

THERMAL STABILITY OF BINDER FOR MINERAL WOOL INSULATIONS

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Abstract

The boundary of the 'analytical' thermal stability of a phenol-formaldehyde-urea binder was determined, assuming the lack of nitrogen losses as a criterion of thermal stability.

Keywords: mineral wool insulations, phenol-formaldehyde-urea binder, thermal stability

Introduction

Mineral wool insulations are normally produced in continuous processes: binder solution is dispersed (usually by injection) on a defibrated mineral material and cured thermally to make it keep the shape of the insulating product, retain its proper mechanical resistance and hydrophobic properties [1]. Binders for mineral wool products are mainly prepared from resol-type phenol-formaldehyde resins [1-3] synthesized at formaldehyde-to-phenol ratios over 3 mol/mol. Such resins contain significant quantities of free formaldehyde which is bound by modification of the resin, most frequently with urea.

As the cost of the binder is an important aspect of commercial manufacture of mineral wool insulations, it is essential to make optimal use of the binder during the manufacturing process. Apart from direct losses the manufacturer is liable to suffer, just partial utilization and/or incomplete curing of the binder will augment the environmental impact and/or impair the quality of final products [4]. In this regard, to optimize the operation of production lines it is necessary to exert on-line control (by measurements) of binder utilization degree.

For a continuous process, binder utilization degree is defined as a ratio of mass flowrate of the cured binder (in the final product) to the mass flowrate of the binder injected during the manufacturing process, in terms of the cured binder. Consequently, the yield of the cured binder produced from the injected binder feed is determined, e.g. by analytical methods to keep control of the momentary values of the binder utilization degree.

The relevant procedure is quite simple and is based on determination of the mass fraction of the cured substance produced by isothermal heating of a binder sample. Selection of proper heating parameters to provide full curing of the binder is not just that simple, as the geometry and the pneumatic conditions involved in curing an analytical sample of the binder have far too little in common with process conditions during manufacture of mineral wool products, e.g. boards. Employment of inappropriate conditions of heating the analytical sample may bring about deviation of results either upward (by way of 'subcuring') or downward (due to the subsequent thermal decomposition of the cured binder).

The present authors have examined the effect of heating conditions of a 10-g analytical sample of the binder on the quality and quantity of dry matter produced, in order to determine the heating regime which is to be applied to obtain a fully cured binder in a minimum time possible, and which can be applied to prevent its thermal degradation: that is in order to set the boundary of the 'analytical' thermal stability of the cured binder.

Thermal stability criterion

Being a thermally reactive phenol-formaldehyde-urea based system, the binder is cured by way of condensation of hydroxymethyl groups to a spatially cross-linked plastic. Water and formaldehyde are the only possible low-molecular (volatile) products of the reactions. The entire nitrogen introduced to the phenol-formaldehyde resin ought to remain in the condensed phase of the cured binder. Loss of nitrogen by heating is then equivalent to crossing the boundary of thermal stability of the cured binder.

Full curing criterion

A fully cured binder ought to be a cross-linked, infusible and insoluble plastic, i.e. to have the properties of a resit (as defined in [2]), obtained from completely cured phenol resins. The nature of the non-volatile residue of phenol resins (obtained while determining its content as set forth in DIN 16916-02-H2) is close to that of the resit: with prolonged heating, its mass will change only slightly.

In the present paper it is assumed that the mass of the non-volatile components of the phenol-formaldehyde resin used for producing the binder – as determined according to the above standard, corrected for dilution of the resin with urea solution and on the assumption that the entire mass of the urea, and just that, remains in the cured binder – by definition, is the mass of the fully cured binder.

Experimental

Material

A phenol-formaldehyde-urea based binder, typically used in Polish mineral wool insulating materials was examined. The binder was prepared from resol-type resin, WR-3 [5], (synthesized under laboratory conditions and stored at below 10°C), containing 36.8% wt non-volatiles (as found according to DIN 16916-02-H2), by its modification with 30% aqueous urea solution added to the resin at such a ratio that the number of moles of urea was twice as low as the number of moles of free formaldehyde contained in the resin. The modification was continued at ambient temperature for 24 h. The nominal value of urea in the binder was 7.34% wt. The yield of the fully cured binder was 35.14% wt, as calculated based on the assumptions above.

Procedure

A few 10-g samples of the binder feed were poured into aluminium foil cups and placed in a ventilated drier preheated to a desired temperature. The cups were then taken out successively to determine the quantity of the cured substance produced. The cured binder samples, of which the mass was close to the calculated mass of the fully cured binder, were then crumbled with a view to determining their nitrogen content by the Kjeldahl method. As the samples were found to reabsorb moisture on crumbling, the nitrogen content was determined in the moistened samples and their moisture content was found by thermogravimetry. The results obtained were expressed in terms of the urea content of the binder feed according to the following equation:

$$w_u = (2.143 \cdot w_N \cdot w_d) / w_1,$$

wherein w_N denotes nitrogen content ($w_1 =$ dry matter) in the remoistened cured substance and w_d denotes the yield of the cured substance obtained from the binder feed.

Discussion

The heating time after which a mass of the fully cured substance is produced at a given temperature and which is equivalent to the previously calculated yield (mass) of the fully cured binder was found by interpolation of the times corresponding to higher and lower masses, to $w_d = 35.14\%$ wt.

The number of samples which were cured at a given temperature and for different time periods, and in which were analyzed to find their nitrogen content

was such that 3 to 4 of the results obtained were monotonically lower than the initial nitrogen content. The intersection point of the regression line found on the basis of the results above (for $w_a = a + b \cdot t$) with the line expressed as $w_a = 7.34\%$ wt was assumed as the heating time for a given temperature, during which the cured substance keeps the entire original nitrogen content.

In the research work described in the present paper the results obtained were consistent with the expected ones. Namely, it was found that the entire original nitrogen content of the binder feed was present in the solid substance obtained by heating only up to a certain threshold temperature which is the higher, the shorter is the time of isothermal heating. The line connecting the points determined by the threshold coordinates above in the T vs. t plane delimits the boundary of the 'analytical' thermal stability of the binder (Fig. 1, curve 1).

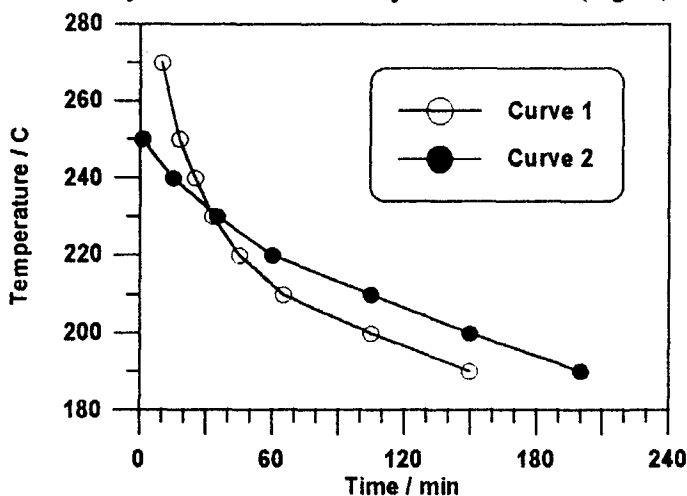


Fig. 1 Boundary of 'analytical' thermal stability (curve 1) and of full curing (curve 2) of the binder

Yet, it was found that at shorter heating times (namely, less than 30 min) the state corresponding to full curing of the binder ($w_a = 35.14\%$ wt) is obtained at a temperature higher than the boundary of the 'analytical' thermal stability of the binder (Fig. 1, curve 2). Only when the heating time is not shorter than 30 min, is it enough for the state of full curing of the binder to be obtained, to heat it at a temperature close to the boundary of the 'analytical' thermal stability of the binder. As a result, only the heating parameters from the area closed up between curve 1 and curve 2 for heating times not shorter than 30 min are useful for analytical purposes. Their employment provides a fully cured, non-degraded binder.

Remarks

In the opinion of the present authors, research works on thermal stability of materials ought to be designed and carried out as research on the kinetics of a process accountable for destruction of certain desirable properties of the materials; these have to be clearly specified. The result of such a research work can not be given as 'points' but must provide the area boundary in the time-temperature plane or the dependence of the rate of the 'destructive' process (or the rate of changes of the desirable property of the material) on temperature. A similar opinion was uttered, and – though in part – rationalized, by J. H. Flynn during the VI Seminar by the name of S. Bretsznajder (Plock, 1993).

Quotation of a single temperature value as information of the thermal stability of the material under study, though, in fact, temperature is just one of the characteristics of a thermoanalytical curve (e.g. TG or DSC curve) recorded during a non-isothermal measurement, is generally not appropriate (which issue was widely discussed by M. Maciejewski in a number of papers, e.g. in [6]). The temperature characteristics of the thermoanalytical curves may only be regarded as indicators and ought to be used solely for comparison of a number of samples, charges or batches of the same type of material. The approach of the authors seems to be an instance of the caution required with regard to the issue of thermal stability.

References

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Zusammenfassung — Es wurde die Grenze der "analytischen" thermischen Stabilität eines Phenol-Formaldehyd-Harnstoff-Bindemittels unter der Annahme ermittelt, daß das Fehlen von Stickstofffreisetzung ein Kriterium für die thermische Stabilität ist.