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Decomposition mechanism of melamine borate in pyrolytic and thermo-oxidative conditions

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ABSTRACT

Decomposition mechanism of melamine borate (MB) in pyrolytic and thermo-oxidative conditions is investigated in the condensed and gas phases using solid state NMR (^{13}C and ^{11}B), X-ray photoelectron spectroscopy (XPS), pyrolysis-gas chromatography–mass spectrometry (py-GCMS) and thermogravimetric analysis coupled with a Fourier transform infrared spectrometer (TGA–FTIR). It is evidenced that orthoboric acid dehydrates to metaboric and then to boron oxide. The melamine is partially sublimated. At the same time, melamine condensates, i.e., melem and melon are formed. Melon is only formed in thermo-oxidative conditions. At higher temperature, melem and melon decompose releasing ammonia which reacts with the boron oxide to form boron nitride (BN) and BNO structures.

1. Introduction

Melamine borate (MB) is a flame retardant used in several polymers such as epoxy resins and flax or cellulose fibers [1–4]. Especially in the world of fire retardancy, it is essential to understand the occurring decomposition reactions of each single compound in a fire retarded material. Costa et al. [5] investigated the decomposition mechanism of MB in pyrolytic conditions using TGA and FTIR analysis in the 90s. In this study, it was proposed that MB dehydrates between 130 and 270 °C evolving water and forming boric anhydrate with melamine. In the second step (270–350 °C), it was shown that melamine is evolved and the formation of an unidentified melamine–boric anhydride structures was proposed. From 350 to 950 °C, a decomposition of the melamine structures was observed and it was proposed that BN or BNO structures are formed, but the presence of these compounds was not clearly evidenced.

Since that paper, the decomposition of MB was not further examined. Thus, this paper deals with the decomposition of MB in pyrolytic and thermo-oxidative conditions. The decomposition mechanism is further investigated using ^{13}C and ^{11}B solid state NMR and XPS for the analysis of the condensed phase. py-GCMS (pyrolytic condition) and TGA–FTIR (thermo-oxidative conditions) are carried out to investigate the gas phase. A decomposition pathway could thus be proposed.

2. Experimental

2.1. Materials

Melagard MB (Fig. 1), melamine borate (hereafter called MB) was received as white powder from Italmatch Chemicals and used without further purification. MB is a chemical mixture of melamine and orthoboric acid at a mass ratio of 2:1.

2.2. Thermal analysis

Thermogravimetric analysis was carried out on a TA Instrument (TGA Q5000IR). The balance purge flow was set to 15 mL/min (nitrogen) and the sample purge flow (air) to 100 mL/min. The powdered samples put in open alumina pan underwent a heating from 50 to 800 °C with a heating rate of 10 °C/min.

2.3. Heat treatments

Heat treatments are carried out in a tubular furnace under air and/or nitrogen at characteristic temperatures determined by TGA. Samples are heated up to the desired temperatures with a heating ramp of about 10 °C/min followed by an isotherm of 2 h. Residues are analyzed afterwards via XPS and solid state NMR.

2.4. Solid State NMR

^{13}C solid state NMR spectra are recorded at 100.6 MHz (B_0 = 9.4 T) on a Bruker Avance II 400 spectrometer using a 4 mm

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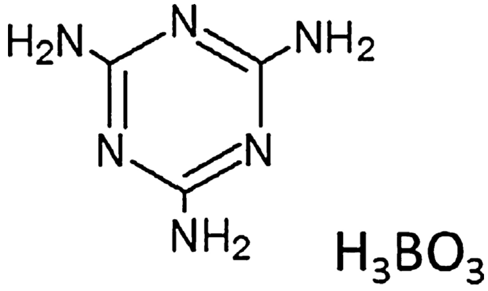

Fig. 1. Chemical structure of melamine borate.

standard probe. The conditions are cross-polarization (CP) ^{1}H–^{13}C (contact time of 1 ms) with dipolar decoupling (DD) and magic angle spinning (MAS) at 10 kHz. The recycle delay between two pulses is 5 s. The number of scans is 1024 and ^{13}C chemical shifts are referenced to tetramethylsilane (TMS).

^{11}B NMR acquisitions are performed at 256.81 MHz on a Bruker Avance 800 (18.8 T) spectrometer with a probe head of 3.2 mm using MAS at 20 kHz. The number of scans is set to 256, recycle delay between two pulses is 4 s. Sodium borohydride is used as reference. Signal coming from the BN stator (probe background signal) is removed by running the same experiment without the sample, then calculating the spectrum difference between the two experiments. BO_3/BO_4 ratios are estimated using Dmfit software [6].

2.5. XPS

The XPS experiments are carried out in an ultra-high vacuum KRATOS Axis Ultra spectrometer using the monochromatized Al Kα (1486.6 eV) source. A constant analyzer pass energy of 40 eV is used. Pressure was in the 10^{-9} Torr range during the analyses. Simulation of the experimental peaks is carried out using the Gaussian–Lorentzian mixture from CasaXPS software. Quantification took into account a linear background subtraction. The core level binding energies are referenced to the C 1s line of carbon contamination at 285.00 eV.

2.6. Pyrolysis GCMS (py-GCMS)

Pyrolysis-gas chromatography–mass spectrometry (py-GCMS) analyses are performed on a device provided by Shimadzu. The device consists of a micro-furnace pyrolyzer (Frontier Lab PY-2020iD) coupled with a GCMS (Shimadzu GCMS QP2010 SE). Experiments are performed under inert conditions using helium. Sample size is about 200 μg.

Samples (in a stainless steel cup) are heated up from 50 to 800 °C with a heating ramp of 10 °C/min. After the decomposition process, evolved gases are introduced into the GCMS system whereas a part of the gases is split to avoid blockage in the column or saturation of the detector. Released decomposition gases are separated using a 30 m long fused silica capillary column. The temperature of the column is set to 35 °C during the desorption process. The column is then heated up to 300 °C with a heating rate of 10 °C/min followed by an isotherm at 300 °C for 30 min. The linear velocity of the carrier gas helium is set to 40 cm/s. The separated gases and fragments are then analyzed with the quadrupole mass spectrometer with an electron-impact (IE) ionization source. The IE spectra are recorded at 70 eV with a mass scan of 2 scans per second. The interface between the pyrolyzer and the GC is heated up to 320 °C; the interface GC–MS to 280 °C. The temperature of the ion source is set to 230 °C. After the experiments data is analyzed using the GCMS post-run analysis from Shimadzu and F-Search from Frontier lab, whereas products are identified using NIST database.

2.7. Thermogravimetric analysis coupled with Fourier transform infrared (TGA–FTIR)

Thermogravimetric analysis coupled with Fourier transform infrared (TGA–FTIR) is performed on a TA Instrument TGA Q5000IR coupled with a Thermo Scientific Nicolet iS10 spectrometer. Analyses are carried out in air in alumina crucibles using around 5 mg of sample. The balance flow is set to 15 mL/min whereas the purge flow is fixed to 100 mL/min. Samples are heated from 50 to 800 °C (10 °C/min) after an isothermal of 10 min at 50 °C. Gases evolved during the TGA experiment are detected continuously by the FTIR device. The spectra are recorded with the OMNIC®

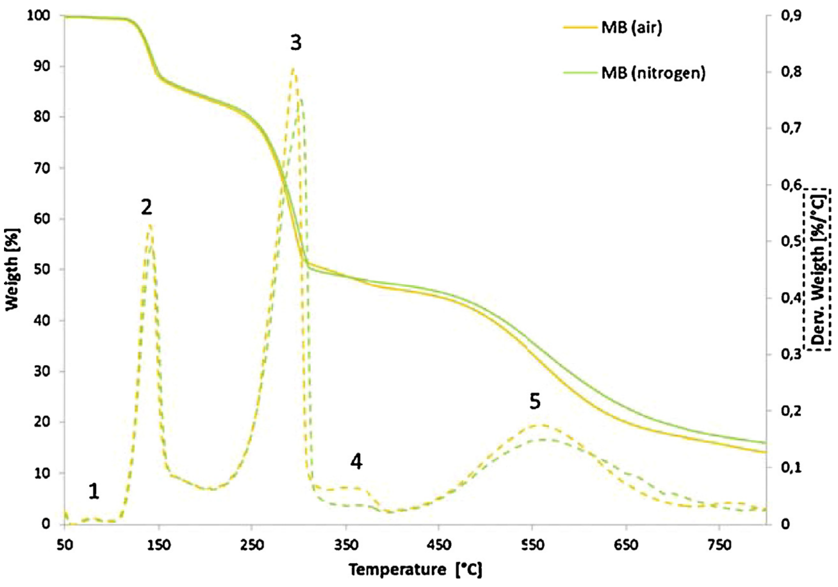

Fig. 2. TG and DTG curves for MB, 50–800 °C, 10 °C/min, in air and nitrogen.