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Parylene C Aging Studies

Komandoor E. Achyuthan, Patricia S. Sawyer, Guillermo Mata, Gregory Von White II,
and Robert Bernstein

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ABSTRACT

Parylene C is used in a device because of its conformable deposition and other advantages. Techniques to study Parylene C aging were developed, and "lessons learned" that could be utilized for future studies are the result of this initial study. Differential Scanning Calorimetry yielded temperature ranges for Parylene C aging as well as post-deposition treatment. Post-deposition techniques are suggested to improve Parylene C performance. Sample preparation was critical to aging regimen. Short-term (~40 days) aging experiments with free standing and ceramic-supported Parylene C films highlighted "lessons learned" which stressed further investigations in order to refine sample preparation (film thickness, single sided uniform coating, machine *versus* laser cutting, annealing time, temperature) and testing issues ("necking") for robust accelerated aging of Parylene C.

ACKNOWLEDGMENTS

We thank Ronald Goeke (Materials Science Department, Org # 01832) for the preparation of free standing and ceramic-coated Parylene C films which were used in the present accelerated aging studies. We also thank Ronald Goeke, Jerome Norris, Mark Stavig, and Rob Sorensen for their fruitful discussions and assistance in testing technique development.

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NOMENCLATURE

CVD	Chemical Vapor Deposition
DLO	Diffusion Limited Oxidation
DMA	Dynamic Mechanical Analysis
DOE	Department of Energy
DSC	Differential Scanning Calorimetry
D-Test	Destructive Test
IR	Infrared
MS	Mass Spectrometry
NDT&E	Non-Destructive Testing and Evaluation
NNSA	National Nuclear Security Administration
P-C	Parylene C
RT	Room Temperature (ambient laboratory temperature, ~23 ^{o}C)
SME	Subject Matter Experts
SNL	Sandia National Laboratories
UV	Ultraviolet
UV-Vis	Ultraviolet-Visible

EXECUTIVE SUMMARY

A key element in a device was the substitution of the Kapton with a Parylene C (polyxylylene) due to the latter's conforming coating capabilities. The goal was to obtain aging data to support the use of Parylene C as a conformable coating to the test body.

Free standing and ceramic (Al_2O_3)-coated Parylene C films were made using a PDS 2010 Labcoter^{TM} 2, sometimes with post-deposition annealing at 109 °C for 1 hour. Parylene C films for accelerated aging studies were prepared using either a punching machine or were cut using a laser. Thickness of Parylene C film was between 20 and 30 µm. Parylene C test coupons were subjected to thermal-oxidative aging at (°C): 40, 64, 80, 109, 124, and 138, and then examined at different time intervals using dynamic mechanical analysis (DMA), tensile testing, and differential scanning calorimetry (DSC).

Difficulties encountered during DMA testing of ceramic-anchored Parylene C films included, limiting the film coating to one side of the surface, aligning the plates exactly parallel, and mixed mode testing (adhesion and tensile). Further studies were limited to free standing films. Films aged at 124 °C and 138 °C led to high rates of polymer degradation. Lower temperature (109 °C and 80 °C) results *initially* looked promising with elongation (% E/E_o) declining proportionally to an increase in aging temperature. However, the data are limited in the number of test samples, test temperatures, and testing period (~40 days). The declining trends were also seen only with elongation (E/E_o) and not with force (F/F_o) values. A different batch of Parylene C displayed different thermo-mechanical profiles. Sample preparation played a crucial role in these properties since these test coupons were not annealed and were cut using a laser device.

Aging profiles of annealed Parylene C test coupons obtained using a cutting tool had different aging profiles with no trends indicative of either increasing or decreasing changes to the tensile properties, reinforcing the need for caution whilst interpreting aging results with limited data, test period, sample batches, and different processing techniques. Using DSC, annealed Parylene C revealed a thermal transition at ~128 °C which increased to 134 °C and 138 °C after 8 and 26.5 hours of annealing times, relative to the non-annealed film. The upper limit of annealed Parylene C aging temperature was therefore fixed at less than 128 °C and preliminary annealing conditions being 109 °C for 1 hour.

In conclusion, data scatter (due to "necking") and batch-to-batch differences made meaningful conclusions regarding Parylene C lifetime difficult. There is a need for uniform (fabrication, thickness, processing, annealing time, temperature) Parylene C film samples aging at 40 °C-109 °C, over longer time frames, in order to make robust lifetime predictions. Spectroscopic tools, DSC, volatiles outgassing, chemical analysis of aged specimens and optical microscopy will also contribute to improved lifetime predictions. Finally, improving the quality of raw material (di-*p*-xylylene), eliminating processing defects and rigorous cleanliness during fabrication will collectively improve data quality. Future studies should also consider aging in thermal only environment, to the exclusion of O_2.

1. INTRODUCTION

An important element in the proposed device was the substitution of the Kapton with a Parylene C. Parylene is the trade name for a variety of polyxylylene polymers. The three most common types of parylenes are Parylene N, Parylene C and Parylene D[1], although a new, heat resistant Parylene HT has been introduced. Parylene C has one chlorine group per repeating unit as shown in Figure 1.

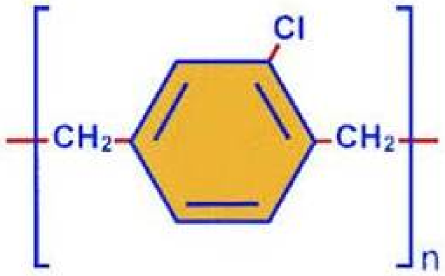


Figure 1. Parylene C Structure

Parylene C offers several advantages, the most important of which is that it can be applied as a conformable coating. Additionally, Parylene C uses an electron beam physical vapor deposition process during production. Starting monomer of Parylene C is commercially available. Ambient temperature, highly precise, pinhole free, chemical vapor deposition (CVD) facilitates uniform coating of the device with Parylene C. Parylene coatings are also hydrophobic, chemically resistant with good barrier properties. They are highly corrosion resistant to metallic surfaces and possess outstanding electrical insulation with high tension strain and low dielectric constant, with low permeability to gases.[1, 2] The goal here was to obtain aging data to support the use of Parylene C as a conformable coating to the test body.

2. EXPERIMENTAL

2.1. Parylene C Mechanical Analysis

2.1.1. Test Facilities

All accelerated aging and testing were performed in building 701, laboratories 2305 or 3331.

2.1.2. Materials

Free standing and ceramic (Al_2O_3)-coated Parylene C specimens were from Ronald Goeke (Department #01832) and were made by using a PDS 2010 Labcoter^{TM} 2 system (Specialty Coating Systems, Indianapolis, IN). The films were deposited on a 0.003" Kapton film which was pre-treated with a 2% cleaning solution of micro-90 in water to aid in the release of the Parylene C film from the Kapton. The films were received "as deposited" or post-annealed at 109 ^{o}C for 1 hour. The post-deposition annealing was carried out in lab 701/3331 or 2305B.

2.1.3. Sample Imaging and Test Coupons Preparation

Parylene C coated samples deposited in a wheel configuration and free standing films (Figure 2) were cut using either a punching machine (MP-5200Z, UHT Corporation, Japan) or a laser and then subjected to accelerated aging studies. The patterns produced ASTM D638-10 Type IV-compliant test specimens.

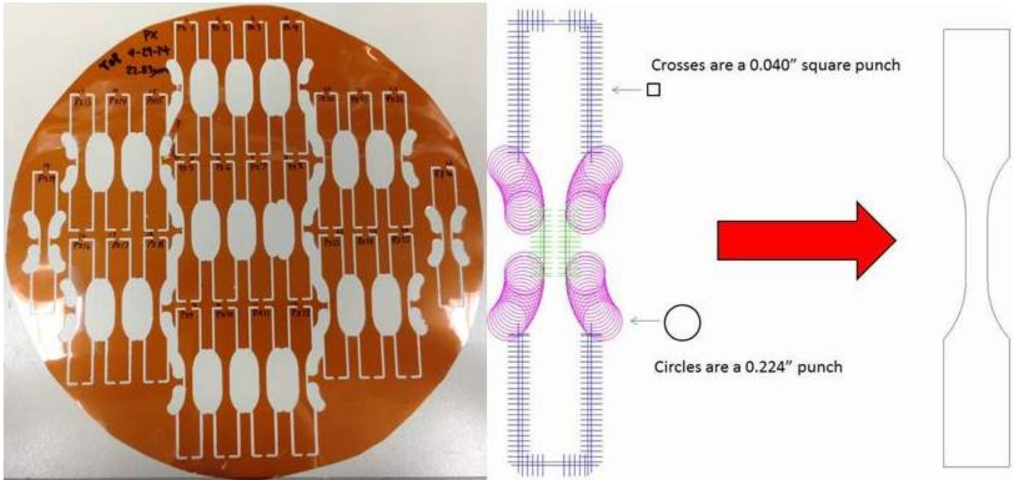
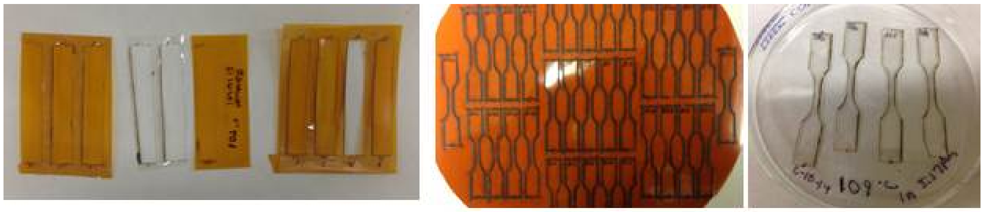
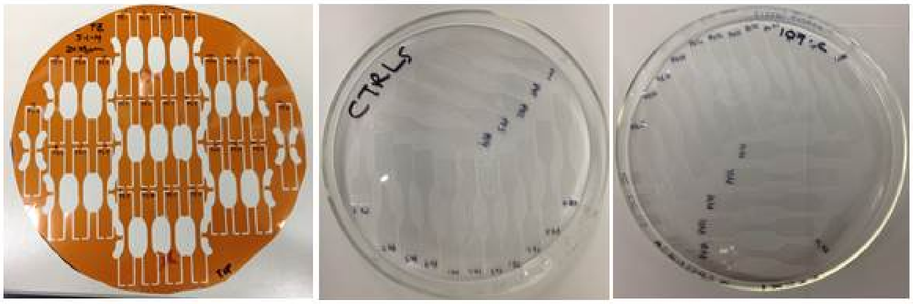


Figure 2. Wheel configuration and schematic of "as deposited" Parylene C

Thickness of Parylene C film was measured optically using normal incidence spectral reflectance (Filmetrics F20, Filmetrics, San Diego, CA) and also by "MEASURE-IT-ALL" gage (Fairfield, OH). Parylene C films were nominally between 20 and 30 µm thickness. The films were manufactured with different amounts of starting monomer and deposited in wheel configurations which were punch or laser cut (Figure 3). Differences in manufacturing and/or processing might have impacted the thermo-mechanical properties of Parylene C described in this report.



Preliminary DMA Samples Laser-Cut Tensile Samples



Punch-Cut Tensile Samples

Figure 3. Parylene C films for accelerated aging studies

Rectangular shaped films (coupons) 1.25 x 0.25 inches (gauge lengths) were prepared as described above. Parylene C films were cut for tensile and dynamic mechanical analysis (DMA). Films were subjected to DMA prior to aging in order to establish "zero point" values and then tested again at different intervals during the aging regimen. Figure 4 shows the photographs of representative examples of room/ambient (23 °C) and 80 °C coupons and the glass petri dishes inside which they were placed for accelerating aging at the indicated temperatures (23 °C to 135 °C). Parylene C films for the remaining temperatures were treated in a similar fashion.

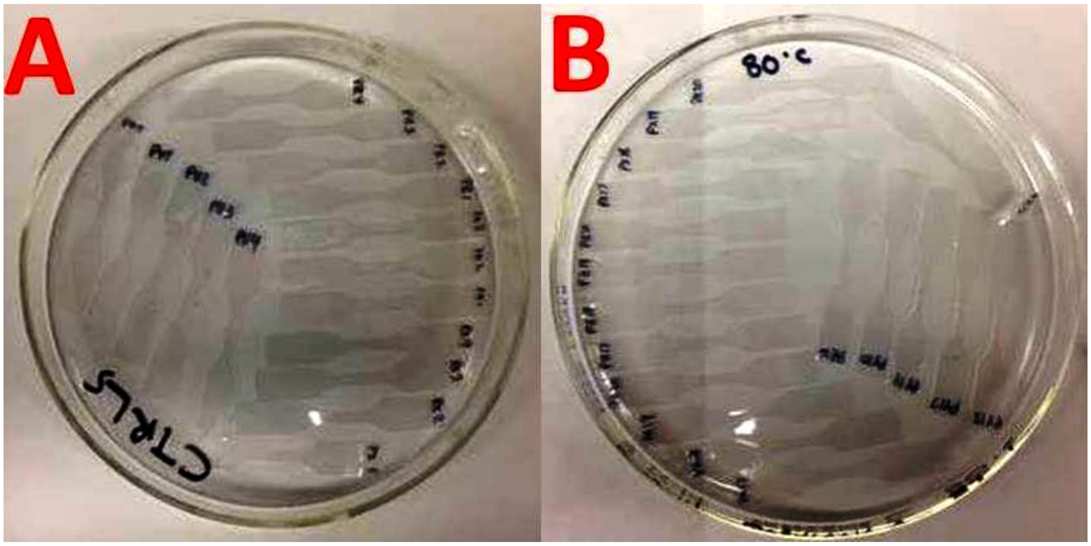


Figure 4. Free standing Parylene C films in glass petri dishes at 23 °C (A) and 80 °C (B)

A general approximation for the magnitude of coupons and their respective accelerated aging temperatures are presented in Table 1 along with ambient, room temperature (RT), ~23 °C. These have not been segregated by their cutting procedure (machined/laser).

Table 1. Approximate number of Parylene C coupons held at aging temperatures.

Aging Temperature	Non-Annealed Coupons	Annealed coupons
109 °C	25	20
80 °C	31	18
64 °C	32	16
40 °C	34	18
23 °C (ambient, RT)	90	16

Ceramic-coated Parylene C films were also prepared to mimic the complex interactions between the ceramic backing and the polymer. These materials were prepared for multi-mode testing for measuring both adhesion and tensile strength on the same sample. The samples were prepared by coating Parylene C onto two ceramic plates placed as close to each other as possible (Figure 5). This way, the two plates could firmly be anchored to a DMA instrument (TA instruments, model # Q800) and stretched to determine the tensile strength of Parylene C film covering the two plates.

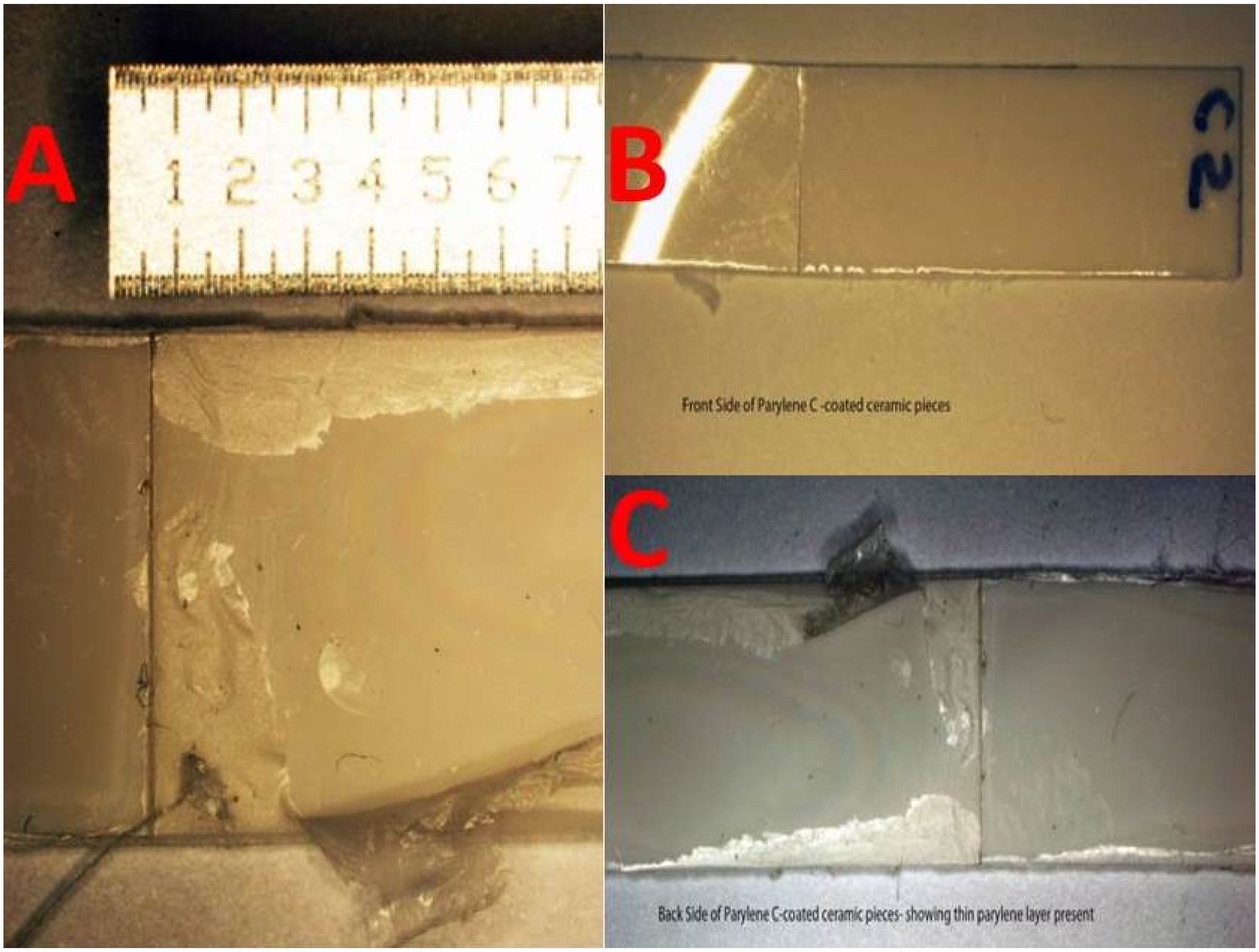


Figure 5. Ceramic coated Parylene C (A) with close up of front (B) and back (C) sides

2.1.4. Accelerated Aging

Parylene C test coupons were subjected to thermal-oxidative aging environments by keeping the coupons in open glass petri dishes with inked labels (Figure 4). The petri dishes containing the coupons were placed inside the various temperature-controlled, air circulating ovens (Lindberg/Blu, Thermo Scientific, USA) at the following temperatures (°C): 40, 64, 80, 109, 124, and 138. Temperatures were monitored using calibrated thermocouple for ± 2 °C accuracy from these target temperatures. As noted in Table 1, coupons were also kept at ambient temperature (23 °C; ~73 °F) in similar, but covered glass petri dishes. Care was taken to ensure that the Parylene C films in the petri dishes did not touch one another while being kept at various temperatures during the course of the accelerated aging study. The coupon section dimensions (thickness, length, and width) were accurately determined as described in the Experimental section. Test coupons were removed at periodic intervals to determine the mechanical properties. Aging period for specific temperatures is listed in the legend to the various figures.

2.1.5. Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) is a widely used technique to characterize changes in a material’s viscoelastic properties as a function of environmental parameters such as time and temperature.[3] A TA Instruments model # Q800 DMA machine was used to measure the tensile modulus of the Parylene C coupons (Figure 6). DMA was performed with a film fixture. Stress-strain curves measured during DMA were analyzed to determine the modulus.

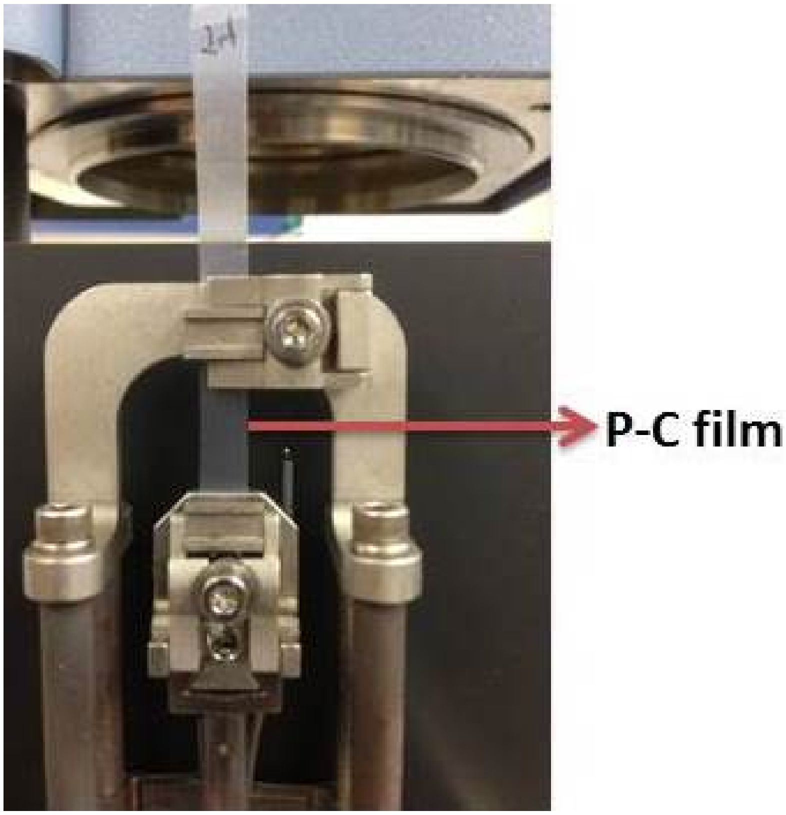


Figure 6. Parylene C (P-C) sample set up for DMA

2.1.6. Free Standing Parylene C Film Tensile Test

Free standing Parylene C film tensile testing was done on an Instron model 5564 Load Frame (Norwood, MA) instrument with a 1000 pounds load cell (Figure 7). Stress-strain curves recorded during measurement were analyzed to determine the maximum tensile stress of each sample.

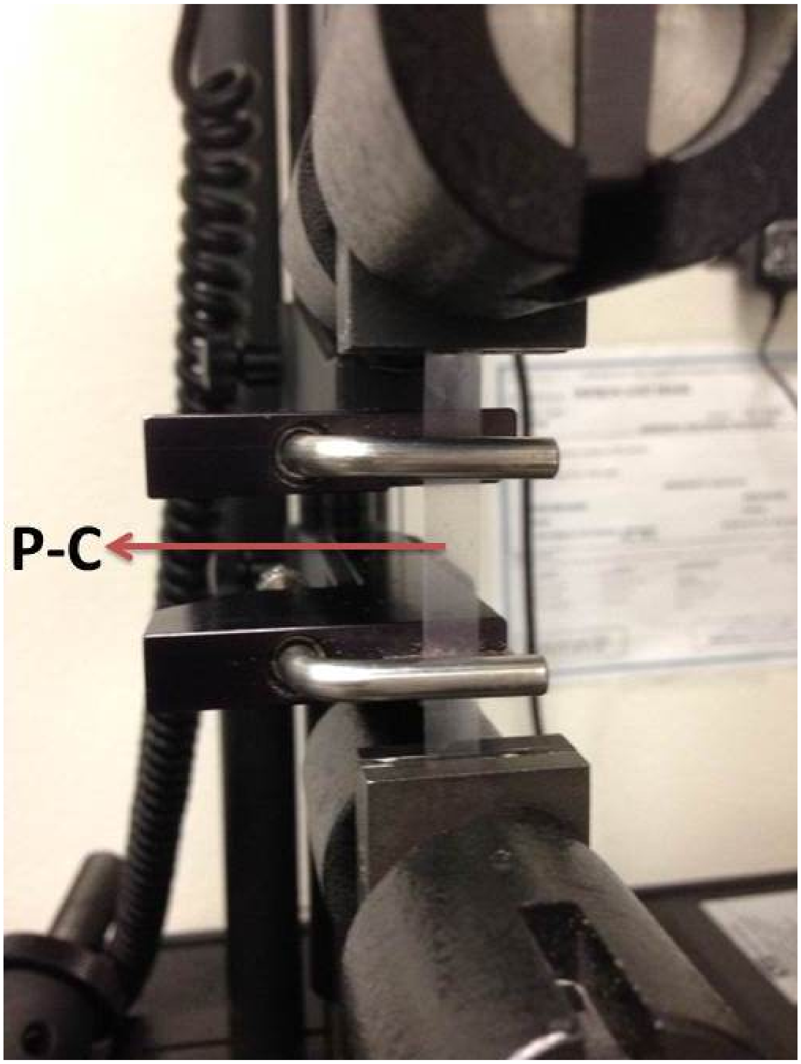


Figure 7. Free standing Parylene C (P-C) film tensile testing

2.1.7. Differential Scanning Calorimetry

Free standing Parylene C films were subjected to differential scanning calorimetry (DSC) using a TA Instrument (New Castle, DE) differential scanning calorimeter model # Q200.

3. RESULTS AND DISCUSSION

3.1. Dynamic Mechanical Analysis

Parylene C film was coated on two closely placed ceramic plates with the idea that the plates anchored the film to the test instrument during DMA (Figure 8). Subsequent stretching of the plates resulted in stretching the Parylene C film as well, thereby providing a metric for changes in the mechanical and/or adhesion properties of the film.

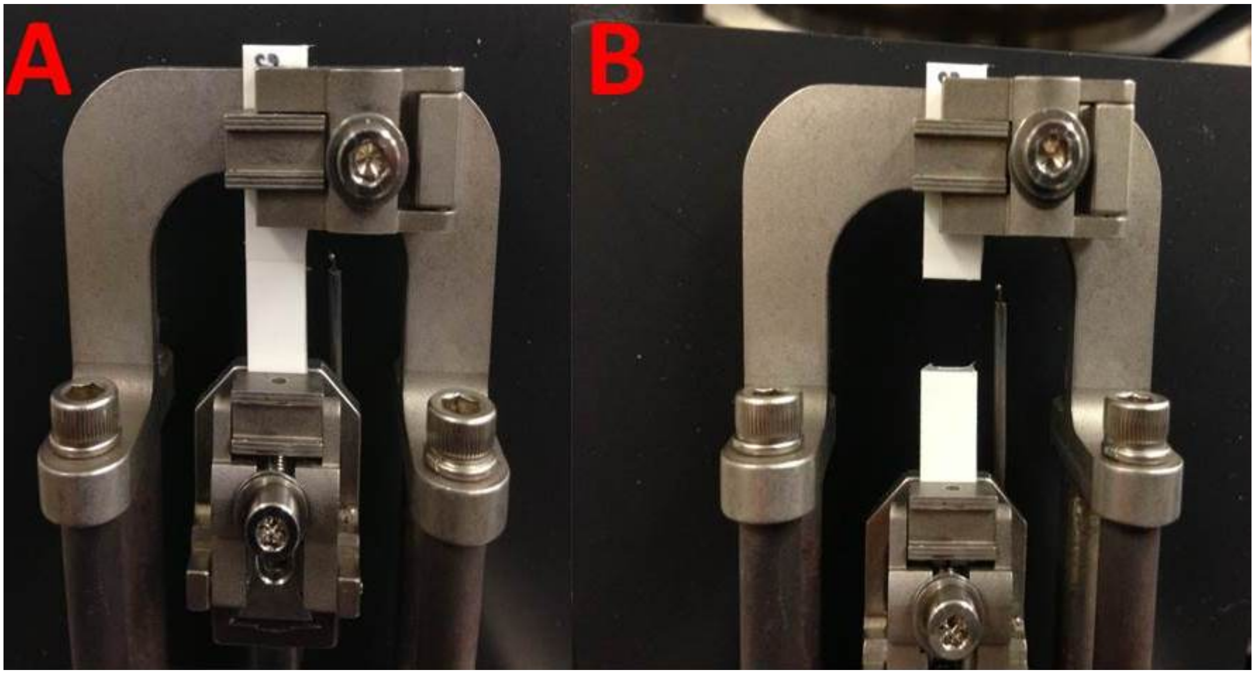


Figure 8. Ceramic-coated Parylene C before (A) and after (B) DMA

While in theory this was a good idea to try, significant difficulties were encountered in keeping the Parylene C coating limited to just one side of the surface (note extensive as well as non-uniform Parylene C coating on the "back side" of the surface in Figure 5). Furthermore, there were also difficulties in aligning the two ceramic plates to be exactly parallel (Figure 9). These two factors complicated data analyses. The mixed mode testing (adhesion strength and tensile strength) also posed problems with this set up. Collectively, the data prompted an exploration of other avenues for testing. Ceramic-Parylene C might be revisited, if the aforementioned difficulties could be overcome.

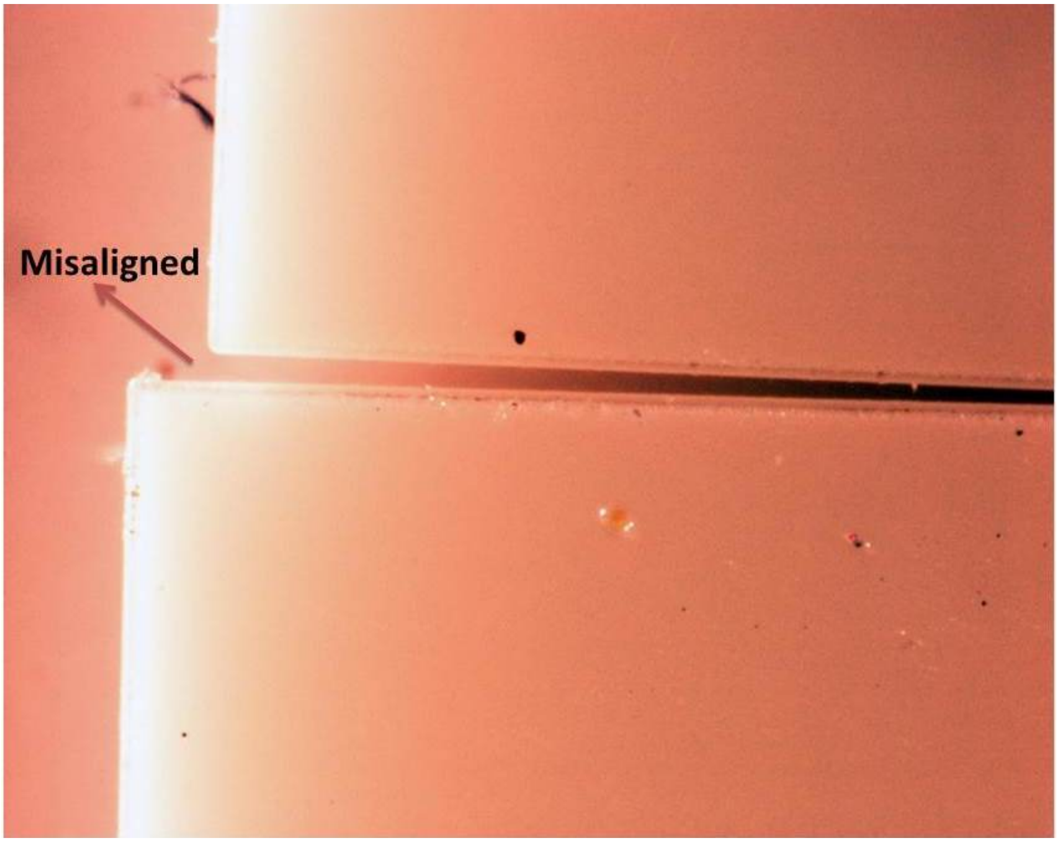


Figure 9. Misalignment of ceramic-coated Parylene C plates

3.2. "Necking" During Tensile Testing

Tensile testing of the free standing Parylene C films using an Instron instrument revealed significant "necking" of the material (Figure 10). It has been reported that "necking" occurs due to tensile deformation when the material's strain is disproportionately localized to a small area on the material and reaches its strain-hardening exponent.[4] With a semi-crystalline polymer such as Parylene C, stress-strain curves are characterized by a linear elastic region; yielding followed by a decrease in stress due to the tangled, intertwined polymer chains becoming untangled and straightening out. If at this point, there is additional stress, then "necking" takes place. Visual observation showed that the control (~23 ^{o}C) Parylene C films displayed a degree of elongation that was different from the thermally-aged samples.

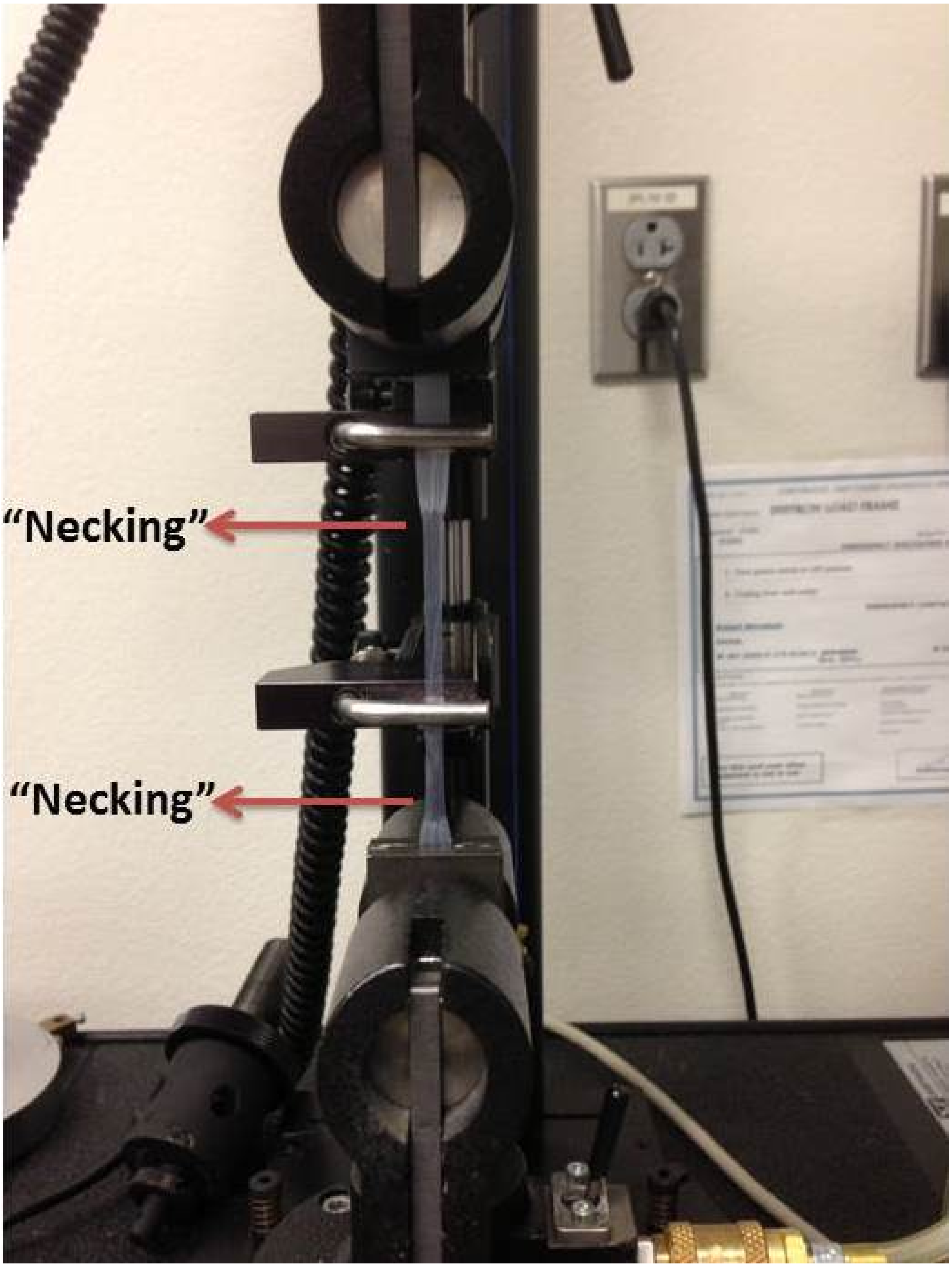


Figure 10. "Necking" of Parylene C film

3.3. Tensile Testing

While tensile stress is arguably not the primary performance characteristic of the component, it is a well-established and well understood testing methodology. Tensile testing (elongation and strength) was performed upon free standing Parylene C films aged at the various temperatures and the data are shown in the following figures. A fundamental problem with all of the work was a lack of consistency in the test coupons. While this should not be construed as a criticism of the manufacturer or of the processes employed for preparing the coupons, it is nevertheless an issue that is inherent to these types of samples. Slight defects are likely along with differences in thickness of the films. Parylene C films exhibited defects such as cloudy films and nodules (Figure 11). Subject matter experts (SME) have suggested that these defects are related to processing, cleanliness and quality of the raw material, which in the case of Parylene C is di-*p*-xylene from which the gaseous monomer is generated during the chemical vapor deposition (CVD) process. Such defects and changes have a profound effect upon the electrical and thermo-mechanical properties of Parylene C.[5, 6] Thus, whilst the design team specification for Parylene C film was set at 20 μm thickness, samples that were supplied for the present study were ~25 μm; a 25% increase in film thickness which will impact the thermo-mechanical properties of the material. Due to the additional concern regarding batch-to-batch variations in Parylene C films, separate data sets were maintained for each batch (unless noted otherwise). However, this approach made data analysis difficult since there was not a large sample size. Nevertheless, the goal was to reduce the experimental scatter in the data, some of which could arise from the "necking" phenomenon described above. A more detailed study could be undertaken in order to address sample variability during fabrication/manufacturing.

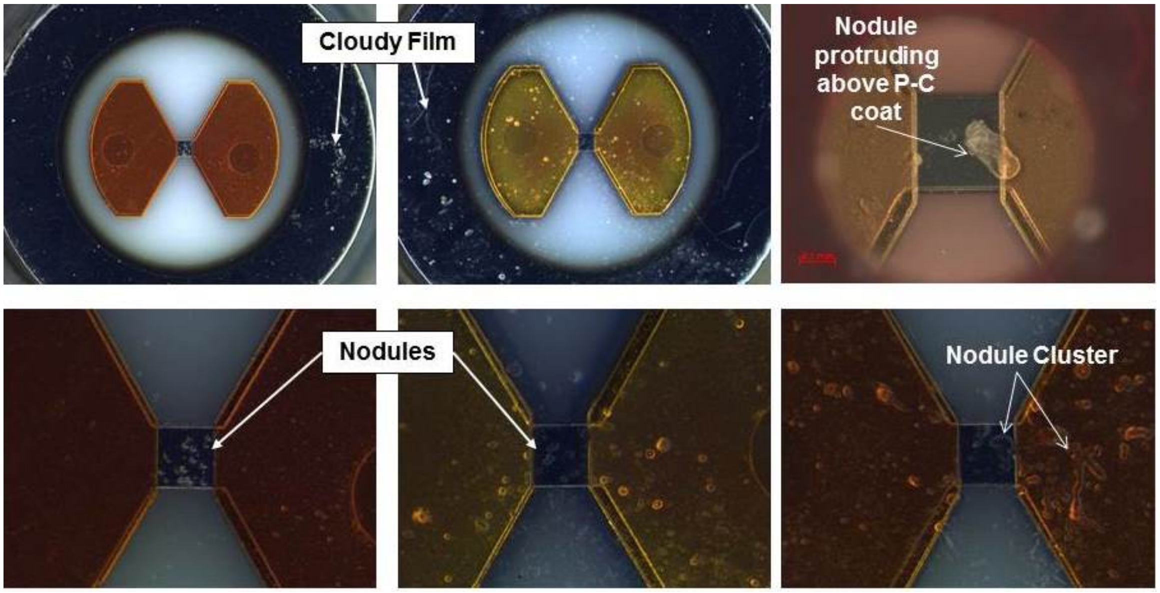


Figure 11. Parylene C defects

3.4. Accelerated Aging

The tensile data showed considerable scatter amongst samples even within a batch. Examination of samples aged for various times and temperatures further highlighted the data scatter. It is likely that differences in film thickness, as a consequence of manufacturing and/or processing variability, could have contributed to data scatter. Even with these caveats, certain preliminary observations were made regarding the aging regimen which will be useful to future studies. First, free standing Parylene C films aging at 124 °C and 138 °C resulted in unacceptably high rates of polymer degradation (Figure 12) turning the ductile polymer brittle. The ratio of elongation of the un-aged and aged films declined extremely rapidly and reached baseline values in approximately 5 days. Such rapid decline in tensile values will not provide meaningful data to enable lifetime predictions. Consequently, these two higher temperatures were eliminated from considerations of the accelerated aging regimen and the focus was on the remaining lower temperatures (23 °C to 109 °C) in order to obtain more realistic and useful Parylene C degradation patterns over time.

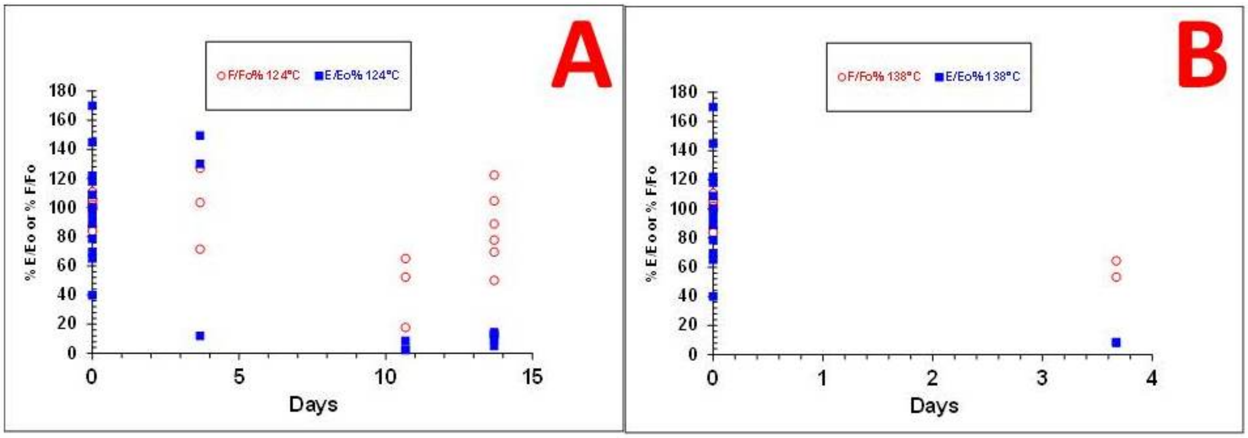


Figure 12. Parylene C films aged at 124 °C (A) and 138 °C (B)

Lower temperature data at 109 °C and 80 °C *initially* looked promising (Figure 13). Whereas the % F/F_o was more or less unchanged at both temperatures, the % E/E_o declined consistently with an increase in the aging temperature. Also, the rate of decline was proportional to the increase in aging temperature (Figure 13). Further, the decline appeared to be slower at 80 °C, occurring over approximately 40 days relative to the faster decline of within 15 days at 109 °C.

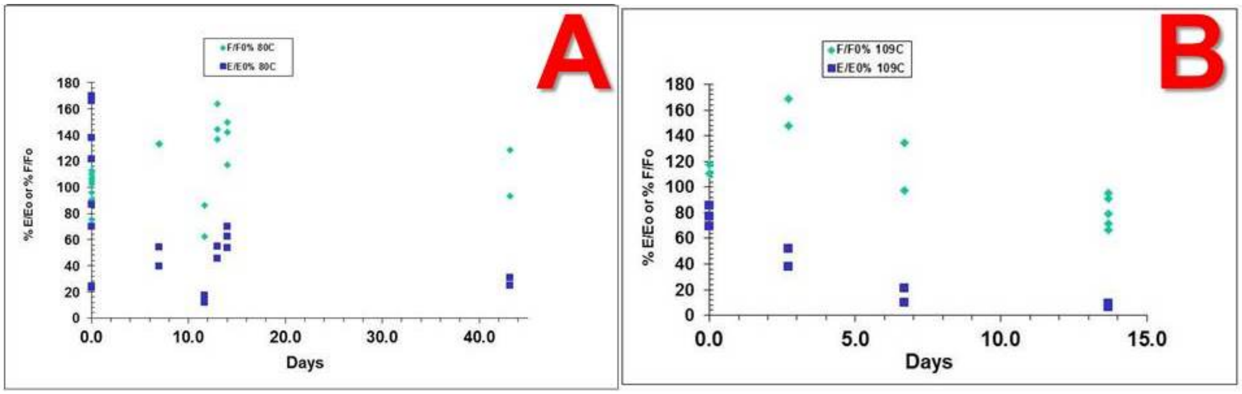


Figure 13. Parylene C films aged at 80 °C (A) and 109 °C (B)

This degradation trend was also similar to the "stud-pull" adhesion strength decline with increase in the aging temperature of Parylene C (Ronald Goeke's data). Parylene C aging and degradation trends (above) also appeared to corroborate literature reports on the thermal properties of Parylene C films. For example, the glass transition temperature (T_g) of Parylene C has been reported to be quite low with values ranging from 35 °C to less than 100 °C.[7-16]The somewhat broad range in reported T_g values is because Parylene C is a semi-crystalline polymer which poses difficulties in clearly identifying this step during DSC measurements.[9]

3.5. Caveat Emptor

Despite the foregoing analysis, caution is advocated against the tendency to rush to extrapolation regarding lifetime predictions for the following reasons. The data presented thus far are limited in both the number of samples tested and test temperatures as well test period (maximum of only ~40 days; Figure 13). Even the declining trends with accelerated aging temperatures were observed only with the elongation ratio (E/E_o), but not with the F/F_o values (Figure 12 and Figure 13). These samples were from one batch of Parylene C fabrication and it is not inconceivable that a different batch of Parylene C might display different thermo-mechanical profiles. Sample preparation might also play a crucial role in the thermo-mechanical properties of the polymer. Thus, the results shown in Figure 12 and Figure 13 were from "as deposited" Parylene C films which had not undergone annealing at 109 °C for 1 hour (post-deposition). These samples were cut using a laser device for preparing the test coupons. Finally, as demonstrated below, when certain sample parameters and preparation methods were altered, significantly different aging profiles could be generated.

Aging profiles of Parylene C films that had been annealed post-deposition (as described above) were investigated next. The test samples described below were obtained using a cutting machine/tool for preparing the test coupons (and were not laser cut). Given these differences, especially with the significant addition of the annealing step at 109 °C for 1 hour, the aging profiles of the free standing Parylene C films were drastically different (Figure 14).

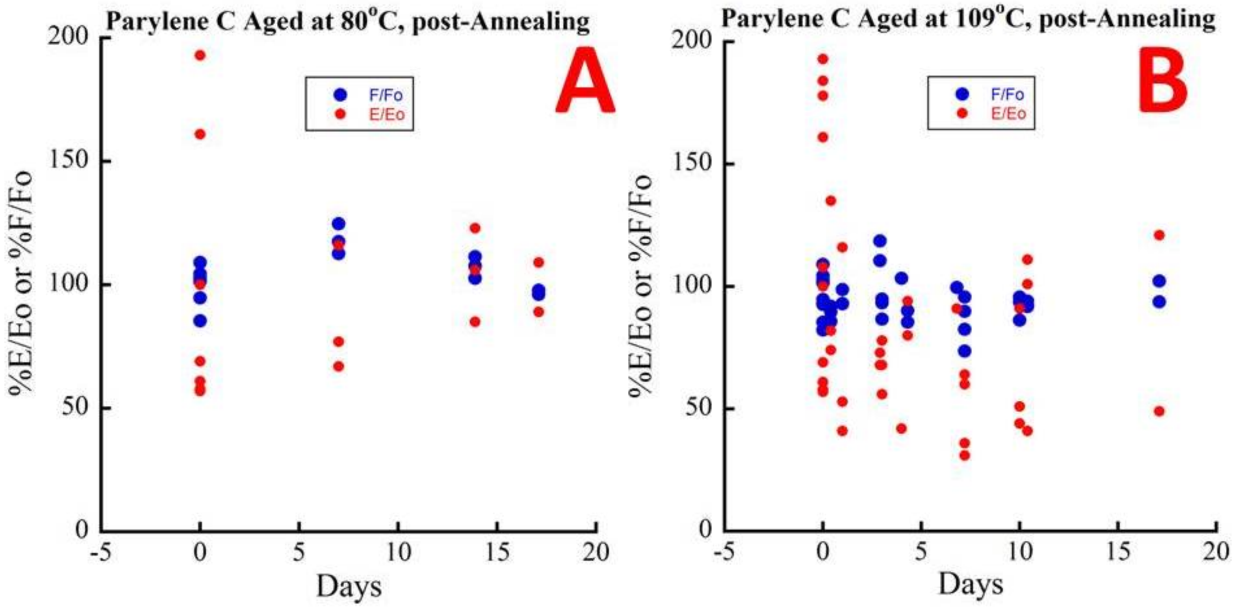


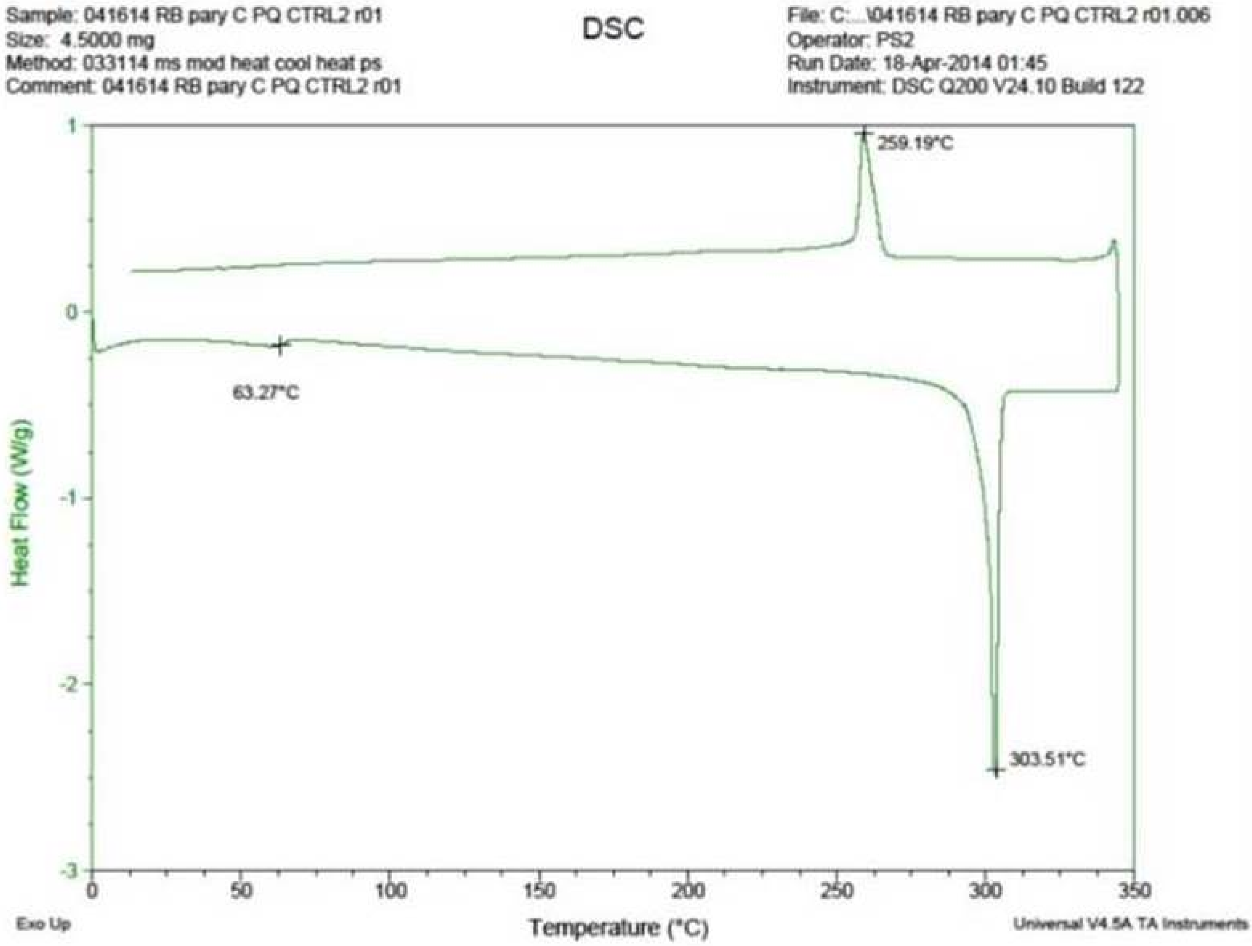
Figure 14. Parylene C films aged at 80 °C (A) and 109 °C (B) post-Annealing

It is obvious that there were no clear trends indicative of either increasing or decreasing changes to the tensile properties (E/E_o or F/F_o) of the Parylene C films aged at 80 °C or 109 °C (Figure

14) when the test coupons were first annealed at 109 °C for 1 hour prior to being subjected to thermal-oxidative aging. The differences in the aging profiles of Parylene C films at these two temperatures were different depending upon whether the films had undergone prior annealing (Figure 14) or not (Figure 13). These results emphasize the aforementioned need for extreme caution whilst interpreting accelerated aging results with limited data, test period, sample batches and sample preparation techniques. These observations may be considered as valuable "lessons learned" which will guide future efforts in the aging studies of Parylene C.

3.6. Differential Scanning Calorimetry

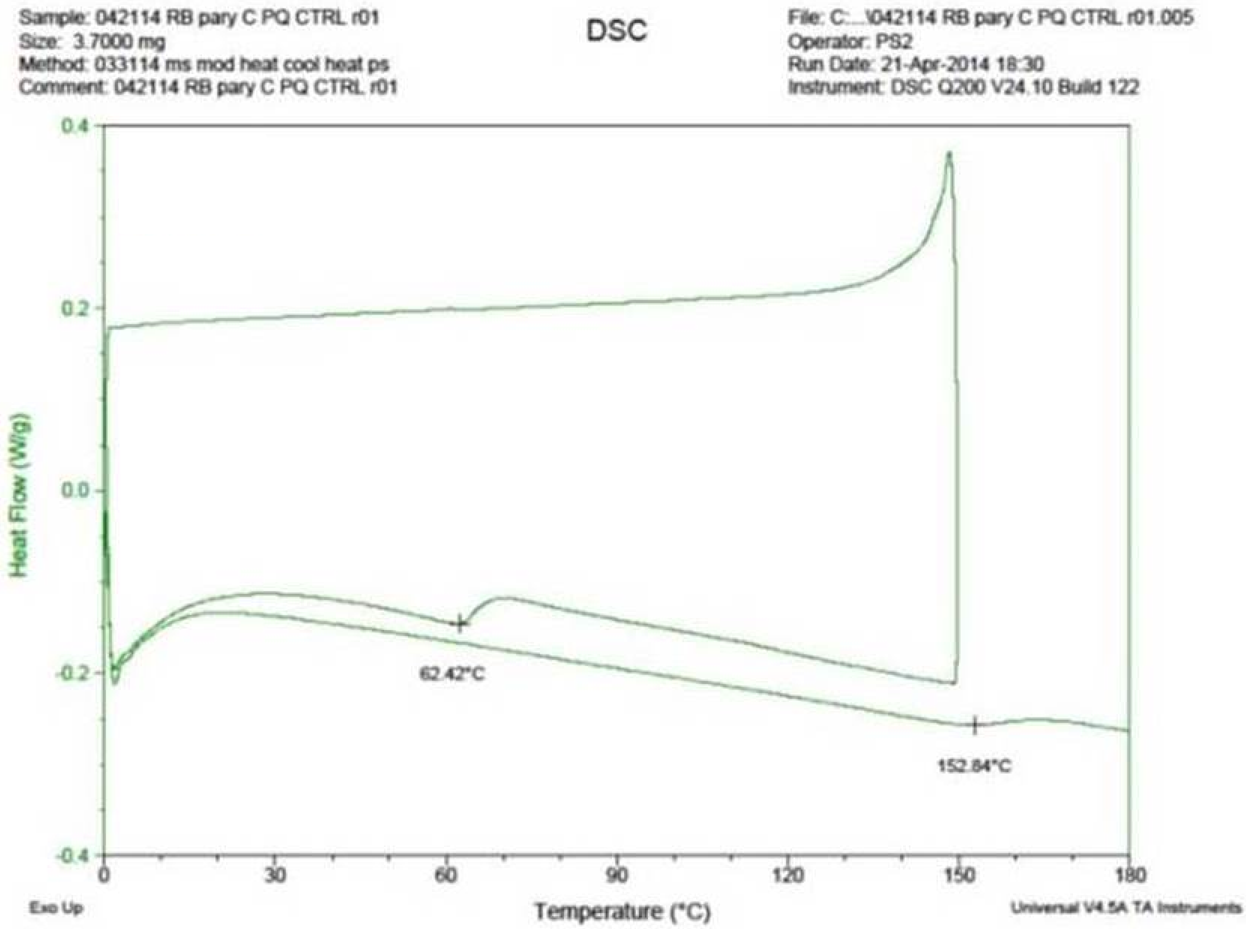
Work on Parylene C films using DSC was mentioned elsewhere in this report. The DSC is a valuable tool for determining polymer thermal properties such as melting point (T_m) and glass transition temperature (T_g) which provide insights during the selection of accelerated aging study temperatures.[17, 18] The T_g values for Parylene C films were reported to be 35 °C to less than 100 °C and T_m was 290 °C.[7, 10, 14] The present DSC data are similar to these values, yielding a T_m of ~260 °C for non-annealed Parylene C film (Figure 15). It has been commented previously that the determination of T_m and T_g for Parylene C using DSC is difficult due to the polymer's semi-crystalline nature,[9] which might explain the small differences observed in the T_g and T_m values. The polymer reaches a thermal transition after about 60 °C.[11] Although Parylenes are thermally stable up to 220 °C and mechanically stable from about –200 °C to + 150 °C, they are nevertheless relatively soft materials with poor oxidative resistance, especially in the absence of an inert atmosphere (in air). The thermal-oxidative degradation temperature range for Parylene C is from approximately 60 °C to 100 °C depending on the failure criteria.[19] As documented in the literature, Parylene C polymers are susceptible to UV degradation.[20, 21] UV causes Parylene C to undergo oxidation, yellowing, stiffening, and lose its protective function. Additionally, these UV-induced changes are irreversible. These factors must be considered during the manufacture and/or processing of Parylene C films as well as during the conduct of accelerated aging studies of this polymeric material.



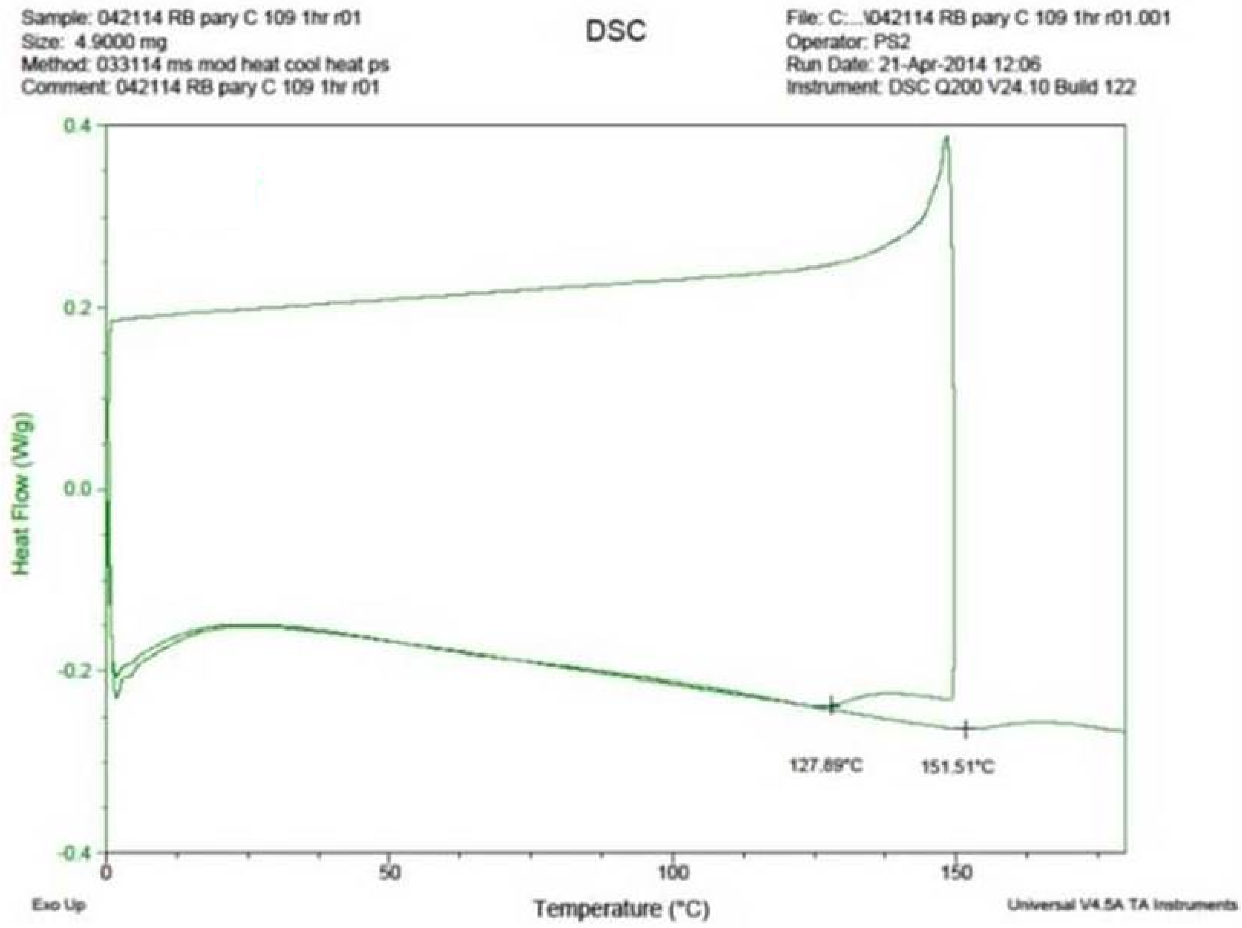
Parylene C Punched sample CONTROL at 23 °C. Temperature was ramped up to 350 °C at 10 °C/min, then back to 0 °C

Figure 15. Melting point of non-annealed Parylene C film using DSC

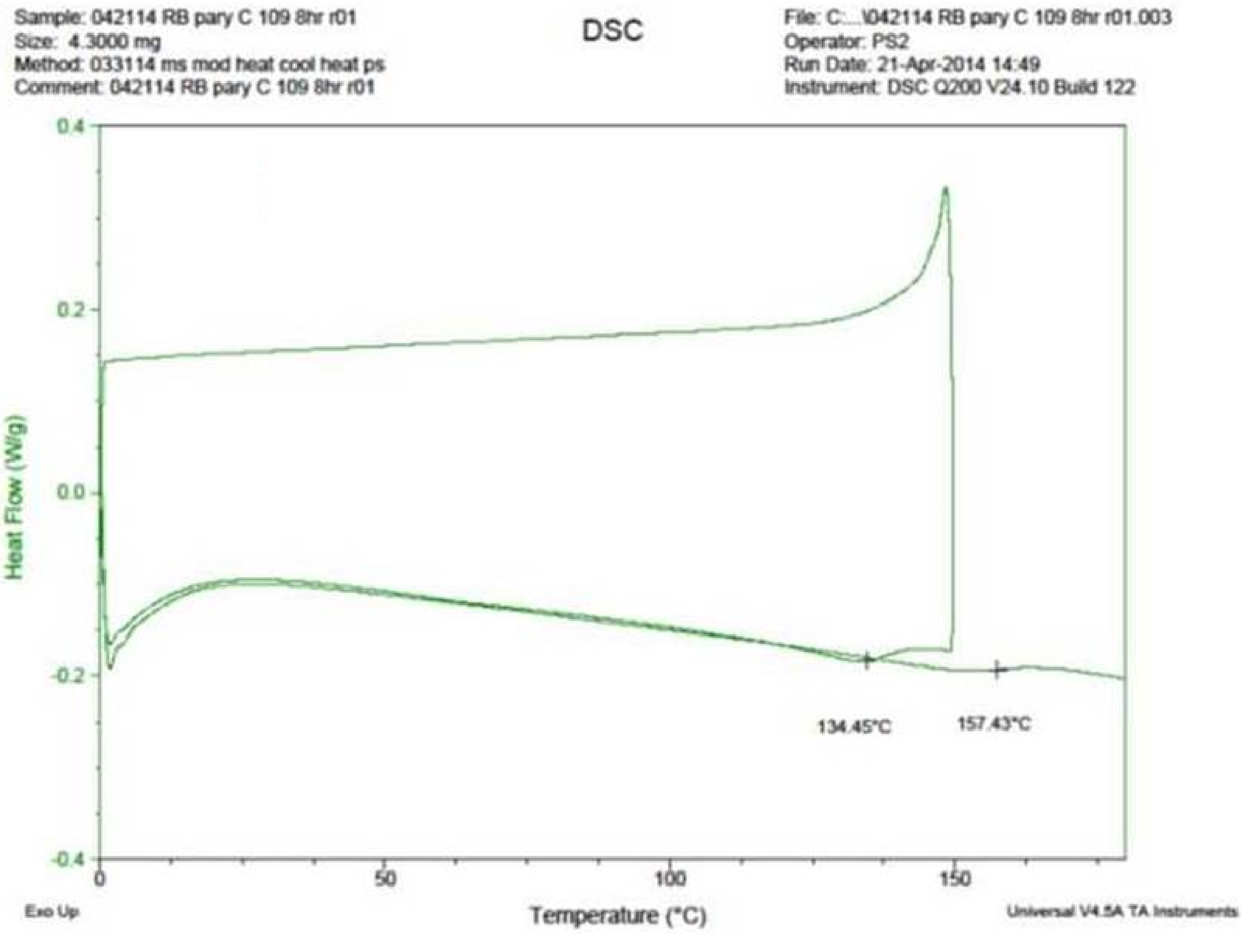
In the following pages, the DSC profiles of Parylene C film annealed at 109 °C for different time periods are depicted. The 109 °C, 1 hour annealed Parylene C revealed a thermal transition at ~128 °C (Figure 16 B) which increased to 134 °C and 138 °C after 8 and 26.5 hours of annealing times, relative to control film (Figure 16, C and D). The DSC profile of non-annealed Parylene C was the control and is included for comparison (Figure 16 A). Based on these data, the upper limit of annealed Parylene C film accelerated aging temperature was determined to be less than 128 °C and the preliminary annealing conditions were set at 109 °C for 1 hour.



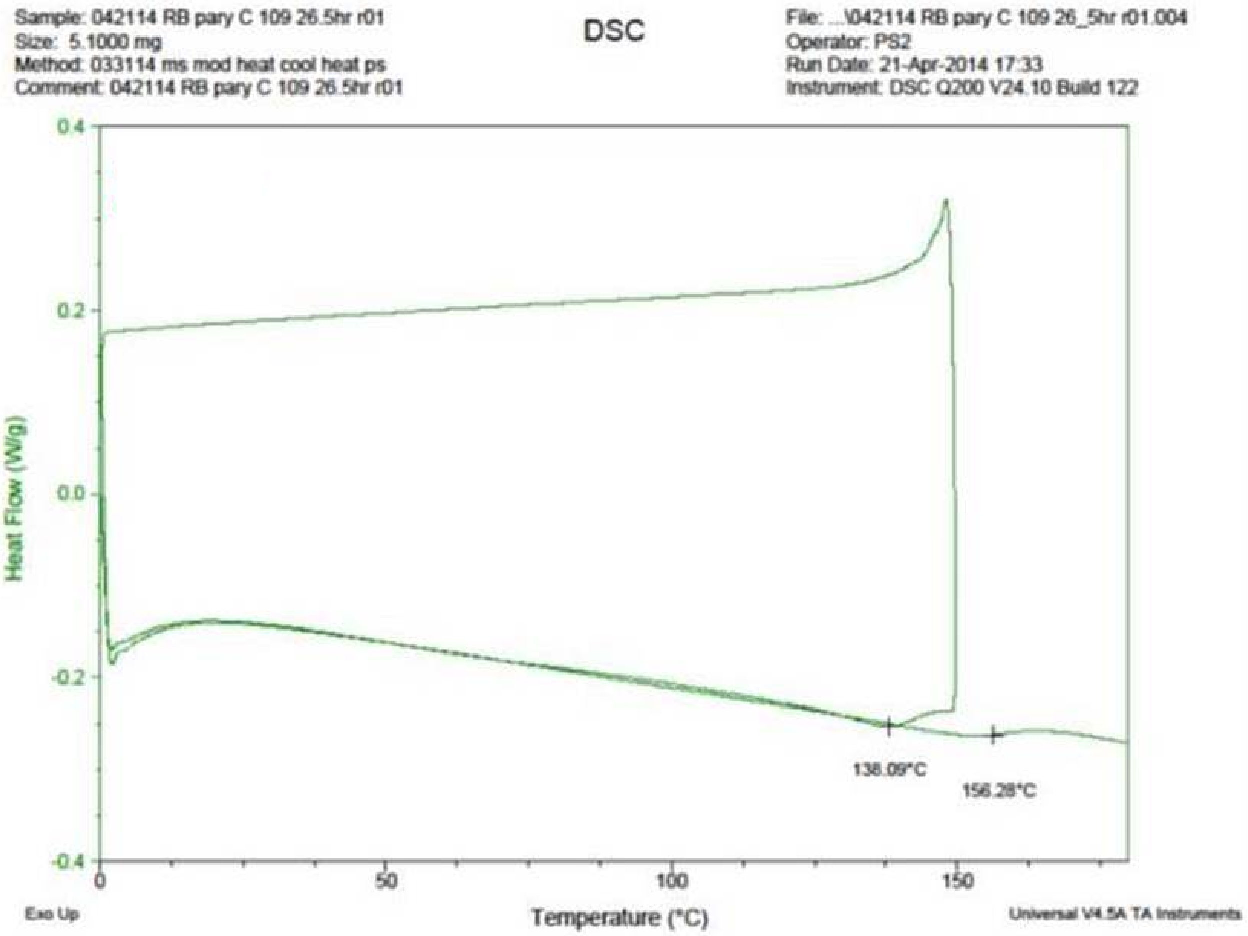
Punched sample CONTROL. Temp ramped up to 150 °C at 10 °C/min, then back to 0 °C, then up again.



Punched sample 109 °C/1 hour. Temp ramped to 150 °C at 10 °C/min, then back to 0 °C, then up again.



Punched sample 109 °C/8 hours. Temp ramped to 150 °C at 10 °C/min, then back to 0 °C, then up again.



Punched sample 109 °C/26.5 hours. Temp ramped up to 150 °C at 10 °C/min, then back to 0 °C, then up again.

Figure 16. DSC of Parylene C non-annealed (A) and annealed at 109 °C for 1 (B), 8 (C) and 26.5 hours (D)

The aging temperature upper limit established here is not unlike the temperature limits imposed during previous aging studies of Nylon 6.6[22, 23] or Kevlar[24].

3.7. Remarks on Parylene C Aging Relevant to Lifetime Predictions

The following remarks provide the context for an in-depth analysis of the current accelerated aging data and also provide thoughts for future experimental designs and conditions to make robust lifetime predictions for Parylene C. Consistent with the current work as well as with earlier polymer accelerated aging studies, Parylene C too is noted for its unsuitability to the Arrhenius approach for making lifetime predictions,[25] since the polymer has been observed to undergo degradation at much lower temperatures compared to theory.[25-28] Thin films of Parylenes N and C were reported to undergo thermal-oxidation at temperatures ranging from 68 °C and 125 °C.[25] There are conflicting reports on changes to film thickness,[20] length and adhesion strength (interestingly with Silquest A-174 promoter, as used in the present study) of

Parylenes depending on (annealing) temperature where the polymer folds into several lamellae before turning into spherulites as a consequence of transitioning from crystallization to glass transition temperatures.[29-32] It should also be noted that certain studies employed films annealed at 100 °C for up to 120 minutes,[31] much like the annealing conditions in this report. These data emphasize the need for careful optimization of the annealing time and temperature for reproducible Parylene C film fabrication. It also suggests that differently cast and differently annealed Parylenes can exhibit different thermo-mechanical behaviors.

UV-exposure was found to enhance oxidative degradation which could be suggested from the chemical structure of Parylene C (Figure 1). It is composed of C-C and C-H linkages with bond energies of 420 and 340 kJ/mol compared to the photon energy of 480 kJ/mol at 250 nm wavelength.[20] Parylene C films also undergo morphological changes at elevated temperatures. For example, an expansion of Parylene C film has been noted above 120 °C and has been attributed to the dominating oxidation effect.[11] Air-instability of Parylene C is also well documented to occur between 65 °C and 125 °C[14, 19] due to oxidative degradation beginning with C-C aliphatic linkages between the aromatic groups, which although not visible at first, can be confirmed by infrared (IR) spectroscopic analysis of the carbonyl (C=O) absorption band at 1695 cm^{-1}.[33] Furthermore, with extended aging in air at elevated temperatures, this absorption band intensifies and the progress of oxidation can actually be quantitated. This provides an additional tool, namely, the IR for monitoring Parylene C degradation during accelerated aging experiments.

Thermal-oxidative instabilities of Parylene C were minimized or even completely eliminated by removing air from the aging environment or by over-coating with inorganics such as SiO_2, SiN or Al_2O_3[33] (ceramic, fortuitously used in the present study; Figure 8 and Figure 9, although it must be conceded that testing conditions of these coated films needs to be improved). It should also be pointed out that certain properties of Parylene C might well be independent of tensile strength changes. Thus, dielectric strength was found to be retained by Parylene C despite its loss of tensile strength during accelerated aging experiments. It was concluded that such data serve only as a guide for considerations of Parylenes for a specific application and further that "questions of thermal endurance tend to have no clear-cut answers."[19]

Changes in the mechanical properties of Parylene C have also been noted between freshly deposited and annealed materials.[19] Specifically, annealing provides a stronger, more rigid and stabilized film compared to material that was not subjected to annealing. This has relevance to the annealed materials tested in this study (Figure 12 through 18). Another property impacting Parylene C lifetime and performance is of course film thickness which impacts the polymer's electrical properties such as breakdown voltage. The design team proposed 20 μm thickness for the Parylene C coatings, although the coupons tested here were of 28 μm thickness, a ~40% departure from specification. It is suggested that in future aging experiments, film thickness be rigorously standardized to 20 μm for consistency. Finally as pointed out above, coating of Parylene C to substrata such as ceramic (Al_2O_3) (Figure 8 and Figure 9), vastly (by 3-10 fold) improves the thermal stability compared to free standing Parylene C films alone.[12, 34, 35]

4. PLANNED STUDIES

4.1. UV-Vis Spectroscopy

Ultraviolet-Visible (UV-Vis) spectroscopy is a useful tool for quantification of color changes in a material as it ages. Since Parylene C film is initially colorless and transparent, it has very little absorption in the visible region. However, at wavelengths of about 280 nm, all Parylenes absorb quite strongly (Figure 19, A and B). These optical charts were reproduced directly from the Specialty Coating Systems (SCS) website, http://www.physics.rutgers.edu/~podzorov/parylene%20properties.pdf and from tufts.edu: http://engineering.tufts.edu/microfab/documents/Parylene.pdf which obtained it from http://www.scscookson.com/parylene/properties.cfm. As noted above, UV-induced oxidation of Parylene C results in the material yellowing which can also be observed using UV-Vis spectroscopy. Therefore, UV-Vis would be a very useful technique to explore the accelerated aging of Parylene C. This work, similar to the IR work proposed below, will be initiated when a more mature aging program is established.

4.2. Infrared Spectroscopy (IR)

Infrared (IR) spectroscopy is a powerful technique for the quantitation of chemical changes in a material as it ages, as the polymer undergoes oxidative degradation (Figure 19, C and D). The IR optical charts were also reproduced directly from Specialty Coating Systems (SCS) and tufts.edu as noted above: http://www.physics.rutgers.edu/~podzorov/parylene%20properties.pdf http://engineering.tufts.edu/microfab/documents/Parylene.pdf http://www.scscookson.com/parylene/properties.cfm. This technique is also useful for its sensitivity and non-destructive testing and evaluation (NDT&E) capabilities.[18, 36] Indeed, this technique has previously been applied to study the oxidative degradation of Parylene C.[33] The availability of reference spectra on the UV and IR properties of Parylene C (Figure 19, A through D) could be useful for the analysis of Parylene C films to measure changes in their spectroscopic properties consequent to aging. Once accelerating aging experimental and sample preparation conditions have been optimized, aged Parylene C samples can be supplied at various timed intervals for UV and IR analysis. This type of work is being performed with IR experts Kathy Alam and Laura Martin. The current research team has collaborated with IR investigators in the past for similar analysis on other types of polymeric materials.

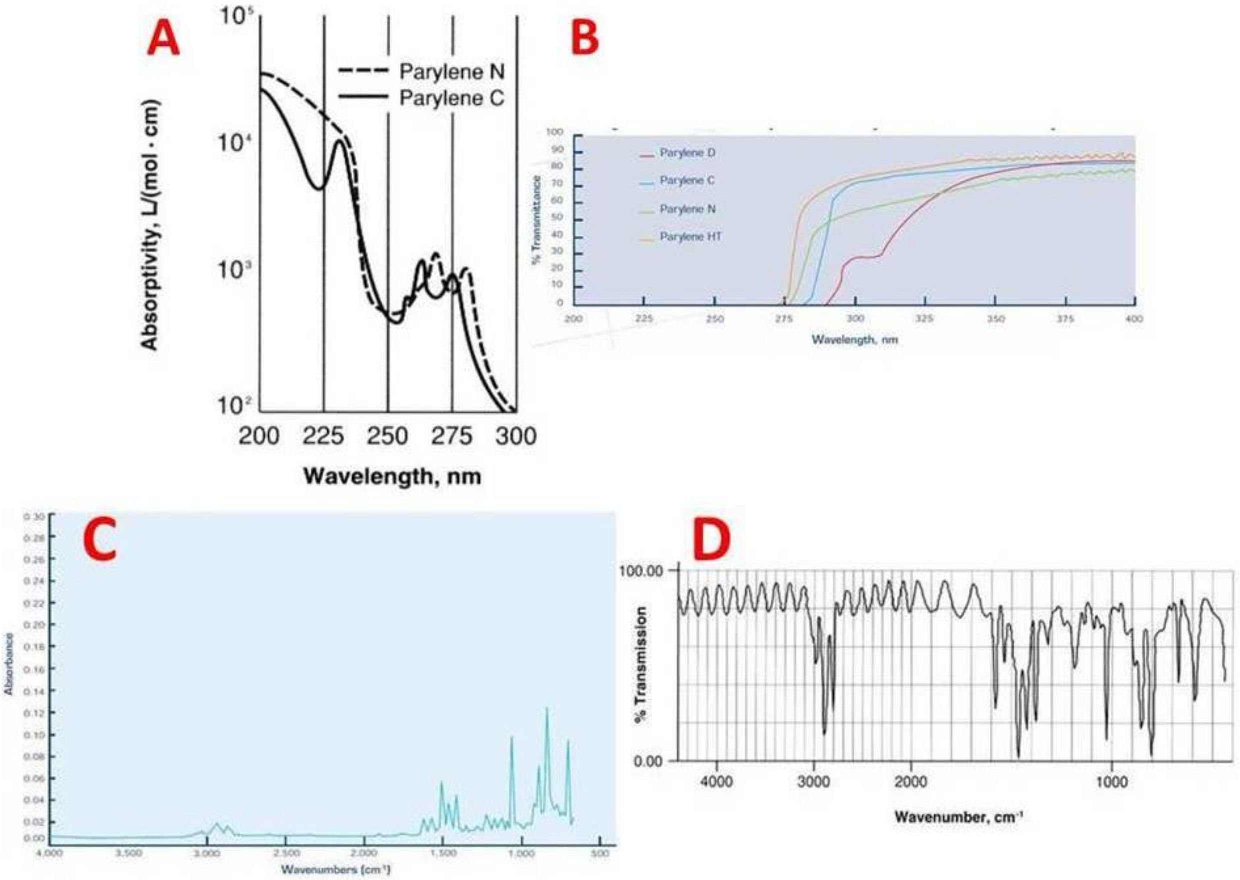


Figure 17. UV-Vis absorbance (top panel, A), transmission (top panel, B) and IR absorbance (bottom panel, A) and transmission (bottom panel, B) spectra of Parylenes. Note: all are copied directly from the cited websites in the text.

4.3. Volatiles Studies

Outgassing studies to understand the amount and nature of volatiles species were not performed in the present study although such work has provided valuable insights into degradation mechanisms of polymers such as Nylon 6.6[23] as well as any compatibility concerns with regard to the materials in the same environment as the Parylene C. This type of work has been performed numerous times in collaboration with the gas analysis expert James Hochrein and should be considered as part of future studies.

4.4. Performance Testing

As an ultimate proof-of-design, nothing can compare to actual performance testing of accelerated aged devices coated with Parylene C. Under this concept, devices coated with Parylene C would be subjected to accelerated aging at various temperatures and time durations and then submitted for performance analysis in the device. This work will be done in collaboration with Jerome Norris.

4.5. Accelerated Aging Films

A final note regarding the accelerated aging studies of Parylene C; test coupons of free standing Parylene C films (annealed and not annealed) are available. The availability of these continuously aging Parylene C coupons will also be useful in scoping studies of UV-Vis, IR and volatiles emission studies described above. These films will be tested for the aforementioned characteristics depending upon time and budget constraints.

5. “LESSONS LEARNED”

“Lessons learned” are summarized below from the present scoping study for designing future robust accelerated aging studies of Parylene C. In constructing this list of “lessons learned” both the present work as well as prior literature references on this topic have been consulted. *The following list is not in any order of priority*.

1) Data scatter and batch-to-batch differences make meaningful conclusions regarding lifetime difficult
2) There is a need for uniform samples based on tensile testing of standard width Parylene C films
3) Parylene C film thickness should be implemented and documented as a quality control metric to be 20 μm as desired by the design team specifications
4) Useful temperature range for future studies of Parylene C need to be definitely below 138 °C, with a particular emphasis upon the temperature range of 40 °C to 109 °C
5) “Necking” is a problem on Instron measurements which in turn led to data scatter
6) Should this be included in any future work, uniform, single-sided coatings of Parylene C upon Al_2O_3 (ceramic) surface need to be developed for enabling fine-tuned measurements. Literature precedence,[12, 34, 35] will be a guide to such efforts, since thermo-mechanical properties of free standing Parylene C and anchored Parylene C films will be significantly different
7) Further optimization of the annealing conditions (time, and especially temperature) is desirable in order to obtain reproducible batches of test coupons and to improve testing conditions and test outcomes
8) There emphatically needs to be more sample uniformity for testing at various temperatures over longer time frames in order to make robust lifetime predictions
9) Coupling tensile/mechanical testing with actual performance testing of devices coated with Parylene C and aged at different temperatures over various times will vastly improve lifetime predictions for this material
10) Additional tools such as UV-Vis, IR, DSC, volatiles emissions/outgassing, chemical analysis of aged specimens, delamination, discoloration, crazing, and optical microscopy will collectively contribute to improved lifetime predictions
11) Combining the adhesion stud pull test with thermo-mechanical aging studies will be overall beneficial to results-based outcome predictions
12) Based upon SME input, improving the quality of raw material (namely, di-*p*-xylylene), eliminating processing defects, and improving cleanliness during fabrication will also greatly improve data quality
13) Test coupon (sample) preparation is critical in determining thermo-mechanical properties of Parylene C films as seen from the present tests of annealed *versus* non-annealed, laser cut *versus* machine punched specimens. Thus, sample preparation technique needs to be standardized for data reproducibility
14) Future studies should consider aging in thermal only environment, that is in the exclusion of oxygen

6. REFERENCES

1. Wadhwani, S., *Parylene coatings and applications.* Paint and Coatings Industry, 2006. **October**: p. 32-44.
2. Hassler, C., T. Boretius, and T. Stieglitz, *Polymers for neural implants.* Journal of Polymer Science B: Polymer Physics, 2011. **49**: p. 18-33.
3. Nair, T.M., et al., *Dynamic mechanical analysis of ethylene-propylene-diene monomer rubber and styrene-butadiene rubber blends.* Journal of Applied Polymer Science, 2009. **112**: p. 72-81.
4. Joun, M., et al., *Finite element analysis of tensile testing with emphasis on necking.* Computational Materials Science, 2007. **41**: p. 63-69.
5. Li, W., et al., *Accelerated-lifetime soak testing of parylene packaging.* Polymer Preprints, 2008. **49**: p. 929-930.
6. Metzen, R.P.v. and T. Stieglitz, *The effects of annealing on mechanical, chemical, and physical properties and structural stability of parylene C.* Biomedical Microdevices, 2013. **15**: p. 727-735.
7. Goda, T., et al., *Photoinduced phospholipid grafting on parylene film: Advanced lubrication and antifouling properties.* Colloids Surfaces B, 2007. **54**: p. 67-73.
8. Kahouli, A., et al., *Ac-conductivity and dielectric relaxations above glass transition temperature for Parylene-C thin films.* Applied Physics A, 2012. **106**: p. 909-913.
9. Kahouli, A., et al., *Structural and dielectric study of parylene C thin films.* Applied Physics Letters, 2009. **94**: p. 152901.
10. Kim, B.J., et al., *Formation of three-dimensional parylene C structures via thermoforming.* Journal Micromechanics Microengineering, 2014. **24**: p. 065003.
11. Lin, J.C.H., et al., *Creep of parylene-C film.* Transducers' 11, 2011. **June 5-9**: p. 2698-2701.
12. Minnikanti, S., et al., *Lifetime assessment of atomic-layer-deposited Al2O3-Parylene C bilayer coating for neural interfaces using accelerated age testing and electrochemical characterization.* Acta Biomaterialia, 2014. **10**: p. 960-967.
13. Niegisch, W.D., *Xylylene Polymers.* Encyclopedia Polymer Science Technology, 1971. **15**: p. 98-124.
14. Noh, H.S., Y. Huang, and P.J. Hesketh, *Parylene micromolding, a rapid and low-cost fabrication method for parylene microchannel.* Sensors Actuators B, 2004. **102**: p. 78-85.
15. Senkevich, J. and S. Desu, *Morphology of poly(chloro-p-xylylene) CVD thin films.* Polymer, 1999. **40**: p. 5751-5759.
16. Youn, S.W., et al., *Control of parameters influencing the thermal imprints of parylene/silicon.* Japanese Journal of Applied Physics, 2007. **46**: p. 6363-6369.
17. Chiu, M.H. and E.J. Prenner, *Differential scanning calorimetry: An invaluable tool for a detailed thermodynamic characterization of macromolecules and their interactions.* Journal Pharmacy BioAllied Sciences, 2011. **3**: p. 39-59.
18. Grabmayer, K., et al., *Accelerated aging of polyethylene materials at high oxygen pressure characterized by photoluminescence spectroscopy and established aging characterization methods.* Polymer Degradation Stability, 2014. **109**: p. 40-49.
19. Beach, W.F., T.M. Austin, and R. Olson, *Parylene Coatings.* Electronics Materials Handbook, 1989. **1**: p. 789-800.

20. Fortin, J.B. and T.M. Lu, *Ultraviolet radiation induced degradation of poly-para-xylylene (parylene) thin films.* Thin Solid Films, 2001. **397**: p. 223-228.
21. Halvorson, B.G. and N. Kerr, *Effect of light on the properties of silk fabrics coated with Parylene C.* Studies Conservation, 1994. **39**: p. 45-56.
22. Bernstein, R., D. Derzon, and K.T. Gillen, *Nylon 6.6 accelerated aging studies: thermal-oxidative degradation and its interaction with hydrolysis.* Polymer Degradation Stability, 2004. **88**: p. 480-488.
23. Smith, J., et al., *Characterization of volatile Nylon 6.6 thermal-oxidative degradation products by selective isotopic labeling and cryo-GC/MS.* Journal American Association Mass Spectrometry, 2012. **23**: p. 1579-1592.
24. Bernstein, R., D. Derzon, and M.M. Shedd, *Kevlar humidity degradation: Oxidative versus inert atmosphere aging.* Polymer Preprints, 2005. **46**: p. 676-677.
25. Bilz, M. and D.W. Grattan, *The aging of parylene: difficulties with the Arrhenius approach.* 11th ICOM Triennial Meeting, 1996. **September 1-6**: p. 925-929.
26. Gratten, D.W. and M. Bilz, *The thermal aging of parylene and the effects of antioxidant.* Studies Conservation, 1991. **36**: p. 44-52.
27. Li, P.Y., et al., *A wireless activated parylene electrothermal valve for mapping brain function in freely moving subjects.* Solid-State Sensors, Actuators, and Microsystems Workshop, 2008. **June 1-5**: p. 32-35.
28. Li, P.Y., et al., *A parylene MEMS electrothermal valve.* Journal Microelectromechanical Systems, 2009. **18**: p. 1184-1197.
29. Hsu, J.M., et al., *Effect of thermal and deposition processes on surface morphology, crystallinity, and adhesion of Parylene C.* Sensors and Materials, 2008. **20**: p. 87-102.
30. Huang, H.L., Y.G. Xu, and H.Y. Low, *Effects of film thickness on moisture sorption, glass transition temperature and morphology of poly(chloro-p-xylylene) film.* Polymer, 2005. **46**: p. 5945-5955.
31. Lin, J.C.H., *MEMS for glaucoma.* Ph.D. Thesis, 2012. **Chapter 5**: p. 145-286.
32. Wu, P.K., et al., *Surface reaction and stability of Parylene N and F thin films at elevated temperatures.* Journal Electronic Materials, 1995. **24**: p. 53-58.
33. Licari, J.J., *Coating materials for electronic applications.* Coating materials for electronic applications, 2003. **Chapter 2**: p. 65-200.
34. Xie, X., et al., *Plasma-assisted atomic layer deposition of Al2O3 and Parylene C bilayer encapsulation for chronic implantable electronics.* Applied Physics Letters, 2012. **101**: p. 093702.
35. Xie, X., et al., *Long-term reliability of Al2O3 and Parylene C bilayer encapsulated Utah electrode array based neural interfaces for chronic implantation.* Journal of Neural Engineering, 2014. **11**: p. 026016.
36. Davies, P. and G. Evrard, *Accelerated aging of polyurethanes for marine applications.* Polymer Degradation Stability, 2007. **92**: p. 1455-1464.

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