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A Thermal Analytical Study of Phenol Formaldehyde Resins

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Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) combined with an infrared absorption study have been used to examine the mechanisms involved in the crosslinking or curing of phenol formaldehyde novolac resins with hexamine. It has been shown that the curing reaction is a three-stage process. The first stage is the physical change of melting and subsequent formation of hexamine solutions. The second and third stages were found to be two, distinct, crosslinking reactions occurring in two, successive, temperature regions. The presence of absorbed moisture modifies the melting and curing processes.

1. Introduction

Phenol formaldehyde resins are of considerable industrial importance and have wide application. The study of the mechanisms involved in hardening and curing them has received considerable attention since their discovery by Baekland in 1907. The complicated nature of the system has lead to the study of model phenols and methylol phenols and their reaction with formaldehyde. This work has enabled the elucidation of the broad, chemical structure of phenolic resins. The detailed examination of the curing mechanisms of industrial resins has not received wide publication. Industrial phenol formaldehyde resins consist of a complex mixture of phenolic compounds and are difficult to study by chemical means. Thermal analysis has been found to be a valuable technique for the study of the hardening and curing of these resins. We have found these techniques to be of special value in the study of novolac resins, which are acid-catalysed, phenol formaldehyde resins in which the formaldehyde/phenol molar ratio is less than one.

Thermal analysis as a method of investigating phenol formaldehyde condensates has been used mainly to study thermal oxidative degradation of cured systems [1-4].

Recently, Popov *et al* [5] have published results on uncured, phenol formaldehyde resins using both DTA and TGA techniques. To our knowledge, this is the only published work on a subject which has wide, industrial importance. The conclusions drawn by these authors are not in full agreement with our findings, but the discrepancy may be due to the high heating rates used by the Russian workers.

The following paper describes some of the work on phenol formaldehyde resins carried out at the Central Research Laboratories of The Carborundum Co Ltd, Trafford Park, during the period 1964-6, using the techniques of DTA, TGA, and infrared absorption.

2. Experimental

2.1. Differential Thermal Analysis (DTA)

The aluminium-block temperature was controlled by F and M silicon-controlled rectifier programme controller. Linear heating rates from 0.5° C/min to 30° C/min can be obtained. A two-channel pen-recorder was used to measure the reference-sample temperature and the differential temperature. The "differential temperature" channel has a maximum full-scale deflection of 1.25° C on a 21 cm chart when using Chromel/Alumel thermocouples. The temperature-measuring channel was calibrated from 0 to 400° C.

In order to avoid spurious differential-temperature fluctuations due to changes in sample geometry during curing, the samples were diluted with glass beads (17 mg of resin with 33 mg glass beads). The reference-sample tube contained 50 mg of glass beads of the same size as those used for the sample dilution (grade 12 Ballotini).

2.2. Thermogravimetric Analysis (TGA)

A Stanton HT Thermobalance (sensitivity 0.5 mg) was used to measure the weight changes which occur on heating the resin in the temperature range 20 to 400° C. A linear rate of heating of 6° C/min was used.

The samples, which were of closely controlled particle size (240 to 300 mesh sieve size), were contained in a 5 ml, recrystallised-alumina crucible. The weight of sample was 0.5 gm. Results were plotted as a percentage weight loss against temperature (TGA) and also as a differential weight loss against temperature (DTGA).

2.3. Infrared Absorption Analysis (IR)

A Unicam SP200G Spectrophotometer was used to examine samples taken from the DTA apparatus at various stages in the curing reaction. Samples were prepared as potassium bromide discs (2 mg of resin to 200 mg potassium bromide).

3. Results

3.1. Differential Thermal Analysis

3.1.1. Novolac Resin R_1 without Hexamine (fig. 1)

Heating rate, 10°/min; chart speed, 720 mm/h; ΔT sensitivity, 0.06° C/cm; water content, 1.36%.

3.1.2. Novolac Resin R_1 with Hexamine (fig. 2)

Experimental conditions as in 3.1.1; water content, 1.36%.

3.1.3. Novolac Resin R_1 with Hexamine and Absorbed Moisture (fig. 3)

Experimental conditions as in 3.1.1; water content, 1.96%.

3.1.4. Novolac Resin R_1 with Hexamine (fig. 4)

Heating rate, 10° /min; chart speed, 180 mm/h; ΔT sensitivity, 0.12° C/cm.

3.1.5. Novolac Resin R_2 with Hexamine (fig. 5)

Experimental conditions as in 3.1.4.

Note Novolac resins R_1 and R_2 are samples of a works production resin (CR1869). Further details are given in section 4.1.4.

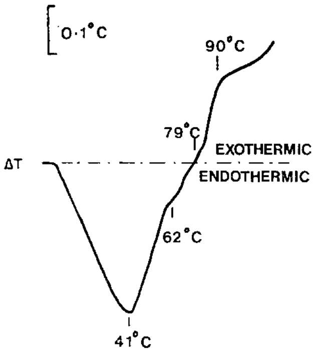
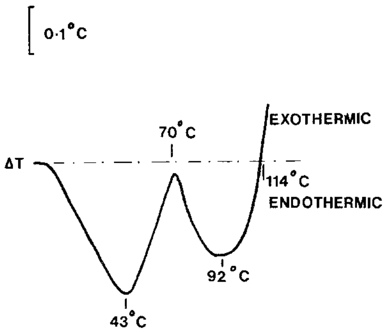


Figure 1



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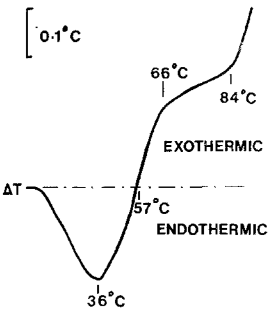

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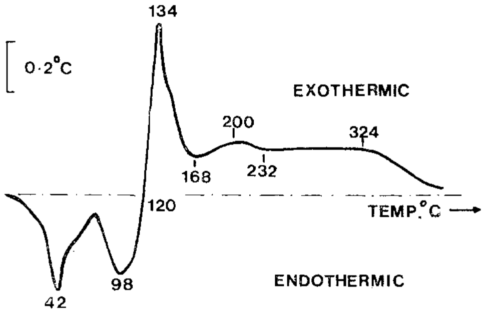

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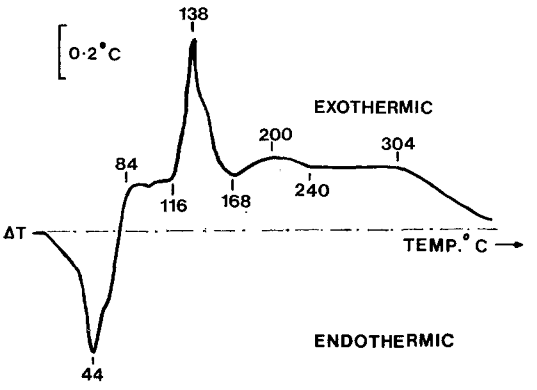


Figure 5

3.2. Thermogravimetric Analysis

3.2.1. Novolac Resin R_3, TGA Curve (fig. 6)
Novolac Resin R_3, DTGA Curve (fig. 7)

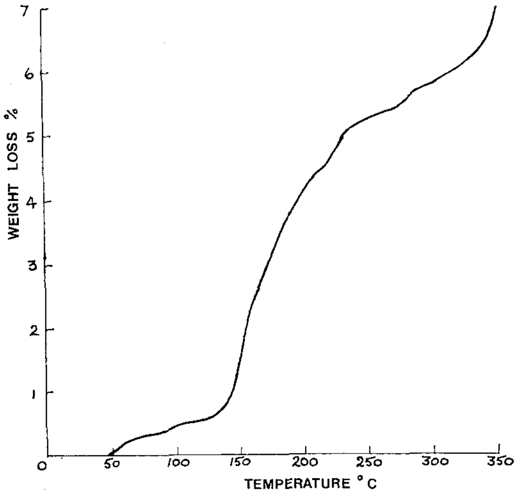
Resin R_3 was synthesised so as to give a high percentage of low-molecular-weight condensate.

3.2.2. Novolac Resin R_4, TGA Curve (fig. 8)
Novolac Resin R_4, DTGA Curve (fig. 9)

Resin R_4 was synthesised so as to give a resin with a low percentage of low-molecular-weight condensate.

3.2.3. Novolac Resin R_1, TGA Curve (fig. 10)
Novolac Resin R_1, DTGA Curve (fig. 11)

3.2.4. Novolac Resin R_2, TGA Curve (fig. 12)
Novolac Resin R_2, DTGA Curve (fig. 13)



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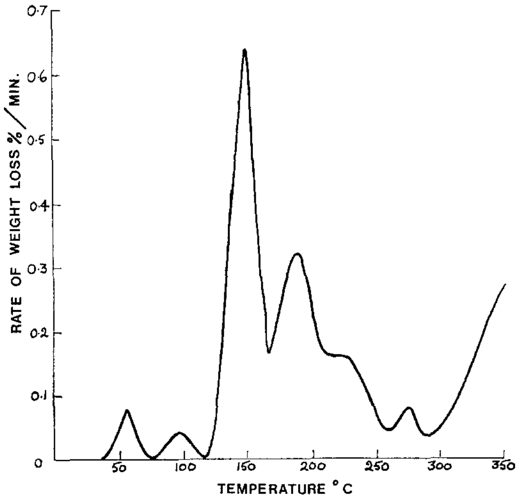

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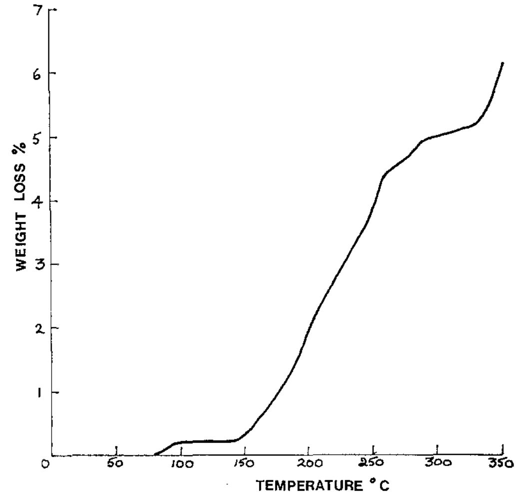

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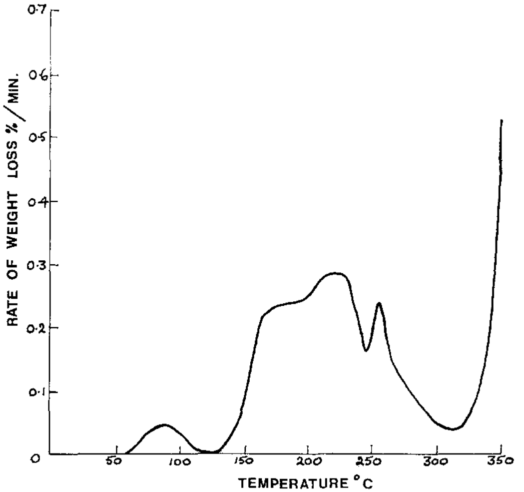

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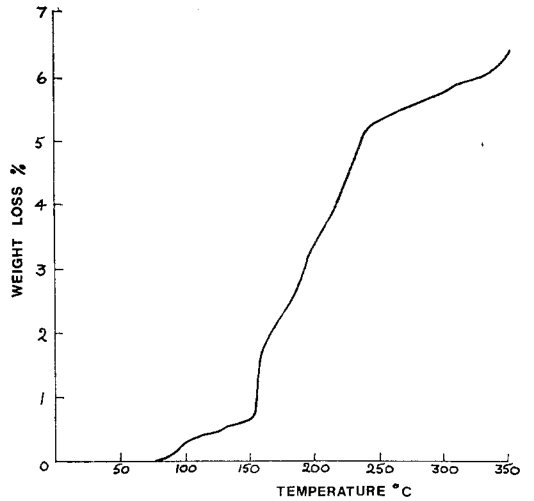

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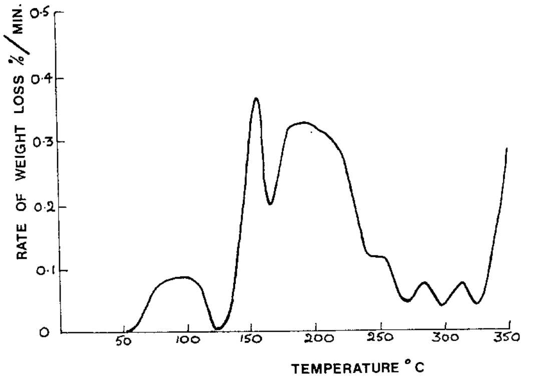

Figure 11

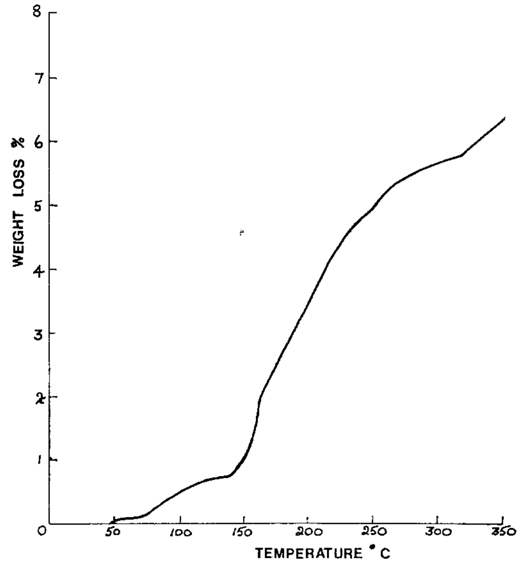

Figure 12

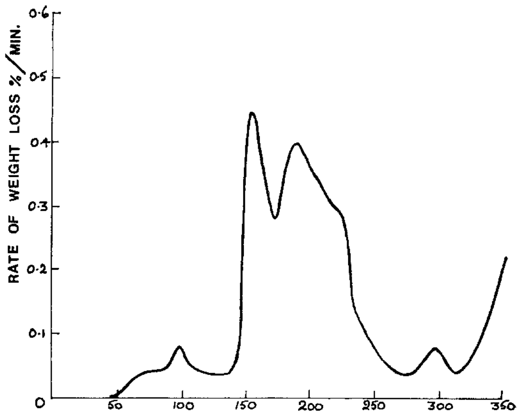

Figure 13

4. Discussion of Results

4.1. General Description of the DTA Curve

All novolacs produce a basically similar pattern with relatively minor variations. Endothermic peaks occur in the temperature range 20 to 110° C followed by a strong exothermic region from 130 to 150, then to 200° C there is a broad but weaker exothermic region. At temperatures higher than 240° C, the curve may become endothermic or exothermic owing to distillation of volatile products and oxidative degradation.

4.1.1. Low-Temperature Endothermic Region

A novolac resin with a phenol/formaldehyde ratio of 1:0.81 in the absence of hexamine gives rise to a DTA curve as shown in fig. 1. There is a broad melting range indicating a spread in molecular weight and a tendency for the molecular weight distribution to be binodal. The same novolac resin with 7% hexamine addition modifies the endothermic region of the DTA curve (fig. 2.)

The first endothermic peak at 41° C becomes broader and the peak temperature is slightly elevated. A secondary endotherm is also present with a peak at 92° C. A sample was taken from the DTA apparatus at this temperature and quenched to room temperature. Examination of this sample by infrared absorption spectrometry showed an identical spectrum to that obtained from the sample prior to heating. It was concluded that the second endotherm was due to the heat of solution of hexamine in the molten resin.

The resin with hexamine addition was exposed to a humid atmosphere for 24 h. This resulted in a water uptake of 0.6% and a marked modification to the DTA curve was observed (fig. 3).

The endothermic peak temperature due to melting of the low-molecular-weight components of the resin was lowered from 43 to 36° C. After the 36° C peak, the reaction rapidly becomes exothermic and the previously observed endotherm at 92° C is suppressed.

The lowering of the endothermic peak temperature indicates plasticisation of the polymer by traces of moisture, a phenomenon well known in the use of phenolic moulding powders. The absence of the 92° C endotherm suggests an acceleration of the exothermic crosslinking reaction owing to the presence of water which enables the exothermic reaction to commence at a lower temperature.

4.1.2. *Exothermic Region of the DTA Curve (fig. 4)*

The first exothermic peak begins at 120° C and has a peak temperature in the region of 140° C. A sample quenched from 144° C was examined by infrared absorption spectrometry.

Approximately 50% of the hexamine was found to have reacted as calculated from the mono-substituted benzene peak at 690 cm^{-1} and the peaks associated with hexamine at 660 cm^{-1} and 1010 cm^{-1}.

The absorption band at 1100 cm^{-1}, which we associate with diphenyl ethers, was markedly reduced in intensity, also the absorption band at 1330 to 1370 cm^{-1} was modified owing to reaction of the resin with hexamine. We conclude that at this stage the curing reaction is approximately 50% complete.

A further sample was taken from the DTA apparatus at 176° C and quenched to room temperature (i.e. after the completion of the first exothermic reaction). Examination of this sample by infrared absorption spectrometry showed that 25% of the free phenol and 8% of the hexamine remained unreacted. A further reduction in intensity of the diphenyl ether band at 1100 cm^{-1} was observed. The curing reaction was estimated to be 90% complete at this stage.

A second exothermic peak appears in the region of 200° C and extends from 180 to 230° C. A sample taken from the DTA apparatus at 200° C and quenched to room temperature shows a similar infrared absorption spectrum to that observed from the sample previously taken at 176° C. The only significant differences being in the region of 1650 cm^{-1}, where a broad band was observed, and the absorption band at 1320 to 1380 cm^{-1} develops a peak at 1330 cm^{-1}. The peak at 1330 cm^{-1} is possibly associated with the formation of azomethins.

A sample taken from the DTA apparatus at 236° C and quenched to room temperature (i.e. after completion of the second exothermic reaction) was found to contain no free phenol and no hexamine. It was therefore deduced that the curing reaction was complete.

4.1.3. *Oxidative Degradation Region*

A further sample was taken from the DTA apparatus at 350° C and quenched to room temperature. This temperature corresponds to the onset of destructive distillation as shown by the DTGA curves (fig. 9), which give a high rate of weight loss in this temperature region. The infrared absorption spectrum showed a severe reduction in intensity of the band at 910 cm^{-1}, which we associate with methylene bridging. A peak also develops at 1010 cm^{-1}, which has not yet been correlated to structure. A further enhancement of the absorption band at 1330 cm^{-1} was observed, indicating an increase in the azomethin content.

4.1.4. *DTA of Resins R_1 and R_2*

These resins were both prepared as standard works production batches at different times. The phenol/formaldehyde ratio was 1:0.81 and the condensation reaction was carried out in the presence of oxalic acid. Hexamine was added to the powdered resin.

A marked difference was observed in the low-temperature region of the DTA curves (figs. 4 and 5), which indicates a difference in molecular constitution of the resin. The higher-temperature regions of the curve were similar.

The previous work described in section 4.1.1 has indicated that the peak at the 90° C region, which was observed with resin R_1, is associated with the solubility of hexamine in the molten resin. The 90° C endotherm is absent in the DTA curve of resin R_2, indicating that the hexamine is not soluble in the melt, which leads to the formation of a heterogeneously cured resin. We have observed microscopically this type of heterogeneous cure, and unreacted hexamine crystals have been extracted from closed pores in samples which had been cured for 24 h at 170° C.

4.2. Thermogravimetric Analysis

In addition to the usual plot of weight loss against temperature (TGA), it has been found advantageous to replot the TGA curves as differential-weight-loss curves (DTGA). The shape of the DTGA curve takes the same general form for all the novolac resins which we have so far examined.

4.2.1. General Description of the DTGA Curve

The small peaks below 100° C are associated with loss of absorbed volatile compounds. The peak observed at 150° C is related to the main curing reaction and is enhanced by the presence of water in the resin and also by the presence of very low-molecular-weight species. This effect is illustrated in figs. 7 and 9. Resin R_3, which gives the high rate of reaction, has a higher proportion of low-molecular-weight material. The reaction peak is associated with the exothermic DTA peak at 144° C.

In all novolac resins so far examined, a broad DTGA peak occurs from 160 to 250° C and is associated with the secondary curing reaction previously observed by DTA at 200° C.

At temperatures greater than 300° C, rapid oxidative degradation and distillation occurs.

4.2.2. DTGA Curves for Resins R_1 and R_2 (figs. 11 and 13)

The DTGA curves of both these resins have the same general form. The overall weight loss up to 350° C is the same (figs. 10 and 12). It is especially interesting that there is no difference in behaviour up to 100° C, indicating that the 90° C endothermic peak observed on the DTA curve (fig. 4) is not associated with loss of volatile components.

A well-defined peak occurs at 155° C with both resins and this is associated with the exothermic DTA peak at 144° C. The temperature discrepancy is attributed to the different heating rates and methods of sample-temperature measurement between the TGA and DTA techniques. Resin R_2 has a higher rate of reaction in this primary curing region.

The secondary curing reaction is defined by the broad DTGA peak from 170 to 250° C. The rate of reaction is higher for resin R_1.

Rapid degradation of both resins begins at 325 to 350° C.

5. Summary and Conclusions

The results show that four distinct regions exist when a novolac resin containing hexamine is heated from 20 to 400° C.

The first region is in the temperature range 20 to 100° C. In this region, only physical changes have been shown to take place. These consist of melting and dissolution of hexamine in the molten resin. It has also been shown that absorption of moisture by the resin/hexamine mixture alters the melting behaviour and accelerates the crosslinking reaction. The crosslinking reaction normally starts at 110° C, but in the presence of absorbed moisture the reaction can commence at 70° C and may mask any endothermic peaks in this temperature region. It is therefore important that any comparative tests should be carried out on resin samples which have the same minimum water content. The molecular-weight distribution in the resins examined has been found to produce variations in DTA curves which are considered to be due to the solubility of hexamine in resin.

The second reaction region occurs between 100 and 180° C and is associated with a crosslinking mechanism, which is referred to in this paper as a primary curing reaction. It has been found for a specific resin that 75% of the available hexamine is utilised in this exothermic reaction. Also, variations in the molecular-weight distribution of the polymer have been shown to modify the observed rates of reaction in this region.

The third reaction region occurs from 180 to 230° C and is characterised by a broad exothermic peak on the DTA curve accompanied by a high weight loss. It is probable that the DTA peak is actually the resultant of an exothermic reaction and an endothermic volatilisation. Consequently, heat of reaction due to the secondary curing process may be much greater than the value suggested by the area under the peak.

In the fourth reaction region from 250 to 400° C, oxidative degradation and distillation of volatile degradation products occur. The DTA curve may deviate either in the exothermic or endothermic direction, dependent on the relative magnitude of the oxidation and distillation reactions. These thermal effects are related to a high weight loss in this temperature region.

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