

DECOMPOSITION OF POLYETHYLENE GLYCOL (PEG) ON HEATING

Tim Padfield, Janne Winsløw, W.B.Pedersen and Jens Glastrup

Abstract

During conservation of a wooden boat, surplus polyethylene glycol (PEG) was melted away. On cooling, the PEG divided itself into three distinct phases: solid, pasty and liquid. These fractions resulted from a rapid oxidative degradation of PEG in warm air. Dry polyethylene glycol degrades significantly within four hours when heated to 75°C. Water protects against degradation, which is perhaps why the phenomenon has not been described before in the conservation literature.

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KEYWORDS

Waterlogged wood, polyethylene glycol, PEG, oxidation, degradation.

Tim Padfield, Janne Winsløw, Walter Batsberg Pedersen* and Jens Glastrup**

The National Museum of Denmark
Department of Conservation
Brede, DK-2800 Lyngby, Denmark

*

Risø National Laboratory
Postbox 49
DK-4000 Roskilde, Denmark

Introduction

The Hjortspring boat was discovered in the beginning of this century in south Jutland and excavated in the early twenties. It is one of the oldest dated boats in the world, about 400 BC. It was, after numerous conservation attempts, most recently conserved in the sixties by impregnation in polyethylene glycol 4000. The boat was discovered in fragments. After the final impregnation the thousands of pieces were left embedded in slabs of solid PEG. Later they were released by placing the slabs in an oven at 80°C for a few hours. The PEG that melted into the tray below, separated into three fractions, one solid, one pasty and a third that was still liquid at room temperature. We suspected that the PEG had partly decomposed at some point in the long conservation process. This paper describes the work done to explore the nature of the decomposition process.

Analytical methods

Thin Layer Chromatography (TLC): This was performed on Silica gel 60(F254) microplates from Merck. The mobile phase was chloroform/methanol/water (6/50/24). The samples were run in a small beaker covered with parafilm. Developing was done by spraying with a 0.005N iodine in potassium iodide solution. To improve visibility the plates can be dried and sprayed with a 0.2% starch solution(1).

Size Exclusion Chromatography (SEC): The samples were dissolved in tetrahydrofuran (THF). 50µl of the solution was injected into a column system comprising a 1000Å, a 500Å and a 100Å column, all from Polymer Laboratories. The chromatographic separation was performed at room temperature by pumping THF through the columns at a flow rate of 1ml/min. The composition of the eluate was monitored by a differential refractometer. A series of PEGs with different molecular weights were chromatographed in order to establish the calibration.

Materials

PEGs of various molecular weights were obtained from Hoechst. The PEG 4000 used in the experiments was dried by bubbling dry pure nitrogen through it. The nitrogen, Quality M from Air Liquide, was passed over a molecular sieve 3Å, Merck, art. 5704, then through the molten PEG at 60°C for 16 hours.

Room air was filtered through glass wool and active carbon filters then dried with silica gel and molecular sieve.

Approximately 76% relative humidity (RH) was maintained over the humid sample (water content 6.5%) by first equilibrating silica gel at room temperature over a saturated sodium chloride solution. This gives an equilibrium RH of 76%. This gel was transferred to a cylinder inside the oven, through which passed a slow stream of dry air at the desired temperature. The equilibrium relative humidity over silicagel is only slightly affected by temperature and the relative humidity can therefore be assumed to be almost the same at high temperature. Fig. 1 shows the experimental system.

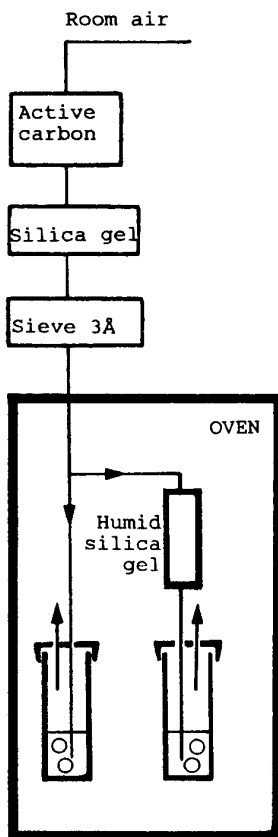


Fig. 1: Experimental system. Dry, filtered air is pumped into one reaction flask. The supply to the other passes through a column of silica gel preconditioned to 76% RH at room temperature.

** Author to whom correspondance should be adressed

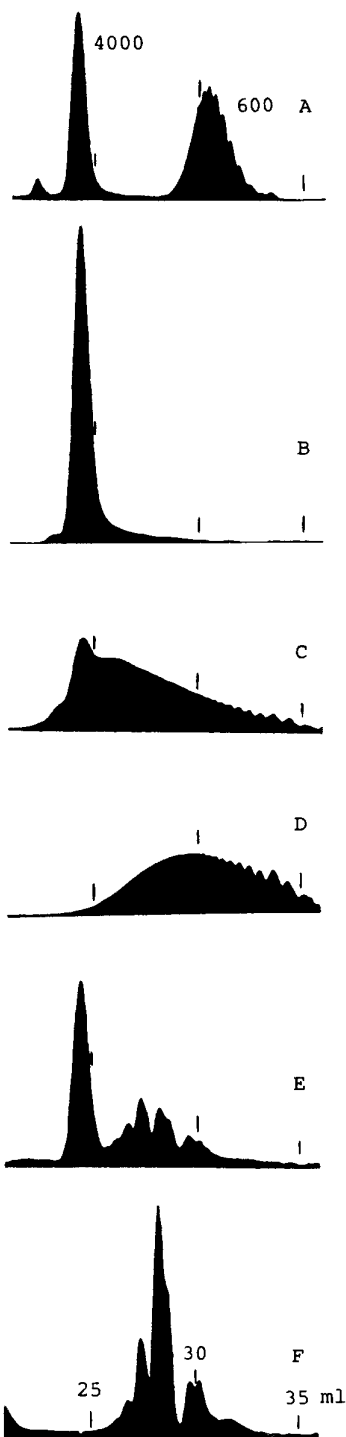


Fig. 2: SEC chromatograms of samples taken before and after melting off the PEG from the boat.

A: Standard made by mixing PEG 4000 with PEG 600.
 B: The hard fraction found in the tray after melting and cooling. C: The pasty fraction. D: The liquid fraction. E: A sample of PEG taken from the boat before melting. F: A sample of pure beeswax.

Experimental

The first indications of PEG 4000 degradation came from the fractionation of the material after melting off PEG from the boat. We first confirmed that this material was decomposed PEG by analysing the three different fractions using SEC. The chromatograms are shown in fig. 2B-D. A mixed standard of PEG 4000 and 600 is shown in 2A. Fig. 2C, which represents the chromatogram of the intermediate sample, demonstrates the presence of both a surviving PEG 4000 fraction and decomposed material.

To prove that significant decomposition occurred during the brief heating period, a sample of PEG was taken from an unheated fragment of wood. The chromatogram is shown in fig. 2E. The minor peaks in the 30 to 35ml region could well be material originating from decomposed PEG. However, the broad shoulder seen in fig. 2C is not seen and is replaced by irregular peaks which probably originate from beeswax, previously used on the boat. Fig. 2F shows a chromatogram of pure beeswax, which resembles the additional peaks in 2E.

We succeeded in decomposing PEG 4000 in the laboratory by simply heating fresh, dried PEG in an oven at 75°C without any special humidity control. This corresponds to 2-3% RH. Samples were taken at intervals between 2 and 120 hours and analysed by TLC. The results are shown in fig. 3B. They show that the PEG, under constant heating at 75°C, rapidly changes in composition. Already after four hours the initially sharp peak defining the fresh PEG shows tailing, demonstrating the formation of components of lower molecular weights. After 16 hours there is virtually no trace left of the original material. This can be seen by comparison with the standards, pure PEG's ranging in average molecular weights from 600 to 20,000 Daltons, shown in fig. 3A.

We were surprised that such a short exposure to heat caused such damage to a material that is held warm for long periods during impregnation of wood. It could be that water, always present during the impregnation process, has a stabilising effect on the PEG.

We therefore set up an experiment in which PEG samples were heated both in dry air and in air in which the relative humidity was approximately 76% at 75°C. Samples were taken out for TLC analysis after 20 hours exposure. We also analysed a sample of PEG 4000 which had been heated under nitrogen. The results are shown in fig. 4. They clearly demonstrate that the PEG decomposed detectably only in dry air. The sample kept under nitrogen showed no sign of degradation. It therefore seems reasonable to conclude that the decomposition noticed during heat treatment of the Hjortspring boat was the result of oxidative degradation caused by oxygen in the absence of water.

Discussion

Our investigations confirmed that the PEG had decomposed and that the decomposition occurred during the brief melting process while handling the wood. A control sample taken directly from the unheated wood showed no detectable breakdown (fig 2E). There had therefore been little damage to the PEG during the long period in hot aqueous solution, nor in the 25 years of its existence in an ordinary room climate.

These experiments show clearly that PEG 4000 can degrade disturbingly fast. This is in sharp contrast to expectations based on work with PEG under normal conditions.

We have not been able to find any literature describing this degradation process in the museum environment. Likewise a search in Chemical Abstracts, back to 1967, gave no results. The work presented here has been confirmed by the Hoechst company (2,3). They, however, used a much higher temperature and a sealed reaction vessel. Under these reaction conditions water was not so effective in protecting PEG, only halving the reaction rate, whereas our results indicate a more complete inhibition. Hoechst also drew our attention to research by Dulog (4) on the instability of polyglycols. This work starts with the words: "Es ist seit langem bekannt, daß niedermolekulare Äther unter milden Bedingungen mit molekularem Sauerstoff reagieren", ("It has long been known that, under mild conditions, the lower molecular weight ethers react with molecular oxygen"). He in turn mentions the thorough work of Riecke and coworkers from the thirties to the sixties (5).

TLC of PEG.

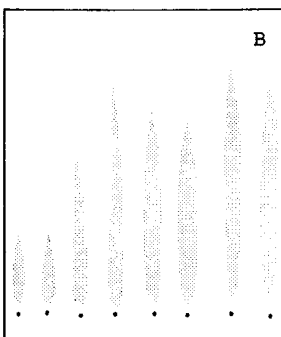
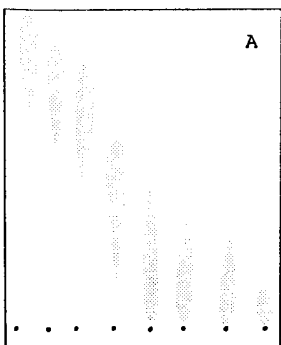


Fig. 3:

A: Chromatograms of samples of PEG of different molecular weights ranging from 600 to 20.000.

PEG standards, from left: 600,800,1000,2000,3000,4000, 6000,20000.

B: TLC chromatograms of PEG dry heated in an oven at 75°C, from which samples were taken at different times.

Samples, from left (hours): 0,2,4,8,16,32,64,120.

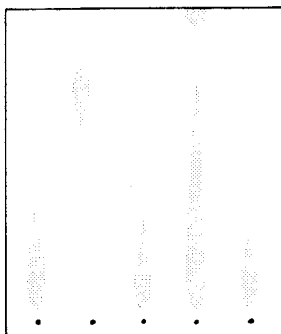


Fig. 4: Influence of different atmospheres on PEG breakdown.

From left:
Standard PEG 4000
Standard PEG 800
PEG 4000 heated in nitrogen.
PEG heated in dry air.
PEG heated in humid air.

This information has some important implications for work with PEG. Surplus PEG on wood is often removed by melting. This inevitably reduces the local RH to a negligibly small value. Small pieces of wood are joined with molten PEG or with "hot melt compounds". These processes should therefore ideally be done under warm nitrogen instead of air.

It can be argued that the oxidation is of minor importance when we talk about wood filled in all pores with PEG, because diffusion of oxygen into the interior is slow. However, PEG is also used to reduce distortion during freeze drying, and here it is more susceptible to oxidation because of the open pore structure in the treated wood. On the other hand, it may be that the close association of the PEG molecules with the lignin/cellulose molecules may alter its susceptibility to degradation.

It should be noted that the oxidation products include esters and aldehydes (3), which in turn may be harmful to wood.

Further work should include measuring the activation energy of the oxidation reaction and from that the approximate oxidation rate at room temperature. Furthermore it is important to measure the relative humidity dependency of the reaction, which may give an indication of the climatic conditions under which PEG conserved objects are best preserved.

Finally it should be kept in mind that this degradation is a result of an oxygen attack on an ether bond. There is therefore a risk that other polyglycols such as polypropylene glycol are also susceptible to this breakdown process.

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