Journal of Thermal Analysis, Vol. 25 (1982) 79–87

THERMAL ANALYSIS OF THERMOSETTING RESINS

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Applications of thermoanalytical methods for the study of the resinification and curing of phenolic resins are reviewed. Examples are given to illustrate the use of DSC for practical industrial systems such as paper impregnants and saturated papers.

Phenolic resins are the oldest and the most common thermosets utilized by the plastics-processing industry. In the cured state they are infusible, covalently crosslinked, thermally stable network polymer structures. The formation of this network structure is responsible for the desirable physical properties which are typical of thermosetting resins over a broad temperature range.

Owing to their intractable nature, the phenolic resins are difficult to study by chemical means. Numerous investigations have shown that thermoanalytical techniques offer valuable tools for the study of the formation, the curing characteristics and the thermal degradation of thermosetting resins.

Phenol-formaldehyde resins

When phenol reacts with formaldehyde the following reactions occur:

a/ Addition reaction to give methylol phenols.

b/ In the presence of acid catalysts, the methylol derivatives condense with phenol to form first dihydroxydiphenolmethane and, on further condensation and methylene bridge formation, fusible and linear low polymers /novolacs/.

c/ In the presence of alkaline catalysts, the methylol phenols can condense either through methylene linkages or through ether linkages. Products of this type, soluble and fusible but containing alcohol groups, are called resols. Resol solutions are used commercially as paper impregnants.

d/ If the reactions leading to resol formation are carried further as is the case in practical applications, large numbers of phenolic nuclei can condense to give network structures.

The nature of the product is dependent on the type of catalyst and the molar ratio of the reactants. Addition and condensation are exothermic reactions, and therefore thermoanalytical methods are particularly suited for the elucidation of thermal effects taking place during the resinification and the subsequent curing reactions. In the following, examples are given to illustrate the use of thermoanalytical measurements for the determination of basic parameters in the resinification and curing reactions.

EXPERIMENTAL AND RESULTS

Resinification reactions

The base-catalyzed reaction between phenol and formaldehyde has been studied using DSC combined with sealed sample cells [1]:

A two-peak curve is obtained, which points to addition and condensation of methylol phenols. Activation energies /determined according to Borchard and Daniels [2]/ of 99.2-80.8 kJ/mole were obtained from the curves for the addition and condensation reactions, respectively. Reaction orders of 2 and 1 were found for the addition and condensation reactions, respectively.

The acid-catalyzed novolac-type reaction between phenol and formaldehyde [3]:

The one-peak curve indicates the simultaneous occurrence of addition and condensation reactions. Activation energies /determined according to Freeman and Carrol [4]/ of 153.4-166.6 kJ/mole were obtained from the curve, which correspond to the sum for the addition and condensation reactions for base-catalyzed resin. Activation energies determined on the mixtures are shown in Table 1. From the results it can be seen that the reaction activation energy decreases with increasing amount of catalyst. A reaction order of 1 was obtained from the plot.

Table 1

Activation energies of reactions between phenol and formaldehyde, determined from DSC traces

Sample	Molar ratio phenol/formaldehyde	Oxalic acid wt, %	Activation energy, kJ/mole
1	1.6	1.6	160.9
2	1.6	3.6	153.4
3	2.4	0.75	166.3
4	2.4	1.7	160.9

A value of 94.2-100.4 kJ/mole was obtained for the heat of reaction, which is in accordance with the literature value of 98.2 kJ/mole found for the total reaction, as determined with other methods [5]. The results indicate that the heat of reaction of the mixture is independent of the phenol/formaldehyde molar ratio.

Reactions between urea and formaldehyde [6]: The course of the reactions is similar to the reactions between phenols and formaldehyde, i.e. addition of formaldehyde to the amine group and condensation of the resulting methylols into high molecular thermosetting resin.

A two-peak curve was obtained, the first relating to the addition and the second to the condensation reaction. Activation energies of 134 kJ/mole were obtained for both addition and condensation reactions. The heat of reaction was found to be 23.6 kJ/mole. The addition and condensation reactions are of second order.

Curing reactions

The curing properties of PF resins have been studied with DTA techniques by several investigators [7,9]. From the thermal curves it is obvious that the exothermic peaks represent processes which occur during the thermal curing of the resin. The inconsistent results obtained in these studies are due to the use of different resin components and reaction conditions, and different methods of sample preparation and instrument techniques. When open cells are used in DTA experiments, the curves may not correlate with the curing behaviour, owing to the endothermic loss of volatile products formed in the curing stage.

Sealed-cell operation simulates actual curing conditions of thermosetting resins under heat and pressure, and additionally the reactive volatiles are retained. The kinetics of curing of base-catalyzed resol resins has been investigated using sealed high-pressure cells in conjunction with DSC [10]. The findings showed that the heating rate exerted a considerable influence upon the resin exotherm. On increase of the heating rate, a shift of the condensation reaction to higher temperatures was observed. An activation energy of 84.5 kJ/mole, a reaction order of 1 and a heat of reaction of 263.7 kJ/g were deduced for a resol resin at a P/F molar ratio of 1:1.2 .

Due to their reactivities under heat and pressure, resol resins are utilized commercially, and therefore the evaluation of their thermal properties is of practical importance. During the curing cycle in the processing stage, the heat liberated from the exothermic reaction gives an indication of the reactivity of resol resins.

To evaluate the effect of the molar P/F ratio with respect to the heat of reaction, curves were run on a series of model compounds with P/F molar rations of 1:1.5, 1:1.7, 1:1.9 and 1:2.1 [11]. A linear correlation was found between the heat of reaction and the P/F molar ratio /Fig. 1/. Prior to DSC measurements, the resins were precured for 10 min at 110°, being simultaneously converted to the resitol stage. Therefore, it can be concluded that a substantial part of the condensation reaction takes place within the heating stage. The advancement of resin cure in this stage may be assumed to be an increasing function of the proportion of formaldehyde in the resins. For this reason the precured resins with a higher proportion of formaldehyde give lower values of the heat of reaction than those having lower F/P ratios.

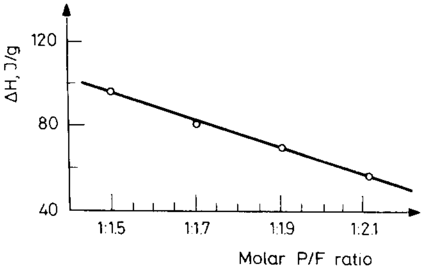

Fig. 1. Heat of reaction vs. P/F molar ration of model compounds

The reactivities of commercial resol resins are commonly evaluated by measurement of the gelation times at 140°. The sudden increase in the viscosity of the resins indicates the formation of polymers.

To evaluate the effect of the heat of reaction with respect to the gelation time, curves were run on freeze-dried commercial resol-resin samples used for paper impregnants. The gelation times of the resins were determined by a standard method. The linear correlation found between the heat of reaction and gelation time for a series of resol resins suggests the use of the basic DSC technique for the quality control of paper-impregnant solutions.

In the preparation of resol resins from phenol and formaldehyde, the viscosity of the solution increases during the cooking, indicating the advancement of addition and condensation reactions. This reaction can also be followed by measurement of the heat of reaction of the samples [12]. A linear correlation was found between the heat of reaction and the viscosity of the samples. The decrease in the heat of reaction of the samples during cooking indicates the advancement of the condensation reaction between methylol groups, leading to polymers of higher molecular weights.

In the resin cooking the P/F molar ratio influences the formation of the condensation products as well as their reactivities in the curing stage. In order to elucidate the effect of the P/F ratio on the reactivities of resol resins, curves were run on samples of varying P/F ratio. From the correlation of the heat of reaction and P/F ratio of the resol resins /Fig. 2/, it can be concluded that resins having a higher formaldehyde content give lower heat of reaction values than those of lower formaldehyde content. This result is in accordance with the previous investigations as concerns the precured model compounds.

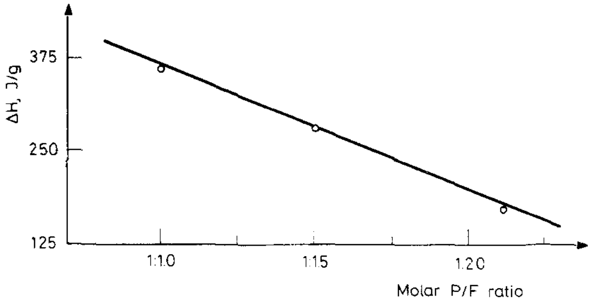

Fig. 2. Heat of reaction vs. P/F molar ratio of resol resins

Resol resin-impregnated paper is an intermediate product in the manufacture of high-pressure laminates. Thermoanalytical methods can be applied for the investigation of thermal effects in saturated paper samples [12].

The heat of reaction was determined on resol resin-impregnated paper samples using sealed sample cells proposed by Freeberg and Alleman [13]. Table 2 presents the values of the heat of reaction calculated with regard to the weight of the paper and the resin. From the results it can be concluded that the heat of reaction of the resin varies between 178 and 279.2 J/g, this being in the range for resol resins with a P/F ratio between 1:1 and 1:2.1 obtained in the previous investigations.

In the following series of investigations the impregnated paper specimens cut from sample 1 were subjected to thermal treatment at 140° for 5, 10, 20 and 30 min. The heats of reaction of the treated samples are presented in Table 3.

Table 2

Heats of reaction of impregnated paper samples

Sample	$\Delta \underline{H}$, J/g calculated on	
	wt. of paper	wt. of resin
1	68.1	226.5
2	55.5	178.0
3	65.2	262.9
4	68.1	214.4
5	82.7	296.8
6	71.4	249.9
7	46.4	182.6
8	79.0	279.6

Table 3

Effect of heat treatment on impregnated paper samples

Sample	Temperature, ^{o}C	Time, min	$\Delta \underline{H}$, J/g calculated on	
			wt. of paper	wt. of resin
1/0	140	0	68.1	226.5
1/5	140	5	59.7	198.9
1/10	140	10	53.0	176.3
1/20	140	20	-	-

The results show that the heat of reaction decreases as a function of time, and after 20 min no thermal effects are to be observed in the curves, which indicates that the curing reaction is completed. It can be concluded that the determination of the heat of reaction allows the evaluation of the degree of curing of resol resins in the impregnated paper, which is of practical importance in the quality control of high-pressure laminates made from resol resin-impregnated papers.

CONCLUSIONS

To summarize the results, it can be stated that

1/ The use of sealed pressure cells allows observation of the exothermic resinification and curing reaction in thermosetting phenolic resins.

2/ A single DSC temperature scan can be analyzed to give reproducible values of overall activation energy, heat of reaction and reaction order for the curing of phenolic resins.

3/ The derived heats of reaction are proving of value with regard to predicting the curing behaviour of practical industrial systems such as paper impregnants and saturated papers.

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ZUSAMMENFASSUNG – Es wird eine Übersicht über die Anwendungen thermoanalytischer Methoden zur Untersuchung der Harzbildung und der Aushärtung von *phenolischen Harzen gegeben. Anhand von Beispielen wird die Verwendung der DSC für praktische industrielle Systeme wie Papierfüllstoffe und gefüllte Papiere aufgezeigt.*

Резюме – Представлено обозрение, касающееся применения термоаналитических методов при изучении смолообразования и вулканизации фенольных смол. Даны примеры, показывающие использование метода ДСК для изучения таких практически важных промышлен ных систем как пропитывающие средства для бумаги и пропитанные бумаги.