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Retention: *Permanent*

Next Generation Solvent – Materials Compatibility with Polymer Components within Modular Caustic- Side Solvent Extraction Unit (Final Report)

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EXECUTIVE SUMMARY

The Office of Waste Processing, within the Office of Technology Innovation and Development, is funding the development of an enhanced solvent for deployment at the Savannah River Site for removal of cesium from High Level Waste. The technical effort is collaboration between Oak Ridge National Laboratory (ORNL), Savannah River National Laboratory (SRNL), and Argonne National Laboratory. The first deployment target for the technology is within the Modular Caustic-Side Solvent Extraction Unit (MCU).^a Deployment of a new chemical within an existing facility requires verification that the chemical components are compatible with the installed equipment. In the instance of a new organic solvent, the primary focus is on compatibility of the solvent with organic polymers used in the facility. This report provides the data from exposing these polymers to the Next Generation Solvent (NGS). The test was conducted over six months.

An assessment of the dimensional stability of polymers present in MCU (i.e., PEEK, Grafoil, Tefzel and Isolast) in the modified NGS (where the concentration of LIX[®]79 and MaxCalix was varied systematically) showed that LIX[®]79 selectively affected Tefzel and its different grades (by an increase in size and lowering its density). The copolymer structure of Tefzel and possibly its porosity allows for the easier diffusion of LIX[®]79. Tefzel is used as the seat material in some of the valves at MCU. Long term exposure to LIX[®]79, may make the valves hard to operate over time due to the seat material (Tefzel) increasing in size. However, since the physical changes of Tefzel in the improved solvent are comparable to the changes in the CSSX baseline solvent, no design changes are needed with respect to the Tefzel seating material. PEEK, Grafoil and Isolast were not affected by LIX[®]79 and MaxCalix within six months of exposure. The initial rapid weight gain observed in every polymer is assigned to the finite and limited uptake of Isopar[®] L / Modifier by the polymers probably due to the polymers porosity and rough surfaces. Spectroscopic data on the organic liquid and the polymer surfaces showed no preferential adsorption of any component in the NGS to the polymers and with the exception of CPVC, no leachate was observed in the NGS from any of the polymers studied.

The testing shows no major concerns for compatibility over the short duration of these tests but does indicate that longer duration exposure studies are warranted, especially for Tefzel. However, the physical changes experienced by Tefzel in the improved solvent were comparable to the physical changes obtained when Tefzel is placed in CSSX baseline solvent. Therefore, there is no effect of the improved solvent beyond those observed in CSSX baseline solvent.

^a Subsequent to the start of this work, the Department of Energy made a programmatic decision to defer deployment of the NGS in MCU in favor of direct deployment in Salt Waste Processing Facility. However, the potential exists that NGS may still be deployed in MCU at a later date. Since some of the materials of construction are similar for the two facilities, the data in this report is also relevant to the newly selected deployment option.

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1.0 Introduction

The Modular Caustic Side Solvent Extraction Unit (MCU) has processed more than one million gallons of supernate waste (as of this writing over 1.8 million gallons have been processed) since 2008.¹ Operations have proven successful thanks to the resilience, reliability, and repeatable performance of the Caustic Side Solvent Extraction (CSSX) process. This same process will be deployed in the Salt Waste Processing Facility (SWPF), currently under construction. Since then, researchers at the Oak Ridge National Lab (ORNL), Savannah River National Laboratory (SRNL), and Argonne National Lab have been developing a next generation solvent (or “improved solvent”) and stripping solution that improves both cesium extraction from supernate and stripping from the current solvent. The development also took into consideration lessons learned from the three years of MCU operation.

In 2010, laboratory scale testing of the improved solvent has demonstrated excellent achievement of performance goals.^{2,3} Those encouraging results are the bases for larger scale test currently conducted at the Savannah River Site which completed in September 2011. Performance verification tests examined mass transfer, hydraulic behavior (such as pumping, phase disengagement, phase carryover), and solvent coalescing. The results from the scale-up test will aid in validating the laboratory scale results as a forecaster for MCU and SWPF operations.

To fully implement the improved solvent at the MCU or SWPF, additional knowledge is needed on the chemical and physical compatibility of the improved solvent with the currently used non-metallic components. These non-metallic components serve a crucial role in sealing and isolating the solvent and solutions from the environment while allowing the flexibility for removing, replacing, and maintaining the different metallic components. When the existing solvent is replaced with the improved solvent in the MCU process, existing non-metallic components will experience a slightly different chemical environment that could lead to a shorter lifetime (that may lead to leaks or binding due to swelling) or duty cycle (or absorption of a key component like the extractant MaxCalix^Σ). For instance, amines are known to degrade polymer performance, and the new suppressor in this solvent, LIX[®]79, may be more reactive in this regards than the trioctylamine in the current solvent formulation.[®] To understand if the chemistry change will affect the gaskets, O-rings and polymer components in MCU, SRNL personnel conducted exposure tests between as received polymers (those currently used at MCU) and the new improved solvent. This report summarizes the findings from this test. This work is a natural expansion of the material compatibility outlined in the original task plan.³

2.0 Experimental Procedure

The solvent systems investigated are shown in Table 1. As shown in Table 1, the new improved solvent has Modifier^f and Isopar[®] L as in the baseline solvent but it also includes MaxCalix and LIX[®]79. The latter two new chemicals may impart more physical changes to the existing polymers used in the MCU process.

^Σ The extractant, MaxCalix, stands for 1,3-*alt*-25,27-Bis(3,7-dimethyloctyloxy)calix[4]arenebenzocrown-6

[®] The suppressor is a derivatized guanidine, N, N'-cyclohexyl, N''-isotridecyl guanidine.

^f Modifier stands for 1-(2,2,3,3-Tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol

The polymers tested – known to be used in MCU and were identified as being the most likely or prominent – are shown in Table 2. With the exception of PEEK (polyether ether ketone) and Grafoil[®], Table 2 shows most polymers used at MCU have fluoride functional groups. Fluorides and aromatic rings impart polymers with chemical and thermal resistance. Despite the fact that the Modifier contains fluorides and alcohol groups that could make the Modifier attractive to the perfluoroelastomers, no detrimental effects have been reported to this date. Polymers were not pretreated (e.g., humidity treated as recommended by some ASTM procedures) nor were they cleaned; they were used as received.

Gaskets and sheets were cut in 2 cm x 1 cm rectangles. O-rings were cut into 2 cm long pieces. The cuts were placed in 15 mL of organic liquid contained in Teflon[™] capped 20 mL glass vials. The composition of the organic liquid was varied as shown in Table 3.

Table 1. A list and structure of the components that make up CSSX and the improved solvent.

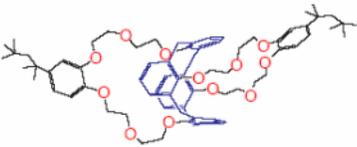
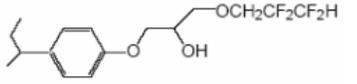
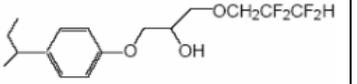
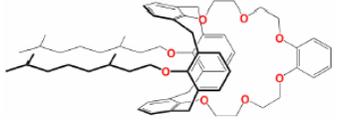
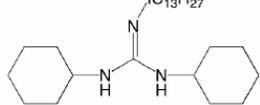
Component	CSSX	Improved Solvent
BoBCalixC6	 7 mM	0 wt %
Modifier	 29 wt %	 21 wt%
TOA	 0.12 wt%	0 wt %
Isopar [®] L	Linear/branched C ₁₂ 69 wt %	Linear/branched C ₁₂ 74 wt%
MaxCalix	0 wt %	 50 mM
LIX [®] 79 (Guanidine)	0 wt %	 3 mM

Table 2. A list of the polymers used in MCU selected for testing.

Polymer Name	Chemical Formula of repeat unit	Shape or Form
Tefzel [®] (DuPont) Grades: 200 and 280	$-(CF_2-CF_2)-(CH_2-CF_2)-(CF_2-CF_2)-(CH_2-CH_2)-$ 	Gasket and Pellets
Isolast [®] (carbon filled). Possible PFR 40		O-ring
Grafoil [®] (GrafTech International)	Particles of C ₆ (SP2 hybridized) pressed together	Sheet
Carbon-filled PEEK (30 wt % carbon filled)		Sheet
Chlorinated polyvinyl chloride (CPVC) ¹		Pipe

The test matrix in Table 3 was designed to investigate the effect of temperature, guanidine derivative and MaxCalix on the dimensional stability of the polymers. The split-plot design is selected to facilitate examination of the two temperatures that bound the operating range of MCU (as shown in Figure 1). Therefore some of the conclusions could be influenced by the particulars of those ovens (for example, heating rate or spatial homogeneity of the temperature inside the oven). The baseline tests in Table 3 capture the effect of presence of Isopar[®] L / Modifier on the polymers (at a 74/21 weight ratio). This effect should be similar to the effect of the current CSSX solvent on these polymers (except that the Isopar[®] L / Modifier weight ratio in CSSX is 69/29). Both molecules, Isopar[®] L and Modifier, can cause polymers to swell. Isopar[®] L is a mixture of linear and branched C9-C13 long hydrocarbons that is attracted to hydrophobic materials. The Modifier molecule has polar and non-polar functional groups that are attracted to hydrophilic materials. We expect the presence of both Isopar[®] L / Modifier to interact (causing swelling) with porous and flexible polymers (such as thermoplastics and slightly cross-linked thermosets). The question to be answered is “does the presence of guanidine derivative and MaxCalix in conjunction with heat (temperature) cause further dimensional instability in these polymers beyond the effect of Isopar[®] L / Modifier alone?”

Since extraction and stripping are conducted at 23 ± 3 °C and 33 ± 3 °C respectively, the tests were at conducted 21 and 36 °C. The 21 °C temperature (instead of 20 °C) was the lowest temperature we could achieve with the oven.

In the experimental design, the concentrations of guanidine and MaxCalix were varied to exceed the expected operating range in the facility but to maintain their relative masses to the total solvent in the same rough order of magnitude.

Given that the ratio of Isopar[®] L / Modifier is higher in our test than in the CSSX solvent, this composition is still within the operating range of MCU since extra Isopar[®] L is added to the CSSX solvent when trimming is conducted to account for Isopar[®] L evaporation. No degradation

¹ CPVC is not used in MCU but will be used as piping on the aqueous streams containing entrained solvent in upcoming testing within SRNL for the contactors and coalescers. A similar approach was used in the prior MCU equipment testing as a cost savings effort.

of the polymers has been reported due to the excess additions of Isopar[®] L that leads to higher Isopar[®] L to Modifier ratio.

Table 3. The chemical composition of the organic liquid used to investigate the effect of MaxCalix and guanidine.

Whole plots	Temperature (°C)	MaxCalix (mM)	LIX [®] 79 (mM)	Isopar [®] L / Modifier
1	21	70	3	Remainder*
1	21	50	10	Remainder *
2	36	70	10	Remainder *
2	36	50	3	Remainder *
3	21	70	10	Remainder *
3	21	50	3	Remainder *
4	36	50	10	Remainder *
4	36	70	3	Remainder *
5 [#]	21	0	0	100% *
5 [#]	36	0	0	100% *

*Isopar[®] L to Modifier weight ratio is 74/21 (improved solvent)

- Some baseline tests were conducted with CSSX solvent.

The polymer samples were exposed to 15 mL of the organic liquid listed in Table 3 for six months. During the exposure some polymers from Table 3 were analyzed periodically to determine the kinetics (speed) of swelling (or shrinkage) or possible reaction that may occur between these polymers and the solvent. The sampling frequency consisted of examining some polymers every 24 hours for the first 120 hours of exposure and then the sampling frequency was reduced to sampling these polymers twice every week. After six months of exposure, all polymers in Table 3 were analyzed to determine the effect of guanidine, MaxCalix and temperature (as well as their two-ways cross products) on the polymers listed in Table 2.

In a separate set of experiments, similar polymer samples are exposed to the baseline solvent. Since a full-factorial experimental design is not used, we will compare the absolute changes for the improved solvent to those observed for the baseline solvent under similar experimental conditions. Property changes that are similar to or less than observed with the baseline solvent should provide a confidence for deployment of the new solvent.

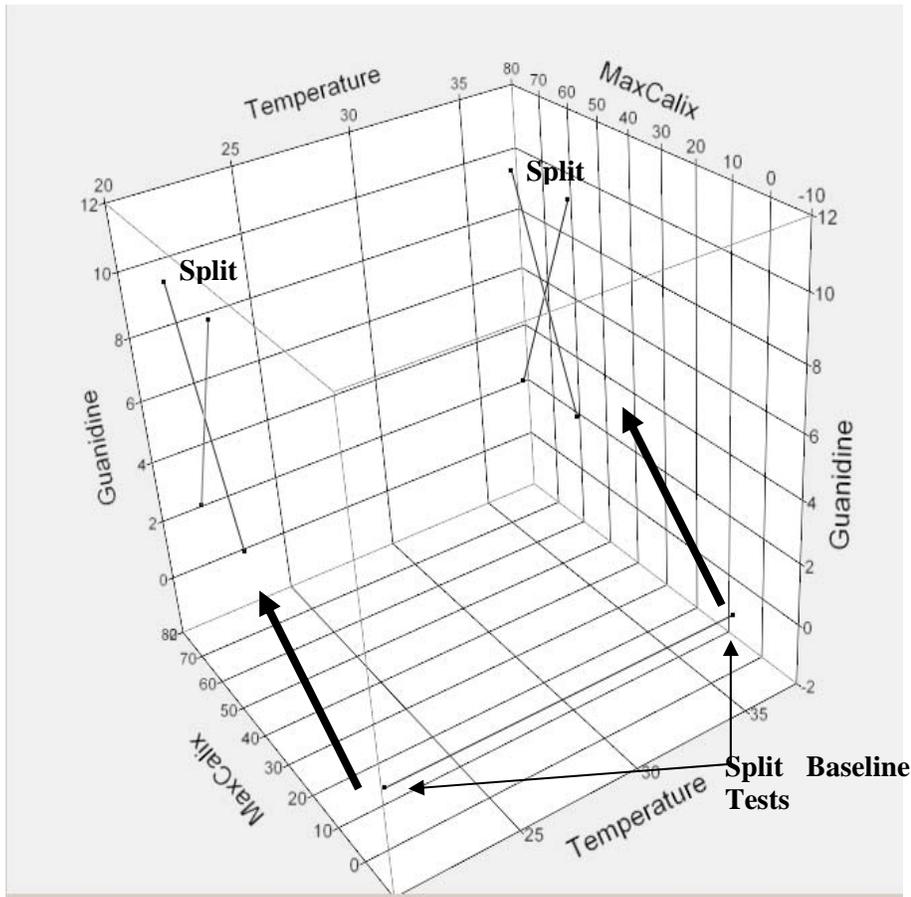


Figure 1. Visual picture of the design matrix listed in Table 3. Two ovens were used in the matrix. Oven variance is not captured in this test.

The polymers will be evaluated in three areas:

1. dimensional stability (e.g., thickness, volume, density, etc.),
2. chemical stability (e.g., absorption, leaching and chemical reactions), and
3. mechanical stability (e.g., flexibility, stiffness, recovery, resiliency, etc.)

Of these areas, this report presents only dimensional data where is applicable. For example, in the case of Ryton this was not possible since Ryton is nonwoven fibrous material that retains solution upon draining. This proved difficult in determining physical changes in Ryton. However, spectroscopic analysis of the solvent was used to determine if adsorption into Ryton or leaching from Ryton occurred in these tests.⁴

3.0 Results and Discussion

3.1 *Comparison between the baseline tests of the modified NGS (Isopar[®] L / Modifier) versus that of CSSX*

The weight, thickness and density data for PEEK, Grafoil, Tefzel, and Isolast[®] is presented in Figures A1 to A12 in Appendix A. Figures A1 to A12 shows appreciable variability at the two temperatures (21 and 36 °C). In general, when the polymer density decreased relative to the as-received polymer it was probably due to the polymer dimensions increased more than it gained weight. It is also possible that the polymers lost (adsorbed or absorbed) water when exposed to the organic fluids thereby affecting the net mass gained or lost. The data indicate that Isolast[®] increased in thickness and weight but the change is consistent with the changes seen when Isolast[®] is placed in CSSX (i.e., the error bars in Fig A11 through A13 larger than any deterministic change). Based on the chemical structure of Isolast[®], Isolast[®] is the most chemically resistant of the polymers studied here and we do not expect any effect of the solvent on Isolast[®].

When trying to evaluate if the baseline test for the improved solvent were equivalent to the test in CSSX solvent, in general due to the variance in the measurements, both solvents had nearly equal impact on the polymers. For example, as shown in Figure A10, the variation in PEEK thickness in CSSX versus PEEK thickness in baseline NGS (with no MaxCalix or Lix[®] 79) is 0.04 mm or 40 microns which is within the variation of the measurement. A similar conclusion was reached in the analysis of Grafoil and Tefzel where their thicknesses and weight change in baseline NGS, although above the measurement noise, were within the changes observed when these materials were immersed in CSSX.

MCU will not replace the polymers when the facility transitions from the CSSX solvent to the improved solvent; however, we foresee no additional effects on the polymers when MCU changes to the improved solvent.

3.2 *t-test of the thickness and weight of PEEK, Grafoil, Tefzel, and Isolast before and after exposure to the solvents listed in Table 3*

A t-test (for paired observation) of the thickness and weight of the individual polymers (i.e., PEEK, Grafoil, Tefzel, and Isolast) is shown in table format in Appendix B. Since the physical dimensions of the pieces of polymers (same pieces) were tracked before and after exposure, a paired t-test analysis will detect the effect of the treatment (i.e., solvent exposure from Table 3). The tables show that the “as received” polymers typically gained weight and lost size (thickness) after 6 months in the solvents listed in Table 3 (with the exception of Grafoil and Tefzel which got thicker see Figure B1). Any probability less than 0.05 (for the two tails curve) is evidence of a significant effect. Such a significant effect was seen in most samples. (The thickness of Isolast and weight of PEEK showed no significant change, which is also seen in the baseline solvent.) These physical changes are believed to be due primarily to the components Isopar[®] L and Modifier shown to cause similar effect for samples exposed to the CSSX solvent (refer to Appendix A).

3.3 *Guanidine and MaxCalix effect on PEEK, Grafoil, Tefzel and Isolast*

To determine if guanidine and MaxCalix affected the dimensional stability of the polymers, least square fitting of the thickness, weight, and density was conducted. Appendix C shows Figures 1C to 4C presenting the least square fitting done with all the possible variables (i.e., guanidine, MaxCalix, temperature, and their two-ways multiplication).

Visual inspection of Figures 1C to 4C clearly shows that, with the exception of Tefzel, the presence of guanidine and MaxCalix had no impact on the dimensional stability of these polymers. The least square fitting (Jump Software version 8.2) could not fit any of the possible variables to the weight, thickness and density data (i.e., the data grouped in a “shot gun” formation).

In the case of Tefzel, the least square fitting was able to find the variable that can fit the systematic variation in thickness and density of Tefzel. That variable was guanidine and at 36 °C the effect of guanidine is more significant. In fact, during the measurements personnel reported the Tefzel sample “bended and twisted” easily (with no memory of its previous shape). The ethylene portion of the ETFE random copolymer is probably being affected by the solvent. Further analysis of the two additional different grades of Tefzel 200 and 280 (Fig. 5 C and Fig. 6C) shows that both LIX[®]79 and temperature has an effect (a cross term effect) on the weight dimensions of Tefzel 200 and Tefzel 280 (the effect is a bit noisy but the noise is attributed to making a film from pellets). High temperature and LIX[®] 79 increases the solvent uptake of Tefzel 200 and Tefzel 280.

The question is “are the changes experienced by Tefzel in 74/21 Isopar[®] L/Modifier solvent containing guanidine and MaxCalix solvent comparable to the changes Tefzel experienced in CSSX baseline solvent?” Appendix E shows the side by side data comparing Tefzel’s weight, thickness, and density change in both solvents. A review of Figures 1E and 2E clearly shows that the physical changes experienced by Tefzel in the improved solvent are within and are comparable to the changes that Tefzel experienced in baseline CSSX solvent. In other words, the changes are within the tolerance since Tefzel is being currently used at MCU with no reports of leaks or degradation. Tefzel is used as the seat material in some of the valves at MCU.⁵ Long term exposure to guanidine, may make the valves hard to operate over time due to the seat material (Tefzel) increasing in size. It may be prudent to test exposed components in an actual valve and tested for performance.

3.4 *Bilayer Effect (NGS-Boric acid and NGS-Salt Solution) on Tefzel, Grafoil, PEEK, CPVC, and Ryton*

All the polymers experienced no physical changes beyond those observed when the polymers were immersed in pure solution (boric acid or NGS). No physical change (thickness) was observed on the polymer or Grafoil at the aqueous-NGS interface (a difficult test to conduct).

3.5 *Kinetics of PEEK, Grafoil, Tefzel and Isolast in the presence of Guanidine and MaxCalix*

Appendix D shows the parameters weight, thickness, and density of PEEK, Grafoil, Tefzel and Isolast in Figures 1D to 4D. Figures 1D to 4D clearly show no additional change (i.e., absence of significant uptake or leaching) when the polymers were evaluated from 24 hours to 120 hours of exposure. The variation in all data was random with time and was within the noise of the system (i.e., variances in treatment, measurement and handling). The initial uptake of solvent discussed previously (assigned to the presence of Isopar[®] L / Modifier) occurred much faster than 24 hours.

In the case of Tefzel, the additional effect of guanidine (discussed in the previous section) must have occurred faster than the initial 24 hours of exposure. Since the whole sample softened this implies that the improved solvent permeated through the sample (not just to the surface). All physical measurements (thickness, weight and density) reached steady state 1.5 months after the start of the test and remain so for the rest of the test (6 months). Taking the log of both thickness (as well as weight) and time showed a non-linear relation (or trend) indicating that the uptake cannot be modeled with a Fickian ($t^{1/2}$) or pseudo ($t^{<1/2}$) or case II (t^1) or super case II (with $t^{>1}$) function.⁶ These functions represent transport limited uptake that include free volume assisted transport (or vacancies in solids) to polymeric segments movements with relaxation times slower than the diffusion of the solvent. The lack of fitting is likely due to a fast uptake and a low sampling frequency.

3.6 FTIR Analysis of the Baseline NGS that contacted PEEK, Grafoil, Tefzel and Isolast

An FTIR evaluation of the NGS solvent that contacted Tefzel, Isolast, CPVC, PEEK, and Grafoil for six months was conducted to determine if any of the NGS components (Isopar[®]L, Modifier, LIX[®] 79, and MaxCalix) is missing or if any impurity leached into the NGS from the polymers or Grafoil. Appendix F contains the FTIR spectra (including the difference spectrum to highlight any change) of NGS after contacting each polymer.

An inspection of the difference spectra in Fig. 1F to 5F shows the same features: loss of Isopar[®]L, in each case, and we believe this is due to loss of containment during sample handling. In addition, the presence of phthalates in NGS that contacted in CPVC was seen in Fig. 4F at approximately 87 ppm. Given that the CPVC polymer was machined down to fit the testing vial, the machined surfaces no longer had the protecting chlorinated surface of CPVC (in fact, the machined surfaces resemble PVC) and thus, the underneath phthalate is exposed to the NGS. Thus, it is not surprising to see phthalates to have leached from machined CPVC (consistent with the brownish color seen on the machined surface of CPVC after contacting NGS for six months). The FTIR difference spectrum also detected the small concentration (~ 10 -15 ppm) of an impurity in the NGS that contacted Isolast. The impurity appears to have unsaturated carbon (C=C), and we believe that sample handling or a manufacturing processes was the method that introduced that impurity into this sample. Therefore, no evidence of NGS composition alteration or leaching of impurities from the polymers was seen.

4.0 Conclusions

An assessment of the dimensional stability of PEEK, Grafoil, Tefzel and Isolast in modified NGS (where the concentration of guanidine and MaxCalix was varied systematically) showed that guanidine (LIX®79) selectively affected Tefzel (by an increase in size and lowering its density). The random copolymer structure, relative crystallinity, and possible porosity of Tefzel allows for the easier diffusion of guanidine. PEEK, Grafoil and Isolast were not affected by guanidine and MaxCalix within 6 months of exposure. The initial rapid weight gain observed in every polymer is assigned to the finite and limited uptake of Isopar® L / Modifier by the polymers probably due to the polymers porosity and rough surfaces. Spectroscopic data of the organic liquid indicates that no chemicals were leached by the polymers tested and not NGS component that can be detected by FTIR was selectively removed by the polymers. The chemicals released by CPVC and Isolast® in this tests were associated with sample handling (CPVC) and processing history as in the case of Isolast®.

The testing shows no major concerns for compatibility over the short duration of these tests. The physical changes experienced by Tefzel in the improved solvent were comparable to the physical changes obtained when Tefzel is placed in CSSX baseline solvent. Therefore, there is no effect of the improved solvent beyond those observed in CSSX baseline solvent. Given that for six months Tefzel did not plasticized (or formed a gel) to the point of losing its physical shape, there is no risk that the current Tefzel components at MCU will not perform as designed.

Appendix A: Comparison of the weight, thickness and density of PEEK, Grafoil and Tefzel polymers for baseline CSSX solvent and 74/21 Isopar[®] L / Modifier weight ratio only.

The following figures examine only the baseline CSSX solvent and the samples with altered Isopar[®] L / Modifier weight ratio (74/21). No guanidine or MaxCalix containing samples are shown. The “as received” data was obtained at room temperature for comparison.

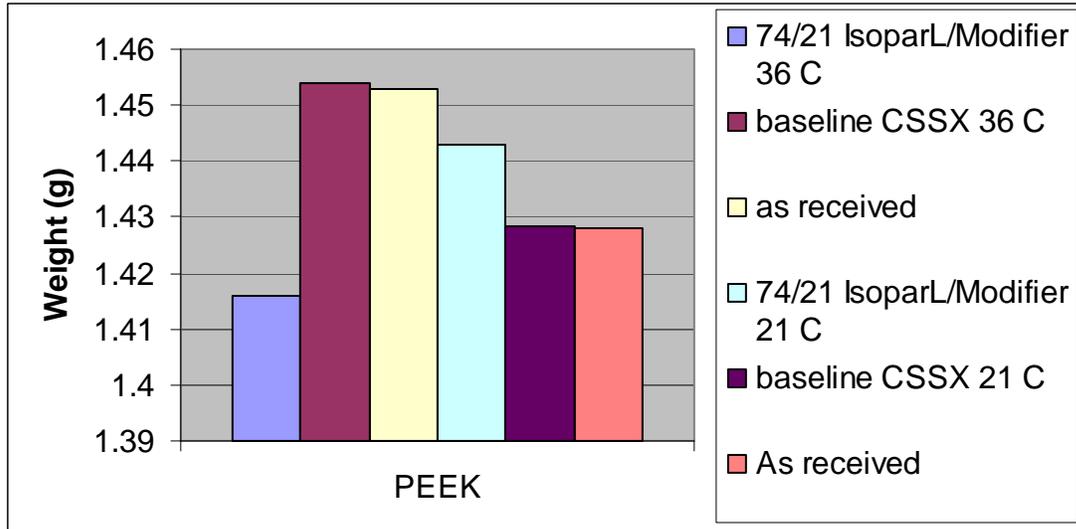


Figure A1. A weight comparison between the baseline CSSX test and the samples with altered Isopar[®] L / Modifier weight ratio (74/21).

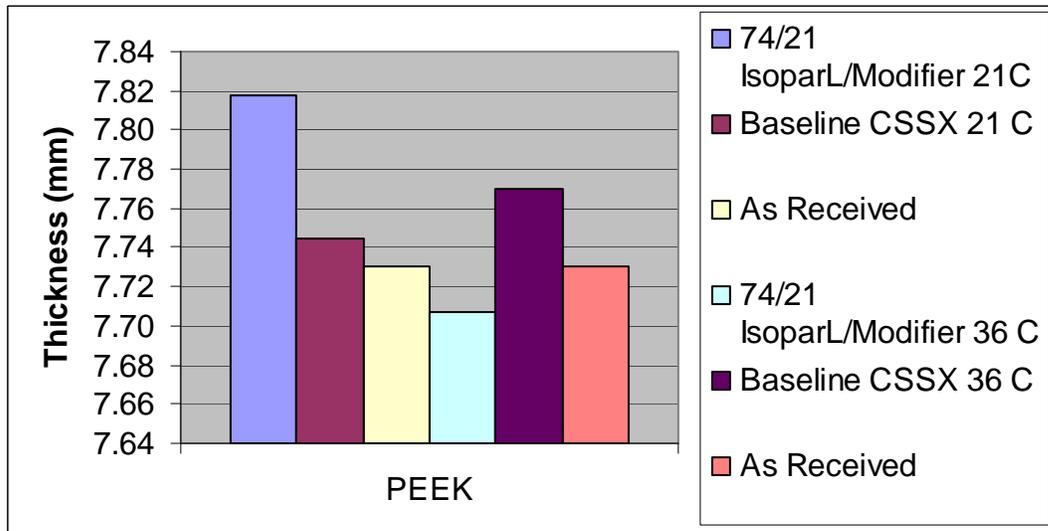


Figure A2. A thickness comparison between the baseline CSSX test and the samples with altered Isopar[®] L / Modifier weight ratio (74/21).

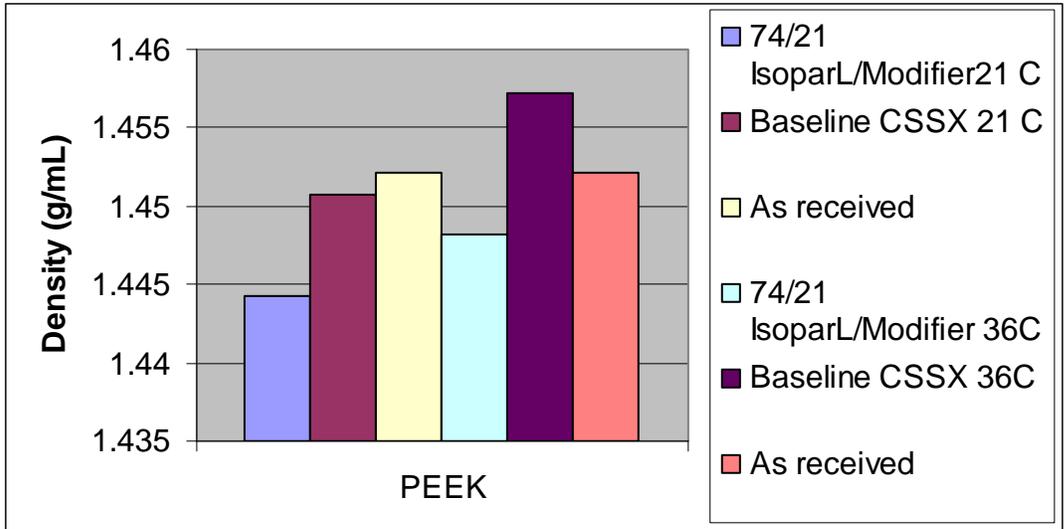


Figure A3. A density comparison between the baseline CSSX test and the samples with altered Isopar® L / Modifier weight ratio (74/21).

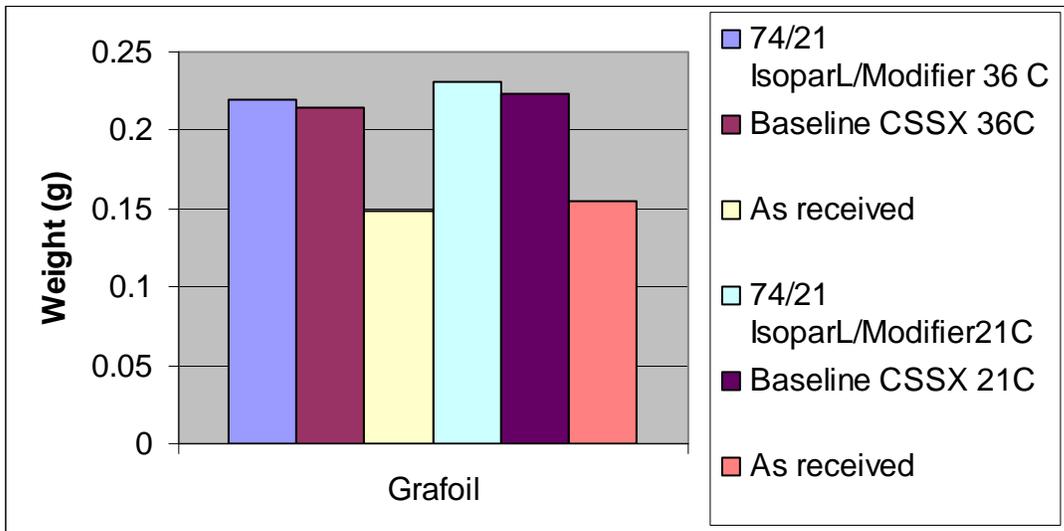


Figure A4. A weight comparison between the baseline CSSX test and the samples with altered Isopar® L / Modifier weight ratio (74/21).

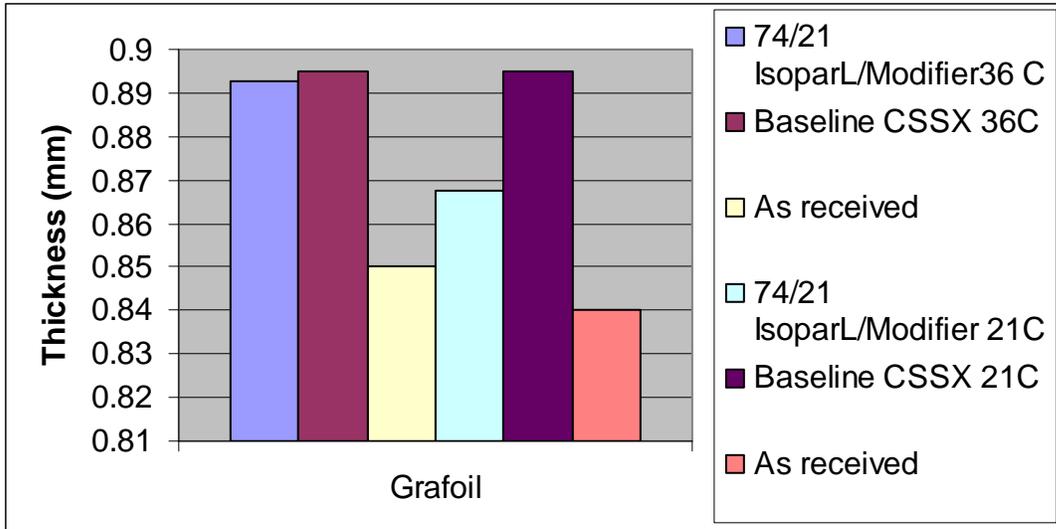


Figure A5. A thickness comparison between the baseline CSSX test and the samples with altered Isopar® L / Modifier weight ratio (74/21).

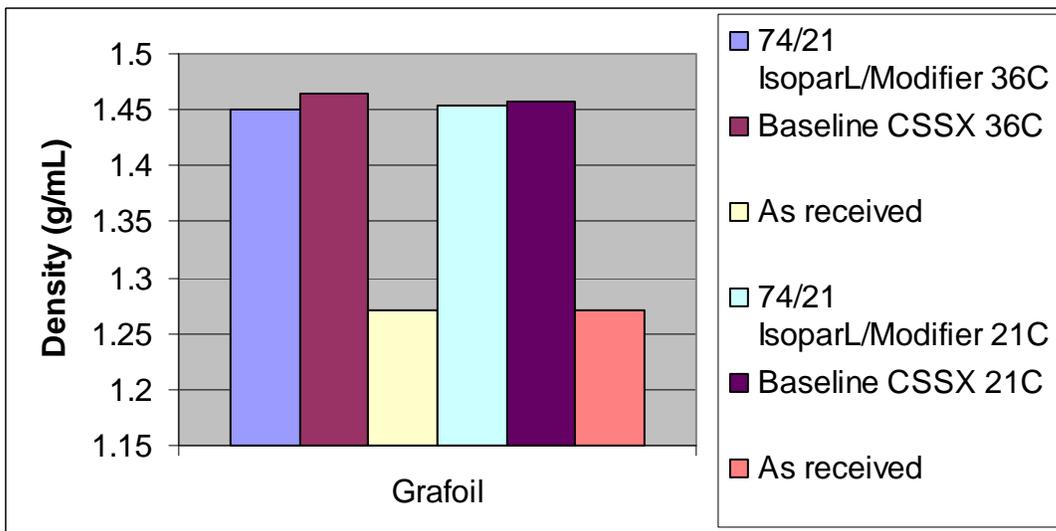


Figure A6. A density comparison between the baseline CSSX test and the samples with altered Isopar® L / Modifier weight ratio (74/21).

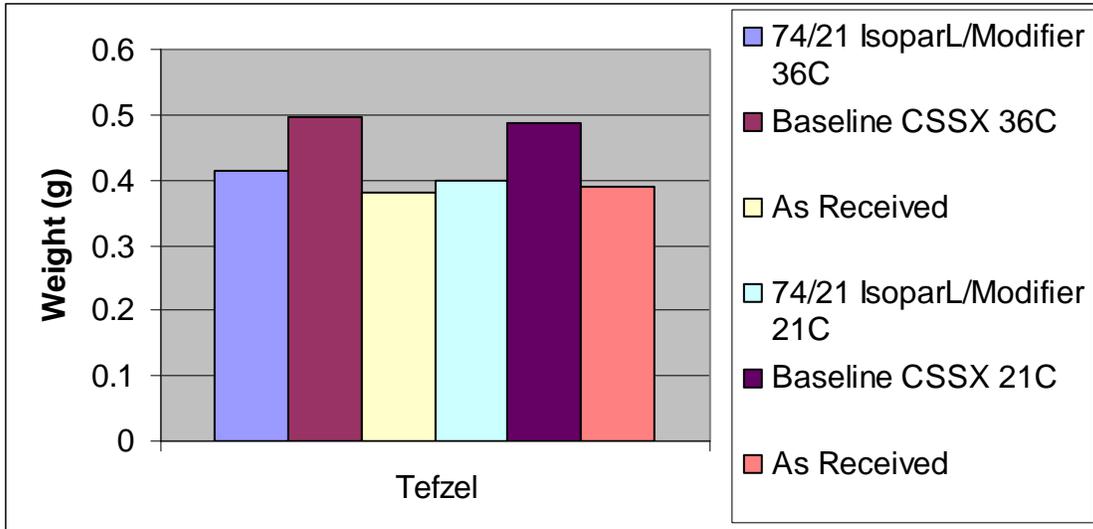


Figure A7. A weight comparison between the baseline CSSX test and the samples with altered Isopar® L / Modifier weight ratio (74/21).

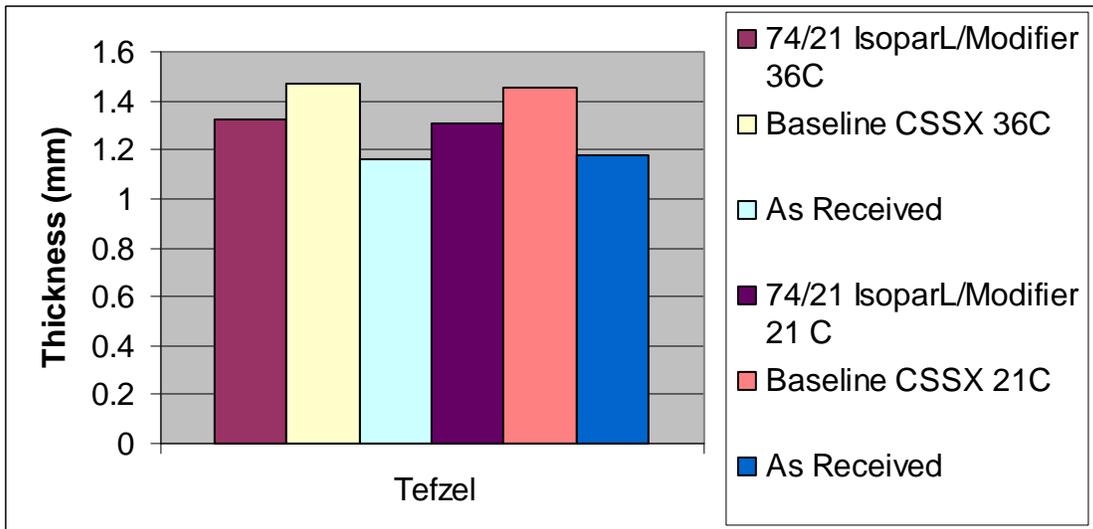


Figure A8. A thickness comparison between the baseline CSSX test and the samples with altered Isopar® L / Modifier weight ratio (74/21).

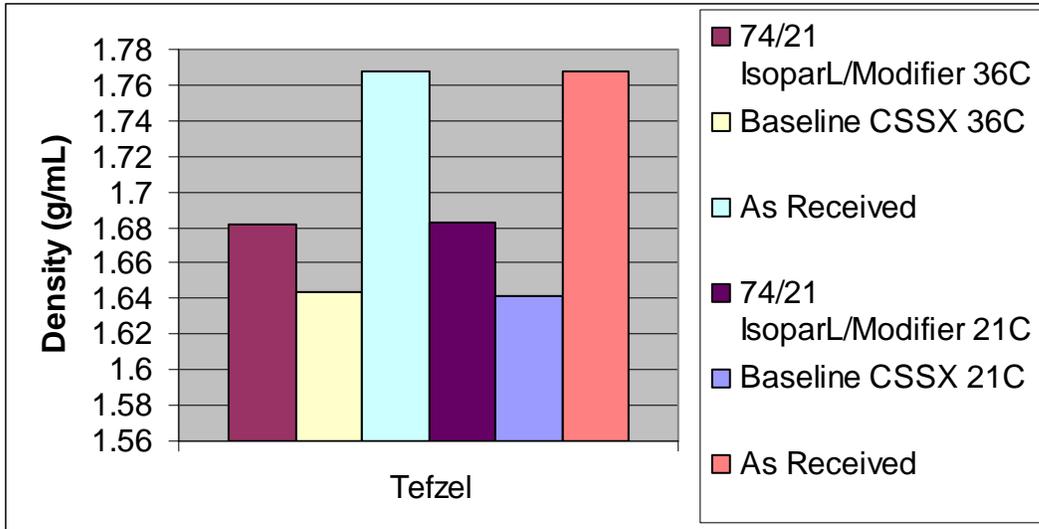


Figure A9. A density comparison between the baseline CSSX test and the samples with altered Isopar® L / Modifier weight ratio (74/21).

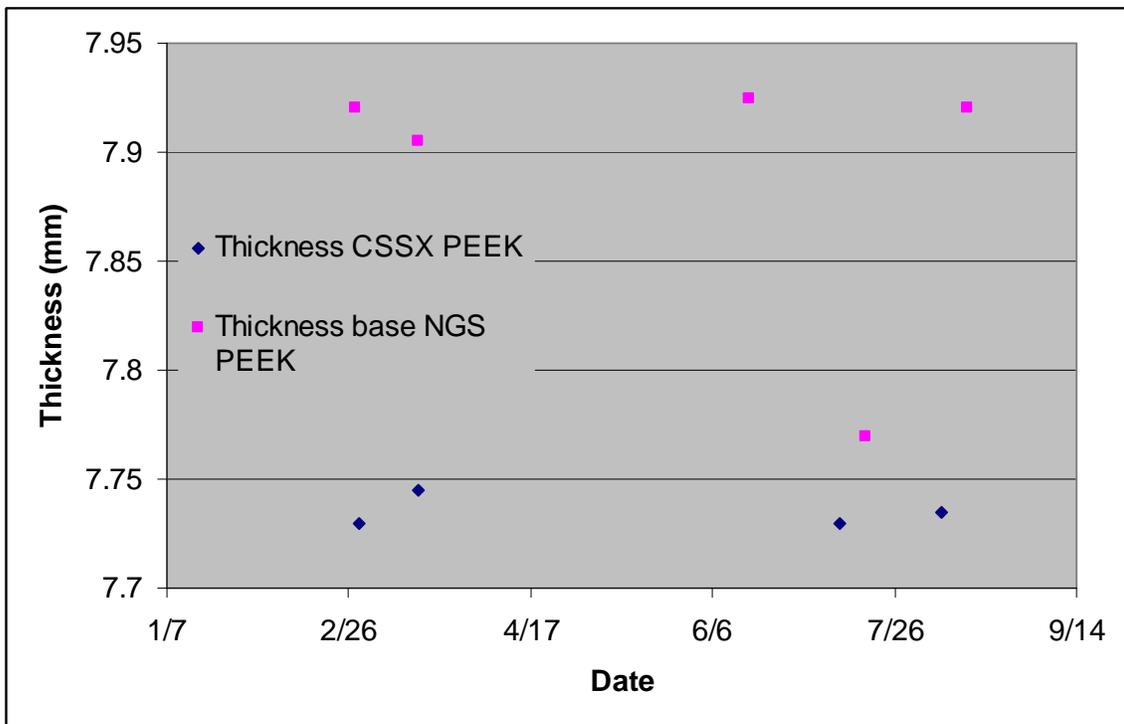


Figure A10. A plot of thickness of PEEK in baseline CSSX and in modified NGS with no MaxCalix and no LIX®79. As can be seen from the figure a maximum difference of 0.04 millimeters (40 microns) in thickness between CSSX and baseline NGS is seen but this difference is within the noise of the thickness measurement.

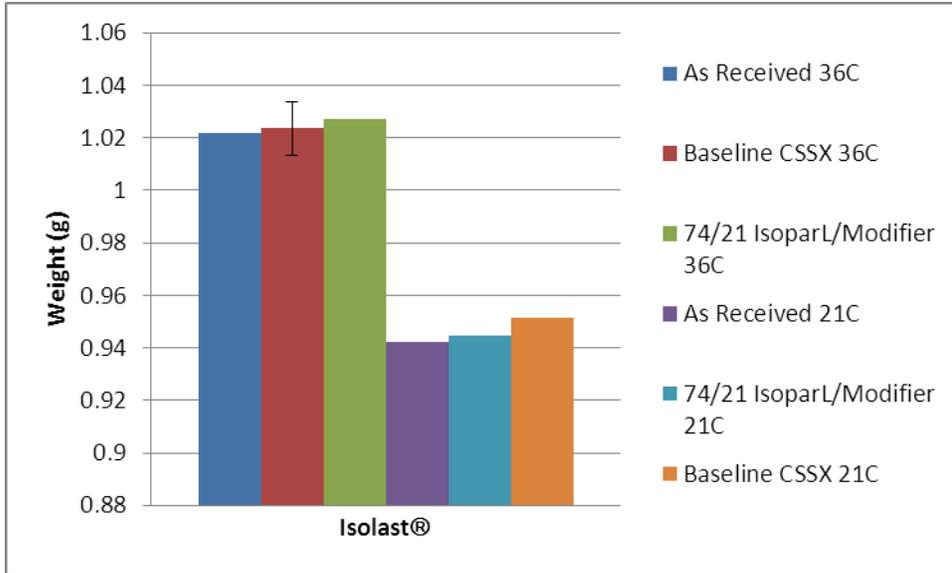


Figure A11. A weight comparison between the baseline CSSX test and the samples with altered Isopar®L/Modifier weight ratio (74/21)

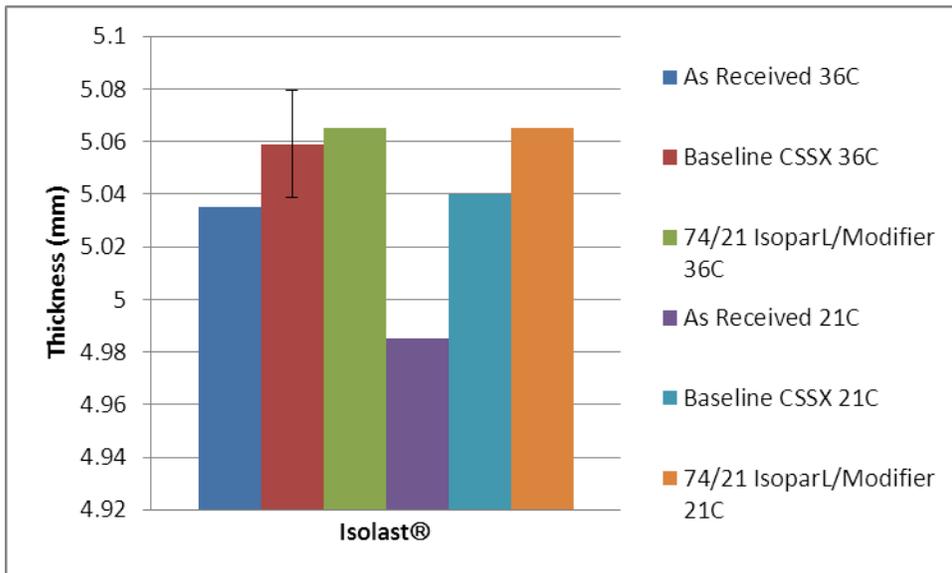


Figure A12. A thickness comparison between the baseline CSSX test and the samples altered Isopar®L/Modifier weight ratio (74/21)

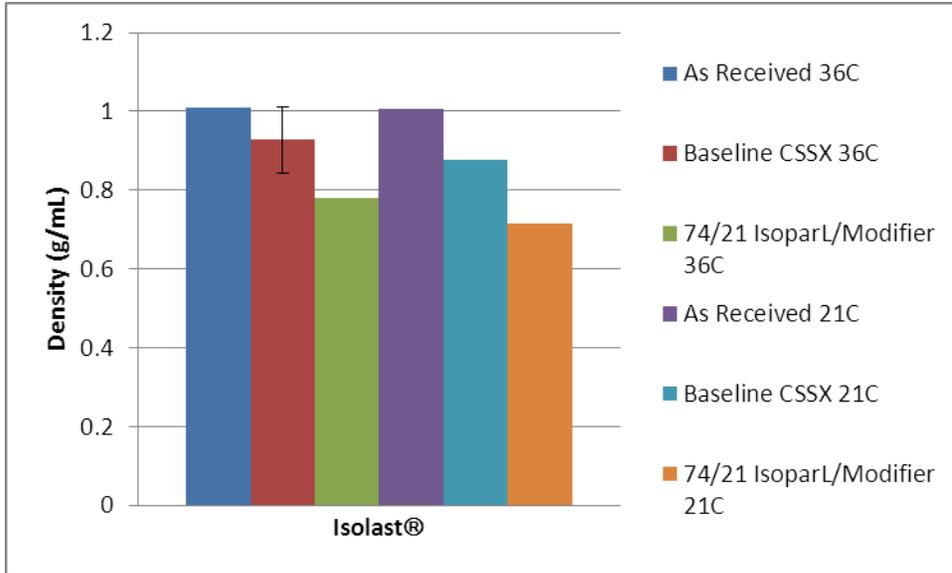


Figure A13. A density comparison between the baseline CSSX test and the samples With altered Isopar[®]L/modifier weight ratio (74/21)

Appendix B: t-test of the weight (g) and thickness (mm) of PEEK, Tefzel, Grafoil, and Isolast before and after exposure to the modified solvents (Table 3).

This data shows the effect of wetting the polymer with solvent containing Isopar[®]L, Modifier, guanidine and MaxCalix (with the composition listed in Table 3) relative to the “as received” polymer (dry).

Table 1B. t-Test: Paired Two Sample for Means thickness
PEEK

	<i>Before</i>	<i>After</i>
Mean	7.74E+00	7.73E+00
Variance	2.65E-02	2.38E-02
Observations	2.40E+01	2.40E+01
Pearson Correlation	9.98E-01	
Hypothesized Mean Difference	0.00E+00	
df	2.30E+01	
t Stat	3.37E+00	
P(T<=t) one-tail	1.32E-03	
t Critical one-tail	1.71E+00	
P(T<=t) two-tail	2.64E-03	
t Critical two-tail	2.07E+00	

Table 2B. t-Test: Paired Two Sample for Means Weight
PEEK

	<i>Before</i>	<i>After</i>
Mean	1.42E+00	1.42E+00
Variance	3.69E-03	3.91E-03
Observations	2.40E+01	2.40E+01
Pearson Correlation	1.00E+00	
Hypothesized Mean Difference	0.00E+00	
df	2.30E+01	
t Stat	1.73E+00	
P(T<=t) one-tail	4.83E-02	
t Critical one-tail	1.71E+00	
P(T<=t) two-tail	9.65E-02	
t Critical two-tail	2.07E+00	

Table 3B. t-Test: Paired Two Sample for Means Weight

Grafoil		
	<i>Before</i>	<i>After</i>
Mean	1.59E-01	2.24E-01
Variance	5.33E-05	1.86E-04
Observations	2.40E+01	2.40E+01
Pearson Correlation	6.51E-01	
Hypothesized Mean Difference	0.00E+00	
df	2.30E+01	
t Stat	3.05E+01	
P(T<=t) one-tail	2.12E-20	
t Critical one-tail	1.71E+00	
P(T<=t) two-tail	4.24E-20	
t Critical two-tail	2.07E+00	

Table 4B. t-Test: Paired Two Sample for Means thickness

Grafoil		
	<i>Before</i>	<i>After</i>
Mean	8.68E-01	8.93E-01
Variance	4.61E-04	3.21E-04
Observations	2.40E+01	2.40E+01
Pearson Correlation	2.44E-01	
Hypothesized Mean Difference	0.00E+00	
df	2.30E+01	
t Stat	5.06E+00	
P(T<=t) one-tail	1.99E-05	
t Critical one-tail	1.71E+00	
P(T<=t) two-tail	3.97E-05	
t Critical two-tail	2.07E+00	

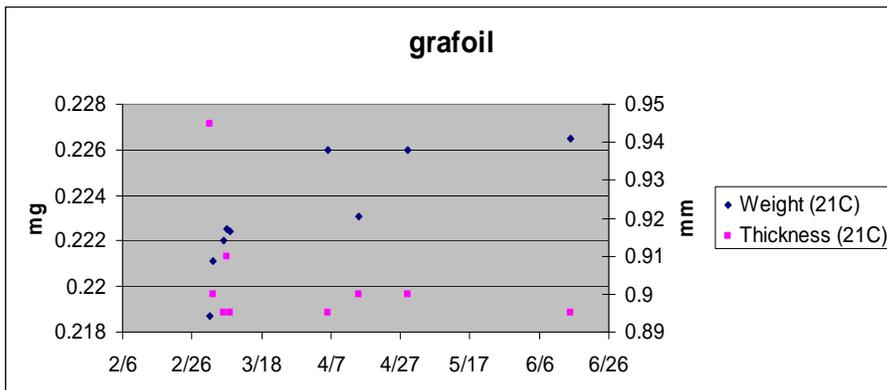


Figure B1. This figure shows that after one month of exposure to NGS, Grafoil absorbed NGS and that weight gain reached steady state approximately two months after. The thickness of the sample remained constant throughout the test (within the 8 % measurement error).

Table 5B. t-Test: Paired Two Sample for Means weight

TEFZEL		
	<i>Before</i>	<i>After</i>
Mean	3.44E-01	4.30E-01
Variance	1.15E-03	2.04E-03
Observations	2.30E+01	2.30E+01
Pearson Correlation	9.80E-01	
Hypothesized Mean Difference	0.00E+00	
Df	2.20E+01	
t Stat	3.01E+01	
P(T<=t) one-tail	1.15E-19	
t Critical one-tail	1.72E+00	
P(T<=t) two-tail	2.30E-19	
t Critical two-tail	2.07E+00	

Table 6B. t-Test: Paired Two Sample for Means thickness

TEFZEL		
	<i>Before</i>	<i>After</i>
Mean	1.15E+00	1.40E+00
Variance	4.32E-04	2.67E-03
Observations	2.30E+01	2.30E+01
Pearson Correlation	5.18E-01	
Hypothesized Mean Difference	0.00E+00	
df	2.20E+01	
t Stat	2.65E+01	
P(T<=t) one-tail	1.67E-18	
t Critical one-tail	1.72E+00	
P(T<=t) two-tail	3.34E-18	
t Critical two-tail	2.07E+00	

Table 7B. t-Test: Paired Two Sample for Means weight
ISOLAST

	<i>Before</i>	<i>After</i>
Mean	9.34E-01	9.35E-01
Variance	5.60E-03	5.64E-03
Observations	2.40E+01	2.40E+01
Pearson Correlation	9.99E-01	
Hypothesized Mean Difference	0.00E+00	
df	2.30E+01	
t Stat	2.79E+00	
P(T<=t) one-tail	5.22E-03	
t Critical one-tail	1.71E+00	
P(T<=t) two-tail	1.04E-02	
t Critical two-tail	2.07E+00	

Table 8B. t-Test: Paired Two Sample for Means thickness
ISOLAST

	<i>Before</i>	<i>After</i>
Mean	5.01E+00	4.84E+00
Variance	5.72E-03	8.53E-01
Observations	2.40E+01	2.40E+01
Pearson Correlation	-5.64E-02	
Hypothesized Mean Difference	0.00E+00	
df	2.30E+01	
t Stat	9.27E-01	
P(T<=t) one-tail	1.82E-01	
t Critical one-tail	1.71E+00	
P(T<=t) two-tail	3.64E-01	
t Critical two-tail	2.07E+00	

Appendix C: Least Square Fitting of Weight, Thickness and Density of Tefzel, Grafoil, Isolast and PEEK

All weights are given in g, all thicknesses are given in mm, and the densities are reported in g/mL.

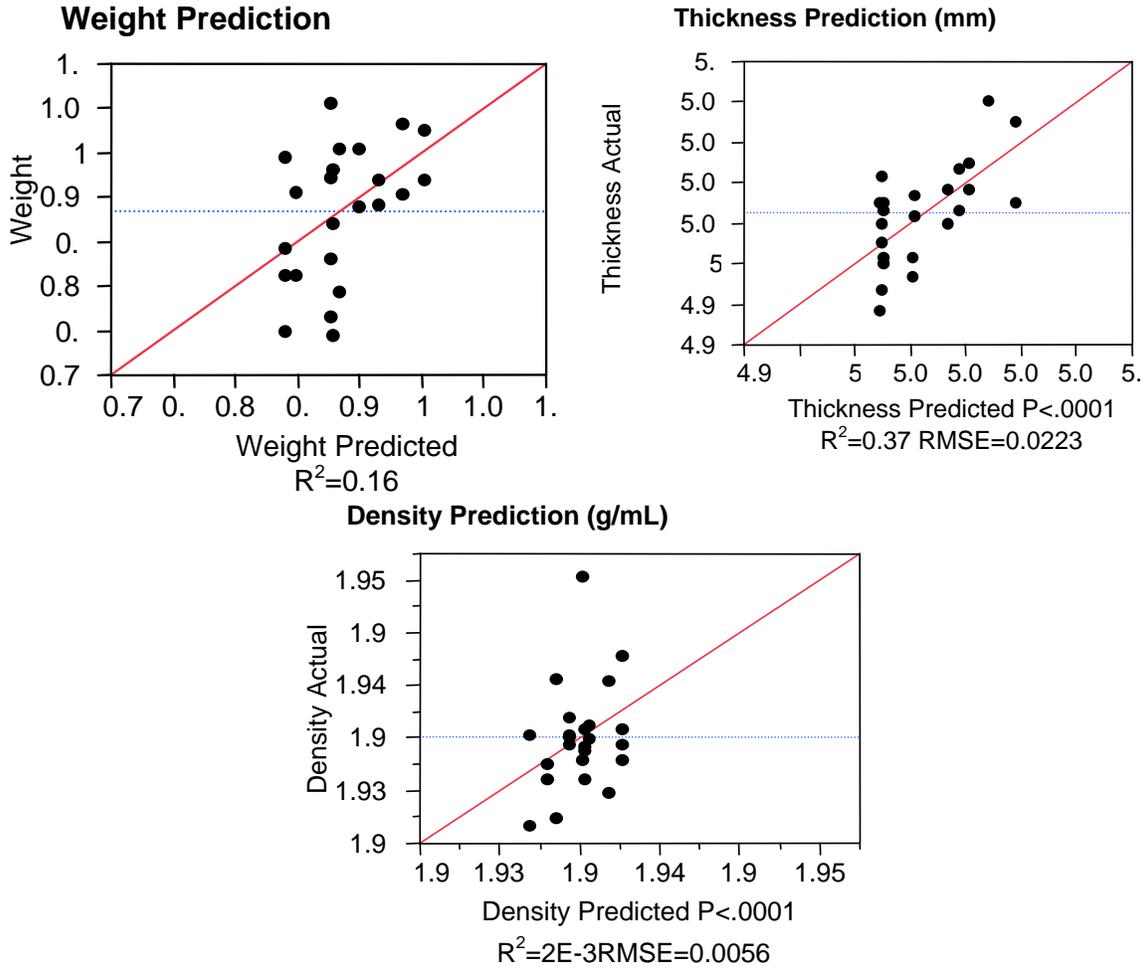


Figure 1C. Least square fitting of the physical dimensions of Isolast.

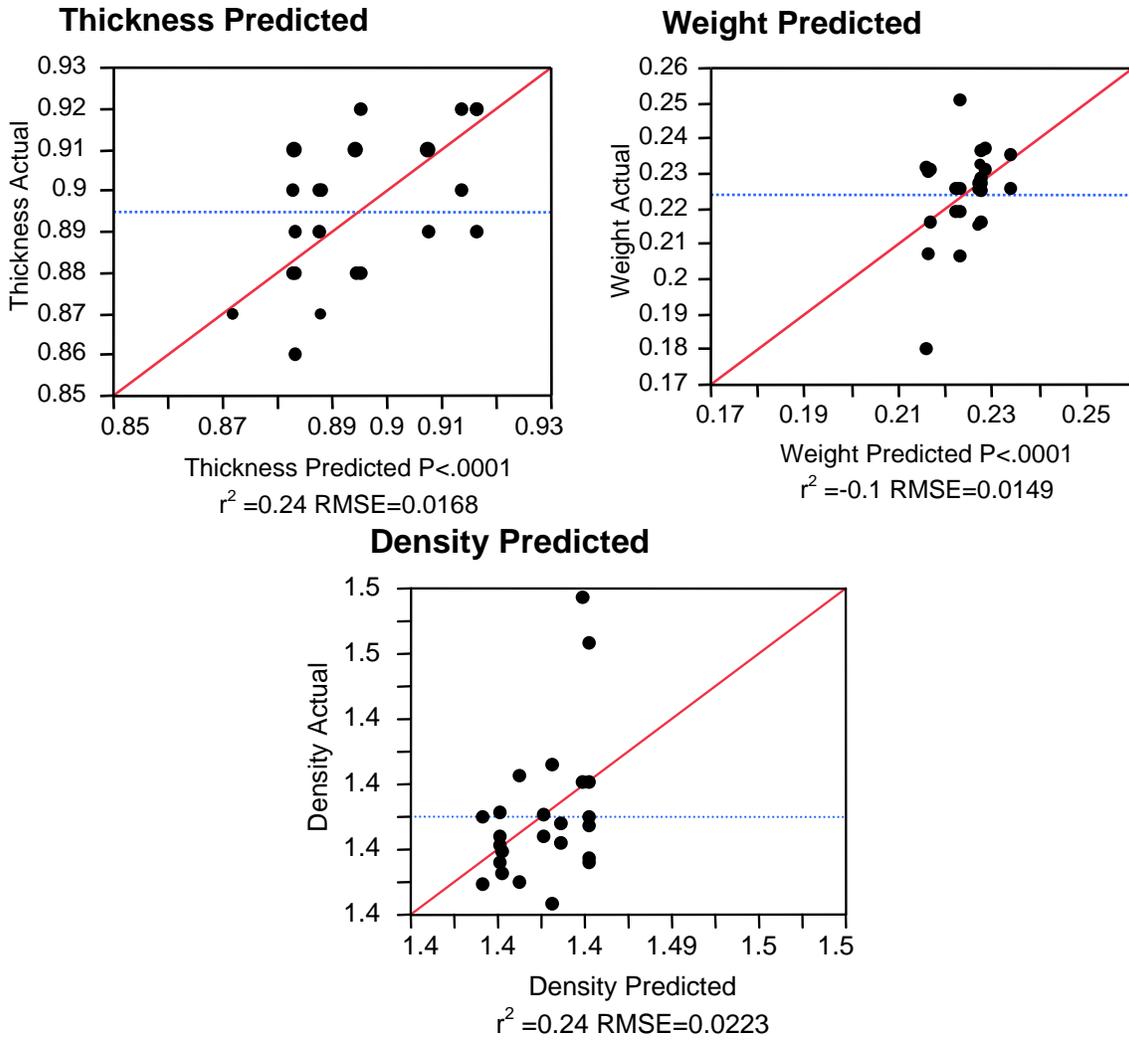


Figure 2C. Least square fitting of the physical dimension of Grafoil

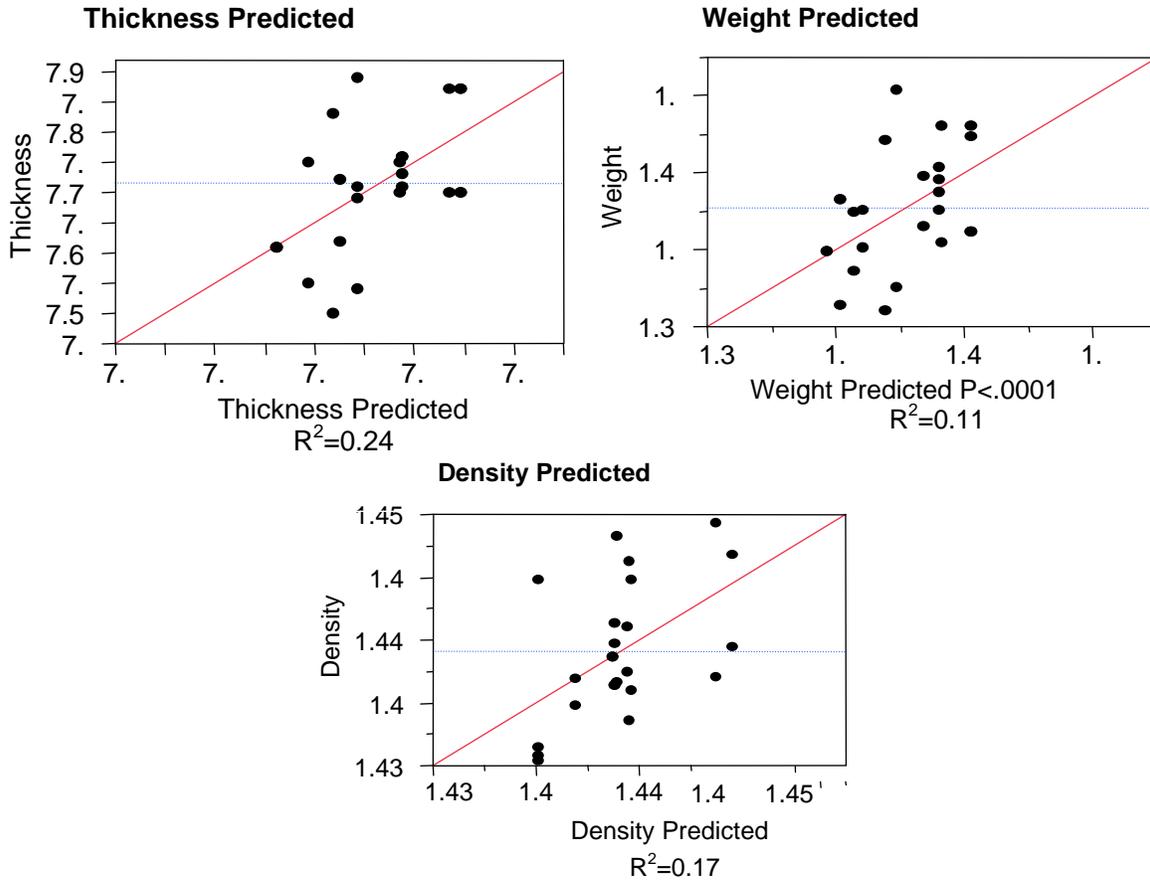


Figure 3C. Least square fitting of the physical dimensions of PEEK

Table 1C. Fixed Effect Tests for PEEK’s thickness after 6 months exposure to modified NGS. The cross term temperature x [MaxCalix] appears to affect (increase) the PEEK thickness.

Source	# parm	DF	DF Den	F Ratio	Prob > F
Temperature(21,36)	1	1	0.744	6.2134	0.31
MaxCalix(50,70)	1	1	6.58	0.0398	0.85
Guanidine(3,10)	1	1	13.67	1.8384	0.20
Temperature*MaxCalix	1	1	16.95	5.1931	0.04*
Temperature*Guanidine	1	1	16.87	1.9076	0.18
MaxCalix*Guanidine	1	1	1.945	0.6028	0.52

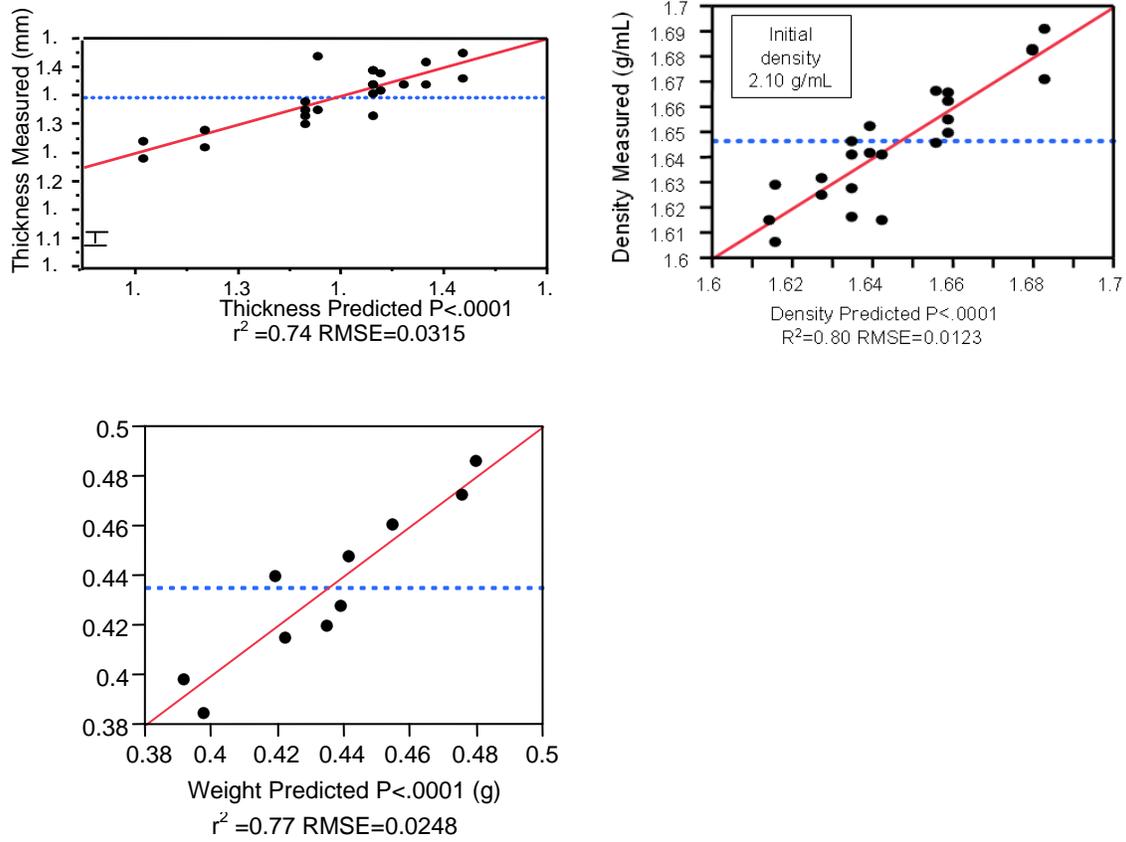


Figure 4C. Least square fitting of the physical dimensions of Tefzel

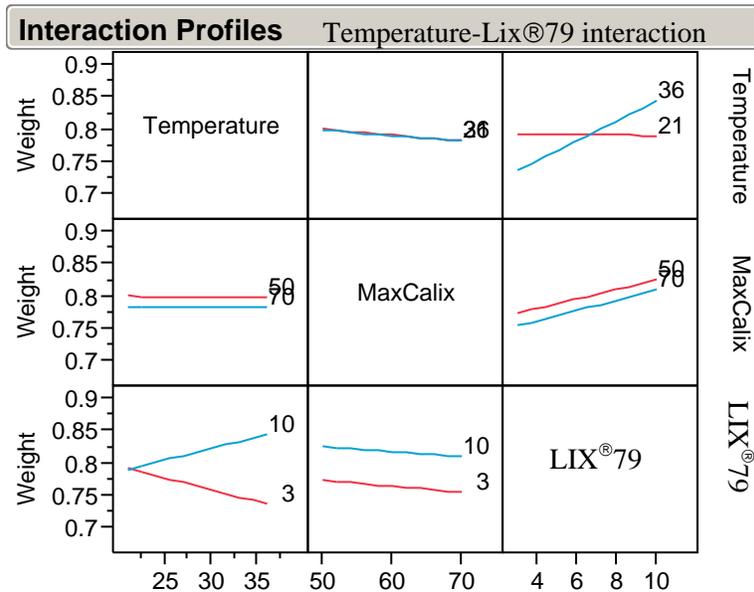
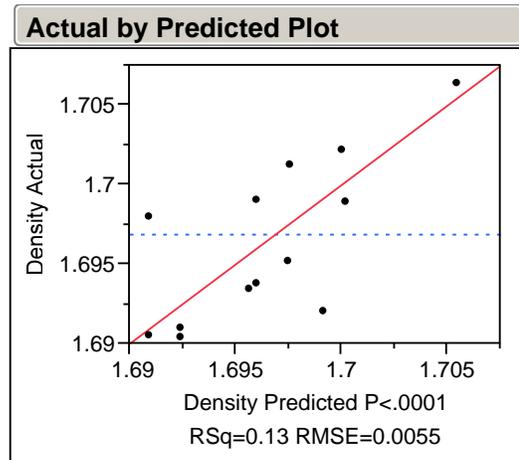
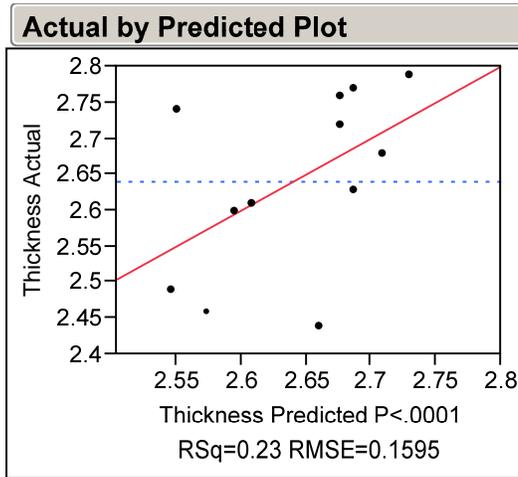
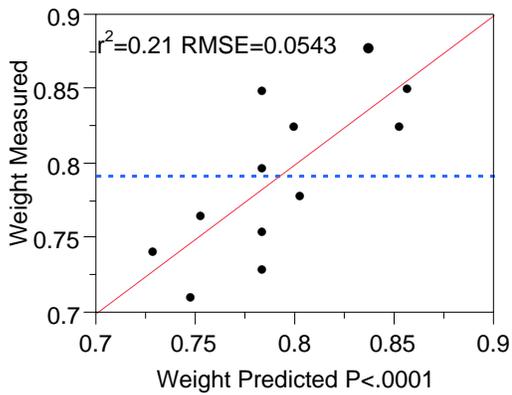


Fig. 5C. This figure shows a correlation between the weight of Tefzel 200 and the concentrations of LIX® 79 (the correlation is stronger with temperature). No correlation with MaxCalix concentration was found.

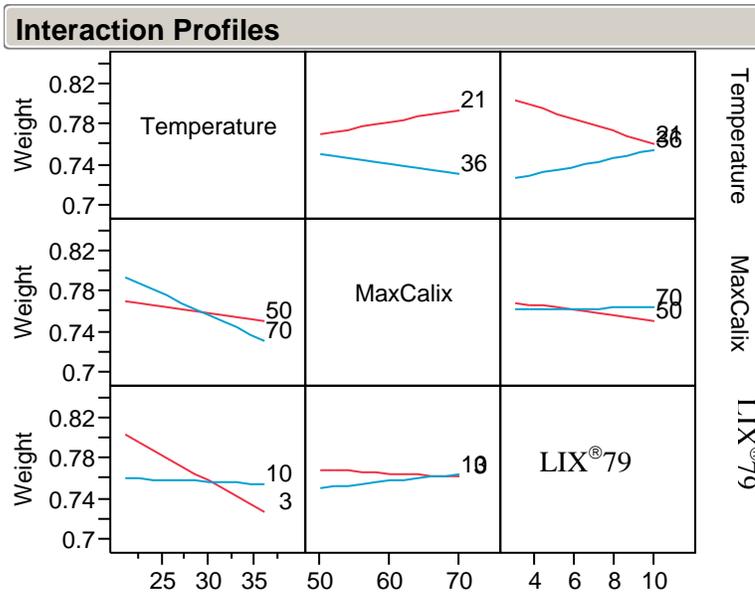
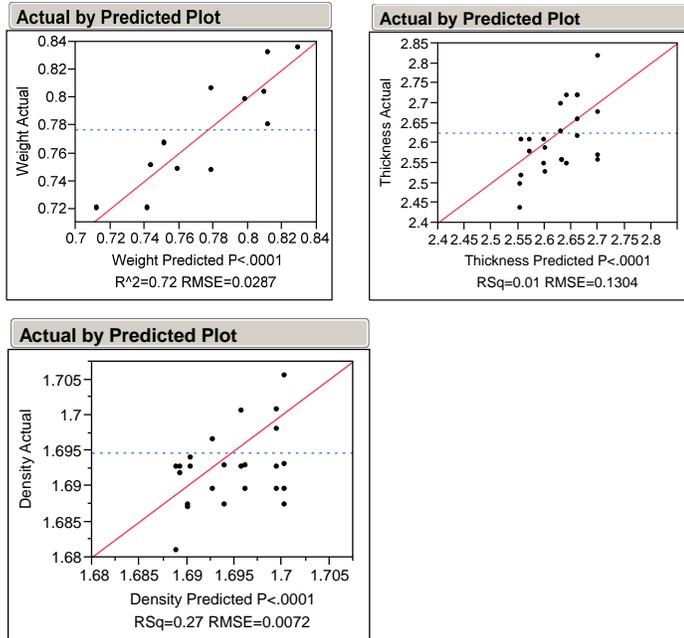


Fig. 6C. This figure shows the lack of correlation between Tefzel 280 and the concentrations of LIX[®]79 and MaxCalix (analysis detected negative interactions between temperature, MaxCalix, and LIX[®]79).

Appendix D: The physical dimensions of PEEK, Tefzel, Grafoil and Isolast as a function of time (hours) and temperature in the presence of LIX[®]79 and MaxCalix. All weights are given in grams, thicknesses given in millimeters, and density given in g/mL.

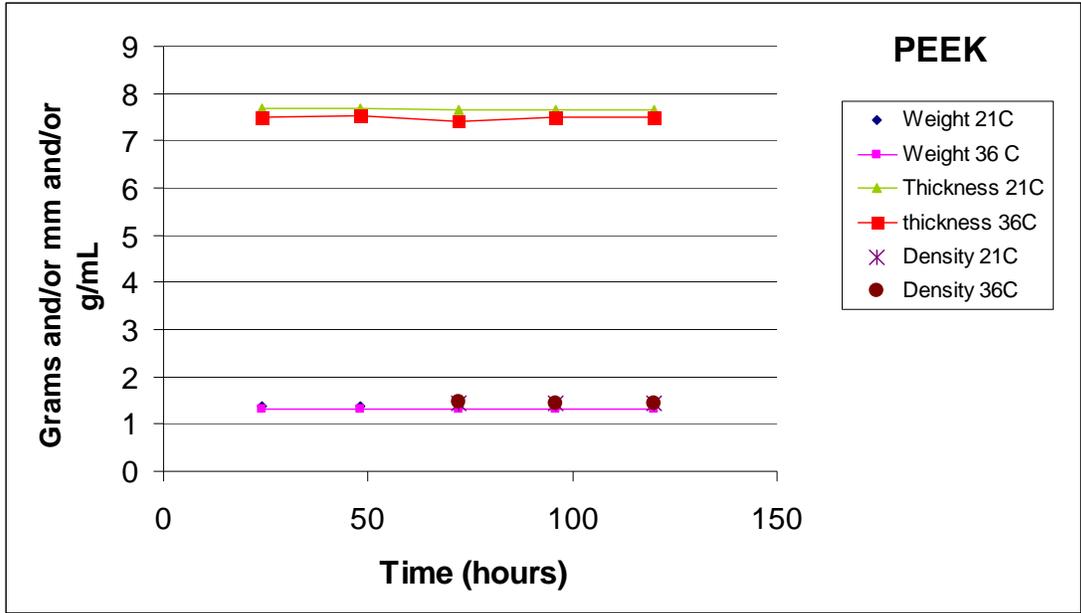


Figure 1D. The physical dimensions of PEEK as a function of time in the presence of LIX[®]79 and MaxCalix.

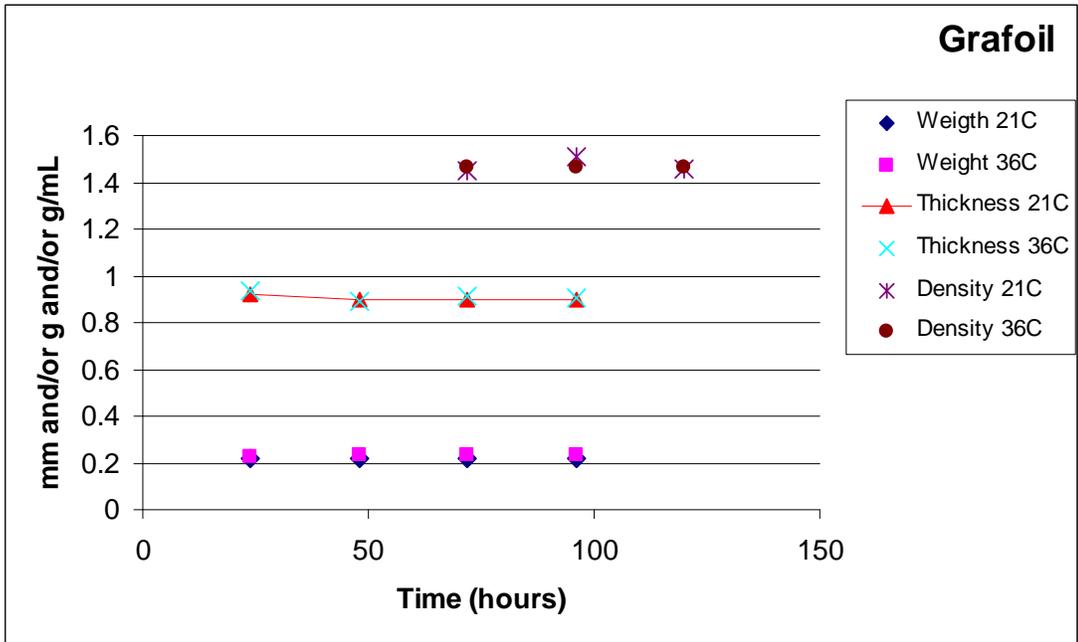


Figure 2D. The physical dimensions of Grafoil as a function of time in the presence of LIX[®]79 and MaxCalix.

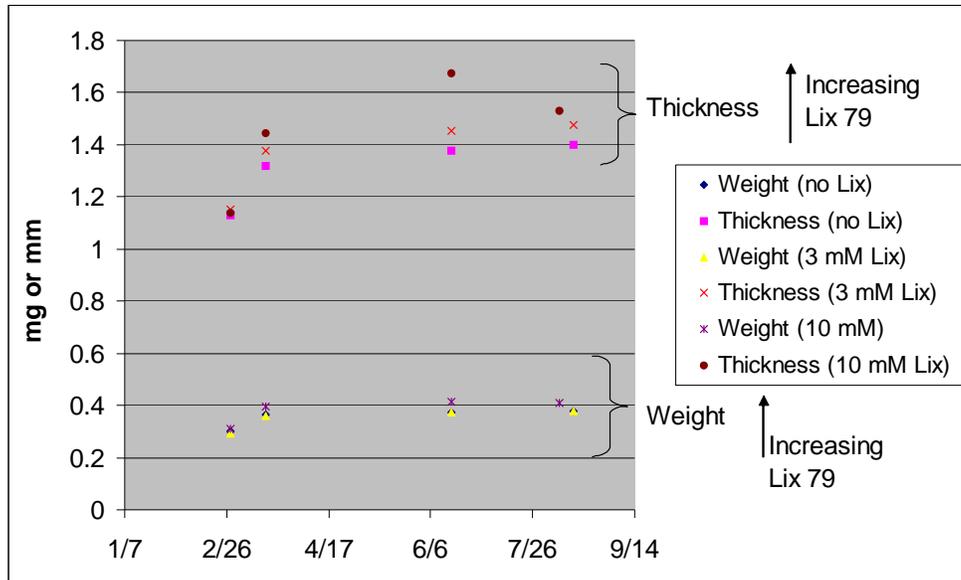


Figure 3D. The physical dimensions of Tefzel as a function of time in the presence of LIX[®]79 (MaxCalix composition remained at 70 mM) at 21 °C.

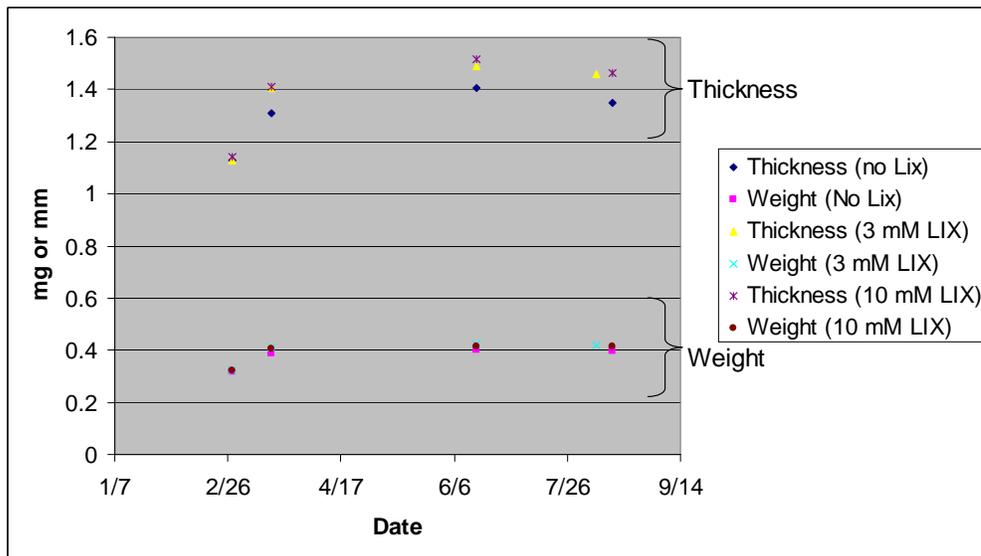


Figure 4D. The physical dimensions of Tefzel as a function of time (date) in the presence of LIX[®]79 (MaxCalix composition remained at 70 mM) at 36 °C.

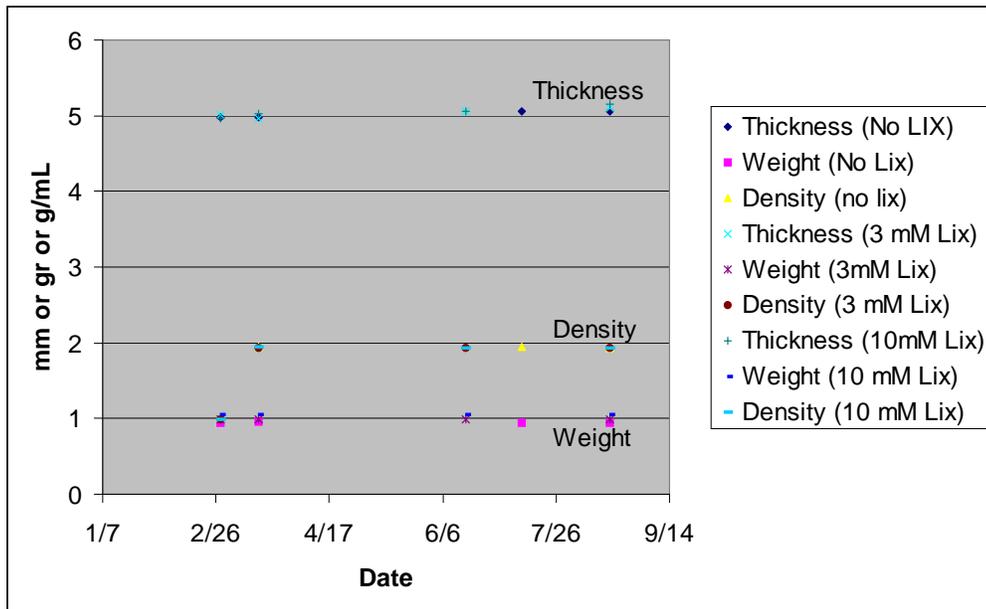


Figure 5D. The physical dimensions of Isolast as a function of time in the presence of LIX[®]79 (MaxCalix composition set at 70 mM).

Appendix E: A comparison of the physical dimensions changes of Tefzel in NGS solvent versus the changes seen in CSSX baseline solvent.

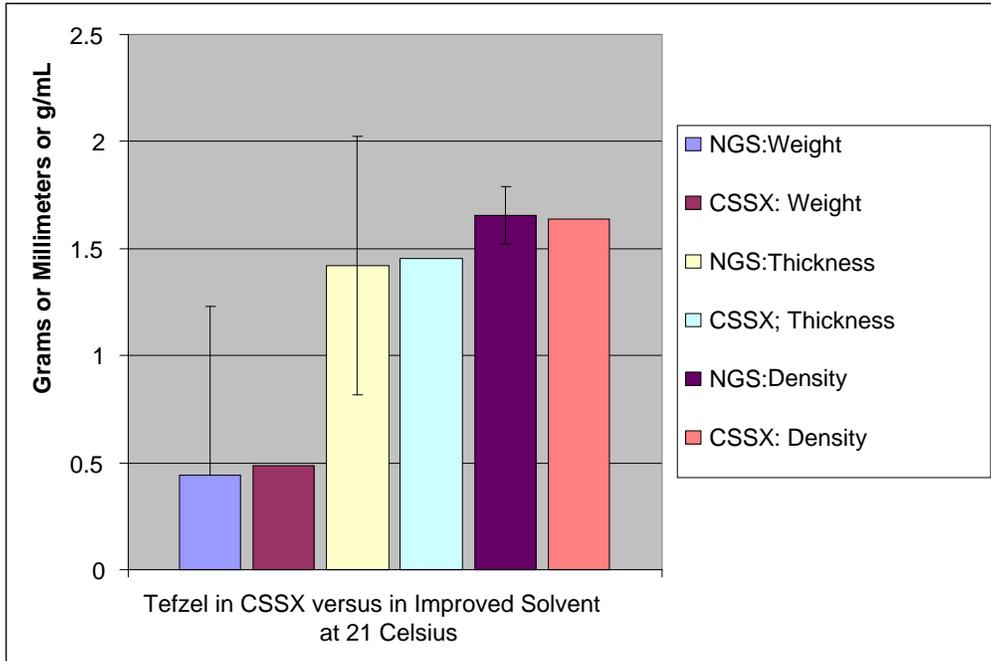


Fig. 1E. The weight, thickness, and density changes of Tefzel in NGS versus that in baseline CSSX.

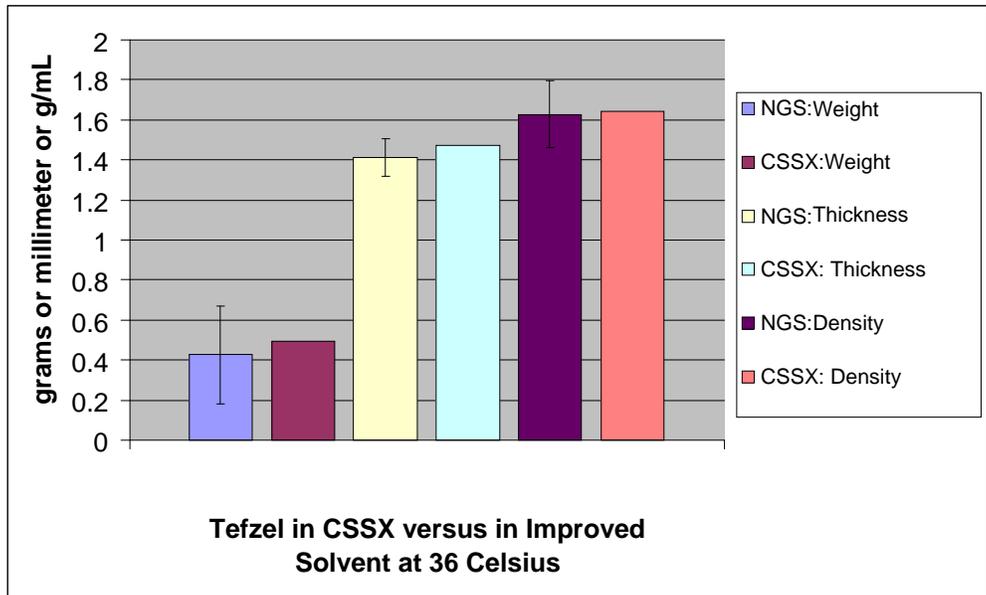


Fig. 2E. The weight, thickness, and density changes of Tefzel in NGS versus that in baseline CSSX

Appendix F: A comparison of the physical dimensions changes of Tefzel in 74/21 Isopar[®]L/Modifier solvent versus the changes seen in CSSX baseline solvent.

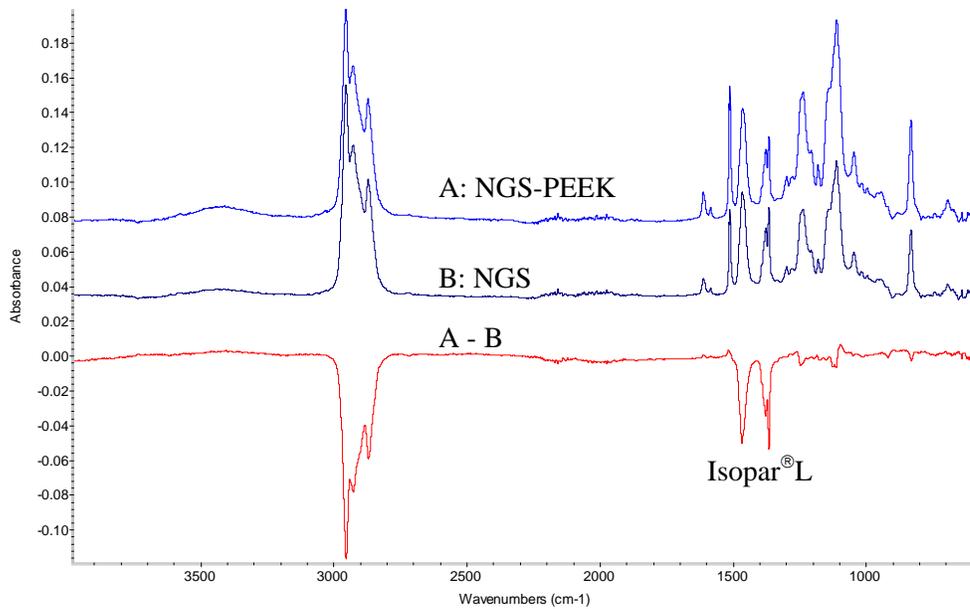


Fig. 1F. The FTIR spectra of NGS after contacting PEEK, of as made NGS, and the difference spectrum.

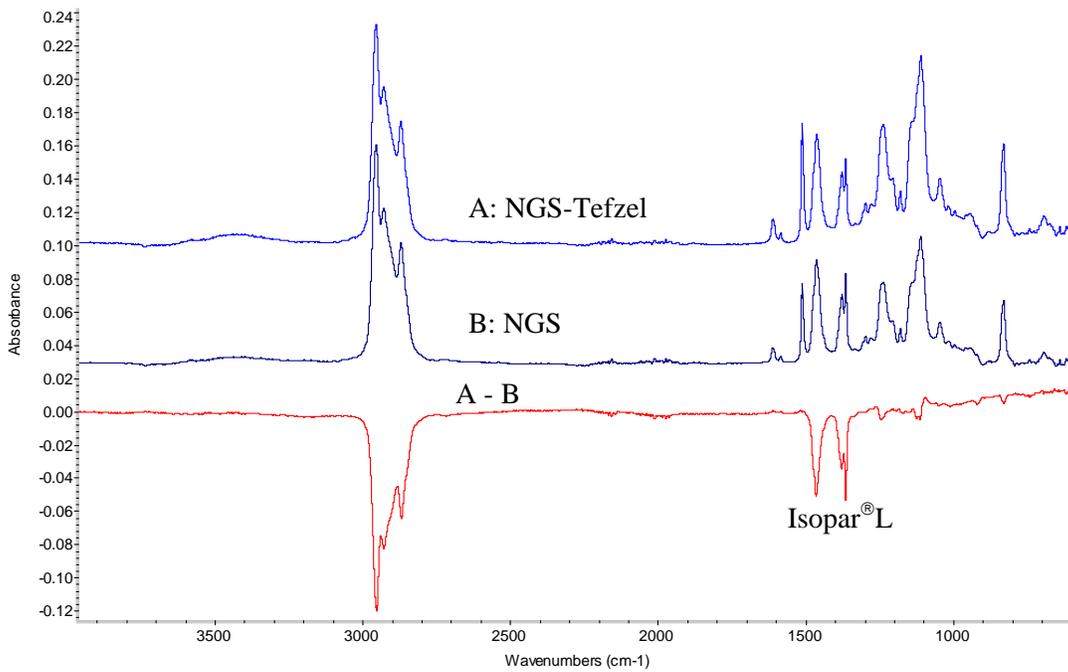


Fig. 2F. The FTIR spectra of NGS after contacting Tefzel, of as made NGS, and the difference spectrum.

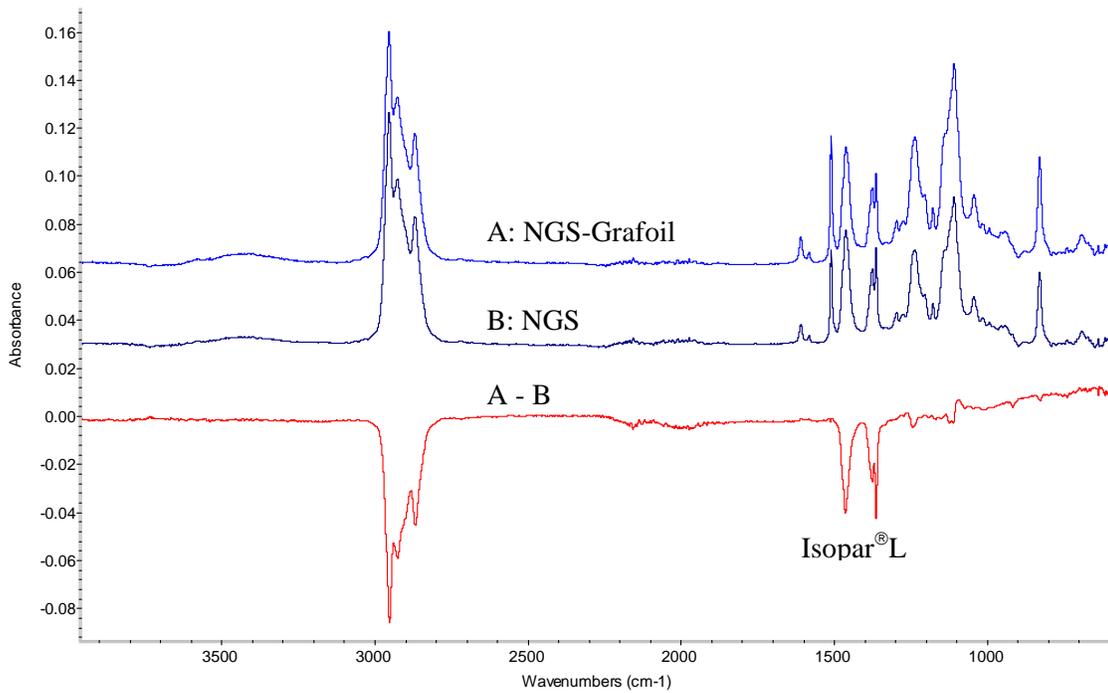


Fig. 3F. The FTIR spectra of NGS after contacting Grafoil, of as made NGS, and the difference spectrum.

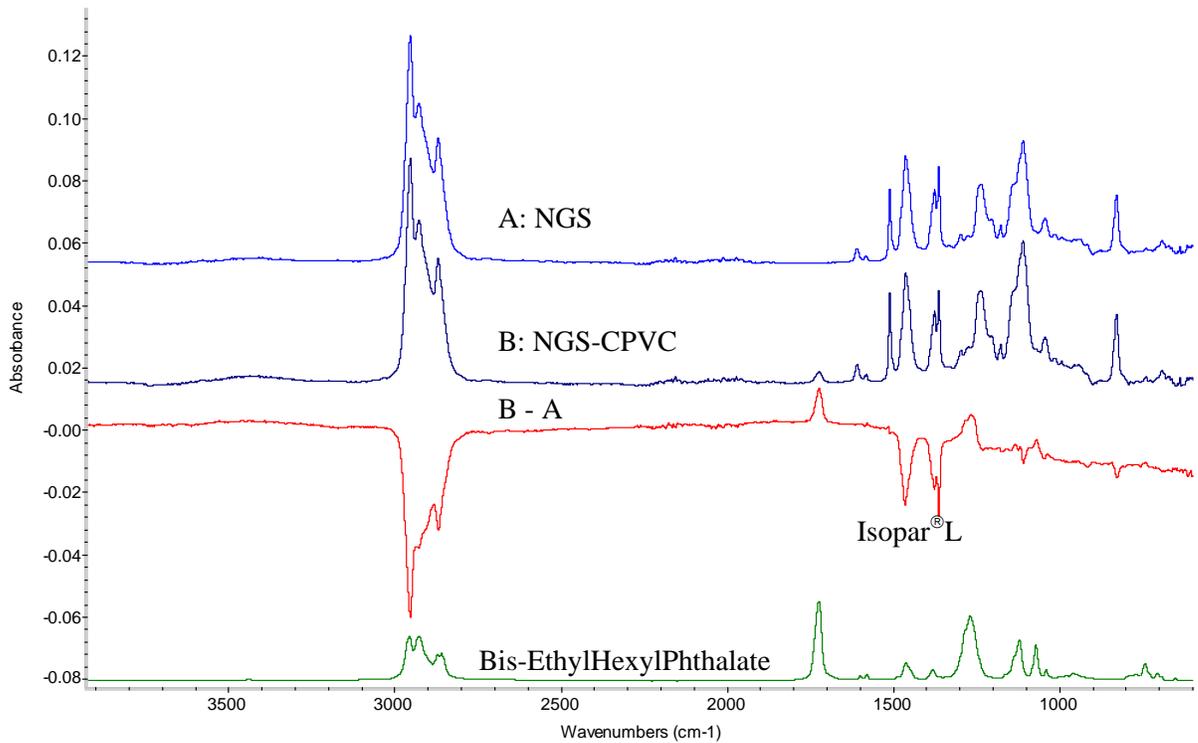


Fig. 4F. The FTIR spectra of NGS after contacting CPVC, of as made NGS, and the difference spectrum.

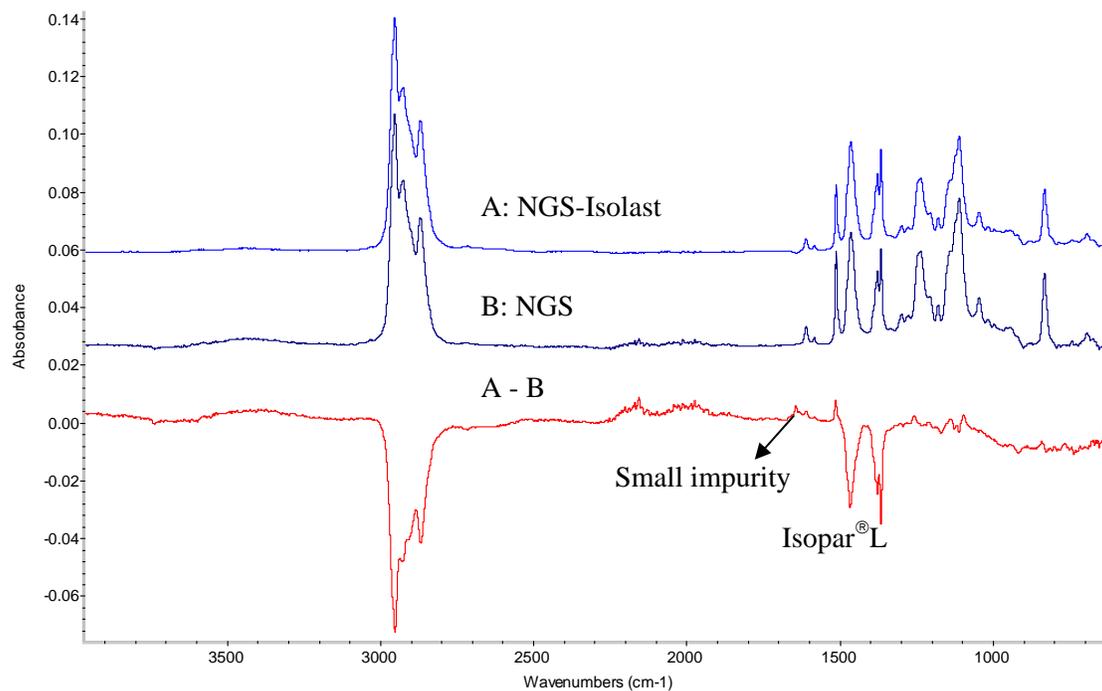


Fig.5F. The FTIR spectra of NGS after contacting Isolast, of as made NGS, and the difference spectrum.

5.0 References

- ¹ B. Moyer, J. F. Birdwell, L. H. Delmau, D. L. Schuh, E. L. Stoner, N. J. Williams, S. D. Fink, T. B. Peters, R. A. Pierce, R. A. Leonard, and M. W. Geeting, "Next Generation Cesium Solvent," EM Technical Exchange Meeting, Atlanta, GA, Nov. 16-18, 2010.
- ² B. A. Moyer, P. V. Bonnesen, L. H. Delmau, F. V. Sloop, Jr., N. J. Williams, J. F. Birdwell, Jr., D. L. Lee, R.A. Leonard, S. D. Fink, T. B. Peters, and M. W. Geeting, "Development of the Next-Generation Caustic-Side Solvent Extraction (NG-CSSX) Process for Cesium Removal from High-Level Tank Waste", WM2011 Conference, February 27–March 3, 2011 (Phoenix, AZ).
- ³ T. B. Peters, S. D. Fink, "Results of the First Extraction-Scrub-Strip Testing Using Improved Solvent Formulations", SRNL-STI-2010-00586, Rev 0, September 2010.
- ⁴ F. F. Fondeur and S. D. Fink, "Chemical Stability of Polyphenylene Sulfide in the Next Generation Solvent For Caustic-Side Solvent Extraction," SRNL-STI-2011-00738, December 2011.
- ⁵ D. D. Larsen and M. A. Pelicone, "MCU Task Requirements and Criteria Design Constraint Verification (U)," LWO-SPT-2007-00149, July 2007.
- ⁶ S. L. Rosen, "Fundamental Principles of Polymeric Materials," second edition, John Wiley & Sons, New York, 1988.

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