T-12
Theoretical Chemistry & Molecular Physics

Chemical Mechanisms and Kinetics of Estane Aging

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Estane, specifically Estane 5703 made by B. F. Goodrich, is a polyester-polyurethane elastomeric polymer that is used as a binder (glue) in Plastic-Bonded Explosives (PBX) to decrease their mechanical sensitivity and thus make them safer to handle. These PBX's are used in weapons applications. Like all polymers, Estane slowly degrades with time. As part of the Science-Based Stockpile Stewardship and Enhanced Surveillance programs, it is important to know the effect of the aging of the Estane on the mechanical properties of the PBX's to much longer times than the current ages of any of the weapons in order to predict with confidence the useful lifetime of the explosives with respect to safety and reliability.

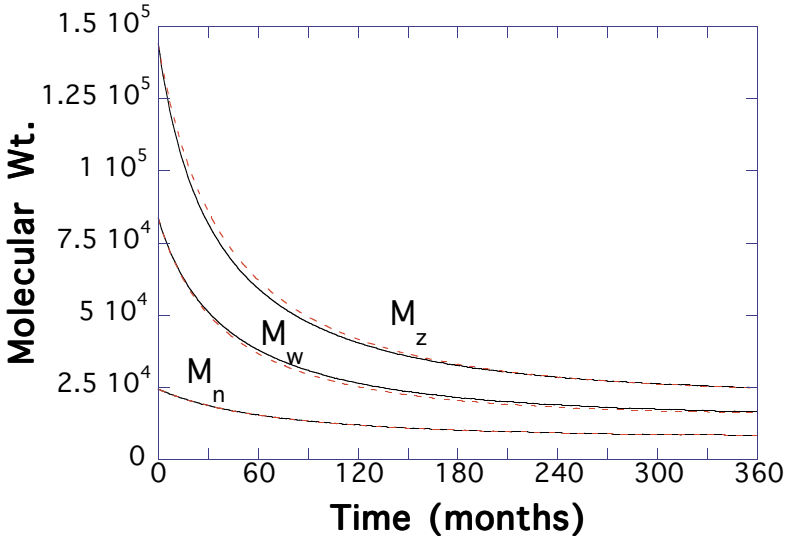

Figure 1: M_n, M_w, and M_z as functions of time for the aging of a simple polymer. The black lines result from the exact solution of 2325 coupled differential equations. The red lines result from the solution of four moment equations.

Before predicting the mechanical properties of an explosive containing aging Estane, one must know what is happening chemically, i.e., what molecular species are present as a function of time. Accordingly, a study is underway to determine the chemical mechanisms of Estane aging and develop kinetics models to predict its future chemical composition and molecular weight distribution with confidence. A master equation formulation of the chemical kinetics is being used in two approaches: In the first, the *detailed kinetics* model, we consider only one aging reaction mechanism but keep a large number of species (up to 7000) representing the many possible polymer fragments. The concentrations of these species are followed in time by direct numerical solution of up to 7000 coupled first-order differential equations to get a detailed distribution of polymer fragments as a function of time. In the second approach, the *realistic chemistry* model, all reactions thought necessary for a realistic representation of the aging chemistry of Estane are included. This leads to too many equations to then follow each polymer fragment as a separate species. Instead, equations for the mass or number moments of the polymer distribution are derived from the master equations. A simple but accurate approximate truncation of the moment equations allows their rapid numerical solution. The number-average (M_n), weight-average (M_w), and z-average (M_z) molecular weights obtained from the moments give a good average picture of the polymer fragment distribution as a function of time (Figure 1).

The Estane degradation chemistry is complicated, and, in our semiempirical approach, estimates of experimental rate constants are used to do model calculations. These, in turn, suggest new experiments to refine the rate constants. This close interplay of experiment and theory is essential to the success of this work. Estane

is a copolymer; i.e., its chain consists of alternating soft segments and hard segments. The soft segments are polyester oligomers (short polymers) containing 4 to 10 repeat units. The hard segments are short polyurethanes with only 1 to 3 repeat units. The hard segments tend to cluster together into domains and produce a partial phase separation. It is the hard segment domains that hold the Estane together and make it tough, and the soft segment domains that make it soft and rubbery.

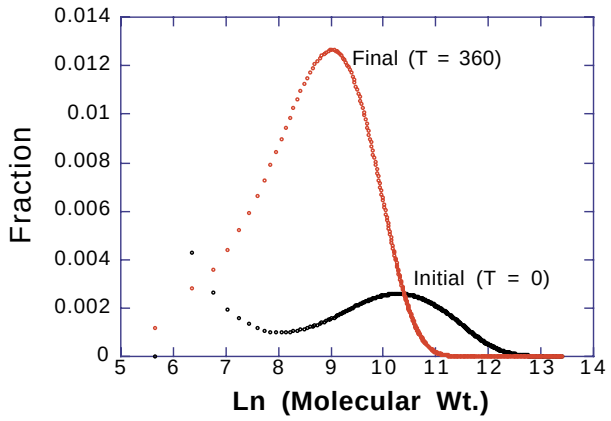

Figure 2: Detailed initial (black) and final (red) molecular weight distributions. The weight fractions of polymers of a given molecular weight are plotted against the natural log of their molecular weight.

Early in the lifetime of Estane in PBX, an observed increase in the molecular weight implies that crosslinking is occurring. Later on, degradation dominates, due to bonds in the polymer molecules being scissioned, leading to a decrease in the molecular weight and a loss of elastomeric mechanical properties. The degradation mechanisms we have identified as most important are (1) oxidative scission of the urethane links by NO_X and/or O_2; (2) hydrolysis of the ester links; and (3) scission of bonds by free radicals produced by ionizing radiation and thermal degradation. In accelerated aging experiments any of these three mechanisms can be made to dominate. One of our objectives is to determine which dominates under the conditions in which Estane is stored in weapons.

In Figure 1 the average molecular weights as functions of time from the detailed kinetics model are compared with those from the truncated moment equations for the aging of a simple polymer with just one mechanism for polymerization and depolymerization. The moment approximation is seen to do rather well. In Figure 2, we plot the initial and final detailed molecular weight distributions from the detailed kinetics model calculations of Figure 1.

The realistic chemistry model contains all the reactions mentioned in an earlier paragraph and also those of a nitroplasticizer mixed with the Estane, free radical production and recombination, and the reactions of added free radical inhibitors. At present, it has 28 species and 36 reactions besides any moment equations for the polymer distributions. With this model it is very easy to fit the weapons data. Figure 3 compares the predictions of this model with actual Estane weight-average molecular weights obtained from surveillance data. However, the present predictions of the model for times longer than the data can not be trusted because the rate constants have not yet been adjusted to fit all known Estane aging experiments. Such work is ongoing.

In addition to kinetics modeling, we have started using X-ray data and quantum chemistry and molecular mechanics codes to determine the packing of the polymer molecules in solid Estane and the size and shape of the hard segment domains.

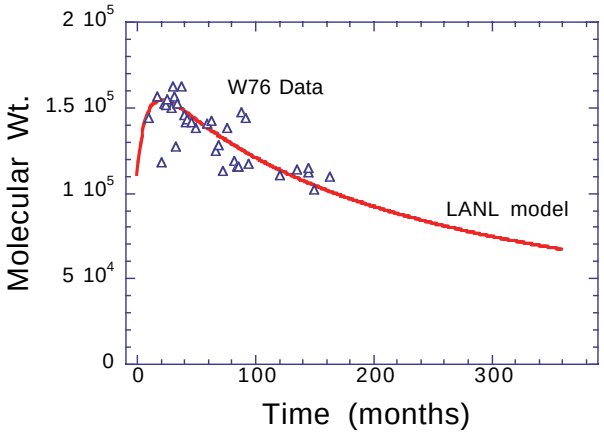

Figure 3: Estane molecular weight as a function of time. Comparison of model calculations with actual surveillance data.

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