

Comparisons of the Cure of Phenol-Formaldehyde Novolac and Resol Systems by Differential Scanning Calorimetry

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Synopsis

Comparisons were made of differential scanning-calorimetric (DSC) thermograms of both liquid and powdered commercial phenol-formaldehyde resins. By a combination of the results from analyses under a variety of conditions, such as ambient pressure, high pressure, using freeze-dried samples, and also by direct observation of the resin-curing process in wood-veneer assemblies, the curing reactions of phenol-formaldehyde resins were found to differ for resol and novolac systems. At a heating rate of 10°C/min, the resol resin showed endothermic curing reactions at temperatures of about 150°C, while the novolac-type resin showed an exothermic peak maximum at about 160°C. Results are presented to show how DSC can be used to differentiate between a resol and novolac system.

INTRODUCTION

Thermal analysis studies of thermosetting resins have been reported extensively in the literature in recent years.¹⁻⁷ The availability of reliable instrumentation and the realization that this thermal information provides an understanding of the curing properties and thermal stability of these resins are major reasons for the popularity of this technique. Unfortunately, in the case of phenol-formaldehyde (PF) resins, many conflicting results have been presented in the literature.⁴⁻⁷

These inconsistencies have been discussed in detail in a previous article.¹ Briefly, some workers have reported only exothermic peaks in the ranges of 60-75° and 135-180°C during cure of base-catalyzed PF resins.^{5,6} Others have observed only endothermic peaks at 60, 125, and 180°C for both base- and acid-catalyzed resins.⁷ In still another article, several different thermograms were found for a PF resin cured in the presence of hexamethylenetetramine ("hexa").⁴ These various observations were attributed to the use of different resin components and reaction conditions, different methods of sample preparation, and different instrumentation techniques.¹ This article is an attempt to clarify these inconsistencies through a survey of commercial PF resins primarily used in the forest products industry. Novolac and resol systems were examined, with the latter involving both liquid and solid types. In order to resolve the effects of sample preparation, liquids were run under ambient and high-pressure conditions and in some cases after freeze drying. In addition, the influence of heating rate was studied to detail differences in the curing of resol and novolac resins with softening temperature measurements used to determine the physical property changes associated with the thermograms.

EXPERIMENTAL

Adhesives

Eight commercial resins, four resols, and four novolacs described in Table I were studied in detail. A further 16 PF resins were obtained from commercial sources to give a total of 24 resins surveyed, 15 of which were dry powders and the other nine were liquids. The formaldehyde-to-phenol ratio (F/P) of the liquid resins was more than 1.5. Except for resin C, which had a pH of 5, all liquid resins had a pH of 9 or greater. All liquid resins were classified by adhesive suppliers as resol types.

The 15 powdered PF resins consisted of nine novolacs, four resols, and two intermediate types, according to the information provided by adhesive companies. The novolacs used, except for resin H, contained hexa as a hardener component. For convenience these will be referred to as novolac-hexa resins.

Thermal Analyses

All ambient-pressure, differential scanning-calorimetric analyses (DSC) were performed on a Perkin-Elmer DSC-2 instrument equipped with a baseline stabilizer. For liquid resin analyses, a sample of 4 ± 0.5 mg was placed in a gold sample pan without a cover lid. Aluminum sample pans were not used to avoid the interaction with sodium hydroxide in the resin. A sample was then heated in a DSC sample cell at a constant or varied heating rate to 250°C with a dry nitrogen gas flow sweeping it during analysis. It is understood that exclusion of the sample lid allows water evaporation to take place freely, resulting in an endothermic peak at a relatively low temperature. The powdered resins were analyzed in an aluminum sample holder sealed with a crimped lid.

Pressure Cell Study

The use of the DSC pressure cell to eliminate the interference of water evaporation during thermal analysis is a recognized method (12) for analysis of water-containing samples. In this experiment, two dry powdered PF resins (novolac-hexa E and resol G) and two liquid resins (resins B and D) were analyzed

TABLE I
Description of Resins Studied

Resin	Type	Molar F/P^a	% Methylol ^a	% Resin solids
Liquids				
A	resol	2.2	57	43
B	resol	1.7	52	65
C	resol	2.1	44	77
D	resol	1.8	52	60
Solids				
E	novolac	0.8 ^b	0	99
F	intermediate	1.3	19	99
G	resol	1.8	51	99
H	novolac	0.7 ^b	0	98

^a Determined by ¹H-NMR analysis of acetylated products.¹⁰

^b Exclusive of hexa hardener.

by the Forest Products Laboratory, University of California, using a Du Pont pressure-cell DSC analyzer. A sample was hermetically sealed in a gold pan and placed inside a pressure cell. The analysis was performed at ambient pressure and 500 psi, under nitrogen gas with heating temperature from 24 to 250°C at a heating rate of 5°C/min.

Freeze Drying Study

Liquid resins A and C were continuously freeze dried in a film form for 72 hr and then stored at -10°C before DSC analysis at one atmosphere.

Heating Rate Study

One-Step Heating. All resins were analyzed at a constant heating rate of 10°C/min. However, one liquid resin (A) and two powdered resins (novolac-hexa E and resol G), which represent the common characteristics of the majority of the PF resins, were also studied at heating rates of 5, 10, 20, 40, and 80°C/min.

Two-Step Heating. Because the DSC-2 instrument can readily change the heating rate instantaneously during analysis runs, the influence of varying heating rates on the peak temperatures of thermal reactions was studied for three resins, A, E, and G. To simulate a curing condition of resin during wood composite product production, two experimental conditions were examined. (i) Individual samples of the same resin were first heated at a fast rate of 80°C/min until 120°C, and then the heating rates were changed to either 5, 10, 20, or 40°C/min until 300°C. (ii) Individual samples were separately heated at a rate of 20, 40, and 80°C/min to 120°C, and then the samples were heated at a constant rate of 10°C/min to 300°C.

Glueline Study

This study was designed to examine the thermogram of a liquid PF resin in a wood assembly during hot pressing and relate this to the thermogram of resin cure obtained from DSC studies at ambient pressure. Veneers $\frac{1}{8}$ in. thick of white spruce (8 × 8 in.) were dried to a moisture content of about 5%. Resin A (liquid) was applied at a spread rate of about 80 pounds/1000 ft² to half the surface of each veneer. The other half of the veneer surface was either not spread with resin or spread with aluminum oxide (Al₂O₃) powder. The sample thermocouple from an Aminco differential thermal analyzer (DTA) was inserted between two veneers with the PF resin as a glueline, while the reference thermocouple was placed in the adjacent location between veneers where either no resin was applied or where Al₂O₃ powder was present. The two-veneer cross-band assembly was then pressed in a Carver press at a temperature of 180°C and pressure of 200 psi and a DTA thermogram recorded.

Softening Temperature Determination

To determine the relationship between softening temperature and DSC peaks, several 300-mg samples of resins E (novolac-hexa), F (intermediate), and G (resol) were separately heated in an Aminco thermogravimetric analyzer oven

at a heating rate of $9^{\circ}\text{C}/\text{min}$. At specific, designated temperatures (see Fig. 8) the scan was stopped and the sample immediately removed from the TGA oven and rapidly cooled in Dry Ice. Resin solids were then pulverized and their thermal softening temperatures determined by a method described previously.¹¹ The heating rate for the softening temperature determination was $9^{\circ}\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Liquid Resins

The DSC thermograms of liquid PF resins used in wood particleboard and waferboard are shown in Figure 1. The thermograms consist of a large expected endothermic peak, due to the heat of water evaporation, at 80 to 120°C and one or more smaller endothermic peaks in the 130 to 170°C region. The much larger endothermic peak of resin A compared to resin B can be attributed to its much larger water content (Table I). This endothermic nature of the liquid PF resins has been described in previous reports^{1,9} and needs no further elaboration. Upon freeze drying of the liquid resins, the first large endothermic peak decreased substantially, while the magnitude of the second endothermic peak was enhanced. An example of the thermogram of freeze-dried resin C is shown in Figure 1.

The high-pressure cell study of liquid resin D at 500 psi (Fig. 2) showed a similar trend to that of the freeze-dried sample (resin C) analyzer at ambient

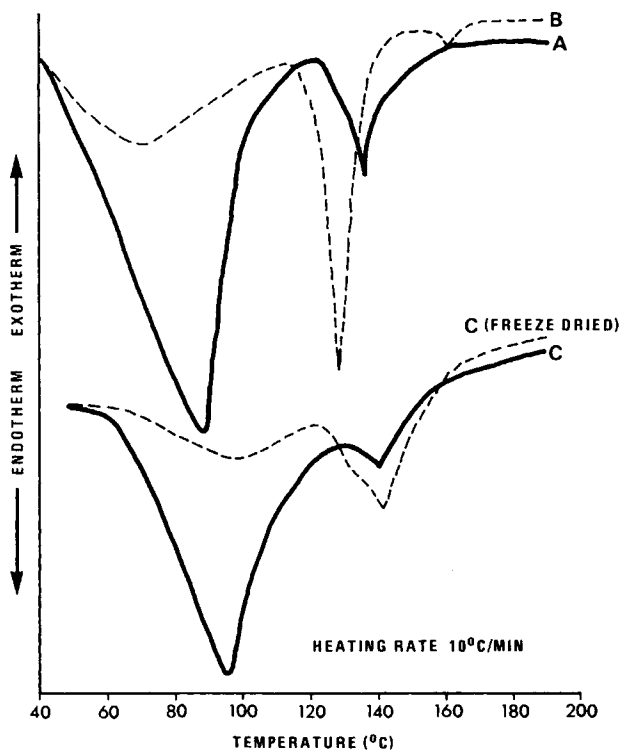


Fig. 1. DSC thermograms of liquid resol PF resins A, B, and C at ambient pressure.

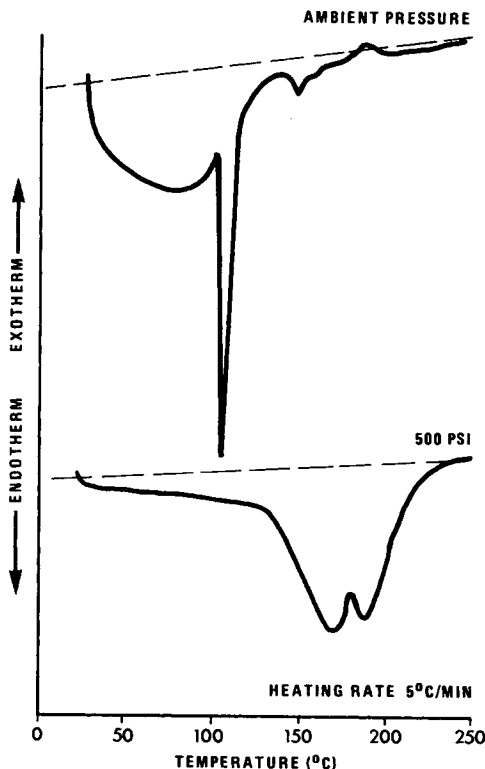


Fig. 2. DSC thermograms of liquid resin D at ambient pressure and 500 psi pressure.

pressure (Fig. 1). The large endothermic peaks of water evaporation (50 to 120°C) under ambient conditions (Fig. 2) were completely suppressed, while the originally small endothermic peaks at 130 to 160°C were significantly enlarged.

The general preference to run DSC scans of liquid resins at high pressure instead of ambient pressure relates to attempts to suppress the endothermic water evaporation peak in order to resolve any exothermic reactions occurring at the same time.¹² However, in bonding wood substrates with these resins using both elevated temperature and pressure, the effect of the heat of water evaporation cannot be ignored. Figure 3 shows the DTA thermogram of liquid PF resin A measured during curing of the glueline of a dry spruce veneer-resin assembly pressed under 200 psi pressure. The large endothermic response near the 100°C region in the glueline is due to the heat absorption of water in the resin. A second endothermic peak appears in the 150°C region. When heating rate is taken into consideration, the second endothermic peak temperature is essentially the same as the peak temperature shown in the DSC thermogram of the resin alone (Fig. 1, resin A). The two thermograms in Figure 3 show the differences between placing the reference thermocouple in an area with wood contact only and an area where contact is with Al₂O₃. When Al₂O₃ is used as reference, an extra endothermic peak was observed in the 110 to 120°C range. This 110 to 120°C endothermic peak was also present previously⁷ in DTA thermograms of wood where Al₂O₃ was used as reference.

These DTA thermograms of PF resin cure in a veneer-resin composite pressed

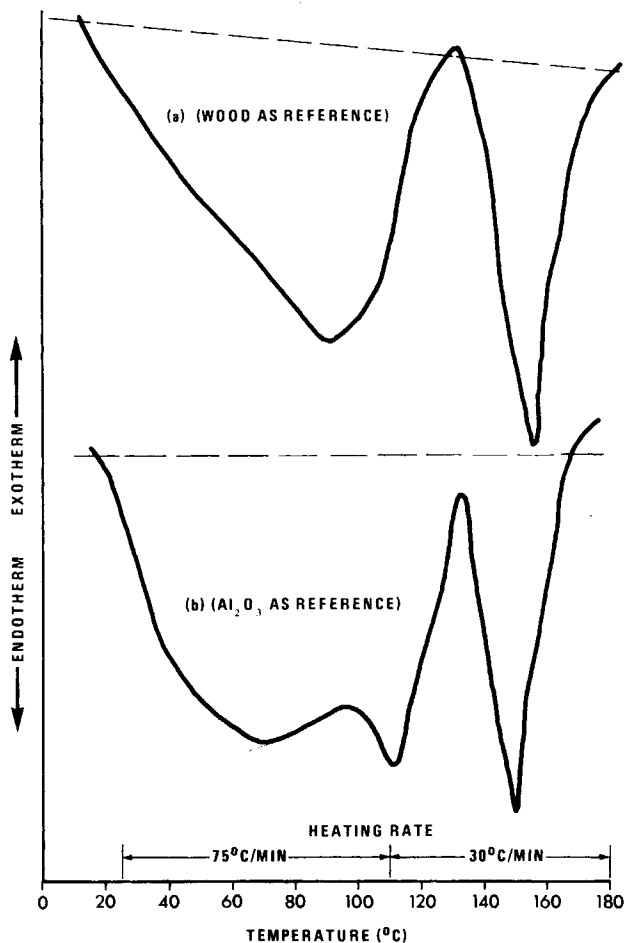


Fig. 3. DTA thermogram of liquid resin A in veneer assembly under 200 psi press pressure and 180°C press temperature: (a) reference thermocouple in wood; (b) reference thermocouple in Al_2O_3 .

at 200 psi thus show thermal responses similar to the DSC thermogram of the PF resin alone, under ambient pressure, in the temperature range considered. DSC thermograms of resin at ambient pressure condition therefore can be useful for predicting the curing behavior of adhesives in wood–glue composites. It should be emphasized here that the existence of the second endothermic peaks (130 to 160°C) in the freeze-dried and high-pressure systems indicates the overall endothermic polymerization nature of the resol adhesive in aqueous solution.

Powdered Resins

The DSC thermograms of three representative powdered dry resins are shown in Figure 4. The powdered resins all initially gave endothermic peaks in the 40 to 110°C regions due to the melting of the resins. Beyond this temperature region, the thermogram depends on the resin formulation. For the novolac–hexa resin type where the initial $F/P = 0.8$, the thermal reaction is essentially exothermic, peaking at 150 to 160°C (resin E). When the resin is a resol type, with

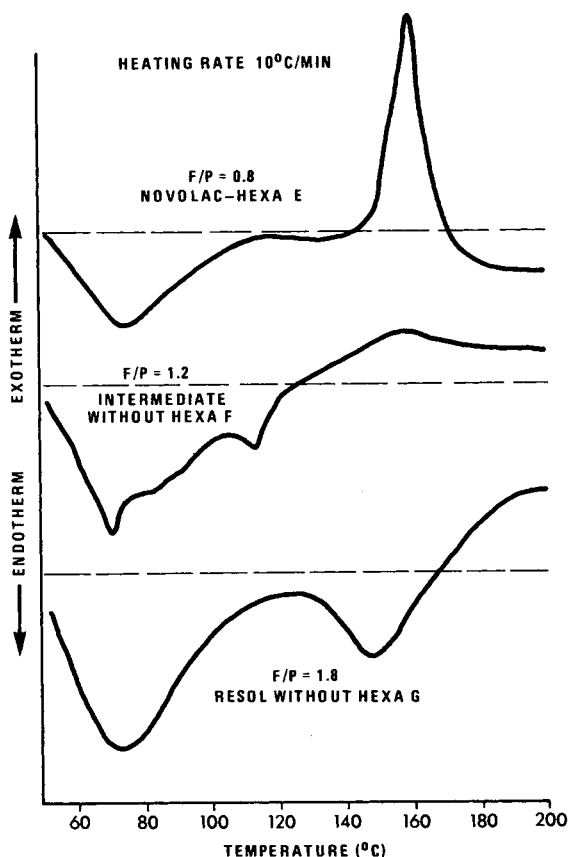


Fig. 4. DSC thermograms of powdered phenolic resins at pressure of 1 atm. Resin E (novolac, F/P about 0.8, hexa hardener added); resin F (intermediate, F/P about 1.2), and resin G (resol, F/P about 1.8).

molar F/P ratio = 1.8 (resin G), the thermogram showed a broad endothermic peak at about 150°C . The intermediate resin F, which is a novolac-resol combination (molar $F/P = 1.2$), shows a thermal reaction which is mainly exothermic (150 to 160°C) but also has a small endotherm at about 115°C .

High-pressure cell study of both powdered resol G and novolac-hexa E resins (Fig. 5) showed similar respective endothermic and exothermic peaks as those found in the ambient-pressure thermogram. The endothermic peak of the powdered resol resin further substantiates the endothermic nature of the reactions for all resol resins, as was previously indicated for the high molar F/P liquid resins in Figure 1. It should be mentioned here that at most the internal water vapor pressure inside a wood-composite panel pressed at 200°C would be 225 psi.¹³

The above results may now help clarify some of the inconsistencies in the literature on DSC of PF systems, especially when comparing high-pressure cell and ambient-pressure methods (Fig. 5). A novolac will usually show exothermic peaks at ambient and high pressure. A resol system will show only endothermic peaks at normal pressure, with the intensity of the endotherm in the 100°C region being suppressed as the pressure is increased, whereas the intensity of the second

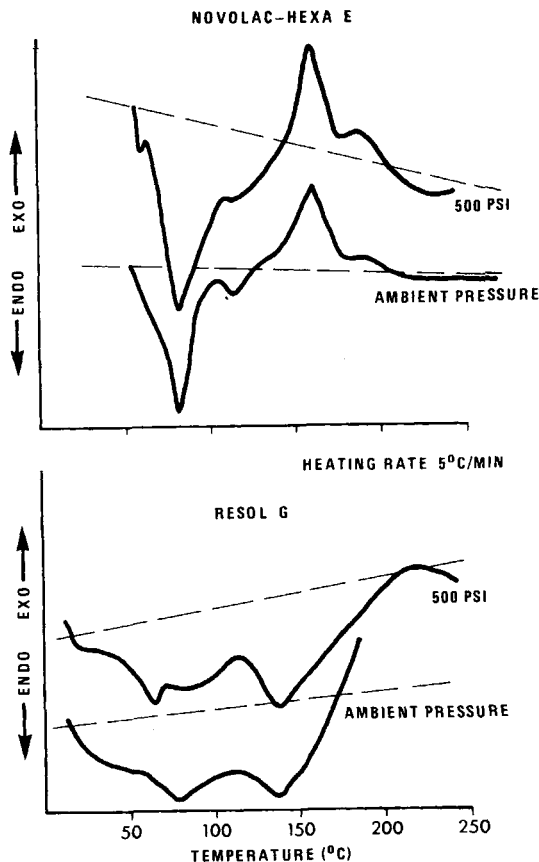


Fig. 5. DSC thermograms of powdered PF resin at 1 atm and 500 psi pressure.

endotherm in the 150°C region is enhanced. An intermediate resin, near the novolac-resol borderline, may show either exothermic or endothermic peaks, depending on resin preparation and catalyst present. For example, if this resin contains many hydroxymethyl groups but little free formaldehyde, the DSC thermogram will show the endotherm(s) of the condensation reaction during cure. However, if the resin is prepared in such a manner that few hydroxymethyl groups are available but formaldehyde is released during cure, then an exotherm representing the addition of formaldehyde to the phenolic will be observed. Thus, the inconsistencies present in the previous literature relate primarily to a poor definition of the PF system.

Heating Rate Effects

The application of DSC thermogram information to actual bonding situations requires a thorough understanding of heating rate effects on peak temperature. The relationship between heating rate and the peak temperature of liquid resol resin A, powdered novolac-hexa E, and resol G are shown in Figure 6. Because the reproducibility of the peak temperature is within $\pm 2^\circ\text{C}$, only the average temperature is shown in the figure. The peak temperatures of all resins increased with increasing heating rate. In general, at the same heating rate the second

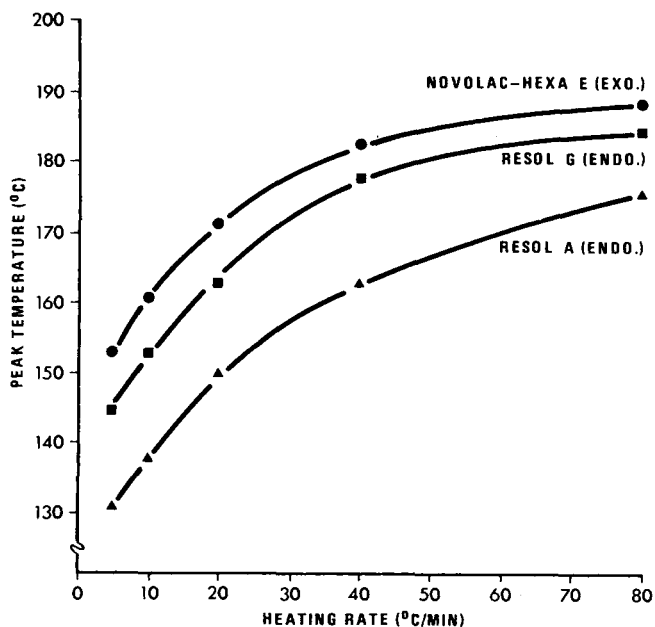


Fig. 6. Peak temperatures and heating rates relationship for liquid PF resin A (resol) and powdered resins E (novolac-hexa) and G (resol).

endothemic peak of the liquid resin occurs at a lower temperature range than that for the dry-powdered resol, while the latter is about 5 to 10°C less than the novolac-hexa exothermic peak.

Figure 7 shows further an example of the variation of peak temperature in

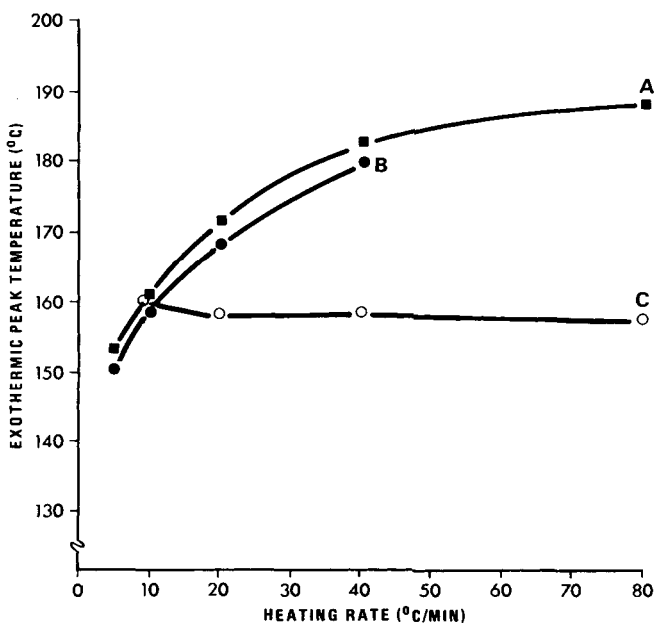


Fig. 7. Example of the heating rate and peak temperature relationship: A, one-step heating; B, two-step heating, first to 120°C with 80°C/min rate, then the heating rates designated on the x-axis; C, two-step heating, first heating to 120°C and then at a rate of 10°C/min.

one-step and two-step heating systems for powdered novolac-hexa resin E. Curve A is the result of one-step heating procedure, which was also shown in Figure 6. Curve B shows the relationship between the peak temperature of the exothermic reaction with a two-step change in heating rates. The instrument was first set at a heating rate of 80°C/min and scanned to a temperature of 120°C, and then the heating rate was changed to the respective heating rates of 5, 10, 20, and 40°C/min as indicated on the horizontal *x*-axis. The trends for curves A and B are similar, and the peak temperatures of the exothermic reaction for the two heating curves differ by only 3 to 4°C. In another experiment, this resin was first heated to 120°C at different heating rates, and then the heating rate was changed to a constant 10°C/min. The exothermic peak temperature of the resin was then recorded. As indicated in curve C of Figure 7, at a 10°C/min heating rate the exothermic peak appeared almost at the same temperature (157°C) as that of the one-step heating procedure regardless of the original heating rate used in the two-step procedure. Although results are not presented here, the other resins showed similar trends to that of Figure 7.

The above heating rate study indicates that the peak temperature for resin cured by multiple-heating steps can be determined using the curve of the one-step heating procedure as reference. The initial, fast rise of temperature in the first stage of heating in the two-step heating system was not a critical factor in defining the curing peak temperature of the resin. The heating rate during the last step is the main factor that decides the curing peak temperature.

Softening Temperature

Figure 8 shows the relationship of the initial softening temperature and the final curing temperature (heating rate 9°C/min) for resins E, F, and G. The arrows indicate the temperature at which the exothermic or endothermic peak of the respective resin occurred. Although all resins show an increased softening temperature as the heating temperature approaches the thermal-reactive areas, the rate of increase varied. For example, up to a cure temperature of 150°C novolac-hexa resin E showed little change in softening temperatures (70 to 80°C). The softening temperature of the resin then rapidly increased with increasing cure temperature. This hardening temperature range (150 to 190°C) corresponds to the DSC exothermic peak temperature of the resin (160°C). In contrast, resol G has already approached its maximum softening temperature as novolac-hexa E starts to show an increase in softening temperature. It should be recalled here that the novolac-hexa resin peak is exothermic, while that of the resol resin is endothermic.

The low *F/P* molar-ratio resins (E and H) contain few methylol groups (Table I). Making them thermosetting requires addition of hexa or paraformaldehyde to the resin prior to cure. The cure temperature releases some ammonoformaldehyde¹⁴ or free formaldehyde from the additives which react with the phenolic rings. This addition process, an exothermic reaction, is thus a necessary step during composite pressing involving resins E and H. However, reaching this exothermic peak does not necessarily result in a completion of cure. To achieve a completely cured resin, crosslinking must take place through the condensation reaction involving methylol units with other moieties of the resin. As shown in Figure 8, attaining the temperature of the addition exothermic peak

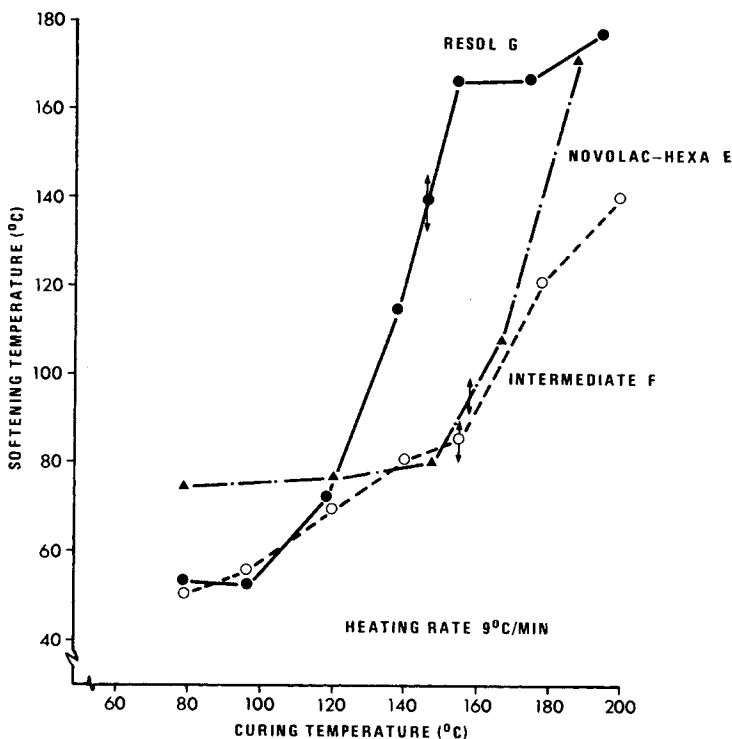


Fig. 8. Curing temperature and softening temperature relationship for powdered PF resins E (novolac-hexa), F (intermediate), and G (resol). Arrows indicate the temperature at which the curing exothermic or endothermic peak of the resins occurred.

in the novolac-hexa resin and to some extent in the intermediate resin produces only a limited increase in softening temperature. The softening temperature of the resin increases greatly only after completely passing the exothermic region (Fig. 4, resins E and F).

To expand on this concept, one can further examine the thermograms of powdered resol and novolac resins in the presence of hexa (Fig. 9). The dry-powder resol, G, already contains a large methylol content. Comparison of the thermograms for this resin itself and with 15% hexa (Fig. 9, ii and iii) indicates almost identical thermal reactions. The curing reaction of this resin in the 150°C range is not influenced by hexa or, in fact, paraformaldehyde, since it does not necessarily depend on the methylolation of the resin, but can proceed directly through a condensation-dehydration process into a crosslinked system. Thus, the overall reaction is endothermic and once the endothermic peak at 150°C is reached, the softening temperature of the resol is near its maximum. In contrast, thermograms for novolac resin H, with and without hexa (Fig. 9, v and iv), show different reactions. The presence of hexa produces an exothermic peak (160 to 170°C), the necessary first-stage addition reaction, which is then followed almost immediately by the second stage condensation reaction. Thus, DSC provides a means of differentiating these two types of reactions, in effect, a convenient method of defining a resol or novolac PF resin. In other words, for a novolac-hexa resin, a two-step process occurs, part of which is characterized by the presence of an exothermic peak. In a resol, a one-step process occurs

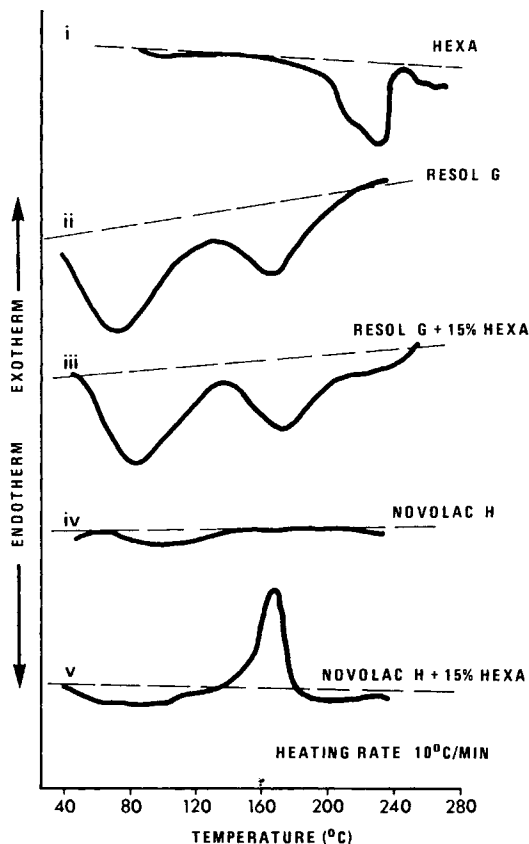


Fig. 9. DSC thermogram of resol G and novolac H with and without addition of hexa.

which is endothermic only. This "definition" of PF systems may be more accurate than the classical one involving molar F/P ratio greater or less than one.*

SUMMARY

Previous literature inconsistencies in PF resin DSC thermograms can be explained by examining both liquid and solid resins of the resol and novolac type. The mechanism of cure for these resins is different. The novolac-hexa type of phenolic resin does not attain thermosetting properties until the exothermic peak temperature at 160°C is passed (about 180°C). The resol type of phenolic resin, regardless of whether it is liquid or powder, depends on the endothermic cur-

* Perhaps in simplistic terms, a novolac is a resin requiring additional formaldehyde to become thermosetting, while a resol needs no further formaldehyde to form a thermoset. The reader should be aware that because of various synthetic procedures and catalysts used in making PF resins, unexpected situations can arise. For example, a resin with a loaded molar $F/P < 0.8$ would be expected to be a novolac, but if the initial cooking procedure results in a large amount of free phenol, which is removed during concentration, the resulting resin may in fact have a much higher molar ratio and really be a resol. Similarly, a resin with a loaded molar $F/P > 1.0$ may turn out to be a novolac rather than a resol if some formaldehyde does not react during the cooking process and is subsequently removed on resin concentration.

ing-reaction peak at about 150°C for thermosetting. Once the resin temperature reaches this endothermic peak, the cure is almost completed.

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