Thermal Characteristics of Unsaturated Dicarboxylic Acid Durable Press Finishing Systems *

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SYNOPSIS

Thermoanalytical (TA) studies including differential scanning calorimetric (DSC) and thermogravimetric (TG) analyses were carried out to measure characteristics of dried mixtures based on two unsaturated polycarboxylic acids. Model 9% treatment (pad) solutions of maleic (M) and/or itaconic (I) acid, with and without potassium peroxydisulfate (K) as the free-radical initiator, were prepared with sodium hypophosphite (H) as the catalyst and vacuum oven-dried. DSC thermograms varied with each component; even the presence of a small amount of component K was evident. TG residue production and maximum rates of weight loss were the most useful thermal parameters. Residue/rate factors, used previously as predictors, were calculated. Previous studies indicated that high residues and low rates were indicators of combinations of reactants that resulted in good durable press treatments for fabrics. Residue/rate factors were used to rank the six mixtures that reflect actual fabric treatment combinations: MH, IH, MIH, and those same three with the initiator present. Rankings indicated that the presence of the initiator significantly increased the residue/rate factor for IHK and for MIHK. The presence of the initiator appears more beneficial to itaconic acid than to maleic acid. The rankings by the TA predictor agreed with textile properties measuring appearance and strength. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Research on durable press (DP) finishing of cotton textiles involves a variety of chemical reactants capable of forming cross-link bonds with cotton cellulose. These bonds produce a fabric that has a smooth appearance after washing and tumble drying. A variety of studies that dealt with thermal characteristics of DP reactants have been reported. The research began with studies of N-methylol compounds.[1] When DP research was shifted away from such formaldehyde-based finishes due to concerns for textile workers health, thermal analyses were performed on 10 polycarboxylic acids (PCAs)[2] including maleic and aconitic acids. The latter are both

unsaturated. Early fabric trials found that results were poor with the unsaturated acids.[3] Maleic and aconitic were also poor choices according to important thermal parameters. Residue production was smaller with the unsaturated acids than with the bench mark, 1,2,3,4-butanetetracarboxylic acid (BTCA), and the rates of weight loss were much higher. If a reactant volatilizes too early or decomposes totally and very rapidly, it will not be readily available for reaction with cotton cellulose. Unsaturated bonds are associated with higher rates of thermal reactions. It was evident from thermal results that good acids for DP treatment of cotton textiles were tri- or tetrafunctional.

After thermal analytical (TA) examination of acids alone, thermal research moved next to the effects of catalyst on the thermal characteristics of PCAs.[4] The ability of TA test results to correlate with and predict good durable press properties found in fabric research was a significant achievement of this research.[5]

As Welch and Andrews continued to improve fabric durable press properties from PCAs,[3] Choi studied dicarboxylic acids as starting materials of new durable press reactants.[6] His system uses a free-radical-initiated vinyl polymerization of unsaturated dicarboxylic acids to form longer-chain polycarboxylic acids followed by esterification cross-linking of the cellulose via the mechanism proposed by scientists at this center.[7] This mechanism involves formation of an anhydride and reaction with cellulose that restores one carboxylic acid group. If there is no third acid group available to form another anhydride, a cross-link cannot be formed. There is thermoanalytical and mass spectrometric evidence in support of this mechanism.[8]

The objectives of the current collaborative research were to measure the basic thermal characteristics of these processes with dicarboxylic acids and to compare thermal parameters and actual fabric durable press properties for agreement and possible predictability of the latter as had been reported for other reactants.[5]

EXPERIMENTAL

The materials tested in this research were all commercial-grade chemicals. Individual materials were tested neat. When two or more reactants were tested together, an aqueous solution of the mixture was prepared, as if one were preparing a fabric pad solution. An aliquot was then dried in a vacuum oven at $60°C$, stored in glass containers, and kept in a desiccator. Two unsaturated dicarboxylic acids, maleic [HOOC—CH : CH—COOH] (M) and itaconic [HOOC—C(:CH$_2$)CH$_2$—COOH] (I), formed the basis of the study. Only one catalyst was used— the one that consistently performs best with PCAs, i.e., sodium hypophosphite (NaH$_2$PO$_2 \cdot x$H$_2$O) (H). A single, free-radical initiator was studied: potassium peroxydisulfate (K$_2$S$_2$O$_8$) (K). Solutions were prepared with 9% individual acid or 4.25% M and 4.75% I (1 : 1 molar ratio between M and I) when the acids were mixed. The catalyst was in a 1 : 1 molar ratio with the acid(s) and ranged from 7.3 to 8.2% in solutions. The initiator was 1.5% on weight of the monomer or 0.135% of solutions. In Table I are the abbreviations used throughout the article for materials and the percentages of materials in the dried samples.

Table I. Material Abbreviations/Concentrations for TA Samples

M_{100}	$MK_{98.5/1.5}$	$MH_{52/48}$	$MHK_{52/47/0.8}$
I_{100}	$IK_{98.5/1.5}$	$IH_{55/45}$	$IHK_{55/45/0.8}$
$MI_{47/53}$	$MIK_{46.5/52/1.5}$	$MIH_{25/28/46}$	$MIHK_{25/28/46/0.8}$
	K_{100}	H_{100}	$HK_{98/1.7}$

Samples enclosed in the double-lined box are ones that correspond to actual fabric treatment conditions.

All thermal analyses were performed using a TA Instruments 2100 thermoanalyzer.† A differential scanning calorimetric (DSC) module 910 and a thermogravimetric (TG) module 951 were used. DSC samples were 4.5–5.5 mg; TG samples were 10–12 mg. All samples were tested under flowing nitrogen and were heated under programmed conditions. Samples were held at $60°C$ for 3 min, heated at a rate of $15°C$/min to $400°C$, and held isothermally for 3 min. All samples were tested in duplicate.

When thermal parameters were compared to actual fabric treatment data, the fabrics were specimens of 100% cotton print cloth weighing approximately 109 g/m^2 that had been desized, scoured, and bleached. The fabrics were impregnated for 5 min in the appropriate pad bath containing a nonionic polyethylene emulsion softener, Cyanalube TSI, and Triton X-100 wetting agent. Samples were then padded with two dips and two nips to give a wet pickup of 80–95% on weight of the fabric. Fabrics were dried 10 min at $100°C$ and cured at $180°C$ for 1.5 min. They were tested for durable press rating according to AATCC test method 124-1987 and for retained fabric breaking strength using ASTM-1682-64 (strip method).

RESULTS AND DISCUSSION

The DSC and TG thermograms of sodium hypophosphite (H) are overlaid in Figure 1. The DSC curve [Fig. 1(a)] contained both endothermic (downward) peaks and exothermic (upward) peaks. Endothermic reactions, in which the sample absorbs heat as it is being heated, include water loss and melting peaks. Exothermic peaks represent thermal reactions that give off heat as the sample is heated. DSC thermograms showed early multiple endothermic peaks, all apparently due to water loss or melting.

The TG data are represented by two curves. Figure 1(b) represents variations in the sample's weight as it was heated. Weight loss occurred even during
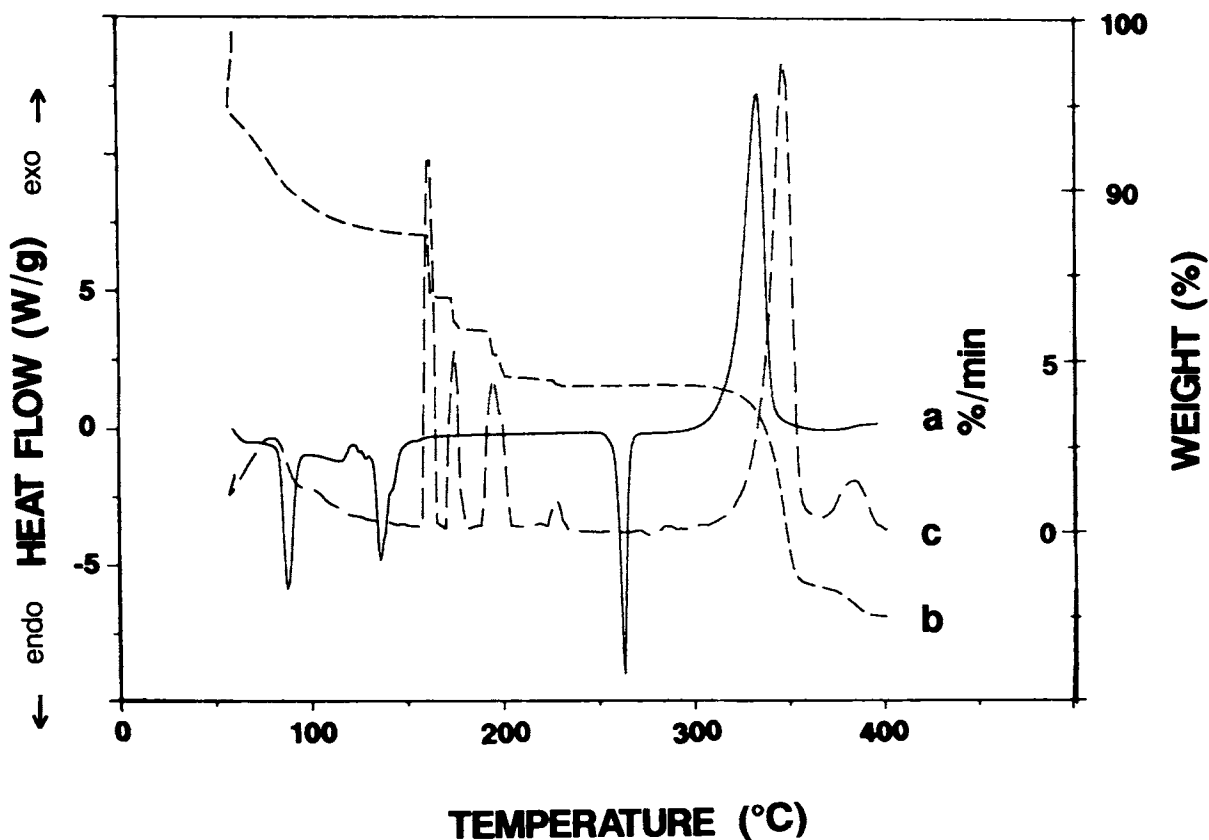
Figure 1   Overlaid thermograms of sodium hypophosphite catalyst. Curves are (a) DSC heat flow in W/g, (b) TG % weight, and (c) DTG rate of weight loss in %/min.

the initial isotherm and was found to be formed due to water loss. Gradual loss continued until we found a region of rapid, stepwise weight losses that had different patterns in different runs. This weight loss region ended at about 225°C. Hypophosphite foams and bubbles during heating and we believe this to be occurring during this period. When the foam broke, it released mass. The material was inert for a period between 250–300°C and then the final weight loss occurred above 300°C.

Differential thermogravimetric (DTG) data are plotted in Figure 1(c). The data are reported as percentage weight loss/minute. DTG peaks occur in temperature regions of rapid weight loss. DSC and DTG curves are often similar. The rapid stepwise weight loss of hypophosphite that was associated with foaming and breaking bubbles was not reflected in the DSC and DTG thermograms at the same temperatures, although the material foamed up during heating in DSC analyses also. The explanation is not certain at this time, but we believe that the temperature-range differences were due to the openness of the TG pan where bubbles could form and break easily vs. the closed (but vented) DSC

aluminum pan. These temperature differences would be lessened if we could run concurrent TG/DSC analyses.

Some members of the textile industry were concerned that sodium hypophosphite catalyst would produce phosphine in the workplace. TGA/FTIR runs were performed and confirmed that only water loss occurred in the temperature range from 60 to 300°C with sodium hypophosphite.[9] The final peak was identified in TGA/FTIR analyses to contain phosphine. Morris et al. published the TGA/FTIR results that no phosphine was found at temperatures employed by the textile industry (i.e., well below 300°C) and that the catalyst was safe under textile finishing conditions.[9]

In Figure 2 are the thermograms of the initiator, K. The simpler DSC curve [Fig. 2(a)] is on the same heat-flow scale as the catalyst was in the previous figure. There was some exothermic activity between 200 and 300°C. TG weight loss [Fig. 2(b)] occurred above 200°C, and above 300°C, the weight loss stopped. The DTG curve [Fig. 2(c)] showed that the most rapid weight loss occurred over the same temperature range as seen in the TG ther-
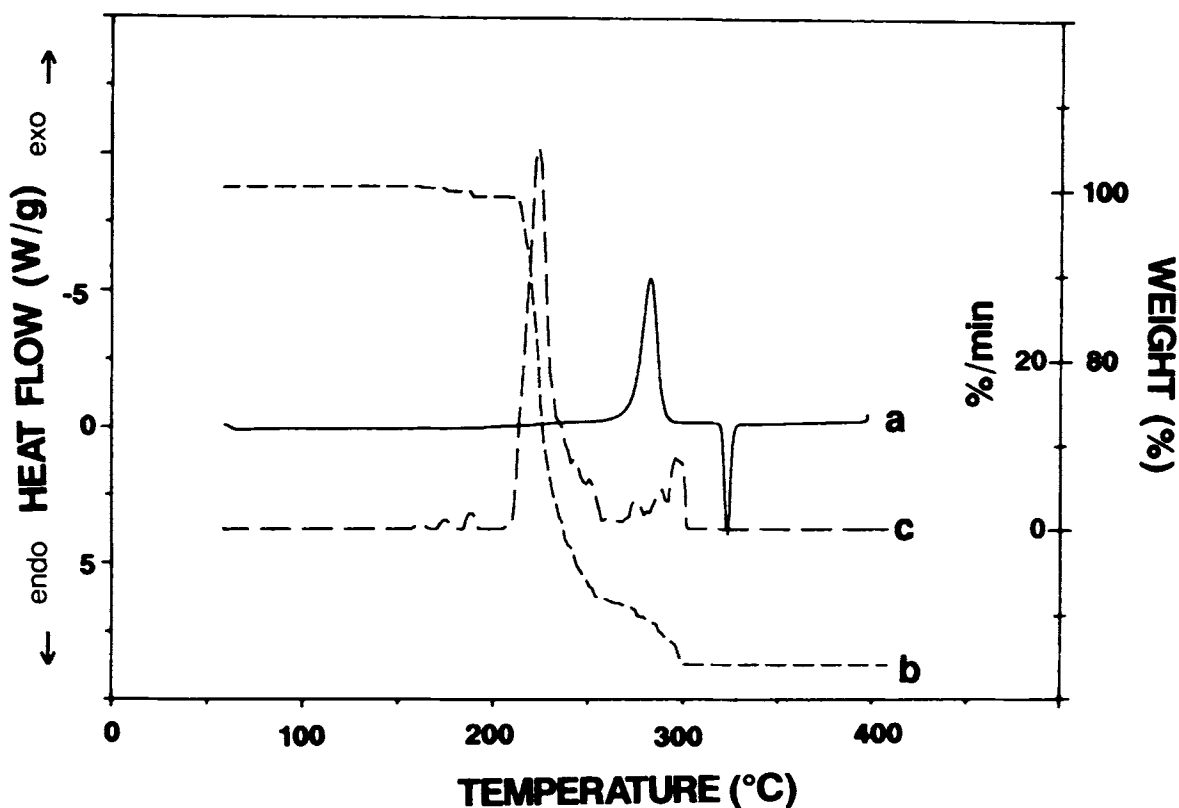
Figure 2 Overlaid thermograms of potassium peroxydisulfate initiator. Curves are (a) DSC heat flow in W/g, (b) TG % weight, and (c) DTG rate of weight loss in %/min.

mogram and peaked at about 225°C. The thermal characteristics of the initiator, shown here, were those of the pure material; however, it was present in our dried, pad solutions in smaller amounts. A major objective in this study was to learn if its relatively small presence would be measurable in thermoanalyses.

Because one of the DP finishes examined in this study involved a mixture of maleic and itaconic acids, Figure 3 contains the DSC thermograms of the two acids and their combination. Itaconic was thermally more stable than was maleic. There are differences in melting peaks of the two, and when they were mixed, a double peak occurred, at slightly lower temperatures. This was an indication that the two were not chemically reacting when mixed in solution but were each reacting like impure compounds with depressed melting points. The peak intensities for the mixtures were diminished due to the lower concentrations of each individual acid. In both acids, endothermic decomposition after melting may be attributed to dehydration and decarboxylation.

Figure 4 is an overlay of four DSC thermograms involving maleic acid. The two curves representing mixtures containing hypophosphite catalyst (MH)

and the combination of catalyst and initiator (MHK) showed that the presence of these components dramatically changed the thermal activity. Where there were endothermic peaks for the acid alone (M), there were now exothermic peaks in both samples. These two mixtures appear to thermally behave more like hypophosphite than like maleic acid. The presence of initiator (MHK) caused a further change in peak temperature (lower) and intensity (higher). The thermogram for the control mixture of acid and initiator (MK) was little different from that for maleic acid alone.

Figure 5 includes the DSC thermograms for itaconic acid and mixtures containing it. We found thermal responses with this acid in the presence of catalyst (IH) that were similar to those for maleic acid, but different responses when the initiator was added (IHK). Although there was still exothermic activity when the initiator was present because the endotherms have disappeared, the thermal activity with itaconic acid appears to be moderated, almost as if endothermic and exothermic reactions were balanced. As with maleic acid, simply adding the initiator to itaconic acid (IK) caused minimal effects.
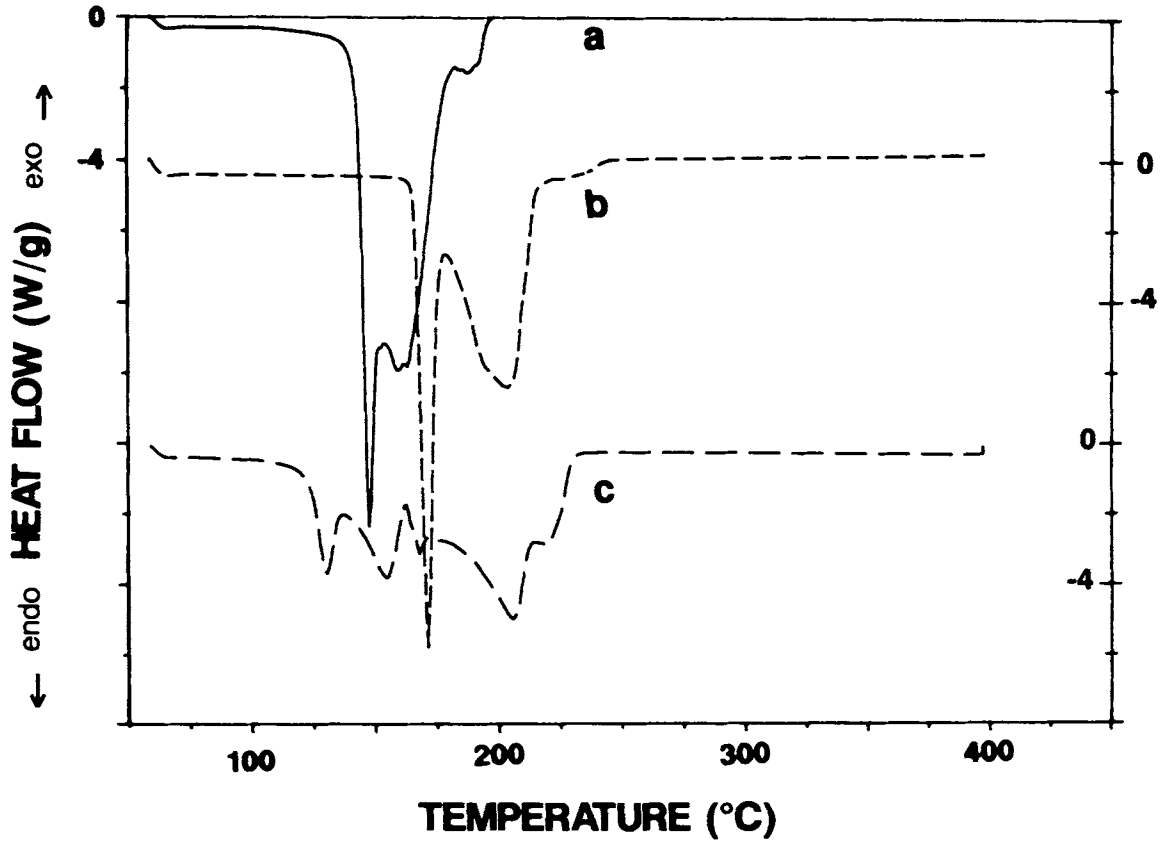
Figure 3 Comparison of DSC thermograms of acids in study on same heat-flow scale, offset. Curves are (a) maleic acid, (b) itaconic acid, and (c) maleic/itaconic acid mixture.
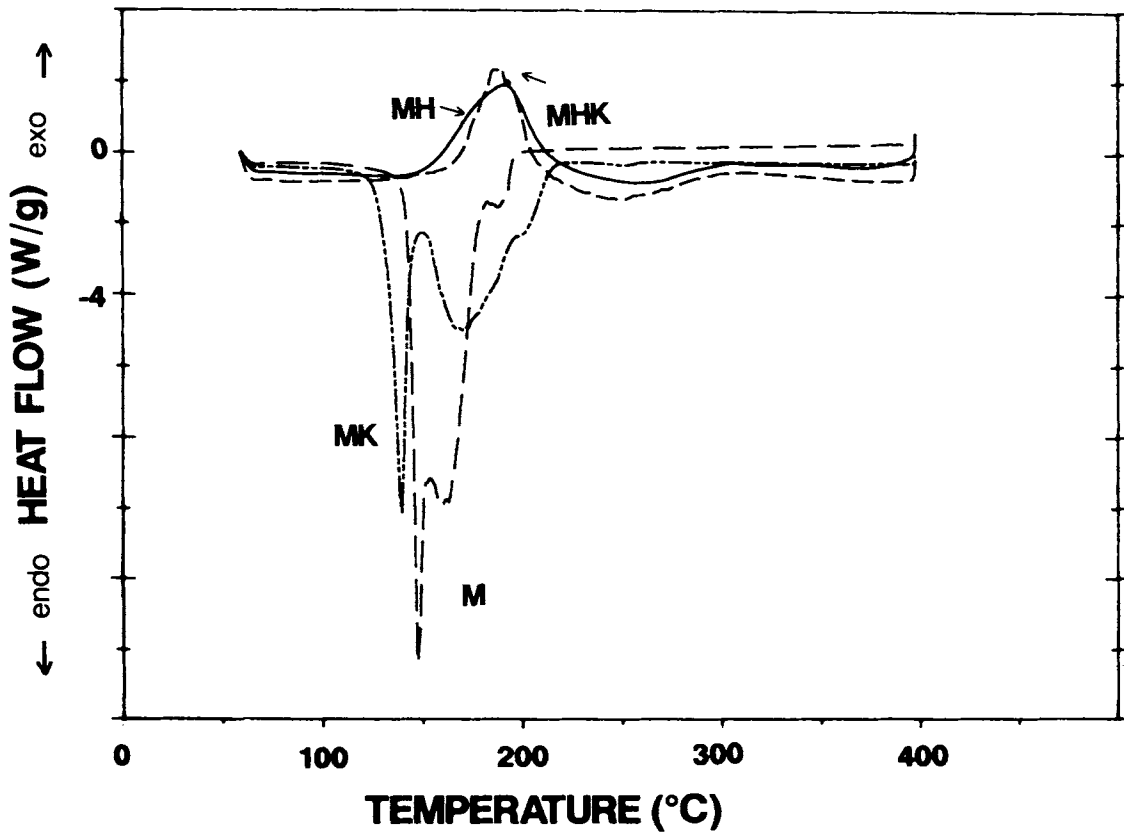

Figure 4 Comparison of DSC thermograms of four samples containing maleic acid alone and in three combinations. Abbreviations are given in Table I; heat flow axes are identical for all samples.
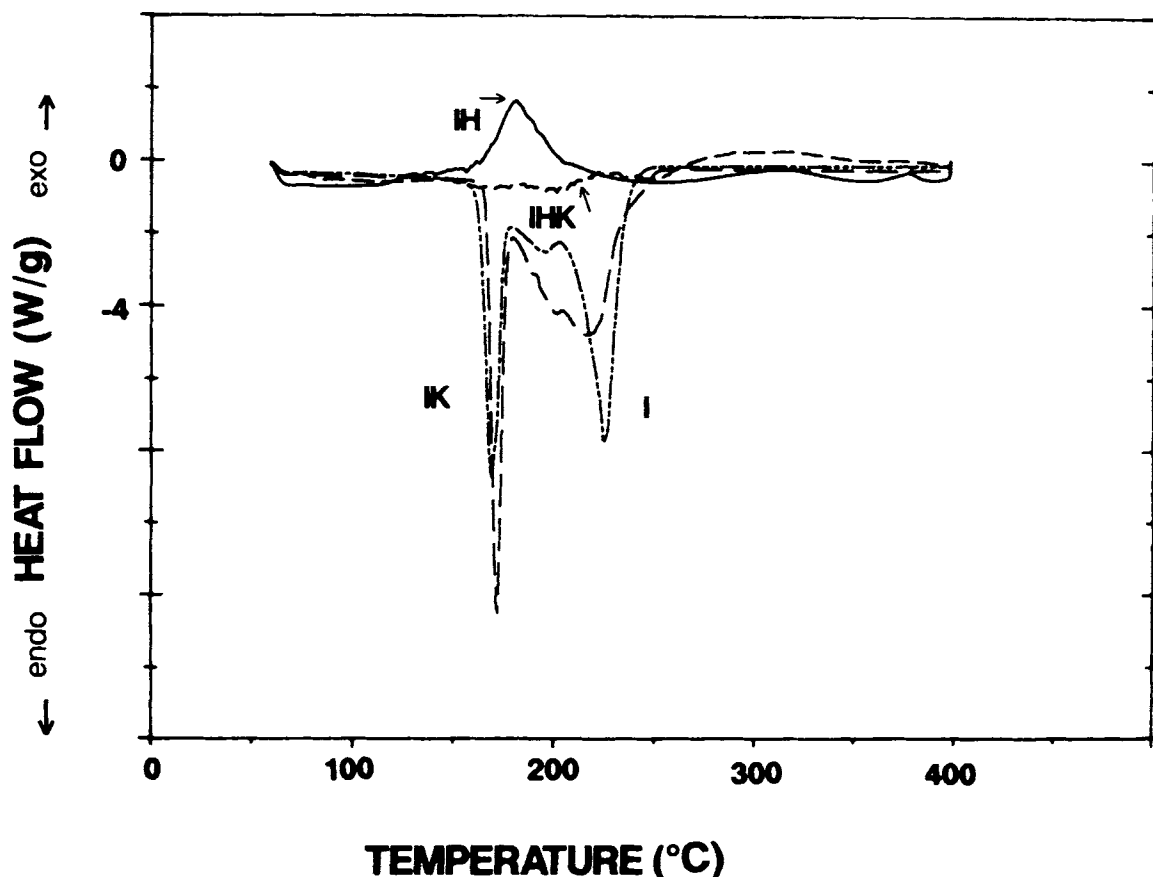
Figure 5   Comparison of DSC' thermograms of four samples containing itaconic acid alone and in three combinations. Abbreviations are given in Table I; heat flow axes are identical for all samples.

The third set of curves in Figure 6 illustrates the DSC thermal responses of the two-acid mixture. The addition of hypophosphite catalyst (MIH) generated exothermic shifts; when catalyst and initiator were both present (MIHK), there was again an exothermic peak, although it was less intense than the one observed for maleic acid/catalyst/initiator. When only the mixed acid/initiator (MIK) was present, dual melting point peaks were still evident. The DSC peaks are less intense because both acids are present in a smaller quantity.

DSC analyses enabled us to recognize changes in thermal characteristics brought about by both the catalyst (evidence showed large changes) and the free-radical initiator (which led to measurable changes despite being present only in small amounts).

TG data are very straightforward. In Figure 7(a) are the weight-loss curves for the four samples containing maleic acid. Maleic acid rapidly lost weight

and at a much lower temperature than any of the mixtures except acid plus initiator (MK). Residue production was negligible with acid (M) and acid plus initiator (MK) and very large with the other two mixtures. The corresponding DTG curves are shown in Figure 7(b). Clearly, the maximum rates of weight loss for M and MK were the two highest. There were large differences when the catalyst (MH) or catalyst plus initiator (MHK) were added.

The next series of figures compares TG percent residue (hatched bars) and DTG maximum rate of weight loss (solid bars) data averaged and shown with standard error bars. Based on past research, we want the former to be high and the latter to be low as an indication of good DP performance potential. Figure 8 contains the TG data for the controls and their combinations. Figure 8(a) includes the data for the sodium hypophosphite catalyst and the potassium peroxydisulfate initiator. The catalyst (H) produced high residue—the highest of any sin-
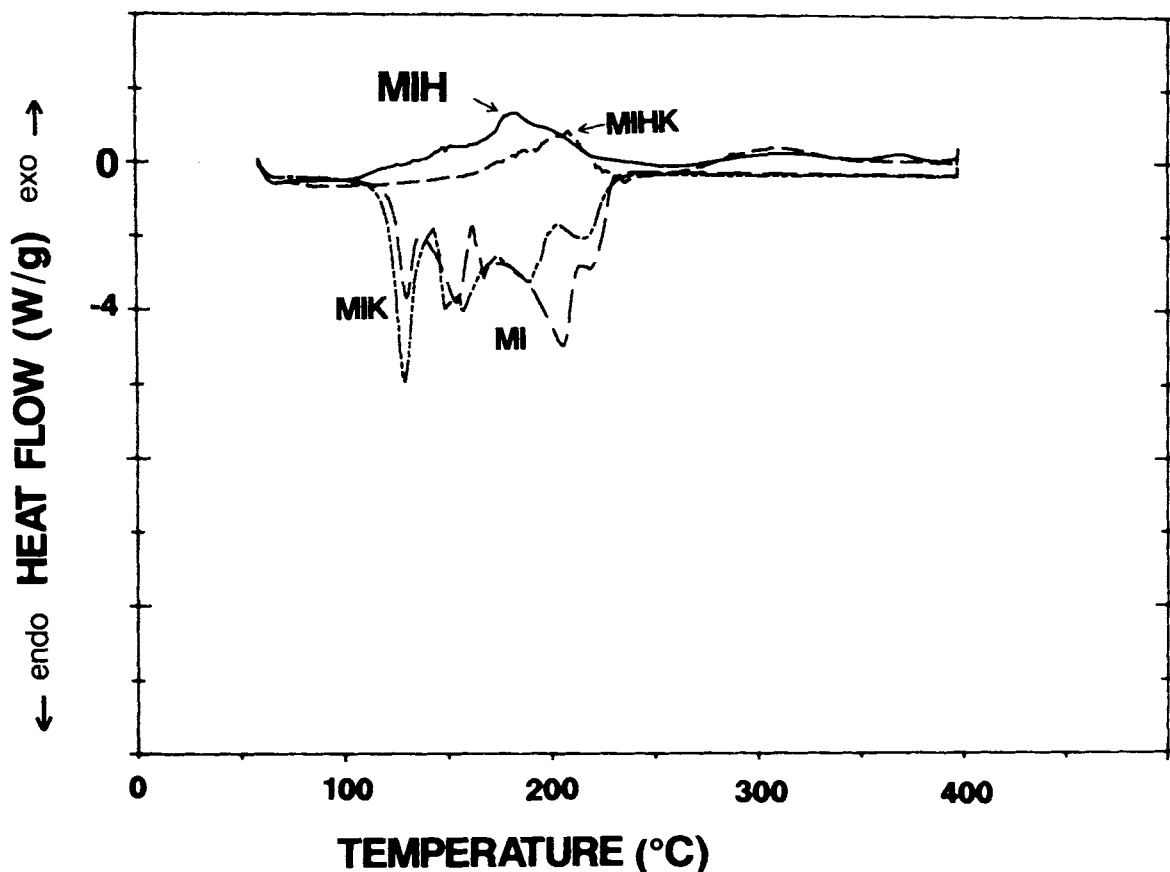
Figure 6 Comparison of DSC thermograms of four samples containing mixed maleic/
itaconic acids alone and in three combinations. Abbreviations are given in Table I; heat
flow axes are identical for all samples.

gle component in this study—and a moderate rate
of weight loss. The pure initiator (K) produced lower
residue (40%) and a rate that was more than twice
as fast as measured for pure catalyst; it was the sec-
ond highest rate in this study. The combination of
the two components (HK) was impressive, however.
The residue was the highest in the whole study and
rate was among the lowest. By thermoanalytical
standards, the combination was excellent and in-
dicated a possible synergistic effect between catalyst
and initiator.

Figure 8(b) illustrates how the acids compare
with each other. The acids alone produced no sig-
nificant residues and had moderate to high rates of
weight loss. Rate results of itaconic acid were slightly
better. Combining the two acids (MI) caused a
probable additive residue and a rate slightly better
than itaconic acid alone.

Figure 8(c) shows how the acids compare when
in the presence of initiator. Residues are slightly

higher due solely to the presence of the small quan-
tity of initiator in the sample. Maximum rates of
weight loss dropped as we compared maleic and ita-
conic to the mixed acids, MI.

Figure 9(a) presents the residue and rate data
for the samples containing maleic acid. Maleic acid
alone produced negligible residue and had the high-
est rate of weight loss of this study. The combination
of acid/catalyst (MH) was excellent, i.e., high res-
idue and a low rate of weight loss. The acid plus
initiator (MK) was a little better than was acid
alone. The combination of acid, catalyst, and initi-
ator (MHK) was slightly poorer according to residue
and rate data than was the sample with the catalyst
alone. The addition of the initiator did not seem to
help.

The same format was used to compare results for
itaconic acid [Fig. 9(b)]. The acid alone (I) had no
significant residue and a fairly high rate of weight
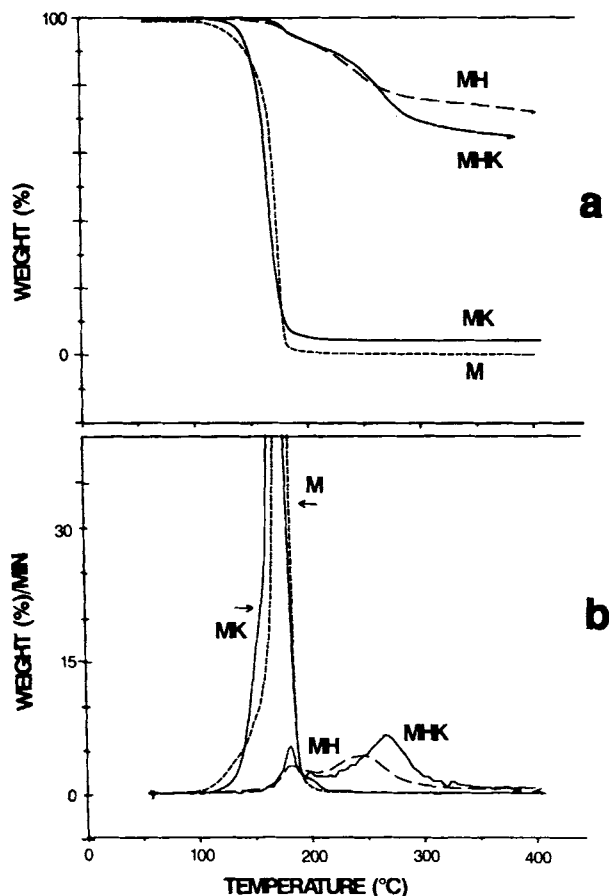loss. Again, hypophosphite (IH) caused improve-

Figure 7 Thermogravimetric data for samples containing maleic acid. Examples are (a) TG % weight curves and (b) DTG rate of weight loss curves, in percent/minute units. Abbreviations are given in Table I.

ments in these thermal parameters. The presence of initiator did not seem to help when added to itaconic acid (IK). However, the combination of all three components (IHK) was still excellent.

When both maleic and itaconic were combined (MI) [Fig. 9(c)], residue production was not significant and the rate of weight loss was modest. Catalyst (MIH) made large improvements in both parameters. The addition of initiator to the mixed acids (MIK) provided slight improvements in both thermal measurements. The formulation of all four components (MIHK) produced high residue and a low rate of weight loss. However, there was less residue than for the sample without the initiator.

Figure 10 compares acids in combinations that would be found in actual pad solutions, i.e., those containing acid and catalyst. Residue and rate data are compared in Figure 10(a); maleic (MH) appeared better than itaconic (IH) because it produced

higher residue and a lower rate of weight loss. When the two acids were combined (MIH), the results were slightly better. All three acid–catalyst combinations appear suitable based on thermal characteristics.

When we added a small amount of initiator, as shown in Figure 10(b), maleic (MHK) lost a little of its advantage; itaconic (IHK) was slightly improved, and the mixed acid sample (MIHK) was the best.

If there were no chemical interactions between the components of our mixtures, the amount of residue from the mixtures would be the total of the residues produced by each component corrected for its proportion in the mixture. These calculations were made and Figure 11 shows a comparison of the individual component contributions to an additive residue vs. the actual residue found in the mixtures. Figure 11(a) represents the data for maleic/itaconic acids with only the hypophosphite catalyst added
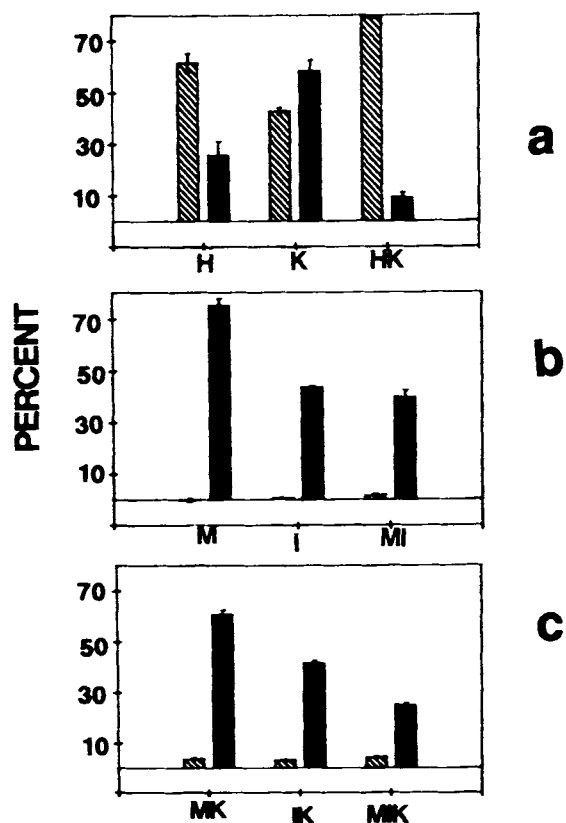

Figure 8 Comparison of averaged percent residue (hatched bars) and averaged maximum rate of weight loss data for controls: (a) catalyst and initiator; (b) acids; (c) acids/initiator. High residue and low rates of weight loss are desired. Abbreviations are given in Table I.
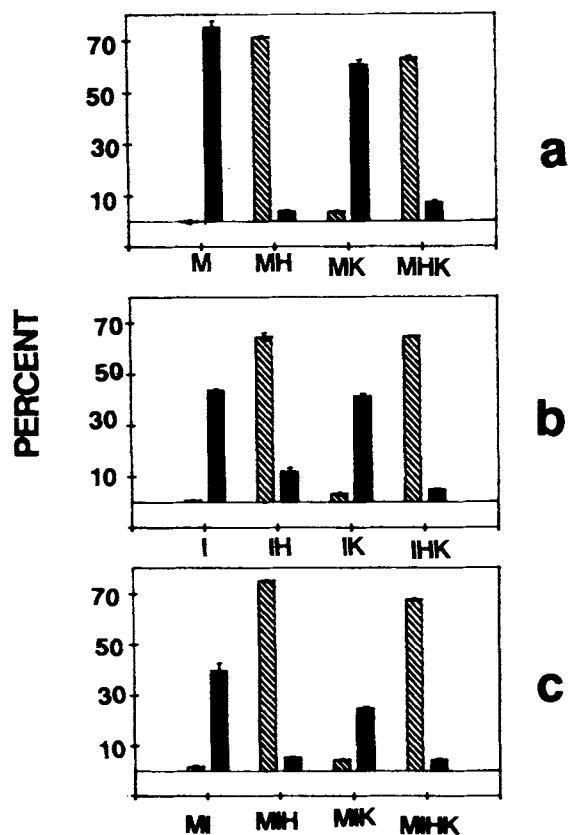
Figure 9 Comparison of averaged percent residue (hatched bars) and averaged maximum rate of weight loss data for samples (2) arranged by acid: (a) maleic; (b) itaconic; (c) mixed acids. High residue and low rates of weight loss are desired. Abbreviations are given in Table I.

Thermoanalytical parameters have been used successfully to rank catalyst effectiveness with PCAs. A predictor factor was developed to study PCA interaction with three inorganic salts of phosphorous acids.[5] 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, in examining the data from this study, we calculated a partial predictor factor with the two available TG parameters. Because good DP properties correlated with high residue and low rates, we defined the residue/rate factor as the percent residue divided by the maximum percent weight loss/minute. A higher factor should indicate a better DP finish.

The residue/rate predictor factors are presented in Figure 12. These factors are not intended as absolute numbers—they are used to compare a series of samples based on one acid at a time. Standard error bars are included to indicate that the factors are statistically different. From this figure, it is clear
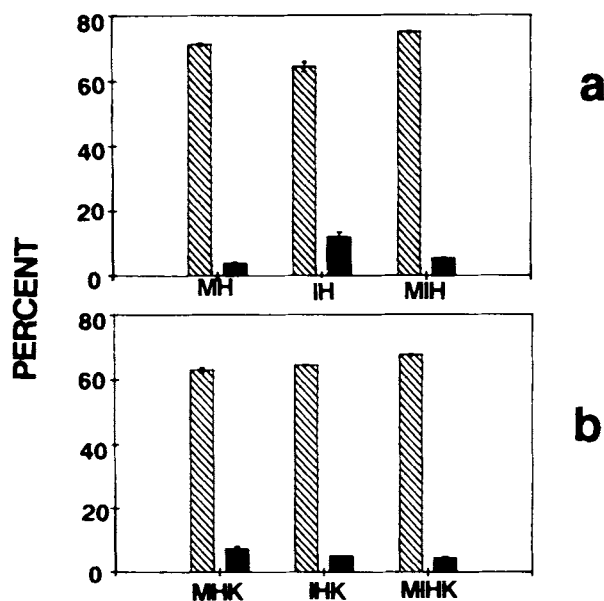
(MIH). The bar on the left represents the calculated residue data and the solid one on the right represents the actual residue found for that combination. Figure 11(b) shows similar data for the samples that also contained the initiator (MIHK). These residue data indicated that component interaction was occurring. Although not shown, similar results were seen when the individual acids were compared. All results indicated component interaction. Residue is an important parameter to measure in our study of thermoanalytical characteristics of finishing agents because high values have consistently been indicative of good agents. Higher residues are produced when mixtures have chemically reacted, such as polymerizations and condensations, and respond to heat through a more complex mechanism. With polycarboxylic acids, we are stabilizing the normal decarboxylation reaction, with its water and carbon dioxide formation; hence, the greater residue.

Figure 10 Comparison of averaged percent residue (hatched bars) and averaged maximum rate of weight loss data for samples comparable to those used in actual fabric treatments. Abbreviations are given in Table I.
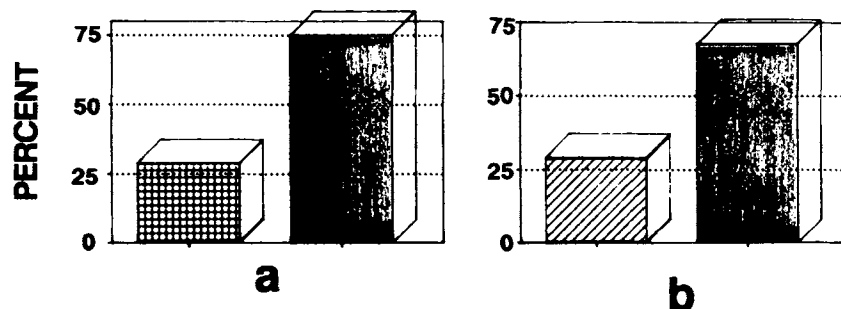
Figure 11   Illustration of reactant interaction: (a) comparison of stacked bars (left) to produce additive residue vs. actual residue found for maleic/itaconic mixture with catalyst only; (b) similar comparison with initiator present.

that only samples that contained catalyst had substantial predictor factors. Figure 12(a) illustrates the factors for samples containing maleic acid. With MH, the addition of the initiator (MHK) appeared to be detrimental. Figure 12(b) shows the itaconic acid data. With that acid, the initiator was apparently of value (IHK). The predictor factors for the
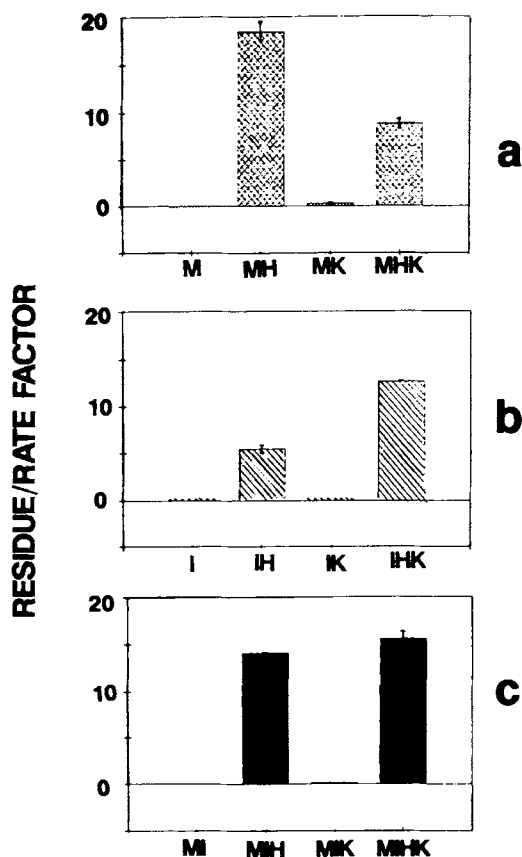

Figure 12   Residue/rate predictor factors for samples based on (a) maleic acid, (b) itaconic acid, and (c) maleic/itaconic acids mixed. Abbreviations are given in Table I.

combined acids are plotted in Figure 12(c). Again, there was improvement due to the presence of initiator (MIHK), although it appeared to exert a smaller influence than it did with itaconic acid. This was probably because it seemed to help only one of the acids.

In the study where we compared three catalysts using the TA predictor factors,[5] we successfully predicted the best catalyst—the one that produced the best balance of smooth drying appearance without excessive loss of fabric strength. As in the previous study, we compared the same two fabric properties with our TA residue/rate factors calculated in the present study. The physical properties that we chose were durable press rating and percentage retained breaking strength (BS). High values of both of these fabric parameters are desirable, so the fabric predictor was the product DP × BS. The actual durable press fabric parameters, as well as the fabric and TA predictor factors from fabrics treated with the six combinations of acids with and without initiator, are presented in Table II.

The rankings are the same for both thermal and fabric predictors within a comparable group. Our thermal predictor indicated that maleic acid samples were poorer with the initiator and this was supported by actual fabric data. Itaconic and the mixed acids were improved by the presence of initiator according to thermal parameters. Again, these rankings agreed with fabric properties. With these thermal analytical results, we have moved basic scientific research closer to the practical world of the textile-finishing chemist.

SUMMARY AND CONCLUSIONS

Using differential scanning calorimetry and thermogravimetry, we examined combinations of two

Table II   Comparison of Fabric Predictor Factors with Thermal Predictor Factors

Finish	DP Rating	% BS Retained	Fabric Predictor (DP × BS)	TA Predictor (Residue/Rate)
M/H	2.3	65	150	18.5
M/H/K	2.0	62	124	8.7
I/H	3.2	74	237	5.5
I/H/K	3.7	65	241	12.6
MI/H	2.0	74	148	14.0
MI/H/K	3.7	67	248	15.5

polycarboxylic acids, maleic and itaconic; a single catalyst, sodium hypophosphite; a free-radical initiator, potassium peroxydisulfate; and all the individual reactants as controls. We found new examples of the usefulness of thermoanalytical techniques to characterize and better understand reactants for durable press finishing of cotton textiles.

DSC thermograms of individual materials changed as the agents were mixed and chemically reacted. Addition of the catalyst led to the greatest changes. When the relatively small quantity of the initiator was added, its presence was detectable.

As in previous research, percent residue production and maximum rates of weight loss continued to be the most useful thermal parameters to examine. Experience has shown us that high residue production and low rates of weight loss correlate with good DP performance. A reactant system needs to resist thermal decomposition long enough to allow reaction with cellulose to occur. In this study, we found that the addition of the catalyst caused the greatest changes in these two thermal parameters and that the changes were in the desired directions. Although the quantity of the initiator was very small in these mixtures, its presence could be detected in TA. Interactions between mixture components in samples of acid/catalyst or acid/catalyst/initiator were evident because changes in residue production were not simply additive. They were the result of a free-radical-initiated vinyl polymerization of unsaturated polycarboxylic acids.

Thermal predictor factors based on residue and rate data were calculated and compared with a fabric predictor factor incorporating DP rating and breaking strength data. The thermal predictor agreed with actual fabric data. This research offers textile scientists a bridge between basic scientific research using sophisticated analytical techniques and the practical needs of the textile finisher.

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