

## Phenolic resins

### Part 6. Identifications of volatile organic molecules during thermal treatment of neat resols and resol filled with glass fibers

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#### Abstract

The physicochemical characterization of resols before and after cross-linking in the presence and absence of fiberglass was carried out using spectroscopic and chromatographic techniques.

Experiments involving gas chromatographic thermodesorption coupled with mass spectrometry (GC–MS) led to the identification of the different volatile organic compounds present during the heat treatment of neat resol and resol filled with glass fibers.

The results show that the knowledge of initial resol structures are very important data for kinetically following the departure of volatile compounds during resol manufacture. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Phenol–formaldehyde resin; Degradation; Volatile organic compounds

#### 1. Introduction

In continuation of our work on phenolic resins [1–5], we have investigated and characterized volatile organic compounds released during the cross-linking of filled systems [6,7]. This was done in the framework of a modeling study of the degradation of phenolic resins in the presence of a filler (glass wool).

The work involved resols obtained in a basic medium having a formol/phenol ratio (F/P) higher than 1. On the basis of published data [6,7,11] and our own results in the laboratory [1–5], the prepolymers obtained are single- and/or poly-ring hydroxymethylphenols.

These prepolymers are cross-linked by the action of heat in the presence of an acid or a base. They form a three-dimensional network acting as binders in materials filled with fiberglass.

There were three objectives for this work:

- The first involved the characterization of the raw prepolymer in order to determine reactivity as a function of the F/P ratio and of the catalyst used to prepare the resol.
- The second was to determine the degree of cross-linking of fiberglass-filled products after precure and postcure.
- The third was to identify the volatile organic compounds

(VOC) released during the different heat treatments in the polymerization process.

For the first two points, a dynamic physicochemical study using thermal techniques, e.g. differential scanning calorimetry (DSC) and pyrolysis, was carried out. They were coupled with chromatographic methods in order to analyze the products formed in resins during the polymerization cycle, with or without glass fiber.

An experimental system described in this publication was developed to study the third point. It included, desorption, coupled with gas chromatography–mass spectrometry, enabling the analysis of VOC in solid compounds without prior extraction. There prepregs were heated at different degradation temperatures and the products trapped were characterized directly.

#### 2. Experimental part

##### 2.1. Samples

###### 2.1.1. Raw materials

Phenol P (98%), formaldehyde F (37% solution (w/w)) and an alkaline hydroxide, Ba(OH)<sub>2</sub> (98%), were obtained commercially (Aldrich) and used as received.

###### 2.1.2. Synthesis of resols

Phenol (P) and formaldehyde (F) were mixed at 60°C in a

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defined ratio  $R = [F/P]$  (mol/mol). The pH was adjusted to 8 with titrated solutions of alkaline hydroxide.

The characteristics of the resol studied were:

Resol R:  $F/P = 3.2$  mol/mol, catalyst  $Ba(OH)_2$  free formol (%liq) less than 7, free phenol (%liq) < 1).

### 2.1.3. Resol–glass wool composite preparation

**2.1.3.1. The binder.** The binder was a mixture of the resol R with a basic cross-linking (ammonia and urea).

**2.1.3.2. Preimpregnate.** The prepreg was obtained by blending the binder with the glass wool (15% weight) using an industrial process (the products were provided by Iover Saint Gobain.)

**2.1.3.3. Cured product.** The prepreg was heated with a precise thermal cycle in various baths and ventilated ovens.

## 2.2. Experimental techniques

### 2.2.1. Thermal measurements

A Du Pont Model 10 DSC heat flux apparatus was used to determine temperatures and heats of reaction. Masses of about 30 mg (prepreg) and 10 mg (neat resol) were placed in a loosely covered aluminum crucible. They were heated with an argon blanket from 30 to 450°C at the rate of 5°C min<sup>-1</sup>.

### 2.2.2. Separation methods

**2.2.2.1. High performance liquid chromatography.** A Hewlett Packard HP-1090 chromatographic system was used. It was composed of quaternary pumping (four different solvents), an automatic injector and a diode array detector covering the wavelength range of 190–600 nm. Acquisition was with HP software for High performance liquid chromatography (HPLC) (G 2170 AA).

The separation system was composed of a precolumn and elution from a column of Inerstil ODS (C18, particle diameter = 5 μm) 3 mm × 25 cm. The eluent was a gradient of water/methanol/tetrahydrofuran at a flow-rate of 0.4 ml min<sup>-1</sup>.

**2.2.2.2. Preparation of neat resol and preimpregnate samples for HPLC analysis.** The resol was dissolved in de-ionized water, filtered and injected. The peaks detected were identified with respect to standards and integrated to determine the relative quantities of each mono- or polycondensed species.

Preimpregnated extracts were prepared from the resol as described below.

Five grams of preimpregnate was added to a 150 ml flask, followed by 100 ml of de-ionized water. After mixing for 2.5 h, the preimpregnate was removed from the flask. The extract was filtered and injected directly into the HPLC system.

The same procedure as that used for the resols was applied for the quantification of the present species.

**2.2.2.3. Size exclusion chromatography.** Size exclusion chromatography (SEC) analyses were carried out with a Varian chromatography system including a CPL 9012 pump, a fixed UV detector set at 254 nm, followed by a UV 9065 diode array detector and software for piloting and data processing.

The mobile phase was tetrahydrofuran (THF) a the flow-rate of 1 ml min<sup>-1</sup>. An external 20 μl loop was used for injection. The separation system was composed of an HXL PRD01N precolumn and two columns in series.

The first column was TSK gel G 2000 HXL, 7.8 × 30 cm packed with 5 μm particles and with the exclusion limits of 0–10,000 Da. The second column was TSK gel G 1000 HXL of the same size and particle diameter but whose exclusion limits were 0–1000 Da.

The calculation of masses was based on the retention volumes of the eluted compounds. Polymer Laboratories software carried out these calculations from the chromatograms obtained with the fixed wavelength detector (254 nm). The calibration curve of retention volume vs. log molar mass was established with polystyrene standards of increasing mass.

**2.2.2.4. Preparation of samples for SEC chromatographic analysis.** Products were dissolved in the mobile phase (THF). 0.0256 g of resol R was dissolved in 5 ml of THF. The solution was filtered before injection.

For the preimpregnate, an extract was prepared in the same solvent. 5.0195 grams of glass wool preimpregnate was added to a 150 ml flask followed by 100 ml of THF. After stirring for 2 h and extraction of the glass wool, the solution was filtered and injected.

## 2.3. Analysis of volatile compounds

### 2.3.1. System + CT/PIT-GC–MS (thermal desorption cold trap injector/purge and trap injector) coupled gas chromatography–mass spectrometry

- Thermal desorption cold trap injector/purge and trap injector) (TCT/PTI). The TCP/PIT used was Chrompack model CP-4010. The instrument was composed of a heating block in which a Pyrex or glass tube was placed. The tube outlet was connected to a cold trap composed of a portion of column chilled to an adjustable temperature between 0 and –150°C. (chilled with a stream of liquid nitrogen)

The temperature of the trap during injection increased from –100°C (for example) to 280°C in less than 30 s.

### 2.3.2. Gas chromatography–mass spectrometry

Analyses were carried out with a Varian model CX 3400 equipped with a Saturn ion trap. The column was a

moderately polar DB 17, 30 m long, with inner diameter 0.25 mm and film thickness 0.25  $\mu\text{m}$ .

### 3. Analyses of the results

#### 3.1. Mechanisms of polycondensation and cross-linking

Fig. 1 summarizes the mechanisms of prepolymer formation in basic catalysis. Fig. 2 shows the general mechanisms of cross-linking in basic medium in the presence of urea.

There are several mechanisms for explaining the formation of the first reaction intermediates. These mechanisms are more or less probable depending on the conditions of synthesis. The first one (Fig. 1) involves a C-alkylation [6,7] of phenol or rather the phenoxide ion in basic medium. This reaction occurs preferentially on the *ortho* and *para* positions, leading to the formation of two hydroxymethylphenol monomers (HMP). Condensation reactions on these two compounds by the same mechanism yield di- and trisubstituted species (formation of 2,4-DHMP, 2,6-DHMP and 2,4,6-THMP).

Another mechanism [6,7] involves first the formation of the hemiacetal of phenol (Fig. 1b). The HMPs are then formed by the tautomeric rearrangement of this hemiacetal.

A third mechanism was proposed by Price [8], involving the chelated form of the phenol salt formed in basic medium. This can be compared to the mechanism proposed by De Jong and De Jong [9] and Peer [10] (Fig. 1c). These mechanisms explain the formation of 2-HMP but cannot be envisaged for the formation of 4-HMP.

When polyhydroxymethylphenols are heated, they react mutually by co-condensation to form a three-dimensional network. Three mechanisms have been proposed to explain the formation of the network resulting from thermal activation. They are all possible as a function of the conditions in which cross-linking was carried out. They yielded two structures involving two different bridging groups (Fig. 1d–f).

In the presence of urea and ammonia, cross-linking can be conducted in basic medium [12–14], which improves the non-flammability of the resins. This reaction is highly pH-dependent and is often buffered. This results in formol–urea linkages (Fig. 1g).

#### 3.2. Characterization of the resol and glass wool prepreps by HPLC and SEC chromatographies

HPLC made it possible to assay the various initial monomers (Table 1). The results show that the quantity of 2,6-DHMP varied little between the resol and the preimpregnated fiberglass. On the contrary, there were greater quantities of 2,4,6-THMP in the fiberglass.

In addition, monosubstituted and disubstituted compounds disappeared in favor of higher molecular weight molecules after the onset of cross-linking. This

was confirmed by SEC analysis (Table 2). First of all, number of products were found both in the resin and the preimpregnate. As in the case of HPLC, the trisubstituted compound 2,4,6-THMP increased, but new, higher molecular weight products (A, B, C) appeared in the preimpregnate extract, confirming that the process for preparing the preimpregnates involved co-condensation reactions. In light of the molecular weight shift due to the steric volume of the model compounds, we were able to calculate the molar masses of the new compounds detected. They were condensation products of two substituted phenolic molecules.

#### 3.3. Thermal behavior of the resol and the prepreg

In order to determine the quantity of binder in the preimpregnated glass film, a complete pyrolysis of the preimpregnate was carried out in the temperature range of 50–500°C. Pyrolysis was coupled with an elemental analysis. Carbon, hydrogen and nitrogen (in %) could be assayed during the heat cycle. Carbon and hydrogen were present at all temperatures, with maxima around 165, 230, 300 and 485°C, while nitrogen (from the decomposition of urea bridges) appeared only starting at 180°C.

The preimpregnate was weighed before and after pyrolysis. The residue was situated at around 85%, confirming an organic binder approaching 15%, as expected from the preimpregnation process used.

Polymerization temperature and enthalpies were obtained from the thermograms of the resol and the preimpregnate (Table 3). The results show that a first peak was observed around 130°C, that could have resulted from the transformation of dimethylene ether bridges into methylene bridges. The peak reached its maximum at 185°C (cross-linking of the resin). The third peak, observed at high temperatures, resulted from degradation of the resin [15,16].

The differences between the filled and neat resin were minimal.

#### 3.4. Identification of volatile organic compounds

The aim of this part was to first characterize the organic matrix and then to identify the volatile compounds presents during heating of the preimpregnate in the course of its manufacture.

#### 3.5. Search for probable molecules

The molecules formed by the polymerization and condensation reactions were taken into consideration and those that could have been present were inventoried. It is consistent to believe that the reactions with urea and ammonia, as well as probable dehydration reactions, would occur preferentially on 2,4,6-THMP, which is the majority monomer. The possible reactions and molar

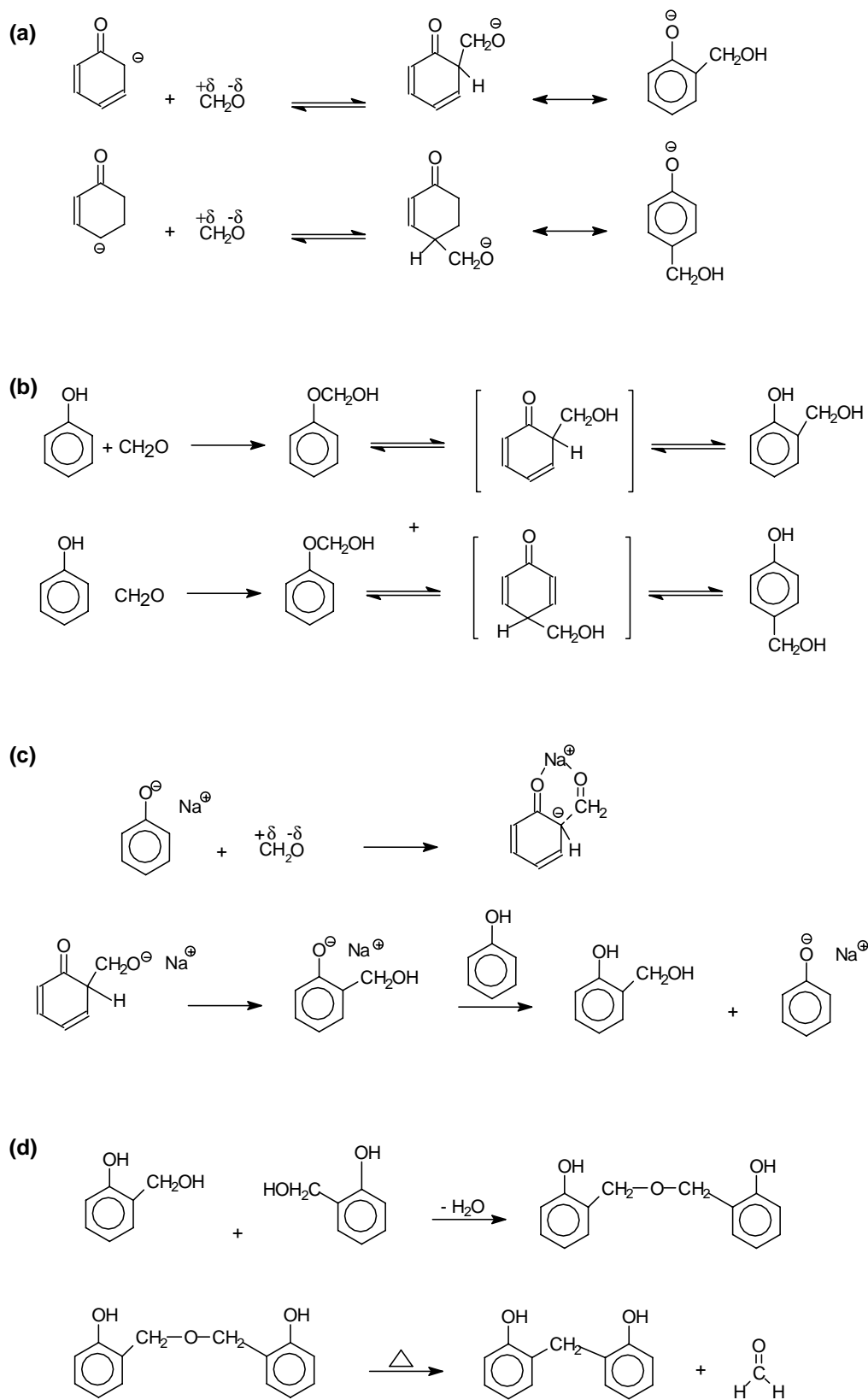


Fig. 1. Mechanisms of condensation and cross-linking: (a) mechanism of C-alkylation; (b) reaction mechanism involving a hemiacetal intermediate; (c) reaction mechanism involving the chelated form; (d) reaction mechanism leading to the formation of the dimethyl ether bridge; (e) reaction mechanism of the formation of the methylene bridge by loss of formaldehyde; (f) reaction mechanism of condensation; and (g) condensation mechanism of urea on a hydroxymethylphenol.

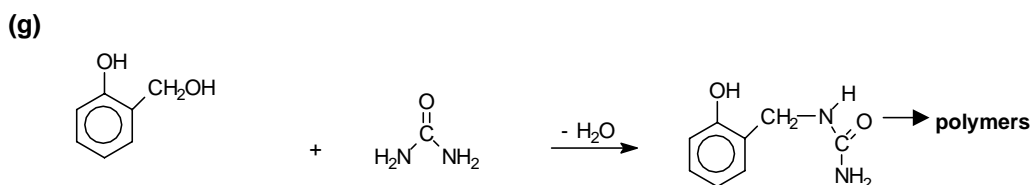
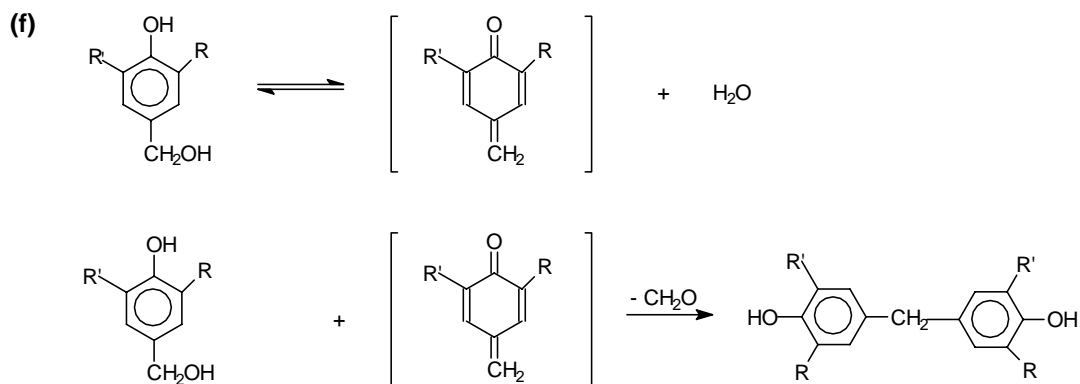
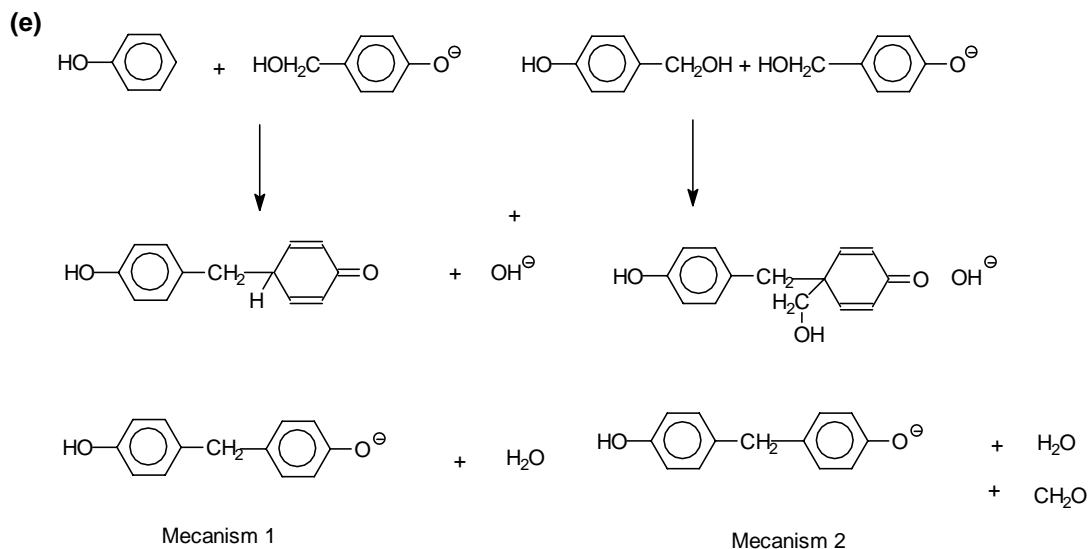


Fig. 1. (continued)

masses associated with the different products expected are shown in Fig. 2.

The different reactivities of the monomers show that the molecule present in the initial resol can react once or twice with ammonia and/or urea. The reaction with urea thus increased molar masses by 42, while the reaction with ammonia decrease mass by one AMU.

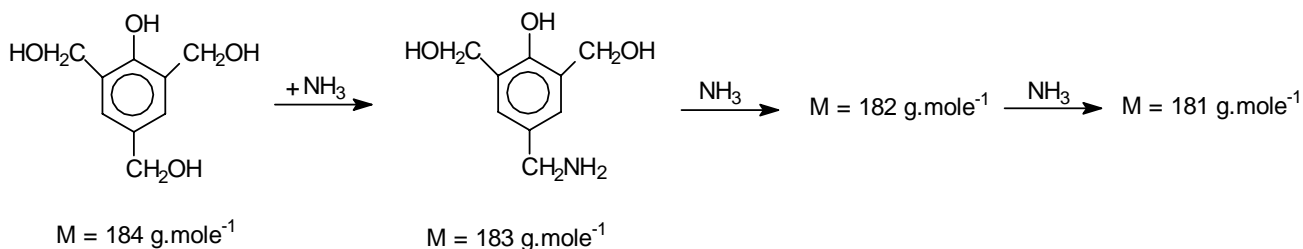
These reaction hypotheses are not exhaustive, since the preimpregnate contains mono- and disubstituted molecules that could also react with ammonia and urea. Condensation

reactions between two phenolic compounds could occur in parallel and yield, as expected, the three-dimensional network. Since these possibilities are numerous, we initially carried out a modeling study based on the initial substituted phenols that we isolated and characterized in prior work [2].

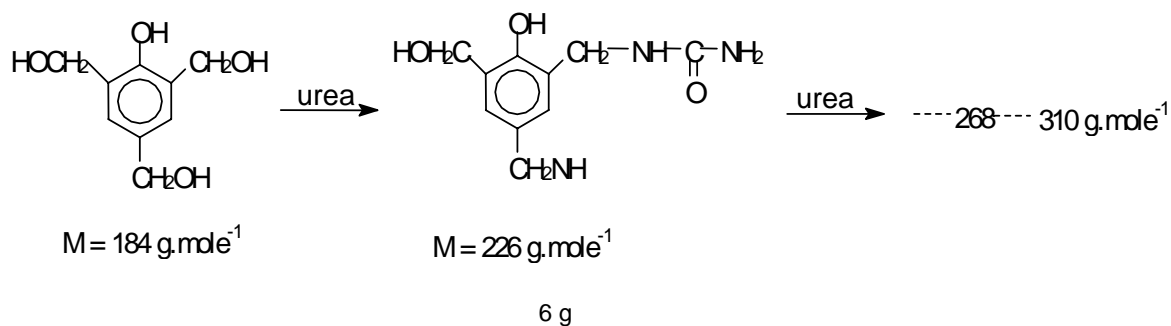
### 3.6. Characterization of monomers present in the preimpregnate

A model mixture was analyzed by coupled GC–MS. A

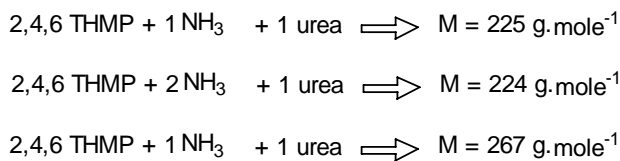
(a)



(b)



(c)



(d)

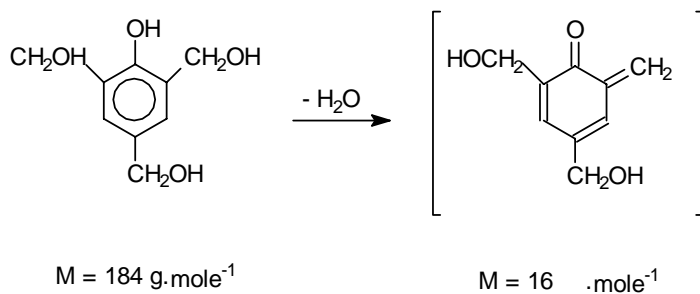


Fig. 2. Modeling the predictable reactions of 2,4,6-THMP: (a) with ammonia; (b) with urea; (c) ammonia and urea; and (d) dehydration reaction of 2,4,6-THMP.

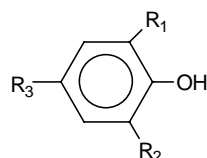
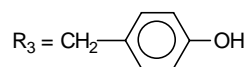
spectrum library was established. Table 4 summarizes the principal fragments whose presence was expected (2,4 and 2,4,6-HMP were not examined since they are insoluble in the medium). These compounds all contain the same type of

fragment and although they all exhibit their own mass spectrum, they all contain practically the same functions and the fragments are not especially characteristic of a molecule (Fig. 3).

Table 1  
HPLC analysis results

Compounds	Resol		Prepreg	
	$R_t$ (min)	Surface (%)	$R_t$ (min)	Surface (%)
2,4,6-THMP	4.31	50.27	4.33	61.40
2,4-DHMP	4.58	19.28	4.61	16.45
4-HMP	5.59	8.16	5.62	6.37
2,6-DHMP	7.04	2.01	7.08	2.39
2-HMP	9.00	8.76	9.04	3.92
Phenol	13.62	10.67	13.66	9.12
4-4'-DHDMP	20.40	0.84	20.39	0.35

a

2,4,6 THMP-  $R_1 = R_2 = R_3 = CH_2OH$ 2,4 DHMP -  $R_2 = R_3 = CH_2OH = R_1 = H$ 4 HMP -  $R_1 = R_2 = H = R_3 = CH_2OH$ 4,4 DHDMP-  $R_1 = R_2 = H$ 

## 3.7. Analysis of preimpregnates with the TCT-GC-MS system

In light of the previous pyrolysis results, four analysis temperatures were determined. The aim of this work was to identify the molecules released by evaporation as a function of the temperature and those resulting from cross-linking of the preimpregnate. Setting the cold trap to  $-100^\circ\text{C}$  guaranteed optimal trapping of desorbed molecules.

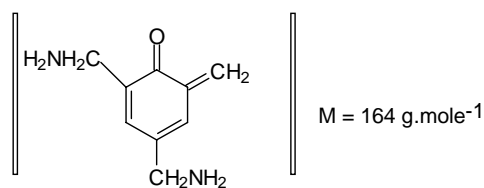
Four chromatograms obtained at the four analysis temperatures were recorded. The results (Table 4) show that the molecules were not all released at the same temperature. Some were present in the preimpregnate from the onset, especially those desorbed at  $75^\circ\text{C}$ .

Phenol appeared with a retention time of about 10.5 min. Similarly, a peak of dioxane (from formaldehyde) was present. These products are the starting reagents.

The chromatograms obtained at  $75$  and  $180^\circ\text{C}$  reveal the

presence of HMP, eluted around 21 min. This would indicate that the monosubstituted compound is not especially reactive towards ammonia and urea. The chromatogram obtained at  $300^\circ\text{C}$ , however, contained a peak at 26.96 min with a mass of 166 and that contained a fragment at MW 108 (loss of 58 mass units). This could be the formol-urea monomer synthesized from monohydroxy-methylphenol.

Similarly, there was a peak of molecular mass 164, which could be attributed to dehydrated THMP that reacted with two  $\text{NH}_3$  molecules as shown below:

Table 2  
SEC results

Compounds <sup>a</sup>	Resol		Prepreg		Calculated molecular mass (g mol <sup>-1</sup> )	Resol molecular mass (g mol <sup>-1</sup> )
	%	RV (ml)	%	RV (ml)		
Produit A	N.I. <sup>b</sup>	–	16.04	12.8	600	Unknown
Produit B	57.12	13.29	37.88	13.45	490	Unknown
Produit C	4.52	13.9	Ni <sup>b</sup>	–	316	Unknown
2,4,6-THMP	20.38	14.6	30.1	14.6	290	184
2,4-DHMP	7.64	15.00	7.87	14.98	227	154
4-HMP	5.55	15.47	5.26	15.47	195	124
2-HMP	3.94	15.9	2.25	15.9	158	124
Phenol	6.85	16.66	Ni <sup>b</sup>	–	136	94

<sup>a</sup> See Table 1 for the identification of compounds.

<sup>b</sup> Non identified.

Table 3  
Thermal data for the resol and the preimpregnate

Compounds	$T$ (°C)	$T_{\text{end}}$ (°C)	$T_{\text{max}}$ (°C)	$H$ (J g <sup>-1</sup> )
Resol	110	190	260	135
Prepreg	79	157	130	12
	157	230	185	16
	308	376	354	25

A product with molar mass 226 was eluted around 11 min in the analyses at 75 and 180°C. Considering the hypotheses presented (Fig. 2), this would be the formol–urea monomer formed from 2,4,6-THMP. The latter compound would have reacted with one urea molecule. It is present in large quantities, since this molecule is the basis of the expected three-dimensional network.

At 230°C, water was released around 8.6 min, confirming that intermolecular condensations were occurring at this temperature. Similarly, since urea was included in the composition of the binder, the presence of *N*-methyl urea ( $M = 74 \text{ g mol}^{-1}$ ) and/or *N,N*-dimethylurea ( $M = 88 \text{ g mol}^{-1}$ ) is entirely justified.

Methylphenols with varying degrees of substitution were identified. Methylphenol ( $M = 108 \text{ g mol}^{-1}$ ) eluted at around 12.7 min and also around 13.5 min (*ortho* and *para* isomers). Dimethylphenol was identified in the 300°C chromatogram, as well as two molecules of trimethylphenols.

The presence of naphthalene-like compounds was also possible in the same series. They were detected in the high temperature analyses (230 and 300°C). A hydroxybenzaldehyde ( $M = 122 \text{ g mol}^{-1}$ ) was also identified and could be

attributed to the oxidation of the alcohol function on the methoxy group.

At 230°C, *N,N*-dimethylbenzene methanamine ( $M = 135 \text{ g mol}^{-1}$ ) was detected at the retention time of 10.9 min. Pyridinol ( $R_t = 7.49 \text{ min}$ ,  $M = 96 \text{ g mol}^{-1}$ ) was also detected in the analysis at 300°C.

Several molecules with relatively high masses were also observed, but considering the numerous possibilities for condensation reactions, they could not be unambiguously identified.

They were few in number, since during formation of the network, high molecular weight molecules remained in the fiberglass. Even an analysis at 300°C could not volatilize them for identification.

#### 4. Conclusion

The aim of this work was initially to characterize the reactivity of resols and to determine the degree of cross-linking of semi-finished and finished products. The next step was to identify the VOC arising from the manufacture of glass wool, from these perfectly characterized base products.

The resols of the base resin and the preimpregnate were identified by liquid and size exclusion chromatographies. This enabled us to demonstrate a slight reaction advancement during preparation of the preimpregnate.

We subsequently investigated the VOC in the gaseous effluents by gas chromatography coupled to mass spectrometry.

A thermodesorption system led to the identification of a certain number of molecules arising from condensation and

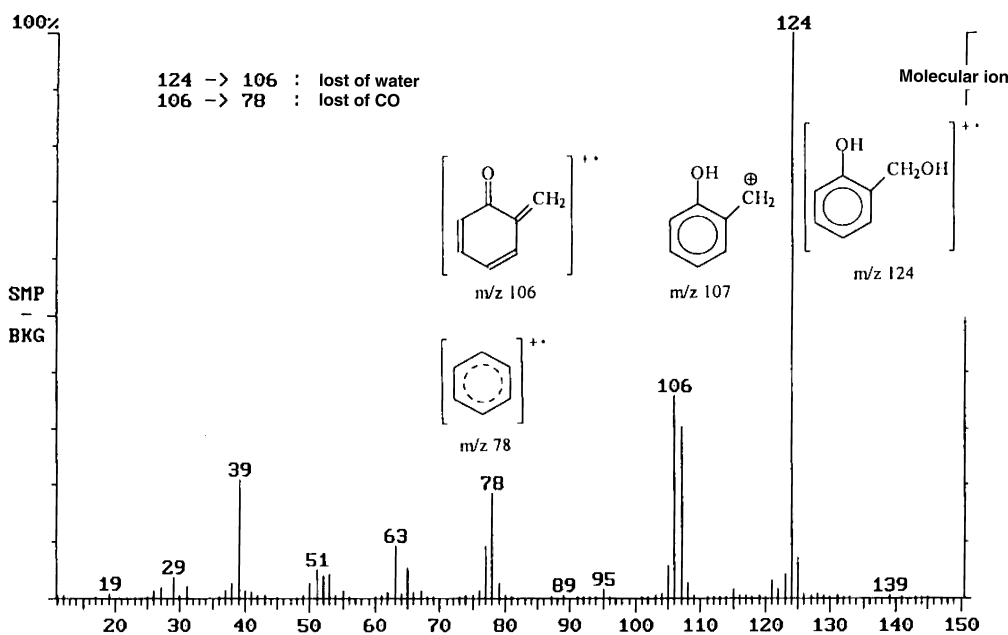


Fig. 3. Example of GC–MS spectra: 2-HMP.



Table 4

Volatile organic compounds detected and identified by TCT-GC-MS coupling ( $T = 75, 180, 230, 300^{\circ}\text{C}$ )

Proposed structure	$M$ (g mol <sup>-1</sup> )	Fragments (in italic basic peaks)	Retention time (min)			
			75°C	180°C	230°C	300°C
CO <sub>2</sub> ,NO <sub>2</sub> ,H <sub>2</sub> O ?		44-30-18			1.66	
?		70-57-56-41	1.81			
Dioxane	88	88-57-43	3.29			
Dimethylaminoacetonitrile	84	83-58-42			4.33	4.38
<i>N</i> -methylurea	74	74-60-30			6.10	6.01
Phenol	94	94-65-39				6.78
Pyridinol	95	95				7.49
H <sub>2</sub> O	18				8.58	
Phenol	94	94-65-39	10.76		10.51	
Benzenemethanamine, <i>N,N</i> -diméthyl	135	135-134-91-58			10.96	
Formol trisubstituted urea	226	226-136-134-58	11.01	11.10		
Methylphenol	108	108-107			12.89	12.79
Hydroxybenzaldehyde	122	122-121-65		12.89	12.79	
Methylphenol	108	108-107-77		13.31	13.31	13.76
Dimethylphenol	122	122-107-77				14.40
?	122	103-89-44			15.51	
Dimethylurea	89	89-72			16.24	18.73
Trimethylphenol	136	136-121-04				17.46
?	89				18.06	
2-hydroxy-3-methoxybenzaldehyde	152	152-151-75		18.66		
	152	135-134-75			18.85	
2-HMP ou 4-HMP	124	39-78-106	20.89	21.73		
Bis dimethylethylphenol	206	206-191			24.69	
Formol-urea monomer	166	166-108-107				29.96
Naphthalene (heterocyclic 2N)	158	157-128-56			27.29	
?	144	144-143-56	28.25			
?	224	148-132-61				28.66
?	194	194-158-132				29.44
Trimethylphenol	136	136-121-91...				29.78
?	161	161-146-121				30.88
Naphtalene	144	144-142-75...				32.03
?	164	164-106-78				32.33
Chlorophenol	128	130-128-42	33.38			
Naphthalene	144	144-142-132			33.38	
?	144	144-142-132				33.53
?	132	132-101				34.50
Chlorophenol	128	130-128-85-71	34.59			
?	150	150-106-78		34.51	35.53	
Dehydrated formal + 2NH <sub>3</sub>	164	164-120-91				36.81
?	176	176-130				38.01
?	178	178-130				38.63
?	256	256-72-59		39.56		
?	282	282-72-59		43.02		
Benzene acetonitrile...	290	290-91s		49.16		49.19

cross-linking reactions. The molecules identified were numerous and varied, in light of the diversity of the products in the composition of the reagents. Nevertheless, a more detailed study will be carried out, taking into account the different catalyses (acidic and basic cross-linking).

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