

Chemical Kinetics of Estane Aging

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Estane, 5703, made by B. F. Goodrich and herein called Estane, is a poly(ester urethane) used as a glue in the plastic-bonded explosive PBX 9501 which is used extensively in weapons. Because it is an elastomeric polymer, Estane markedly decreases the mechanical sensitivity of the PBX. However, Estane slowly degrades in time, and the effect of that on the mechanical properties of the PBX raises safety and reliability concerns. Hence, the study of Estane aging is an integral part of the Enhanced Surveillance Campaign.

Our objective is to understand the chemical mechanisms by which Estane ages and develop kinetics models that can reliably predict the chemical composition and molecular weight of the Estane to times longer than the ages of any of the weapons. Others are developing models to calculate the mechanical properties of the PBX from the output of these chemical models.

The chemistry of Estane degradation is very complicated, and the approach is necessarily a joint experimental-theoretical one. Estane is known to degrade by: (1) scission of urethane links by slow thermal degradation; (2) hydrolysis of the ester links by water; (3) crosslinking and/or scission of polymers by oxidizing free radicals, such as NO_2 and ROO (peroxyl), or by free radicals R produced by ionizing radiation. Work on all these mechanisms is being pursued; in this report we discuss mechanism (2) which we have proved dominates the aging of Estane exposed to the atmosphere at ambient humidities.

The overall hydrolysis reaction is



where E is an ester link, A is an acid end, L is an alcohol end, and H_2O is water. One sees that the acid catalyzes the reaction between the water and the ester link, the ester link is broken, and an alcohol end and another acid end are formed. Because the reaction forms more acid, which

catalyzes further hydrolysis, it is autocatalytic; i.e., it speeds up as it proceeds.

As one part of the refinement of our treatment of hydrolysis, we are analyzing experiments on the amount and rate of water absorption by the components of PBX

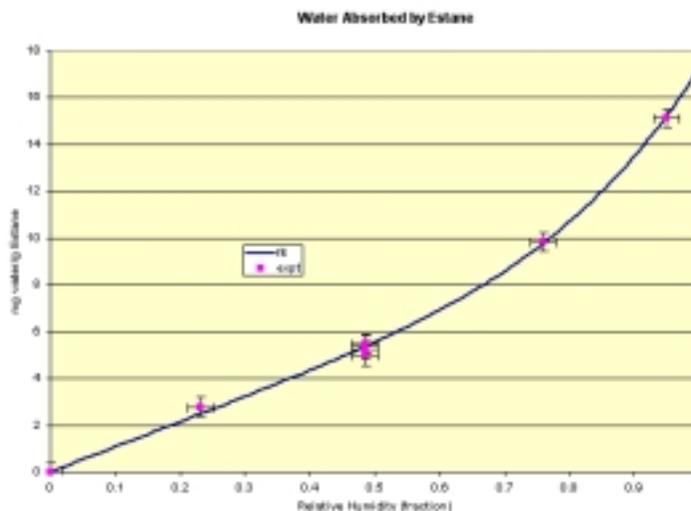
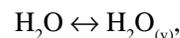


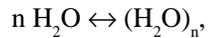
Figure 1: Water absorbed by Estane (in mg water/g Estane) versus relative humidity (as a fraction) at room temperature. The points are experimental; the line is the fit.

9501. Samples are stored at one relative humidity then transferred to a balance kept at another relative humidity, and the weight of the sample is recorded as a function of time. Coupled with a numerical solution of Fick's second equation, the data determine both (1) the water absorbed as a function of the relative humidity and (2) the diffusion coefficient of water in the material. It appears that, in all the components examined thus far, water absorption is primarily due to the Estane present. Absorption for neat Estane, 5703 is shown in Figure 1.

The nonlinearity of the absorption at high relative humidity can be understood as being due to water being absorbed from the vapor,



occupying monomeric sites where hydrogen bonding is favorable, and then forming clusters,



at high-relative humidity. The value of n which best fits the data is about 5, which is a reasonable value for the number of water molecules that can cluster around a single hydrogen bonding site. It appears that the monomers attach to existing sites and do not change the structure of the solid Estane; however, we believe that the clusters do distort the structure and produce the well-known swelling of wet polyurethanes.

the familiar hydrogen-bonded ring-type dimer that all carboxylic acids form readily. Rather, it is an ion-pair formed from such a dimer. In a water solution it would ionize, but the dielectric constant in solid Estane is not large enough to support ions. This mechanism seems able to fit all the data we have yet seen. It has been successfully applied to fit literature data taken under a wide range of conditions and is now being applied to all the Estane hydrolysis data obtained over the past several years at various DOE laboratories and plants. It is also being applied to the aging of Estane in PBX kept in the atmosphere and in weapons storage. This work will result in a robust model of the hydrolytic degradation of Estane that can be used to make long-time predictions and thus enable informed decisions about when PBX 9501 stored in various conditions needs to be replaced.

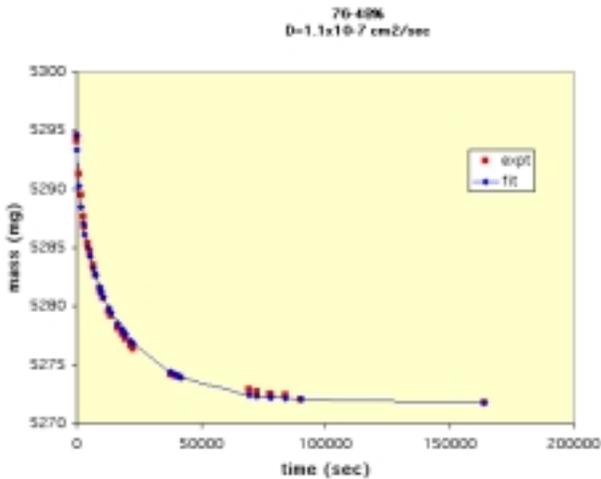
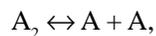


Figure 2: Weight loss versus time of Estane® 5703 when the RH changes from 76 to 48%.

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An example of the time dependence of the water absorption or loss by neat Estane is shown in Figure 2.

We have tested several possible kinetics mechanisms for the hydrolysis (and esterification) of Estane. The mechanism now being used for it is known as an abbreviated $A_{AC}2$ mechanism,



and is the mechanism most often observed for such reactions. Here the acid dimer, A_2 , is more than simply