A Materials Aging Problem in Theory and Practice

Lawrence W. Hunter, James W. White, Paul H. Cohen, and *Paul J. Biermann*

Polyesters are widely used in plastic objects, films, and fabrics. A recurring mechanism of polyester aging is attack by humidity (hydrolysis), whereby the long chain molecules are cleaved and the material softens. This article offers an approach for modeling the hardness/aging behavior of commercial polyesters. The model is qualitatively consistent with exposure tests on fresh polyester plastic material made from a commercially available resin and hardening agent. It expresses the rate of polyester hydrolysis in terms of the relative humidity, and then connects the degree of hydrolysis to hardness using a relation that accounts for stabilizers that are present in commercial polymers to counter the hydrolysis. (Keywords: Balance of life, Environmental exposure, Ester hydrolysis, Materials aging, Polyester hydrolysis, Polyesters.)

INTRODUCTION

Any model that predicts when a material will break down, reach the end of its service life, or stop performing as required offers many benefits. With safety and performance assured, it becomes possible to achieve the maximum service life and the most economical schedule for disposals and upgrades. In practice, the price can be continuous monitoring of environmental exposure conditions like temperature, humidity, shocks, and vibrations. In addition, model accuracy is impacted by the complexities of commercial materials.

This article offers a model of the hardness/aging of commercial polyester materials exposed to heat and humidity. Polyester materials have a wide range of applications including filter wool, photographic film bases, packaging films, magnetic media, textiles, soft drink bottles, furniture parts, and numerous other plastic objects.

The entanglements that occur between long molecular chains give a polymer its hardness. However, the molecular chains in polyesters have weak links, namely, the ester links, which can be cleaved by chemical reaction with water as follows:
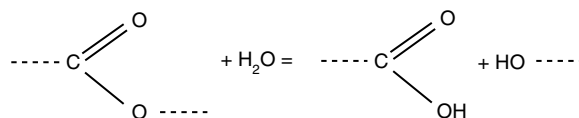
The first member of this equation is the weak ester link. The chemical bonds shown as dashed lines connect to the remaining parts of the polymer. These parts become disconnected, and hence the polymer chains become less entangled. The material tends to soften as a result. After the reaction, the two loose ends terminate, as shown on the right side of the equation, as a "carboxylic acid" group and an "alcohol" group.

The literature on ester chemistry[1,2] shows that the cleavage reaction is promoted ("catalyzed") by a trace of acidity in the water. For example, the reaction goes

much faster with a trace of hydrochloric acid (HCl) in the water. Interestingly, one of the loose ends created is itself acidic, i.e., the carboxylic acid group, as its name indicates. Thus, the reaction promotes itself once it starts (the reaction is "autocatalytic").

The preceding chemical equation is a simplification of the sequence of molecular collisions that actually occur to achieve the same net result. We will examine the more detailed description later in the article. Meanwhile, we begin with the one-step reaction as given, since it turns out that this provides a very good start.

EXPOSURE TESTS

We made fresh commercial-grade polyester material by combining a resin with a curing (hardening) agent in a mold and then applying heat. Air Products and Chemicals, Inc., supplied the ingredients: Voranol 630 (a trifunctional polyol) and Versathane A-8 (a toluene diisocyanate polyester prepolymer). With this new material, we were able to reset our clocks back to time 0 and maintain control over the complete history of environmental exposures.

The fresh samples were exposed to 100% relative humidity (RH) at three temperatures (Fig. 1). Results showed that higher temperatures promoted softening. The temperature effect was consistent with the hypothesis that the softening is caused by a chemical reaction with water, since the rates of chemical reactions typically increase as temperature increases.

The data points in Fig. 1 show some fluctuations due to experimental precision and reproducibility. It becomes a matter of judgment to identify underlying trends that reflect the chemistry. Our interpretation is that hardness tends to remain initially constant and that the time of constant hardness decreases as temperature rises; then hardness starts to fall at a rate that increases as temperature increases; and finally, the softening tends to accelerate slightly with time. Similar qualitative trends have been reported in the literature.[3]
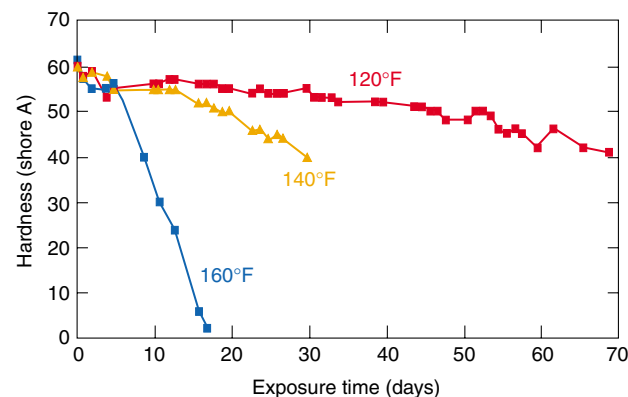

Figure 1. Tests of fresh material in 100% relative humidity exposed to three different temperatures.

PRELIMINARY MODEL OF AGING

The next step is to extrapolate the results to ambient temperatures. Our preliminary model of the temperature dependence evolved from a simple picture of the chemical reactions, since simple models are best, if they work. Commercial polyesters like ours contain an additive called a stabilizer that reconnects broken ester links until the stabilizer is depleted (Wirpsza[3] lists three classes of stabilizers, including "carbodiimides" whose structure and mechanism of action were explained by Shoffenberger and Stewart.[4]) Hence, retention of hardness depends on the amount of stabilizer present. The initial rate of reaction between unstabilized ester links and water at various temperatures was measured by Brown et al.[5] These results were combined with an *ad hoc* model of hardness in terms of the number of ester links and the amount of stabilizer. The result is a preliminary model of hardness versus temperature and humidity for commercial (stabilized) polyesters.

The concentration ϵ of ester links in an unstabilized polyester decreases with time according to[5]

$$\epsilon = \epsilon_0 e^{-kRHt},$$

in which ϵ_0 is the concentration at time 0, k is the "rate constant," and t is time. All of the temperature dependence is concentrated in k, which has the "Arrhenius" form

$$k = Ae^{-E/RT},$$

where $R = 1.984 \times 10^{-3}$ kcal mol^{-1} K^{-1}. The "frequency factor" A and "activation energy" E were adjusted to fit our data:

$$A = 2.41 \times 10^{14} \text{ day}^{-1}$$

and

$$E = 24.8 \text{ kcal mol}^{-1}.$$

As a footnote, the values of A and E would be different if we had chosen to write the concentration of ester links in terms of the partial pressure of water vapor rather than the relative humidity, but the form of the equations would be identical. All of the dependence on temperature would still be isolated explicitly in an Arrhenius exponential factor whose pre-exponential coefficient and activation energy are independent of temperature. It turns out that our activation energy E, for example, is actually the activation energy forester hydrolysis minus the activation energy for water vaporization.

This rate law implies that, as soon as the material is exposed to humidity, the ester links begin to break. Hardness is assumed to be tied to the sum of the ester links and the replacement links created by the stabilizer. This sum remains constant even though the number of actual ester links is declining, as long as a stabilizer is present. After the stabilizer supply has been exhausted, the sum starts to decline with the ester links, one for one. Hence, the relationship between (nondimensional) hardness and the (nondimensional) concentration of ester links is assumed to be like that shown in Fig. 2. For the best fit to our data, we assumed that a fraction $s = 0.07$ of the ester links can be stabilized. Specifically, hardness is assumed to be proportional to the concentration of ester links after a fraction $s = 0.07$ has been hydrolyzed. Surely, the true relation between hardness and links is much more complex. Still, it is interesting to pursue this approach to see what qualitative conclusions may be possible.

The results, for comparison with the measurements, are shown in Fig. 3. Clearly, the predicted curve at 160°F is less severe than the observations. Less dramatic but still evident is the tendency of the predicted curves to level out with time, whereas the observations show a slight tendency to accelerate downward. In addition, the predictions say nothing about acidity. In fact, acid autocatalysis is a potential cause of the acceleration. (Another mechanism contributing to the acceleration may be the expected increase in water absorption as bonds begin to break and porosity increases.)

Still, overall, the model is quite successful. Despite its simplicity, many of the qualitative features of the data are captured, including the presence of a delay time that decreases as temperature rises, as well as the tendency of the downward rate to increase as temperature rises.

APPLICATION TO CONDITIONS IN THE FIELD

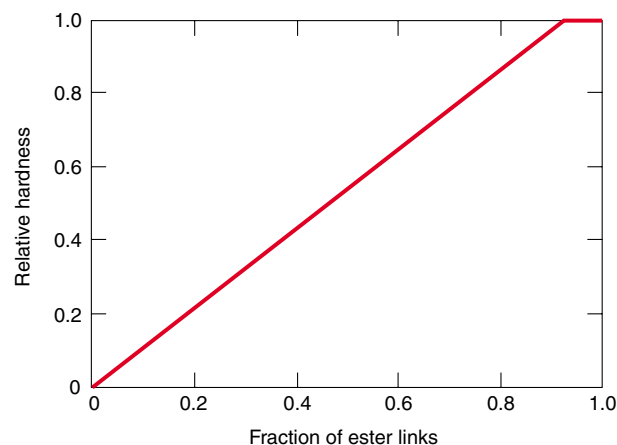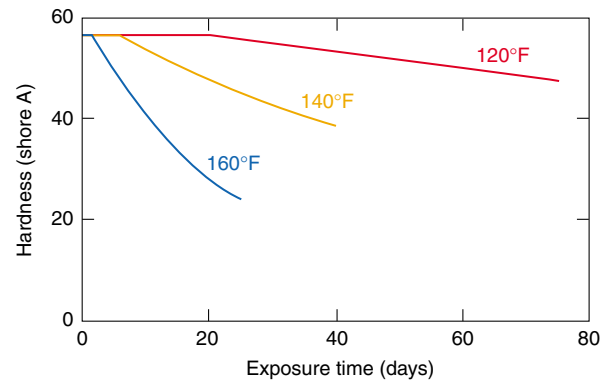Our laboratory tests accelerated the aging of the samples through the use of elevated temperatures. The

Figure 3. Calculations for fresh material in 100% relative humidity.

reasonableness of the model under test conditions suggests using it to extrapolate to conditions more like those expected in the field, where temperature and humidity vary depending on the time of day, the local climate, and the seasons. What is needed is a procedure to estimate the cumulative effects, including the effects of temporary excursions to high temperature and humidity. The correct procedure turns out to be as follows, considering that the fluctuations in temperature and humidity occur on a much shorter time scale than the chemical degradation:

$$\epsilon_1 = \epsilon_0 \exp\left(-\int_{t_0}^{t_1} k\mathsf{RH}\ dt\right),$$

with $k = Ae^{-E/RT}$ as before, but now RH and T are functions of time: $\mathsf{RH} = \mathsf{RH}(t)$, $T = T(t)$. The integral, which is straightforward to calculate, provides increased weight to humidity exposures that occur at high temperature during the time period between t_0 (at manufacture) and t_1 (the present). The resulting value for the concentration of ester links is substituted into Fig. 2 to get the predicted hardness, as before.

The results in Fig. 4 are calculated for constant humidity and temperature conditions just to show the kind of aging rates that might be expected under ambient conditions. It can be seen that dry and cool conditions favor a long life.

A CLOSER LOOK AT THE CHEMISTRY

Although the preliminary model is quite helpful, a closer look at the chemistry is of interest to show how the simpler model is at least consistent with a more rigorous approach that addresses the phenomena not included in the simpler model. Specifically, the results outlined here offer additional insights into the observed catalysis by trace amounts of acid[2,3] and the tendency for the reaction to accelerate. The solution also provides a possible explanation for a further observation
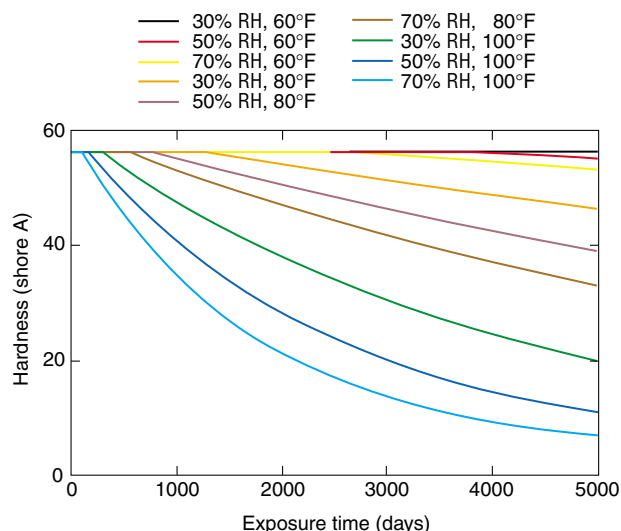
Figure 2. Assumed relationship between hardness and ester links.

Figure 4. Calculated effect of relative humidity and temperature on polyester aging.

by Cuddihy,[6] i.e., hot air actually promotes the re-formation of polyester links if the humidity level is low enough. These improvements in the model come at the price of additional parameters whose values are not readily available for commercial polymeric esters.

We start with a set of chemical reactions that represent actual molecular collisions whose net effect is the same as the overall reaction used earlier. These reactions were proposed before by Gould[2] but not, to our knowledge, solved mathematically. Stabilizers are absent, and the water is assumed to start out slightly acidic.

We will continue to use k to denote a rate constant, with subscripts such as Es (for ester) to identify which reaction, and an underline to denote a reverse reaction. We also follow a convention employed by organic chemists and use R (and R′) to denote a remainder of a molecule not directly involved in the reaction of interest. Concentrations will be denoted by brackets.
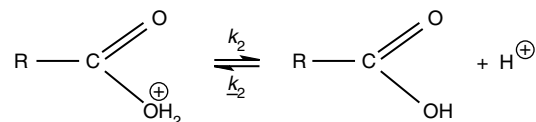
Protons attach to ester links and rapidly attain equilibrium with the reverse reaction
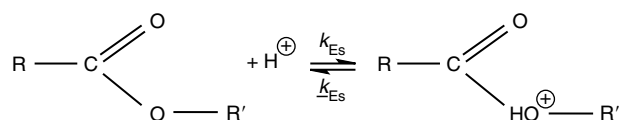
except that a very small fraction of the resulting "conjugate acids" slowly breaks and re-forms,
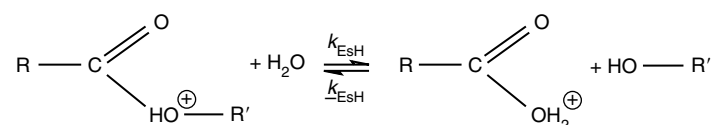
The products are the final alcohol and protonated carboxylic acid, which in turn rapidly equilibrate with the unprotonated carboxylic acid end product and the free protons

In these reactions, protons act as a catalyst by facilitating the breakage and re-formation of ester links without any net change in their own concentration. The generation of additional protons by the carboxylic acid is described by the equilibrium:
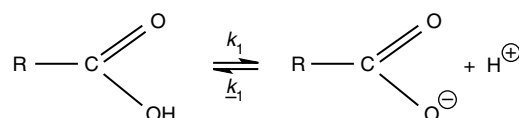
This completes the set of molecular reactions that have the same net effect as the single overall reaction used in the preliminary model.

The challenge now is to write a closed set of corresponding governing equations that can be solved for species concentrations as a function of time. There are eight unknown species concentrations in the reaction set. In addition, we chose to identify ϵ as the total concentration of all species with ester links and to define α as the total concentration of all species with acid loose ends:

$$\epsilon = [\text{Es}] + [\text{EsH}^{\oplus}]$$

$$\alpha = [\text{RCOO}^{\ominus}] + [\text{RCOOH}] + [\text{RCOOH}_2^{\oplus}] .$$

(Here the notation has been collapsed somewhat for simplicity.) This brings the total number of unknowns to 10, but of course the last two equations will count toward the total number of equations needed to solve for the unknowns.

To begin writing the governing equations, the three equilibria satisfy the following equilibrium conditions (drawing upon the symbols for the chemical kinetic rate constants introduced in the previous reactions):

$$\frac{[\text{EsH}^{\oplus}]}{[\text{Es}][\text{H}^{\oplus}]} = \frac{k_{\text{Es}}}{\underline{k}_{\text{Es}}} \equiv K_{\text{Es}} ,$$

$$\frac{[\text{RCOOH}][\text{H}^{\oplus}]}{[\text{RCOOH}_2^{\oplus}]} = \frac{k_2}{\underline{k}_2} \equiv K_2 ,$$

$$\frac{[RCOO^{\ominus}][H^{\oplus}]}{[RCOOH]} = \frac{k_1}{\underline{k}_2} \equiv K_1.$$

The charge balance is written

$$[EsH^{\oplus}] + [H^{\oplus}] + [RCOOH_2^{\oplus}] = [RCOO^{\ominus}] + [Cl^{\ominus}].$$

This accounts for trace hydrochloric acid added as a catalyst. Since new acid loose ends and new alcohol loose ends are produced together, they can be assumed to be in stoichiometric balance:

$$\alpha - \alpha_0 = [R'OH].$$

The remaining slow reactions are described by differential equations, which we write in terms of ϵ and α:

$$
\begin{aligned}
\frac{d\epsilon}{dt} &\equiv \frac{d[Es]}{dt} + \frac{d[EsH]^{\oplus}}{dt} \\
&= -k_{Es}[Es][H^{\oplus}] + \underline{k}_{Es}[EsH^{\oplus}] + k_{Es}[Es][H^{\oplus}] \\
&\quad - \underline{k}_{Es}[EsH^{\oplus}] - k_{EsH}[EsH^{\oplus}][H_2O] \\
&\quad + \underline{k}_{EsH}[RCOOH_2^{\oplus}][R'OH] \\
&= -k_{EsH}[EsH^{\oplus}][H_2O] + \underline{k}_{EsH}[RCOOH_2^{\oplus}][R'OH].
\end{aligned}
$$

Similarly,

$$\frac{d\alpha}{dt} = k_{EsH}[EsH^{\oplus}][H_2O] - \underline{k}_{EsH}[RCOOH_2^{\oplus}][R'OH]$$

subject to the initial conditions

$$\alpha = \alpha_0, \epsilon = \epsilon_0.$$

We assume that the H_2O is absorbed by the polyester much faster than the reaction occurs and write

$$[H_2O] = S \cdot RH,$$

where S is the solubility at 100% relative humidity.

We now have 10 equations, namely, the 5 algebraic equations and the equations for ϵ and α, the 2 differential equations, each with initial conditions, and the equation for H_2O. Hence, we have closure.

Solving is next. It may be shown that the concentrations of the intermediate species remain small, and thus the total concentration of ester links ϵ may be obtained from

$$\frac{d\epsilon}{dt} \approx -k_{EsH}K_{Es}\epsilon[H^{\oplus}]S(1-D)RH$$

in which

$$D = \frac{\alpha(\epsilon_0 - \epsilon)}{K_{EsH}K_{Es}K_2 S\epsilon RH}, \quad K_{EsH} = \frac{k_{EsH}}{\underline{k}_{EsH}},$$

and

$$\alpha = \alpha_0 + \epsilon_0 - \epsilon.$$

In addition, the concentration of hydrogen ions is approximately

$$[H^{\oplus}] \approx \frac{[Cl^{\ominus}] + \sqrt{Cl^{\ominus}]^2 + 4(\epsilon K_{Es} + 1 + \alpha/K_2)\alpha K_1}}{2(\epsilon K_{Es} + 1 + \alpha/K_2)},$$

and the initial condition is

$$\epsilon = \epsilon_0.$$

Thus, the solution may be readily calculated with a first-order differential equation solver or written as an explicit integral to be evaluated with an integration routine.

DISCUSSION

Initially, when hydrolysis predominates, the solution of the differential equation reduces to the simplified model with the identification

$$k = k_{EsH}K_{Es}[H^{\oplus}]S.$$

Notice that the reactions given here can start up only with the hydrochloric (or other) acid present. With no hydrochloric acid at time 0, the formula for the hydrogen ions reduces to 0, and hence the right side of the differential equation is 0. Segreda[7] has studied the spontaneous hydrolysis of esters in which ester molecules are directly attacked by water molecules to start the process.

Notice too that the solubility S enters the differential equation as an overall factor. This provides a simple way for hydrolysis to accelerate. When the ester links break, the polymer network opens up and water can penetrate the polymer more easily.

The full differential equation, including the effects of the reverse reactions, shows that the number of ester

links decreases (hydrolysis) when $D < 1$; the number is stable (at equilibrium) when $D = 1$; and the number increases if $D > 1$. Thus, D serves as a discriminant. As a corollary, consider a polyester that has been equilibrated at a given humidity. The hydrolysis will proceed further if the humidity increases and reverse itself if the humidity decreases. Such a phenomenon was observed by Cuddihy.[6]

The detailed model just solved is therefore consistent with the simple model and adds an explanation of catalysis by trace acidity, auto-acceleration, and the possibility of equilibrium for some polyesters. The drawback of the detailed model is the number of parameters needed in practical cases. However, when the values of the parameters are known, the formulas may be readily applied to estimate the aging behavior of polyesters.

SUMMARY

The usefulness of models of aging increases with the amount of data available. Service and storage logs provide only a qualitative indication of past exposure conditions, when a few hours in the sun can sometimes make a big difference. Thus, continuous environmental data logging is advisable, as well as detailed property characterizations at the time of manufacture. With this information, models can potentially provide the balance of life of each individual item in the inventory.

REFERENCES

[1]Fieser, L. F., and Fieser, M., *Organic Chemistry*, D.C. Heath and Co., Boston, MA (1944).
[2]Gould, E. S., *Mechanism and Structure in Organic Chemistry*, Holt, New York (1959).
[3]Wirpsza, Z., *Polyurethanes*, Ellis Horwood, Chichester, UK, p. 25 (1993).
[4]Shoffenberger, C. S., and Stewart, F. D., *Advances in Urethane Science and Technology, Vol. 1*, Technomic Publishing Co., Stamford, CT (1971).
[5]Brown, D. W., Lowry, R. E., and Smith, L. E., *The Kinetics of Hydrolytic Aging of Polyester Urethane Elastomers*, Technical Report TR-3, Sep 1978 to Aug 1979, Polymer Science and Standards Division, National Bureau of Standards, Washington, DC (1979).
[6]Cuddihy, E. F., "Aging of Magnetic Recording Tape," *IEEE Trans. Magn.* **MAG-16**(4), 558–565 (1980).
[7]Segreda, J. F. M., "Spontaneous Hydrolysis of Ethyl Formate: Isobaric Activation Parameters," *Int. J. Chem. Kinet.* **32**(1), 67 (2000).

THE AUTHORS

LAWRENCE W. HUNTER is a member of APL's Principal Professional Staff. He holds a 5-year equivalent "B.Sc. (hons.)" degree, first class, in chemistry from Carleton University, Ottawa, Canada (1967), and a Ph.D. in theoretical chemistry from the University of Wisconsin, Madison (1972). Dr. Hunter has worked at APL since 1973 on projects related to combustion, propulsion, high-temperature materials, and rocket propellant aging. He has contributed to 55 refereed journal articles, including one listed in "The Twenty-Two Most Frequently Cited APL Publications," *Johns Hopkins APL Tech. Dig.* **7**(2), 221–232 (1986). Dr. Hunter is a member of AIAA and the Combustion Institute. His e-mail address is l.w.hunter@jhuapl.edu.
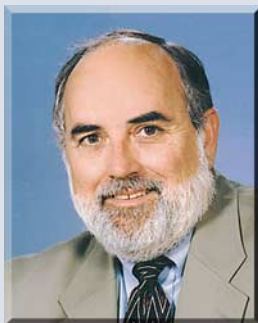
JAMES W. WHITE received his undergraduate degree in engineering physics from the University of Oklahoma in 1972, a master's degree in mechanical engineering and an engineer degree in ocean engineering from MIT in 1980, and a master's degree in business administration from Loyola College of Maryland in 1992. He spent 21 years in the Navy as an Engineering Duty Officer. After leaving the Navy, he founded Ocean Systems Research and was its president for 7 years. Mr. White came to APL in 1993 and now works in the Engineering Group of the Air Defense Systems Department. He has conducted several failure analyses for Navy systems and has participated in the development of new Navy equipment such as the F/A-8 E/F aircraft and the Standard missile. Mr. White is a member of the American Society of Naval Engineers. His e-mail address is james.white@jhuapl.edu.

PAUL H. COHEN received his B.E. in metallurgy from the New York University School of Engineering and Science in 1975 and an M.S. in metallurgical engineering from the Polytechnic Institute of New York in 1979. After joining the Metallurgy Laboratory at Consolidated Edison in New York, he performed failure analysis investigations of equipment in nuclear-powered and fossil-fueled generating stations. Mr. Cohen was a Senior Engineer in the Materials Laboratory of APL's Technical Services Department from 1989 to 1998, where he evaluated failures of missile components and served as a technical resource in areas ranging from metallurgy to nondestructive testing and materials evaluation. He is currently with the Engineering Materials Laboratory at Atlantic Research Corp., Gainesville, VA, where he performs failure analysis investigations and materials evaluation. His e-mail address is cohen@arceng.com.

PAUL J. BIERMANN earned a B.S. in materials engineering at Rensselaer Polytechnic Institute in 1980. He is a materials and process engineer and a member of the Senior Professional Staff at APL, with over 18 years of experience in the manufacture and characterization of composite materials and engineering polymers. He has an extensive background in composite cure and assembly techniques, polymer molding and casting, tooling and mold fabrication, and adhesive bonding. Mr. Biermann spent 6 years in the aerospace industry at Bendix Corp., Allied Signal, and Martin Marietta Corp., performing research and development related to composite material fabrication and characterization. In 1986 he joined APL to establish and operate a composite materials and engineering polymers fabrication facility. Mr. Biermann has published 17 papers. He holds 2 U.S. patents, 2 patents that are pending, and 12 other invention disclosures. His e-mail address is paul.biermann@jhuapl.edu.