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Characterization of phenolic resins with thermogravimetry–mass spectrometry [α]

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Abstract

As part of an advanced material research program, thermogravimetry–mass spectrometry (TG–MS) analysis of a phenolic resin was carried out recently for the study of the curing of the prepolymer, solvent extraction and carbonization of the polymer at high temperature in an inert atmosphere. These steps are critical to the quality of the produced advanced material.

In addition to TG–MS, several other complementary techniques were also employed for the analysis of the phenolic resin prepolymer and its curing and thermal degradation products. These techniques include pyrolysis–gas chromatography–mass spectrometry, direct insertion probe–mass spectrometry and gas chromatography–mass spectrometry.

EXPERIMENTAL

The present TG–MS system [1] consists of a Stanton Redcroft TG-761 thermogravimetric analyzer (TGA) and an Extranuclear quadrupole mass spectrometer. An IBM PC-based data system (Vector One, Teknivent Corp.) is employed for the control of mass spectrometric operation and data acquisition. Several modifications were made recently to improve the overall TG–MS performance. One major achievement is the capability of TG operation at any pressure, ranging from near vacuum to atmospheric. In addition to the existing interface line with molecular jet separator, a direct gas line was installed between the TGA and the mass spectrometer ion source for vacuum TG operation.

All the pyrolysis and direct insertion probe analyses were done in a Kratos MS-25 mass spectrometer. Both this and a Finnigan ion trap detector were employed for the gas chromatography–mass spectrometry (GC–MS) studies.

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The phenolic resin used in the present study is a one step resole prepolymer [2] with a phenol–formaldehyde ratio of 0.37. It came as yellow–brown chunks and must be crushed to small pieces prior to analysis. The sample may contain some absorbed moisture owing to its long storage time of more than one year.

RESULTS AND DISCUSSION

GC–MS

The phenolic resin was first analyzed by GC–MS to identify the starting material composition in this prepolymer. In this analysis, 1 mg of the phenolic resin was dissolved in 1 ml and methanol, and 1 μl of the resulting solution was injected into the GC injector, which was maintained at 250 °C. It is expected that the resin, which exists in a dilute solution, once vaporized inside the injector will have little chance of further polymerization before it is swept into the GC column by the carrier gas (He).

The GC column chosen for this work is a non-polar SPB-1 capillary column (Supelco, Inc.) which was programmed from 50 to 250 °C at 10 °C min^{-1}. The effluent from the GC column was subsequently analyzed by the ion trap detector, which repetitively scans over a mass range of m/z 45–650. The result of this analysis is shown in Fig. 1. A similar analysis result was also obtained using the Kratos MS-25 mass spectrometer.

The two major peaks in the total ion chromatogram trace are identified as phenol and methylphenol (cresol). This is somewhat different from the most common phenolic resin prepolymer [3], which has only phenol as a major

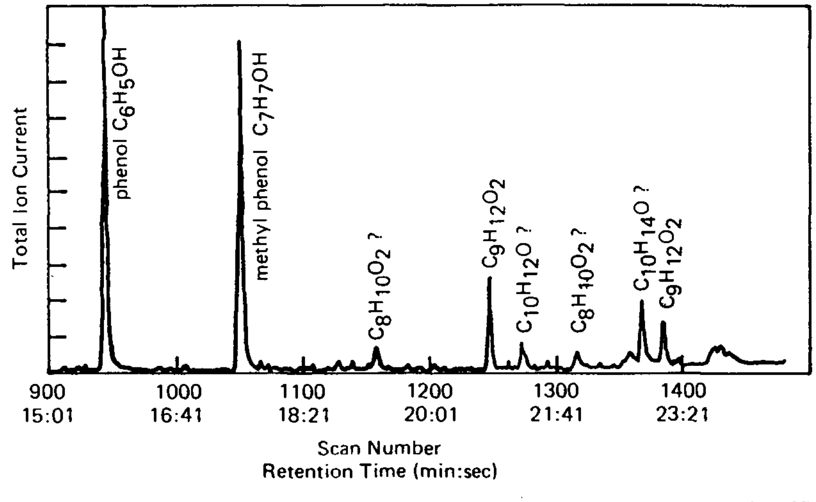

Fig. 1. Total ion chromatogram of the phenolic resin prepolymer by GC–MS.

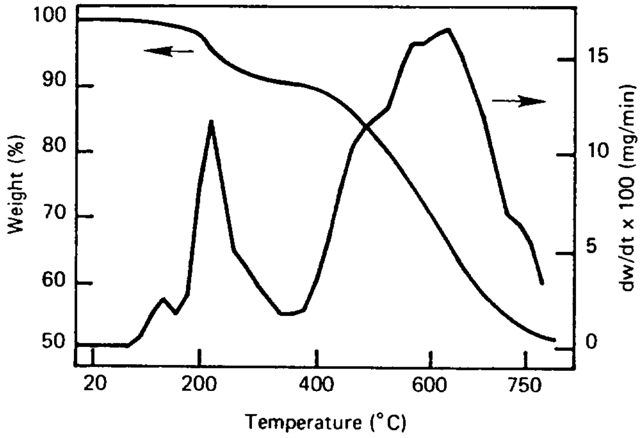

Fig. 2. TG and DTG traces of the phenolic resins.

constituent. A total of six peaks appear beyond the cresol peak. Two of them are tentatively identified as $C_9H_{12}O_2$, with unknown structural formula. Both are likely to be certain substituted methylols, which are known [3] to be the major components in a phenolic resin resole prepolymer. The four other chromatographic peaks remain unidentified.

It should be noted that other components may also exist in the resin, but they fail to elute through the GC column and be detected. Any prepolymer that polymerizes inside the GC injector or column will not be shown in the chromatogram either.

TG–MS

Figure 2 shows the TG and DTG traces of the phenolic resin which was heated from 20–750 °C at 5 °C min^{-1} in a helium atmosphere. As clearly seen in the DTG trace, the resin sample experiences three distinctly different regions during the heating process. The first region (20–180 °C) corresponds to a weight loss of 1–2%, representing the loss of the absorbed water, as made clear through simultaneous MS analysis. The second region (180–300 °C), with weight loss of 8%, signifies the curing of the phenolic resin. Beyond 300 °C, the polymer thermal degradation begins to take place, and will continue throughout the heating process. At the end of the TG run, a fused black char remains, which consists of approximately 50% of the original sample weight.

Figure 3 displays the traces of all major ions obtained during the mass spectrometric monitoring of the evolved gas. Each of these traces is individually normalized for clarity. The full-scale intensity for each trace is indicated as shown. Gas species contributing to these ions are also displayed in the figure.

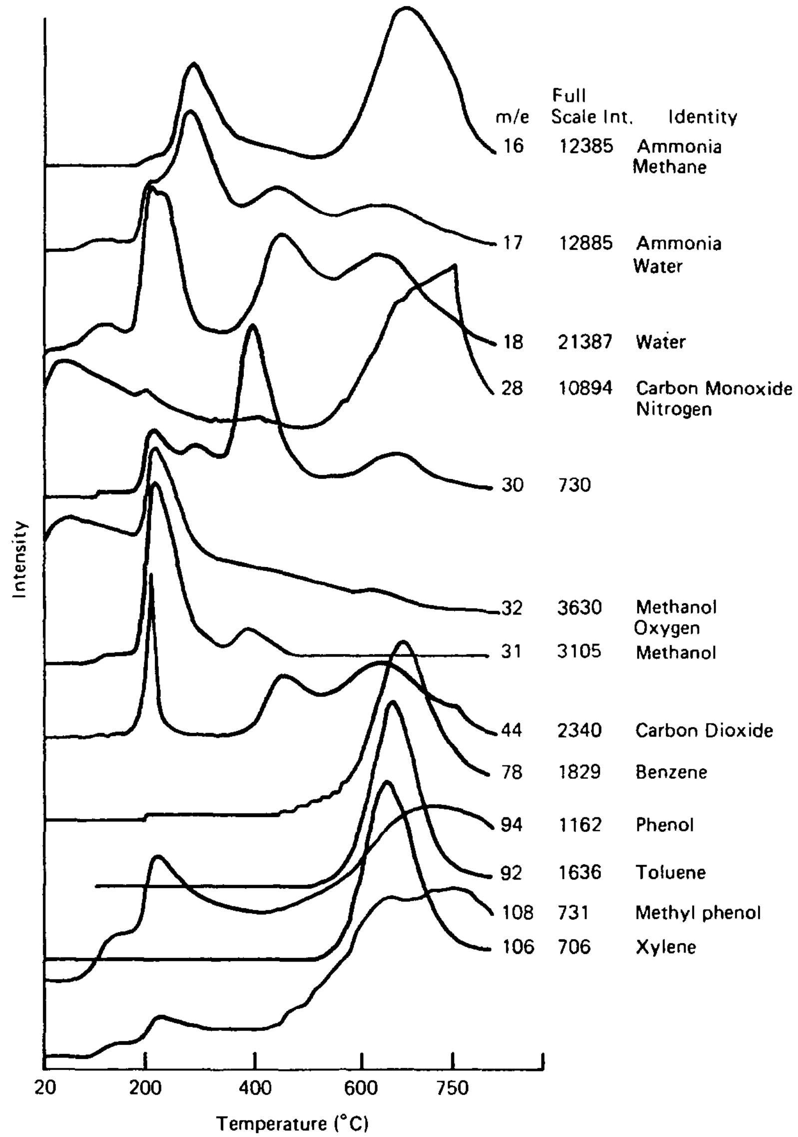

Fig. 3. Traces of major ions from the evolved gas.

Positive identification of all the evolved gases based on the TG–MS data alone is very difficult, owing to mass spectrometric interference problems. This is especially true at several TG temperatures (e.g., 200° and 615°C) during which several different gases contributing to the same ions observed were evolved simultaneously. Positive identification of the evolved gases was finally achieved with the assistance of the complementary information obtained from the pyrolysis–GC–MS analysis, which will be discussed in a later section.

TABLE 1

List of gases evolved during the phenolic resin TG–MS experiment

Peak temperature (°C)	Gas	Estimated weight loss (%)
120	Water	0.8
145	Phenol	0.3
210	Water	4.4
	Phenol	1.8
	Methanol	1.2
	Carbon dioxide	0.4
270	Ammonia	2.7
370	Unidentified	0.3
420	Water	5.0
	Carbon dioxide	0.7
580	Water	5.7
	Carbon dioxide	1.3
650	Methane	3.8
	Benzene	3.4
	Toluene	2.7
	Xylene	1.3
	Trimethylbenzene	0.2
720	Phenol	4.1
	Cresol	2.6
	Dimethylphenol	1.1
	Trimethylphenol	0.1
	Carbon monoxide	6.1
20–750	Total	50

Listed in Table 1 are all the identified gases evolved at each peak temperature, as represented by the ion traces in Fig. 3. Also listed in this table are the estimated weight loss (%) contributed by each identified gas centered at the given peak temperature. In this estimation, it is assumed that (1) all gas species have the same ionization sensitivity factor (base ion intensity per mole); and (2) the total weight loss of 50% as obtained from the TGA experiment (Fig. 2) is entirely attributed to the gases listed in the table.

As discussed previously, the water evolved at 120 °C is due to the loss of the absorbed water in the phenolic resin. Phenol detected at 145° and 210 °C probably results simply from the evaporation of phenol near the surface of the phenolic resin chunks.

The evolution of water at 210 °C has been well established [3] as resulting from the condensation reactions among phenols and methylols. These reactions rapidly lead to the formation of a three-dimensional macromolecule crosslinked by methylene and ether bridges. It is believed that the release of methanol may also result from the similar condensation reactions in which the methoxy branch of the methylol is extracted.

The source of the formation of CO_2 at 210 ° C is not clear. The sharp peak shape of the m/z 44 trace as seen in Fig. 3 differs from the shape of all other ion peaks at this temperature. The possibility of oxidation of certain additives in the resin mixture cannot be ruled out.

Clearly, the ammonia detected at 270 ° C must be released from certain ammonia-containing additives in the phenolic resin. Ammonia is a well known alkaline catalyst in the one-step resins [3]. On the other hand, ammonia was also detected [4] in a novalac–hexaphenolic resin after heating to near 200 ° C.

As seen in Table 1, the thermal degradation of the polymer and its resulting weight loss largely occur over four temperature zones. At 420 ° and 580 ° C, water is the major gas evolved, and is accompanied by a small amount of carbon dioxide. Large amounts of methane were observed at 650 ° C. At the same temperature, significant quantities of benzene and substituted benzenes were also released. At the final temperature of 720 ° C, the major gas detected is carbon monoxide. Some phenol and substituted phenols also evolve continually until the end of the heating cycle.

The thermal degradation of the phenolic polymer has been studied extensively by Jackson and Conley [5]. In their study, pyrolysis–GC was employed for analyzing volatile gas evolved from the polymer sample. A detailed mechanism for the thermal degradation was also postulated, based largely on the infrared spectral analysis of the thermally degraded polymer.

Table 2 provides a direct comparison of the released volatile gas composition from the present TG–MS work and from the pyrolysis–GC study [5]. Overall agreement is very good in spite of the crudeness in the assumption adopted for the present weight loss computation. Except for several minor species, as indicated in the table, all major evolved gases are reported in both works. The most serious disagreement is in the yield of carbon dioxide, which may suggest some difference in the thermal degradation of the phenolic polymer under a low TG heating rate (5 ° C min^{-1}) in contrast to the high heating rate (310 ° C s^{-1}) of pyrolysis.

It is interesting to note that the present TG trace is almost identical to that in previously reported work [6] using a phenolic resin with a phenol–formaldehyde ratio of 0.36. The only difference is the much smaller loss of water during the first stage in the earlier work. This is expected in view of the relatively long storage period of the present sample, during which some absorption of moisture may take place

In this same work [6], the elemental compositions of both the starting phenolic resin and the char residue after the thermogravimetric analysis were also determined with the use of a carbon–hydrogen analyzer. It is not unreasonable to assume that the phenolic resin of the present work will have the same elemental composition as the one used in the reported work [6] in view of their identical TG trace. With this assumption, it is possible to calculate the final elemental composition of the char residue resulting from

TABLE 2

Comparison of the released volatile gas compositions from the present TG–MS work and pyrolysis–GC [5]

Product	Weight loss (%)	
	TG–MS [a]	Pyrolysis–GC [b]
Water	15.9	[c]
Carbon dioxide	2.4	8
Methanol	1.2	[d]
Methane	3.8	2.5
Benzene and substituted benzene	7.6	2.0 [e]
Carbon monoxide	6.1	5
Phenol and substituted phenols	10.00	9.5 [f]
Benzaldehyde	[d]	0.2
Paraformaldehyde	[d]	[c]

[a] Water (0.8% at 120 °C), ammonia (2.7%), and unidentified (0.3%) not included.

[b] Pyrolysis condition [5]: sample (precured 3 h at 120 °C) heated to 800 °C at a heating rate of 310 °C s^{-1} with a total heating time of 10 s.

[c] Detected, weight loss amount not reported.

[d] Not detected.

[e] Xylene and trimethylbenzene not detected.

[f] Dimethylphenol and trimethylphenol not detected.

the present thermogravimetric analysis based on the evolved gas information in Table 1. The result of such calculation is shown in Table 3. The agreement is acceptable, which again validates the accuracy of the present gas analysis.

The present TG–MS data generally supports the postulated thermal degradation mechanism [5], in which the methylene bridge in the polymer will first undergo oxidative degradation to form dihydroxybenzophenone linkages accompanied by the release of water. At higher temperature this linkage will be further converted to carbon char through the formation of a quinone-type linkage as well as evolution of carbon monoxide. Methane is

TABLE 3

Comparison of calculated elemental composition of the phenolic residue from the present TG–MS work and the reported value [6]

	Elemental composition					
	This work			Reported value [6]		
	C (%)	H (%)	O (%)	C (%)	H (%)	O (%)
Initial sample	72.37 [a]	5.31 [a]	22.32 [a]	72.37	5.31	22.32
Residue	95.2	2.2	2.6	94.12	1.13	4.75

[a] Assumed value; see text.

thought to be formed largely via a hydrogen abstraction process by methyl radicals. Water can also be formed similarly by hydroxyl radicals.

The pyrolysis study [5] shows that most phenol, cresols and higher phenolic species are formed at quite a low temperature (500 ° C). This leads to the conclusion that these products are most likely formed from dihydroxydiphenylmethane and slightly higher homologs entrapped in the cured resin system. However, this rationale may only partially explain the present thermogravimetric process in which the majority of the phenols, cresols and higher phenolic species appear only above 600 ° C and continue to be evolved until the end of the heating process.

It was suggested [5] that carbon dioxide is formed mainly through a decarboxylation process following the polymer oxidative degradation. This process may not be significant in view of the much lower yield of carbon dioxide from the thermogravimetric heating (see Table 2). Since the ion curve for m/z 44 closely tracks the m/z 18 ion curve over the entire thermal degradation temperature range (400–750 ° C), any plausible carbon dioxide formation mechanism must be compatible with the scheme under which water can also be formed concurrently.

Pyrolysis–GC–MS

Figure 4 shows the mass chromatogram traces obtained from the pyrolysis–GC–MS of the phenolic resin. In this experiment, the phenolic resin sample is heated to 750 ° C for 10 s at a heating rate of 1000 ° C s^{-1}. The volatile gas evolved is swept into the GC column (SPB-1, 30 m × 0.53

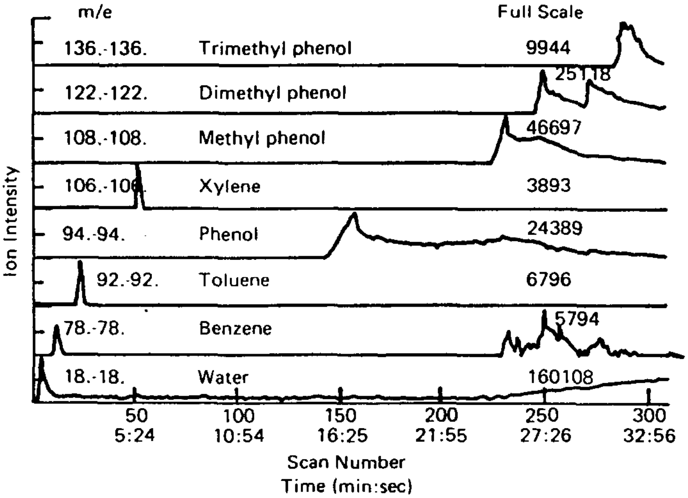

Fig. 4. Mass chromatograms of phenolic resin (pyrolysis–GC–MS).

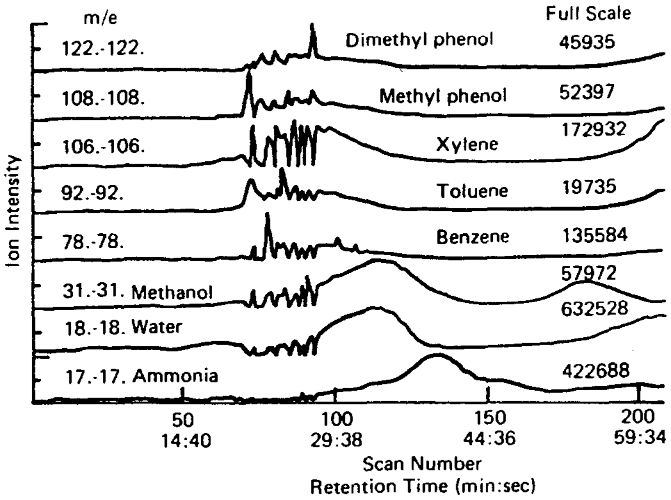

Fig. 5. Mass chromatograms of phenolic resin (direct insertion probe–MS).

mm × 0.5 μm; Supelco Inc.) which is programmed from 30–250 °C at 5 °C min^{-1} with an initial hold at 30 °C for 20 min.

As seen in the figure, the pyrolyzed gas detected includes water, benzene, toluene, xylene, phenol, cresols and xylenol. Because of the GC column used, other expected products such as methane, ammonia, carbon monoxide and carbon dioxide were not detected. Similar experiments with pyrolysis temperatures of 200° and 300 °C were also carried out. Only phenol and cresol were detected in such experiments. All these experiments were intended solely for facilitating the identification of gases evolved in the TG–MS analysis. No quantitation is intended.

Direct insertion probe–MS

In the present experiment the phenolic resin was placed within the direct insertion probe, which was heated from 30–280 °C at 5 °C min^{-1}. The obtained mass chromatograms for several major ions are shown in Fig. 5. The detected species include ammonia, water, methanol, benzene, toluene, xylene, phenol, cresol and xylenol. All these were seen in the TG–MS trace and thus further validate the TG–MS results.

It is interesting to note that there are significant fluctuations in all ion signals at 20–30 min (120–170 °C). These fluctuations are random but reproducible in all runs. Furthermore, the fluctuation patterns of all ion traces are not identical. All these fluctuations reflect the random nature in the condensation/thermal degradation process of the phenolic resin and the difference in mechanism for the formation of all the gases evolved. A similar fluctuation was also observed in the TG–MS study [7] of a methylol allyl phenyl ether type phenolic resin.

CONCLUSIONS

A phenolic resin used in Mound production was characterized in detail by thermogravimetry–mass spectrometry. A GC–MS analysis provides a better understanding of the chemical composition of the starting material. Other techniques including pyrolysis–GC–MS and direct insertion probe–MS provide complementary information, which greatly facilitates the identification of gases evolved in the TG–MS analysis.

The obtained TG profile is in excellent agreement with that for reported TG work with a similar phenolic resin. The evolved gas composition is also in good agreement with that of a reported pyrolysis–GC analysis.

The detailed temporal profile of the gas evolution from the thermogravimetry process allows a close examination of the postulated thermal degradation pathways of the cured polymer. This results in general support of the established mechanism. However, the process for the formation of carbon dioxide and phenol and higher phenolic species, which was originally based on the pyrolysis study, was found less suitable in accounting for the present thermogravimetric phenomena.

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