

A Thermoanalytical Study of Chemical Reactions of Durable Press and Acrylic Soil Release Textile Finishing Agents

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Synopsis

Chemical reactions in systems with durable press reagents and acrylic soil release polymers are analyzed using differential scanning calorimetry. Self-condensation of N-methylol compound is the preponderant chemical reaction when a film with 70% methacrylic acid/30% ethyl acrylate copolymer and dimethylolethylene urea (DMEU) or dimethyloldihydroxyethylene urea (DMDHEU) is heated. This reaction proceeds through formation of transitory methylene ether bridges with methylene bridges as the thermodynamically favored product. An exotherm is observed under certain circumstances in DSC thermograms of films containing DMEU or DMDHEU and is attributed to a rapid shift of methylene ether to methylene bridges. Appreciable anhydride formation occurs in the polymer only above about 160–170°C. Esterification of polymer by methylol reagent probably also occurs to a limited extent, especially above about 160–170°C. Soil release of fabrics treated in a one-bath process is often unsatisfactory because polymer is embedded in a matrix of condensed N-methylol compound which restricts swelling of polymer and, therefore, its utility as a soil release agent. The limited extent of reaction between polymer and methylol compound is of minor importance compared with this adverse morphology. However, in some cases, ester formation may be responsible for significantly inferior soil release of fabrics cured at higher temperatures, for example 210°C/30 sec rather than 160°C/3 min. In such cases, polymer may be trapped chemically as well as physically in the resin matrix.

INTRODUCTION

Emulsion copolymers containing a substantial proportion of carboxylic acid, such as 70% methacrylic acid/30% ethyl acrylate, are very effective soil release top finishes for durable press textile fabrics. However, when such polymers are applied with durable press reagents in a one-bath application, soil release initially is often inferior to that obtained with a two-step application. The degree of inferiority depends upon the durable press and soil release agents used. In contrast, durability of the soil-releasing effect to laundering is better when reagents are applied in a one-bath application.

Durable press reagents are generally bifunctional or multifunctional N-methylol compounds which diffuse into cotton fibers and crosslink cellulose, thereby increasing the resilience of the fibers. However, these compounds

also self-condense to oligomeric or macromolecular products on the surface of fibers. In earlier work,¹ soil release of treated fabrics was concluded to be dependent upon the morphology of the dual-purpose finish. There is very little coalescence of polymer dispersion particles when reagents are applied in a one-bath system. Polymer is embedded in a matrix of condensed methylol compound which restricts swelling of polymer, in some cases to such an extent that its usefulness as a soil release agent is impaired. If polymer is applied alone in a separate second step, soil release initially is excellent, regardless of the durable press reagent used. In this case, polymer is at most amalgamated with durable press reagent and not trapped within it. Polymer is therefore free to swell and function efficiently as a soil-releasing agent.

Self-condensation of methylol reagent is responsible for the matrix surrounding polymer in the one-bath system. However, there may also be other chemical reactions, such as reaction between N-methylol compound and soil release polymer. Polymer might then be crosslinked and trapped chemically as well as physically in the matrix of condensed methylol reagent. For example, soil release of fabrics treated in a one-bath process and cured 210°C/30 sec is generally significantly worse than that of fabrics cured 160°C/3 min. It is questionable if morphology is substantially altered by curing. Thus, the difference in soil release may be due to differences in chemical reactivity of the reagents at different temperatures. The objective of this investigation is to determine which chemical reactions occur to a significant extent between the two principal components used in the one-bath process, soil release polymer and N-methylol compound, and, more specifically, which reactions contribute to unsatisfactory soil release of treated fabrics.

Determining which reactions occur and are significant is more difficult than might be expected. N-Methylol compounds self-condense as well as react with cotton; they may form esters or imides with the polymer; also, intra- or intermolecular anhydride formation is possible in the polymer. Analysis is complicated by the heterogeneity of the system. Polymer dispersion particles consist of tightly coiled chains with hydrogen bonds between carboxylic acid groups and hydrophobic bonds between methyl groups.² N-Methylol compounds penetrate the polymer dispersion particles to only a limited extent,¹ and therefore the majority of carboxylic acid groups are not available for reaction with N-methylol compounds. An investigation with model compounds would not be sufficiently pertinent to the present objectives. The question is not whether N-methylol compounds react with polymers containing carboxylic acid; there is good evidence that they should.³⁻⁵ The relevant question is to what extent commonly used durable press reagents, such as DMEU and DMDHEU, react with emulsion copolymers containing appreciable carboxylic acid.

A 70% MAA/30% EA emulsion copolymer; two durable press reagents, DMEU and DMDHEU; and zinc nitrate catalyst were chosen for study. Softeners and other textile modifiers were not considered. Films were

prepared in which the relative proportions of the components were equivalent to those recommended for commercial treatment of fabrics. Differential scanning calorimetry was chosen as the principal means of analysis. Heat flow in millicalories per second is recorded as a function of the programmed temperature. The area under an exothermic or endothermic peak is directly proportional to the enthalpy change of a chemical or physical transformation. Fabrics were excluded from investigation owing to difficulties involved in obtaining and interpreting thermograms of chemically treated fabrics. This exclusion is not believed to be critical because chemical reactions which interfere with soil release undoubtedly occur at the surface of fibers where soil release polymer is located and most likely do not necessarily involve reaction with cotton or polyester.

Thermogravimetric analysis (TGA) and infrared spectroscopy were used to a limited extent.

MATERIALS AND METHODS

The reagents used, procedure for casting films, and composition of films are reported elsewhere.¹ A Perkin-Elmer DSC-1 differential scanning calorimeter was used for enthalpic analysis. Film samples, 10–25 mg, were weighed into aluminum sample pans and in most cases sealed with crimped-aluminum cover discs. A programmed temperature rate of 20°C/min and a nitrogen atmosphere were used. DSC thermograms are reported schematically and are generally composites of at least three relatively reproducible curves.

Films containing DMEU or DMDHEU may expand drastically upon heating due to escaping water vapor. There were, therefore, occasional problems in thermal contact, resulting in noisy thermograms. Sealed pans often burst when vigorous chemical reactions occurred. In such cases, the thermograms in the figures appear to abruptly terminate, usually during an endotherm.

Unless otherwise specified, films were aged at room temperature for at least a week before thermograms were run. This must be taken into consideration in interpreting thermograms. For example, reactions during film formation may have reversed; formaldehyde may be lost; water may be lost or gained.

A Perkin-Elmer 421 instrument was used for infrared spectroscopy. Scans were run on film samples mulled in mineral oil. A Sartorius-Werke Elektronal 99223 instrument was used for TGA measurement. A modified Gehman apparatus was used for torsional modulus measurements; the procedure in ASTM D 1053-58T was followed, except that a heating rate of 10°C/15 min was used.

INFRARED SPECTROSCOPY

Infrared spectroscopy is a useful means of determining chemical reaction products. The limitations of this technique in satisfying the objectives of the present work are shown as follows.

A film sample of 70% MAA/30% EA copolymer, DMDHEU, and zinc nitrate cast at room temperature was heated in a forced-circulation oven for 5 min at 160°C. A film of equivalent composition cast at 80°C was placed between the plates of a Carver press at 180°C for 20 min and then pressed at 170 psi. The film was heat treated in this manner for another purpose, but a sample was used in this study to determine the chemical consequences of such severe heat treatment. Also, samples from a film cast at room temperature from low molecular weight polymethacrylic acid solution polymer (pMAA), DMEU, and magnesium chloride were cured 160°C for 2 or 10 min.

Infrared spectra were obtained from both untreated and heat-treated samples of each film. The spectra were difficult to interpret because of the many chemical structures present, and they differed with degree of heat treatment, but no significant decrease in carboxyl groups and corresponding increase in ester groups could be detected in films with MAA/EA copolymer. No ester was detected in cured films with pMAA. Furthermore, there was no evidence of imide formation between soil release polymer and N-methylol compound in any of the films. Less of this reaction product than ester would be expected.

A change of less than about 5–10% ester content would not be differentiated by IR. It can be concluded, then, that ester formation is not substantial, although it may occur to a limited extent. Esterification is limited in the case of emulsion polymer by the heterogeneity of the system because a large proportion of carboxylic acid groups are inaccessible to methylol reagent.¹ To obtain further useful information, analysis with infrared spectroscopy would have to be sensitive and quantitative as well as qualitative in nature. In general, infrared spectroscopy is limited in utility for detecting small quantitative changes. In view of the limitations, it was decided to concentrate exclusively on thermoanalytical studies.

DIFFERENTIAL SCANNING CALORIMETRY

The thermal behavior of films of the individual components is reported first, and then that of films consisting of both durable press reagent and soil release polymer together.

DMEU, DMDHEU, and Zinc Nitrate

Surprisingly, there are few thermoanalytic data in the literature for durable press reagents and catalysts. Miller has done the majority of the pertinent work using differential thermal analysis (DTA) and TGA to study trimethylol melamine⁶ and DMEU⁷ with zinc nitrate. In the present work, DSC thermograms of films cast at room temperature consisting of DMDHEU, with or without zinc nitrate, or DMEU without zinc nitrate, are similar to DTA thermograms reported by Miller for DMEU: a broad endotherm beginning at about 100°C, accelerating at about 130°C, and peaking at about 150–160°C. A limited number of TGA experiments

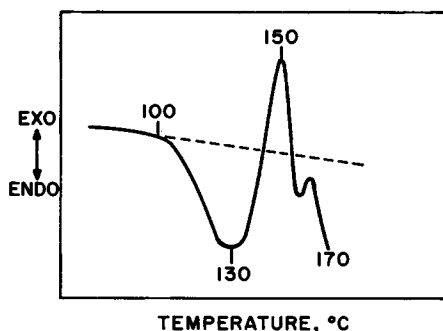


Fig. 1. DSC thermogram of DMDHEU and zinc nitrate, film cast at 50°C.

were run at 4°C/min under vacuum. In the presence of zinc nitrate, DMDHEU begins to lose weight at about 60°C, and has lost about 10% at 75°C and about 30% at 225°C. Without zinc nitrate, significant weight loss does not begin until 100°C is reached, but total weight loss is about the same.

A DSC thermogram (Fig. 1) of DMDHEU and zinc nitrate cast at 50°C begins in a similar fashion to that of samples prepared at room temperature; but at about 130°C, an exothermic drift begins, culminating in a sharp exothermic peak at about 150°C, and immediately followed by a series of sharp endotherms. The endotherm beginning at 100°C was very reproducible, but the exotherm was variable. It was sometimes broad, sometimes sharp, and peaked somewhere in a 20–30°C temperature interval. To investigate the exothermic peak, programmed heating was stopped and samples held at a fixed temperature. At fixed temperatures below 130°C, only endotherms appeared. At a fixed temperature of 130°C or above, weak exotherms were observed after about a minute and a half, superimposed upon a general endothermic trend. To investigate further the exothermic peak, DMDHEU samples without zinc nitrate cast at room temperature were heated to 130°C at the programmed rate, cooled to 50°C, and then reheated. A sharp exotherm appeared at about 135°C, then a sharp endotherm. The sample was then held at 140°C; there was again a general endothermic trend with a superimposed exotherm. It is apparent, then, that the appearance and intensity of exotherms in films of DMDHEU and zinc nitrate are dependent upon the thermal history of the samples and not necessarily upon the presence of zinc nitrate.

The temperature which must be reached to observe exotherms, 130°C, is significant in durable press finishing. Bille and Conrad⁸ plotted conditioned crease recovery angle versus cure temperature (5 min) for a series of fabrics treated with DMEU or DMDHEU. The curve for DMEU increases linearly with increasing cure temperature and levels off at about 130°C. The curve for DMDHEU has nearly zero slope until about 130°C, where it abruptly begins to rise, and thereafter rises rapidly with increasing cure temperature. This would seem to indicate that below 130°C, DMD-

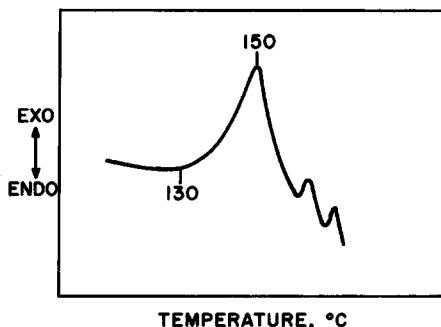


Fig. 2. DSC thermogram of DMEU and zinc nitrate, film cast at 23° or 50°C.

HEU condenses principally with itself rather than with cotton, while DMEU reacts more with cotton.

A film of DMEU and zinc nitrate cast at 50°C softened with aging.¹ Thermograms were run after it had begun to soften. There is no significant difference between these thermograms (Fig. 2) and those for a film cast at room temperature. The heated film apparently reverts to a structure similar to that of the film cast at room temperature. The first endotherm is absent, which suggests chemical reaction prior to thermal analysis.

70% MAA/30% EA Copolymer

A glass transition in the interval 120–150°C is evident in DSC thermograms (Fig. 3) of films cast at 80°C. This is somewhat lower than that evident in the torsional modulus–temperature curve (Fig. 4). The transition occurs over a temperature interval in which fabric finishes are commonly cured. The glass transition is much weaker in thermograms of films cast at room temperature (not shown). Also in films cast at room temperature, there is an apparent vitrification transition between 80°C and 100°C, which is most likely due to sintering of poorly coalesced polymer dispersion particles. These results with films of polymer cast at different temperatures suggest that the glass transition is related to motion of side groups rather than the backbone chain. Since interchain carboxyl groups

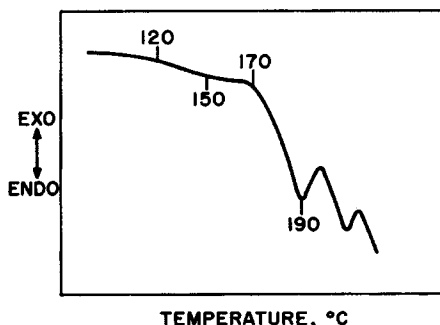


Fig. 3. DSC thermogram of 70% MAA/30% EA copolymer, film cast at 80°C.

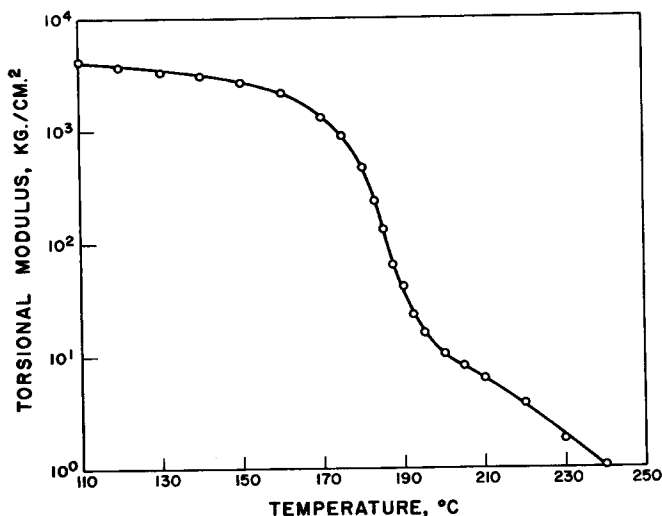


Fig. 4. Ten-second torsional modulus vs. temperature, 70% MAA/30% EA copolymer film cast at 80°C.

dimerize through hydrogen bonds,^{9,10} the glass transition is most likely a response to relaxation of these bonds. This type of transition is in accord with Andrews' thermodynamic conception of the glass transition as a thermal breakdown of intermolecular secondary bonds in the solid state.¹¹

There are no first-order transitions below 160°C in films cast at 80°C or room temperature. Above about 160–170°C, there is a series of endotherms, presumably associated with degradation of the polymer. Grant and Grassie¹² used infrared spectroscopy to investigate the thermal degradation of polymethacrylic acid at temperatures near 200°C. They concluded that the principal chemical reaction is intramolecular anhydride formation with little intermolecular reaction or chain splitting. Some chain splitting might be expected in MAA/EA copolymer since the polymer contains ethyl acrylate.

A polymer film was heated at 40°C/min under vacuum to 330°C in a thermobalance. There was a gradual weight loss which totaled 23% of the sample at 330°C. Grant and Grassie reported 10–20% weight loss on heating predried pMAA under vacuum at 200°C until the production of volatile materials ceased.

The rubbery-flow portion of the 70% MAA/30% EA copolymer torsional modulus curve has a significantly negative slope, indicating an absence of crosslinking. This is in agreement with the conclusion of Grant and Grassie. There is, therefore, no apparent evidence for appreciable crosslinking through primary bonds in films of 70% MAA/30% EA copolymer, whether heat treated or not. This is not to deny strong secondary bonding, however, particularly interchain dimerization of carboxyl groups.

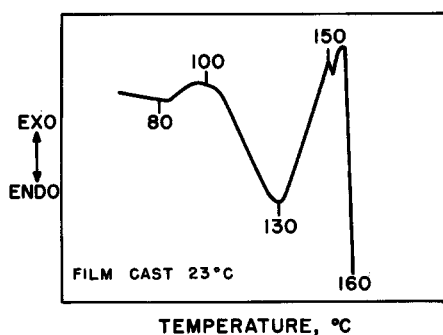
On the basis of thermoanalytic and torsional modulus data, it is concluded that the endotherms observed in films of 70% MAA/30% EA co-

polymer above 170°C are representative of intramolecular anhydride formation reactions equivalent to those discussed by Grant and Grassie.

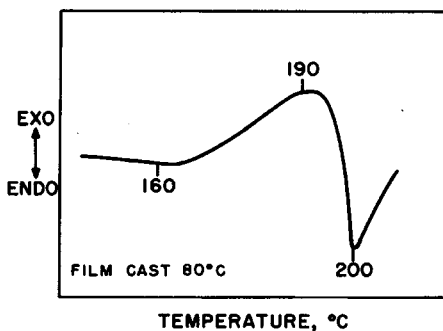
70% MAA/30% EA Copolymer and DMDHEU

In films cast at room temperature, an endotherm begins at 100°C (Fig. 5), much the same as with DMDHEU alone. At about 130°C, an exothermic drift begins, resulting in two or three exothermic peaks in the 140–160°C range. These peaks are immediately followed by a sharp endotherm at 160°C. Samples could not be run beyond about 160°C. Thus, films of DMDHEU cast at room temperature exhibit an exotherm with polymer present, but not without. It is likely that the acidity of the polymer catalyzes self-condensation of DMDHEU.

A vitrification transition is evident in the interval 80–100°C, similar to that observed in thermograms of films of polymer alone cast at room temperature. It is again probably associated with sintering of dispersion particles and is further evidence that DMDHEU does not mix well with polymer in films cast at room temperature.¹ The transition is not observed in films of equivalent composition cast at 80°C, because DMDHEU hardened in film formation blocks sintering of polymer dispersion particles.



(a)



(b)

Fig. 5. DSC thermograms of 70% MAA/30% EA copolymer and DMDHEU.

The initial endotherm is absent in films cast at 80°C (Fig. 5). A broad exotherm begins at about 160°C, immediately followed by an endotherm peaking at about 200°C. These samples were run as high as 270°C without cells bursting. Weight loss below 200°C is less than 10%, in contrast to polymer alone, where it is at least 10%. There is undoubtedly chemical reaction in film formation. There is also reaction during thermal analysis of a different nature than that observed in films of the same materials cast at room temperature or in films of either component alone.

70% MAA/30% EA Copolymer, DMDHEU, and Zinc Nitrate

The thermogram of film cast at room temperature is similar to that without zinc nitrate, except that the exotherm begins about 20° higher in temperature (Fig. 6). The thermogram of film cast at 80°C is similar to that without catalyst, except that the exotherm begins about 20–30° lower in temperature. If these temperature differences are significant, they are most likely related to the influence of catalyst on methylolamide self-condensation reactions.

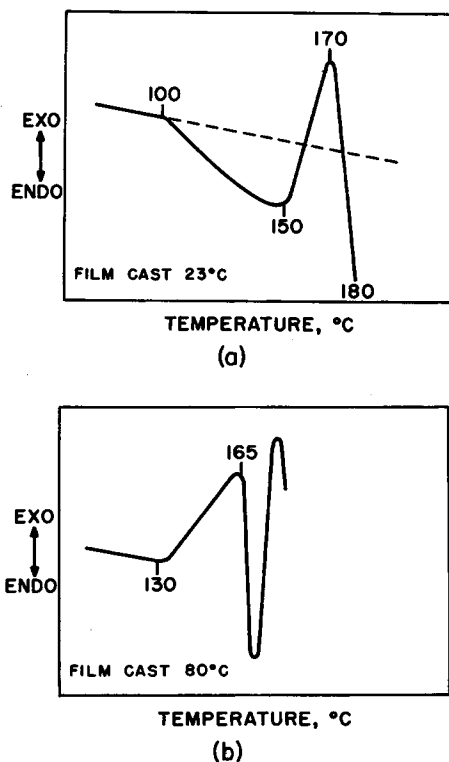


Fig. 6. DSC thermograms of 70% MAA/30% EA copolymer, DMDHEU, and zinc nitrate.

70% MAA/30% EA Copolymer and DMEU

In films cast at room temperature, the endotherm beginning at 100°C is much weaker than that with similar films containing DMDHEU (Fig. 7). This indicates a greater tendency for DMEU to react during film formation. There are no exotherms. The vitrification transition in the 80–100°C interval observed with similar films containing DMDHEU is

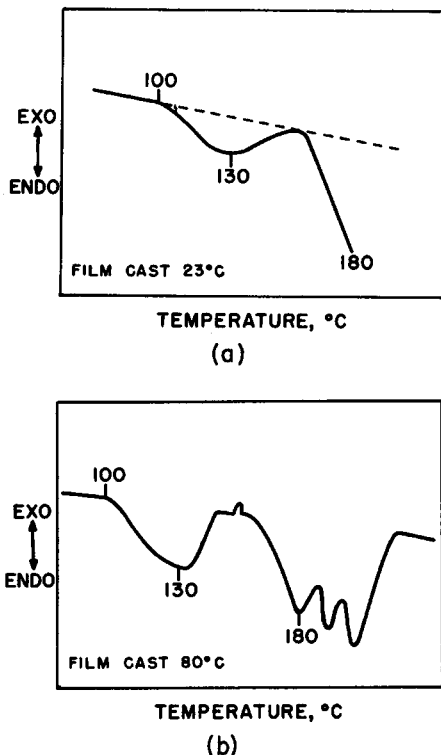


Fig. 7. DSC thermograms of 70% MAA/30% EA copolymer and DMEU.

absent. This is further evidence for better mixing of DMEU than DMDHEU with polymer.¹ With film cast at 80°C, the endotherm beginning at 100°C is again weak (Fig. 7). There is a questionable slight exotherm shortly before 180°C. A series of sharp endotherms similar to those with polymer alone begins at about 170°C. These samples were run well beyond 200°C without cells bursting.

70% MAA/30% EA Copolymer, DMEU, and Zinc Nitrate

With film cast at room temperature, there is an exotherm beginning at 130°C that is absent when zinc nitrate is omitted (Fig. 8). It is followed by a sharp endotherm at about 140°C. Since these events occur well below

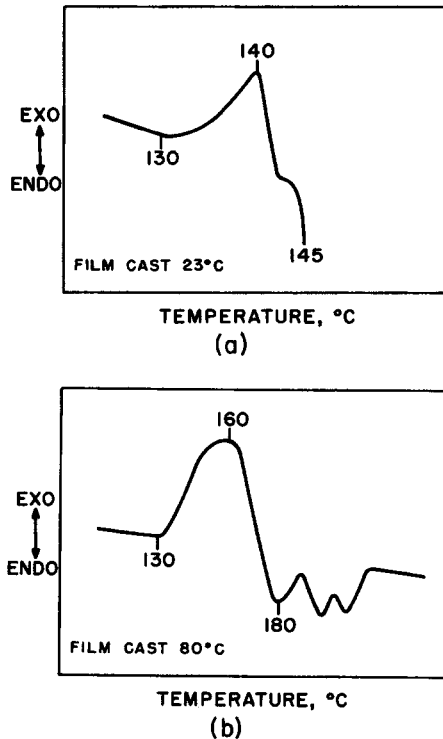


Fig. 8. DSC thermograms of 70% MAA/30% EA copolymer, DMEU, and zinc nitrate.

160°C, they are probably associated with self-condensation of DMEU. There is an exotherm beginning at 130°C in films cast at 80°C, but it is much broader. Above 160°C, variable results were obtained in four different samples. In one, there was no endotherm following the exotherm; the curve returned to the baseline. In another, there was a single, relatively broad endotherm. In two others, there was a series of two or three sharp endotherms. Marginal chemical reaction of polymer and DMEU can be implied from these data.

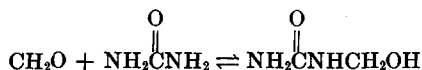
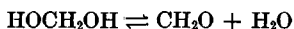
INTERPRETATION OF THERMOANALYTICAL RESULTS

Self-Condensation of N-Methylol Compounds

DSC thermograms of durable press reagents alone or with catalyst are discussed in this section. The exotherms appearing in the vicinity of 130°C are of particular interest because an explanation of their existence has not appeared in the literature. However, a general analysis of the condensation reactions of N-methylol reagents must be presented first.

It is of interest to consider the kinetics and thermodynamics of methylation of amides and the condensation of the products. Landquist¹³ re-

ported kinetically and thermodynamically consistent data for the methylation of urea, 20–40°C, pH 6.7–10:



$$\Delta H = E_f - E_r = 15.4 - 20.4 \text{ kcal/mole} = -5 \text{ kcal/mole}$$

where E_f and E_r are the activation energies for the forward and reverse reactions and ΔH is the heat of reaction. Results are equivalent for the dimethylolated product. Steele¹⁴ reported 21.2 and 20.2 kcal/mole activation energy for hydrolysis of dimethylolurea (DMU) from cotton in 0.05N HCl. It is not unreasonable to assume that activation energies are similar for self-condensation of DMU and, in general, for self-condensation of most N-methylol compounds. Thus, heats of reactions are slightly exothermic. However, if water is vaporized, an additional +10.5 kcal/mole must be considered. Overall, then, the observed ΔH is about +5.5 kcal/mole (endothermic). The heat of vaporization of water is greater than the heat of reaction and dominates the observed enthalpy change. Thus, in thermograms of DMEU and DMDHEU, the endotherms beginning at 100°C are mainly a consequence of vaporization of formaldehyde and water. However, the subsequent exotherms may be a consequence of the actual condensation reactions.

Smets and Borzee¹⁵ reported the following activation energies for condensation of monomethylol and dimethylolurea: 21 kcal/mole in neutral solution, 8–10 kcal/mole in pH 3–5 solution. Reaction rate data were based upon titration of formaldehyde. Saxon and Lestienne⁵ reported an activation energy of 14.5 kcal/mole for self-condensation of hexakis(methoxymethyl)melamine. Capped methylol compounds are less reactive, so the activation energy is higher. Considering the literature data, then, it is reasonable to assume activation energies of less than 10 kcal/mole for self-condensation of DMEU and DMDHEU in acidic media to methylene ether or methylene bridged structures.

There is little doubt that N-methylol compounds are capable of self-condensing to higher molecular weight structures, but the resultant chemical structure of these products is seldom fully elucidated. In acid catalyzed reaction of DMU, only methylene bridges are formed.¹⁴ However, methylene ether as well as methylene bridges are believed to form in condensation of methylolated imidazolidinone-type reagents, the proportion of the former decreasing with harder cures. The importance of the methylene ether bridge in the present investigation is developed in the following analysis.

Assume for simplicity of analysis that the action of a latent acid catalyst (zinc nitrate) can be interpreted in terms of the presence of protons and that the crosslinking agents are fully methylolated. Upon heating, DMEU or

methylene bridge is the more thermodynamically stable compound. As reaction progresses, methylene ether bridges are rapidly broken and few eventually remain. Further reaction takes place only through loss of more water and formaldehyde. At this point, there is sufficient amide present so that essentially only methylene bridges are formed. The reaction now appears to be endothermic again due to vaporization of formaldehyde and water.

The experimental results indicate that addition of zinc nitrate to DMEU or DMDHEU, or heat treatment of DMDHEU prior to thermal analysis, results in either the existence of an exotherm or a more intense exotherm. Considering the preceding analysis, this is explained by the formation of methylene ether bridges during film formation or in subsequent heat treatment. Zinc nitrate apparently promotes their formation and subsequent transfer to methylene bridges.

Reaction of 70% MAA/30% EA Copolymer and N-Methylol Compounds

A critical question to be confronted in this study is whether there is chemical reaction between soil release polymer and durable press reagent. If not, a thermogram of polymer, N-methylol compound, and zinc nitrate should be a linear combination of the thermograms of the individual components. Before interpreting thermograms of polymer and N-methylol reagents, however, it is advantageous to specify which chemical reactions might take place between the two species and also to consider their thermodynamics and kinetics.

Saxon and Lestienne⁵ interpreted the crosslinking of methacrylic acid/methyl methacrylate copolymers with hexakis(methoxymethyl)melamine (HMM) in terms of ester linkages. Polymers containing carboxylic acid groups were shown to be less reactive than those with hydroxyl groups. There was no evidence of HMM reaction with poly(methyl methacrylate) control polymer. Ester formation is believed to be the most likely reaction other than self-condensation of the N-methylol compound in the present study. Imide formation is possible, but less likely. For simplicity, imide formation will not be considered, and the discussion will be confined to the possibilities of ester formation.

Enthalpy change for esterification reactions is generally¹⁶ of the order of ± 1 kcal/mole, nearly isenthalpic. For example, for reaction of ethyl alcohol and acetic acid at 25°C, $\Delta H = +1.8$ kcal/mole and $\Delta G = +0.4$ kcal/mole, calculated from Denbigh's data.¹⁷ If water is vaporized, its heat of vaporization must be added to obtain the total enthalpy change, $\Delta H = +12.3$ kcal/mole. Thus, enthalpy changes in esterification reactions in which water is vaporized are dominated by the heat of vaporization of water. A similar situation was shown earlier to exist for self-condensation of N-methylol reagents. Discrimination between self-condensation and esterification reactions based upon enthalpy changes is therefore more difficult to analyze than might be expected because enthalpy changes are similar.

Flory¹⁸ and Fairclough and Hinshelwood¹⁹ reported activation energies of 11.5–13 and 15 kcal/mole, respectively, for esterification of primary acids. With 70% MAA/30% EA copolymer, acid groups are in a secondary position and more restricted in mobility. Substituents on the β -carbon of an aliphatic carboxylic acid significantly hinder esterification reactions,²⁰ and therefore the methyl group of MAA would be expected to sterically interfere with chemical reaction. The activation energy for esterification of soil release polymer with methylolamides should be higher, therefore, probably in the 10–20 kcal/mole range. Higher activation energy may be needed for reaction with DMDHEU than DMEU. It was assumed earlier that activation energy for self-condensation of DMEU or DMDHEU is less than 10 kcal/mole. Thus, self-condensation is probably the kinetically favored reaction, especially at low temperatures. Since the system is heterogeneous, the self-condensation reaction should be even more favorable than predicted by the assumed activation energies.

It was concluded earlier that anhydride formation takes place in polymer above 160°C. Grant and Grassie¹² reported an activation energy of $37 \pm$

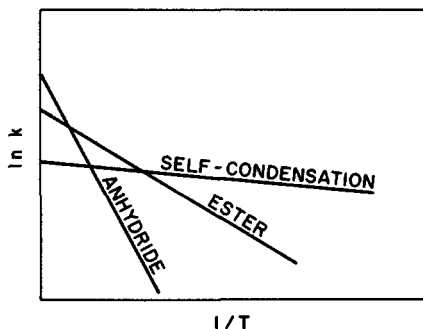


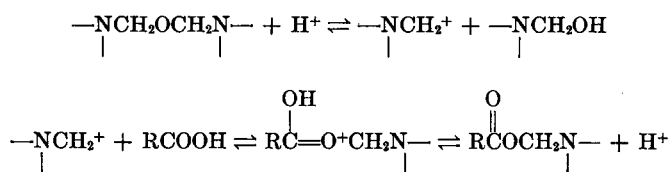
Fig. 9. Hypothetical intersections of three Arrhenius rate-equation curves.

3 kcal/mole for anhydride formation in pMAA. The activation energy for thermal degradation of polyacrylates is generally of the order of 30–50 kcal/mole.²¹ Thus, it can be reasonably concluded that more activation energy is needed for anhydride formation or chain splitting than esterification of polymer with N-methylol compound.

Reasoning thus far concerning reaction selectivity has been based upon a consideration of activation energies only; frequency factors were neglected. In comparing two reactions, if the frequency factor of the reaction with lower E_a is greater than that with higher E_a , then the reaction with lower E_a is more favorable at all temperatures. However, if the opposite is true, the rate-temperature curves intersect, and above a certain temperature the reaction with higher E_a becomes more favorable. Thus, if curves intersect as in Figure 9, ester formation would be more favorable at moderately high temperatures than self-condensation of N-methylol reagents, but less favorable than anhydride formation.

It can be inferred from literature data that the frequency factor for anhydride formation in acrylic acid²² is greater than that for esterification of primary acids,¹⁹ which is in turn greater than that for self-condensation of dimethylolurea.¹³⁻¹⁵ Arrhenius curves may therefore intersect as shown in Figure 9. However, the frequency factor is much more sensitive than activation energy to reaction conditions and the specific reactants used. There are not sufficient data available to predict with certainty if or how the curves intersect. Nevertheless, it can be reasonably predicted that ester formation becomes more favorable relative to self-condensation of methylol reagents with increasing temperature and that it is quite probable that some esterification of polymer takes place, especially above 160–170°C.

DSC thermograms of films containing polymer and a N-methylol compound, with or without zinc nitrate, are now considered. There is no obvious indication in the thermograms that N-methylol compounds necessarily react with polymer below 160°C. However, exotherms may be a manifestation of esterification of polymer as well as the formation of methylene bridges in N-methylol compounds. Carbonium ions generated from decomposition of unstable methylene ether bridges may become involved in esterification reaction with polymer as well:



The latter reaction, like that for methylene bridge formation, is believed to be exothermic and could contribute to the exotherm observed in thermograms. Esterification can also proceed through protonation of a carboxyl group, but this reaction involves loss of water directly and should therefore be endothermic.

Portions of thermograms above 160°C are of particular interest because the crude estimates of reaction rate parameters indicate that esterification becomes more favorable at high temperatures. Also, the polymer is above its glass transition, so carboxyl groups should be more reactive. Interpretation is difficult though, because above 160°C, condensation of N-methylol compound, anhydride formation, and esterification are endothermic due to volatilization of water. Nevertheless, there are distinct differences in some cases between films with polymer alone and those with N-methylol compound also. For example, in Figure 5, the exotherm in the film of polymer and DMDHEU cast at 80°C persists beyond 190°C before an endotherm begins. Also, with polymer, DMEU, and zinc nitrate cast at 80°C, variable results were obtained above 160°C with each sample. In one curve, there is no endotherm in the vicinity of 200°C, indicating an absence of anhydride formation; it is likely that carboxyl groups were involved in another reaction beforehand, presumably ester formation.

In conclusion, it can be surmised from examination of DSC thermograms that there is reaction other than self-condensation of N-methylol compound and anhydride formation in the polymer. This additional reaction is believed to be ester formation between polymer and N-methylol compound. It is emphasized that the extent of this reaction is much less than that of self-condensation of N-methylol reagent.

RELEVANCE OF RESULTS TO SOIL RELEASE OF TREATED FABRICS CURED AT TEMPERATURES NEAR 200°C

It has been concluded from thermal analysis that self-condensation of N-methylol compound is the preponderant chemical reaction when films of polymer and DMEU or DMDHEU are heated. Esterification of polymer is believed to have little effect on soil release when fabrics are cured 160°C/3 min. However, ester formation becomes kinetically more favorable with increasing temperature and may be very important when fabrics are cured at temperatures higher than 160–170°C. Soil release of fabrics treated in a one-bath process and cured 210°C/30 sec is often significantly worse than that of fabrics cured 160°C/3 min. If fabrics are treated with polymer but not with durable press reagent, and cured at 160° or 210°C, soil release is excellent in each case. The difference for fabrics treated in the one-bath process could be due to more self-condensation of methylol reagent at the higher temperature. This would result in more insoluble matrix which restricts swelling of polymer and therefore its effectiveness as a soil release finish. The following analysis shows that this conclusion is questionable and that esterification of polymer by methylol compound may be responsible for inferior soil release of fabrics cured at 210°C.

Assume that one reaction, or multiple reactions with nearly equivalent activation energies, is responsible for the difference in soil release of fabrics cured at 160° and 210°C. Assume also that the degree of conversion, and therefore soil release, is equivalent in fabrics cured 160°C/3 min and 210°C/30 sec. Since chemical reaction rate and temperature are related through the Arrhenius rate expression, the activation energy can be estimated from the ratio of the rate expressions

$$\frac{t(T_1)}{t(T_2)} = \exp \left[\frac{-E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

where t = time of cure, T = cure temperature (absolute), and E_a = activation energy. Substituting times and temperatures, E_a is calculated to be 17 kcal/mole. In general, though, soil release is worse with the 210° cure. For such treatments the estimate of the activation energy is too low, the true E_a being higher to some unknown degree depending upon the specific crosslinking agent, catalyst, and soil release polymer used. The order of magnitude of such an activation energy is more characteristic of esterification reactions than self-condensation of N-methylol compounds. In other words, the difference in soil release is too temperature sensitive to be attrib-

uted simply to more self-condensation of N-methylol reagent. Thus, it would seem that ester formation may be at least partly responsible for the sometimes deleterious effect of high-temperature cures on soil release of fabrics treated in a one-bath process. Soil release of fabrics cured 210°C/30 sec is worse to some degree with various combinations of N-methylol compounds and acrylic soil release polymers which have not been considered in this article (e.g., N,N-dimethylolalkyl carbamates, copolymers with less MAA). The generality of the effect suggest the influence of a common determinant, which is believed to be ester formation.

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