



Chemical Resistance of Antero 800NA



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Antero™ 800NA is a Stratasys-proprietary polyetherketoneketone (PEKK) material that's part of the polyaryletherketone (PAEK) family. It's a semi-crystalline, engineering-grade thermoplastic resin known for its strength, high temperature tolerance and excellent chemical resistance.

Chemical Resistance of Antero 800NA

The objective of this white paper is to document the results of experiments to characterize [Antero 800NA's](#) chemical-resistant properties when exposed to typical aviation industry chemicals. Specifically, the study looked at what chemicals had a detrimental effect and to what extent. A specific group of chemicals that would cause the most harmful effects were chosen. The selection was based on PAEK manufacturer literature and the prevalence of these chemicals in the aviation industry. The chemical reagents are:

- Methyl Ethyl Ketone (Butanone) – organic solvent
- Toluene – aromatic hydrocarbon solvent
- Dichloromethane (DCM) – geminal organic solvent
- Ethyl Acetate – organic solvent
- Skydrol 500B-4 – aviation hydraulic fluid
- Jet-A – aviation fuel

The results showed lower chemical resistance to halogenated solvents for the non-annealed material. However, Antero 800NA exhibited good to excellent resistance for the remaining chemicals prior to annealing. Additionally, all annealed specimens exhibited excellent chemical resistance to the gamut of chemicals tested. Based on these results, Antero 800NA demonstrates a competitive advantage among aerospace materials.

Methods

Test specimens were generated using [FDM® technology](#) on one [Fortus 450mc™ 3D Printer](#). A T20D tip was used to achieve a 0.010" bead thickness. The test specimens were generated using identical parameters and software versions over a two-week period. Mechanical and dimensional specimens were printed using four separate spools from the same lot of material and tracked throughout the experiment.

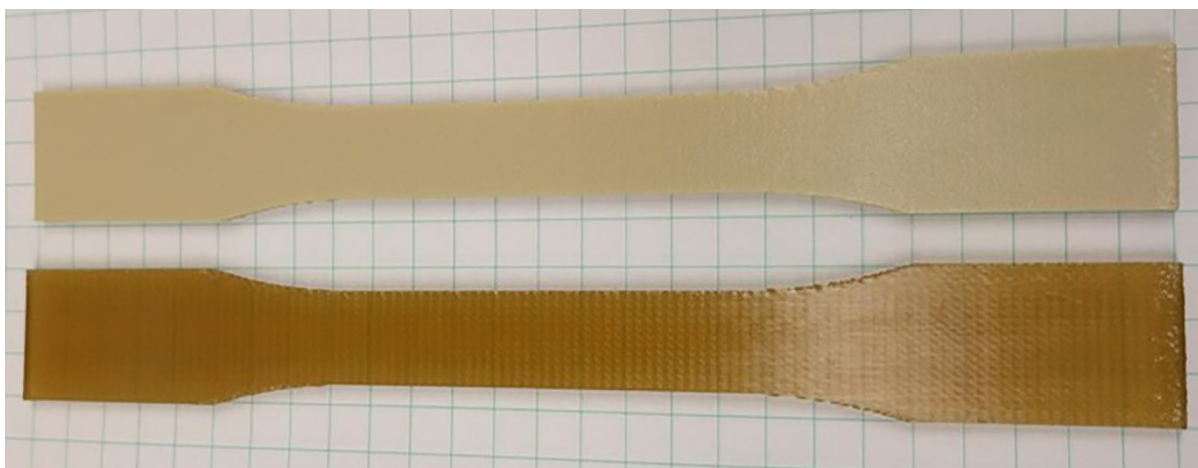


Figure 1: Annealed (top) vs. non-annealed tensile specimens.

Chemical Resistance of Antero 800NA

The specimens were separated into annealed vs. non-annealed groups after building in both on-edge (XZ) and upright (ZX) orientations. They were immersed in the previously mentioned chemicals for 168 hours per ASTM D543. After immersion, the specimens were evaluated for visual and dimensional changes. They were also mechanically tested for tensile and flexural variation. Additionally, another group of test specimens was exposed to the same chemicals under a 1% strain during the 168-hour chemical exposure.

Unstrained Chemical Resistance

For these tests, the specimens were not subjected to strain during chemical exposure. A simultaneous test comparison was conducted on annealed versus non-annealed sample parts. See the Annealing Protocols section in the appendix of this paper.

Test specimens were immersed in their respective solvents for seven days in sealed, non-reactive containers under standard controlled laboratory conditions. The specimens were separated from each other and lightly agitated every 24 hours per ASTM D543.

After the solvent bath immersion, the samples were removed and dried in the hood for up to two minutes, depending on the solvent, before mechanical testing. Tensile and flexural testing was conducted per ASTM D638 and ASTM D790 respectively. The Skydrol specimens were first cleaned with a cloth before drying to remove as much hydraulic fluid as possible from the surface prior to testing.

Dimensional characterization was conducted with a balance and a set of calibrated calipers, both before and after chemical exposure. The same exposure protocols as outlined for the mechanical specimens were used. Laboratory conditions were kept constant throughout testing.

Strained Chemical Resistance

A variable strain fixture was fabricated and a representative specimen was tested for 24 hours prior to selecting strain values. This test determined how much strain (0.5, 1.0, 1.5, and 2.0% strain) a specimen could endure while exposed to the solvents.



Figure 2: Variable Strain Fixture - shows the extent of deformation under various strains with chemical exposure. Some samples broke above 1% strain with certain chemicals.

Chemical Resistance of Antero 800NA

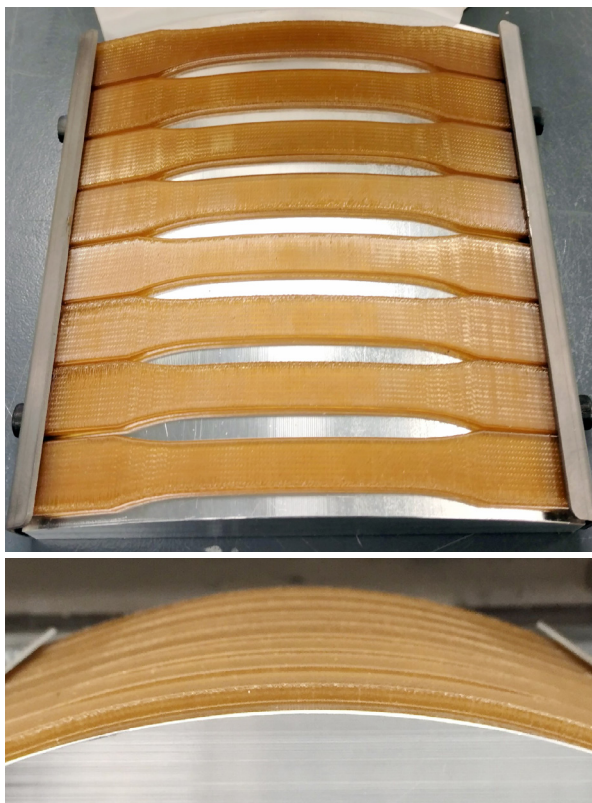


Figure 3: Non-annealed Antero 800NA ZX tensile samples in 1% strain fixture pre-exposure.

A 1.0% strain fixture was fabricated that could withstand repeated and various chemical exposures. This fixture was used to test tensile variability and to make a direct visual comparison between Antero 800NA and [ULTEM™ 9085 resin](#) after strained chemical exposure.

Strain fixtures were fabricated from stainless steel in accordance with ASTM D543 to achieve a consistent and accurate 1% strain along the length of the specimens' test area. Extra room was given on each fixture to account for extra specimens needed for outliers during testing.

A soaked cloth was used to expose the strained specimens to the various chemicals throughout testing, per ASTM D543. Saturated fixtures were placed in airtight non-reactive containers to prevent evaporation of chemicals during exposure.

The cloths were examined regularly and saturated as needed throughout the 168-hour exposure.

Visual comparison to ULTEM 9085 resin was conducted for each of the chemicals with simultaneous strained exposure.

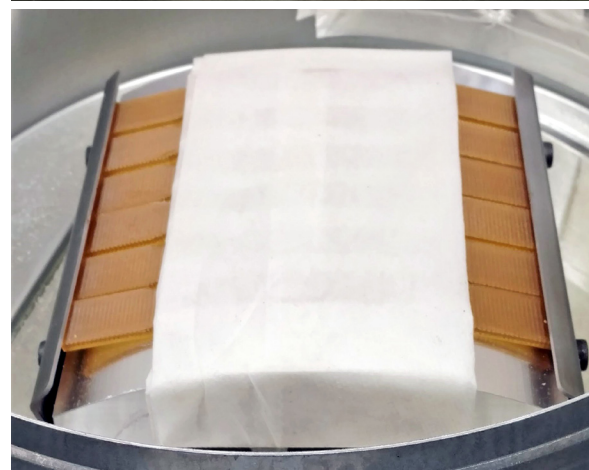


Figure 4: Tensile 1% strain test set-up - cloth in position across test area (annealed - top, non-annealed - bottom).

Chemical Resistance of Antero 800NA

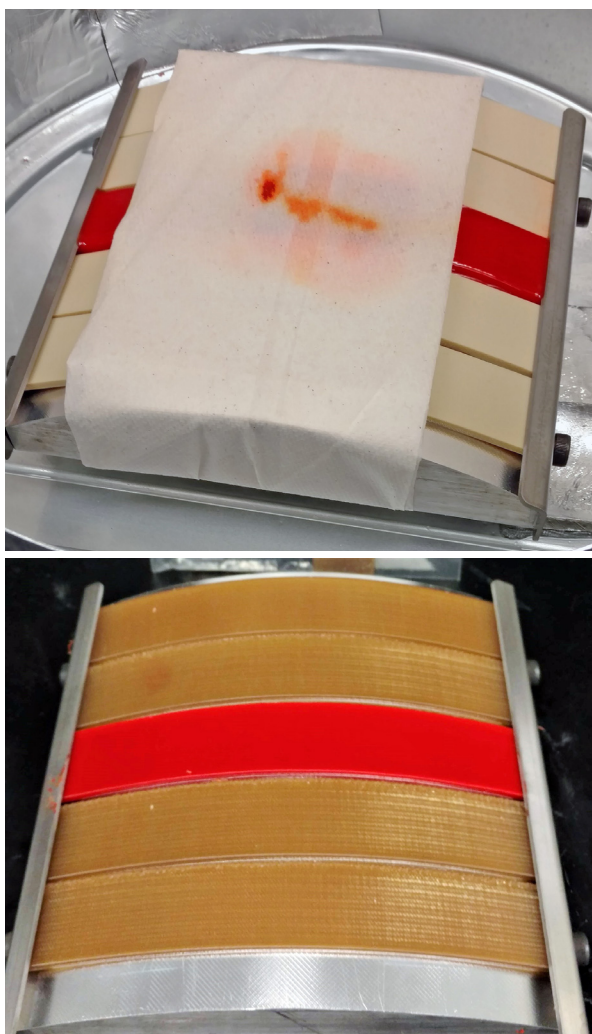


Figure 5: Visual testing Antero 800NA vs. ULTEM 9085 (orange) set-up (annealed – top, non-annealed – bottom).

Results

Overall, Antero 800NA exhibited very good chemical resistance to most chemicals except for Dichloromethane (DCM). The material's reaction to DCM was especially significant, resulting in an immediate color change, as well as significant deformation and decrease in mechanical properties over the duration of the submersion. However, once the material was annealed, its exposure to DCM did not result in any change in properties or appearance. Likewise, with the other chemicals tested, annealing negated any adverse

effects that the exposure to each of the chemicals may have caused.

Unstrained Chemical Resistance

DCM, being halogenated, has an immediate and severe effect on non-annealed Antero 800NA. Once crystallinity is augmented by annealing, the material's chemical resistance is greatly improved. Non-annealed Antero 800NA exhibited excellent chemical resistance to the other chemicals tested.

- Tensile strength improved, or remained comparable, for both orientations after annealing.
- Elongation-at-break improved or remained comparable for both orientations after annealing. The exception was Jet A and Skydrol, which seemed to have a plasticizing effect on the material, making it more pliable/ductile.
- With the exception of DCM, the tensile modulus remained the same throughout testing, regardless of chemical or annealing.

Chemical Resistance of Antero 800NA

Change in Dimension and Weight - Non-Annealed Antero 800NA (ASTM D543)

	Print Orientation	Weight Change (%)	Length Change (%)	Width Change (%)	Thickness Change (%)
Skydrol 500B-4	Horizontal	1.7%	-0.1%	0.3%	1.2%
	Vertical	0.4%	0.1%	0.1%	1.5%
Jet-A	Horizontal	1.2%	0.0%	0.0%	0.5%
	Vertical	0.2%	0.1%	0.1%	3.7%
MEK	Horizontal	0.4%	0.1%	0.2%	-0.7%
	Vertical	0.1%	0.0%	0.0%	0.5%
Toluene	Horizontal	0.7%	0.0%	0.0%	0.7%
	Vertical	0.2%	0.0%	-0.1%	2.8%
Dichloromethane	Horizontal	43.0%	1.8%	3.3%	30.6%
	Vertical	44.7%	1.1%	4.0%	29.4%
Ethyl Acetate	Horizontal	0.4%	0.1%	0.3%	1.0%
	Vertical	0.1%	-0.1%	0.2%	1.3%

Change in Dimension and Weight - Annealed Antero 800NA (ASTM D543)

	Print Orientation	Weight Change (%)	Length Change (%)	Width Change (%)	Thickness Change (%)
Skydrol 500B-4	Horizontal	1.6%	0.0%	0.1%	0.8%
	Vertical	0.4%	-0.1%	0.0%	0.6%
Jet-A	Horizontal	1.1%	0.0%	0.2%	-0.5%
	Vertical	0.2%	0.1%	0.1%	-0.2%
MEK	Horizontal	0.2%	0.1%	0.1%	1.0%
	Vertical	0.2%	0.0%	0.1%	-0.8%
Toluene	Horizontal	0.7%	0.0%	-0.8%	0.2%
	Vertical	0.1%	0.2%	0.0%	0.0%
Dichloromethane	Horizontal	0.4%	0.0%	0.0%	-0.3%
	Vertical	0.6%	0.0%	0.1%	-0.3%
Ethyl Acetate	Horizontal	0.5%	0.0%	0.2%	0.7%
	Vertical	0.2%	0.1%	0.0%	1.8%

Apart from DCM on non-annealed samples, the chemical reagents had little to no effect on the dimensional weight change during exposure. Annealing the samples negated any of the chemical susceptibility the samples previously showed.

Chemical Resistance of Antero 800NA

Change in Mechanical Properties - 168 hour Chemical Exposure (ASTM D543)

	Reagent	Non-Annealed XZ	Non-Annealed ZX	Annealed XZ	Annealed ZX
Tensile Strength	Dichloromethane	-88%	-81%	-15%	1%
	Ethyl Acetate	-20%	-4%	-19%	-7%
	Jet A	-14%	-3%	11%	-1%
	Methyl Ethyl Ketone	-17%	-7%	-16%	-7%
	Skydrol	-5%	-16%	19%	-9%
	Toluene	17%	-11%	-14%	-9%
% Elongation @ break	Dichloromethane	1,135%	2,264%	-11%	0%
	Ethyl Acetate	9%	-1%	3%	-5%
	Jet A	25%	-1%	45%	2%
	Methyl Ethyl Ketone	21%	-2%	16%	-2%
	Skydrol	24%	26%	48%	-7%
	Toluene	8%	-7%	12%	-7%
Tensile Modulus	Dichloromethane	-92%	-93%	-1%	-1%
	Ethyl Acetate	-3%	-4%	-3%	-1%
	Jet A	-3%	-3%	-4%	-3%
	Methyl Ethyl Ketone	-2%	-6%	-4%	-4%
	Skydrol	-3%	-4%	-1%	-4%
	Toluene	-1%	-4%	-3%	-3%

Flexural property changes followed the same trends as the tensile testing. The only chemical that had a significant effect on non-annealed test specimens was Dichloromethane. Annealing the flex samples negated the adverse effects of the DCM.

Chemical Resistance of Antero 800NA

Change in Flexural Properties -1-Week Chemical Exposure (ASTM D543)

	Reagent	Non-Annealed XZ	Non-Annealed ZX	Annealed XZ	Annealed ZX
Flexural Strength	Dichloromethane	-91%	-88%	-6%	-7%
	Ethyl Acetate	2%	-20%	-20%	-1%
	Jet A	0%	3%	-3%	-1%
	Methyl Ethyl Ketone	2%	-15%	-17%	-2%
	Skydrol	4%	-5%	-2%	-4%
	Toluene	-3%	-19%	-10%	-1%
Flexural Modulus	Dichloromethane	-91%	-92%	3%	-2%
	Ethyl Acetate	2%	-4%	0%	0%
	Jet A	3%	-6%	1%	-1%
	Methyl Ethyl Ketone	3%	-11%	4%	1%
	Skydrol	6%	-5%	3%	5%
	Toluene	5%	-7%	2%	9%

Strained Chemical Resistance

Introducing a 1% strain during chemical exposure simulates how Antero 800NA parts will react to simultaneous exposure to environmental stress and chemicals. The strain exacerbated some of the tensile properties when compared to the unstrained test specimens.

- Tensile strength improved for the XZ specimens between non-annealed and annealed; but for the ZX specimens, the UTS decreased significantly after annealing the samples, highlighting the embrittlement caused by annealing.
- Elongation for the strained specimens was more variable when compared to the unstrained, but roughly followed the same trends as the unstrained exposures.
- Tensile modulus was also more variable, but didn't follow the same trends for reagents like DCM and Skydrol.

Chemical Resistance of Antero 800NA

Change in Mechanical Properties - 1-Week Chemical Exposure under 1% Strain (ASTM D543)

	Reagent	Non-Annealed XZ	Non-Annealed ZX	Annealed XZ	Annealed ZX
Flexural Strength	Dichloromethane	-91%	-72%	-2%	-69%
	Ethyl Acetate	-32%	-15%	-8%	5%
	Jet A	-8%	28%	0%	11%
	Methyl Ethyl Ketone	-50%	-23%	-35%	-22%
	Skydrol	-19%	17%	2%	-4%
	Toluene	-34%	-25%	-20%	6%
Flexural Modulus	Dichloromethane	567%	1,049%	35%	-74%
	Ethyl Acetate	44%	29%	28%	23%
	Jet A	21%	56%	50%	15%
	Methyl Ethyl Ketone	-12%	11%	7%	15%
	Skydrol	13%	44%	25%	29%
	Toluene	48%	-7%	33%	22%
Tensile Modulus	Dichloromethane	-94%	-86%	83%	26%
	Ethyl Acetate	21%	33%	3%	0%
	Jet A	-5%	-8%	-7%	-7%
	Methyl Ethyl Ketone	24%	7%	-11%	-1%
	Skydrol	-7%	10%	-5%	-22%
	Toluene	35%	69%	4%	-6%

Chemical Resistance of Antero 800NA

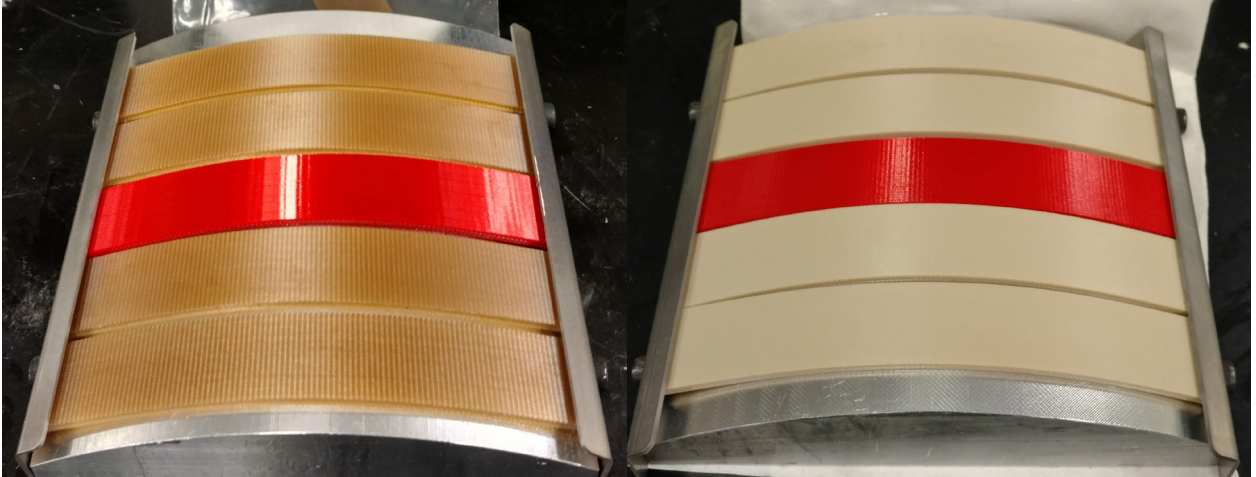


Figure 6: Visual specimens in fixture prior to chemical exposure (non-annealed – left; annealed – right) (orange = ULTEM 9085 resin)



Figure 7: Non-annealed (left) and annealed (right) specimens after exposure to Skydrol (orange = ULTEM 9085 resin)

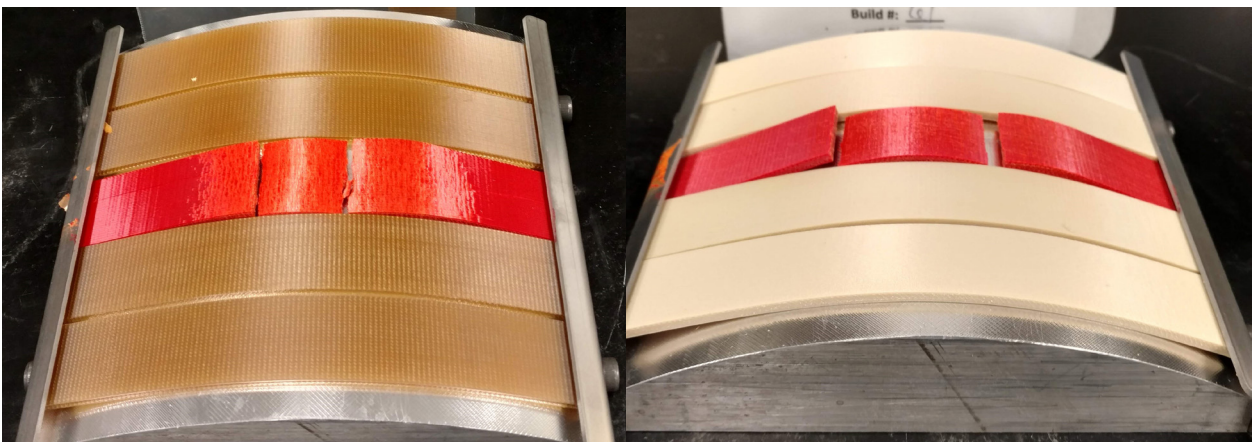


Figure 8: Non-annealed (left) and annealed (right) specimens after exposure to Ethyl Acetate (orange = ULTEM 9085 resin)

Chemical Resistance of Antero 800NA

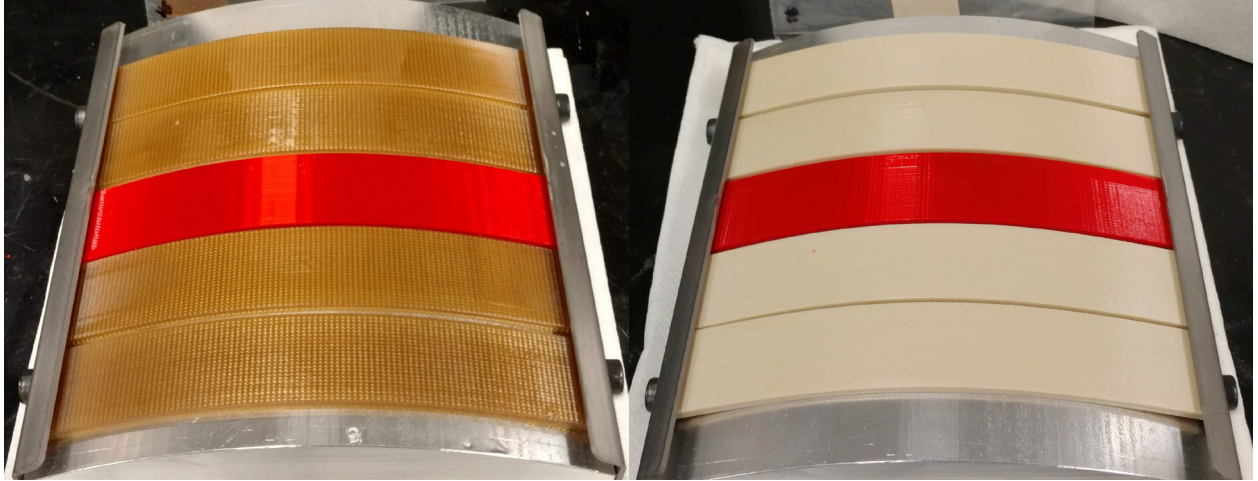


Figure 9: Non-annealed (left) and annealed (right) specimens after exposure to Jet A (orange = ULTEM 9085 resin)

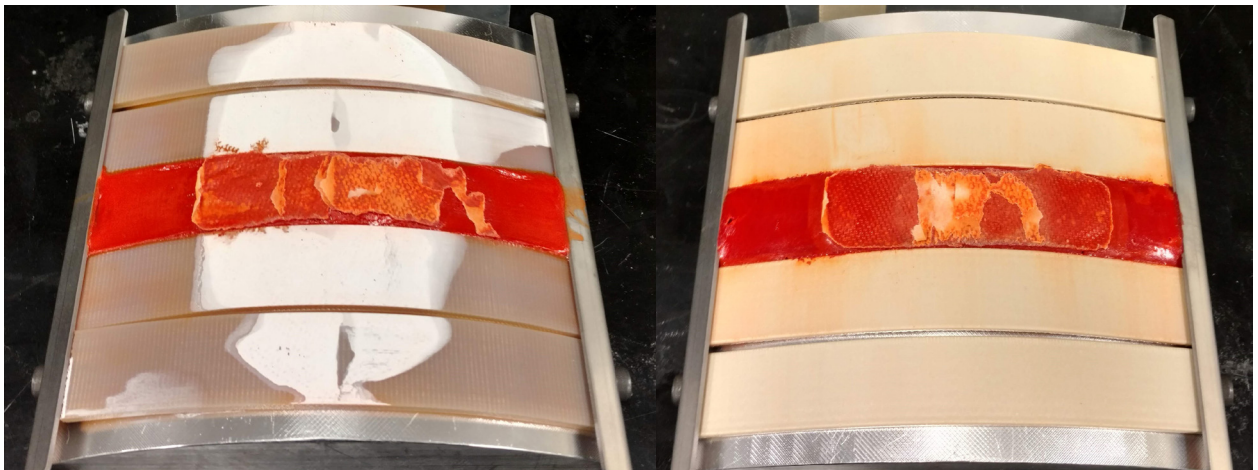


Figure 10: Non-annealed (left) and annealed (right) specimens after exposure to Dichloromethane (orange = ULTEM 9085 resin)



Figure 11: Non-annealed (left) and annealed (right) specimens after exposure to Toluene (orange = ULTEM 9085 resin)

Chemical Resistance of Antero 800NA

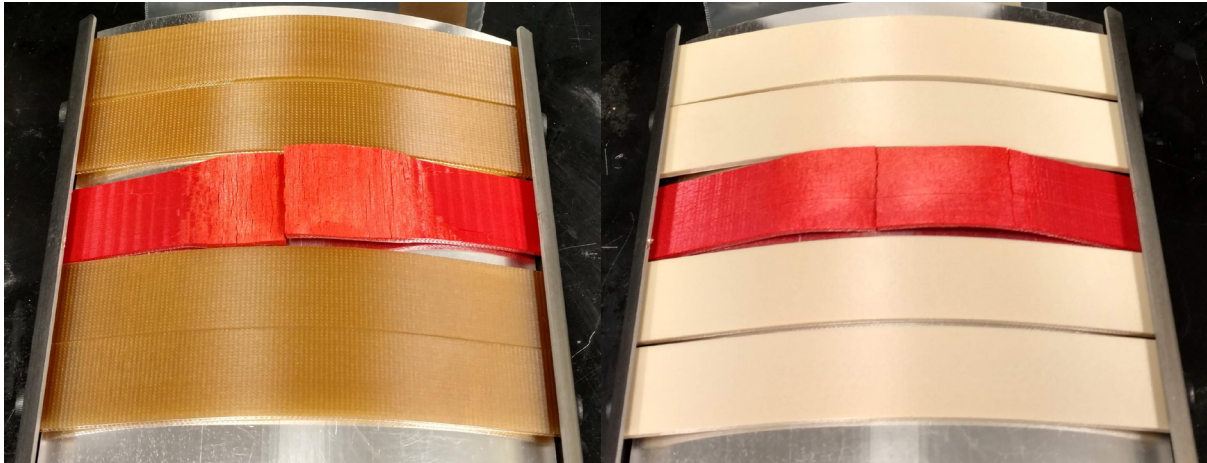


Figure 12: Non-annealed (left) and annealed (right) specimens after exposure to MEK (orange = ULTEM 9085 resin)

Discussion

Overall, halogenated chemicals appeared to have a more significant effect on Antero 800NA than any other chemical tested within the bounds of this experiment. However, annealing resulted in an augmented chemical resistance for substances like Dichloromethane, as well as other chemicals traditionally destructive toward plastics. This enhanced chemical resistance from annealing resulted in a more robust material, and gives customers the ability to choose the level of needed chemical resistance based on the application.

Exposure under strained conditions increased the variability of the results and diminished annealing's effectiveness on the chemical resistance.

Each application is unique in the environment and conditions to which the material will be exposed. However, the data shows that Antero 800NA exhibits exceptional resistance to chemicals typically used in the aerospace, oil and gas, and automotive industries and will withstand exposure to those chemicals while maintaining properties.

References

- ASTM D543: Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents
- ASTM D638: Standard Test Methods for Tensile Properties of Plastics
- ASTM D790: Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials

Appendix

Annealing Protocol

Note: See Antero 800NA data sheet for un-annealed vs. annealed material properties.

Annealing is the process of using heat to relieve residual stress in material after processing. This allows recrystallization to occur, affecting properties such as strength, hardness, ductility and chemical resistance.

Chemical Resistance of Antero 800NA

Process Overview

1. Set the oven to 392 °F (200 °C) and allow the oven to reach this temperature while completing the steps below.



Figure 1: Annealing can be completed in standard industrial ovens.

2. Arrange samples to be annealed in a half-full container of fine sand so they are not touching. (Salt can be used as an alternate to sand, and by soaking the samples in water after annealing the salt will dissolve, removing all of the packing media from the samples.) Cover them so they are completely submerged in the sand. The sand will prevent the specimens from moving in an uncontrolled manner and warping or deforming as the temperature exceeds the recrystallization point. It also lets the specimens anneal slowly, which prevents any undue stresses associated with rapid heating/cooling.



Figure 2: Samples should be placed in a sand bath to prevent deformation while being annealed.

Chemical Resistance of Antero 800NA

3. Place the sand bath containers in the oven. Allow the oven to reach the set point temperature of 392 °F (200 °C) after inserting the samples (when the oven is opened it will lose heat and will need time to get back up to the set point). Remove the samples three hours AFTER the oven reached the set point.
4. Once removed from the oven, allow the specimens to cool to ambient temperature before removing them from the sand bath. Note: The sand will retain the heat for a period of time. One hour is typically the minimum amount of time for the sand to cool.
5. After cooling, remove the samples from the sand. Clean off as much sand as possible into the container. The remaining sand can be washed off with water or removed with other appropriate means if water cannot be used.



Figure 4: Samples in the oven.

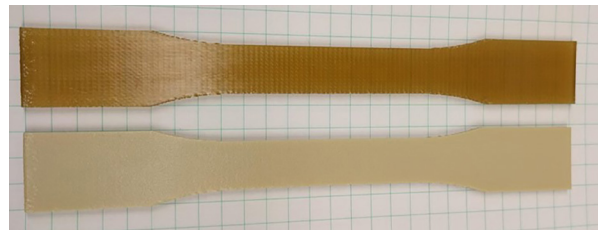


Figure 5: Un-annealed (top) vs. annealed (bottom) PEKK Specimens.

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