

ALKALINE HYDROLYSIS OF POLYMERS IN CONTACT WITH CEMENT BASED MATERIALS

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ABSTRACT

Hydrolysis of polymers is a common degradation mechanism under alkaline conditions such as found in contact with humid or wet concretes and mortars. Common building related products that are susceptible to alkaline hydrolysis are flooring adhesives, concrete admixtures, polymeric reinforcement materials and PVC plasticizers. We have developed a method based on isothermal calorimetry – the measurement of heat production rate at constant temperature – that can be used to quantify hydrolysis rates. The method relies on that the heat produced by hydrolysis is close to zero, but that the acid produced by the hydrolysis reaction is neutralized in the alkaline solution, and that the heat produced by this process is high and almost constant (per mol of reaction). With knowledge of this heat (the neutralization enthalpy) it is possible to directly measure the number of hydrolysis events taking place per second, i.e., the true kinetics of the process. Measurements can be made under different pH and temperature conditions, and the result can be used develop kinetic models of hydrolysis. We will in this paper exemplify this with data from calorimetric measurements on flooring adhesives, and discuss the use and limitations of kinetic models developed from such data.

1 INTRODUCTION

Hydrolysis is a common type of chemical reaction between organic substances and water. The most common type of hydrolysis is that of ester bonds, in which a water molecule cleaves the hydrolysed molecule at the ester bond, forming one alcohol and one carboxylic acid. This process is can be exemplified by the simple case of ethyl acetate hydrolysis, in which ethanol and acetic acid are formed.

The rate of hydrolysis increases both under acidic and under alkaline conditions. In the construction field, hydrolysis of polymers is a common degradation mechanism under alkaline conditions, such as found in contact with humid or wet concretes and mortars. Common building related products that are susceptible to alkaline hydrolysis are flooring adhesives, concrete admixtures, polymeric reinforcement materials and PVC plasticizers[1,2].

We have developed a method based on isothermal calorimetry – the measurement of thermal power – to quantify hydrolysis rate [2]. All processes (physical, chemical, biological) produce heat, which often can be measured with isothermal calorimetry. Generally, the following two equations describe the relation between calorimetric measurements of thermal power P (W) and heat Q (J), and the rate v (mol/s) and extent of reaction ξ (mol/mol):

$$v = \frac{P}{\Delta H} \quad (1)$$

$$\xi = \frac{Q}{\Delta H \cdot n_0} \quad (2)$$

Here, ΔH (J/mol) is the reaction enthalpy and n_0 (mol) is the amount of reacting substance at the start of the process. Note that the isothermal calorimeter continuously measures the thermal power, which can then be integrated between any two times during a measurement to yield the heat. Typically, the reaction starts at time zero and the result can be shown in two graphs: the thermal power as a function of time, and the heat produced as a function of time.

As the thermal power is proportional to the rate of the process, and the heat is proportional to how much that has reacted, isothermal calorimetry is a powerful method to study kinetics if the reaction rate times the enthalpy is high enough to be measured by the calorimeter used. In the case of hydrolysis, the enthalpy is close to zero so the thermal powers produced by the primary reaction are low, but the produced acid will react with the hydroxide ions and this secondary reaction (neutralization) has a high enthalpy, which is close to constant if a strong base like sodium hydroxide is used [2]. The enthalpy of neutralization is -55.81 kJ/mol and we found total reaction enthalpies of -57.3 kJ/mol for poly(vinyl acetate) and -57.9 kJ/mol for poly(lactic acid) [2] indicating that we can determine rates of alkaline ester hydrolysis of all polymers to within a few percent by measuring the produced thermal power [2]. We thus have two reactions: the hydrolysis reaction that we are interested to study the rate of, and the extremely rapid neutralization. The first is rate determining and the second produces the heat that is measured with an almost constant enthalpy. We will in this paper show some examples of results from measurements on polymer dispersions.

2 MATERIALS AND METHODS

Three commercial polymer dispersions commonly used in flooring adhesives were used in the present studies:

1. A vinylacetate/ethylen/vinylester-terpolymer
2. An acrylate/vinylacetate/ethylen-terpolymer
3. A styren-acrylate-copolymer

All measurements were made on about 1 g of polymer dispersions added to about 16 mL of NaOH(aq). Measurements were made at 20, 30, 40 and 50 °C and the following concentrations of NaOH prepared from Fixanal (Merck) ampoules were used: 1.0 M, 0.5 M, 0.25 M and 0.10 M. All hydroxide solutions were pre-thermostated to the temperature of the measurement before the polymer was added. This significantly decreases the initial disturbance of the calorimeter.

The measurements were made in eight channel TAM Air isothermal calorimeters (Thermometric AB; now TA Instruments) using 16 mL water as reference. The results were evaluated by the following steps:

- Subtraction of baseline (offset) measured with ampoules with water.
- Multiplication with the calibration coefficient obtained from electrical calibrations.
- Division with the mass of polymer dispersion.
- Tian correction for the thermal inertia of the instruments (time constant 600 s).

3 RESULTS

To exemplify the use of the method we here present selected results. In Fig. 1 are seen results for the three dispersions at 40°C, and in Fig. 2 the results for one dispersion at different temperatures are shown. It is seen that the hydrolysis of dispersion 3 follows

different kinetics than the hydrolysis of dispersions 2 and 3, and that the kinetics are temperature dependent.

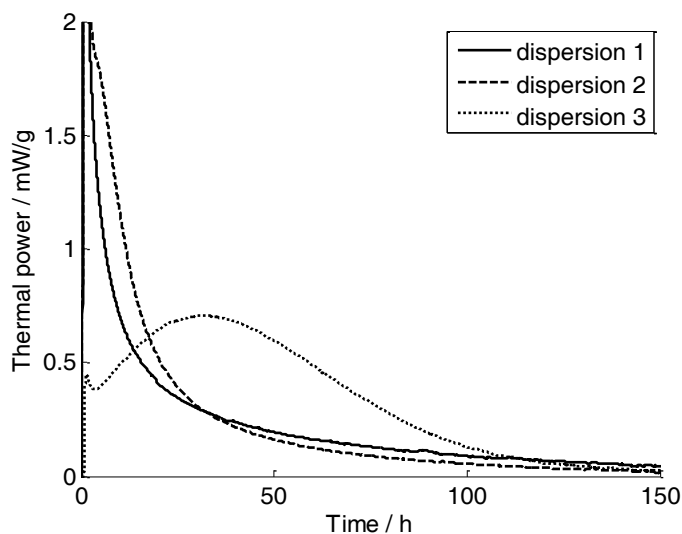


Figure 1: Thermal powers per mass of dispersion measured for the three dispersions hydrolysed at 40 °C and 1 M NaOH.

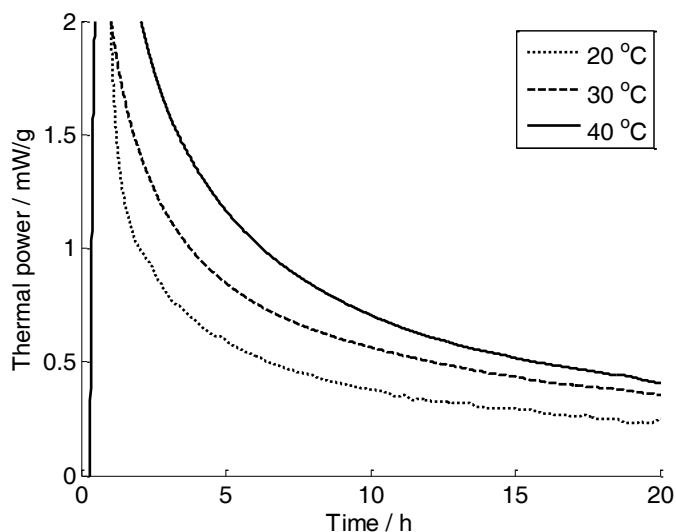


Figure 2: Thermal powers per mass of dispersion 1 measured at different temperatures for dispersion 2 in 1 M NaOH.

4 DISCUSSION

As noted in the introduction, there is proportionality between the thermal power and the rate of reaction. This means that we can calculate the rate of hydrolysis from the measured thermal power. As an example, the peak thermal power of dispersion 3 in Fig. 1 after about 40 h is about 0.75 milliwatt per gram dispersion. Using -57 kJ/mol as reaction enthalpy the 0.75 mW (=0.75 mJ/s) corresponds to a rate of about 13 nmol/s. Every second, 13 nmol hydrolysis events take place per gram dispersion.

If the whole peak seen for dispersion 3 in Fig. 1 is integrated, a value of about 380 J/g is found. If we assume that the hydrolysis has come to an end after 150 h, we can recalculate this heat into amount of hydrolysable ester bonds: 0.066 mol per gram dispersion.

As we can measure the reaction kinetics at different temperatures, we can calculate the activation energy of the rate determining hydrolysis reaction. This is made by plotting the thermal power (proportional to the rate) as a function of the heat (proportional to the extent of reaction), and using the thermal powers for different temperatures, but at the same heat, as input to the Arrhenius equation.

As the result from a calorimetric measurements directly shows the kinetics of the studied hydrolysis process, it is possible to use the calorimetric results to optimize kinetic models. In Fig. 1 it is seen that dispersions 1 and 2 possibly follow first order (exponential) kinetics, while dispersion 3 behaves more as if it was an auto-catalysed process that accelerates, peaks and then deaccelerates. Kinetic modelling based on data from isothermal calorimetry has been described by Beezer and co-workers in a series of papers; see for example references [4-5].

5. CONCLUSIONS

Isothermal calorimetry is an interesting method to study alkaline ester hydrolysis as the produced thermal power and heat are proportional to the reaction rate and the extent of reaction. The proportionality constant (the reaction enthalpy) is known to within a few percent.

6. ACKNOWLEDGEMENT

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