Alkaline hydrolysis of polymers with ester groups studied by isothermal calorimetry

Lars Wadsö [a,*], Ola J. Karlsson [b]

[a] Building Materials, Lund University, Box 118, 221 00 Lund, Sweden
[b] Physical Chemistry, Lund University, Box 124, 221 00 Lund, Sweden

ABSTRACT

Alkaline hydrolysis of polymers produces heat that can be measured with isothermal calorimetry to monitor the hydrolysis. We here report on two studies to measure the enthalpy of alkaline hydrolysis of polymers containing esters of carboxylic acids. The heat from the hydrolysis of films of poly(vinyl acetate), PVAc, was followed for up to 42 days and correlated with the amounts of acetic acid produced. The enthalpy per hydrolysed repeat unit was -57.3 kJ mol^{-1} for PVAc. For poly(lactic acid), PLA, fibres the enthalpy of hydrolysis was determined by integrating the heat produced during complete hydrolysis. For PLA, the result per hydrolysed repeat unit was -57.9 kJ mol^{-1}. The determined values are within a few percent of the enthalpy of neutralization of the carboxylic acids formed, as the hydrolysis itself has a low enthalpy; it is the neutralization of the acid that produces most of the measured heat. Isothermal calorimetry is thus a general quantitative method for the investigation of the rate and extent of alkaline hydrolysis of esters of carboxylic acids in polymers and other organic substances.

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1. Introduction

The degradation by alkaline hydrolysis of polymers in contact with cement based materials like concrete, screeds and mortars is of significant practical interest. The high pH in such materials is caused by the high content of hydroxides in the Portland cement from which such products are made. The pH of a newly cast Portland cement concrete is normally above 13, but may decrease to about pH 11 if it carbonates, i.e. reacts with the carbon dioxide present in the air. As cement based materials have nanometre-sized pores that hold the highly alkaline pore solution by capillary condensation even at moderately high relative humidity [1,2], there is a risk of alkaline hydrolysis in materials in contact with concrete, even if there is no "free" water present.

A large number of polymers are used in contact with concrete and similar alkaline materials. In many cases hydrolysis is not a problem, e.g. when non-hydrolysable polymers like polyolefins are used; or when the relative humidity is too low for the hydrolysis to take place at an appreciable rate. However, several polymers used also in potentially alkaline environments contain hydrolysable ester linkages, for example poly(vinyl acetate), poly(ethylene terephthalate), poly(methyl methacrylate) (acrylics), poly(lactic acid) and a range of co- and ter-polymers. There are also other polymers that contain other hydrolysable groups, for example polyamides (nylon), polysaccharides and polycarbonates that can undergo alkaline hydrolysis.

Two examples of where alkaline polymer hydrolysis has caused problems in the construction sector are:

- Flooring adhesives used to bond PVC-flooring to concrete floors are typically co- or ter-polymers with butyl- and/or 2-ethylhexyl-acrylates that will form odorous butanol and 2-ethyl hexanol if they are hydrolysed [3].
- Casein (natural milk protein) is used as a flow agent in screeds, and if these contain Portland cement and are not dried properly, the casein will be hydrolysed and release amines, ammonia and other compounds that may discolour flooring materials and give unacceptable odours [4].

To be hydrolysable, a polymer must contain functional groups susceptible to hydrolysis. This is most commonly ester groups, but also other groups (anhydride, amide (peptide), oxime etc. [5]) can be hydrolysed. In the following we will limit the discussion to the hydrolysis of esters of carboxylic acids (RCOOR′, where R and R′ are

* Corresponding author. Fax: +46 46 2224427.
E-mail address: lars.wadso@byggtek.lth.se (L. Wadsö).

the groups forming an acid and an alcohol, respectively) as this is the most common hydrolysable bond type.

Polymers containing ester groups can have very different rates of hydrolysis. The rate is highly dependant on both physical factors such as chain mobility, crystallinity and permeability [6] and the chemical structures neighbouring the bond [7] controlling the accessibility of the ester groups to the hydrolysis agents (water, oxonium ions, hydroxide ions, enzymes and other catalysts). Generally, increased chain mobility, decreased crystallinity and increased permeability will increase the accessibility and thus the rate of hydrolysis.

Hydrolysis of carboxylic acid esters takes place when the ester bond is broken by the reaction with a water molecule. This reaction divides the molecule into two parts: an alcohol and a carboxylic acid. For non-crosslinked polymers, hydrolysis can be divided into three types:

- If the ester linkages are in the backbone, hydrolysis leads to backbone scission. This is a desirable degradation mechanism for biodegradable polymers as the final result after complete hydrolysis is the monomers from which the polymer was originally built. A typical example of a polymer that is hydrolysed in this way is poly(lactic acid), PLA, which degrades into lactic acid. Also other polyesters like poly(ethyleneterephthalate), PET, and poly(caprolactone), PCL, will degrade by backbone scission. For such degradation two stages have been identified [6,8]. The first stage consists of random hydrolytic cleavage of the polymer chains during which the mass is essentially unchanged, but the morphology and mechanical properties change. The second stage starts when the molecular mass of the polymer has decreased to a point where the diffusion of small fragments out of the polymer becomes significant. This results in a catastrophic loss of mechanical strength [6].
- If the ester linkage is in a side-chain with the carboxylic acid residue *outside* the oxygen bridge (−O−), hydrolysis will lead to the formation of a free carboxylic acid, while the remaining side chain will end with a hydroxyl group. This is the case with for example polyvinyl acetate, PVAc, for which hydrolysis forms acetic acid and the remaining part of the side group is a hydroxyl group.
- If the ester linkage is in a side chain with the carboxylic acid part *inside* the oxygen bridge (−O−), hydrolysis will lead to the formation of a free alcohol, while the remaining part of the side chain will end with a carboxyl group. This type of hydrolysis is seen, for instance, in poly(methyl methacrylate), PMMA, and in dispersion acrylates like butyl acrylate. Hydrolysis of such materials can give negative environmental effects from produced alcohols like methanol, butanol and 2-ethyl hexanol.

It is of general interest to study the rate of hydrolysis of polymers as a function of parameters such as temperature and pH. This normally involves exposing a number of samples to a degrading environment and at suitable times measuring for example mechanical properties [9], molecular mass [10,11], decomposition temperature [10] or mass loss [10−12]. Many of these techniques to assess the level of hydrolysis are destructive and a large number of samples may be needed for a study. It is also possible to continuously follow the hydrolysis by measuring pH of the solution in which the degrading sample is placed [12]. For biodegradation, composting tests in which oxygen uptake and carbon dioxide production from the microbiological processes are measured are also used [8].

The present work concerns a method to quantify hydrolysis kinetics that is especially suitable for alkaline hydrolysis. It is based on isothermal calorimetry (microcalorimetry), by which measurements of thermal power (heat production rate) can be made [13]. For a chemical reaction like alkaline hydrolysis, the thermal power P (W or J s^{-1}) is proportional to the rate of the process dn/dt (mol s^{-1}):

$$P = \Delta H \frac{dn}{dt} \tag{1}$$

Here, n (mol) is the amount of reaction sites (hydrolysable bonds). There is a certain heat produced for every ester functional group that is hydrolysed. The proportionality constant is the reaction enthalpy ΔH (J mol^{-1}). By measuring the thermal power it is thus possible to directly calculate the hydrolysis rate if the enthalpy is known.

From the thermal power it is possible to calculate the released heat Q (J), as this is the integral of the thermal power. The heat is proportional to the amount of reaction that has taken place:

$$Q = \Delta H(n_0 - n_t) \tag{2}$$

Here, n_0 and n_t (mol) are the amounts of substance at the start of the measurement and at time t (s), respectively, and also here the enthalpy is the proportionality constant. A single measurement in which the thermal power is measured from the start of the process can thus give both the reaction rate and the extent of reaction as a function of time, if the enthalpy of the process is known.

In this paper we will report results from calorimetric experiments on poly(vinyl acetate) and poly(lactic acid). The results show that the overall enthalpy ΔH is approximately constant for the case of alkaline hydrolysis of carboxylic esters, so that there is a direct connection between measured thermal power and number of hydrolysis events per second, and between the measured heat and the extent of degradation.

2. Materials

Two materials were used: poly(vinyl acetate), PVAc, films and poly(lactic acid), PLA, fibres. These were chosen as they are common polymers that are easily hydrolysable.

The PVAc (Sigma Aldrich, beads, molecular mass 100 000, stored under dry conditions in refrigerator before use) was dissolved in acetone (Sigma Aldrich, "ReagentPlus", ≥99% purity). Films were then cast on a float glass support using a 200 mm adjustable doctor blade film applicator (Elcometer 3600/5, Elcometer Ltd., Manchester, UK; a device for manually producing films of an even thickness). The films were left to dry on the glass for about 1 h. They were then softened with 30 °C water for less than 30 s before being removed from the glass and dried hanging in the room for about 1 h. They were then placed in a dry box with molecular sieves for final drying. The thicknesses of the PVAc films were determined with a digital micrometre to be 51 ± 7 μm (mean and standard deviation).

The PLA fibres were kindly provided by Suominen Nonwovens OY (Nakkila, Finland) and are a commercial fibre product (Ingeo from Far Eastern New Century, Taipei, Taiwan) spun from PLA produced by Nature Works LLC (Minnetonka MN, USA). The only additive used in the production was a spin finish (anionic and nonionic surfactants) whose mass fraction in the final product is in the order of 0.1%. According to the manufacturer, the fibre titre is 1.65 dtex (this measure of fibre fineness corresponds to a fibre diameter of 13 μm, a value that was confirmed by scanning electron microscopy).

Sodium and potassium hydroxide solutions were prepared from Fixanal ampoules and deionised water (SigmaAldrich).