

Curing of Resole-Type Phenol-Formaldehyde Resin

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Synopsis

The process of resole-type phenol-formaldehyde resins was studied by differential thermal analysis and infrared spectroscopy. It was shown that in neutral media the first reactions that occur are those between free phenol present in the resin and monosubstituted methylol phenol with free reactive positions on the benzene ring. The formation of methylene linkages is followed immediately by the condensation of methylol groups to give dibenzyl ether linkages. These are subsequently destroyed at about 210°C. It is believed that the entire curing process is governed by a free-radical mechanism. It is also shown that oxidation of the resin occurs slowly at room temperature and humidity.

INTRODUCTION

The curing of phenolic resins has not been studied adequately in view of their extensive commercial development and application and the fact that phenol-formaldehyde resins represent the first synthetic polymers produced. The reason lies perhaps in the complex nature of the processes of condensation and curing and the rather intractable nature of the resin. Yet in recent years, owing to the intensive use of thermal and spectroscopic methods of investigation in polymer chemistry, an approach has been made to the better understanding of these intricate processes. Ravich and Frolova¹ were the first to use differential thermal analysis (DTA) for the investigation of the acid- and alkali-catalyzed condensation reactions of phenol-formaldehyde resins. In the case of NaOH as the catalyst, they observed two thermal effects. The latter, lying in the range 160-180°C. and corresponding to the curing process of the resin, was designated by the authors as one which could give an important insight into the chemistry of these processes. Hardening of novolac-type resins and methods of quality control have been described by Nakamura² and Popov and co-workers.³ The possibility of identification of the type of the resin involved and the type of phenolic component used was pointed out by Mil-lane;⁴ White and Rust⁵ showed by this technique the effect of temperature, catalyst, water content, and degree of resin advancement on the rate of cure. Learmonth⁶ used DTA in conjunction with thermogravimetric analysis (TGA) for the investigation of thermal degradation of phenolic resin-based laminates. The first detailed analysis by infrared spectroscopy of phenolic resins and their intermediate products was made by Richard

and Thomson.⁷ Igonin and co-workers⁸ were the first who followed, by this technique, the curing of resole type phenolic resins in the range 70–200°C., observing changes in the spectrum during the hardening. Secret⁹ discusses infrared spectra of different types of phenolic resins made from phenol and substituted phenols. Hummel¹⁰ has collected a number of infrared spectra of commercial phenolic resins and discusses their absorption bands and changes that take place during heating at elevated temperatures. Reed and Favero¹¹ and Brown and Murray¹² developed methods for the control of resin advancement to the B stage, a condition otherwise very difficult to define in the production of preimpregnated materials. Conley and co-workers used infrared spectroscopy in many valuable investigations of oxidative degradation of phenol-formaldehyde polycondensates.^{13–16}

EXPERIMENTAL

Preparation of Resins

The phenolic resins were prepared in the usual manner at various phenol/formaldehyde molar ratios ($P/F = 1:1.3, 1:1.5, \text{ and } 1:2.0$) with 0.03 mole NaOH per mole phenol as catalyst. The mixtures were condensed until the tolerance for water was 1:1; this required approximately 90 min. at reflux temperatures. After cooling to room temperature the mixtures were neutralized to pH 7 with 10% acetic acid. The resinous layers were washed several times with distilled water, dissolved in acetone, dried over anhydrous sodium sulfate, and evaporated at 10^{-4} mm. Hg and 40°C.

Apparatus

DTA was carried out on a Fa. Gebrüder Netzsch, Type 404 apparatus with modified metal block. Resin samples, about 0.1 g. each, were put in glass tubes, 25 mm. long and 5 mm. in inside diameter. The reference substance was calcined alumina. The differential thermocouple was made from chromel–alumel wire. The infrared spectroscopic determinations were conducted on a Perkin-Elmer Model 221 spectrophotometer. Film samples were cast from acetone solutions of resins on polished salt plates and cured directly on them.

RESULTS AND DISCUSSION

Figure 1 shows a typical DTA curve obtained during thermal hardening of a dehydrated resole made with P/F ratio 1:1.3. The DTA curve obtained in a similar experiment conducted in a nitrogen atmosphere is shown in Figure 2. From these thermograms it is obvious that the exothermic peaks represent processes which occur during the thermal curing of the resin, and are not associated with oxidative reactions. It can also be concluded that the exothermic peak at 156°C. is not evident until it reaches its maximum, i.e., until the thermic effect of this reaction is greater than the preceding one, which begins to slow down rather quickly. In order to get

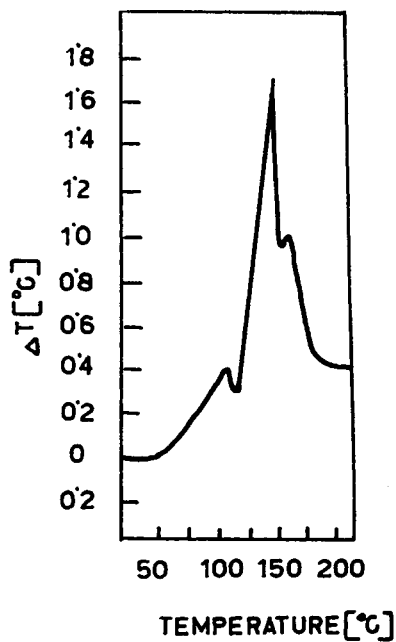


Fig. 1. Thermogram of the resole prepared at P/F 1:1.3. Heating rate 5°C./min.

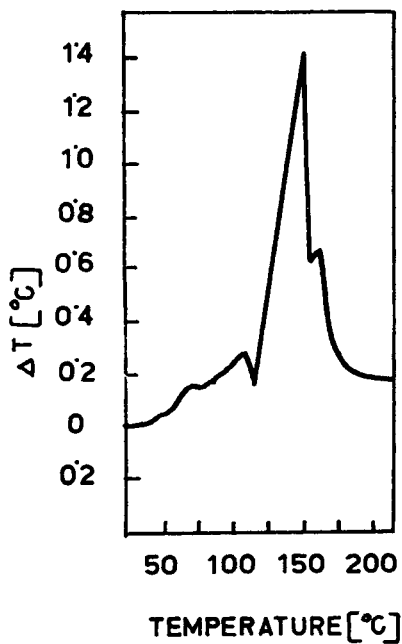


Fig. 2. Thermogram of the resole prepared at a P/F = 1:1.3 under nitrogen. Heating rate 5°C./min.

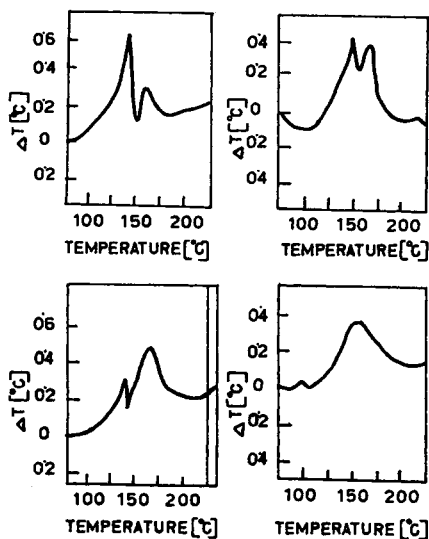


Fig. 3. Thermograms of resole resins (P/F = 1:1.3) after heating of sample for various times: (a) 2 hr.; (b) 3 hr.; (c) 5 hr.; (d) 10 hr. Heating rate 5°C./min.

better resolution of these peaks, the samples of the resin were heated in an oven at 90°C. for varying times, cooled, and examined again by DTA. The thermograms shown in Figure 3 indicate that two processes, represented by exothermic peaks at 148 and 156°C., take place almost immediately one after another but with different speeds. After this treatment the resin was red-brown in color, opaque, and could not be dissolved in acetone or ethanol. From the infrared spectra obtained before and after the 10-hr. heating period at 90°C., one can see that significant changes take place at 690, 755, and at 1010 cm^{-1} , the latter to a very small extent. As the vibrations at 690 and 755 cm^{-1} correspond to monosubstituted and *ortho* disubstituted benzene rings, respectively, i.e., to free phenol and *o*-methylolphenol, the first exothermic peaks are evidently due to the reactions of these two species; presumably the first one at 110°C. is due to reactions of phenol and the second at 148°C. to reactions with *o*-methylolphenol, both resulting in methylene bridge formation. This assumption can be proved if one works with resins prepared at lower phenol-formaldehyde ratios. In such runs, the quantities of free phenol and *o*-methylol phenol decrease at lower P/F ratios, giving greater proportions of di- and trisubstituted phenol. Figures 4 and 5 show DTA curves of resins prepared at P/F ratios of 1:1.5 and 1:2.0, respectively. It is obvious that the peak corresponding to the reaction of *o*-methylolphenol is proportionally smaller in the case of P/F ratio 1:1.5 than in the case of P/F 1:1.3, while at P/F = 1:2.0 the DTA curve shows only a point of inflection at this temperature. Exothermic peaks previously not present are now noticed at 200 and 210°C., respectively, and with much greater amplitude in the case of P/F = 1:2.0. In order to explain the exotherms at 164 and 200°C., a glass tube with

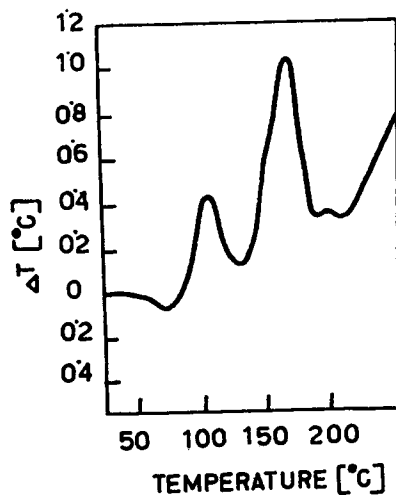


Fig. 4. Thermogram of the resin prepared at a molar ratio $P/F = 1:1.5$. Heating rate 20°C./min.

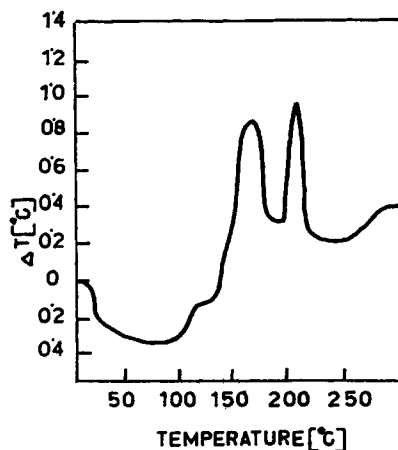


Fig. 5. Thermogram of the resin prepared at a molar ratio $P/F = 1:2.0$. Heating rate 10°C./min.

resin was immediately taken from the block and cooled in an ice bath at the moment the DTA curve reached its maximum. Infrared spectra were obtained on these samples. From Figures 6 and 7 it can be seen that the exothermic peak at 164°C. corresponds to the disappearance of the frequency at 1010 cm.^{-1} , while a new one at 1050 cm.^{-1} appears immediately after. As these vibrations are attributed to $-\text{C}-\text{OH}$ and $-\text{C}-\text{O}-\text{C}-$ groups, respectively, this means that the exothermic peak at 164°C. corresponds to the formation of dibenzyl ether linkages. In the same way, the DTA peak at 210°C. (P/F ratio $1:2$, Figs. 8 and 9) could be attributed to the cleavage of the ether bridge, i.e., it is associated with the disappear-

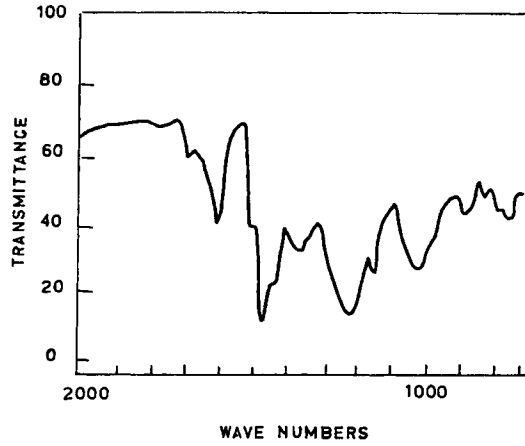


Fig. 6. Infrared spectrum of phenolic resin before appearance of the DTA peak at 164°C.

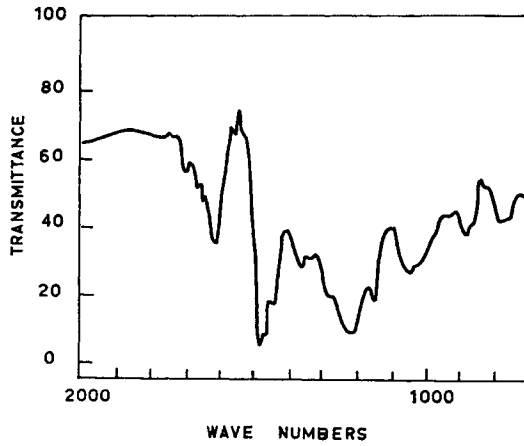


Fig. 7. Infrared spectrum of phenolic resin after appearance of the DTA peak at 164°C.

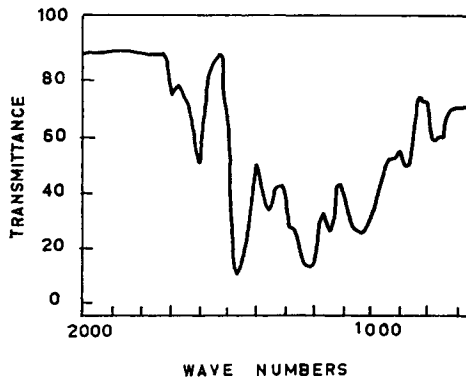


Fig. 8. Infrared spectrum of phenolic resin (P/F = 1:2) before the peak at 210°C.

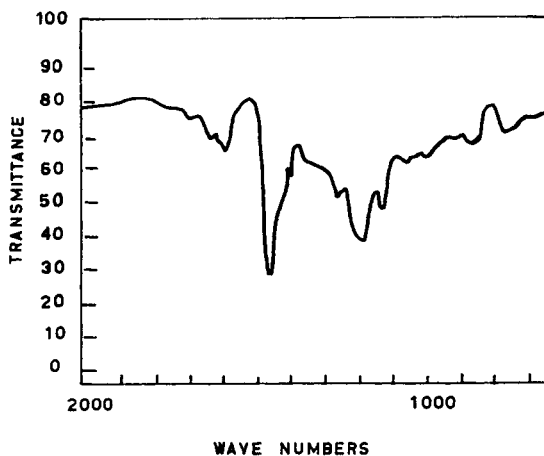


Fig. 9. Infrared spectrum of phenolic resin (P/F = 1:2) after the peak at 210°C.

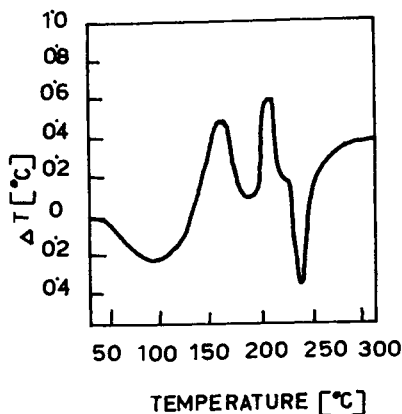


Fig. 10. DTA thermogram of phenolic resin (P/F 1:2) after 2 months at room temperature and ambient humidity.

ance of the band at 1050 cm.^{-1} . As the proportion of ether bridges is greater with P/F ratio 1:1.5 and particularly with the 1:2 ratio, it follows that the height and area under the peak will be greater in the latter case.

Conley and Jackson,¹⁵ recently observed that when phenolic resins are exposed to humid conditions, oxidation occurs even in an inert atmosphere; this was confirmed by leaving samples of the resin at room conditions for 2 months and then analyzing them by DTA (Fig. 10). During this period the resin became opaque from water of condensation.

The thermogram of this sample shows a new endothermic peak at 234°C . not found if the experiment were conducted in an inert atmosphere. From the infrared spectrum, which shows the appearance of a new band at 1720 cm.^{-1} , it can be concluded that this is due to the oxidation of methylol groups to carboxyl groups, as proposed by Conley.¹⁵

Lilley's views¹⁷ regarding the free-radical mechanism for the second stage of the curing process were confirmed for novolacs and for resoles made from substituted phenol,^{18,19} but not for resoles made from pure phenol. In order to find the precursors of the free radical at the curing temperature, DTA was performed on a resin sample containing 2.5% benzoyl peroxide. The thermogram (Fig. 11) shows that the peak at 164°C. has moved to 117°C., while a new one, although very small, appears at 170°C.; this peak was previously overshadowed by the higher peak at 164°C. It is obvious that the curing of resoles made from pure phenol is also governed by a free-radical mechanism. The appearance of the small peak at 170°C. could possibly be attributed to the reaction of phenolic hydroxyl, because in this temperature range the infrared spectrum shows disappearance of the band

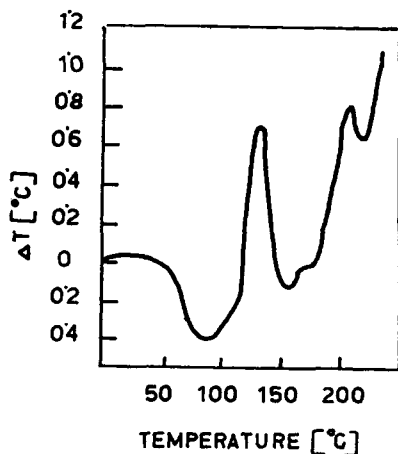


Fig. 11. DTA thermogram of phenolic resin (P/F = 1:2) with 2.5% benzoyl peroxide.

at 1350 cm.^{-1} and appearance of a new band at 1260 cm.^{-1} , probably associated with formation of some diphenyl ether bridges, but not to a great extent because of steric hindrance. This does not correspond to the results of Smirnova and Serenka,²⁰ who found that during the hardening of resoles with deuterated methylol and hydroxyl groups the quantity of heavy water formed during the curing process corresponds to the content of methylol groups. However, they conducted their experiments between 100 and 160°C. and in this range the infrared spectra do not show changes at these frequencies.

From the results of these experiments it can be concluded that DTA in combination with infrared spectroscopy is a valuable tool for the study of curing processes of phenolic resins. Under neutral conditions the main reactions that can be detected are those leading to the formation of methylene bridges and especially to dibenzyl ether linkages. The latter reaction gives the greatest thermic effect and is governed by a free-radical mechanism.

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Résumé

On a étudié la durcissement de résines phénol-formaldéhyde de type résol au moyen de l'analyse thermique différentielle et de la spectroscopie infrarouge. En milieu neutre les premières réactions ont lieu entre le phénol libre dans la résine et le phénol monométhylolique aux positions libres du noyau benzénique. La formation de pont méthyléniques est suivie immédiatement de la condensation de groupes méthyloliques et formation de liens du type éther dibenzylque. Ceux-ci sont ultérieurement détruits à environ 210°C. On admet que le processus entier de durcissement est régi par un mécanisme par radicaux libres. On montre également que la résine s'oxyde à température de chambre et à l'humidité.

Zusammenfassung

Der Härtungsprozess von Phenolformaldehydharzen vom Resoltyp wurde mittels Differentialthermoanalyse und Infrarotspektroskopie untersucht. In neutralen Medien treten zuerst Reaktionen zwischen dem freien, im Harz vorhandenen Phenol und monosubstituiertem Methylolphenol mit freien Stellungen im Benzolring auf. Darauf folgt unmittelbar die Bildung der Methylenbrücken durch Reaktion der Methylolgruppen und Bildung von Dibenzylätherbrücken, die bei etwa 210°C zerstört werden. Es wird angenommen, dass für den ganzen Härtungsprozess ein Radikalmechanismus bestimmend ist. Schliesslich tritt Oxydation des Harzes auch bei Einwirkung von Feuchtigkeit bei Raumtemperatur während einer bestimmten Zeitdauer ein.

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