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HIGH PRESSURE DSC OF PHENOLFORMALDEHYDE MOULDING COMPOUNDS

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The influence of pressure on the polycondensation reaction between novolac resin (N) present in commercially available moulding compounds and hexamethylenetetramine (HMTA) was studied up to 80 bars under air and in an inert atmosphere. For a low HMTA content (N/HMTA=98/2 mass ratio) high pressure enables the detection of two successive curing reactions. With increasing HMTA content the peak due to the first curing reaction becomes less pronounced at high pressure, while the enthalpy of the second increases. In an inert atmosphere both curing reactions are well observable even at ambient pressure and for lower HMTA content take place at lower temperatures, as expected. For the sample with N/HMTA=98/2 the curing reaction was followed using TG-MS.

Keywords: *composite material, curing reaction, hexamethylenetetramine, high pressure DSC (HP DSC), novolac, phenolformaldehyde resin, thermoset*

Introduction

Phenolformaldehyde (PF) moulding compounds are composite materials consisting of three basic components: novolac resin as a binding material, glass fibres to improve the mechanical properties and an inorganic filler to ensure dimensional stability (Fig. 1).

PF resins are divided into two main groups: resoles and novolacs. Both are obtained during polycondensation reaction between phenols or their derivatives and aldehydes. In the case of an aldehyde excess and in alkaline media resoles are formed, while under acidic conditions and a phenol excess novolacs are formed. Novolacs are cured by the curing agent which results in methylene linkages between the phenols. During the injection moulding process of PF moulding compounds a polycondensation reaction (Scheme 1) between the novolac oligomers (N), already present in the commercially available raw material, takes place in the presence of hexamethylenetetramine (HMTA), which serves as a curing agent. The first step of the curing reaction occurs within a short time (around 2 min) in the hot cavities (T=150°C). The temperature of the cavity and a high

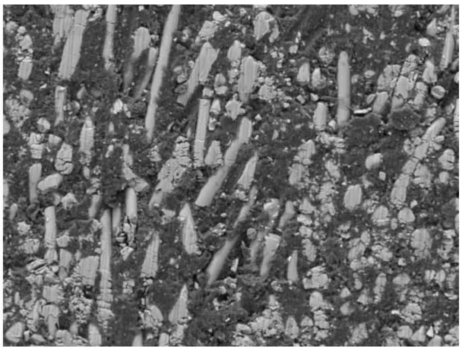
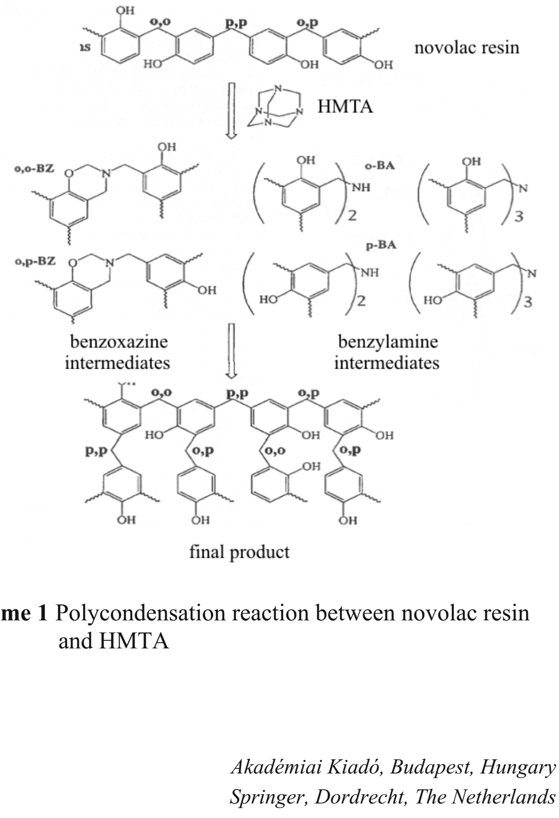


Fig. 1 SEM micrograph of the cross section of a PF moulding compound. Glass fibres (light colour) with an average diameter 12 μm are seen in various orientations in the matrix of cured novolac resin and fine-grain filler



Scheme 1 Polycondensation reaction between novolac resin and HMTA

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pressure (200 bars) enable the moulding compound to fill the cavity and irreversibly harden. During the second reaction, also called the post-curing process, the structure cross-links together 3-dimensionally. This process takes several hours; the temperature is increased in ramps up to 200°C. After the thermal treatment described, the final thermosetting material is obtained, having excellent dimensional, thermal, chemical and insulating properties [1, 2].

Differential scanning calorimetry (DSC) is one of the most widely used analytical methods for studying polymeric materials [3]. In 1967 Burns and Orrell [4] studied the curing reaction of PF novolac resin with HMTA using differential thermal analysis (DTA) at ambient pressure under an air atmosphere. They found that the cross-linking reaction occurred in two successive temperature regions; in the first exothermic reaction from 120 to 180°C some free phenol and HMTA remained unreacted, while their peaks disappeared after the second exothermic reaction taking place from 180 up to 230°C. They pointed out that the second DTA peak is the result of an exothermic reaction and an endothermic volatilization. Consequently, the heat of reaction due to the secondary curing process may be much greater than the value suggested by the measured peak area.

During the curing process volatilization of the small gaseous by-product can hide the exothermic polycondensation reaction. In this case, encapsulation of the sample or high pressure (HP) is required [5–7]. In a pressurized system the pressure can be controlled, whereas in sealed pans this is not possible. The advantage of a pressurized cell, besides exact pressure control, is the choice of atmosphere, which can be inert, oxidative or reductive, while in a sealed pan only a self-generating atmosphere is possible.

In 1971, Kurachenkov and Igonin [8] published results carried out in a home-made DTA instrument which enabled pressures up to 5000 bars to be achieved. They observed radical changes in the shape of the polycondensation reaction between PF novolac and HMTA at high (>3000 bars) pressures. The first step of the curing reaction (120–160°C) nearly disappeared while the second one (230–260°C) increased in intensity. Although curing of novolacs by HMTA under high pressures has not yet been fully investigated, they presumed that the curing mechanism under high pressure differs significantly from the mechanism taking place under the usual conditions. Studies of the influence of pressure therefore generate basic practical knowledge of the final properties of the materials produced under high-pressure processing conditions (injection moulding) [9]. For the present it is regrettable that it is virtually impossible to carry out measurements at pressures from 100 to 10000 bars, because they would be highly relevant from the point of view of both theory and industrial practice.

With the help of ^{13}C and ^{15}N solid-state NMR studies Zhang and coworkers in 1997 showed that the curing reaction between novolac resins and HMTA is very complex. During the polycondensation reaction a large number of intermediates was detected [10]. The HMTA content influences the rate and the mechanism of the curing reaction, as well the composition and properties of the final product. When the amount of HMTA is lower, the initial intermediates appear at lower temperature and decompose at lower temperature; the temperature required to form methylene linkages is also lower. In the finally cured resins there is a lower content of nitrogen-containing structures.

The aim of our work was to follow the curing reaction of PF moulding compounds using thermal methods of analysis: high pressure DSC (HP DSC), DSC, TG, and evolved gas analysis (EGA). We investigated the influence of pressure on the shape of the DSC curve and the influence of HMTA content on the course of the curing reactions (the curing mechanism was compared for samples with N/HMTA=98/2, 94/6, 88/12 and 80/20 mass ratios). A comparison between air and argon atmospheres was made by HP DSC for all of the mentioned samples and TG-MS analysis for the sample with N/HMTA=98/2.

Experimental

Commercially available composite material containing approximately 30 mass% of novolac resin and 2.0 mass% HMTA was used (sample N/HMTA=98/2). Samples with higher HMTA content were prepared by carefully weighing pure powdered HMTA (Merck, p.a.) and the commercial sample. The two components were mixed together and homogenized in an agate mortar. For analysis, all samples were pressed in a hand-press to obtain a thin pellet.

HP DSC measurements were performed on a Mettler Toledo DSC827^e instrument in 40 μL standard aluminum open pans in static air or argon atmospheres. The temperature range was from 25 up to 350°C. The heating rate was 20 K min^{-1} in air and 10 K min^{-1} in an argon atmosphere. An empty pan served as a reference. Temperature and enthalpy were calibrated using indium and zinc, both supplied from Mettler Toledo. Masses of samples were around 5 mg.

TG measurements were performed on a Mettler Toledo TGA/SDTA 851^e instrument from room temperature up to 500°C in a dynamic air or argon atmosphere with a flow rate of 100 mL min^{-1} at a heating rate of 10 K min^{-1}.

TG-MS analyses were carried out in a Mettler Toledo GmbH, Switzerland. The TGA/SDTA 851^e

instrument was coupled to a Pfeiffer (Balzers) Thermostar mass spectrometer (MS). The heating rate was 10 K min^{-1}, masses of samples around 100 mg and the flow rate of air or argon 30 mL min^{-1}.

Results and discussion

In Fig. 2 a comparison of DSC curves measured at normal pressure and at higher pressures is presented for the sample with N/HMTA=98/2. At ambient pressure, a glass transition of the raw material occurred at around 70°C. A small and broad peak positioned at 163°C appeared due to the 1st step of the curing reaction. During this step various substituted benzoxazines and benzylamines were produced. Their decomposition, oxidation and/or further reactions of these initial curing intermediates produced methylene linkages between phenolic rings [10]. The second step, in which various amide and imide structures with aromatic ring –CO–N< bonds were formed [10], could not be separated from the general exothermic process occurring at temperatures higher than 200°C. With increasing pressure the peaks on the DSC curve became more and more intense. At pressures higher than 40 bars the second curing reaction became separated from the decomposition process; the peak occured at around 245°C. After that, the signal did not return to the baseline, but increased further in the exothermic direction. In this range most probably some further oxidation processes occurred, which might also take place in fillers or additives present in the moulding compounds. All the processes could be clearly distinguished at 80 bars pressure, namely the glass transition, melting of the additives at 120°C, the 1st and the 2nd step of the curing reaction (especially the 2nd is superimposed on the oxidative exothermic peak) and the beginning of thermal decomposition. In Fig. 2 the ‘post-curing process’ is given in quotation marks because in the injection moulding process the heating rate is very low within this temperature range. The temperature of both curing reactions was shifted towards lower temperatures in [10] (the beginning of the 1st curing reaction to 90–120°C for instance; the end of the 2nd curing reaction after isothermal treatment for 4 h at 205°C) due to the very slow heating rate (the heating rate was 0.062 K min^{-1} up to 135°C, and from 135 to 205°C it was 0.20 K min^{-1}). The second reason was the difference in the chemical system since our samples contained only 30% PF (see Fig. 1; the residue being glass fibres, fillers and additives).

There are two major differences in the curing rate and the chemical structure of the fully cured resins between samples with a low or a high HMTA content [10]: (*i*) many reactive sites of novolac remain in the system with low HMTA content (98/2, 96/4) after the formation of the initial intermediates and these ‘free’ sites can react with those intermediates to produce further methylene linkages for cross-linking. In the system with a higher HMTA content (88/12), the reactive sites are used up after the formation of the initial intermediates. No additional reactive sites are available to react with these intermediates and many more nitrogen-containing intermediates are still present after curing. (*ii*) Novolacs are acidic polymers while HMTA is a basic compound. The ability of the system to form initial curing intermediates is higher at lower pH, which means at lower HMTA content. On the basis of these facts, we expected that a higher HMTA content in the sample would only shift the DSC curves towards higher temperatures. The curves of the sample with N/HMTA=80/20 obtained under an air atmosphere are presented in Fig. 3. There is no

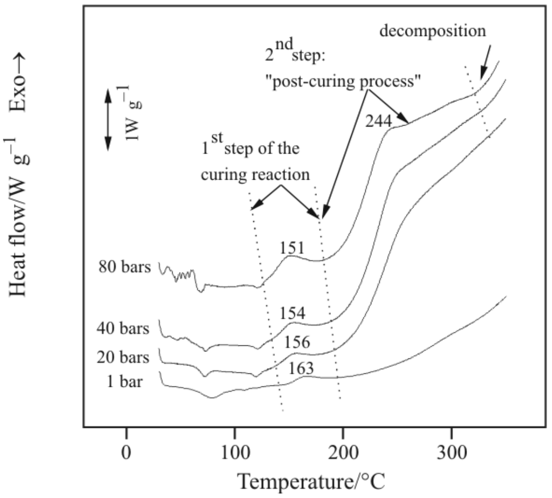

Fig. 2 Influence of pressure on the shape of the DSC curve for a sample with N/HMTA=98/2 under an air atmosphere. The heating rate was 20 K min^{-1}

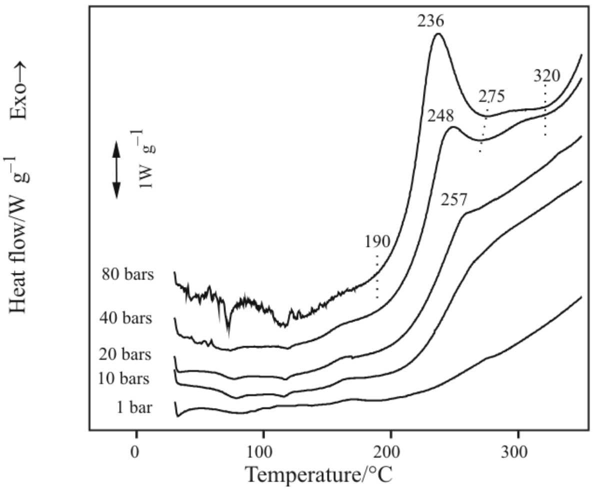

Fig. 3 DSC curves of a sample with N/HMTA=80/20 under an air atmosphere; heating rate 20 K min^{-1}

explicit difference in the shape of the DSC curves for samples with N/HMTA=98/2 and 80/20 up to a pressure of 20 bars because the peak of the 2nd curing reaction is hidden under the exothermic signal from the oxidation process. But at higher pressures (40, 80 bars) the peak for the 1st curing reaction is less pronounced, whereas the second increases in intensity. This behaviour was observed already in 1971 [8] for the system with N/HMTA=90/10. At much higher pressures (3000 bars) the 1st curing reaction was totally inhibited, while the enthalpy of the second was large. We observed that after the 1st curing reaction the baseline does not return to zero but increases in the exothermic direction. This means that at higher pressures oxidation of the sample occurs at lower temperatures, so the 1st curing reaction and the oxidation process take place simultaneously and consequently the peak area is lower. On the other hand, oxidation itself could prevent the curing reaction from proceeding. At normal pressure oxidation under an air atmosphere during the curing reaction has been observed at higher temperatures (205°C), leading to a 20–30% oxygen gain [10]. For the sample with N/HMTA=98/2 the majority of the curing reaction at high pressure takes place in the temperature range from 190 to 275°C.

In the next figure (Fig. 4) the influence of the HMTA content on the curing reaction in an air atmosphere at a pressure of 80 bars is presented. In samples with a higher HMTA content the first peak decreases due to the higher degree of oxidation at lower temperatures, while the second peak is more and more pronounced. It is evident from the figure that the greater the HMTA content in the sample, the larger the enthalpy released during the curing reaction. Enthalpy values are not given because the right hand limit after the second curing reaction could not be exactly determined. If the initial amount of HMTA is very small, the curing pathways can be different, and result in a cross-linked network containing different kinds of side-products [10]. There are therefore two reasons for the larger enthalpy release during the curing of samples with a higher HMTA content: (*i*) a different curing mechanism leading to formation of more stable bonds and/or a higher degree of cross-linking; (*ii*) a higher degree of oxidation in these samples, i.e. a larger oxygen uptake.

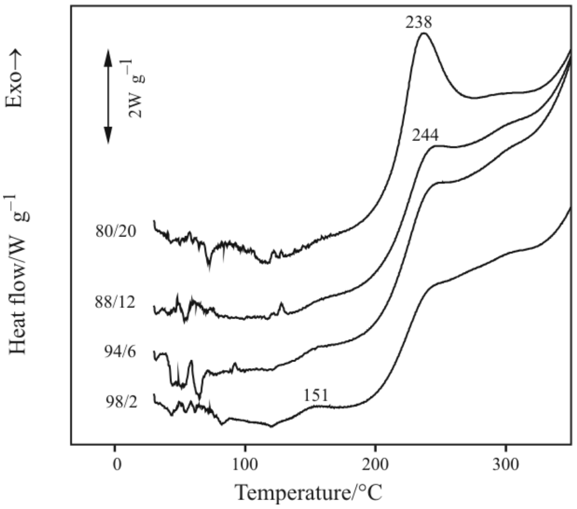

Fig. 4 Influence of HMTA content on the shape of a DSC curve under an air atmosphere (pressure 80 bars)

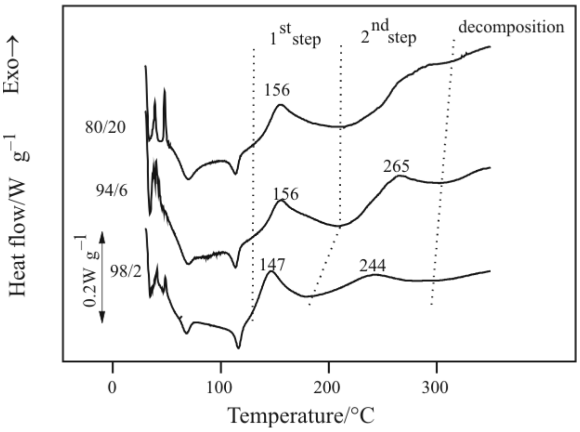

Fig. 5 Influence of HMTA content on the curing reaction in an argon atmosphere (pressure 50 bars, heating rate 10 K min^{-1})

In an argon atmosphere (Fig. 5) the DSC curves follow one another with increasing HMTA content in the expected series, that is, for lower HMTA content lower temperatures for the beginning and completion of both the 1st and the 2nd curing reactions [10]. For all samples the differences in temperature are not very large, but observable. The curves were recorded at a pressure of 50 bars because at 80 bars the noise was too large at the beginning of the measurement. The heats evolved during the curing reaction are one order of magnitude lower (note the scales of the left-hand axes in Figs 4 and 5) in comparison with those obtained in an air atmosphere, indicating that oxygen plays a major role in the reaction taking place in an air atmosphere. However, also in an argon atmosphere there seems to be some oxidation during the 2nd curing reaction of samples 94/6 and 80/20. The reason is probably insufficient purging before measurement.

A comparison of TG and DSC curves for the sample with N/HMTA=98/2 under air and argon atmospheres at normal pressure is shown in Fig. 6. Up to 200°C the mass loss curves and DSC curves of the sample are almost identical in both atmospheres. At higher temperatures the signal on the DSC curve turns in an exothermic direction in an air atmosphere, while on the TG curve the mass loss from 230 up to 330°C is lower due to oxidation of the sample. However, already at ambient pressures up to 230°C the curing reaction follows a different path with respect to the atmosphere used (Figs 7a and b). The first step in the TG curve occurs from room temperature up to 130°C and in both atmospheres is associated with the removal of water molecules (mass peaks 18 and 17), which are added to the moulding compound to obtain an appropriate fluidity. In this region the observed mass loss is around 1%. During the first step of the curing reaction in an air atmosphere ammonia (mass peak 17 and 15) and formaldehyde (mass peak 30) are released from the sample. At higher temperatures (>300°C) the signal for CO_2 (44) becomes predominant, but also a lot of water is evolved. On the DSC curve the exothermic reaction starts at temperatures higher than 200°C (under ambient pressure) and this is connected with water release. Oxygen which reacts with the sample is probably quickly released in the form of water molecules. In an inert atmosphere higher peak intensities for NH_3 and HCHO are observed between 150 and 230°C, and a signal for CO_2 was detected. The mass peak 31 (evolution of NO and NO_2) shows up only in an inert atmosphere.

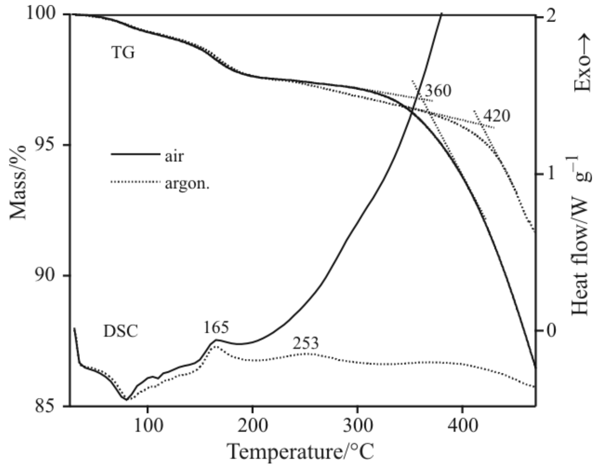

Fig. 6 TG and DSC curves of a sample with N/HMTA=98/2 under air and argon atmospheres (normal pressure)

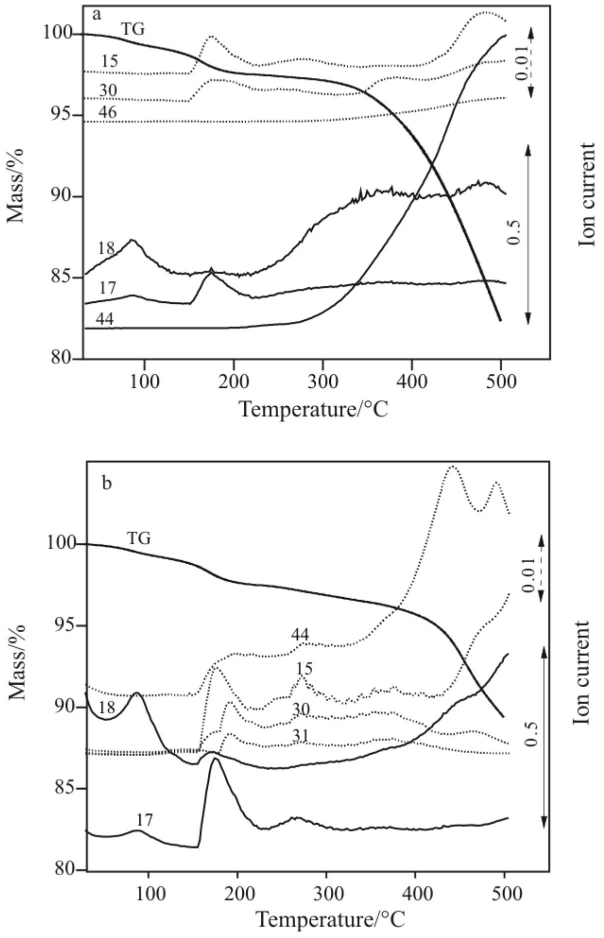

Fig. 7 TG-MS curve of a sample with N/HMTA=98/2 under a – air and b – argon atmosphere

Conclusions

- The curing reaction between novolac oligomers and HMTA occurs in two successive steps. Under an inert atmosphere the curing reaction is complete at lower temperatures for samples with lower HMTA content, as was expected on the basis of results published on the curing mechanism [10]. Both peaks (positioned at 165 and 253°C – Fig.5) are clearly distinguished already at ambient pressure. Under the normal conditions (air atmosphere, pressure of 1 bar), the second curing reaction is overlapped by an exothermic process taking place at temperatures higher than 200°C. At the pressure of 80 bars the second peak becomes superimposed on the exothermic process. From approximately 275 to 320°C, where decomposition begins, some exothermic processes are still going on, most probably oxidation of additives or fillers present in the moulding compounds. With increasing HMTA content, oxidation is shifted toward lower temperatures to the region of the first curing reaction. The peak corresponding to it therefore becomes less pronounced, while the peak of the second curing reaction increases in intensity. This may be due to a different curing mechanism on one hand, and on the other a higher degree of oxidation. The TG-MS result shows that the curing mechanism is different in the two atmospheres (air, inert) at temperatures higher than 130°C.
- Some additional measurements should be made in order to fully explain the DSC curves obtained. Our suggestion is that DSC measurements of the 'pure' system consisting of well-defined novolac oligomers and HMTA should be performed. To resolve the mechanism of the curing reactions for PF moulding compounds with different HMTA content at higher pressures under an air atmosphere

(injection moulding conditions), solid-state NMR of ^{13}C and ^{15}N-enriched intermediates, quenched during DSC measurements, would probably be the most helpful.

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