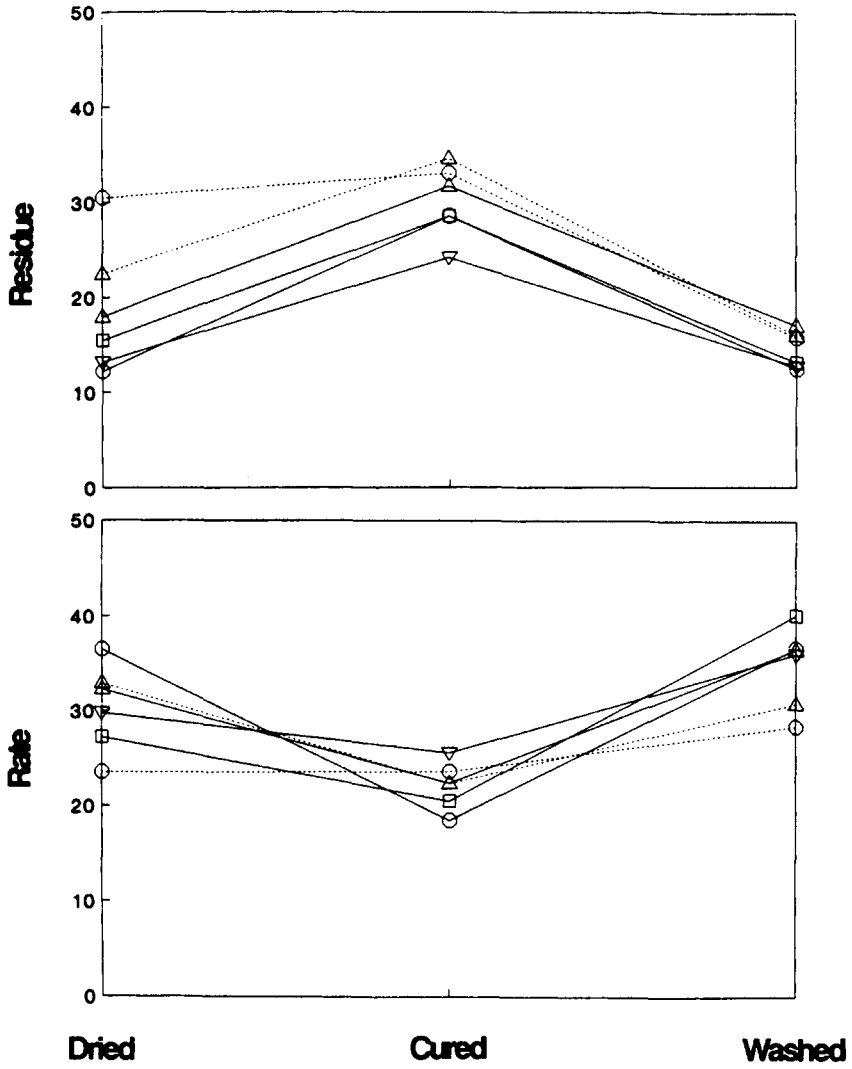

Figure 6 Comparison of six fabrics treated with polycarboxylic acid durable press finishes. (——) PCA samples catalyzed with Na_2; (- - -) are the tetracarboxylic acid samples catalyzed with HYPO. [(▽) 1,2,3-propanetricarboxylic acid; (□) citric acid; (○) 1,2,3,4-butanetetracarboxylic acid; and (△) all-cis cyclopentanetetracarboxylic acid]. Top graph compares percent residue at 575°C for three sets of fabric: those fabrics padded and dried (left); same fabrics cured (middle); and same fabrics cured and washed (right). Bottom graph shows comparable maximum rate of weight loss data in % weight loss/min.

are not available, the average DSC major-peak temperature was plotted against the residue/rate factor. These results, with error bars in both directions, are shown in Figure 8 and illustrate the extent to which we can separate and distinguish among fabrics treated with some DP finishes to date. Symbols containing a "dot" represent fabrics catalyzed with Na_2. Washed and unwashed samples are still discriminated; unwashed samples are all above the arbitrary dotted line and washed samples are all below the line. Error bars parallel to the X-axis are within the area of the symbols except for the sample treated with BTCA/Na_2. This fabric is the only one with this catalyst that appears among the fabrics treated with PCAs/HYPO. Error bars parallel to the Y-axis are largest for samples treated with Na_2 catalyst and washed. Additional analyses of the washed samples after storage for more than 6 months revealed that increases in percent residue had occurred for the fabrics on which this catalyst had been used.

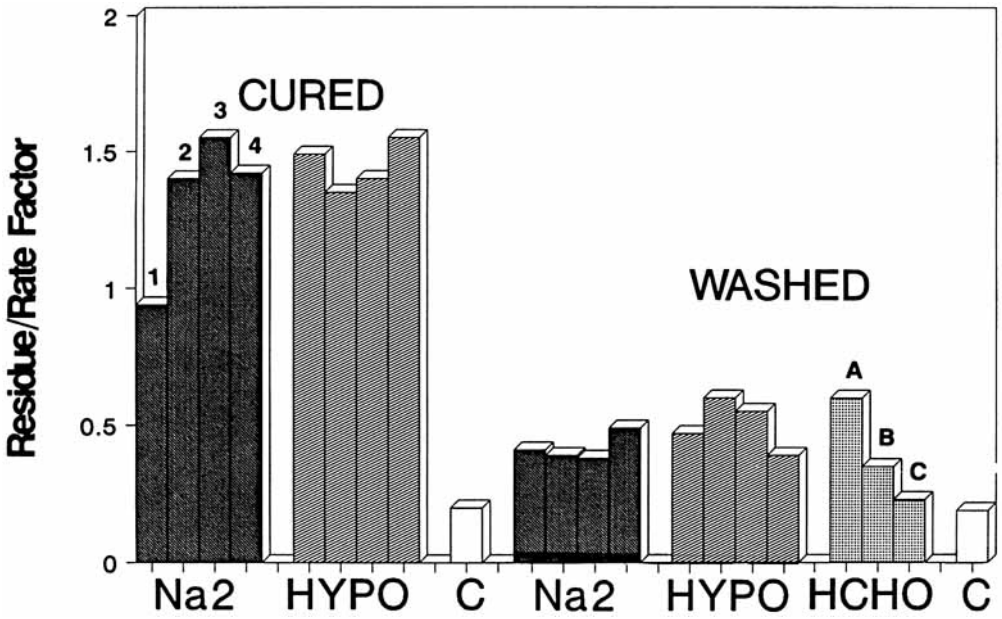

Figure 7 Comparison of residue/rate factors. From the left, the first two sets of four bars represent data for fabrics treated with (1) 1,2,3-propanetricarboxylic acid; (2) citric acid; (3) 1,2,3,4-butanetetracarboxylic acid; and (4) all-cis cyclopentanetetracarboxylic acid with catalysis by Na_2 or HYPO, respectively, after samples were dried and cured. A cotton control bar (C) is next. Corresponding bars after a wash appear next. The final set of three bars represents the single analysis data for DMDHEU-based finishes: (A) 1,3-dimethylol-4,5-dihydroxyethyleneurea; (B) partially methylated DMDHEU; and (C) tetramethylated DMDHEU.

Reproducibility for HYPO catalyzed fabrics was better.

We are not able to separate individual PCAs/catalysts from each other when they were unwashed. After unreacted materials were washed off, however, data points for PCA-treated fabrics were grouped according to catalyst, those for HYPO-catalyzed samples appearing at lower DSC peak temperatures.

The points from single analysis of fabrics finished with DMDHEU-based agents and washed are separated from each other. However, only the 4Me-DMDHEU sample is separated from the other washed DP fabrics plotted in this figure.

We believe that, with additional research, a discrete set of thermal parameters can be found and a means developed to eliminate overlap of finished and unwashed fabrics. Future research involving multiple series of fabrics, additional control fabrics, different crosslinking finishes and monitoring of storage effects is needed. Our goal, to identify durable press finishes on cotton fabric using thermoanalysis, is closer to achievement.

CONCLUSIONS

Differential scanning calorimetric and thermogravimetric analyses of cotton fabrics treated with a variety of durable press finishes have been performed. Finishes studied included three based on *N*-methylol compounds and newer formaldehyde-free DP finishes that are based on four polycarboxylic acids. As found in earlier research, the TG parameters of percent residue at the end of the analysis and the maximum rate of weight loss are two important thermal parameters and are readily measurable. They can be used alone to distinguish between treated and untreated cotton fabrics and those given a wash and between those given none. With the addition of a single DSC parameter, peak temperature, we were better able to distinguish among those same fabrics and able to discriminate between samples from two catalysts used in finishing with polycarboxylic acids after a single wash. With further refinements, we should be able to distinguish among many DP finishes on cotton cellulose in-

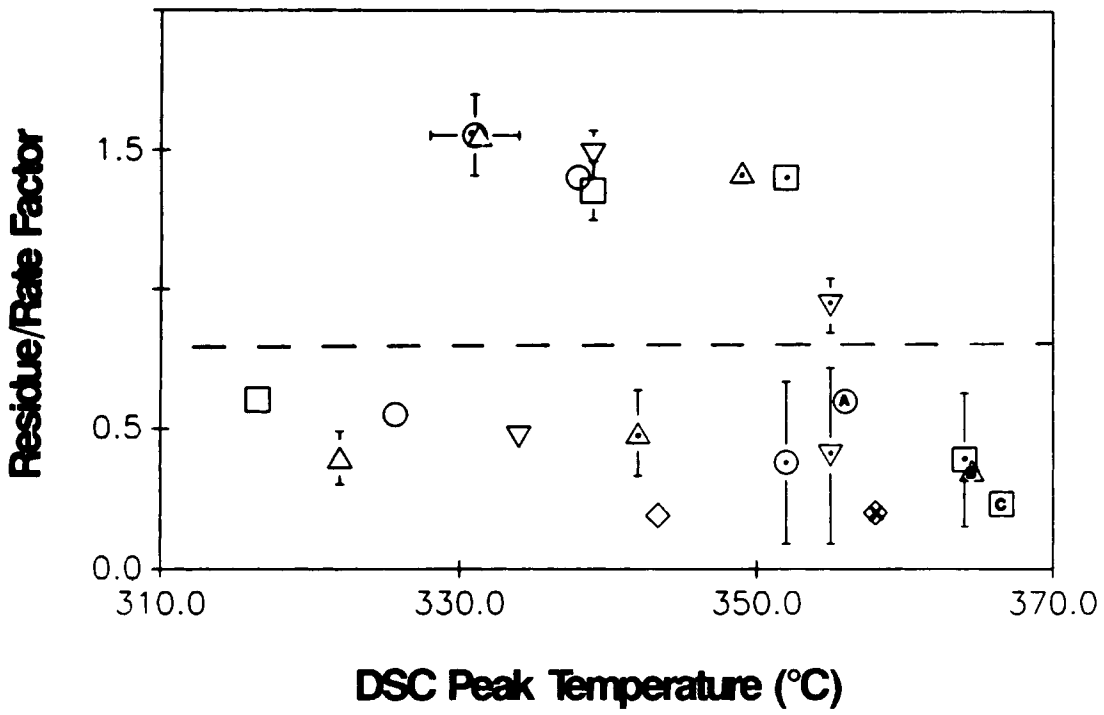

Figure 8 Scatter plot of the residue/rate factor vs. average DSC peak temperature. Each point represents a specific fabric sample: [(▽) 1,2,3-propanetricarboxylic acid; (□) citric acid; (○) 1,2,3,4-butanetetracarboxylic acid; (△) all-cis cyclopentanetetracarboxylic acid; (A) 1,3-dimethylol-4,5-dihydroxyethyleneurea; (B) partially methylated DMDHEU; and (C) tetramethylated DMDHEU. (◇) Cotton controls]. Points above the dotted line are dried and cured fabrics. Points below the line are for fabric samples treated and washed (except cotton control with "x"). Symbols for samples treated with PCAs and HYPO catalyst are open; those for Na_2 catalyzed PCAs contain a "dot."

cluding those reactants based on formaldehyde and polycarboxylic acids. Finish identification of durable press treated cotton fabrics using thermoanalysis may be a realistic goal.

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