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Thermogravimetry/Fourier transform infrared coupling investigations to study the thermal stability of melamine formaldehyde resin ☆

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Abstract

This work reports new results obtained for a stable melamine formaldehyde resin intermediate. Using thermogravimetry/Fourier transform infrared (TG/FTIR) coupling, qualitative and quantitative analyses of the effluents which appear during a thermal cycle were performed. Four successive mass losses appear on the thermogravimetric curve (between 40 and 145°C, 145 and 225°C, 225 and 440°C, and for $T > 440$°C). The TG/FTIR coupling analysis identifies most of the effluents (water, methanol, formaldehyde, CO_2, amino compounds, ammonia).

Keywords: Environment application; Melamine formaldehyde resin; TG/FTIR coupling analysis

1. Introduction

Melamine resins provide a wide variety of useful products. For instance, in coating technology they may be used to modify the adhesion properties of other materials [1]; they also may be included as curing elements for other resins [2] or as fire retardant

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additives for polymeric products [3, 4]. Whatever the goal, a suitable thermal cycle, in which the temperature can reach values greater than 200°C, must be performed. During this thermal cycle, crosslinking reactions occur [5, 6] and volatile products are released [5–7].

In this work, a melamine formaldehyde modified resin is studied. Instead of using model compounds which extremely difficult to synthesize [5], it was decided to use commercially available melamine formaldehyde modified resin. Before studying the curing process itself, it is very important for reasons of environmental protection, to determine the nature and the amount of effluents which could be released during the thermal curing cycle.

This work deals with thermogravmetry/Fourier transform infrared coupling investigations performed on a melamine formaldehyde resin.

2. Methods

The melamine resin used is supposed to contain about 20% by weight of water and to be composed of 2.6 mol% (per melamine mole) of methanol, and 3.7 mol% of formaldehyde (supplier's data). The aqueous solution contains about 0.5 mol% of free formaldehyde. This resin is designed as a highly methylated, high-NH melamine formaldehyde resin and may be written as $MF_{3.7}Me_{2.6}$, where M represents the melamine, F the formaldehyde, Me the methanol and the different indices are the combined molar ratio of formaldehyde and methanol per melamine.

The thermal cycle shown in Fig. 1 was chosen because it has a reasonable experimental duration and because the levels of gas released are sufficient for the analysis. The same thermal cycle was performed on a TG.DTA 92 Setaram thermobalance and on a Dupont 951 TGA thermobalance connected to a Fourier transform infrared spectrometer (TGPLUS BOMEM) by mean of a multipass gas cell (more details of this instrumentation are given in Ref. [8]). A mass of 12 mg of liquid was heated and weighed in the furnace of the balance, while a carrier gas transported the effluents through a gas cell interface for continuous quantification by infrared analysis. Infrared spectra were acquired each thirty seconds. To calibrate the infrared signal, a known flow of the compound to be calibrated was mixed with the fixed flow of sweep gas and passed through the gas cell. The flow associated with each reference spectrum is calculated from the weight loss given by the balance. Water, methanol, CO, CO_2, and ammonia were calibrated in this way.

3. Results

The weight losses observed during the heating program on the melamin formaldehyde resin (curve a) and the derived curve (curve b) are displayed in Fig. 2. Four peaks are observed on the derived curve. We may define four temperature ranges where weight losses appear: from 40 to 145°C, 145 to 225°C, 225 to 440°C and the last one for

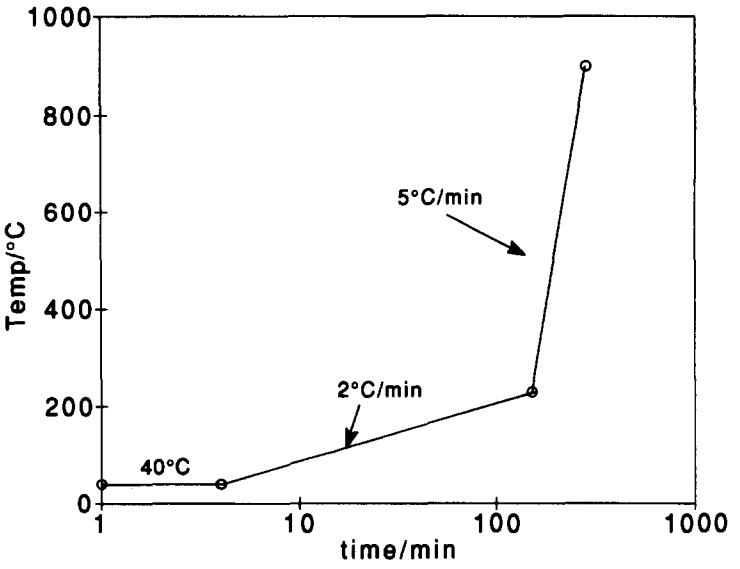


Fig. 1. Temperature program used for thermogravimetry investigations.

temperatures higher than 440°C. For each temperature range, the values of the partial weight losses and their characteristic temperatures determined from the minimum of the peak observed on the derived curve are reported in Table 1.

On Fig. 3, the infrared spectra performed at 175°C (curve a), 265°C (curve b), 395°C (curve c), 410°C (curve d), 525°C (curve e) and 660°C (curve f) are displayed. On each spectrum we have identified different molecular species (the results are reported in Table 1). For temperatures greater than 100°C and for wavelengths $3500\ cm^{-1} > \lambda > 3100\ cm^{-1}$, the strong absorption peak is an artefact of the experimental method.

Fig. 4 shows, for each gas, the cumulative weight percent passing through the gas cell of the TG/FTIR coupling detector versus time. These data are also reported in Table 1.

4. Discussion

During the first weight loss ($T_m = 78°C$), the TG analysis gives 14% weight loss while the IR signal suggests 13.8% of weight loss calculated from water loss. Thus, we may conclude that this first weight loss is mainly due to the evaporation of water.

During the second weight loss ($T_m = 185°C$), methanol, formaldehyde and amine are detected by IR spectrometry. By TG/FTIR we found that methanol effluents represent 12% of the 22.7% weight. The difference, i.e. 10.7%, is due to the evaporation of formaldehyde and amine. The evaporation of methanol and formaldehyde in this temperature range is not really surprising and is generally discribed by the following set

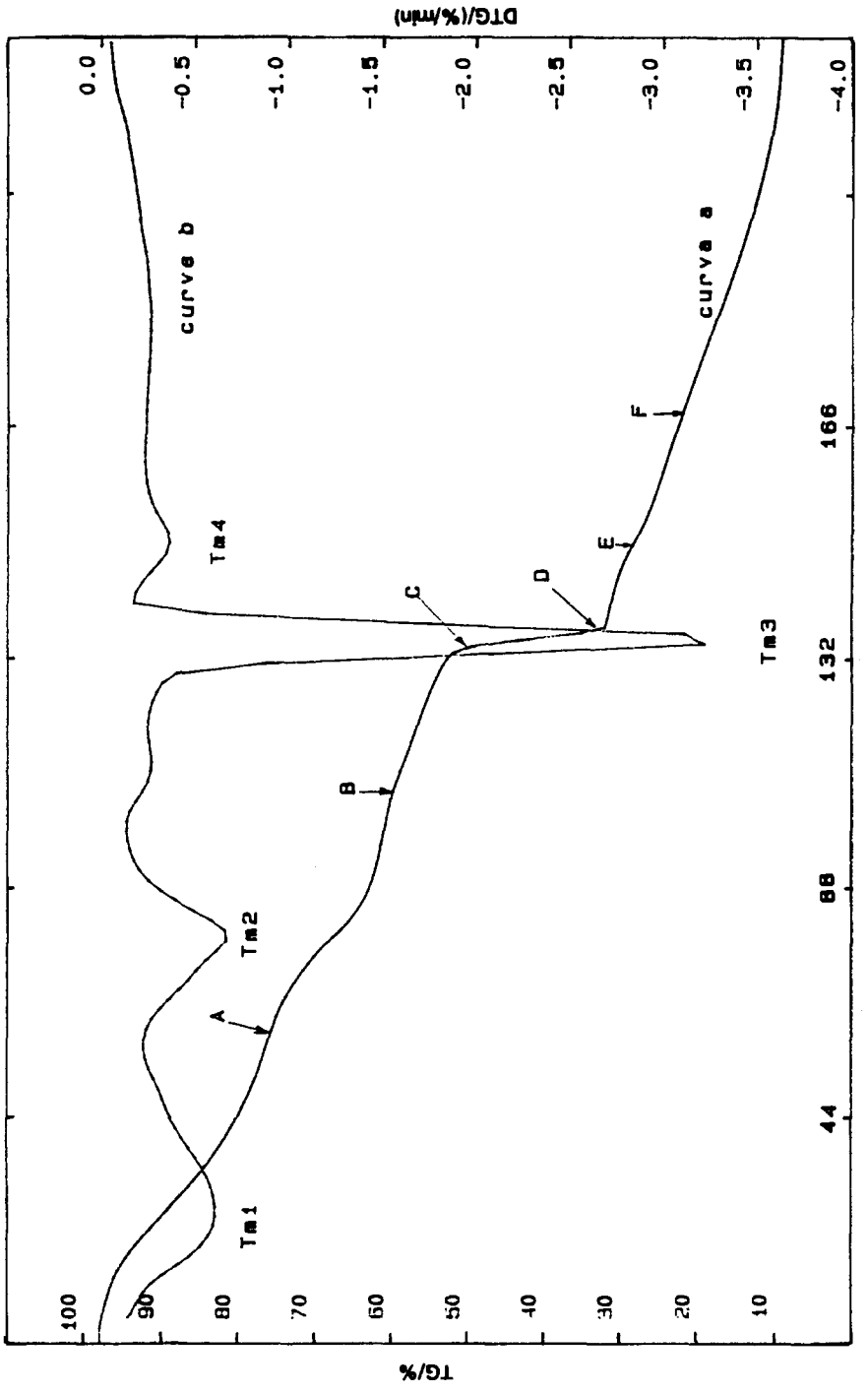


Fig. 2. Curve a, Thermogravimetric curve obtained on the melamine formaldehyde resin (initial mass = 12 mg), according to the heating program given in Fig. 1: A, B, C, D, E, F indicate the temperatures at which a FTIR spectrum was performed to determine the nature of the effluents. Curve b, derived curve.

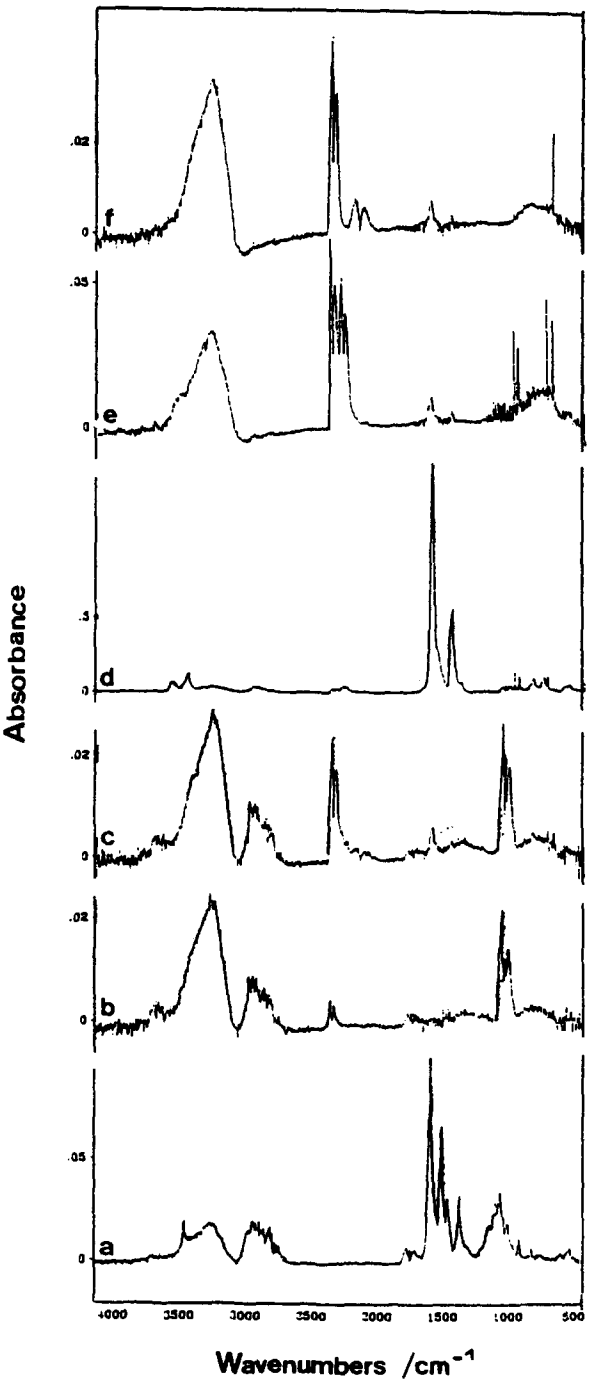


Fig. 3. FTIR spectra performed at: a, 175°C; b, 265°C; c, 395°C; d, 410°C, e, 525°C; f, 660°C.

Table 1
Thermogravimetry, infrared spectrometry and thermogravimetry/infrared coupling analysis data. In this table, the quantity $A + B = 20.4\%$

Thermogravimetry analysis			IR analysis			TG/FTIR coupling analysis	
Temperature range/(°C) ±1°C	T_m/(°C) ±1°C	Partial weight losses (%) ±10% relative	Temperature/ (°C) ±1°C	FTIR wave number/(cm^{-1}) ±4 cm^{-1}	Detected gas	Partial weight losses from IR (%) ±10% relative	Temperature range/(°C) ±1°C
40–145	78	14	70		H_2O	13.8	40–115
				1034	CH_3OH	12	
145–225	185	22.7	175	1780/1720	HCHO	11	115–200
				3464/1593/1504	Amines		
				1034	CH_3OH	A	
		9.5	265	1745	HCHO		200–360
				2364/2341	CO_2	0.6	
				1745	HCHO		
225–440	407			3577/3458	Amines		
		16.5	395	1595/1452			
				1034	CH_3OH	B	360–435
				2364	CO_2	0.9	
			410	966	NH_3	5.9	
			525	1595/1452	Amines		
				966	NH_3	9.7	
				2364/667	CO_2	1.6	
				2281/2250	HCH or CH_3CN		435–900
440–900	498						
		24.1	660	2183/2119	CO	11.8	
				1600	Amines		
				2364/667	CO_2	4.8	

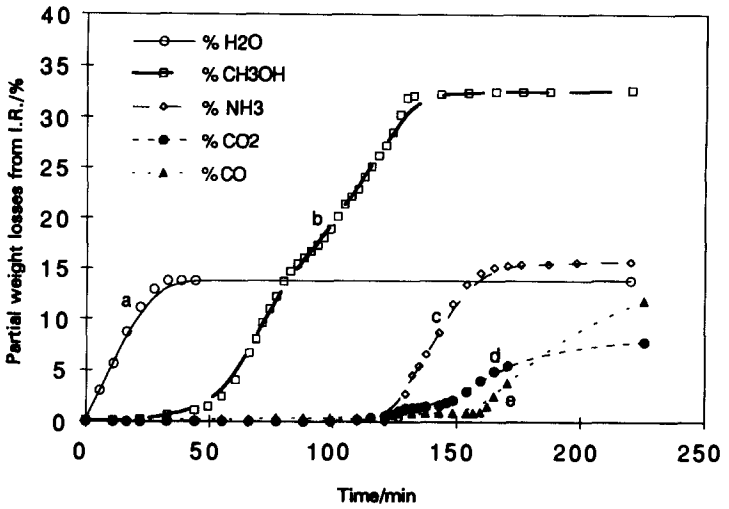


Fig. 4. Partial FTIR spectra for quantitative analysis performed on: a, H_2O gas; b, CH_3OH gas; c, CO_2 gas; d, CO gas; e, NH_3 gas.

of reactions [9].

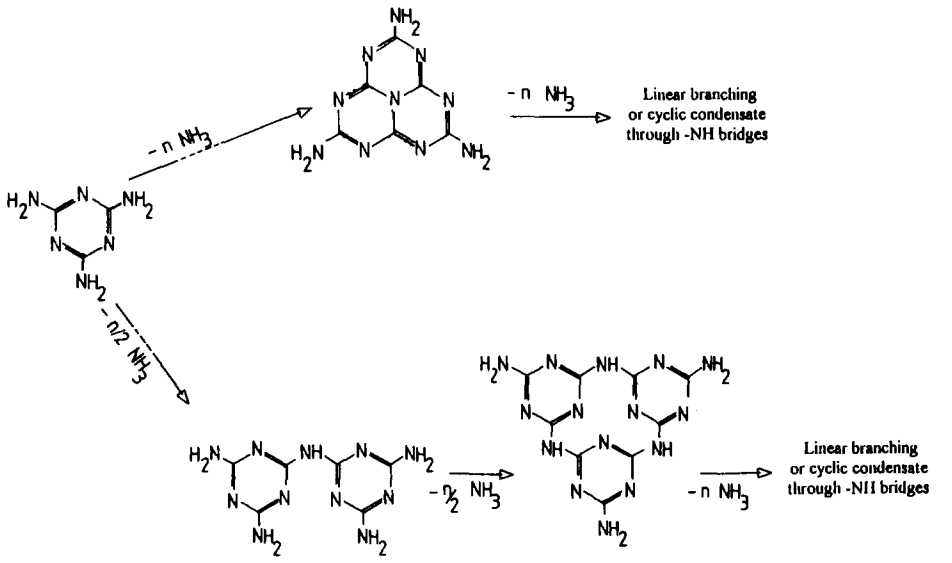
$$-NH-CH_2OCH_3 + H_2O \longrightarrow -NH-CH_2OH + CH_3OH$$

$$-NH-CH_2OH \longrightarrow \diagdown NH + CH_2O$$

However, the absorption bands of the triazine ring (1504 and 1462 cm^{-1}) and of the primary amine groups (3464 and 1593 cm^{-1}) which appear on the IR spectra performed at this weight loss indicate that the amine effluents come from evaporation of the melamine. This means that some molecules of melamine can be sublimated at a temperature lower than the sublimation temperature generally observed ($\approx$ 345°C).

During the third weight loss (T_m = 407°C), formaldehyde, methanol, amine, and also CO_2 and NH_3 gas are detected by IR analysis. The origin of the small quantity of CO_2 (0.6%) observed during this step is not clear. Indeed, no acid or ester are included in the resin formulation; thus, the origin of CO_2 cannot be explained by the degradation of a part of the resin. Although all our experiments are made under nitrogen or helium flow, the presence of some traces of O_2 in the apparatus may explain the presence of CO_2. The existence of some impurities, like catalysts, is also a probable cause of the presence of CO_2.

The characteristic absorption peak at 966 cm^{-1} indicates that the thermal condensation of the melamine takes place with elimination of ammonia [7]. This mechanism is described by Costa et al. [7]



However, the presence of methanol, formaldehyde and amine shows that other reactions also take place, in particular the sublimation of a part of the melamine.

For the last weight losses (temperature greater than 435°C), the results are consistent with what is generally observed for the thermal degradation of melamine [7], except for the presence of CO and CO_2. For temperatures in the range 410–525°C, IR analysis shows that HCN or CH_3CN are evaporated (Table 1). Thus according to Costa et al. [7], we assume that melamine formaldehyde progressively deaminates forming cyameluric structures.

Above 660°C, the melamine formaldehyde condensate undergoes extensive degradation with quantitative formation of volatile products among which HCN, CO and CO_2 have been identified at this stage by TG/FTIR coupling analysis.

Taking into account the different weight losses observed by TG and TG/FTIR coupling methods, we observe that the actual quantities of methanol which are evaporated are greater than those expected from the supplier's formula. In fact, it appears that our melamine formaldehyde resin must be written as $MF_{\geqslant 4.4}Me_{4.4}$.

5. Conclusion

We have determined the different natures of the effluents which appear during a heating program by thermogravimetry, infrared spectroscopy and thermogravimetry/infrared coupling analysis. From the calculation of the partial weight losses we have found that the actual formula of the commerical resin is $MF_{\geqslant 4.4}Me_{4.4}$ instead of $MF_{3.7}Me_{2.6}$ proposed by the supplier. We have also observed that melamine effluents may be obtained in a temperature range lower than that expected one.

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References

[1] R. Brainbridge, Sail, 8(1) (1977) 142.
[2] Chem. Eng. News, 61(18) (1983) 13; 61(24) (1983) 93.
[3] M. Kay, A.F. Price and I. Lavery, J. Fire, Retardant Chem., 6 (1979) 69.
[4] J.R.A. Broadbent and M.M. Hirschler, Eur. Polym. J., 20 (1984) 1087.
[5] W.J. Blank, J. Coating Technol., 51 (1979) 61.
[6] U. Samaraweera and F.N. Jones, J. Coating Technol., 64 (1992) 69.
[7] L. Costa and G. Gamino, J. Therm. Anal., 34 (1988) 423.
[8] A. Fafet, E. Ubrich and L. Le Squer, Proc. Journées de Calorimétrie et d' Analyse Thermique, Corte, Cal. Therm. Anal., 24 (1993) 117.
[9] H.P. Whonsiedler, A.C.S. Div. Org. Coatings & Plastics Chem., 20/2 (1960) 53.