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The Thermal Degradation of Tetraethylene Glycol, a Model Molecule for Polyethylene Glycol

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Abstract

Tetraethylene glycol (TEG) was aged at 70°C in a stream of gas. TEG is stable in nitrogen but decomposes in dry air. Water vapour in the air reduces the rate of degradation. Copper acetate and ferric chloride inhibit degradation, and nickel sulfate accelerates degradation. The main degradation product is of higher molecular weight. The sensitivity of TEG, and therefore presumably of all polyethylene glycols, to small alterations in the chemistry of its environment casts doubt on the wisdom of accepting PEG impregnation as a standard preservation technique for waterlogged wood.

Keywords

Tetraethylene glycol, polyethylene glycol, thermal degradation, gas chromatography

Introduction

In a previous article we demonstrated that PEG 4000, a synthetic polyethylene glycol wax which is extensively used for the stabilisation of waterlogged wood, suffered degradation through heat treatment (1).

To examine the degradation more systematically we chose a model molecule, tetraethylene glycol (TEG). This molecule is small enough that both it and its degradation products can be analysed directly by gas chromatography (GC) and by mass spectrometry (GC/MS). TEG is one of the two main oligomers in the commercial product PEG 200. TEG was heated to 70°C while a stream of gas was blown through it. We measured the decomposition rate of pure TEG in nitrogen and in air at different relative humidities. We also bubbled air at 75% RH through samples of TEG contaminated with 10mM of $FeCl_3$, $Cu(CH_3COO)_2$ and $NiSO_4$.

Materials and methods

The chemical used as a model for the degradation af PEG is tetraethylene glycol (TEG, CARN 112-60-7). The experiments were performed in an oven at 63°C. The oven contained a flask of water through which the gas was bubbled. The reaction vial was 5 ml 33-expansion borosilicate glass from Wheaton. 2.0 ml of TEG was put in the vial which was then placed in an aluminium block sitting in the oven. The block was heated to 70°C. The saturated gas stream from the water flask at 63°C was further heated to 70°C in a coil in the aluminium block. This lowered the RH to 75%. The gas then bubbled through the TEG. For the dry experiments the water flask was empty and for the 5% RH experiments the water flask was outside the oven.

All tubing was 1/8" and 1/16" Teflon. The nitrogen and air were passed through Molecular Sieve 3A and activated charcoal (Merck 2514 & 5704). The air pressure was set at 170 kpa. The flow was controlled by restrictors made of polyimide-coated fused silica with an internal diameter of 60 μm (J&W Scientific, Folsom, California). The flow rate is determined by the Poiseuille equation: 1, 2, 4 and 10 cm lengths give a flow of 10.0, 5.0, 2.5 and 1.0 cm^3/min, respectively, at this pressure.

We first measured the degradation rate of TEG in the reaction vials with different air flows in order to find the minimum air flow that ensured the maximum reaction rate. At air flow rates of 10 and 20 ml air/minute, the slope of the curve, i.e., the degradation rate, is the same, whereas at 5 ml/min the degradation rate is somewhat lower. We chose 10 ml/min for all the experiments. Nitrogen was also tested at this bubbling rate. TEG showed no degradation under these circumstances.

For the analysis, 2 μl aliquots were withdrawn from the reaction flask and transferred to a vial with 1.0 ml acetone spiked with 0.5 mg methyl palmitate as internal standard. The samples were analysed by a Varian 3500 Gas Chromatograph. The experimental parameters were as follows: carrier gas H_2, initial column temperature 110°C, hold 0.5 min, ramp rate 40°C/min to 175°C, hold 0.3 min; injector 275°C, split 25, column flow 2.0 ml/min; detector 230°C, att. 32; and column BP-5, 4 m long, 0.32 mm i.d., coating 0.25 μ (J&W Scientific).

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Analysis of the degradation products was performed on a Varian Saturn II GC-MS. The GC carrier gas was helium. The experimental parameters for GC were as follows: initial column temperature 110°C, ramp rate 10°C/min to 210°C, hold 3 min; injector on column, initial temperature 60°C, ramp rate 200°C/minute to 275°C, hold 12 min; transfer line 230°C; and column 20 m BP-5, 20 m long, 0,18 mm i.d., coating 0.40 µ from J & W Scientific. The experimental parameters for MS were as follows: manifold temperature 220°C, electron emission current 10 µA, scan segment from 50 to 399 amu, and 1 scan /sec.

The reaction kinetics

Figure 1 shows the effect of relative humidity (RH). Note that even 5% RH noticeably protects the TEG and 75% RH reduces the decomposition rate by about 30%. At this RH the TEG contains about 27% water.

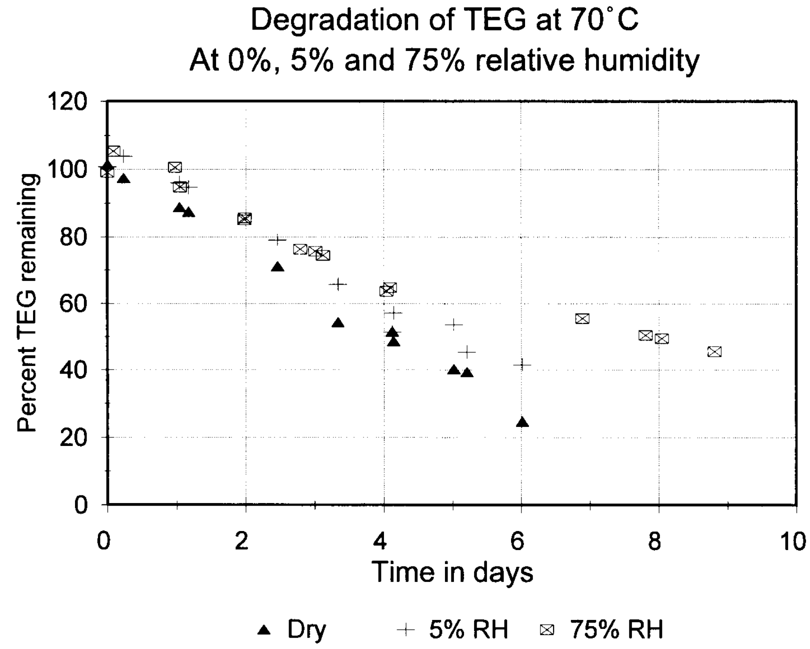

Fig. 1: The decomposition rate of TEG at 70°C in air at different RH values.

Figure 2 shows the effect of 10 mM of metal salts added to the TEG. Minor amounts of ferric chloride and of copper acetate completely protect against oxidation, while nickel sulfate accelerates the reaction.

Figure 3 shows the decomposition of TEG in dry air at 40°C, compared with the rate at 70°C. After one week of apparent stability the TEG begins to decompose.

The reaction products

The reaction products from the degradation have been examined by GC-MS. Figure 4A shows the chromatogram from fresh TEG and figure 4B shows the chromatogram of TEG which has been treated with dry air at 70°C for one week. The primary degradation product comes out at 524 seconds. This component comes out later than the TEG peak at 458 seconds, which indicates that the degradation product results from an addition to the TEG molecule. This is supported by the fact that we found in the mass spectrum of the degradation product an ion at 223 atomic mass units (amu) and probably another ion at 239, whereas in TEG we found a molecular ion at 195 amu (M+1). A third component at 580 seconds appears as degradation proceeds. It has more or less the same fragmentation pattern as the peak at 524 seconds and is probably a result of further reaction with this primary degradation product. The degradation products are presently under examination.

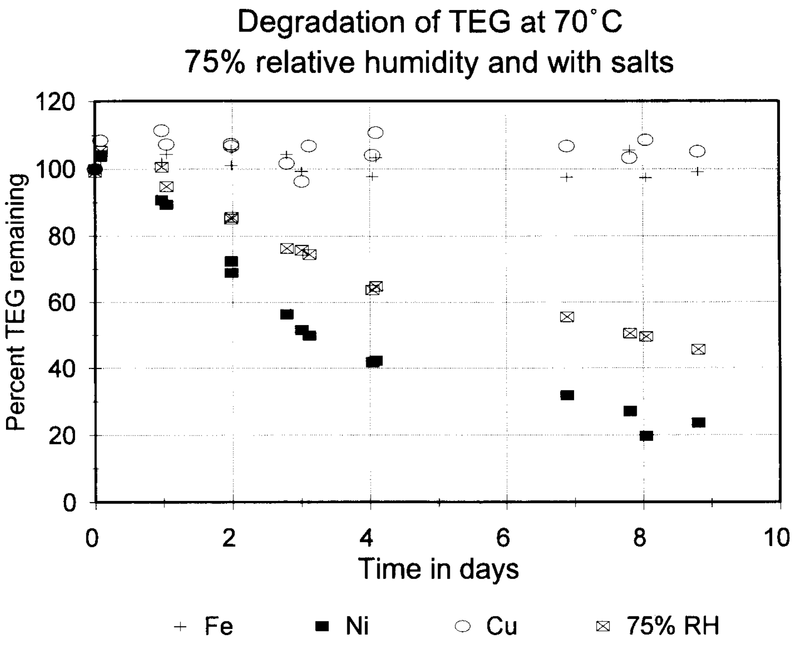

Fig. 2: The decomposition rate of TEG contaminated with metal salts at 70°C in air at 75% RH.

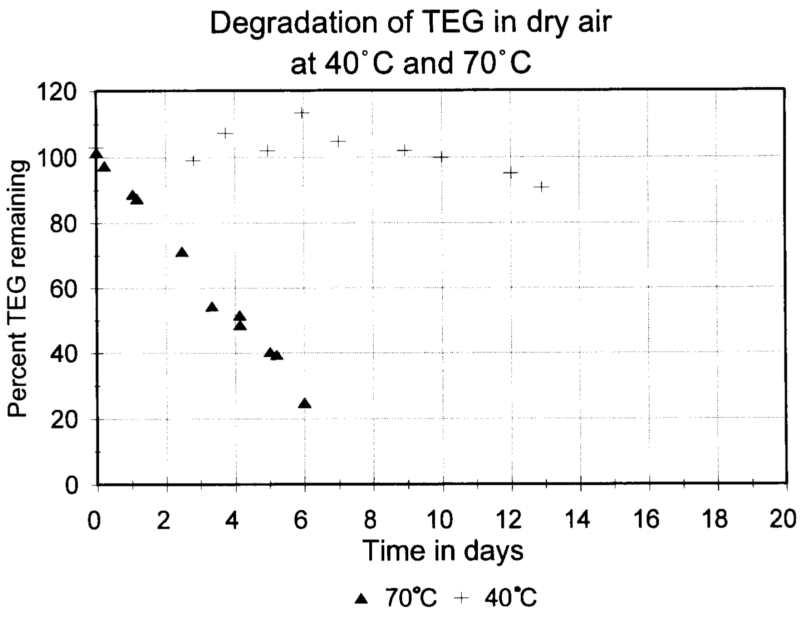

Fig. 3. The decomposition of TEG in dry air at 40°C and at 70°C.

Discussion

Polyethylene glycol (PEG) is a material of vast industrial importance. Besides its use in the conservation industry, it is used in large amounts in medical, pharmaceutical and cosmetic formulations, in the battery industry and in chromatographic applications. However, most of the research on the stability of PEG has been done under severe conditions: ultrasonic radiation (2), gamma radiation (3,4), under high oxygen pressure at 120°C (5,6) and at high temperatures (280–420°C) with or without oxygen present (7,8,9). At high temperatures (200–300°C) the degradation of PEG takes place in days or hours, even at ppm and ppb levels of oxygen (10,11). Riecke and coworkers demon-

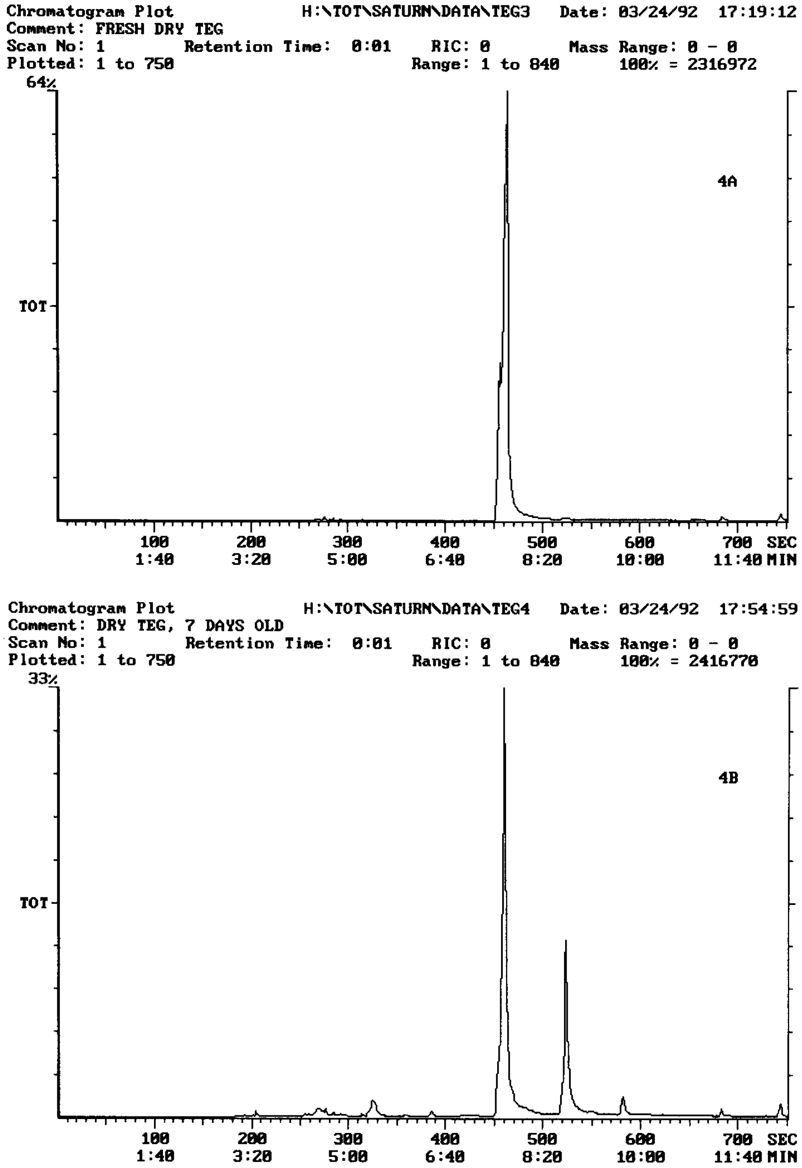

Fig. 4. (A) Gas chromatogram of fresh TEG, and (B) TEG after exposure to dry air at 70°C for seven days.

strated in the fifties that organic materials containing ether groups suffer degradation through peroxide formation next to the ether bond (12,13). At relatively low temperatures (120–160°C) in pure oxygen, the main degradation is caused by peroxide formation, and the degradation products are water, carbon dioxide, formaldehyde, acetaldehyde, methylformate and ethylformate (14). This is generally in agreement with other studies of the oxidative degradation of PEG (5–9,15). The results seem to support peroxide formation and degradation through a radical mechanism. McGinity et al. have demonstrated that peroxides are found in all commercial PEG products and that removal or inhibition of these peroxides stabilises the product. Water seems to inhibit the peroxide formation (16). Inorganic salts have previously been demonstrated to have a stabilising effect on the oxidation of PEG (7).

In work more directly related to conservation, de Witte et al. showed decomposition of PEG 4000 in water during a two year treatment of a wooden boat at 65°C (17). The decomposition appears to accelerate in the later stages when the PEG bath was nearly free of water. There was approximately 20% degradation of the PEG during the first 22 months during which the PEG concentration increased from 10% to about 80%. During the next six months, while the PEG became water-free there was a further 15% degradation. Recently, de Simone et al. have performed a series of experiments with PEG 200 and hexaethylene glycol at 80°C (18). The main conclusions were that fast degradation could be seen with dry glycol whereas water slowed degradation. Gallic acid and iron salts stabilised the glycol. These experiments were performed in sealed ampoules which lost oxygen during the exposure, and the results cannot be directly compared with ours.

Our earlier experiment on commercial PEG showed degradation to lower molecular weight compounds (1). This we now attribute to the influence of minor impurities. In the experiments on pure TEG reported here the higher molecular weight degradation product seemed relatively stable. In early experiments, however, with stainless steel used as the nozzle, we have seen results ranging from almost complete stabilisation of the TEG in the presence of water to a degradation proceeding as fast as in dry TEG. No addition product was found in this case but brown deposits were found on the stainless steel nozzle which also showed light signs of corrosion. We believe that the deposits or the corrosion products from the stainless steel have influenced the stability of the addition product.

Conclusions

We have found that tetraethylene glycol can decompose disturbingly fast in the presence of air at relatively low temperatures. In less than a week in dry air at 70°C only 30% of the TEG remains. The main reaction product of this fast degradation is probably an addition product, because it comes out later than TEG in the gas chromatogram (Fig. 4) and shows a higher molecular weight in the mass spectrum.

These experiments on tetraethylene glycol, the previous results from polyethylene glycol and results extracted from the literature show without doubt that polyethylene glycol is not inherently stable. In the presence of air it decomposes. This decomposition is markedly slowed by the presence of iron and copper, somewhat slowed by water, and accelerated by nickel. These observations are compatible with anecdotal evidence for the erratic behaviour of PEG in conservation. There have been reports of surface stickiness, whitening of surfaces (probably through phase separation), instability in the impregnation bath, and deliveries of unused but already decomposed batches of PEG. These reports, together with many examples of apparently satisfactory stability of treated objects, confirm the sensitivity of PEG to stabilisation or destabilisation by subtle changes in its chemical environment.

Some of the degradation products that have been reported are toxic. There is a threat to the health of conservators from the unpredictable risk of rapid breakdown of PEG during the conservation process.

We have found a degradation path of tetraethylene glycol which is different from the previously described peroxydation of ethers (11) which leads to scission of the ether bond and the formation of smaller degradation products (14). This degradation can be stabilised or destabilised but at this stage it is difficult to envisage a reliable stabilisation technique.

PEG impregnation has achieved the status of a standard conservation procedure, almost universally used in the treatment of waterlogged wood. This is quite clearly undeserved. We are not suggesting that all wood treated in this way will fall apart in a few years. Air can only diffuse slowly through the solid PEG on the surface of the wood. Traces of iron may further stabilise the PEG. It seems unwise, however, to rely on a basically unstable material for a process designed to protect wooden relics for a very long time.

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