Investigating the curing of amino resins with TGA-MS and TGA-FT-IR

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Introduction

The monomers used for preparing amino resins (aminoplasts) are urea (for UF resins) or melamine (for MF resins) and formaldehyde. The latter undergoes an addition reaction with amino groups with the formation of N-methylol groups. In principle, with a primary amine, two methylol groups can be formed. With melamine (Figure 1), the addition reaction of formaldehyde to the primary amine group (Figure 2) is faster than to the secondary amine group; there is nevertheless the possibility of six-fold methylolation. Urea, however, only undergoes two-fold methylolation. Amino resins are available commercially in precondensed form, usually in aqueous solution, with molar masses of 500 to 1500 g mol^{-1}.

During curing, the amino resin undergoes cross-linking as a result of condensation reactions (Figure 3). The curing reaction is acid-catalysed; *p*-toluenesulfonic acid (PTS) is normally used. The methylol groups react with amino or other methylol groups and form either methylene bridges according to reaction (1), or ether bridges according to reaction (2). The methylol groups of the MF resin are present in partially methylated form. Correspondingly, the cross-linking reaction results in the liberation of not only water but also methanol. The conversion of ether bridges to methylene bridges with the elimination of formaldehyde according to reaction (3) does not occur until higher temperatures. The cross-linking density of the cured aminoplast is determined by the number of methylol groups per amine.

The aim of the thermogravimetric analysis-mass spectrometry (TGA-MS) and the thermogravimetric analysis-Fourier transform infrared (TGA-FT-IR) spectroscopy measurements was to gain an insight into the reactions taking place by analysing the volatile substances evolved. The detection of methanol, for example, should enable one to decide whether the MF prepolymer is involved in the cross-linking reaction or whether it serves only as an external plasticiser.

It should also be possible to obtain information on the reaction kinetics. The evolved gases were to be identified by coupling the TGA thermobalance with MS and FT-IR.

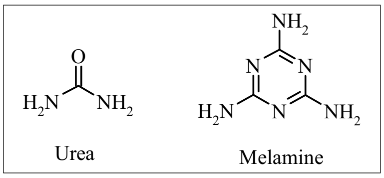

Figure 1. Structural formulae of urea and melamine.

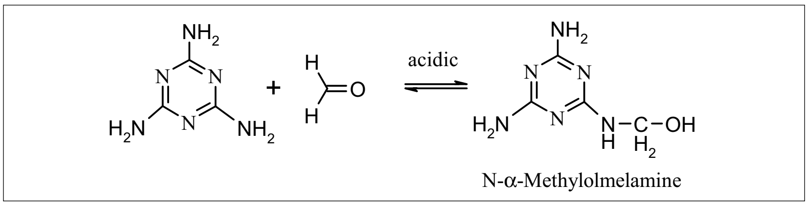

Figure 2. Acid-catalysed addition of formaldehyde to an amine group with the formation of a methylol group.

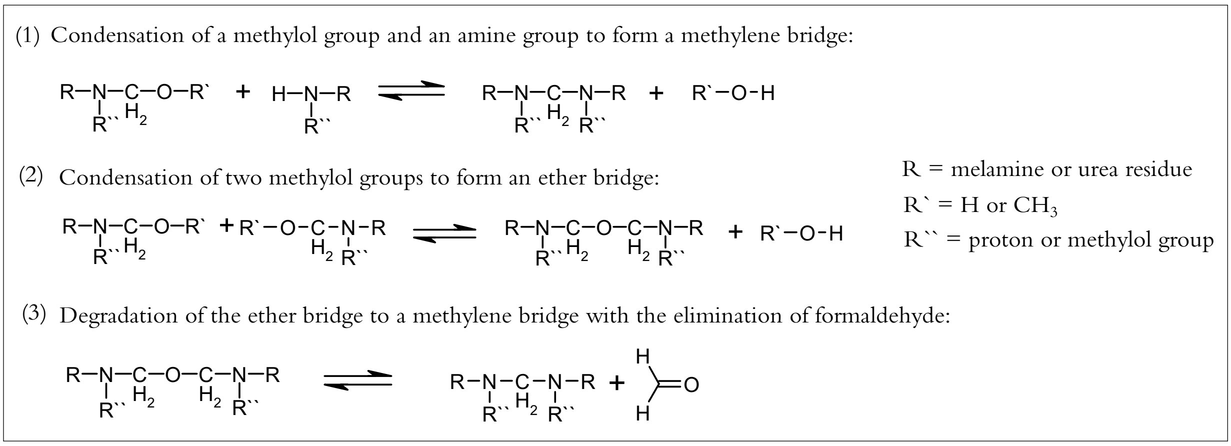

Figure 3. The most important reactions in the curing of amino resins.

Table 1. Peak assignment in MS analysis.

m/z	Gas
17	water (OH), ammonia (NH_3)
18	water (H_2O)
30	formaldehyde (CH_2O)
31	methanol (CH_3OH)

Table 2. Absorption band assignment in the IR analysis.

Wavenumber (cm^{-1})	Gas
3325	ammonia (NH_2 stretching vibration)
3200–2700	methanol (O–H stretching vibration)
2340, 2360	carbon dioxide
1770	formaldehyde (carbonyl stretching vibration)
1620	ammonia (NH_2 scissoring vibration)
1340	methanol (O-H deformation vibration)
1035	methanol (C-O stretching vibration)
965, 930	ammonia (fingerprint)
670	carbon dioxide

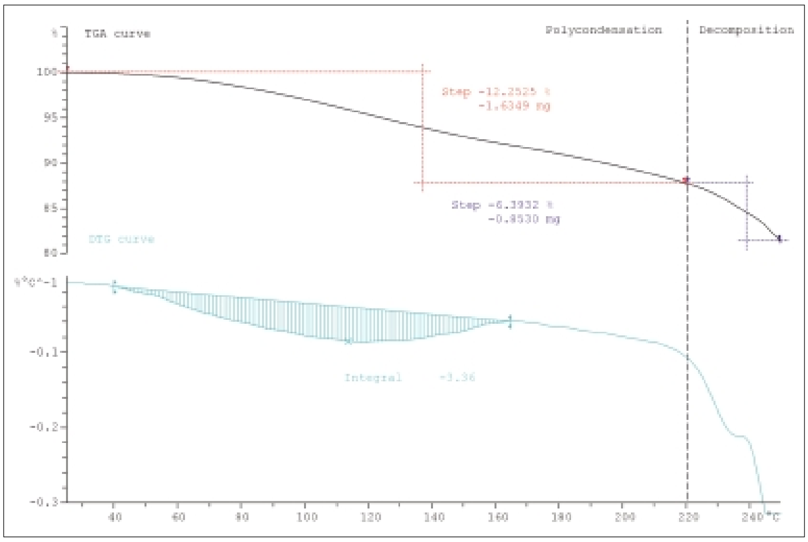

Figure 4. TGA curve (black curve), 1st derivative of the TGA curve (blue-green line).

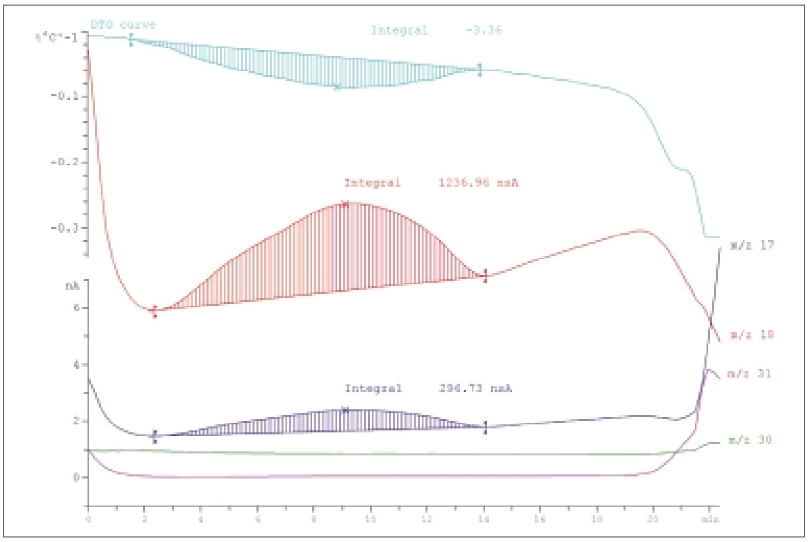

Figure 5. DTG and MS fragment ion curves.

Experimental details

An open aluminium crucible of 100 µL volume was used for the measurements. The TGA temperature program ran dynamically from 25 to 250°C at a heating rate of 10 K min^{-1}; nitrogen was used as inert gas with a flow rate of 70 mL min^{-1}. The gaseous components evolved were detected by coupling the Mettler Toledo TGA/SDTA851e thermobalance either to a mass spectrometer (Balzers Thermostar) or a FT-IR spectrometer (Nicolet Nexus). The mass spectrometer was set to record masses with *m/z* values of 17, 18, 30 and 31 (see Table 1). The FT-IR measured and averaged 16 scans at a resolution of 4 cm^{-1} for each spectrum. UF and MF resins were mixed well in a ratio of 90:10 by weight with 0.4% PTS catalyst and then weighed. Precuring was done at 60°C for 90 min in a differential scanning calorimeter (DSC). The assignment of the IR absorption bands is shown in Table 2.

Results

The TGA curve (Figure 4) shows that the sample loses weight during the curing reaction from room temperature to 220°C; the total weight loss is 12.2%. The products eliminated during the reaction vaporised continuously. Above 200°C the weight loss increased markedly. This can be clearly seen in the TGA curve and its 1st derivative. From this we assumed that the residual curing had been completed by 220°C. Afterwards, degradation began causing the sample to lose weight rapidly. The sample foamed and turned brown.

The mass spectrometer was set so that fragment ions of particular mass/charge ratios were detected throughout the measurement time (multiple ion detection, see Table 1).

As expected, in the initial heating phase, the MS ion curves (Figure 5) showed a strong signal for water. In contrast neither methanol nor formaldehyde were detected during this curing reaction. In the second temperature segment (from 220 to 250°C) the MS curves of formaldehyde (*m/z* 30) and methanol (*m/z* 31) showed a sharp increase. The signal from water (*m/z* 18) became weaker. At temperatures above 240°C (20 min), the *m/z* 17 signal increased rapidly while the *m/z* 18 signal decreased. This indicates the beginning of the elimination of ammonia (*m/z* 17) (compare with Figure 6). The degradation products of the aminoplast are therefore formaldehyde, ammonia and methanol.

The results from the FT-IR spectra (Figure 6) agreed with those obtained from the MS curves. Here again only water was detected in the initial heat-

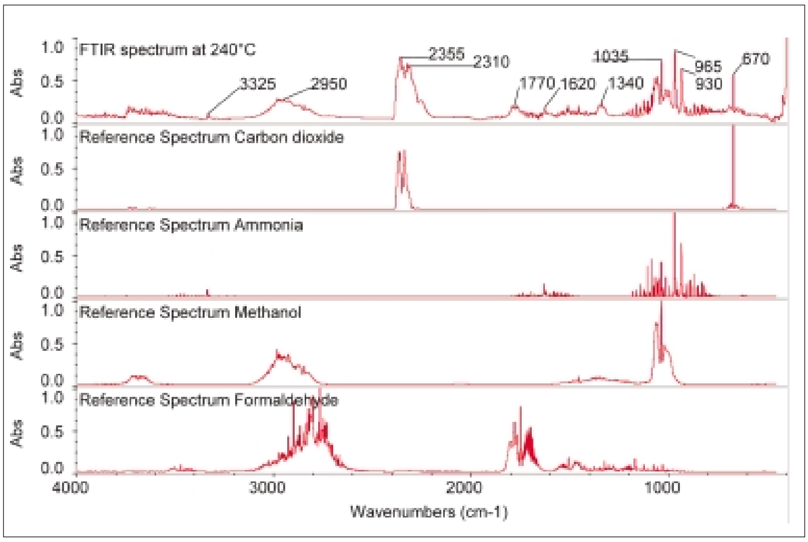

Figure 6. FT-IR spectrum at 240°C and reference spectra of methanol, ammonia, formaldehyde and carbon dioxide.

ing phase. When sample degradation occurred, formaldehyde and methanol, as well as ammonia and carbon dioxide were found. Although the sensitivity of FT-IR spectroscopy for the substances investigated was less than that of mass spectrometry.

Conclusions

The objectives were to a large degree achieved through a combination of the use of TGA coupled with MS and FT-IR spectrometers:

- The analysis of volatile gases up to 220°C showed that during the curing reaction only water was eliminated in agreement with reactions (1) and (2) in Figure 3. During the degradation of the aminoplast (220–250°C) methanol, ammonia, formaldehyde and carbon dioxide were liberated.
- The quantity of water eliminated was determined quantitatively and was found to be 12.2 weight%.
- Methanol was not detected until above 220°C. This indicates that the ether methylol groups do not take part in the curing reaction. It does not exclude the participation of melamine in the reaction because this was only partially but not completely etherified.
- The FT-IR measurements confirmed that methanol, carbon dioxide and ammonia as well as smaller amounts of formaldehyde were liberated.

Acknowledgement

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