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THERMAL ANALYSIS OF PHENOLIC RESIN BASED PYROPOLYMERS

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The formation and thermal behaviour of pyropolymers based on novolak resin synthesized under carefully controlled processing conditions have been studied by various thermoanalytical techniques. A suitable reaction scheme has been proposed for the formation of these pyropolymers. Only a small (3–8%) weight loss has been observed up to 800 °C in static air. DTA curves confirmed multistage exothermic processes predominantly due to two different linkages which control their thermo/thermo-oxidative stability. Hot metal filtration (≈700 °C) in an inert atmosphere exhibited only negligible weight loss.

Many high polymers when heated above 300° in an inert atmosphere tend to degrade and much of their non-carbon content is lost as gases leaving behind different forms of carbon. This process commonly known as carbonization gives rise to coke and/or char formation. The elimination of the non-carbon content is not complete until heat treatment temperature exceeds 1000°. Samples heated between 300 and 1000° exhibit properties intermediate between those of the polymer and carbon and are termed as "pyropolymers". The nature and properties of these pyropolymers depend on the chemistry of the starting material as well as on the processing conditions. Some of these pyropolymers are being used as surface coating, fibres etc. for various applications such as hot-filtration, microwave absorbers, bio-compatible surfaces, semiconducting layers etc. Although the chemistry of pyrolysis of polymeric materials has been studied in detail by thermoanalytical techniques, hardly any attempt has been made to analyse the complicated structure/property relationship of these intermediate pyropolymers. In the present investigation a high-char yielding phenolic resin and pyropolymers obtained from it through heat treatment were studied with thermoanalytical and spectroscopic techniques.

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Experimental

Novolak based pyropolymers were prepared in an inert atmosphere using a specially fabricated furnace having an accuracy of ± 1 deg to ± 3 deg depending upon the furnace temperature. IR spectra were recorded on a Perkin–Elmer (Model No. 598) instrument. A Stanton–Redcroft thermal analyzer STA–780 was used and a heating rate of 10 deg/min was applied. The amount of samples taken varied from 15 to 17 mg.

Results and discussion

Acid-catalysed phenol formaldehyde (Novolak) resin of the following structure (Fig. 1) has been used for the present work. It is a relatively short, low molecular weight, linear polymer soluble in conventional organic solvents. When heated slowly in an inert atmosphere, relatively small amounts (1–2%) of water and phenol evolve between 100 and 350°. Above this temperature it has been shown that small quantities of CO, CO_2 and CH_4 along with other aromatics (low mol.wt.) will be formed leaving behind 75–85% by weight of pyropolymers. The linear nature and low molecular weight of the starting material permits the evolution of water and phenol at such a low temperature. In the case of highly cross-linked material, water is not evolved until above 400°. Above 300° one can visualise the condensation of hydroxyl group on the neighbouring chain to form an ether linkage. Simultaneously the hydroxyl group may react with the methylene group in a neighbouring chain to form a closer crosslink similar to diphenylmethane structure. Figure 2 shows the weight loss curves of novolak resin (PF) and/or hexamethylenetetramine (HMTA) during pyrolysis as a function of temperature in an inert atmosphere. The nature of the curves is essentially similar although both the rate of weight loss and the final weight loss decrease with increasing molar concentration of HMTA as curing agent, levelling off at about 700°. Furthermore, one can easily visualise that the loss of water and/or phenol will be directly related to the initial 40% contraction in volume below 500° (Fig. 3) beyond which there may be a significant loss due to removal of hydrogen only. Both the above mentioned carbonization and

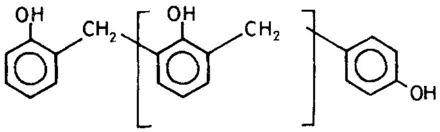


Fig. 1 Structure of novolak resin

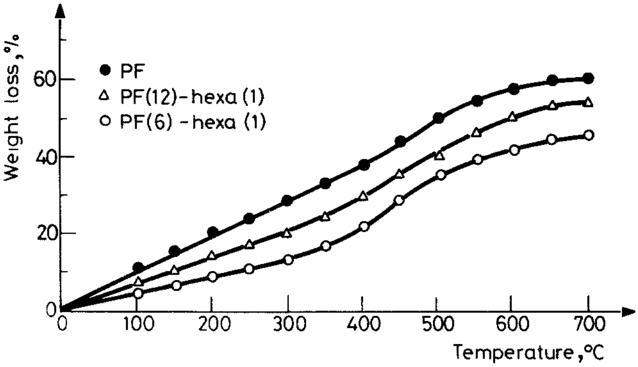


Fig. 2 Weight loss of novolak resin (PF) during pyrolysis

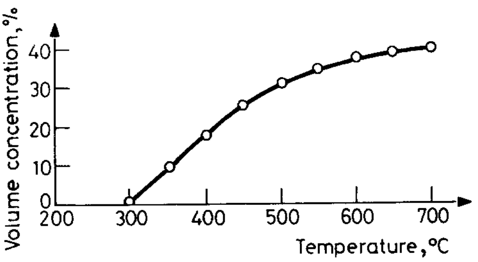
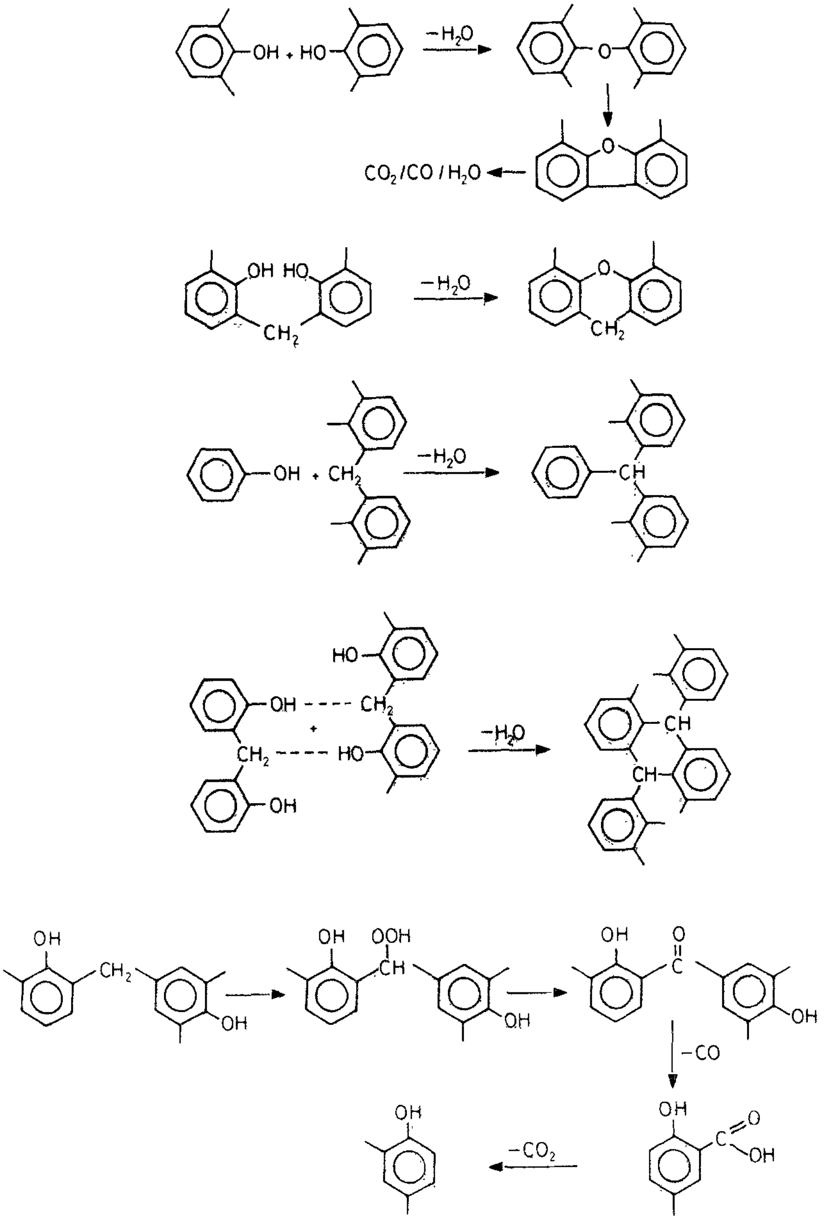


Fig. 3 Volume contraction of novolak resin/HMTA during pyrolysis

dehydrogenation step can be further distinguished by plotting the change in bulk density of the resulting pyropolymer against the weight loss of compacted discs (Fig. 4). The carbonization step weight loss also corresponds to a decrease in the bulk density (taking into account any loss due to foam formation) above which the density increases linearly with temperature due to dehydrogenation step and formation of a close-cell microporous structure [1]. Within the temperature range of our interest, the possible reactions taking place during the formation of pyropolymers of phenolic resins are shown in Scheme-1 [2]. In addition, IR absorption spectra of these pyropolymers also confirmed the presence of hydroxyl and carboxyl groups as evidenced by their bands around 3500 cm^{-1} (broad) and 1700 cm^{-1}, respectively. A tentative thermo-oxidative reaction sequence (300–500°) in nitrogen atmosphere is outlined in Scheme-2 [3].

The results of DTA, TG and DTG analysis of these pyropolymers are given in Table 1 and a typical plot is shown in Fig. 5. These experiments were performed in air and nitrogen atmospheres at a heating rate of 10 deg/min. It can be seen that all these pyropolymers show very high thermal and thermo-oxidative stability, degradation occurs between 375–400° and 500–550° in the majority of cases. The



Scheme1 and **2** Possible reactions taking place during formation of thermo-oxidative degradation of novolak pyropolymers

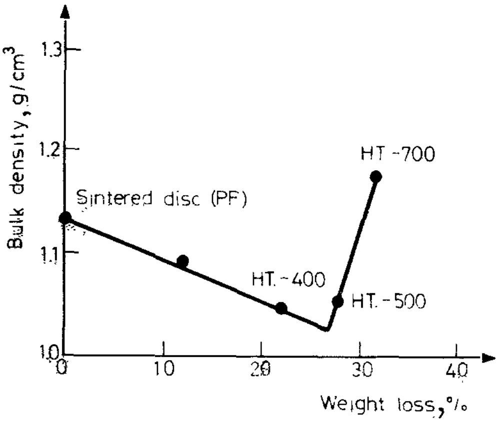


Fig. 4 Change in bulk density of novolak resin during pyrolysis as a function of weight loss

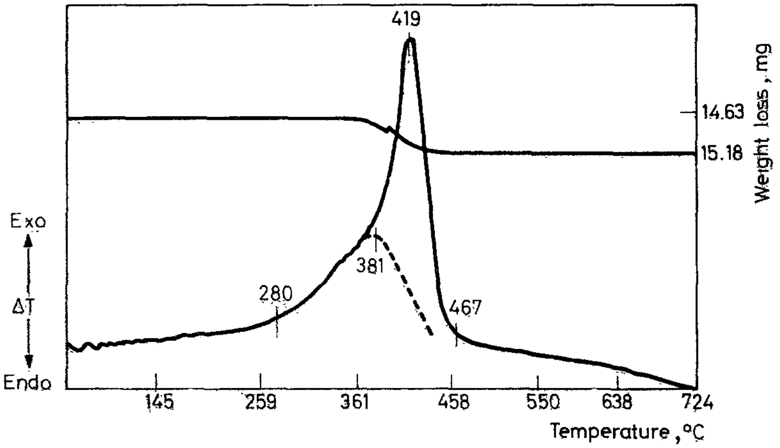


Fig. 5 DTA/TG curves for a typical novolak pyropolymer, B–II (post heat-treated at 400 °C for 3 h in N_2). Heating rate: 10 deg/min, atmosphere: static air

plot of the rate of weight loss process shows very clearly that in air the degradation is a multistage process, whereas in nitrogen there occurs essentially a single stage reaction with the formation of a fairly stable char in both the processes representing 90–95% by weight of the starting pyropolymers. it is interesting to note that the primary mode of breakdown is essentially thermo-oxidative. Thermal breakdown is negligible and it seems that char formation proceeds through X-linking. The multistage thermo-oxidative process signifies the predominance of two types of linking units present, which are known to pyrolyse around 400–450° and 500–550°, respectively. Initial decomposition temperature may be attributed to furan linkages which are only stable up to 250–275°. Processing conditions shift the rate of

Table 1 Effect of processing conditions on the thermal behaviour of phenolic pyropolymers

Sample number	Processing conditions	DTA peaks, °C				Wt. loss, %
		A	B	C	D	
B–I	100 °C (4 hrs) Air 400 °C (2 hrs) N_2	259	351	405	480	7.82
B–II	100 °C (4 hrs) Air 400 °C (3 hrs) N_2	280	381	419	467	3.60
B–III	100 °C (4 hrs) Air 450 °C (2 hrs) N_2	311	406	448	509	8.65
B–IV	100 °C (4 hrs) Air 500 °C (2 hrs) N_2	371	439	486	532	4.81

A – Initial decomposition temperature; B – Maximum rate of weight loss (1st stage); C – Maximum rate of weight loss (2nd stage); D – Burn out temperature.

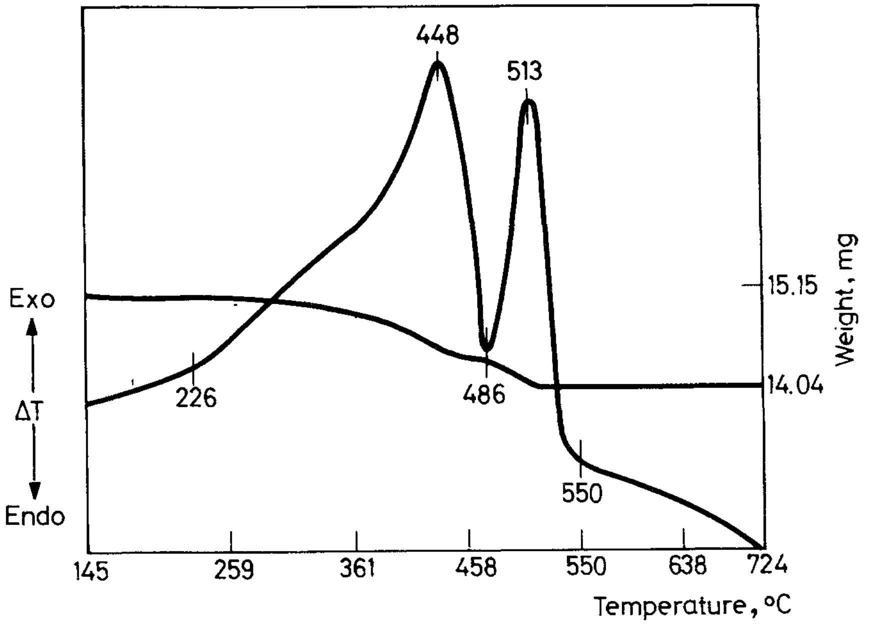


Fig. 6 DTA/TG curves for a speciality novolak pyropolymer. Heating rate: 10 deg/min, atmosphere: static air

maximum weight loss peak towards higher temperatures, probably signifying the conversion of furan linkages to other stable moieties. Furthermore, for suitably modified phenolic pyropolymers the two principle exotherms can further be shifted towards higher temperatures (Fig. 6) to enhance its thermal/thermo-oxidative stability. The preparative aspects of these systems will be published elsewhere [4]. During hot metal filtration ($\approx 700°$) in an inert atmosphere only negligible weight loss has been observed. In addition, preliminary studies confirmed their reasonably good mechanical, electrical, adhesion and biocompatibility properties.

References

1 E. Fitzer and W. Schäfer, Carbon, 8 (1970) 597.
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3 R. T. Couley, Thermal Stability of Polymers, Chapter 11, Marcel Dekker Inc., NY 1970.
4 A. K. Banthia and V. Jha, unpublished results.

Zusammenfassung — Mittels verschiedener thermoanalytischer Verfahren wurde Bildung und thermisches Verhalten von Pyropolymeren auf Novolackbasis unter streng geregelten Reaktionsbedingungen untersucht. Zur Bildung dieser Pyropolymere wurde ein geeignetes Reaktionsschema entwickelt. In unbewegter Luftatmosphäre kann bis 800 °C nur ein geringer (3–8%) Gewichtsverluft beobachtet werden. Die DTA-Kurven zeigen einen exothermen Mehrstufenprozeß, der hauptsächlich auf zwei verschiedene Verkettungen zurückzuführen ist, welche die thermische/thermisch-oxidative Stabilität bestimmen.

Резюме — Различными термоаналитическими методами изучено образование и термическое поведение пирополимеров на основе новолачной смолы и синтезированных в тщательно контролируемых условиях. Предложена приемлемая реакционная схема образования таких пирополимеров. В статической атмосфере воздуха до температуры 800° наблюдалась только незначительная (3–8%) потеря веса. Кривые ДТА подтвердили многостадийность экзотермических процессов, обусловленных преимущественно двумя различными звеньями цепи, определяющие их термо/термическую окислительно-восстановительную устойчивость. Горячая металлическая фильтрация ($\approx 700°$ в инертной атмосфере показала только незначительную потерю веса.