An example of a microcalorimetric solid state compability test

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1998

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Rapport TVBM-7127
Lund, 1998

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Introduction

If two materials are compatible they do not degrade each other. This is an extremely important aspect of product development as incompatible materials loose their desired properties earlier than necessary. Compatibility testing may be used for:

- explosives and packaging materials
- fuels and polymer containers
- foods and packaging materials
- many-component washing powders
- other reactive products like sealants and adhesives, and proposed packaging materials

A complication in compatibility testing of solid materials is that it is difficult to bring two solids together in a reproducible way. It is important to divide the solids as much as possible to increase the contact surfaces between the materials. Mixing, grinding and pressing are three ways of further increasing the contact.

Compatibility tests may often be done in simple closed glass ampoules. Only in cases where one wants to simulate more complex situations, e.g. the continuos removal of a reaction product or a high oxygen concentration, will one need to use a flow-through system.

Here I describe a compatibility test between a hydrogen peroxide producing bleaching agent and two different types of papers. One of the papers had been impregnated with a copper salt as copper is a well-known catalyzer of hydrogen peroxide degradation; "The presence of heavy metals (such as Fe and Cu) in hydrogen peroxide can increase the rate of decomposition by many orders of magnitude..." (Kirk and Othmer). This type of measurement is of practical interest to producers of bleaching agents and manufacturers of washing powders, but is given here as it was developed for a student experiment in isothermal microcalorimetry.

Method and materials

An house-hold "percarbonate" bleaching powder was used. This consisted of quite pure $Na_2CO_3 \cdot 1.5\ H_2O_2$ (it also contains some enzymes and already reacted percarbonate). Three glass ampoules (3 ml) were half-filled with approx. 1.5 g of bleaching powder. To two of these was added approx. 4 cm^2 of two types of papers (A and B), each cut into pieces approx. 2 mm x 4 mm. The ampoules were then closed and the samples were mixed by shaking. Before the ampoules were entered step-wise into the TAM microcalorimeter (Thermometric AB, Järfälla, Sweden) care was taken so that the paper was as evenly distributed in the powders as possible. Baselines were measured before and after the measurement with sealed glass ampoules half-filled with water. The measurements were made at +40°C.

Two papers were used. Paper A was an ordinary brown packaging. Paper B was the same paper which had been impregnated with an aqueous solution of $CuSO_4$. The copper content of

the paper was 1.5 mg/cm^2 of $CuSO_4 \cdot 5\ H_2O$ or 0.4 mg/cm^2 of Cu. The paper in each ampoule contained approx. 2 mg copper.

Result and discussion

The thermal power measured for the ampoules with only bleaching agent was in the order of 5 μW. A slightly higher value was found for the sample with the untreated paper A. Figure 1 shows the results. The effect of the copper was quite remarkable. Already when the ampoule has just come down to the measuring position (less than 1 hour after the paper and the percarbonate were mixed) a thermal power of 45 μW is measured. During the 20 h measuring period this increases to nearly 70 μW. The compatibility problems between the percarbonate and paper B containing copper is thus clearly demonstrated.

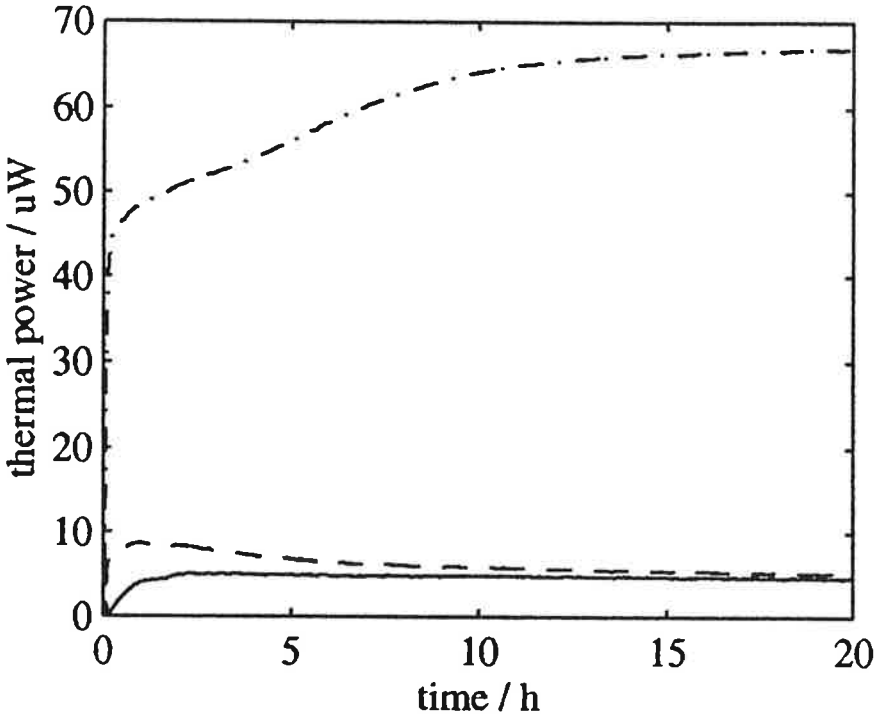

Figure 1. Examples of results from three experiments with percarbonate-paper compatibility. Solid line: only percarbonate; dashed line: percarbonate and paper A; dash-dotted line: percarbonate and paper B. All samples contained 2 g percarbonate.

A more quantitative discussion of stability and compatibility should be based on an understanding of the chemical process responsible for the degradation of the bleaching agent:

$Na_2CO_3 \cdot 1.5H_2O_2 \rightarrow Na_2CO_3 + 1.5H_2O_2 \rightarrow Na_2CO_3 + 1.5H_2O + 3/2\ O_2$

ΔH of the first reaction is assumed to be small compared to the ΔH of the second reaction which is large: ΔH=-95 kJ/mol = -500 J/g.

If we assume that a degradation process is *not* autocatalytic, i.e. the reaction products do not catalyze further degradation, then the degradation can be modeled as a first order "decay"-process with the following equations:

$M(t) = M(0) \exp(-kt)$

$k = P(0) / \Delta H / M(0)$

Here P is the thermal power, M is the mass of percarbonate used in the measurement, and k is the rate constant. The fractional degradation (D) during a time period t may be calculated as:

$D = 1 - M(t) / M(0) = \exp(P(0)\, t / \Delta H / M(0))$

For the percarbonate without paper and with paper A approx. 20% of the percarbonate is degraded per year, but for the sample mixed with paper B the same figure is 93%. It is thus clear that paper B is not a good material to use together with the percarbonate, e.g. in a package.

The above equations should be used with caution as many solid-state processes are auto-catalytic and will accelerate with time. The process here may speed up as the water produced may increase the mobility of the copper and also generally increase the rate of the percarbonate reaction.

Conclusion

This report describes a quite straightforward testing of the compatibility between a bleaching agent and different types of papers. The method is sensitive to even low-rate degradation and can be used as a method to screen and test product combinations.