JOURNAL OF Applied Polymer SCIENCE

Rheological Properties of Neat Epoxy Exposed to In-Service Aerospace Contaminants

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ABSTRACT: We present an experimental study on the rheological properties of a commonly used epoxy resin system (EPIKOTE-862 resin and EPIKURE-W curing agent), exposed to a variety of fluids typical of aerospace operations (jet fuel, hydraulic fluids, deicing, detergents, etc.), for a period of up to 6 months, at room temperature for most conditions, and with no concurrent mechanical loading or prior degradation. The specimens were subjected to stress and frequency sweeps with a shear rheometer, while a limited set received also a temperature sweep in a range consistent with aircraft operations. Results indicate that the treated resin samples are linear viscoelastic under these testing conditions. The resin has reasonable chemical resistance to most contaminants of this study, with the exception of two commonly used detergents: an aircraft surface cleaning compound, Penair C5572, and a nonionic detergent, Methyl Ethyl Ketone (MEK). The durability change of the first compound appears triggered by high temperatures only, while the second compound causes a very drastic stiffness loss under several conditions. This drop of performance occurs within a 3-months period, with no apparent color change or fracture that could prompt visual inspection and repair. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 3961–3971, 2013

KEYWORDS: composites; rheology; thermosets; viscosity and viscoelasticity

Received 16 February 2013; accepted 8 June 2013; Published online 3 July 2013
DOI: 10.1002/app.39654

INTRODUCTION

Fiber-reinforced polymer (FRP) composites have been adopted for many engineering applications since the 1970s, because of properties such as their high specific stiffness and strength, their tailorability to design requirements and their corrosion resistance. Interest in these materials has been recently reinvigorated as they are employed as primary, load-carrying structures in wind turbines, in new and retrofitted pedestrian and vehicular bridges (e.g., Miyun bridge built in 1982 in China), in new aircraft (e.g., Boeing 787, Airbus A350, F-35 Lightning II, Learjet 85), or in repairs of legacy aircraft, in ships (e.g., Visby Corvette, M80 Stiletto), in transportation (e.g., electric or high-end combustion engine cars, the composite car body of the South Korean tilting train).

When in service, it is expected that these materials will be subjected to a complex loading history that may not be fully captured by laboratory and field testing. For example, in aerospace composite structures, the focus of this article, mechanical loading will be coupled with material degradation due to water and synthetic chemicals, and high thermal fluctuations. As an example of high thermal fluctuations, skin temperatures for a subsonic aircraft structure vary between −55°C and room temperature, while in a supersonic aircraft they reach +130°C, see Ref. 1.

The problem of the vulnerability of polymers and FRPs to temperature-dependent moisture* sorption and diffusion-driven chemical reactions has been documented since the 1970s (e.g., work of Springer and coworkers[2,3]). The study of polymers' and FRPs' hygrothermal behavior caused by partial or full immersion in water is still a subject of active research, see for example the review by Masaro and Zhu[4], and the work of Merdas et al.,[5] Loh et al.,[6] Popineau et al.,[7] Dao et al.,[8–10] Mensitieri et al.,[11] Papanicolau et al.,[12] Weitsman,[13] Yang et al.,[14] just to name a few recent contributions.

*"Moisture" here is intended as "liquid (water, jet fuel, salt water or any other liquid) which is [...] present in quantity sufficient for immersion of an object" (ASTM D5229 standard).

Additional Supporting Information may be found in the online version of this article.

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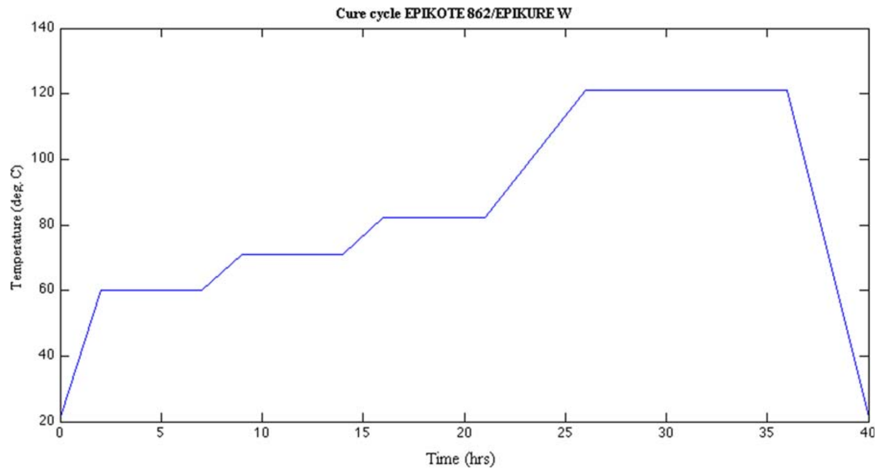

Figure 1. Cure cycle for the epoxy/hardener system of this study. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

There is also limited literature on the durability of polymers and FRPs exposed to contaminants typical of aerospace operations, such as jet fuel or deicing sprayed on the wings, or anti-icing jet fuel additive (mixed in jet fuel) or hydraulic fluid (Loos and Springer[3], Curliss[15], Rider and Yeo,[16] work of La Saponara et al.,[17–20] Landry et al.[21]). Various levels of durability reduction are shown, ranging from insignificant (e.g., effect of hydraulic fluid on the composite materials in Refs. 3 and 21) to serious (impact of hydraulic fluid and anti-icing jet fuel additive on laboratory-scale composite materials in Refs. 16–21). The majority of these works do not address the effect of commercial paints, primers, and gel coats that will be applied to the actual in-service aerospace structures. However, no material, whether coated or not, is completely impermeable and durable, as shown by the occurrence of delamination in commercial composites such as Airbus A300 composite rudders, caused by nearby hydraulic fluid leaks (US National Transportation Safety Board[22]).

This article presents new rheological data for a type of epoxy commonly used in out-of-autoclave composites, with cured samples fully immersed in several fluids typical of aerospace operations. The article does not address the state of cure of the epoxy as tracked by viscosity changes, and is not meant to provide recommendations for the processing of the resin. Instead, our objective is to apply rheology for quality assurance of the resin under simplified in-service conditions and in a laboratory setting, which is one of the uses of rheology in MIL Handbook 17.[23]

The findings demonstrate the susceptibility of the conditioned epoxy to two very common and nominally harmless cleaning solvents, which was an unexpected outcome. The level of degradation of the epoxy due to immersion in hot water is consistent with the literature, and expected. Moreover, within the limits of this investigation, the conditioned epoxy did not exhibit statistically significant degradation due to hydraulic fluid, contrary to other epoxies in the Refs. 16–21.

On the basis of these results, use of these solvents on structures manufactured with this resin system should be prevented or severely limited, for operations within the temperature and frequency ranges of this study.

EXPERIMENTAL

Specimens Preparation

The resin investigated in this work was EPIKOTE-862 resin (Momentive Performance Materials), a Bisphenol-F epoxy, previously known as EPON-862. It is a common low-viscosity resin used in out-of-autoclave applications such as filament winding, pultrusion, Vacuum Assisted Resin Transfer Molding. This resin was mixed with EPIKURE-W curing agent, an aromatic amine curing agent, at the nominal ratio of 100 : 26 parts by weight. Once epoxy and hardener were mixed, they were poured into a mold prepared with a release agent (MS-122AD Miller-Stephenson PTFE) and cured at the cycle shown in Figure 1. This cycle maximizes resin wetting and helps prevent the formation of voids in a filament winding application of interest.

After the resin/hardener panels were cured (Figure 2), they were machined to a 3 mm thickness with a multiaxis milling machine. Both sides of each sheet were sanded with an orbital sander using 120, 240, and 320 grit papers. The 300 and 24 resulting specimens were cut with a multiaxis router to dimensions 60 mm L × 13 mm W, with the exception of small tabs that held them in place. The tabs of each sample were cut with a Dremel® tool and their edges were sanded with 320 grit paper. Each sample was scribed with a unique serial number, which also referenced the original sheet of resin it came from (Figure 2). The samples were then cleaned with isopropyl alcohol. The weight of the specimens was measured to a 1000th g with an Ohaus scale model number AP2500, and the specimen dimensions were measured with a 0.0254 mm resolution.

Five specimens per set were fully immersed (at a relative humidity, RH, equal to 100%) in 11 undiluted contaminants typical of aerospace service, ranging from hydraulic fluid, jet fuel, diesel, to solvents (Table I, Figure 3). The tests took place at room temperature, except for the sets of specimens immersed in water at 74°C, a temperature typical of a composite aircraft structure on the ground.[9] Specimens were typically selected from two panels, and the exposure time varied from 2 weeks to 6 months (see Table I). After conditioning, the specimens were

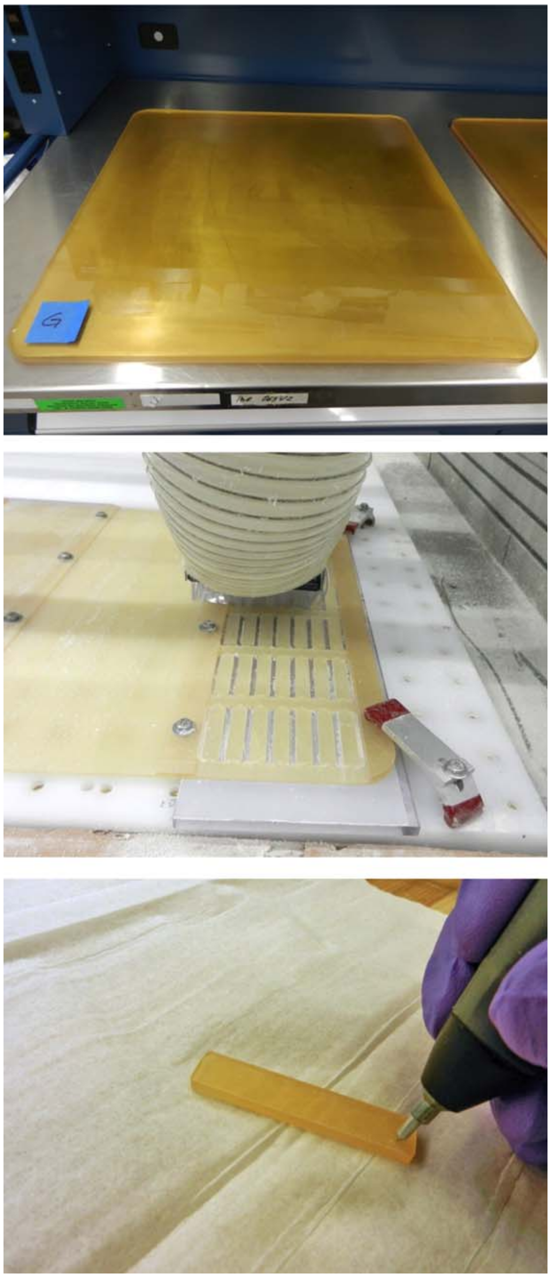

Figure 2. Steps of specimens' machining process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dried, assessed for their physical properties (volume and weight), and then were tested on the following day in a rheometer using torsional dynamic material analysis (TA Instrument AR 2000ex Rheometer). Control specimens were kept in plastic bags without desiccant until they were tested. In addition, nine control specimens were assessed after 10 months.

To briefly describe the rheometer operations, its electric motor applies an oscillating torque to the top of the sample, with the bottom of the sample fixed. The twist of the sample is measured with an optical encoder, and the data acquisition system records torque and angular displacement as a function of time. The shear strain is measured as $\gamma=\theta \cdot \frac{t}{L}\left(1-\left(0.378\left(\frac{t}{W}\right)^2\right)\right)$, where θ is the measured angular displacement and t, L and W are respectively the specimen's thickness, width and length in millimeter. The shear stress is computed as $\tau=M \cdot G_c \cdot 1000 \cdot \left(\frac{3+\left(1.8\frac{t}{W}\right)}{Wt^2}\right)$, where M is the motor torque in 10^{-6} $N\,m$ and G_c is equal to 98.07 $\frac{\text{kg}\cdot\text{m}}{\text{N}\cdot\text{s}^2}$.

In this rheometer, the specimens were first preloaded in compression, to ensure that the clamps around them were tight. Then, two sweeps were applied sequentially: (a) an isothermal stress sweep at the nominal temperature of 25°C and at the fixed frequency of 1 Hz, with the torque amplitude being incrementally increased from 9×10^{-3} N to 7×10^{-2} N, to reach a shear strain of 4,000 microstrain; (b) an isothermal frequency sweep from 1 to 100 Hz, at the nominal temperature of 25°C and at the fixed shear strain amplitude of 4,000 microstrain. Furthermore, two samples per set were also subjected to a temperature ramp from −48°C to 107°C, a typical range for an aircraft.[1] This test occurred at a heating rate of 2.78°C/min, at the fixed frequency of 1 Hz and at the fixed shear strain amplitude of 1,000 microstrain. Furthermore, four 10-months old control specimens were also subjected to the temperature sweep.

Other studies report the viscoelastic behavior of the EPON 862/W polymer as a function of cure state,[24,25] or its hygrothermal behavior under different loading conditions than those of the current study.[26] To the best of our knowledge, the outcome presented in this article is new.

RESULTS AND DISCUSSION

Physical Properties

After a 6-months exposure, most specimens showed barely visible discoloration with respect to yellow/light orange color of the 6-months-old baseline specimens [Figure 4(a)], and did not appear fractured. On the other hand, three out of five specimens contaminated in nonionic detergent (MEK) fractured by the end of the 6-months testing [Figure 4(d)], while no fracture was observed at 3 months [Figure 4(c)]. Specimens immersed in hot water had a very noticeable color change, to a dark orange/red [Figure 4(f)].

Regarding mass, m, and volume, V, most samples exhibited minor gains, measured in terms of $\frac{m_{\text{final}}-m_{\text{initial}}}{m_{\text{initial}}}\times 100$ and $\frac{V_{\text{final}}-V_{\text{initial}}}{V_{\text{initial}}}\times 100$, respectively up to 2.5% and 3% (these are median values, see for example Figure 5 for the aircraft surface cleaning compound, Penair C5572). The water samples gained a median value of ~2% mass after 6 months (see Supporting Information), this being a small mass sorption with respect to those recorded in recent literature for different epoxies and conditioning temperatures (up to ~10%, see Table I in Ref. 19). The only significant mass and volume changes are those for the nonionic detergent, MEK, respectively up to ~25% and ~33% (median values, Figure 6). Although no visible color changes occurred by 3 months, the specimens had already considerable dimensional/mass variations. Pictures and plots for the other contaminants are given in Supporting Information.

Table I. Specimens' Matrix, with Contaminant Type and Exposure Times

Contaminant	Product name	2 weeks	1 month	2 months	3 months	6 months	10 months
Control	–	–	–	G[a]	G	G	H (4), I (5)
Aircraft engine lubricating oil	Aeroshell 500	F	H	H	H	F	–
Aircraft fuel (JP8)	JP8	H	H	I	I	H	–
Aircraft hydraulic fluid, petroleum base	Royco 782	F	H	I	I	F	–
Aircraft hydraulic, synthetic hydrocarbon base	Braco 881	F	H	I	I	F	–
Diesel fuel	Diesel red	F	H	I	I	F	–
Diesel fuel	Diesel clear	F	H	I	I	F	–
Aircraft surface cleaning compound	Penair C5572	F	F	I	I	F	–
De-icing fluid water/glycol (85%/15% mixture)	Avail TKS fluid	F	F	I	I	F	–
Solvent, dry cleaning	Inland tech	F	F	I	I	F	–
Isopropyl alcohol	IPA	H	H	I	I	H	–
Nonionic detergent Ethyl	Methyl Ethyl Ketone -MEK	F	H	I	G	H	–
Tap water, 74°C	Tap water	H	H	H	H	H	–

Letters from F to I indicate the panels from which the specimens were cut. There were 5 specimens per condition, with the exception of control specimens conditioned for 10 months (9 specimens overall, 4 from panel H, 5 from panel I).
[a] Actual time was 2 months and 3 weeks.

The mass was recorded at the beginning and at the end of the exposure times, hence it is not possible to learn whether the diffusion behavior is Fickian or not, and whether saturation was achieved when the specimens were removed from their containers. It should also be noted that the specimens do not actually meet the dimensions' requirements dictated by ASTM D5229/D5229M-92(2004) standard for predominant through-the-thickness diffusion. Their dimensions were established for compatibility with the rheometer.

Rheological Properties

The rheology results of this study are given in terms of complex (or dynamic) shear modulus G, storage modulus G', loss modulus G' and tangent of the phase angle δ between the peak shear stress and the peak shear strain, parameters often reported in the literature. In particular, G' and G'' are associated to the elastic (in phase with the applied shear stress) and viscous contributions (out of phase with the applied shear stress) of the polymer, respectively. Values of complex viscosity η and dynamic viscosity η', not directly presented in this work, may be instead obtained through eq. (1) (see also Ref. 27,28):

$$\eta = \frac{G}{i\omega} = \frac{G' + iG''}{i\omega} = \eta' - i\eta'' \tag{1}$$

where ω is the angular frequency.

Figure 3. Selected conditioned specimens. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Stress Sweeps. The isothermal and isofrequency stress sweep tests confirm the results from the mass and volume gains, highlighting once again the seriously damaging behavior of the nonionic detergent (MEK) with respect to other aerospace contaminants. In fact, the MEK-treated specimens exhibit a decrease of the norm of the complex shear modulus $\frac{|G_{\text{treated}}|-|G_{\text{control}}|}{|G_{\text{control}}|}\times 100$ respectively equal to $\sim -52\%$ and -69% for 3 months and 6 months treatments (median values), for all strain levels. The impact of MEK conditioning on the samples' durability could be quantified already within the first month of exposure.

Aside from MEK conditioning, there were very few cases with a small increase (up to ~8% for fuel JP8, and hydraulic

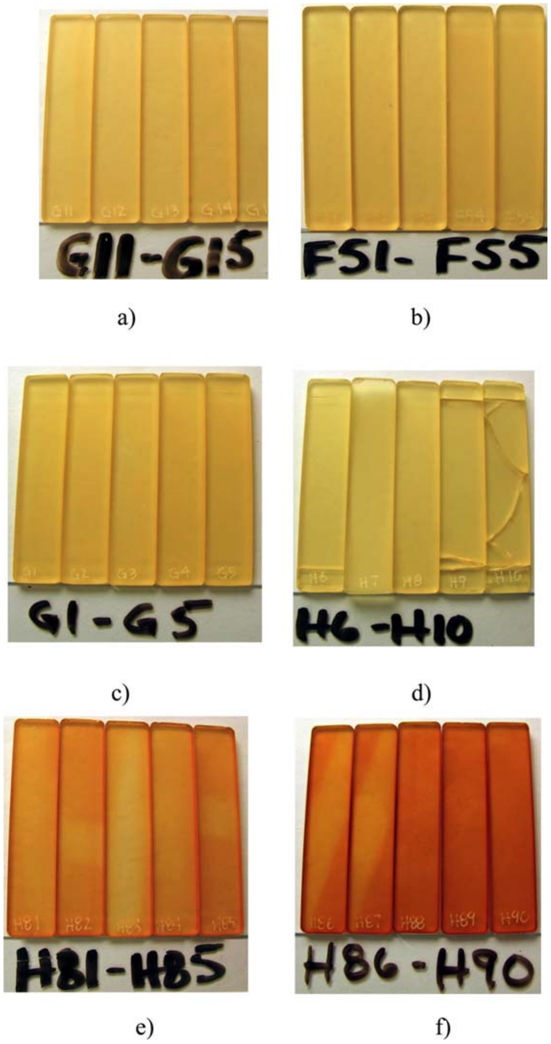

Figure 4. Selected specimens after 6 months exposure. (a) 6-months-old control specimens, with nominal dimensions 60 × 13 mm^2; (b) aircraft surface cleaning compound (Penair C5572) after 6 months; nonionic detergent (MEK) after (c) 3 months and (d) 6 months; hot water after (e) 3 months and (f) 6 months. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

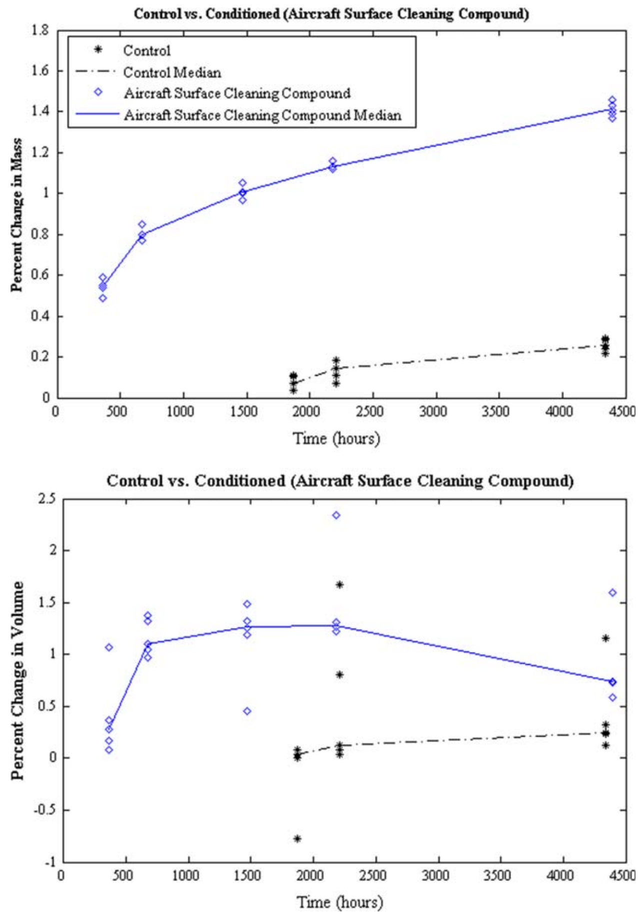

Figure 5. Mass change (top) and volume change (bottom) for specimens conditioned in aircraft surface cleaning compound (Penair C5572). The legend for the symbols in the bottom figure is the same as for the top figure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fluid Royco 782) or a slight loss (~6% for hot water) of complex shear modulus, typically up to ~2,000 microstrain. We will show in "Frequency sweeps section" that the largest contributor to the complex shear modulus is the elastic shear modulus (the loss modulus is typically less than 2% the storage modulus), and hence the assessment on the complex shear modulus allows a direct evaluation of durability and stiffness performance.

In all cases, the complex shear modulus appears to be independent of the shear strain, in the strain range of the isothermal and isofrequency stress sweeps of this study, for baseline and treated specimens. On the basis of this outcome, the specimens are linear viscoelastic,[29] up to ~4,000 microstrains. This was demonstrated through boxplots, which provide a clear and statistically-robust picture of the variability of the samples with respect to each other, and are independent of the type of data distribution[†].

Results for the samples treated in aircraft surface cleaning compound (Penair C5572) are given in Figure 7, for strains ranging from ~500 microstrains up to ~4,000 microstrains. This condition is representative of the behavior of the majority of the contaminated specimens, where control and treated specimens are statistically similar within the parameters of this study. The MEK data is in Figure 8. Details for the other contaminants are enclosed in the Supporting Information.

Regarding Figures 7 and 8, it is observed that the scatter of the control specimens seems high, but it is actually associated to a

[†]Boxplots, or box and whiskers plots, are conventional graphical statistical tools that are independent of the type of data distribution (see for example A. C. Tamhane and D. D. Dunlop, Statistics and Data Analysis–from Elementary to Intermediate, 2000, Prentice Hall, Inc.). The box represents the first, second and third quartiles. The second quartile, or median, is represented with a red line. The whiskers are drawn to the most extreme data value. Potential outliers are shown as a cross.
With the Lilliefors normality tests, many data sets were found not to be normally distributed. No data was excluded from the analysis.

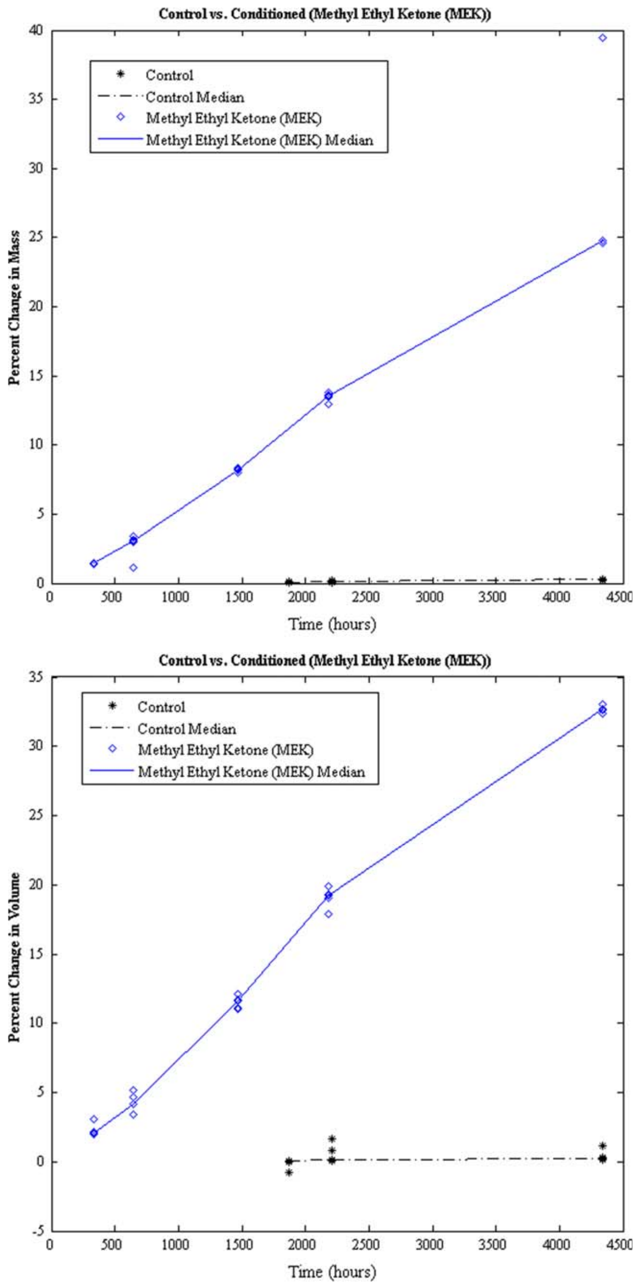

Figure 6. Mass change (top) and volume change (bottom) for specimens conditioned in nonionic detergent (MEK). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

coefficient of variation of just 2.5–3.5% (about twice that of the conditioned specimens).

Frequency Sweeps. Results from the isothermal and isostrain frequency sweeps are given in two forms: boxplots of the complex shear modulus, and plots of storage and loss moduli (G' and G''), and tangent of the phase angle (δ). The frequency sweeps are supposed to take place at levels of strains within the linear viscoelastic regime,[29] and this is indeed the case for this study, based on the behavior at 4000 microstrain presented in "Stress weeps section".

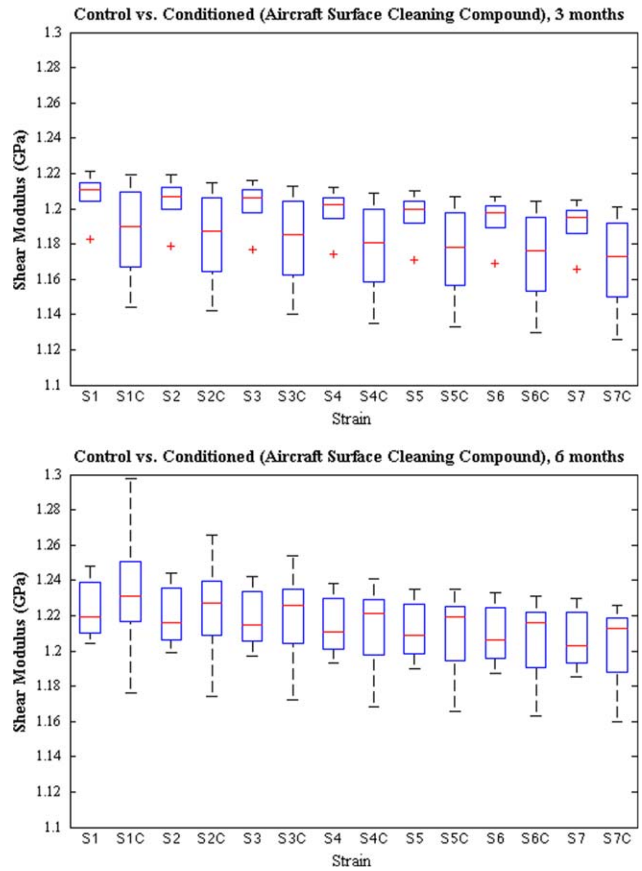

Figure 7. Boxplots of complex shear modulus resulting from the stress sweep of specimens immersed in aircraft surface cleaning compound (Penair C5572), for 3 and 6 months, as compared with control specimens ("C"). All following data is in microstrain, ranging from ~500 microstrain up to ~4000 microstrain: S1 = 493, S1C = 593; S2 = 785, S2C = 943; S3 = 990, S3C = 1190; S4 = 1576, S4C = 1894; S5 = 1988, S5C = 2389; S6 = 2508, S6C = 3015; S7 = 3165, S7C = 3727. The red "+" indicates potential outliers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

We start discussing Figures 9–11, for a representative contaminant (aircraft surface cleaning compound, Penair C5572). In Figure 9, due to scatter, control and conditioned samples are statistically equivalent to each other. There is a minor increase of complex shear modulus of the 6-months-old control specimens with respect to the 3-months-old control specimens, but only up to 63 Hz.

A more complete picture is given in Figures 10 and 11: first of all, a review of the values of complex shear, storage and loss moduli demonstrate the much higher impact of the elastic portion, G', over the viscous/dissipative portion G'' in the selected frequency range. We can compare G', G'', and tan(δ) with the theoretical behavior of a linear viscoelastic solid, Figure 12.[28] The trend of the storage modulus in Figures 10 and 11 is quite consistent with the theory, approaching steady-state towards the highest values of frequency in these tests. The loss modulus and tan(δ); however, would be flat lines if plotted in the same range of values as the storage modulus. The trends are otherwise increasing without achieving a maximum in the

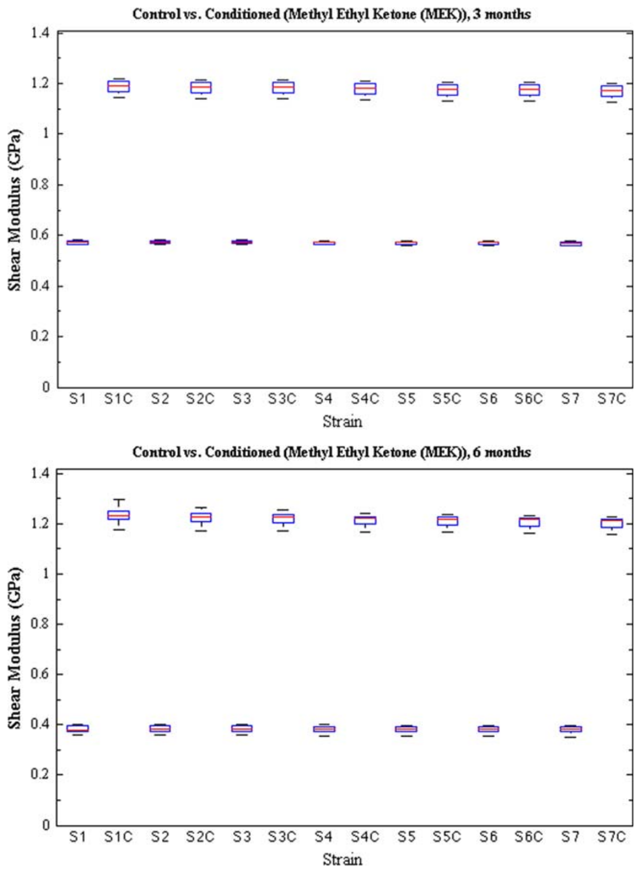

Figure 8. Boxplots of complex shear modulus resulting from the stress sweep of specimens immersed in nonionic detergent (MEK), for 3 and 6 months, as compared with control specimens ("C"). All following data is in microstrain, ranging from ~500 microstrain up to ~5,000 microstrain: S1 = 783, S1C = 593; S2 = 1242, S2C = 943; S3 = 1564, S3C = 1190; S4 = 2485, S4C = 1894; S5 = 3134, S5C = 2389; S6 = 3954, S6C = 3015; S7 = 4992, S7C = 3727. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

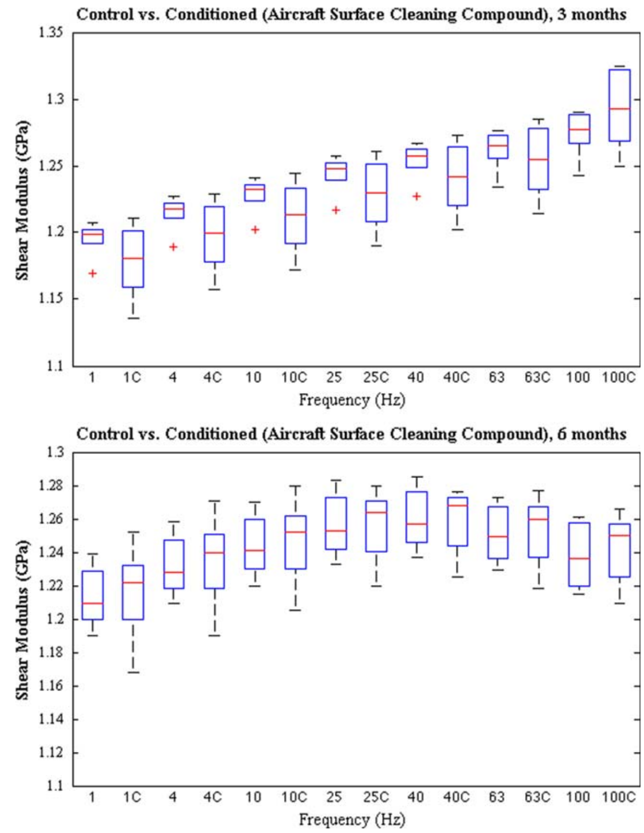

Figure 9. Boxplots of complex shear modulus resulting from the frequency sweep (selected frequencies of 1, 4, 10, 25, 40, 63, and 100 Hz) of specimens immersed in aircraft surface cleaning compound (Penair C5572), as compared with control specimens (same frequencies, but followed by "C"). The red "+" indicates potential outliers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

frequency range of the current tests. The 10-months-old baseline samples (Figure 11) exhibit a slight stiffening (increase of storage modulus) with respect to the conditioned and 6-months-old control, but only between 63 and 100 Hz. Other than this, the storage moduli of control and conditioned samples appear very close to each other, as reflected by the statistical equivalence of the complex shear moduli for those samples. The conditioning does not seem to affect the amount of dissipation in the material, since the loss modulus is not significantly changed.

On the other hand, the complex shear modulus of the MEK-treated samples is distinctly different with respect to the control. The considerable drop of complex shear modulus that occurs at 1 Hz with the stress sweeps (Figure 8) is observed also at higher frequencies (Figure 13). Figures 14 and 15 suggest that the conditioning in MEK increases the viscous/dissipative contribution of the complex modulus, although the elastic content is still higher by comparison.

Plots related to other contaminants are in the Supporting Information.

Temperature Sweeps. The outcome of the temperature sweep is presented in Figure 16 (for aircraft surface cleaning compound, Penair C5572), Figure 17 (for nonionic detergent, MEK) and Supporting Information (for all other cases). Boxplots are not appropriate here because of the small number of specimens per set (two) in the large majority of cases.

We analyzed the storage modulus trends with temperatures, Figures 16 and 17. The data can be accurately fitted to lines $G' = p_1 T + p_2$ (with coefficients of determination R^2 varying between 0.948 and 0.997). The differently-aged control specimen trends are very consistent with each other, especially when considering the 95% confidence bounds for the slope and the G'-axis intercept, respectively coefficients p_1 and p_2 (Table TI in the Supporting Information). The aircraft surface cleaning compound (Penair C5572) data exhibits the same trend for 3- and 6-months conditioning, when accounting for the 95% confidence bounds for p_1 and p_2. These outcomes are likely to be due to the absence of significant physical aging for the control specimens as well as significant damage for this set of treated specimens. For this contaminant, after a period of 6 months, the storage modulus variation at 99°C is $\frac{|G_{\text{treated}}|-|G_{\text{control}}|}{|G_{\text{control}}|}\times 100 \approx -18\%$. The Penair C5572 hence causes a clear vulnerability of the resin samples at the highest temperatures ($T \geq 80$°C) of the sweep.

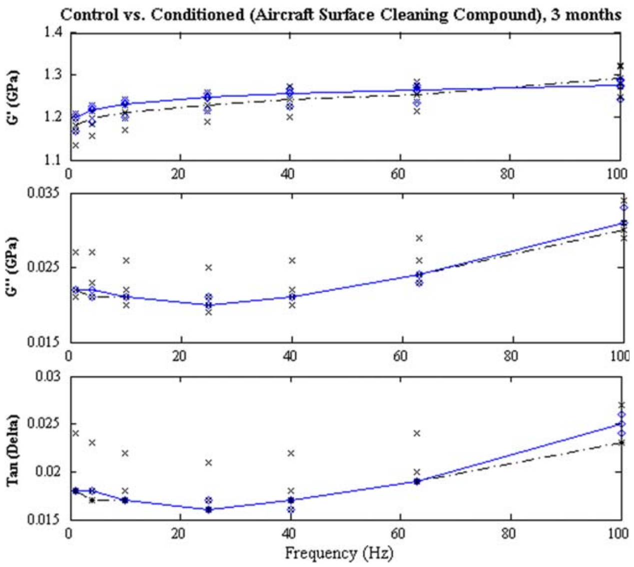

Figure 10. Storage shear modulus G' (top), loss shear modulus G'' (center) and tan(δ) as a function of frequency, for specimens immersed in aircraft surface cleaning compounds (Penair C5572), for 3 months. *Legend: x* = control, with median indicated by dashed-dotted line; ◇ = conditioned, with median indicated by solid line. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

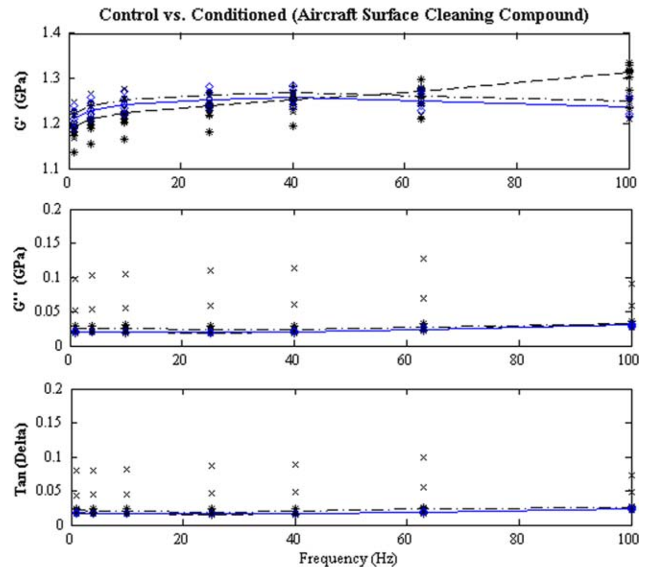

Figure 11. Storage shear modulus G' (top), loss shear modulus G'' (center) and tan(δ) as a function of frequency, for specimens immersed in aircraft surface cleaning compounds (Penair C5572) for 6 months. *Legend: x* = control, 6 months, with median indicated by dashed-dotted line; $*$ = control, 10 months, with median indicated by dashed line; ◇ = conditioned for 6 months, with median indicated by solid line. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Regarding the MEK-treated specimens' data, the slopes and intercepts for the 3- and 6-months conditioning are comparable to each other, but there is a very strong variation with respect to the slope of the control data. For the previous contaminant, Penair C5572, the slope of the fitted lines for the treated specimens with respect to the slope of the control data fitted line was steeper, and equal to $\frac{(p_1)_{\text{median,treated}}-(p_1)_{\text{median,control}}}{(p_1)_{\text{median,control}}}\times 100=27\%$, where the $(p_1)_{\text{median,treated}}$ and $(p_1)_{\text{median,control}}$ are the median of the slopes of all the treated data and all the control data, respectively (collected together independently of the age). For MEK-treated specimens, $\frac{(p_1)_{\text{median,treated}}-(p_1)_{\text{median,control}}}{(p_1)_{\text{median,control}}}\times 100=81\%$, indicating a much more drastic loss of stiffness with temperature. This behavior, once again, confirms the seriousness of the impact of this latter contaminant on this otherwise chemically robust resin system. Both specimens in this sweep fractured.

Finally, reviewing the behavior of loss modulus and tangent of phase angle, we can notice that the contaminants and conditioning times impact the specimens differently at different temperatures, which is not a surprising result *per se*. The viscous component of the specimens treated in Penair C5572 increases for $T \geq 60°C$.

The complex shear modulus is still dominated by the storage modulus within the parameters of this study, and thus an evaluation of the extent of chemical- and temperature-dependent degradation of the samples may be based on the previous discussion on the storage modulus.

SUMMARY AND CONCLUSIONS

Cured samples made of a common out-of-autoclave epoxy were immersed in various contaminants typical of aerospace operations for up to 6 months, typically at room temperature. The specimens were tested in a shear rheometer, with three different sequential sweeps (stress, frequency, and temperature). Within the parameters of this work, the resin samples behave as linear viscoelastic materials, but with a predominantly elastic behavior. The resin samples exhibit a reasonably

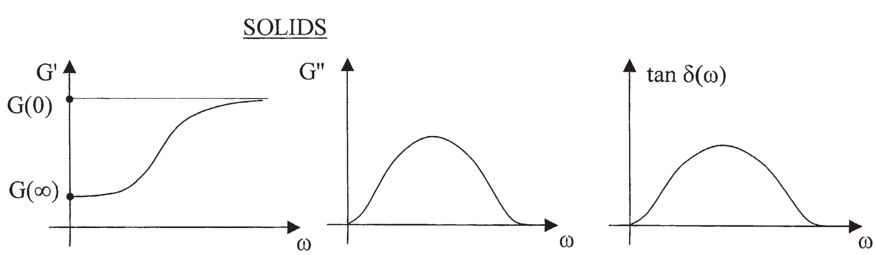

Figure 12. Behavior of (left to right) storage modulus, loss modulus and tangent of phase angle as a function of frequency, for a linear viscoelastic solid (from Ref. 28, reprinted with permission of Cambridge University Press. Copyright © 2000 Cambridge University Press).

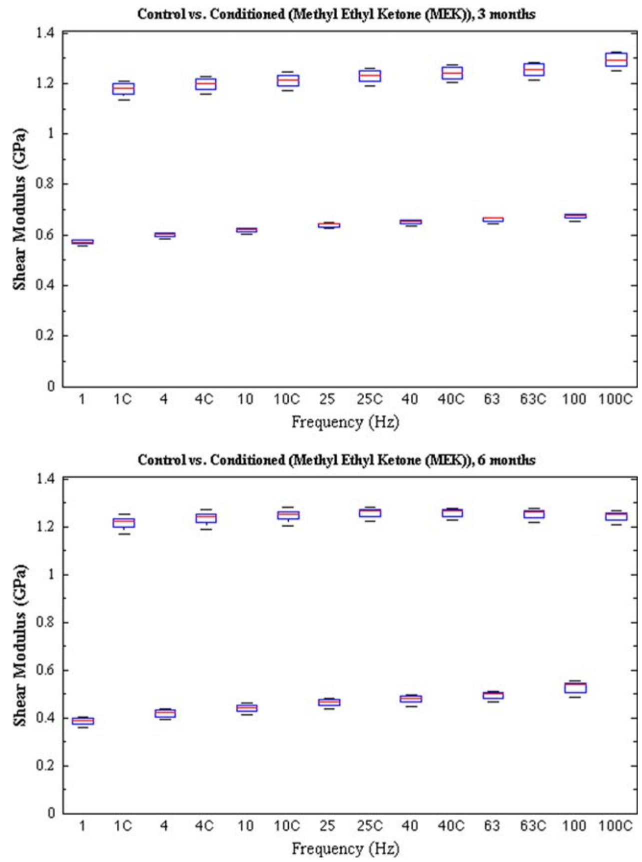

Figure 13. Boxplots with complex shear modulus resulting from the frequency sweep (1, 4, 10, 25, 40, 63, 100 Hz) of specimens immersed in nonionic detergent (MEK), as compared with control specimens (same frequencies, but followed by "C"). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

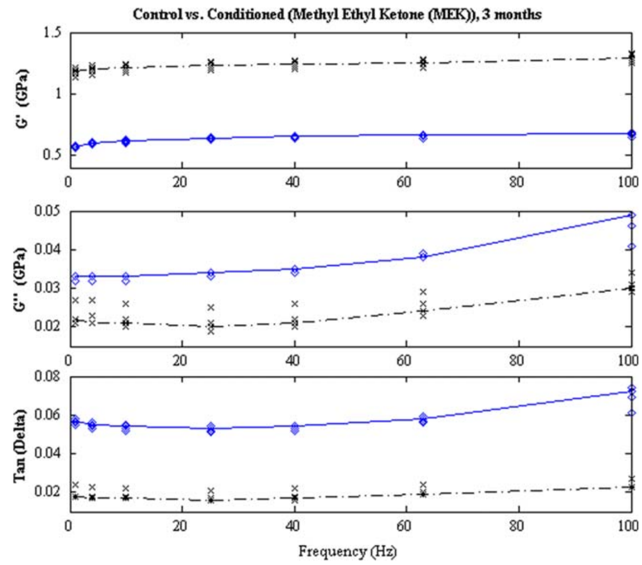

Figure 14. Storage shear modulus G' (top), loss shear modulus G'' (center) and tan(δ) as a function of frequency, for specimens immersed in nonionic detergent (MEK) for 3 months. *Legend:* x = control, with median indicated by dashed-dotted line; ◇ = conditioned, with median indicated by solid line. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

good resistance to all chemicals, with the exception of two commonly used solvents, MEK (during all sweeps) and Penair C5572 (during the temperature sweep only). MEK causes not only a large mass and volume gain of the samples, by comparison with the other chemicals, but also a severe drop of mechanical properties after just 3 months. It eventually leads to fracture of the specimens. There is no meaningful color change, which could trigger a visual inspection after 3 months, by which time the material has already lost half of its stiffness. Exposure to MEK should be minimized, and a substitute chemical should be evaluated.

In use, the aircraft surface cleaning compound, Penair C5572, is diluted and foamed onto the surfaces to clean, and then it is rinsed off. The actual exposure time is thus limited, but it is unknown how much residue is left on the surface. Further testing would be required to quantify these effects on the flight line. Although this chemical was relatively benign during the first two sweeps, it can have detrimental impact at high temperatures.

This study raises a strong safety concern about these two standard aerospace detergents. It is also pointed out that such serious degradation took place in very simplified laboratory conditions (room temperature, no concurrent mechanical loading), and hence it is possible that these detergents' influence may be heightened by a less lenient environment.

ACKNOWLEDGMENT

The authors thank Greg Larsen, Walter Grundler, Roberto Sanchez and Paul Sandoval (Lawrence Livermore National Laboratory) for making over 300 quality samples for testing. Mark Pearson and Wayne Jensen, also from Lawrence

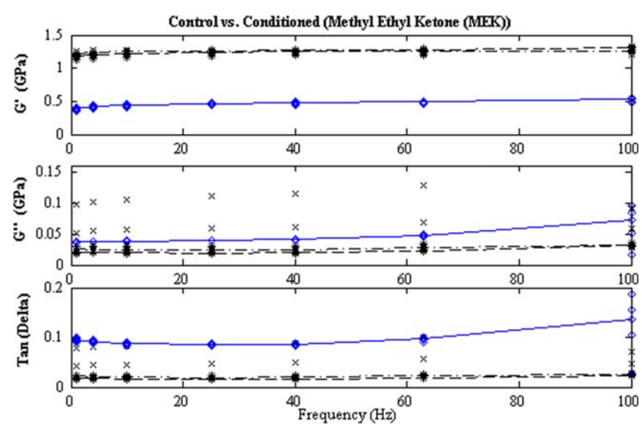

Figure 15. Storage shear modulus G' (top), loss shear modulus G'' (center) and tan(δ) as a function of frequency, for specimens immersed in nonionic detergent (MEK) for 6 months. *Legend:* x = control, 6 months, with median indicated by dashed-dotted line; $*$ = control, 10 months, with median indicated by dashed line; ◇ = conditioned for 6 months, with median indicated by solid line. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

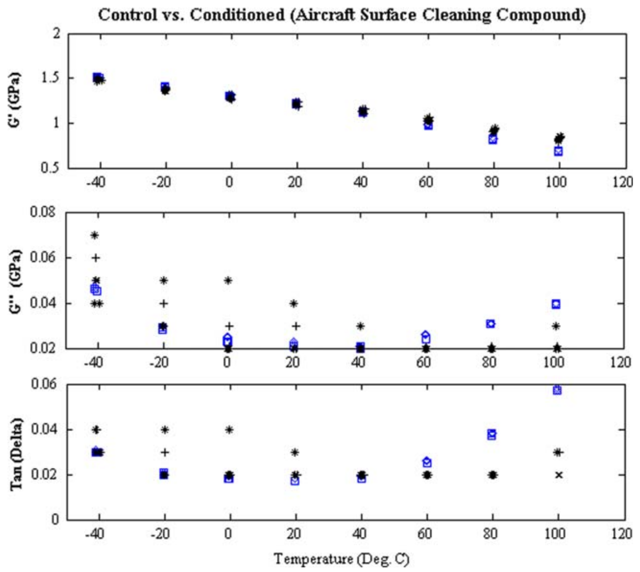

Figure 16. Storage shear modulus G' (top), loss shear modulus G'' (center) and tan(δ) as a function of temperature, for specimens immersed in aircraft surface cleaning compound (Penair C5572). *Legend*: x = control, 3 months, + = control, 6 months, ∗ = control, 10 months; ◇ = conditioned, 3 months; □ = conditioned, 6 months. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Livermore National Laboratory, exposed the samples and subsequently tested them. All their efforts are greatly appreciated.

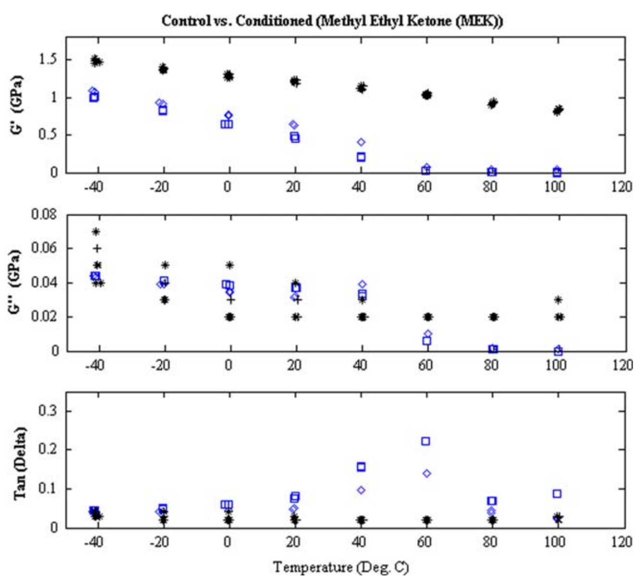

Figure 17. Storage shear modulus G' (top), loss shear modulus G'' (center) and tan(δ) as a function of temperature, for specimens immersed in nonionic detergent (MEK). *Legend*: x = control, 3 months, + = control, 6 months, ∗ = control, 10 months; ◇ = conditioned, 3 months; □ = conditioned, 6 months. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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