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Polymer Grouts for Plugging Lost Circulation in Geothermal Wells

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Abstract

We have concluded a laboratory study to evaluate the survival potential of polymeric materials used for lost circulation plugs in geothermal wells. We learned early in the study that these materials were susceptible to hydrolysis. Through a systematic program in which many potential chemical combinations were evaluated, polymers were developed which tolerated hydrolysis for eight weeks at 500°F. The polymers also met material, handling, cost, and emplacement criteria. This screening process identified the most promising materials. A benefit of this work is that the components of the polymers developed can be mixed at the surface and pumped downhole through a single hose. Further strength testing is required to determine precisely the maximum temperature at which extrusion through fractures or voids causes failure of the lost circulation plug.

Acknowledgements

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Contents

1. Introduction…… 7
2. Experimental Work…… 8
2.1 Polymer Chemistries Studied…… 8
2.2 Material Selection…… 9
2.3 Results and Discussion of Early Testing…… 10
2.4 Water-Activated Samples…… 11
2.5 Water and Heat-Activated Samples…… 11
2.6 Heat-Activated Polyurea…… 11
2.7 Heat-Activated Polybutadiene Resin and Dimethacrylate Monomer…… 12
2.8 Test Procedures and Results…… 12
2.9 Hydrothermal Stability Testing…… 13
3. Chemical Analysis…… 13
4. Discussion…… 18
5. Conclusions…… 27
6. References…… 28

Appendix

1 Polyurethane Grout Hydrolysis Summary of 275°F Experiments…… 29
2 Infrared Spectroscopy…… 49

Figures

1 Absolute Shore Durability 275ºF…… 20
2 Normalized Shore Durability 275ºF…… 20
3 Absolute Shore Durability 300ºF…… 21
4 Normalized Shore Durability 300ºF…… 21
5 Absolute Shore Durability 325ºF…… 22
6 Normalized Shore Durability 325ºF…… 22
7 Absolute Shore Durability 350ºF…… 23
8 Normalized Shore Durability 350ºF…… 23
9 Absolute Shore Durability 400ºF…… 24
10 Normalized Shore Durability 400ºF…… 24
11 Absolute Shore Durability 450ºF…… 25
12 Normalized Shore Durability 450ºF…… 25
13 Absolute Shore Durability 500ºF…… 26
14 Normalized Shore Durability 500ºF…… 26

Tables

1 Summary of Polymer Tests…… 14

1. Introduction

Sandia National Laboratories, through support of the Geothermal Energy initiative within the U.S. Department of Energy, has studied wellbore integrity in geothermal environments. A portion of wellbore integrity research has been directed towards developing materials and methods to more economically solve lost-circulation problems. These environments are hot, with temperatures in the range of 150°F to 600°F and typically wet with hot water, brine, etc. In severe lost-circulation situations, cross flow may be experienced, in which pressure-induced fluid flow may occur through a borehole. When lost circulation of drilling fluid is experienced in geothermal wells, cement plugs are typically used to solve the problem. This is accomplished by stopping drilling, placing the cement plug, allowing the cement to cure, and re-drilling. However, high cross flow rates, low pore pressures, and/or large voids can present more difficult circumstances for conventional cement plug deployment. For example, cement can be washed out by cross flow before it has set, may drift away, or the amount of cement placed simply may not fill the void present.

This paper reports on polymer grouts that have been developed to help overcome some of the deficiencies of the cement grouts. It reviews the chemistry and mechanical/chemical stability (hydrolysis) of the polymer grouts that have been tested for hydrothermal stability. These grouts flash set upon contact activation with water, and when constrained during placement through a packer, they will flow (low viscosity) and expand to fill the accessible volume by the nature of the chemical reaction through which they are formed.

In 2001, Green Mountain International, Inc., Sub-Technical, Inc., Resource Group, and Sandia National Laboratories joined forces to deploy a polyurethane-based grout to plug a lost-circulation zone at Rye Patch, Nevada. Over twenty conventional cement plugs and other common plugging techniques had already been tried on this well without success. A two-part polyurethane grout (Mountain Grout ISP) was used to plug the lost-circulation zone and permit completion of the well. The two-part system was chosen because of its availability for application to the relatively shallow depth, 740 ft, and low temperature 170°F (Mansure et al, 2001) well.

The success at Rye Patch inspired a more rigorous laboratory study of polyurethane-based grouts. The goals of this work were to include development of a better understanding and improvements upon (1) the deployment technique(s) of polyurethane-based grout and (2) the chemical/hydrolysis/thermal stability of polyurethane-based grouts. Because lost-circulation zones are commonly encountered at much greater depths and higher temperatures than those at Rye Patch, greater survival temperatures are of interest. Also, simplification of the deployment techniques was desired.

The desired characteristics of polyurethane-based grout systems, in terms of both material development and means of deployment, was established based on the historic Sandia knowledge base with the specific field application at Rye Patch. The two-part polyurethane used at Rye Patch was highly reactive and, therefore, had to be mixed seconds before dispensing into the lost-circulation zone. This problem was resolved by the use of two separate hoses and a static mixer located at the deployment zone. However, a polymer grout that could be dispensed in the lost-circulation zone as a single component (activated by contact with water) would dramatically reduce the complexity of the equipment needs and broaden the window of reaction time.

While the relatively low temperature at the lost-circulation zone (170°F) was not a problem for the Mountain Grout ISP, in preparation for other more severe geothermal lost-circulation problems, the product was tested for hydrothermal stability. The Mountain Grout ISP performed well at temperatures up to 225°F. Literature reviews and discussions with others in the polyurethane industry revealed that little reliable information was available on the stability of polyurethane under the more severe geothermal well conditions.

A program was initiated to screen a variety of isocyanate reaction products and a few other polymers in an effort to optimize the hydrothermal performance. The initial needs included development of a material with no special handling requirements and considered non-hazardous by the Department of Transportation (DOT). The polymer also must be readily pumpable, with a viscosity 200 cps maximum at pumping temperature (maximum 100°F surface temperature). We must be able to control the gel time. The reaction rate needs to be adjustable for varied conditions both at the surface and downhole. For example, it must be chemically stable with no pre-gelation at surface or in the delivery hose. We must be able to control the placement such that it has minimal water solubility, and adheres well to rock surfaces through a single-delivery hose. Once placed, the polymer must be hydrothermally stable for six weeks at temperatures exceeding 300°F. Also, once placed, the grout would have to be sufficiently stiff, to drill with conventional means, and present no unanticipated problems with drill bit plugging. In order to be competitive with cement grouts, the polymer plug must be inexpensive and reliable.

2. Experimental Work

2.1 Polymer Chemistries Studied

In the following, a variety of polymer chemistries are presented. The information is provided as background. These are the fundamental polymer chemistries studied, some of which were ultimately combined in varying amounts to produce materials for evaluation. While most of the work was systematic, there were attempts to sample many of the chemistries on a more limited basis. We were always striving for a material to be developed which ultimately was hydrolysis-resistant. As such, the initial formulations tested were off-the-shelf (materials proclaimed to be water- and temperature-resistant). Chemical attributes of “good survivors” were selectively culled and combined to make polymers believed to be more hydrolysis resistant. The success of this work is demonstrated in the results.

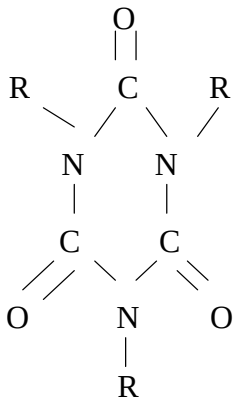
Isocyanate is the primary building block of conventionally produced polyurethane polymers. Isocyanate can also react to produce other chemical linkages. Some of these reactions and the resulting products are shown here:

URETHANE: R-N=C=O + R’-OH = R-NH-CO-O-R’

UREA: 2 R-N=C=O + H2O = R-NH-CO-NH-R + CO2
Note: this urea is formed by reaction with water.

UREA: R-N=C=O + R’-NH2 = R-NH-CO-NH-R’
Note: this urea is formed by reaction with an amine.

ISOCYANURATE: 3 R-N=C=O =



CARBODIMIDE: 2 R-N=C=O = R-N=C=N-R + CO_2

Note: R (and R') is a general symbol used in organic chemistry to represent an undesignated organic portion of a molecule (i.e. a benzene or alkyl group)

There are many other primary and secondary reactions involving isocyanates.

In order to produce a urethane polymer, the isocyanate and other reactants must be polyfunctional. There is a wide array of polyisocyanates, polyols, polyamines and other reactants from which to choose. The most widely used aromatic polyisocyanates are toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI). Aliphatic polyisocyanates such as isophorone diisocyanate (IPDI) and tetramethylxylene diisocyanate (TMXDI) are important for coating applications requiring UV stability. MDI is generally recognized as being easier to handle safely due to its lower vapor pressure.

Typical polyols of the greatest commercial significance are based on polyethers and polyesters. Polyester polyols are known to exhibit relatively poor hydrolytic stability and higher viscosity. Polyether polyols are prepared by alkoxylating a polyfunctional starting material such as glycerine, sucrose, diethanol amine and numerous others.

Polyamines can be aromatic or aliphatic with primary or secondary amine groups. Primary amines tend to be very reactive creating difficulty in achieving an adequate mix with the isocyanate.

The above-mentioned materials represent only a fraction of the variety of compounds that can be used with isocyanate reaction chemistry. This two-year development program involved a sampling of the most promising candidates and evaluating their potential to optimize the hydrothermal performance of the resulting polymer. The program duration permitted hydrolysis testing to determine time-dependent effects. The material development and evolution was based on trial and results with specific chemistries.

2.2 Material Selection

The two-part system used at Rye Patch was used as the base-line material. This system is based on MDI and a combination of ether and aromatic ester polyols.

A single component MDI-based prepolymer was selected for evaluation based on its low viscosity and ease of deployment.

The selection of other materials was guided by knowledge of polyurethane chemistry, experience with commercial applications, literature references, and recommendations from industry sources, test results, material costs, availability and toxicity. Some non- isocyanate-based polymers were also selected for evaluation.

As this work progressed during testing, additional chemistry details were incorporated into the evolution of thoughts and chemistries studied. Polyisocyanurates and carbodiimides are widely used in polyurethane chemistry to improve thermal stability. These reaction products of polyisocyanate with polyisocyanate are obtained by catalyst selection and temperature. Commercial polyureas are often used in place of standard polyurethanes to improve the chemical resistance and thermal performance. Aromatic amines offer greater hydrophobicity than aliphatic amines. P-phenylene diisocyanate (PPDI) was reported to offer improved hydrolytic stability over MDI. Polyether polyols are typically made from ethylene or propylene oxide. Ethylene oxide based polyols are more hydrophilic than the corresponding polyol made with propylene oxide. Polybutadiene polyols have no ether linkages and offer even greater hydrophobicity than those based on propylene oxide. Polybutadiene polyols have unsaturated carbon-carbon bonds that offer sites for additional crosslinking through free radical polymerization. Acrylates and methacrylates were blended with the polybutadiene based prepolymer to increase the crosslinking. Diluents were used with some formulations to reduce viscosity. Propylene carbonate was compared with trimethyl pentanediol diisobutyrate. A commercially available ceramic-filled epoxy that is promoted as offering stability to 400°F at water depths of 2000 feet was included. Crosslinked diacrylate was included based on the manufacturer's claim of stability at 400°F.

2.3 Results and Discussion of Early Testing

The original laboratory test procedure was qualitative; consequently, no definitive time could be assigned for the material's stability. Pieces of the plugs were submerged in water in an aluminum cup and placed in a small high-pressure vessel. The vessel was placed in an oven, and the entire vessel heated while temperature (and sometimes pressure) was monitored. The vessel was removed from the oven periodically (every few days to a week), and the samples were inspected. Materials tended to deteriorate gradually by swelling, softening or breaking. Based on the observations recorded for these tests, the conclusions are as follows:

- The single-component prepolymer performed better than the two-component system used at Rye Patch.
- MDI performed better than PPDI.
- Ethylene oxide polyol performed slightly better than propylene oxide polyol.
- Polybutadiene polyol showed no improvement over ethylene oxide polyol.
- Crosslinking through the unsaturated bonds in polybutadiene improved performance.
- Dimethacrylate performed slightly better than diacrylate.
- TXIB performed slightly better than propylene carbonate.
- Polyurea made from aromatic amine performed better than polyurea made from aliphatic amine.
- Ceramic-filled epoxy failed to perform as advertised (400°F) but performed well at 275°F.

- Crosslinked diacrylate and dimethacrylate did not meet the projected 400°F performance but performed well at 275°F.
- Isocyanurates and carbodiimides failed to improve performance.
- Polyurea outperformed polyurethane.

After consideration of these conclusions, additional samples of some of the material were prepared to refine the initial evaluation. These additional samples produced specimens of more consistent proportions and densities. The evaluation procedure was also modified to provide more objective comparisons (described below). The final series of materials prepared for testing is described as follows:

2.4 Water-Activated Samples

As described earlier, when an isocyanate group is reacted with water, a urea linkage results. A prepolymer (test material[1]: DEG-2-35) was prepared using polymeric MDI and a polyether, ethylene oxide capped triol. In one case, the prepolymer was mixed with 50% polymeric MDI. Both were then blended with TXIB to lower their viscosities (DEG-2-35-1 and DEG-2-35-2).

A second prepolymer was prepared by reacting polymeric MDI with polybutadiene polyol and diluting with TXIB (DEG-2-36-1).

The above formulations were cured by reaction with small amounts of water.

2.5 Water and Heat-Activated Samples

The polybutadiene prepolymer was diluted with a functional dimethacrylate monomer (DEG-2-36-2).

The polybutadiene prepolymer was also blended with a polybutadiene resin and dimethacrylate monomer (DEG-2-36-3).

The above formulations were cured by blending with a small quantity of water and dicumyl peroxide prior to heating to 250°F.

2.6 Heat-Activated Polyurea

As described earlier, the urea linkage can also be prepared by reacting isocyanate with an amine. Because the reaction between isocyanate and amine is so rapid, a dual component metering system would need to be used to deploy the system in the well. Therefore, a blocked amine was chosen so that the two components could be mixed and remain stable until heated.

Samples were prepared in which the ratio of isocyanate to amine index was varied from 1.0 to 1.2 to 1.4 (samples DEG-2-37-1, 2, 3). Curing was initiated by heating to 300°F.

[1] We used a systematic test material identification system that consisted of **DEG-A-B-C**. **DEG** stood for Dennis E. Galbreath, chemical fabricator. **A-B** represented a chemical family, and **C** represented variations on the **A-B** chemistry.

2.7 Heat-Activated Polybutadiene Resin and Dimethacrylate Monomer

Formulations were prepared in which polybutadiene resin was blended with 20% (DEG-2-38-1) and 40% (DEG-2-38-2) dimethacrylate monomer. Samples were prepared by mixing with a small amount of dicumyl peroxide and heating to 250°F.

2.8 Test Procedures and Results

The original test procedure involved placing small specimens of each sample in a water-filled aluminum cup in a Parr Bomb[2]. The specimens were weighted with a metal washer so that they remained submersed in the water. The Parr Bombs were then heated by placing them in an oven and internally pressurized in response to water pressure generated through heating to the desired test temperature. Periodically the specimens would be removed and tested for digestion by manually probing. *Digestion* is the term used to describe the physical/mechanical manifestations of hydrolysis, the chemical process in which water breaks down the polymer bonds. The evaluator would also make notes about any change in appearance or indentation caused by the washer.

As part of establishing this procedure, tests were done at elevated pressures (pressures in excess of the vapor pressure of water) and also with insufficient water such that all the water evaporated. A slight increase in the degradation rate was observed as the pressure was increased to ~1,500 psi, but this increase was on the same order as variability from sample to sample. This increase was attributed to the increased rate that water diffused into the samples at elevated pressures. At pressures below the vapor pressure of water (no liquid phase present) degradation was minimal. This requirement of a liquid water phase for hydrolysis of the polyurethane was interpreted as the explanation of why many materials, claimed to be stable at elevated pressures, do not perform well downhole – they have been temperature-rated based on thermal degradation in air by oxygen attack, rather than in water due to H^+ and OH^- attack. As such, there is a chemical effect of water to degrade the polymers (hydrolysis) which is accelerated/exacerbated by heat.

For the final series of tests, the evaluation procedure was supplemented to include durometer readings, thus improving the objectivity of the testing. This quasi-quantification of the mechanical integrity of final polyurethane grout compositions utilized the standard test method for rubber property, durometer hardness (ASTM 2240), also termed “Shore Hardness or Shore Durability”.

> This test method is based on the penetration of a specified indentor forced into the material under specified conditions. The indentation hardness is inversely related to the penetration and is dependent on the elastic modulus and viscoelastic behavior of the material. The shape of the indentor and the force applied to it influence the results obtained so that there may be no simple relationship between the results obtained with one type of durometer and those obtained with either another type of durometer or another instrument for measuring hardness. This test method is an empirical test intended primarily for control purposes. No simple relationship exists between indentation hardness determined by this test method and any fundamental property of the material tested. (ASTM 2240)

Nevertheless, this method allowed us to provide a valid comparative measure of changes in mechanical integrity of polyurethane resulting from hydrolysis. Other tests were tried (gas chromotography, dynamic modulus, and thermal gravimetric), but were found less repeatable than the durometer.

[2] A Parr Bomb is a commercially available pressure vessel. The vessels were fitted with temperature and pressure-sensing instruments.

2.9 Hydrothermal Stability Testing

All of the above samples were evaluated for hydrolytic stability by placing small wedge-shaped sections of each into the test bomb at 275°F and ~45 PSI; 300°F and ~67 PSI; 325°F and ~96 PSI; 350°F and ~135 PSI; 400°F and ~245 PSI; 450°F and ~420 PSI; and 500°F and ~670 PSI. Durometer readings were taken at regular intervals and plotted. A 50% drop in durometer reading was arbitrarily chosen as the "end point" to obtain days of stability at the test conditions and thereby rank the materials. The results are tabulated in Table 1.

Table 1 Key

Test #: identifies sample number linked to a data notebook
Name: identifies general polymer chemical group evaluated
Species: identifies specific polymer chemical group evaluated (if required)
Material: chemical description
Preparation: curing process
Reaction Temp. ^{o}F: curing temperature
Test Temp. ^{o}F: temperature at which sample tested
Start/High Pressure PSI: starting pressure, highest pressure during test
Days Tested: days at temperature, pressure
Days till Digest: days until sample deteriorated
Comments: comments, observations, etc.

3. Chemical Analyses

A few samples were submitted for chemical analyses using an infrared spectrometer. The samples were fresh polymer samples, as well as those that were subjected to hydrolysis conditions. The detailed report for this work is included in Appendix 2 and is summarized as follows.

Although the geothermal plugs retain much of their physical properties, a lot of chemistry is occurring during aging, including hydrolysis of ester linkages in the methacrylate component and hydrolysis of urethane groups in the urethane component. In addition, there is apparent loss of the butadiene component in aged DEG 2-38-1, of the methacrylate component in DEG 2-38-2, and of both the methacrylate (325°F) and butadiene (350°F) components in DEG 2-36-3. The higher aging temperature tends to enhance the aging effects.

Having tested the polymers to greater temperatures than these samples that were chemically analyzed, we assume that similar and possibly more degradation would have occurred at the greater temperatures. The index test used does not indicate mechanical degradation; however, the analyses suggest more chemical bonds are broken with increasing temperature. Apparently, in this chemical system the broken bonds are not manifested macroscopically in the index testing.

Table 1. Summary of Polymer Tests

Test #	Name	Species	Material	Preparation	Reaction Temp. °F	Test Temp. °F	Start/High Pressure PSI	Days Tested	Days till Digest	Comments
Parr #12	G.M. Flex:1-Part	GM Flex	MDI/Polyether(EO/PO) Prepolymer	Cured by reaction with water to produce urea linkages	250	235	600/780	7	No Digest	
						250	600/770	6	No Digest	
						260	600/810	12	No Digest	Slight Softening, Maybe Early Digestion?
						270	600/800	6	No Digest	Scum Floating on H2O
						285	600/na	7	7	Unable to Determine Digest Day
Parr #16	G.M. Flex:1-Part				400	250	600/780	2	No Digest	
						275	600/810	1	No digest	Softened, Weight Marks, Early Digestion?
						300	600/850	3	3	Close to Being Mushy
Parr #17	Rubinate-1016	Rubinate 1016	MDI Prepolymer thermally stabilized	Cured by catalysis to produce a carbodiimide (Typically used for high thermal stability)	250	235	600/780	7	No digest	
						250	600/770	6	No Digest	
						260	600/810	12	No Digest	Slight Softening, Maybe Early Digestion?
						270	600/800	6	No Digest	Scum Floating on H2O
						285	600/na	7	7	Unable to Determine Digest Day
Parr #17	Rubinate-1016				250	350	600/880	4	4	Unable to Determine Digest Day
Parr #18	Rubinate-1016				350	350	600/880	4	4	Unable to Determine Digest Day
Parr #22	Rubinate-1016				300	275	600/840	3	3	Unable to Determine Digest Day
Parr #23	Rubinate-1104	Rubinate 1104	MDI Prepolymer	Cured by catalysis to produce a carbodiimide (Typically used for high thermal stability)	300	275	600/840	3	3	Unable to Determine Digest Day
Parr #28	DEG-1-135-1	DEG-1-135-1	MDI	Cured by catalysis (1) to produce an isocyanurate (Typically used for high thermal stability)	na	300	0/140	6	3	Slight Digest Day 3, Digest on Day 6
	DEG-1-135-2	DEG-1-135-2	MDI	Cured by catalysis (2) to produce an isocyanurate (Typically used for high thermal stability)	na	300	0/140	6	1	Digest Day 2, Digest on Day 3
Parr #29	DEG/Huntsman	DEG/ Huntsman	MDI	Cured by catalysis (3-heat activated) to produce an isocyanurate (Typically used for high thermal stability)	na	300	0/175	7	7	Unable to Determine Digest Day
Parr #30	Rye Patch: 2-Part	Rye Patch	MDI/polyether-polyester (2 Part)	This 2-part system was used at the Rye patch test because of grouting experience and simplicity	na	300	0/120	2	2	Slight Digest Day 1
	DEG/Huntsman	GM ISP A	MDI	Cured by reaction with water to produce urea linkages - no urethane linkages	na	300	0/120	4	4	No Digest Day 3, Digest Day 4
	G.M. Flex:1-Part	DEG Acylate	Diacrylate	Peroxide/heat cured - no urethane linkages	250	300	0/120	4	4	Slight Digest Day 2, Digest Day 4
Parr #31	Rye Patch: 2-Part	DEG-2-22	MDI Prepolymer/Amine	This 2-part system reacts to produce a polyurea with urethane linkages	na	300	1,250/1,730	2	2	Start Digest Day 1, Disappeared Day 2

Test #	Name	Species	Material	Preparation	Reaction Temp. °F	Test Temp. °F	Start/High Pressure PSI	Days Tested	Days till Digest	Comments
	DEG/Huntsman	DEG-2-28	Ceramic filled epoxy	This commercial 2-part epoxy system was reported to perform well at 400F and 1000 PSI in water	na	300	1,250/1,730	4	4	Start Digest Day 4
	G.M. Flex:1-Part	DEG-2-34	MDI/Polyether(EO/PO) prepolymer	Cured by reaction with water to produce urea linkages - included as a control of restricted expansion sample prep.	250	300	1,250/1,730	4	2	Start Digest Day 3, Digest day 4
Parr #32	Rye Patch: 2-Part	DEG-2-32-I	MDI/Polyether(PO) prepolymer with TXIB diluent	Cured by reaction with water to produce urea linkages - the elimination of EO and Propylene carbonate should make the polymer more hydrophobic resulting in greater hydrolytic stability	na	275	0/50	7	3	Start Digest Day 3, Disappeared Day 7
	DEG/Huntsman	DEG-2-32-II	MDI/Polyether(PO) prepolymer with propylene carbonate diluent	Cured by reaction with water to produce urea linkages	na	275	0/50	14	No Digest	Brittle,Swollen and Warped Day 14
	G.M. Flex:1-Part	DEG-2-33-I	MDI/PolyBD prepolymer with TXIB diluent	Cured by reaction with water to produce urea linkages - Polybutadiene is very hydrophobic and should maximize the resistance to hydrolosis for a linear polyol	250	275	0/50	14	No Digest	Start Softening Day 7, More Softening Day 10
Parr #33	Rye Patch: 2-Part	DEG-2-31-I	PPDI/polyether prepolymer/Blocked amine	Cured by heat release of the blocking agent and production of urea linkages - PPDI is reported to offer improved hydrolytic stability	na	250	0/na	20	14	No Digest Day 14, Digest Day 20
	DEG/Huntsman	DEG-2-31-II	MDI/Blocked amine	Cured by heat release of the blocking agent and production of urea linkages - no urethane linkages	na	250	0/na	41	41	No Digest Day 34, Slight Digest Day 41
	G.M. Flex:1-Part	DEG-2-33-II	MDI/PolyBD prepolymer/Diacrylate	Cured by reaction with water to produce urea linkages and additionally through carbon-carbon double bonds	250	250	0/na	41	20	No Digest Day 14, Digest Day 20
Parr #34	Rye Patch: 2-Part	DEG-2-33-III	MDI/PolyBD prepolymer/ Dimethacrylate	Cured by reaction with water to produce urea linkages and additionally through carbon-carbon double bonds	na	225	0/na	52	35	Start Softening Day 35, Digest Day 45
	G.M. Flex:1-Part	DEG-2-35-1	MDI/Polyether (EO/PO) Prepolymer	Cured by reaction with water to produce urea linkages	250	225	0/na	52	No Digest	
Parr #39	G.M.: ISP-A	DEG-2-35-2	MDI/Polyether (EO/PO) Prepolymer with decreased urethane linkages	Cured by reaction with water to produce urea linkages - less urethane, more urea, more highly crosslinked	200	275	0/na	27	22	No Digest Day 22, Digest Day 27
DEG-Acryl-ate	140	DEG-2-36-1	MDI/PolyBD prepolymer with TXIB diluent	Cured by reaction with water to produce urea linkages - control of DEG-2-33-I	140c	275	0/na	27	No Digest	Rubbery Day 7, Very Rubbery Day 27
	160	DEG-2-36-2	MDI/PolyBD prepolymer with Dimethacrylate	Cured by reaction with water to produce urea linkages and additionally through carbon-carbon double bonds - control of DEG-2-33-III	160c	275	0/na	27	No Digest	Rubbery Day 7, Very Rubbery Day 27
	180	DEG-2-36-3	MDI/PolyBD prepolymer with polyBD resin and Dimethacrylate	Cured by reaction with water to produce urea linkages and additionally through carbon-carbon double bonds - less urethane, less urea, more crosslinking	180c	275	0/na	27	No Digest	Rubbery Day 7, Very Rubbery Day 27
DEG-2-22	Sprayed Polyurea	DEG-2-37-1	MDI/Blocked amine	Cured by heat release of the blocking agent and production of urea linkages - control of DEG-2-31-II	na	275	0/na	14	8	Inspect Day 8, Digest Day Unknown
DEG-2-28	Ceramic Filled Epoxy	DEG-2-37-2	MDI/Blocked amine	Cured by heat release of the blocking agent and production of urea linkages - 20% excess isocyanate allows for additional crosslinking through biuret or urea linkages	na	275	0/na	52	No Digest	Light Surface Softening Day 42

Test #	Name	Species	Material	Preparation	Reaction Temp. °F	Test Temp. °F	Start/High Pressure PSI	Days Tested	Days till Digest	Comments
DEG-2-28	Ceramic Filled Epoxy	DEG-2-37-3	MDI/Blocked amine	Cured by heat release of the blocking agent and production of urea linkages - 40% excess isocyanate for additional crosslinking through biuret or urea linkages	na	400	0/245	21	14	Light Digest Day 14, Severe Day 21
DEG-2-34	G.M. Flex:1-Part	DEG-2-38-1	PolyBD resin/Dimethacrylate	Peroxide/heat cured - 20% Dimethacrylate - no urethane to hydrolyze	na	300	0/67	11	4	Early Digest Day 4, Total Day 11
DEG-2-32-I	G.M. Flex:1-Part	DEG-2-38-2	MDI/Polyether(PO) Prepolymer/TXIB diluent	Cured by reaction with water to produce urea linkages-restricted expansion to simulate down hole results	na	300	0/67	11	4	Early Digest Day 4, Total Day 11
DEG-2-32-II	G.M. Flex:1-Part		MDI/Polyether(PO) Prepolymer/Propylene carbonate diluent	Cured by reaction with water to produce urea linkages-restricted expansion to simulate down hole results	na	300	0/67	4	4	Unable to Determine Digest Day
DEG-2-33-I	PolyBD/MDI		MDI/Polybutadiene polyol prepolymer/TXIB diluent	Cured by reaction with water to produce urea linkages-restricted expansion to simulate down hole results	na	300	0/67	11	4	Early digest Day 4, Total Day 11
DEG-2-31-I	PPI Prepolymer		PPDI Prepolymer/blocked amine	Cured by thermal unblocking of amine to react with isocyanate producing urea linkages	na	300	0/67	4	4	Unable to Determine Digest Day
DEG-2-31-II	Polymeric MDI		MDI/blocked amine	Cured by thermal unblocking of amine to react with isocyanate producing urea linkages	na	300	0/67	11	4	Early Digest Day 4, Total Day 11
DEG-2-33-II	PolyBD/MDI		MDI/Polybutadiene polyol prepolymer/Diacrylate	Cured by reaction with water to produce urea linkages and additionally through carbon-carbon double bonds	na	300	0/67	11	6	Early Digest Day 6, Very Soft Day 11
DEG-2-33-III	PolyBD/MDI		MDI/Polybutadiene polyol prepolymer/ Dimethacrylate	Cured by reaction with water to produce urea linkages and additionally through carbon-carbon double bonds	na	300	0/67	11	6	Early Digest Day 6, Soft Day 11
DEG-2-31-II	Polymeric MDI		MDI/blocked amine	Cured by thermal unblocking of amine to react with isocyanate producing urea linkages	na	275	0/na	30	11	Early Digest Day 11, More Digest Day 30
DEG-2-33-II	PolyBD/MDI		MDI/Polybutadiene polyol prepolymer/Diacrylate	Cured by reaction with water to produce urea linkages and additionally through carbon-carbon double bonds	na	275	0/na	30	14	Early Digest Day 14, More Digest Day 30
DEG-2-33-III	PolyBD/MDI		MDI/Polybutadiene polyol prepolymer/ Dimethacrylate	Cured by reaction with water to produce urea linkages and additionally through carbon-carbon double bonds	na	275	0/na	30	14	Slight Digest Day 14, Slight More digest Day 30
DEG-2-35-1	Flex Prepolymer		MDI/polyether(EO/PO) prepolymer	Cured by reaction with water to produce urea linkages	na	275	0/na	33	20	
DEG-2-35-2	Flex Prepolymer		MDI/polyether(EO/PO) prepolymer with more MDI	Cured by reaction with water to produce urea linkages	na	275	0/na	21	20	
DEG-2-36-1	Flex Prepolymer		MDI/Polybutadiene polyol prepolymer/ TXIB diluent	Cured by reaction with water to produce urea linkages	na	275	0/na	28	20	
DEG-2-36-2	PolyBD/MDI		MDI/Polybutadiene polyol prepolymer/ Dimethacrylate	Cured by reaction with water to produce urea linkages and additionally through carbon-carbon double bonds	na	275	0/na	56	33	
DEG-2-36-3	PolyBD/MDI		MDI/PolyBD polyol prepolymer/ Dimethacrylate/ PolyBD resin	Cured by reaction with water to produce urea linkages and additionally through carbon-carbon double bonds	na	275	0/na	56	n/a	
DEG-2-37-1	Isocyanate Index 1.0		MDI/blocked amine	Cured by thermal unblocking of amine to react with isocyanate producing urea linkages	na	275	0/na	56	56	
DEG-2-37-2	Isocyanate Index 0.8		MDI/blocked amine	Cured by thermal unblocking of amine to react with isocyanate producing urea linkages	na	275	0/na	56	56	

Test #	Name	Species	Material	Preparation	Reaction Temp. °F	Test Temp. °F	Start/High Pressure PSI	Days Tested	Days till Digest	Comments
DEG-2-37-3	Isocyanate Index 0.6		MDI/blocked amine	Cured by thermal unblocking of amine to react with isocyanate producing urea linkages	na	275	0/na	56	56	
DEG-2-38-1			PolyBD resin and Dimethacrylate(20%)	Cured by free radical polymerization by peroxide catalyst	250	275		28	n/a	Test ended to restart at greater T
DEG-2-38-2			PolyBD resin and Dimethacrylate(40%)	Cured by free radical polymerization by peroxide catalyst	250	275		28	n/a	Test ended to restart at greater T
DEG-2-36-3	PolyBD/MDI		MDI/PolyBD polyol prepolymer/ Dimethacrylate/PolyBD resin	Cured by reaction with water to produce urea linkages and additionally through carbon-carbon double bonds	na	300	0/67	40	n/a	
DEG-2-37-1	Isocyanate Index 1.0		MDI/blocked amine	Cured by thermal unblocking of amine to react with isocyanate producing urea linkages	na	300	0/67	19	19	
DEG-2-38-1			PolyBD resin and Dimethacrylate(20%)	Cured by free radical polymerization by peroxide catalyst	250	300	0/67	40	n/a	Test ended to restart at greater T
DEG-2-38-2			PolyBD resin and Dimethacrylate(40%)	Cured by free radical polymerization by peroxide catalyst	205	300	0/67	40	n/a	Test ended to restart at greater T
DEG-2-36-3	PolyBD/MDI		MDI/PolyBD polyol prepolymer/ Dimethacrylate/ PolyBD resin	Cured by reaction with water to produce urea linkages and additionally through carbon-carbon double bonds	na	325	0/96	56	n/a	Stable
DEG-2-38-1			PolyBD resin and Dimethacrylate(20%)	Cured by free radical polymerization by peroxide catalyst	250	325	0/96	56	n/a	Stable
DEG-2-38-2			PolyBD resin and Dimethacrylate(40%)	Cured by free radical polymerization by peroxide catalyst	250	325	0/96	56	n/a	Stable
DEG-2-36-3	PolyBD/MDI		MDI/PolyBD polyol prepolymer/ Dimethacrylate/ PolyBD resin	Cured by reaction with water to produce urea linkages and additionally through carbon-carbon double bonds	na	350	0/135	56	n/a	Stable
DEG-2-38-1			PolyBD resin and Dimethacrylate(20%)	Cured by free radical polymerization by peroxide catalyst	250	350	0/135	56	n/a	Stable
DEG-2-38-2			PolyBD resin and Dimethacrylate(40%)	Cured by free radical polymerization by peroxide catalyst	250	350	0/135	56	n/a	Stable
DEG-2-36-3	PolyBD/MDI		MDI/PolyBD polyol prepolymer/ Dimethacrylate/ PolyBD resin	Cured by reaction with water to produce urea linkages and additionally through carbon-carbon double bonds	na	400	0/245	56	n/a	Stable
DEG-2-38-1			PolyBD resin and Dimethacrylate(20%)	Cured by free radical polymerization by peroxide catalyst	250	400	0/245	56	n/a	Stable
DEG-2-38-2			PolyBD resin and Dimethacrylate(40%)	Cured by free radical polymerization by peroxide catalyst	250	400	0/245	56	n/a	Stable
DEG-2-36-3	PolyBD/MDI		MDI/PolyBD polyol prepolymer/ Dimethacrylate/ PolyBD resin	Cured by reaction with water to produce urea linkages and additionally through carbon-carbon double bonds	na	450	0/420	74	n/a	Stable
DEG-2-38-1			PolyBD resin and Dimethacrylate(20%)	Cured by free radical polymerization by peroxide catalyst	250	450	0/420	74	n/a	Stable
DEG-2-38-2			PolyBD resin and Dimethacrylate(40%)	Cured by free radical poly-merization by peroxide catalyst	250	450	0/420	74	n/a	Stable
DEG-2-36-3	PolyBD/MDI		MDI/PolyBD polyol prepolymer/ Dimethacrylate/ PolyBD resin	Cured by reaction with water to produce urea linkages and additionally through carbon-carbon double bonds	na	500	0/670	74	n/a	Stable
DEG-2-38-1			PolyBD resin and Dimethacrylate(20%)	Cured by free radical polymerization by peroxide catalyst	250	500	0/670	74	n/a	Stable
DEG-2-38-2			PolyBD resin and Dimethacrylate(40%)	Cured by free radical poly-merization by peroxide catalyst	250	500	0/670	74	n/a	Stable

The best performing materials at 275°F (DEG-2-36-3, DEG-2-37-1, DEG-2-38-1 and DEG-2-38-2) were selected for testing at 300°F (The results are tabulated in Table 1.)

DEG-2-36-3, DEG-2-38-1 and DEG-2-38-2 were selected for testing at 325°F and survived beyond 56 days and were subsequently tested at 350°F, 400°F, 450°F, and 500°F.

4. Discussion

The evaluations are based on single specimens representing each formulation variable. In this work, a 50% drop in durometer hardness was chosen as the "end point" for comparative purposes. However, since the initial durometer readings varied, a specific durometer value may offer a more accurate assessment of performance capability.

Although earlier results had suggested that more urea linkages from the isocyanate-water reaction would improve hydrothermal performance (See Parr #39, Mountain Grout ISP A), DEG-2-35-2 failed to demonstrate this enhanced performance.

Polybutadiene (DEG-2-36-1) is very hydrophobic and was expected to offer improved performance over the standard polyether polyol (DEG-2-35-1). The test results did not agree with this expectation. This performance confirms that found in earlier test results with DEG-2-33-1.

Based on the test results of formulations containing significant urethane linkages, the failure of this linkage appears to limit its usefulness to temperatures up to 275°F. No substantial difference in performance was observed between polyols based on propylene oxide or ethylene oxide. Polyols with greater functionality should enhance performance slightly but were not used due to the higher viscosity of the resulting prepolymers. High viscosities make it difficult to pump the material.

When additional crosslinking was introduced through the use of dimethacrylate monomer and the polybutadiene substantial improvement was observed. See DEG-2-36-2, DEG-2-36-3, DEG-2-38-1 and DEG-2-38-2.

The production of polyurea linkages from the reaction of isocyanate and amine appears to be more stable than those produced from the reaction of isocyanate and water. See DEG-2-37-1, 2, 3 vs. Parr #39, DEG-2-35-1, 2 and DEG-2-36-1. This may be due to incomplete conversion caused by stearic hindrance when trying to react the tightly compacted aromatic isocyanate molecules that must first react with water to create an amine that then must react with another isocyanate molecule to form the substituted urea.

The increase in the isocyanate to amine ratio with the DEG-2-37 series from 1.0 to 1.2 to 1.4 failed to improve the hydrothermal performance. DEG-2-37-1 demonstrated good performance while DEG-2-37-2 & 3 showed a progressive decline in performance suggesting a chain-terminating effect or susceptibility of the biuret linkage to hydrolysis.

The elimination of isocyanate reaction products (DEG-2-38-1 & 2) helps to demonstrate that those linkages are limiting the hydrothermal stability of the polymers. Ultimately, these latter compositions were judged to have survived the best (along with DEG-36-3).

The results of the Shore Durability test are shown in Figures 1-14 as a means to demonstrate a measure of the mechanical integrity, and its changes with time of the best of the polymers studied.

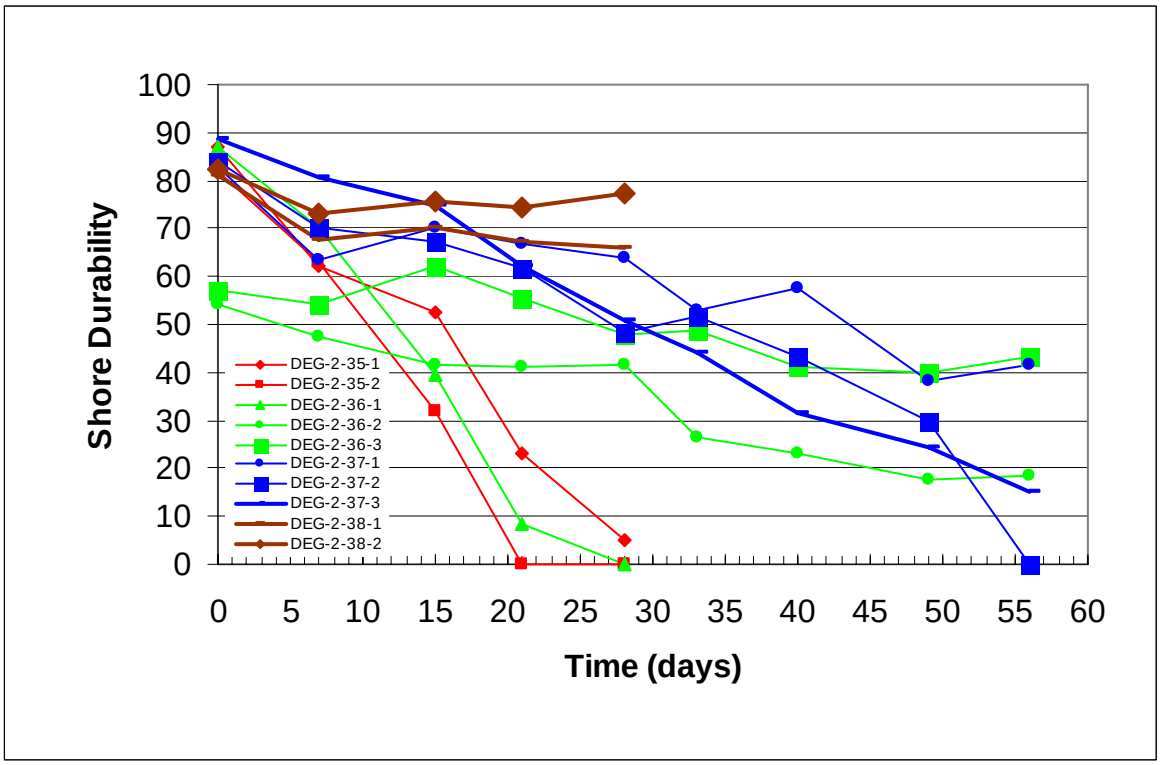


Figure 1. Absolute Shore Durability 275°F

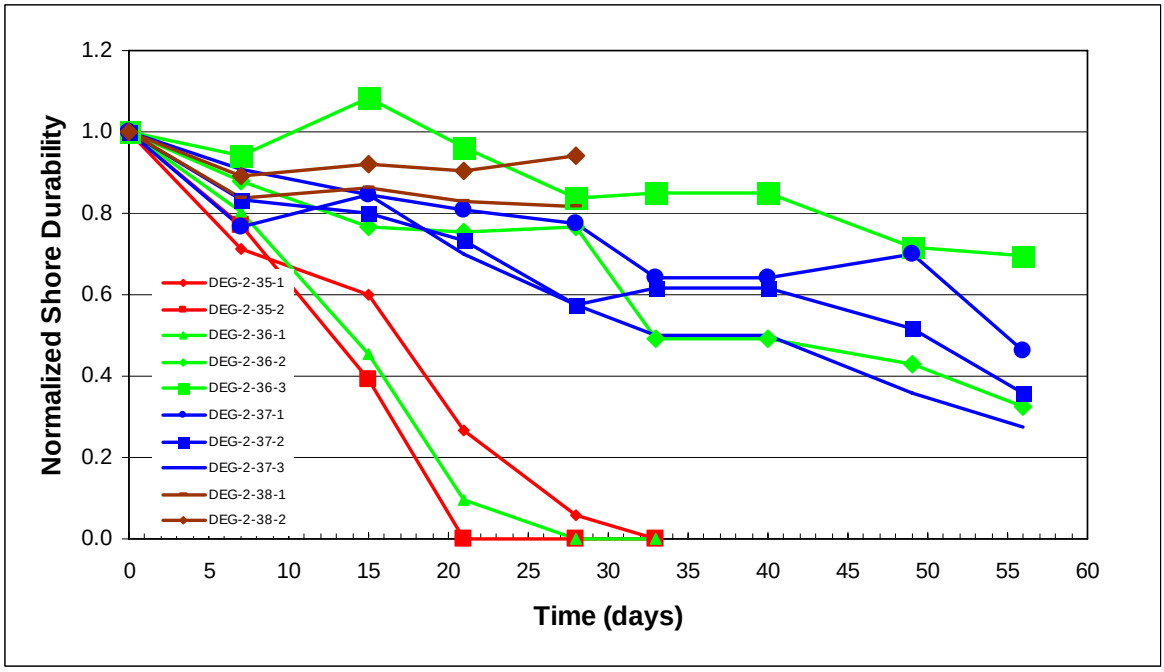


Figure 2 . Normalized Shore Durability 275°F

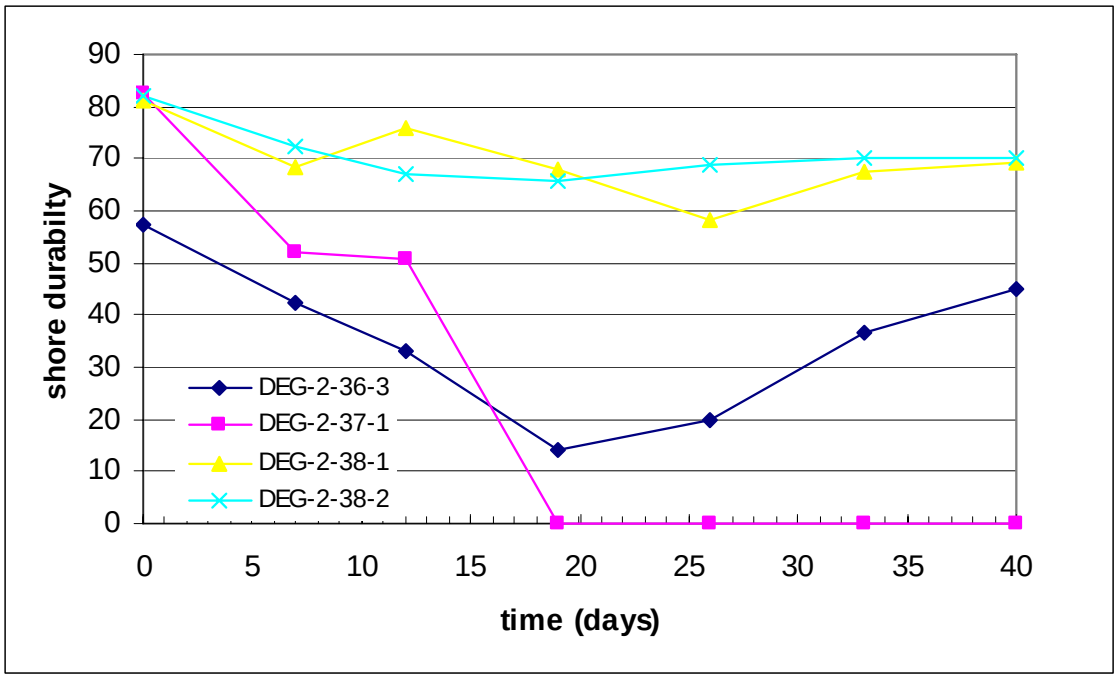


Figure 3. Absolute Shore Durability 300°F

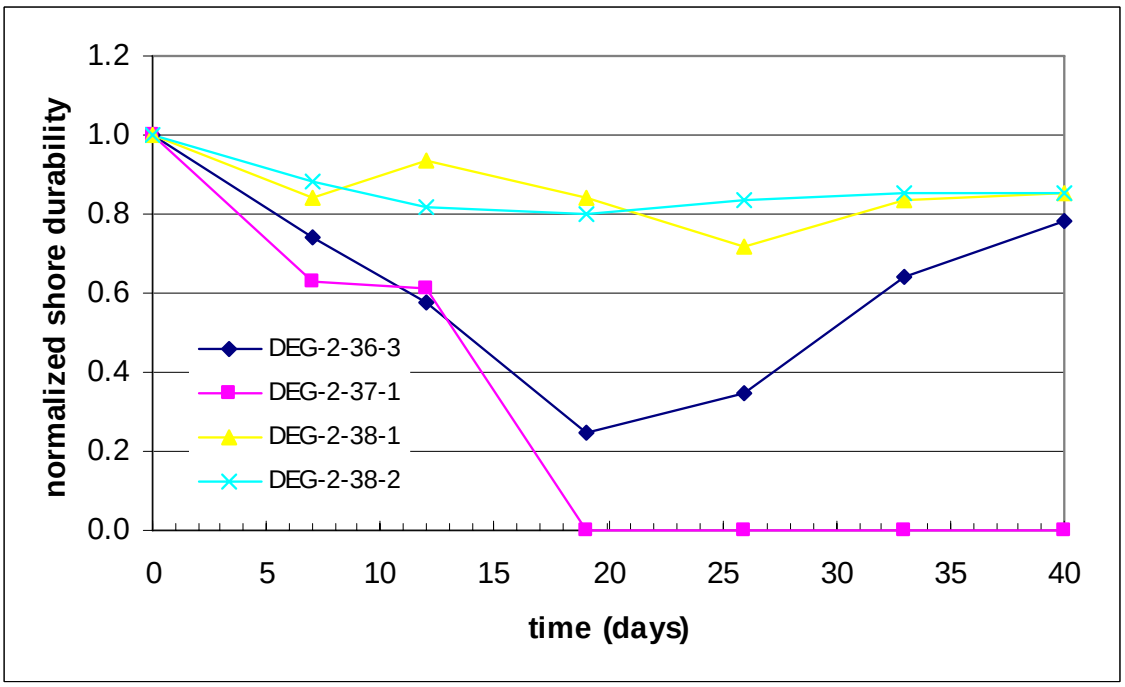


Figure 4. Normalized Shore Durability 300°F

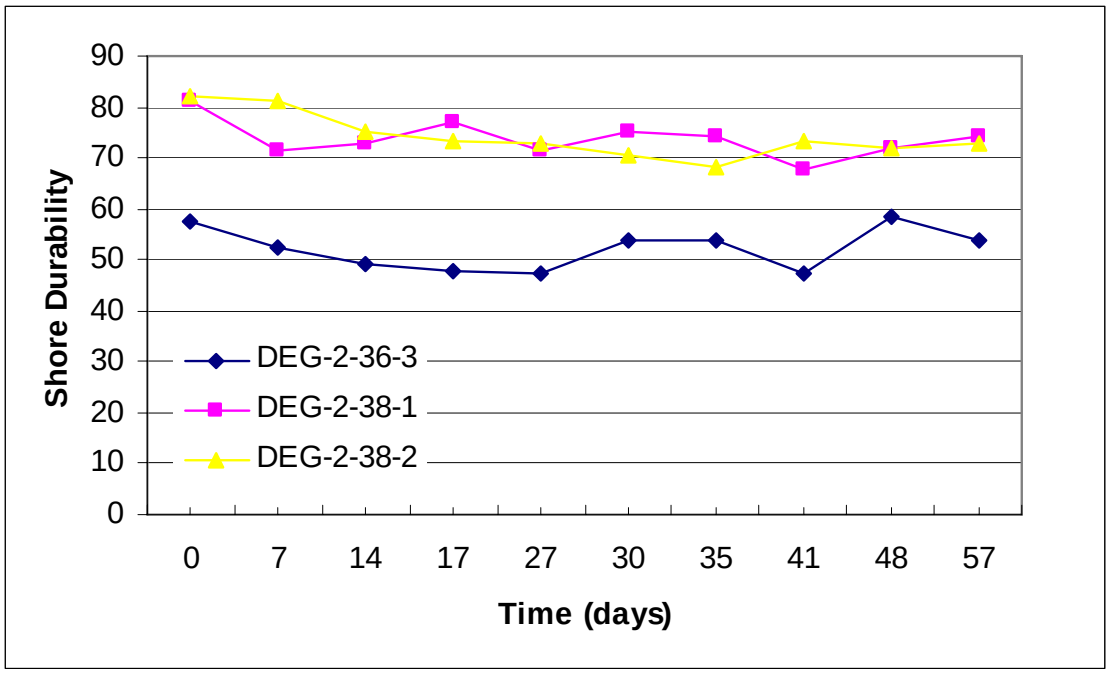


Figure 5. Absolute Shore Durability 325°F

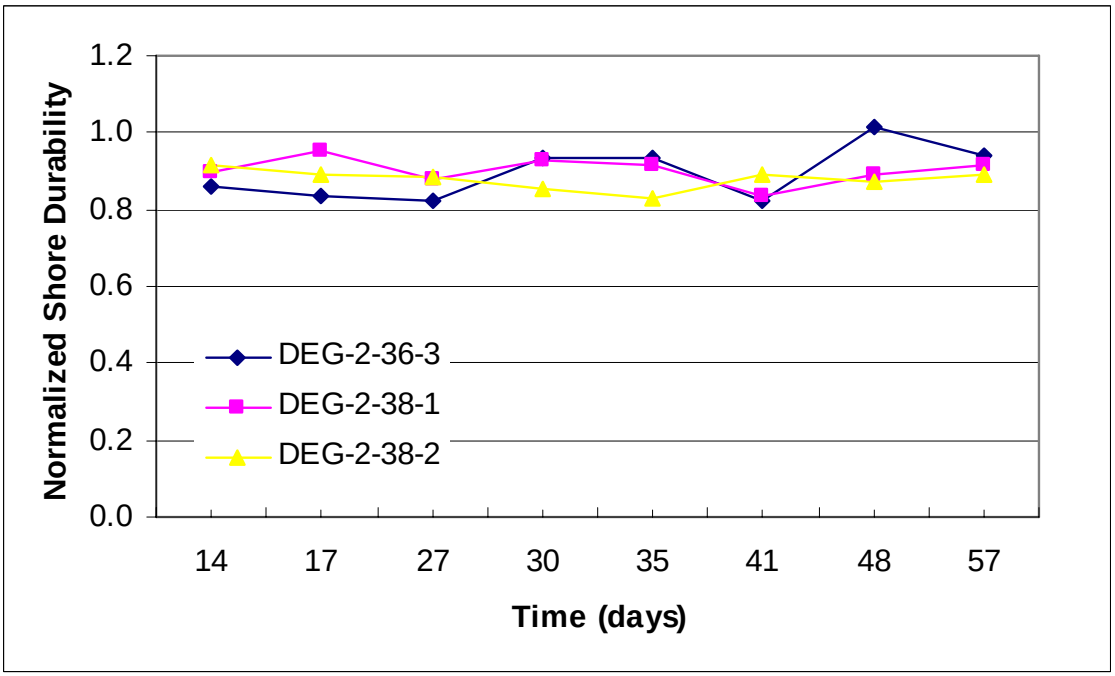


Figure 6. Normalized Shore Durability 325°F

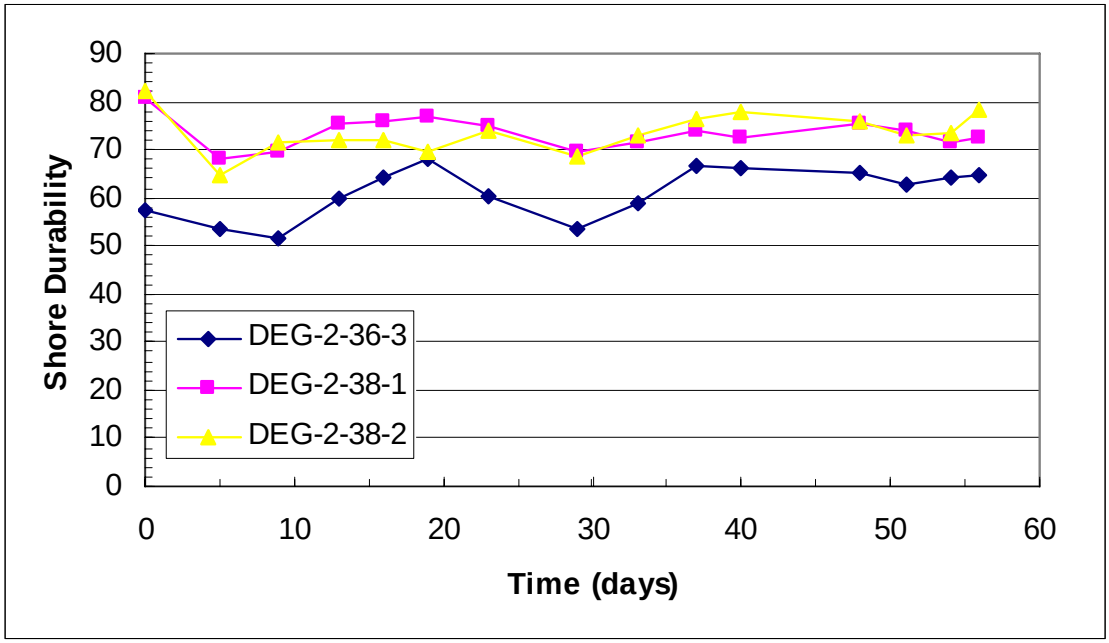


Figure 7. Absolute Shore Durability 350°F

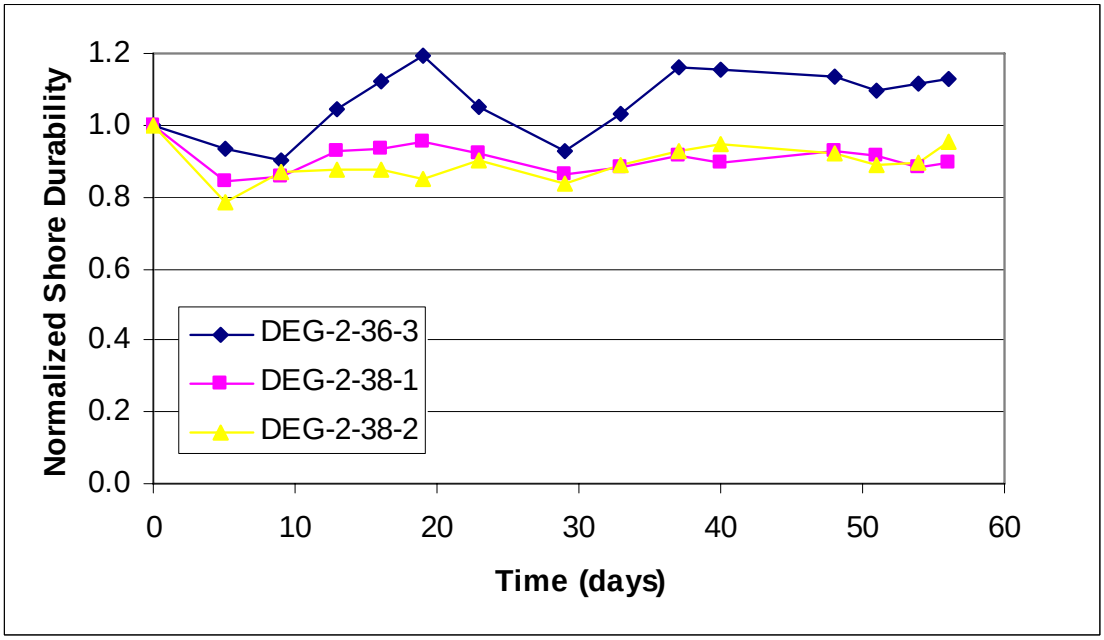


Figure 8. Normalized Shore Durability 350°F

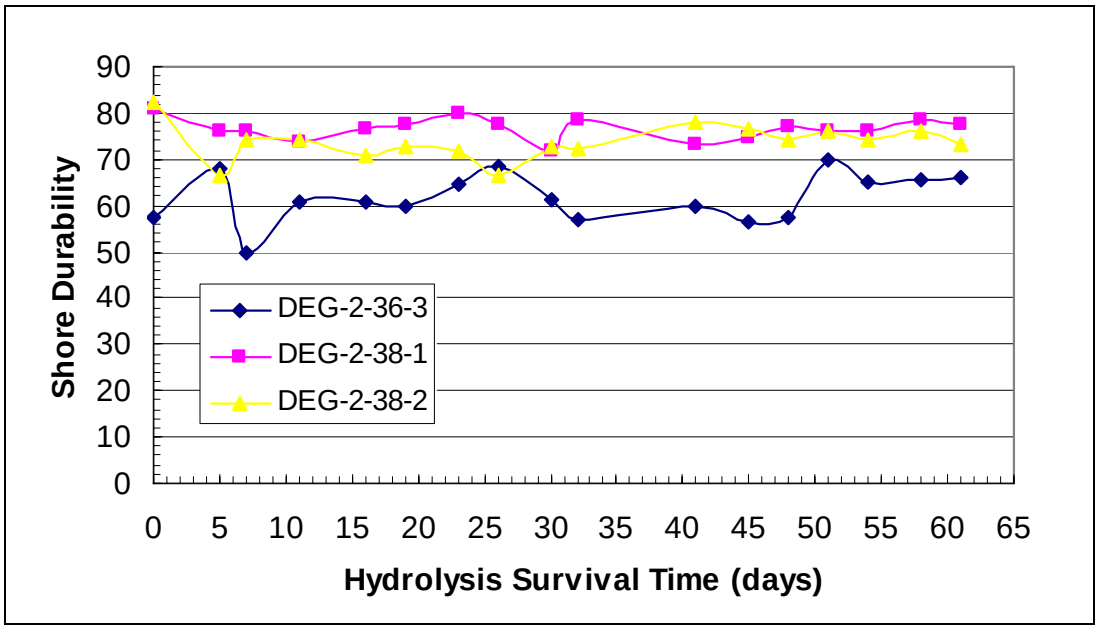


Figure 9. Absolute Shore Durability 400°F

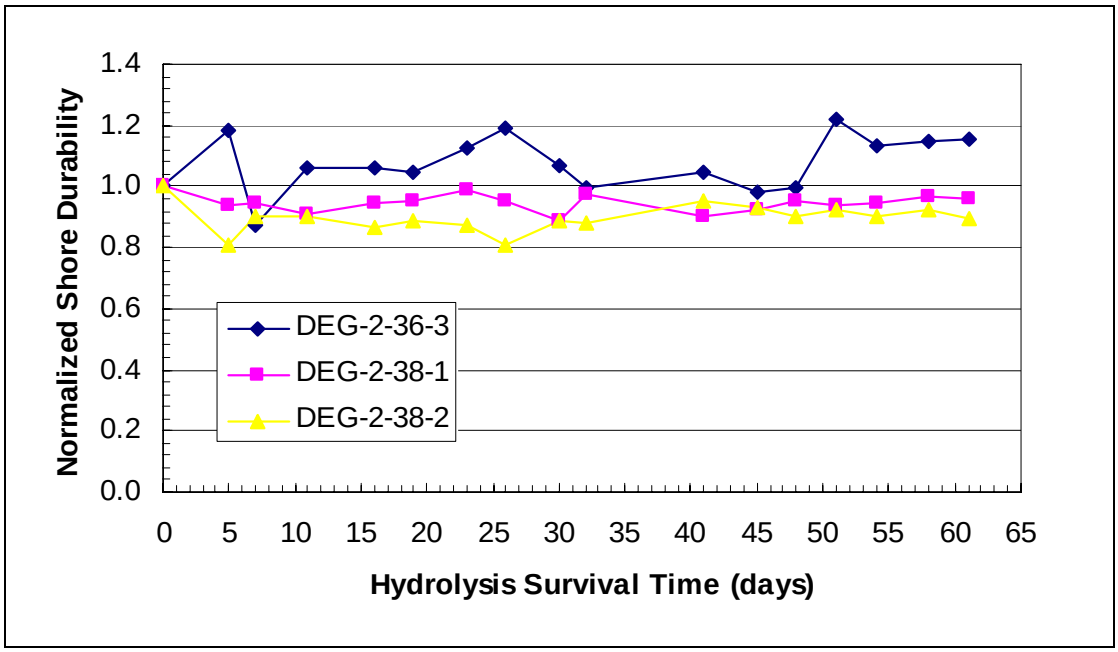


Figure 10. Normalized Shore Durability 400°F

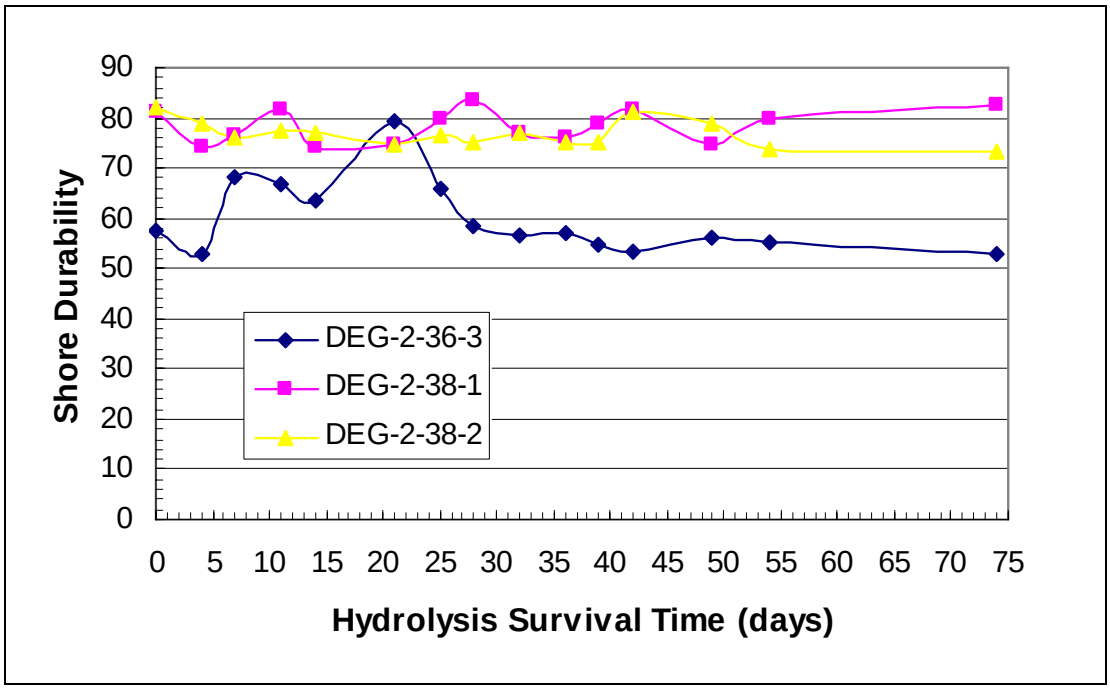


Figure 11. Absolute Shore Durability 450°F

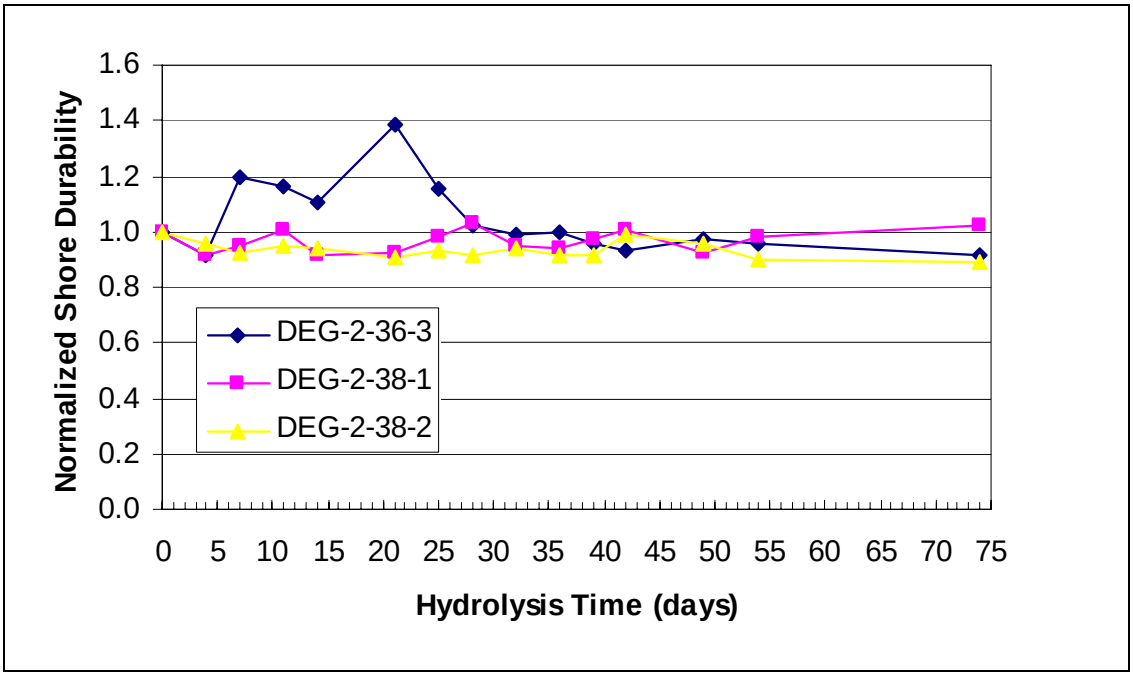


Figure 12. Normalized Shore Durability 450°F

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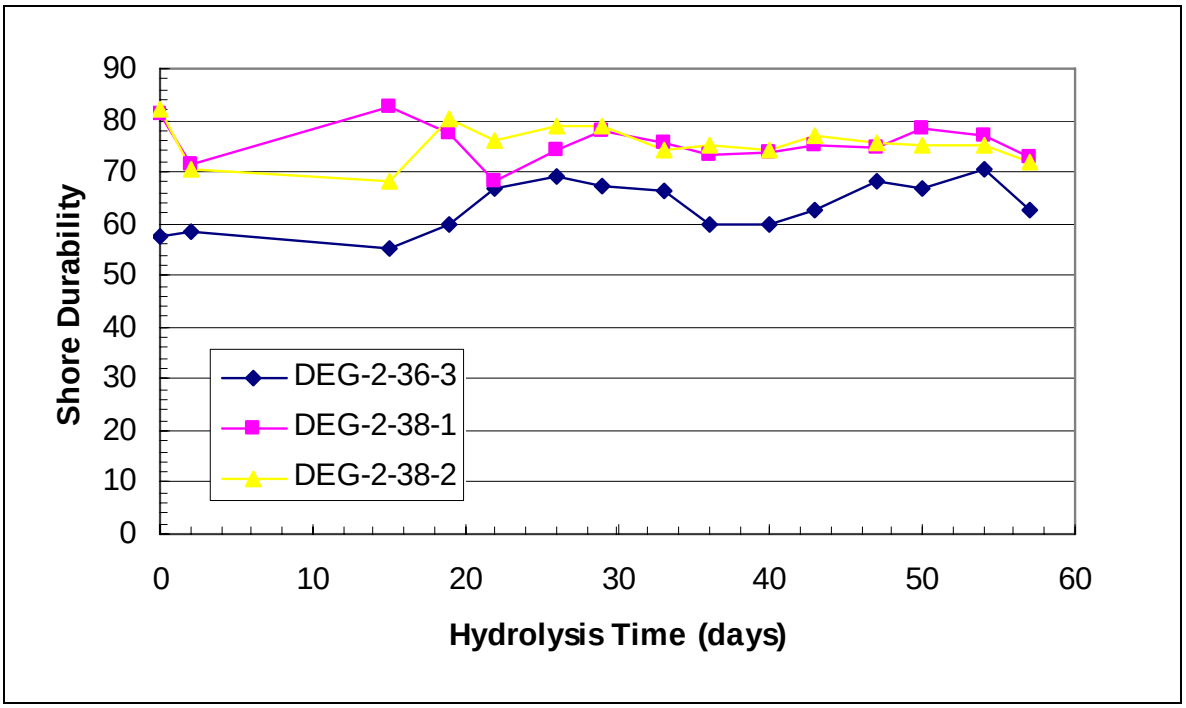

Figure 13. Absolute Shore Durability 500°F

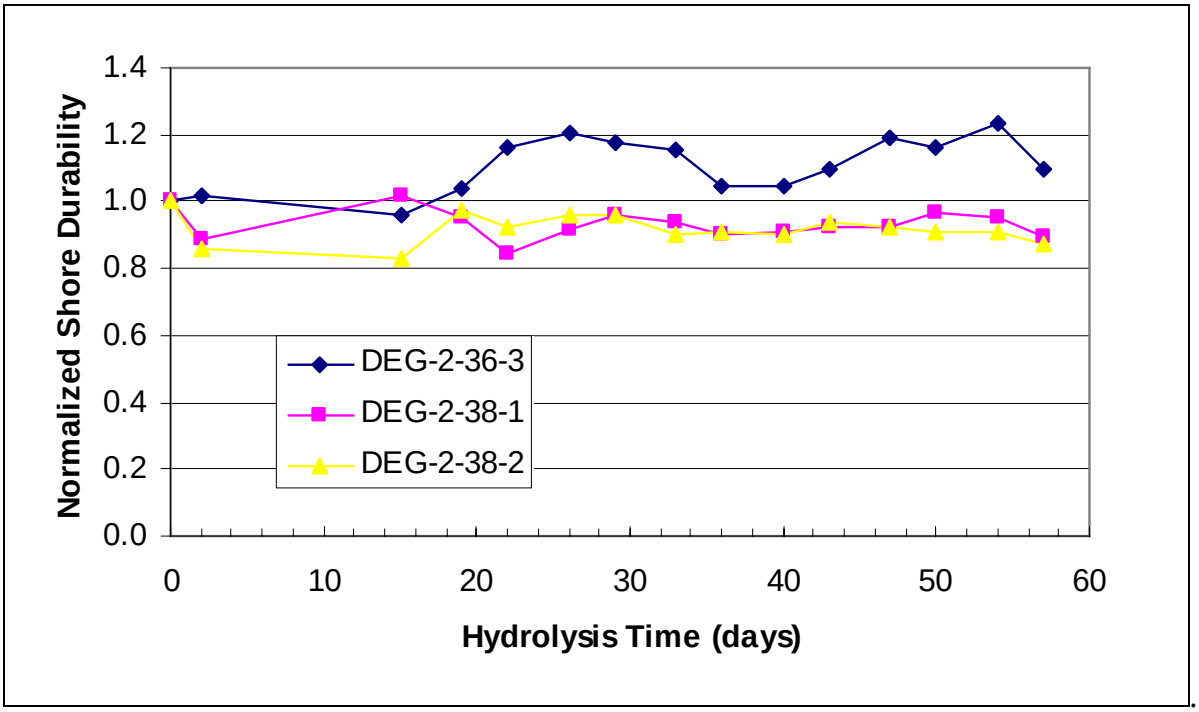

Figure 14. Normalized Shore Durability 500°F

5. Conclusions

We have concluded a laboratory study to evaluate the potential for survival and plugging applications of polymeric materials in geothermal wells of polymeric materials. Early in the study, it was found the polymers were susceptible to hydrolysis, wherein water molecules attacked chemical bonds, breaking them through time, and reducing the mechanical integrity of the polymers. This rendered the polymers useless in the desired range of geothermal temperatures and pressure applications. Through a systematic approach of many potential chemical combinations, polymers were developed which tolerated hydrolysis for eight weeks at 500ºF, and met material, handling, cost, and placement criteria. This screening process identifies the most promising materials. Further strength testing is required to determine precisely the maximum temperature at which they can be used without failure of the lost-circulation plug due to extrusion through fractures or voids.

Specifically, for maximum hydrothermal performance, the crosslink density, types of crosslinks and the ability to perform these curing reactions under field conditions are critical to the ultimate performance of the grouting system. The selection of commercially available and competitively priced raw materials suggests that the standard polyurethane prepolymer and the variations tested will offer about two weeks of useful life at 275ºF. The production of aromatic polyureas or polyurethanes crosslinked with dimethacrylate monomers increases the useful life at 275ºF to four-to-eight weeks. By incorporating a polybutadiene resin and crosslinking with dimethacrylate monomer the useful life at 275ºF is over eight weeks. By eliminating all isocyanate reaction products and crosslinking a polybutadiene resin with dimethacrylate monomer, the useful life at 300ºF is further extended. Testing of final compositions at 325ºF, 350ºF, 400ºF, 450ºF and 500ºF also demonstrated survival from hydrolysis for eight weeks.

These new polymer grouting systems meet most of the previously described desired characteristics but have yet to be tested in a field-type application. Such work should be considered in the future.

6. References

Mansure, A.J., Westmoreland, J.J., Staller, G.E., Jacobson, R.D., Libengood, H., Smith, E., Galbreath, D., and Rickard, W.M., October 2001, "Plugging Polyurethane Grouting of Rye Patch Lost Circulation Zone," *Geothermal Resources Council Transactions*, Vol. 25, Geothermal Resources Council.

Appendix 1

This Appendix consists of a contractor report, with text slightly reformatted.

Polyurethane Grout Hydrolysis Summary of 275°F Experiments

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Contents

Abstract……31
Introduction……..32
Experimental Conditions and Methods ……...32
Results and Discussion…… 34
Conclusions……. 47

List of Figures

Figure 1. Sealed pipes used to conduct hydrolysis experiments at 275°F……..33
Figure 2. Typical sample appearance upon removal from the sealed pipe……33
Figure 3. Weight losses in samples during a 10-day hydrolysis experiment……..34
Figure 4. TMA of sample BCG……... 36
Figure 5. TMA of sample Paddy LC……... 36
Figure 6. TMA of sample P. G. #8……. 37
Figure 7. TMA of sample Rye Patch……... 37
Figure 8. TMA of sample PARR-6……..38
Figure 9. TMA of sample PARR-9……..38
Figure 10. TMA of sample PARR-12……..39
Figure 11. Weight losses in samples during a 19-day hydrolysis experiment……40
Figure 12. Long-Term Hydrolysis TMA of DEG-Hunstman……..41
Figure 13. Long-Term Hydrolysis TMA of Paddy LC……41
Figure 14. Long-Term Hydrolysis TMA of PARR-6……..42
Figure 15. Long-Term Hydrolysis TMA of PARR-9……..42
Figure 16. Long-Term Hydrolysis TMA of PARR-12…… 43
Figure 17. Long-Term Hydrolysis TMA of PARR-26…… 43
Figure 18. TMA plots for Parr 36, 37, and 38 samples…….. 46

List Of Tables

1. Summary of TMA Results for Selected Samples in 10-day Hydrolysis at 275°F ……35
2. Summary of TMA Results for Long-Term Hydrolysis at 275°F……44
3. Tabulated GCMS Data – Identification of Main Degradation Products……45

Polyurethane Grout Hydrolysis Summary of 275°F Experiments

Abstract

This report was a part of a research and development study conducted by Sandia National Laboratories on the hydrolysis behavior of specific polyurethane foam grouts to determine potential impact on their integrity when applied in lost circulation and/or cross flow zones in geothermal wells. During the course of this program, the hydrolysis behavior of several polyurethane foam grout samples at 275°F was evaluated. Samples were subjected to hydrolysis under elevated temperature and pressure conditions. Samples were then analyzed to investigate their retention of properties at the hydrolysis temperature over a period of several days. Thermomechanical analyses (TMA) were primarily employed; these experiments yielded softening temperatures for the materials. Gas chromatography/mass spectrometry (GCMS) was also conducted on the residual water in the sample tubes to identify hydrolysis products that might possibly be of environmental concern. This report serves as a summary of work completed by Adherent Technologies, Inc. on this subject.

Introduction

The Geothermal Research Department at Sandia National Laboratories addresses problems related to well bore integrity as part of more extensive research and development efforts in drilling and completion of geothermal wells for the US DOE. Polyurethane grout is a material that can and has been used to remediate lost circulation and/or cross flow zones that have been encountered in geothermal wells. The research and development in this report is part of a program directed towards determining the chemistry and temperature regime for which certain polyurethane grouts retain their mechanical integrity in the presence of water. Polyurethane is a general class of organic polymers, the specific chemistry polyurethanes can be modified to enhance specific chemical and attendant mechanical characteristics. Here we are interested in enhancing the mechanical stability when the polyurethane is heated, under pressure, and in the presence of water. As such, the study completed by Adherent technologies, Inc. investigated the mechanical response of certain polyurethanes. This work was used to evaluate and screen out compositions for further study. Some of the further evaluations are included in this report, some were studied at Sandia National Laboratories. An important part of the mechanical evaluations was to determine the hydrolysis degradation of the polyurethanes. Hydrolysis is a process in which water diffuses into a polyurethane molecular structure and causes chemical bonds to break, degrading the mechanical integrity of the material.

During the course of this program, the hydrolysis behavior of several polyurethane foam grout samples at 275°F was evaluated (In this report the terms polyurethane and foam are used interchangeably). Samples were provided by Sandia National Laboratories and were subjected to hydrolysis under elevated temperature and pressure conditions as described in the following section. The actual chemical compositions are not stated in this report, but can be obtaied from laboratory notebooks at Sandia National Laboratories. Samples were then analyzed to investigate their retention of properties at the hydrolysis temperature over a period of several days. Thermomechanical analyses (TMA) were primarily employed; these experiments yielded softening temperatures for the materials. Gas chromatography/mass spectrometry (GCMS) was also conducted on the residual water in the sample tubes to identify hydrolysis products that might possibly be of environmental concern.

Experimental Conditions and Methods

Samples in approximately 0.25-in. cubes were placed into test tubes inside sealed pipes with sufficient water to cover the samples. The pipes were then heated to 275°F in an oven. The rack of pipes used for these experiments is shown in Figure 1.

Figure 1. Sealed pipes used to conduct hydrolysis experiments at 275°F.

Pipes were removed after a specified time period, cooled, and opened. A typical sample is shown in Figure 2. The foam samples were air-dried, weighed, and retained for further analysis. Some of the water was also retained for analysis.

Figure 2. Typical sample appearance upon removal from the sealed pipe. The grout sample is at the bottom of the tube, water containing degradation products is above the sample.

Analyses consisted primarily of thermomechanical analysis (TMA) for determination of foam glass transition temperatures, and thermogravimetric analysis (TGA) for determination of foam degradation

temperature. Gas chromatography/mass spectrometry (GCMS) was also conducted on some water samples.

Results and Discussion

Two different series of hydrolysis experiments were conducted. In an initial series of screening experiments, conducted over a period of 10 days at 275°F, the most promising candidates for longer-term application were identified. These results were then used to guide a longer-term series of experiments. Both series of experiments are discussed below.

Initial Hydrolysis Screening

Figure 3 shows the simple weight losses for all samples analyzed during the initial 10-day hydrolysis experiment.

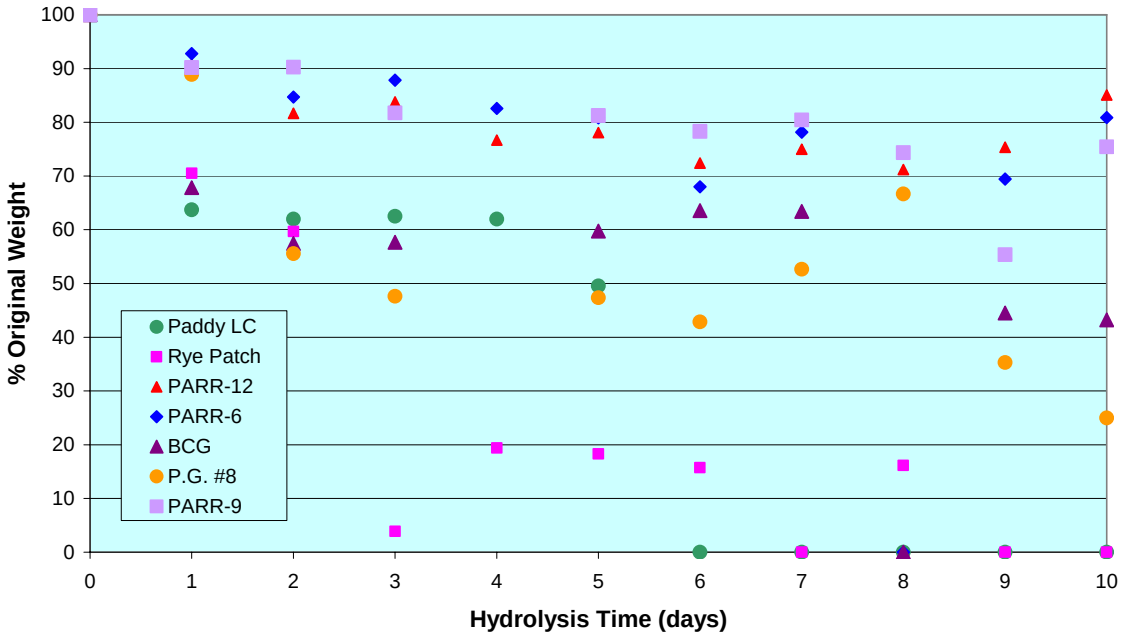


Figure 3. Weight losses in samples during a 10-day hydrolysis experiment. Weight losses are expressed as a percentage of the original sample weight.

Rye Patch degraded very quickly under the hydrolysis conditions explored here; the sample was virtually completely degraded after 3 days. Paddy L.C. showed a longer lifetime, with complete degradation occurring at 4-5 days. BCG and P.G. #8 showed slightly longer lifetimes. PARR-6, PARR-9, and PARR-12 fared the best of all samples tested, appearing to hold up well during the entire course of the hydrolysis experiment. Sample shape was typically retained, as was a significant portion of the original sample weight. The stiffness of the samples did change, however, during the course of the experiment.

Based on these simple weight loss data, several samples of each type were selected for additional thermomechanical analysis (TMA). The softening points of each sample are summarized in Table 1 and detailed in Figures 4-10.

Table 1. Summary of TMA results for Selected Samples in 10-day Hydrolysis at 275°F

Samples	**Onset 1 (°C)**	**Onset 2 (°C)**	**Onset 3 (°C)**	**Comments**
BCG				
Untreated	221.472			
Day 3	87.838	160.403	228.231	
Day 5	65.83	205.487		
Day 6	61.785	121.284		
Paddy LC				
Untreated	261.239			
Day 3	50.148	199.985		* broke
PARR-6				
Untreated	271.582			
Day 5	127.605			
PARR-9				
Untreated	271.446			
Day 3	255.925			
Day 5	49.765	106.365		broke @ 112
Day 7	137.799			
PARR-12				
Untreated	264.402			
Day 5	49.121	103.564		* broke
Day 9	38.38	134.286		
P. G. #8				
Untreated	150.356			
Day 3	103.948			
Day 5	155.266			softens @ 107
Rye Patch				
Untreated	78.321	185.454		
Day 1	68.292			
Day 2	59.367			

TMA analyses show a gradual degradation in the foams over a period of several days. This is most notably observed for BCG. Similar trends are observed for most of the other samples as well. All initial data indicates that the PARR experiments have produced the materials with the longest lifetimes under hydrolysis. These samples, in addition to a few others, were subjected to a longer-term hydrolysis experiment. Results of the long-term hydrolysis are discussed in the next section.

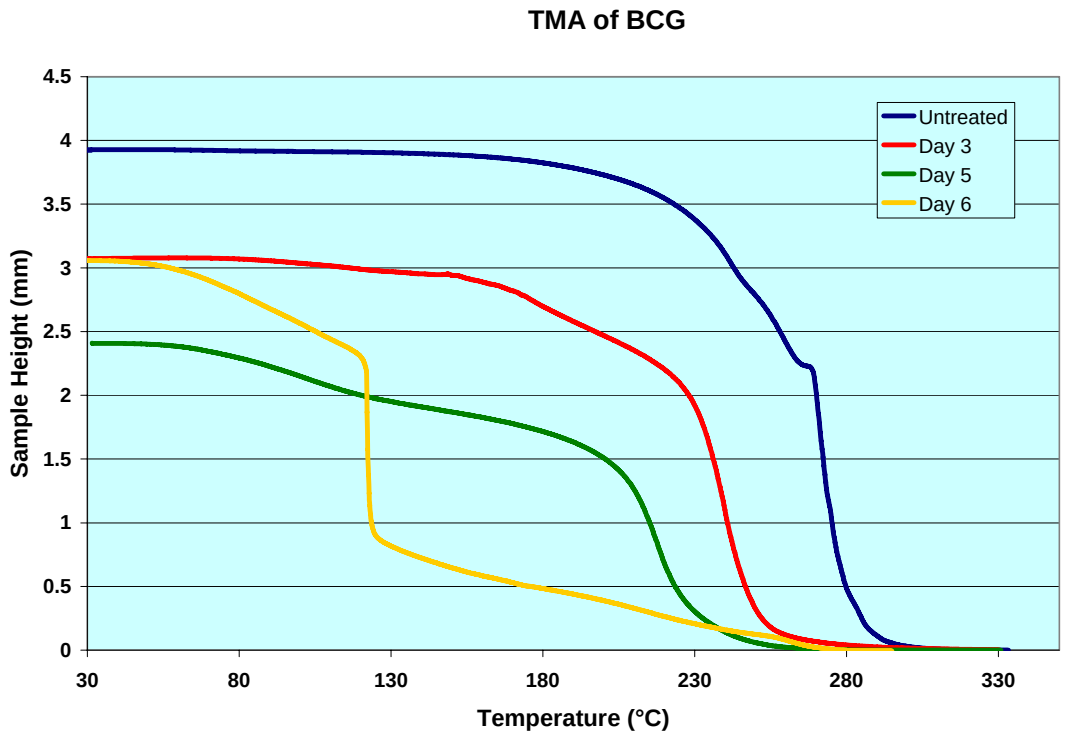


Figure 4. TMA of sample BCG.

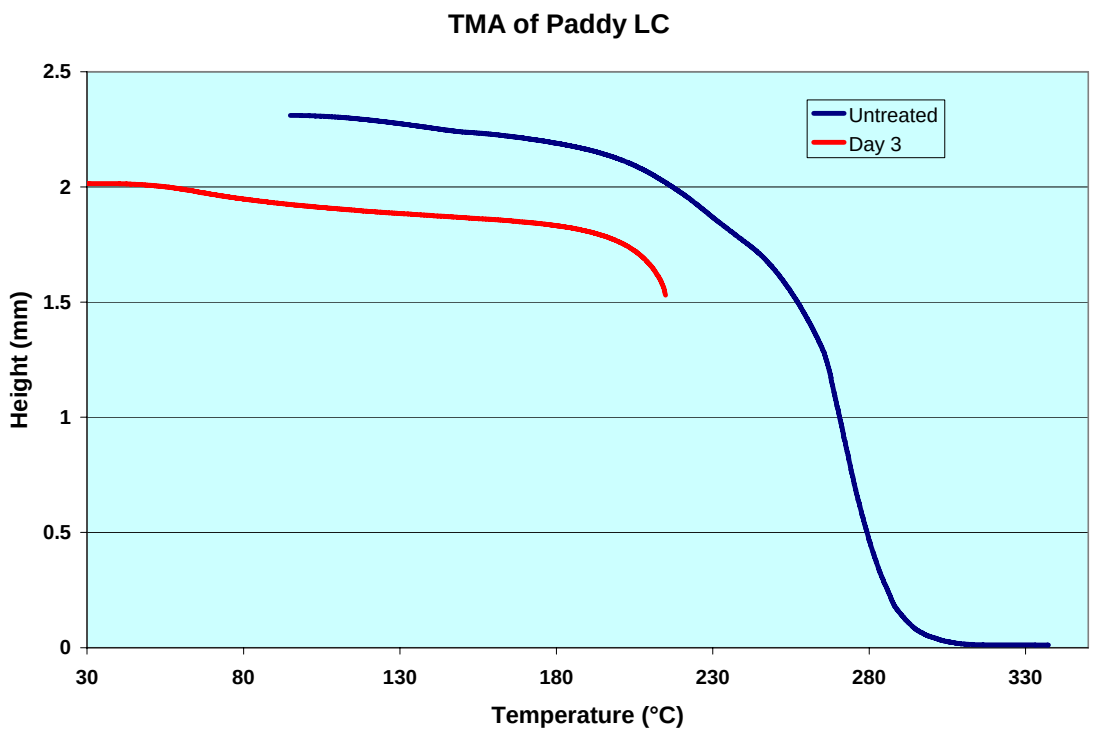


Figure 5. TMA of sample Paddy LC.

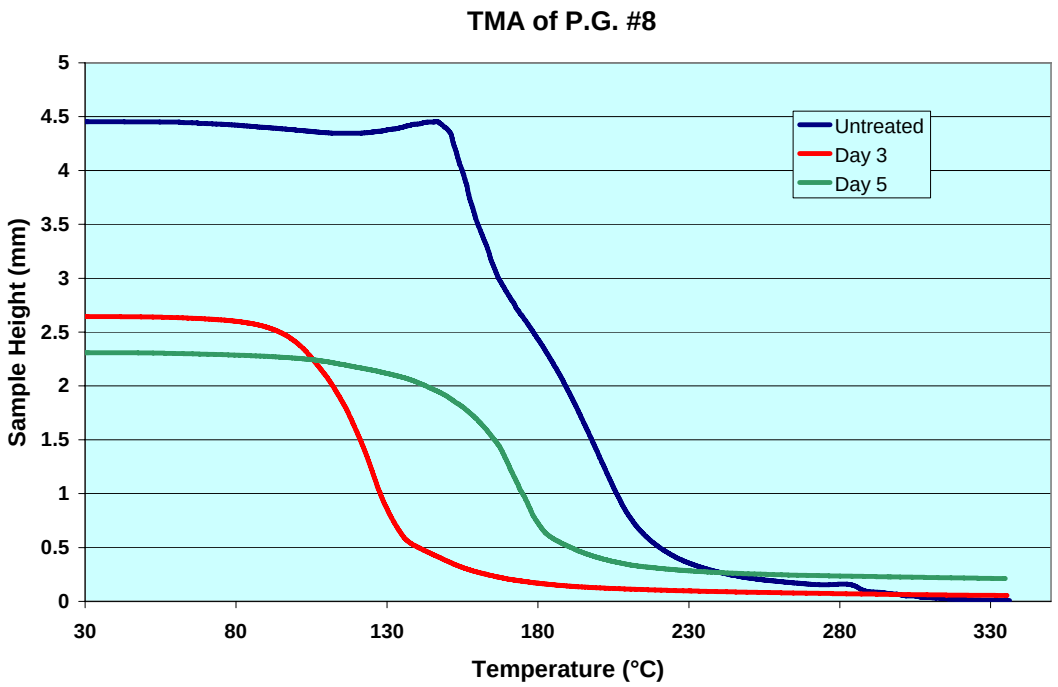


Figure 6. TMA of sample P.G. #8.

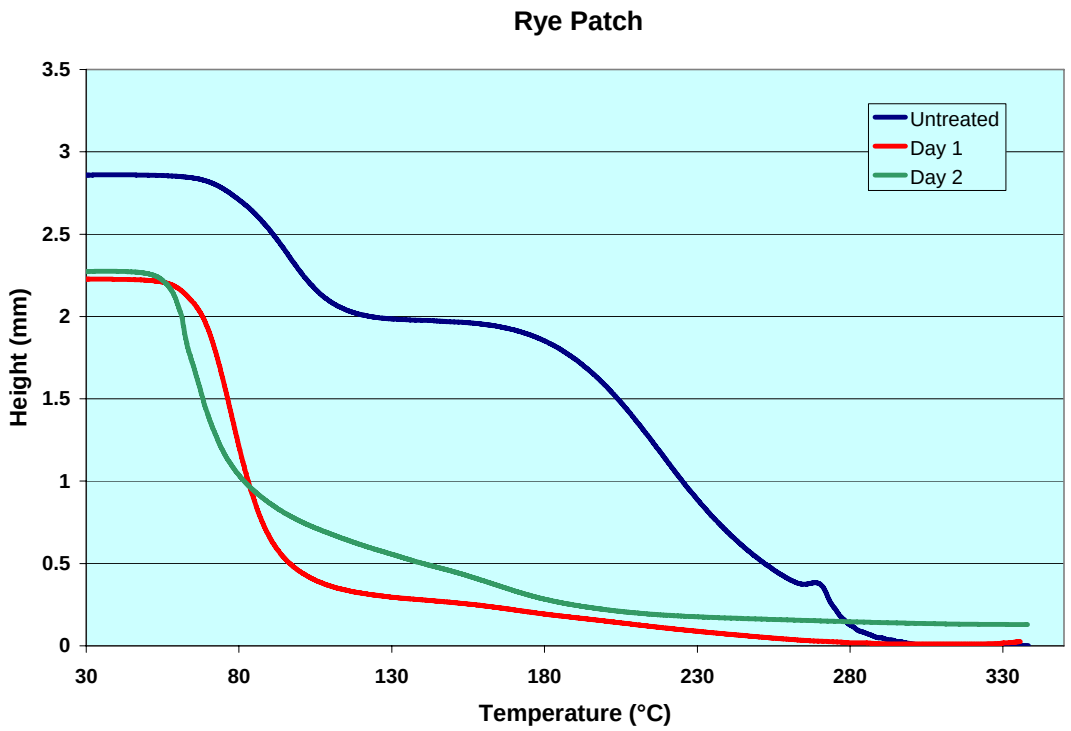


Figure 7. TMA of sample Rye Patch

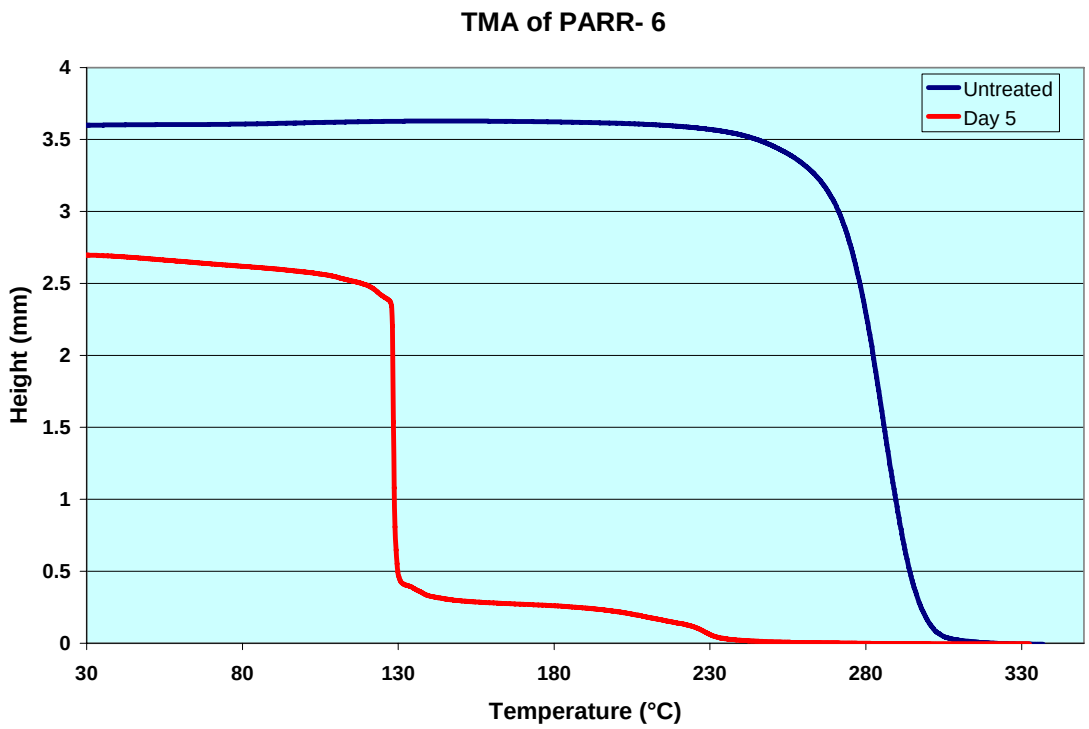


Figure 8. TMA of sample PARR-6

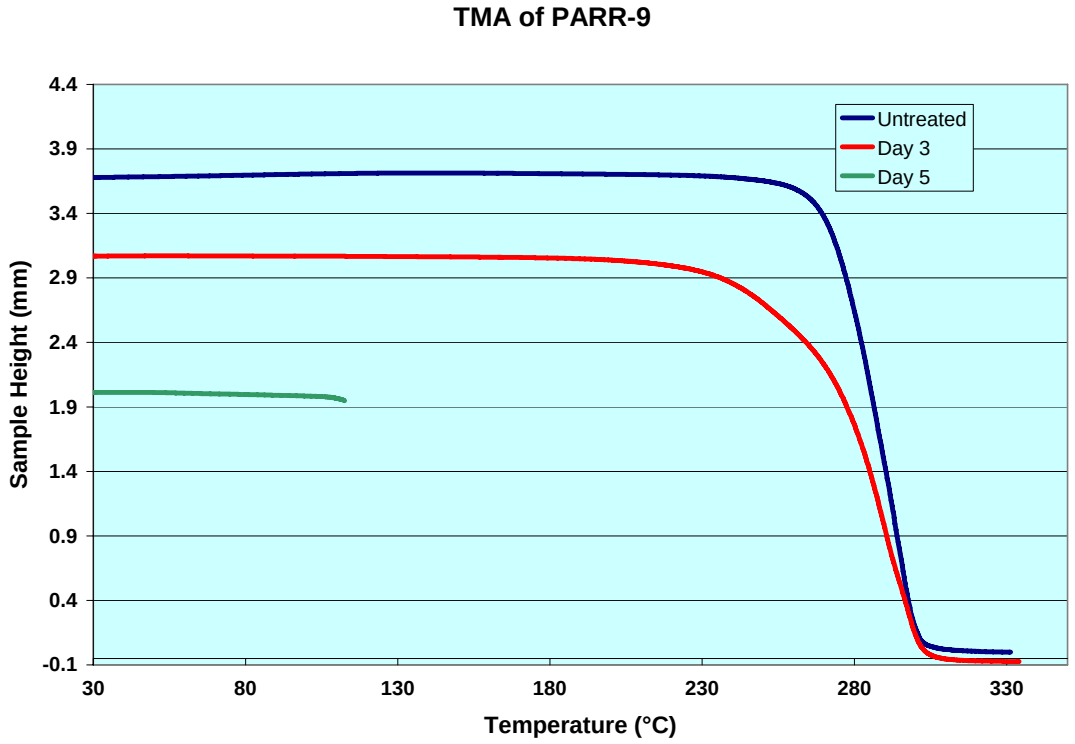


Figure 9. TMA of sample PARR-9

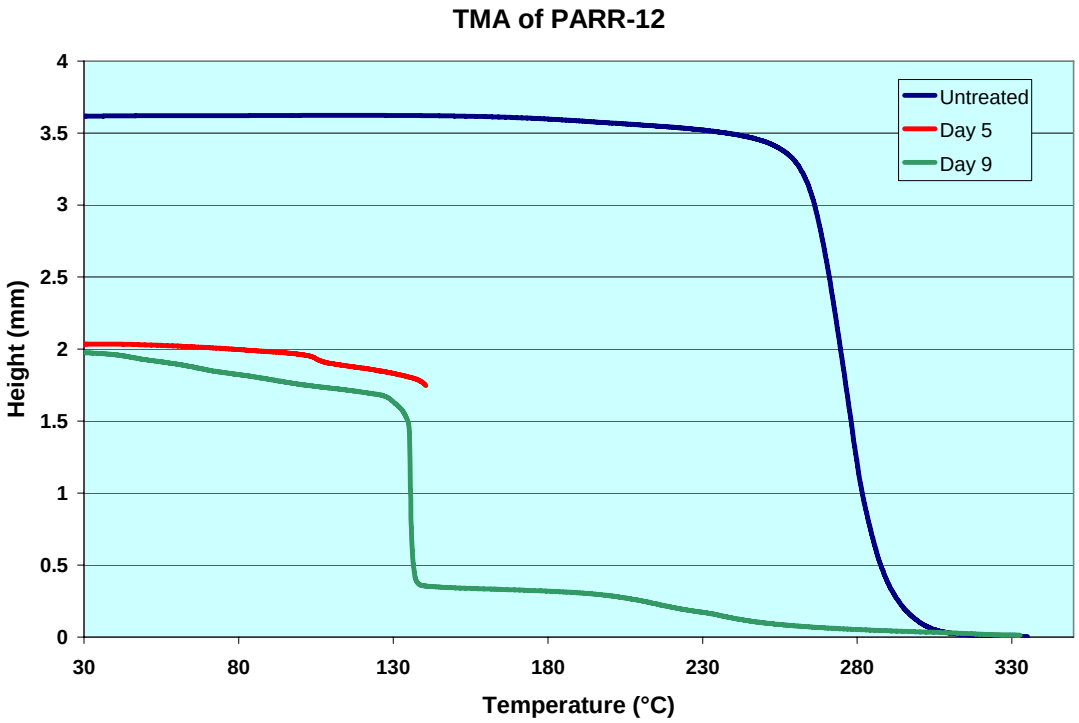


Figure 10. TMA of sample PARR-12

Long-Term Hydrolysis:

Several samples showed some promise in the 10-day hydrolysis experiments and were subjected to a longer-term experiment at 275°F. Three pieces of each sample were hydrolyzed to allow for better analysis of the results. All three pieces were weighed together to generate the simple weight loss data given in Figure 11.

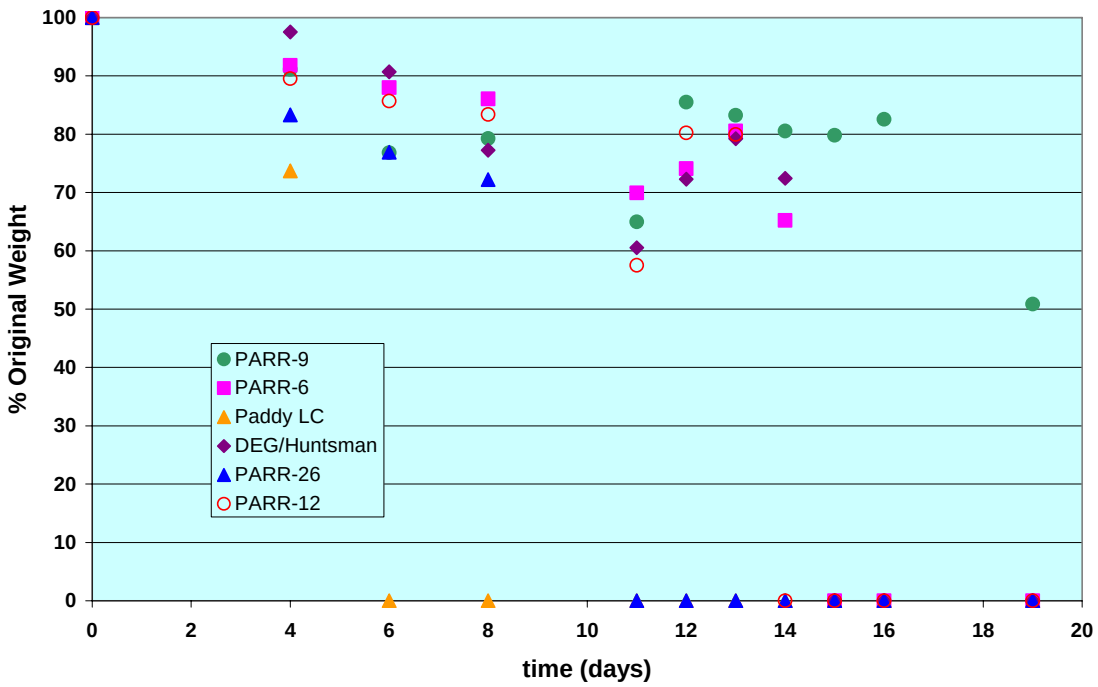


Figure 11. Weight losses in samples during a 19-day hydrolysis experiment. Weight losses are expressed as a percentage of the original sample weight.

PARR-9 survived the long-term hydrolysis for the longest period; samples retained sufficient integrity for basic handling for up to 19 days. The TMA results, however, indicate that 15 days is a more realistic lifetime; samples exposed to the hydrolysis conditions for longer times could not be analyzed. It is interesting that the PARR-9 sample survived so well, particularly in comparison to PARR-6 and PARR-12, which are the same chemistry prepared under different conditions.

The results for the DEG Huntsman sample were somewhat disappointing. This material had been expected to exhibit superior thermal resistance. In fact, it appears that its softening point (untreated) is very similar to that of most of the other materials tested. In addition, degradation occurred very quickly; we were unable to analyze samples after 8 days of exposure to the experimental conditions. This is particularly significant since this sample was in solid form rather than in the porous form of all other samples evaluated. TMA results are summarized in Table 2; all TMA plots for the long-term hydrolysis experiments are given in Figures 12-17.

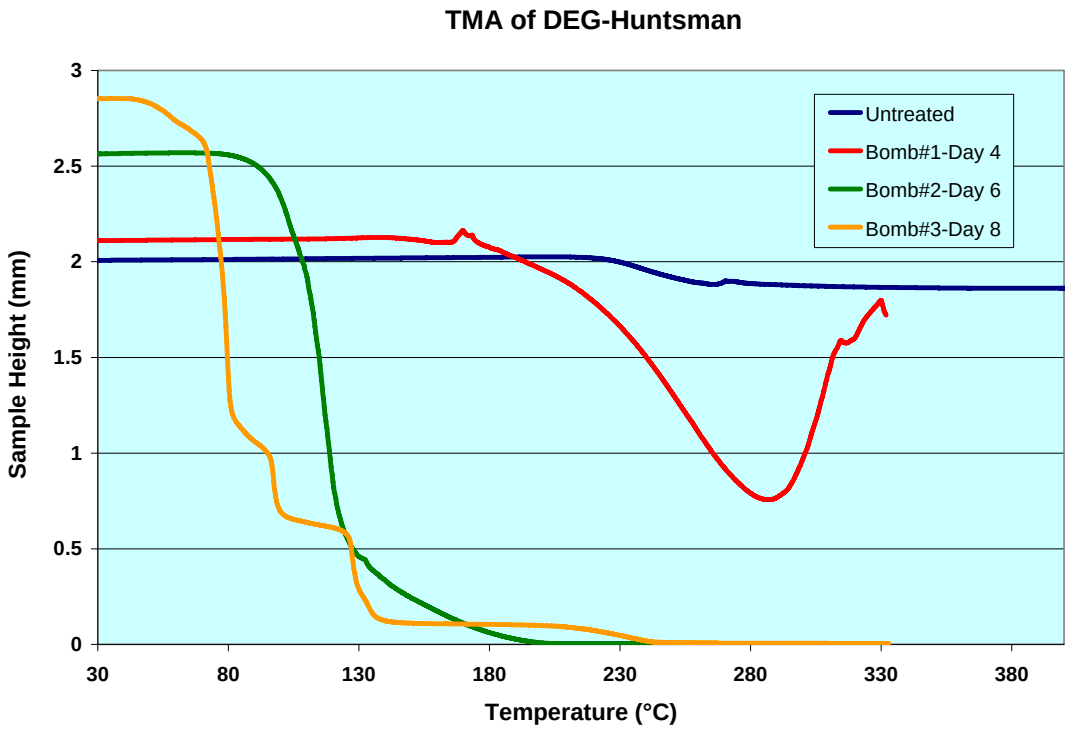


Figure 12. Long-Term Hydrolysis TMA of DEG-Hunstman.

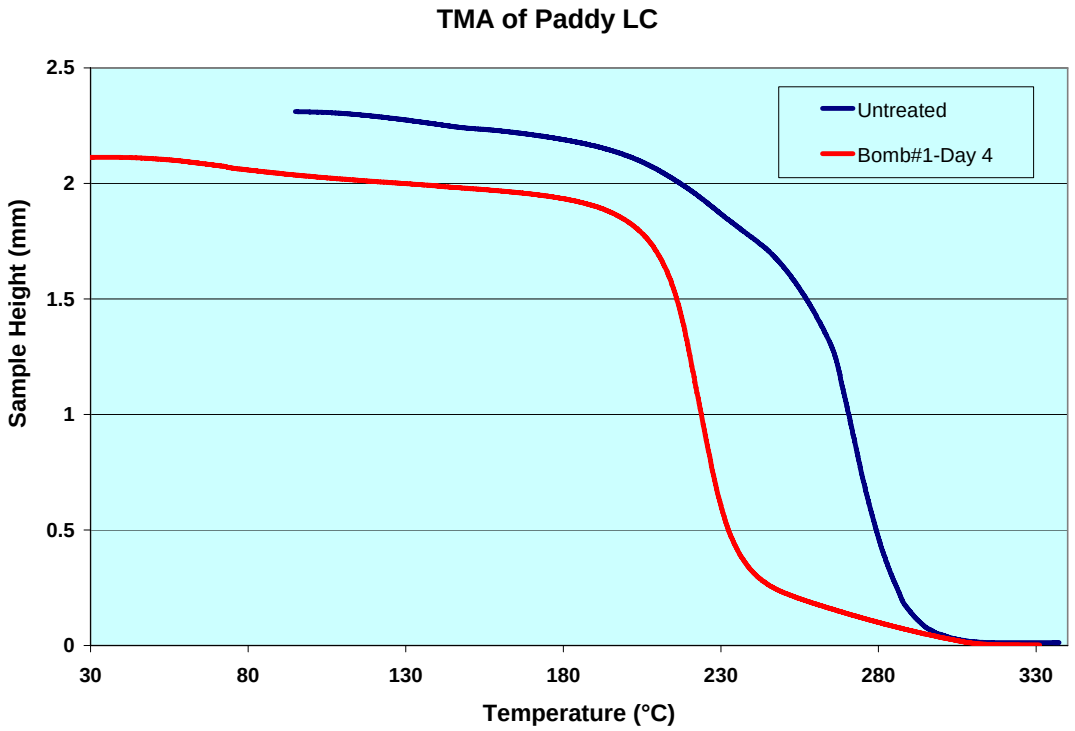


Figure 13. Long-Term Hydrolysis TMA of Paddy LC.

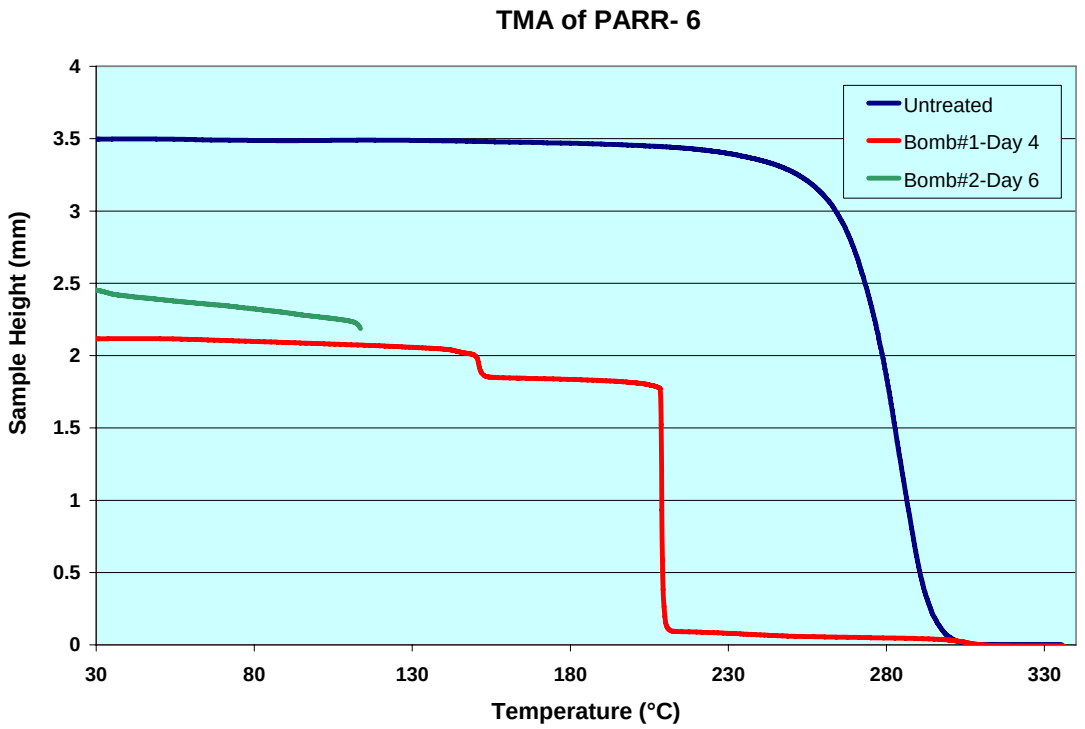


Figure 14. Long-Term Hydrolysis TMA of PARR-6.

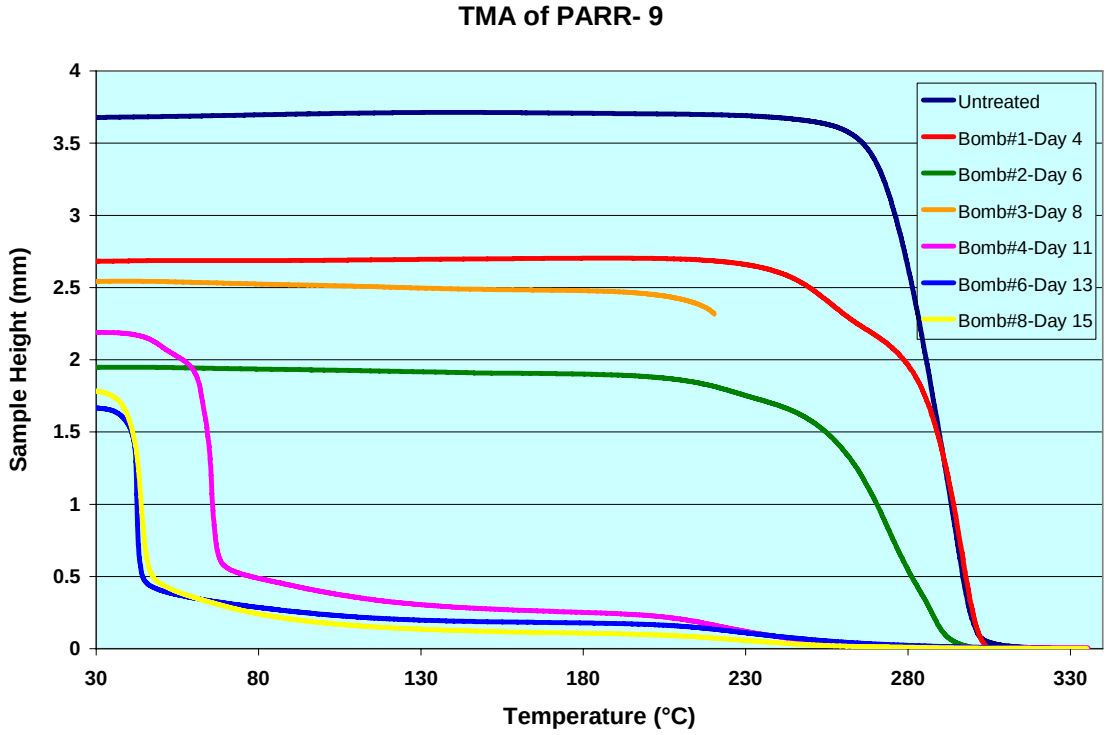


Figure 15. Long-Term Hydrolysis TMA of PARR-9.

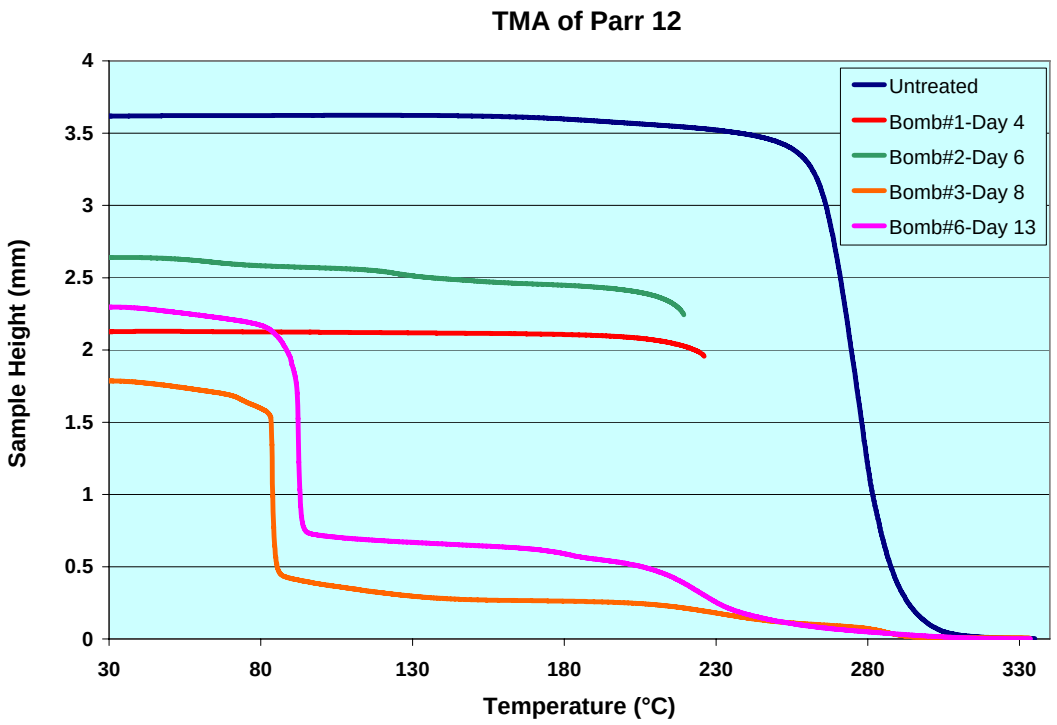


Figure 16. Long-Term Hydrolysis TMA of PARR-12.

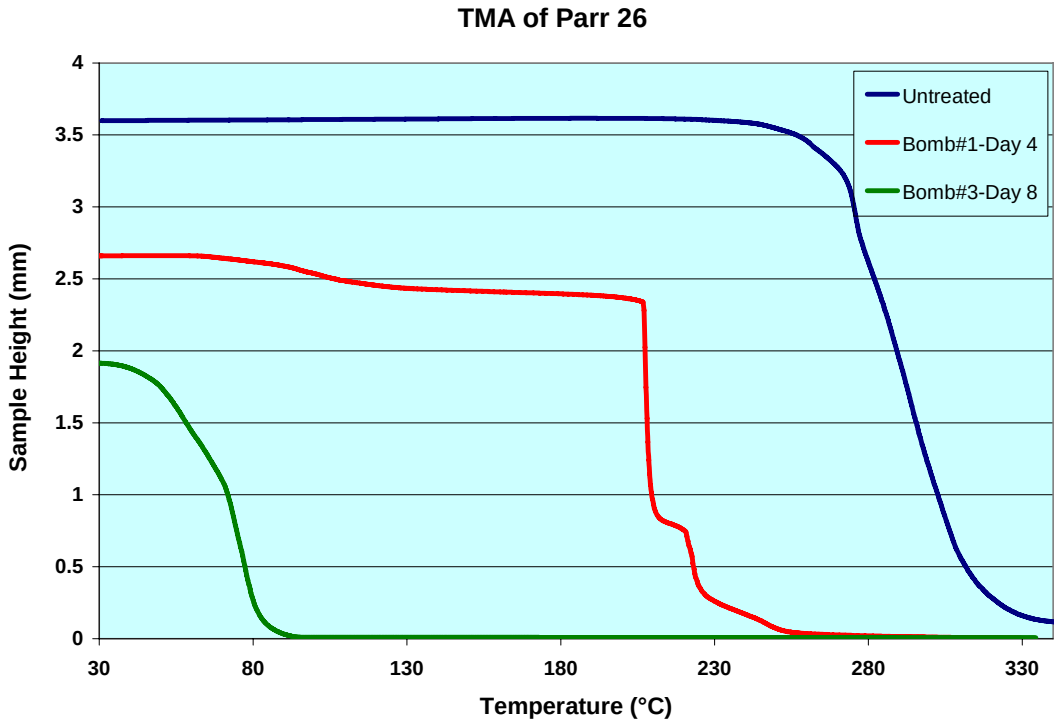


Figure 17. Long-Term Hydrolysis TMA of PARR-26.

Table 2. Summary of TMA Results for Long-Term Hydrolysis at 275°F

Sample	Onset (°C)	Observations
DEG-Huntsman		
Untreated	222.56	Penetrated only slightly into sample
Day 4	198.724	
Day 6	104.082	
Day 8	47.16 (sm), 71.43	Several smaller transitions @ higher T
Days 11-19	-	Like caramelized sugar, very sticky
Paddy LC		
Untreated	206.73 (sm), 261.33	
Day 4	57.36 (sm), 209.16	
Day 6-19	-	Looked like tar
Parr 6		
Untreated	265.419	
Day 4	149.73 (sm), 207.48	
Day 6	Broke at about 111	
Day 8-15	-	Retained shape but too soft to run
Day 16-19	-	
Parr 9		
Untreated	271.446	
Day 4	238.74 (sm), 282.91	
Day 6	Broke at about 247	
Day 6 (repeat)	250.975	
Day 8	Broke at about 180	
Day 8 (repeat)	Broke at about 220	
Day 11	62.071	One smaller transition @ higher T
Day 13	41.526	One smaller transition @ higher T
Day 15	40.055	One smaller transition @ higher T
Day 16	-	Retained shape but was too soft to run
Day 19	-	Too soft and sticky to run
Parr 12		
Untreated	264.402	
Day 4	Broke at about 110	
Day 4 (repeat)	Broke at about 226	
Day 6	Broke at about 219	
Day 6 (repeat)	Broke at about 118	
Day 8	82.033	Several smaller transitions @ higher T
Day 13	89.276	Several smaller transitions @ higher T
Day 14 & 19	-	Too crumbly to to run
Day 15 & 16	-	Too soft to run
Parr 26		
Untreated	269.164	
Day 4	68.18 (sm), 206.71	One smaller transition @ higher T
Day 8	46.774	
Day 11-19	-	Looked like tar

GCMS Analysis

The water obtained from the hydrolysis experiments was highly discolored, indicating the presence of degradation products in the water. It is of potential interest from an environmental standpoint to know the identities and relative quantities of the various components released should these grouts be used in a field situation as some of the degradation products may be toxic.

Gas chromatography/mass spectrometry (GCMS) was used to identify the main degradation products from a few of the samples subjected to the 275°F hydrolysis experiments. No effort was made at this time to determine actual quantities of these materials relative to the amount of material placed into the experiment. This should occur at a later date, when materials are chosen for application in the field.

In general, the expected degradation products were observed. For urethane and isocyanurate systems, various amines, dianilines, and polyols are the most likely products. In fact, these are observed for all samples analyzed. Summary tables of main components and their retention times on the column are given in Table 3.

Table 3. Tabulated GCMS Data – Identification of Main Degradation Products

(a) BCG

Compound	**Retention Time (min)**
Acetic Acid	6.87
2-Butanone	6.94
1-Butanol	8.66
Propylene Glycol	10.64
Aniline	18.98
Ethylaniline Isomer	31.96
Diaminodiphenyl Methane Isomer	50.29

(b) P. G. #8

Compound	**Retention Time (min)**
Acetic Acid	6.87
2-Butanone	6.95
1-Butanol	8.67
Propylene Glycol	10.63
Diethylene Glycol	18.05
Aniline	18.98
Ethylaniline Isomer	31.96
Diaminodiphenyl Methane Isomer	50.29

(c) PARR-9

Compound	Retention Time (min)
Acetic Acid	6.89
2-Butanone	6.95
1-Butanol	8.67
Propylene Glycol	10.63
Aniline	18.98
Diaminodiphenyl Methane Isomer	48.32
Diaminodiphenyl Methane Isomer	50.29

Other Samples

In addition to the hydrolysis experiments described above, three other grout samples were tested for softening points in the TMA. These samples were not subjected to hydrolysis. The plot of the TMA results is given in Figure 18.

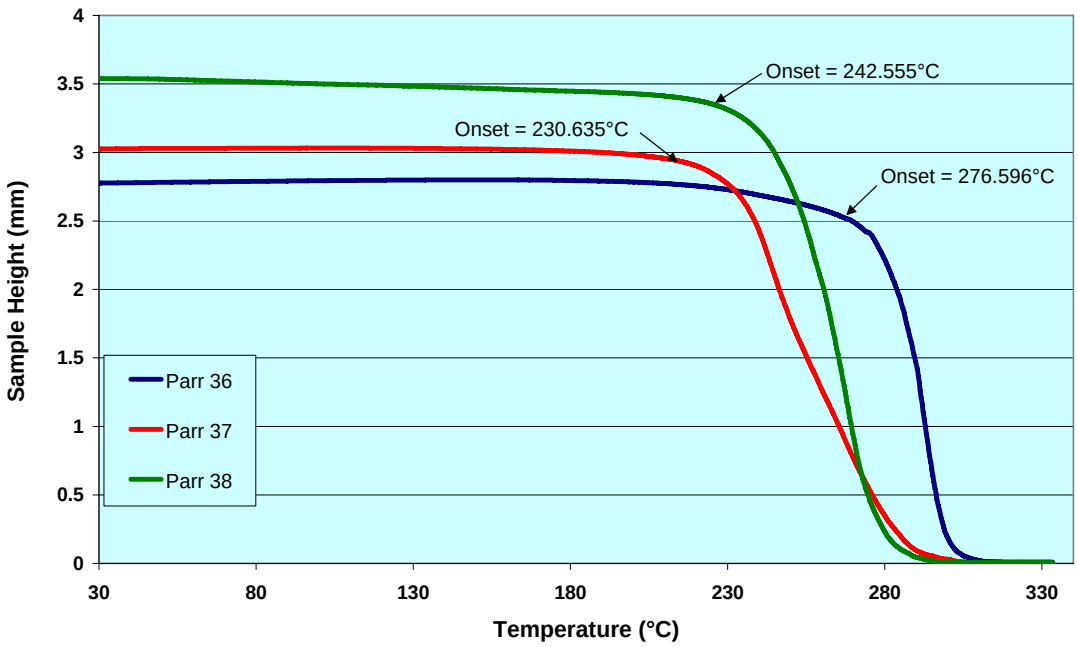


Figure 18. TMA plots for Parr 36, 37, and 38 samples. Samples were not subjected to elevated temperature hydrolysis.

These samples exhibited softening temperatures similar to those of the samples analyzed previously in this program. It is not possible to predict their behavior in hydrolysis without knowing the exact chemistry of the systems. However, unless significant changes in chemistry have been made, these samples are likely to behave very much like the other samples analyzed during the course of this program.

Conclusions

This report presents results for hydrolysis experiments completed on polyurethane grout samples. The work was part of a much larger study by Sandia National Laboratories to evaluate the use of polyurethane grouts to mitigate lost circulation and cross flow problems encountered in some geothermal wells. The results were used to channel subsequent efforts in determining which polyurethane grout formulations should be dropped from further study, and which formulations were potentially useful. Some fairly sophisticated tests were completed on many samples. The formulation used *in situ* at Rye Patch did not fare well in the laboratory testing reported herein, however that grout material performed well in the field. This is because the Rye Patch field application was at a lower temperature then subsequently lab tested.

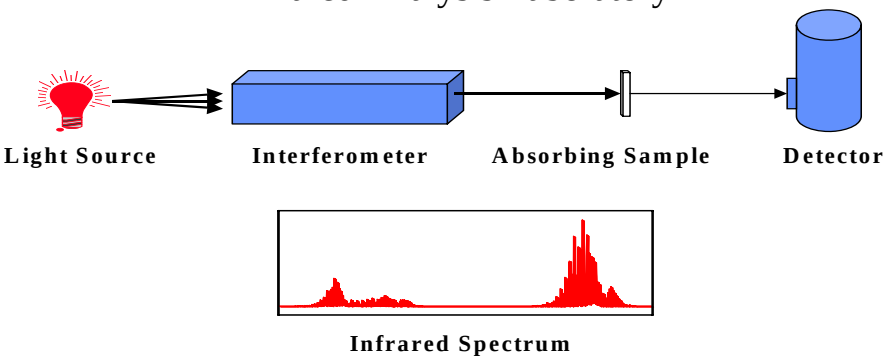
Appendix 2

Infrared Spectroscopy

Sandia National Laboratories

Operated for the U.S. Department of Energy by
Sandia Corporation
Albuquerque, New Mexico 87185-1411

Analysis Report
Infrared Analysis Laboratory



date: 5/3/04

to: Stephen J. Bauer, Org. 06211

Job Number: FTIR04021

File Name: FTIR04021.doc

Program: Geothermal Well Plugs

Description: Analysis of well plugs aged under geothermal conditions

Project/task: 728/15.01 (do not include on any copy of the report which is transmitted outside of SNL)

Requester Info

Name	Org.	Phone		MS	e-mail
		Voice	**FAX**		
Steve Bauer	06211	844-9116	844-3952	1033	sjbauer@sandia.gov

Sample List

Sample #	Description	Date		Delivered	Returned
		Delivered	Returned	By	To
DEG 2-36-3	Urethane/butadiene/methacrylate formulation				
	New (no elevated temperature aging)	5/2004		S Bauer	
	8 weeks @ 325°F aqueous (3/24/04)	5/2004		S Bauer	
	8 weeks @ 350°F/177°C aqueous (5/19/04)	6/2004		S Bauer	
DEG 2-38-1	Butadiene/methacrylate formulation				
	New (no elevated temperature aging)	5/2004		S Bauer	
	8 weeks @ 325°F aqueous (3/24/04)	5/2004		S Bauer	
	8 weeks @ 350°F/177°C aqueous (5/19/04)	6/2004		S Bauer	
DEG 2-38-2	Butadiene/methacrylate formulation				
	New (no elevated temperature aging)	5/2004		S Bauer	
	8 weeks @ 325°F aqueous (3/24/04)	5/2004		S Bauer	
	8 weeks @ 350°F/177°C aqueous (5/19/04)	6/2004		S Bauer	
	Liquid in contact with well plug during aging	6/2004		S Bauer	

Background Information and Work to be Performed

Chemistry of the Well Plug Formulations (Proprietary)

Water and Heat Activated Sample (DEG-2-36-3):
Polymeric MDI (Diphenylmethane diisocyanate) was reacted with hydroxyl terminated polybutadiene resin to produce a polyurethane prepolymer having terminal isocyanate groups. This was blended with a silicone surfactant, a 1400 molecular weight homopolymer of butadiene and a hexane diol dimethacrylate monomer. To polymerize the material 3% water was added to form polyurea linkages with the terminal isocyanate groups and 1% dicumyl peroxide was added to crosslink the butadiene and dimethacrylate through free radical polymerization.

Heat Activated Polybutadiene Resin and Dimethacrylate Monomer (DEG-2-38-1) and (DEG-2-38-2):
A 1400 molecular weight homopolymer of butadiene was blended with hexane diol dimethacrylate monomer at 20 and 40 %. To polymerize the material, 1% dicumyl peroxide was added to crosslink via free radical polymerization.

Analyze the sample materials by infrared spectroscopy (IR), comparing aged to new materials to determine chemical changes related to aging.

Preliminary Report

date:

to:

via: (in-person, telephone, voice mail, e-mail)

Final Report

date: 7/22/04

Multiple, small pieces of each solid sample were removed, squeezed between salt windows and analyzed, using the microscope accessory to our Fourier Transform Infrared Spectrometer. Each resulting infrared (IR) spectrum corresponds to a 100μm by 100μm area of the sample. A portion of the liquid that was in contact with a well plug was evaporated onto a BaF_2 window, and we obtained IR spectra of multiple areas of the residue using the microscope accessory. Where multiple spectra of a sample are very similar, we obtained an average spectrum of them. The resulting spectra are shown in the following figures.

We will start our discussion of the IR results with the DEG 2-38-1 and DEG 2-38-2 samples. These materials are the simpler formulations (see above), consisting primarily of butadiene and methacrylate components. Spectra (averaged) comparing these two formulations are shown in Figure 1. All the major bands in their spectra correspond to the butadiene ("B") or methacrylate ("M") component (or are due to both components) and are so labeled in the figure. The same IR bands are present in the spectra of the DEG 2-38-1 and DEG 2-38-2 samples, but they vary in relative intensity, Specifically, the bands due to the methacrylate component are about three times as intense, relative to the butadiene bands, in DEG 2-38-2 as they are in DEG 2-38-1, indicating a three times larger methacrylate-to-butadiene ratio in DEG 2-38-2.

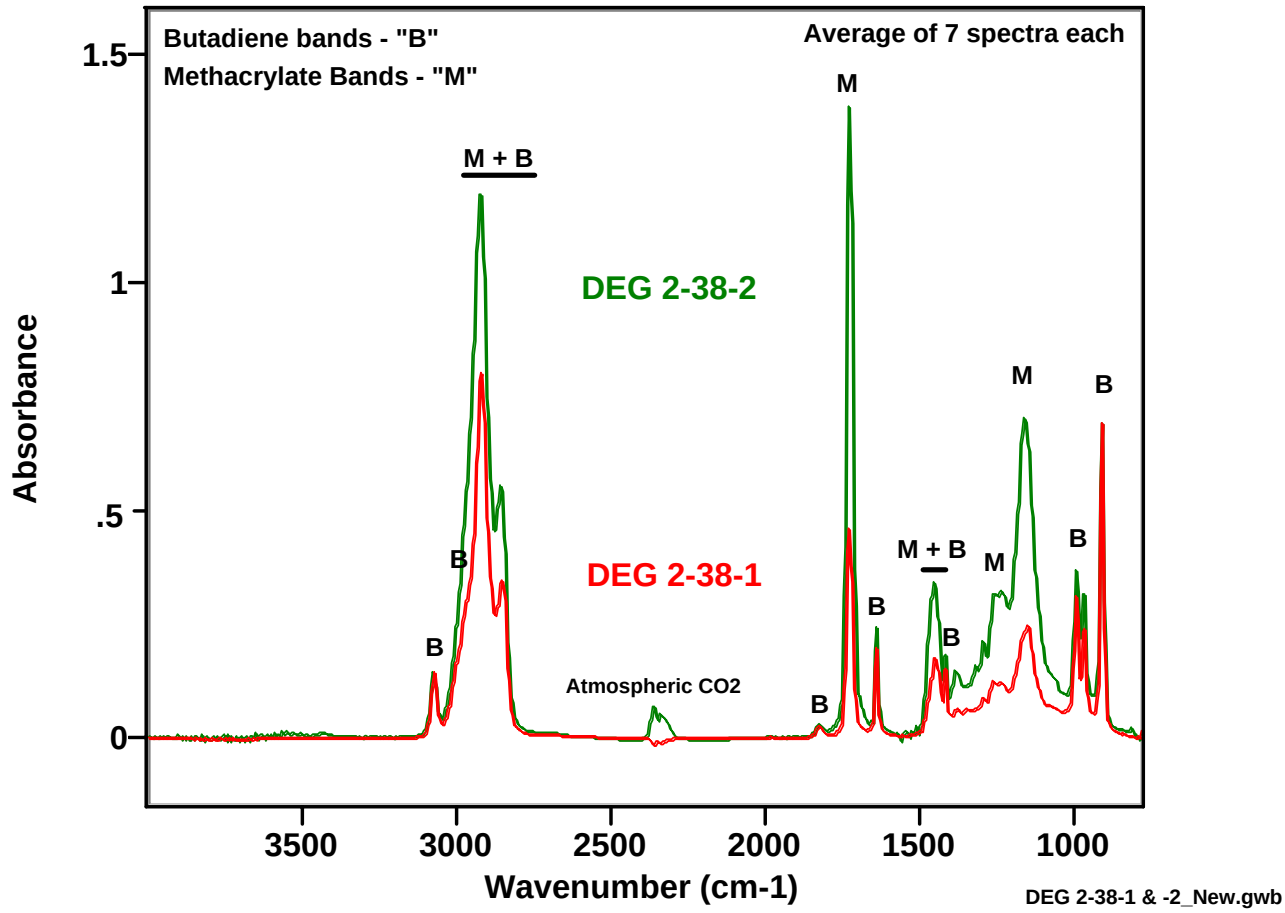


Figure 1. IR spectra from DEG 2-38-1 and 2-38-2 (new materials)

New and Aged DEG 2-38-1

The averaged spectrum of New DEG 2-38-1 from Figure 1 is also shown in Figure 2, along with the spectrum of liquid oozing out of the sample matrix. The spectrum of the liquid has bands due to the butadiene, but not the methacrylate component. Apparently some phase separation of the butadiene component has occurred.

Figure 3 compares IR spectra from New DEG 2-38-1 and DEG 2-38-1 aged at 325°F in aqueous solution for eight weeks. The middle spectrum in Figure 2 is an average of spectra from the bulk of the aged sample. It is similar to the spectrum of the New DEG 2-38-1, except for the appearance of low-intensity, broad band(s) from 3500 to 2500 cm^{-1}. These bands indicate the appearance of carboxylic acid (-COOH) groups. The most likely source of the carboxylic acid groups is hydrolysis of methacrylate ester groups. Since the ratio of bands from the methacrylate and butadiene components in the spectra of New and aged DEG 2-38-1 (top two spectra in Figure 3) is similar, only a small fraction of the methacrylate groups has been hydrolyzed. Further, since the ester groups in methacrylate polymers are not in the polymer chain

backbone, their hydrolysis should not disrupt the methacrylate polymer chain. The (bottom) spectrum of Figure 3 is from a location in the aged sample with only the butadiene component.

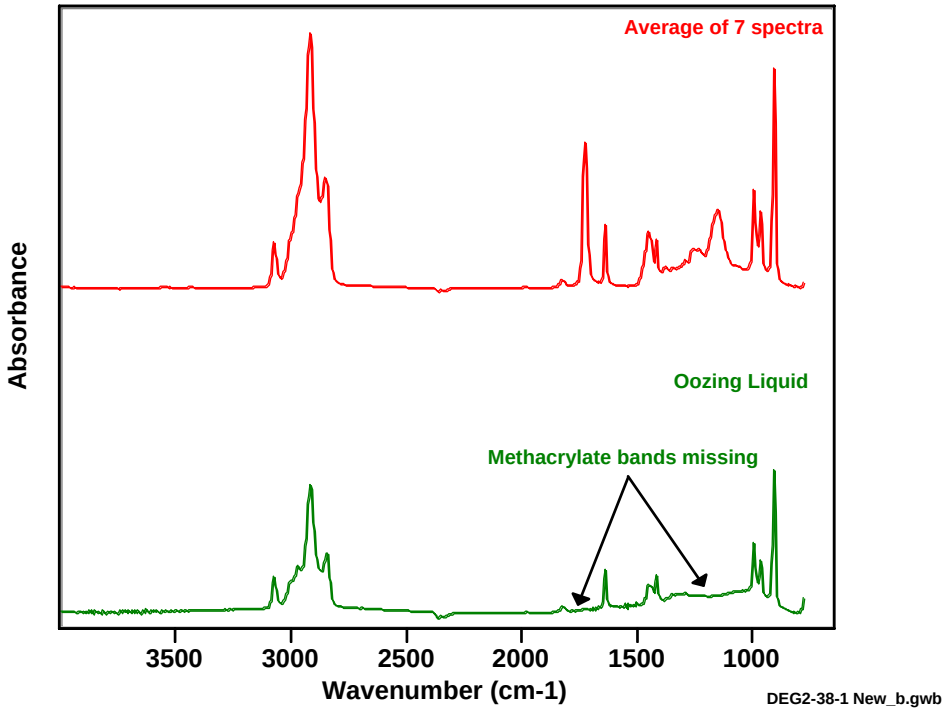


Figure 2. IR Spectra of DEG2-38-1 (New) – Spectra from bulk and oozing liquid

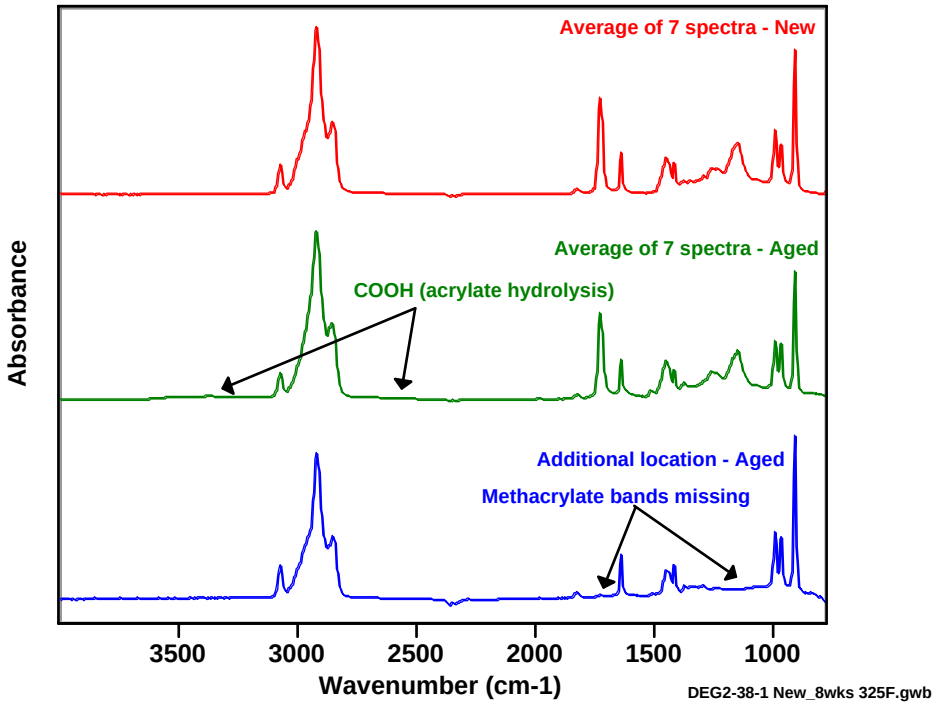


Figure 3. IR Spectra of DEG2-38-1 - New and Aged at 325°F for 8 weeks

Figure 4 compares IR spectra from New DEG 2-38-1 and DEG 2-38-1 aged at 350°F in aqueous solution for eight weeks. IR bands due to carboxylic acid groups are relatively more prominent in the spectrum of DEG 2-38-1 aged at 350°F (Figure 4) compared to the spectrum of DEG 2-38-1 aged at 325°F (Figure 3), indicating more extensive hydrolysis of the methacrylate component. Despite loss of the methacrylate component, the relative intensity of the butadiene bands in the spectrum of 350°F-aged DEG 2-38-1 is less than half of that in the spectrum of New DEG 2-38-1. In addition to hydrolysis of the methacrylate, the aging process at 350°F has leached much of the butadiene component from the sample.

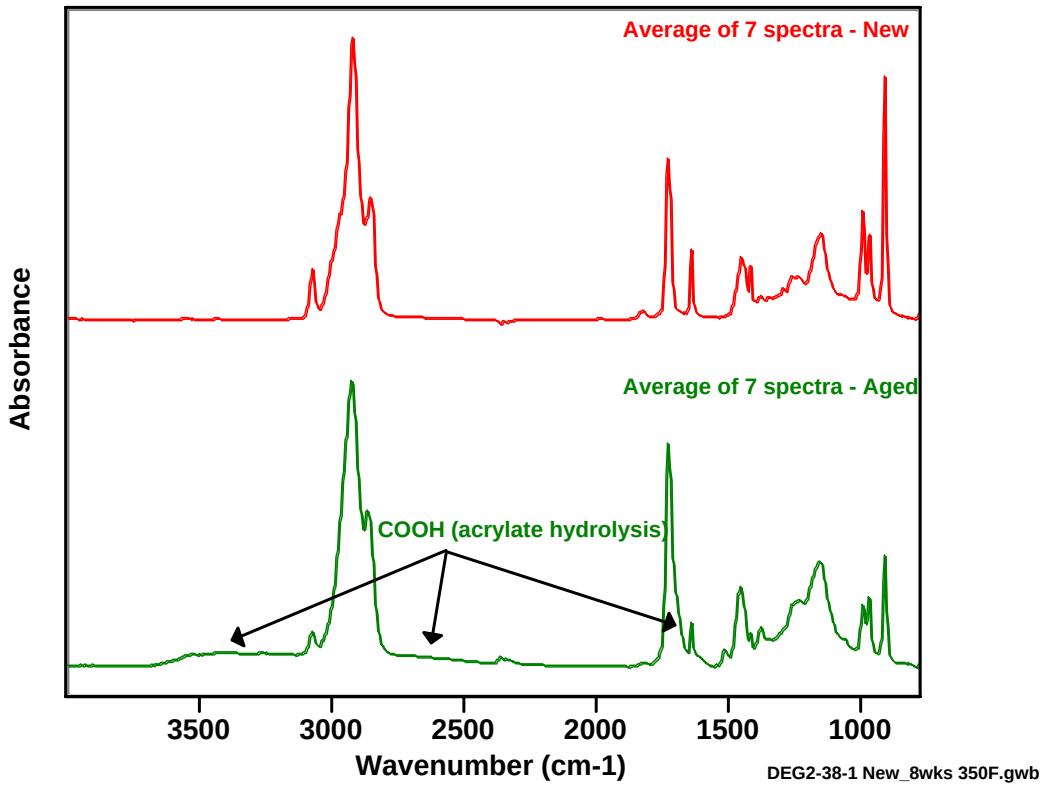


Figure 4. IR Spectra of DEG2-38-1 - New and Aged at 350°F for 8 weeks

New and Aged DEG 2-38-2

Figure 5 shows spectra from the New DEG 2-38-2 sample and from liquid oozing out of it. As with the DEG 2-38-1 sample, the liquid is the butadiene component. Figure 6 compares IR spectra from the New DEG 2-38-2 and DEG 2-38-2 aged at 325°F for eight weeks. As with the aging of DEG 2-38-1 at 325°F, the aging of DEG 2-38-2 at 325°F involves some methacrylate hydrolysis (middle spectrum of Figure 6). The methacrylate bands in the spectrum of aged DEG 2-38-2 are 10 – 15% lower in relative intensity than those in the spectrum of New DEG 2-38-2, consistent with some loss of the methacrylate component. Regions of nearly pure butadiene component are also present in DEG 2-38-2 aged at 325°F (bottom spectrum of Figure 6).

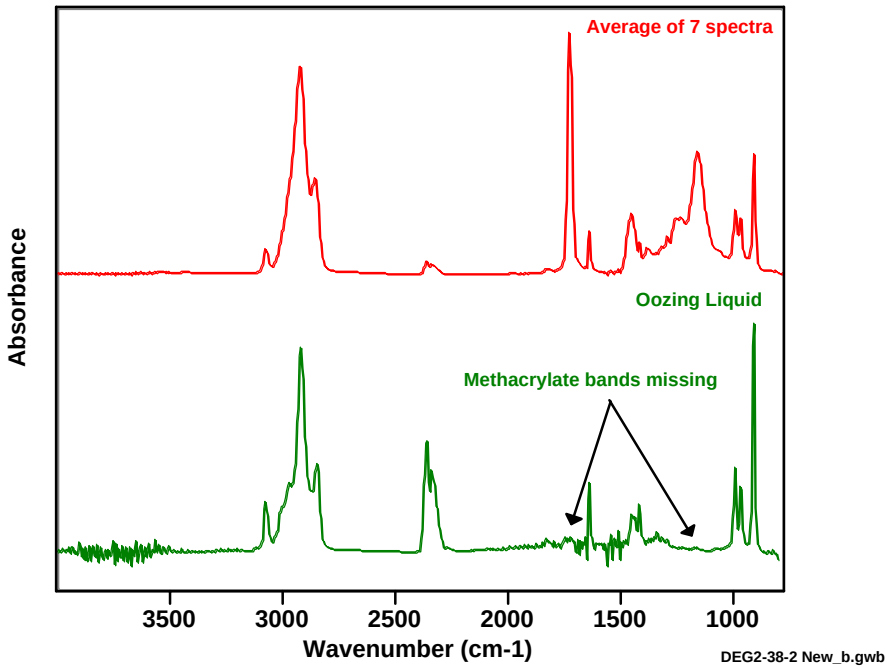


Figure 5. IR Spectra of DEG2-38-2 (New) – Spectra from bulk and oozing liquid

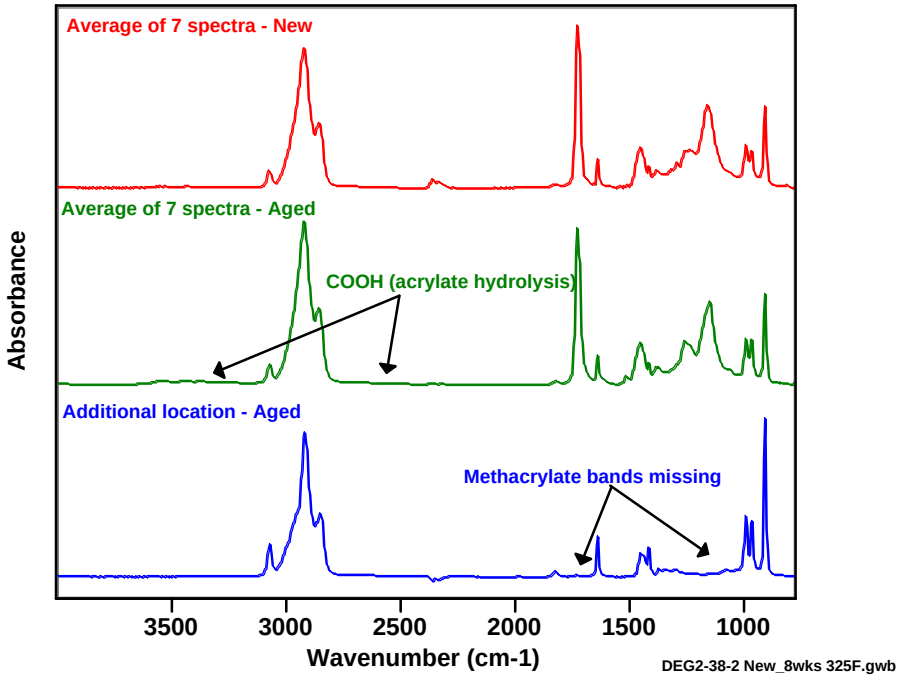


Figure 6. IR Spectra of DEG2-38-2 - New and Aged at 325°F for 8 weeks

The DEG 2-38-2 sample aged at 350°F for eight weeks has an relatively light-colored, center covered by a darker crust. We obtained IR spectra of both the inner (lighter) and outer (darker) regions. Spectra of New DEG 2-38-2 and of the inner material from DEG 2-38-2 aged at 350°F are shown in Figure 7. The spectrum of aged DEG 2-38-2 shows evidence of hydrolysis of some methacrylate groups to form carboxylic acids. In addition methacrylate bands in the aged spectrum are 60% less in relative intensity than they are in the spectrum of New DEG 2-38-2, indicating a significant loss of the methacrylate component. In the spectrum of the outer material from DEG 2-38-2 aged at 350°F (Figure 8), the carboxylic acid bands (from methacrylate hydrolysis) are more prominent, and the methacrylate bands show about a 40% decrease in relative intensity. In addition there is a band (labeled "COO-" in the bottom spectrum of Figure 8) due to a carboxylate salt. The presence of the carboxylate is presumably from association of carboxylic acid groups with cations in the surrounding liquid

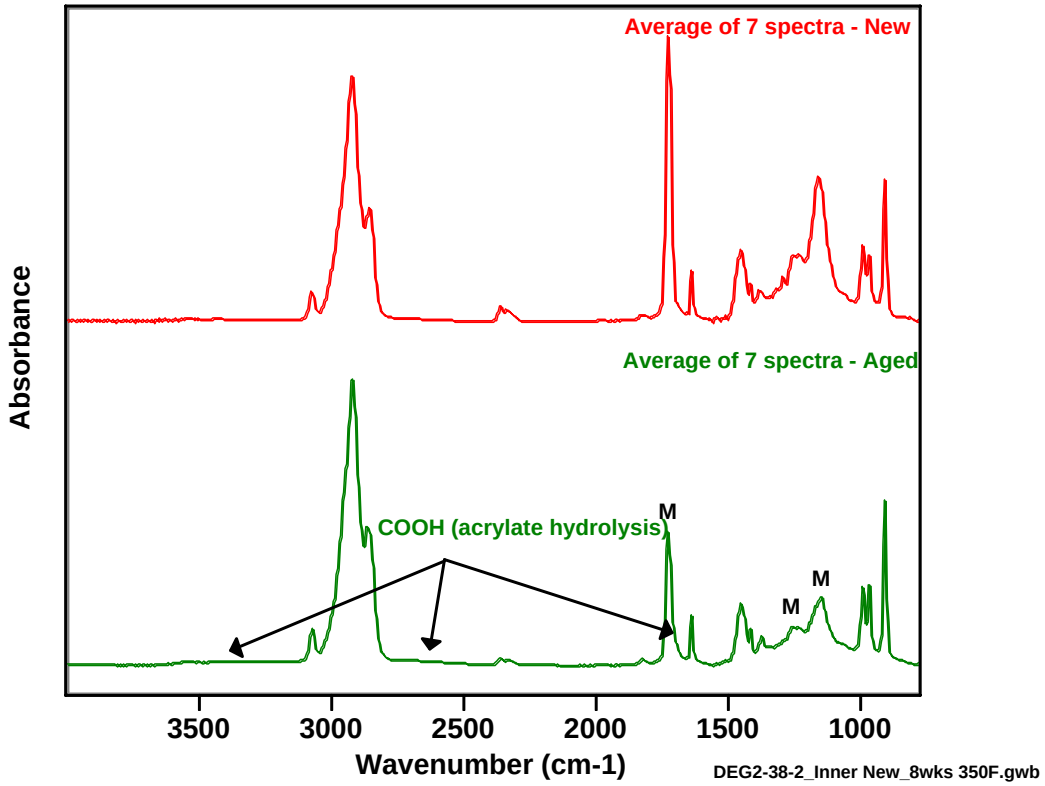


Figure 7. IR Spectra of DEG2-38-2 (inner material) - New and Aged at 350°F for 8 weeks ("M" labels bands of the methacrylate component)

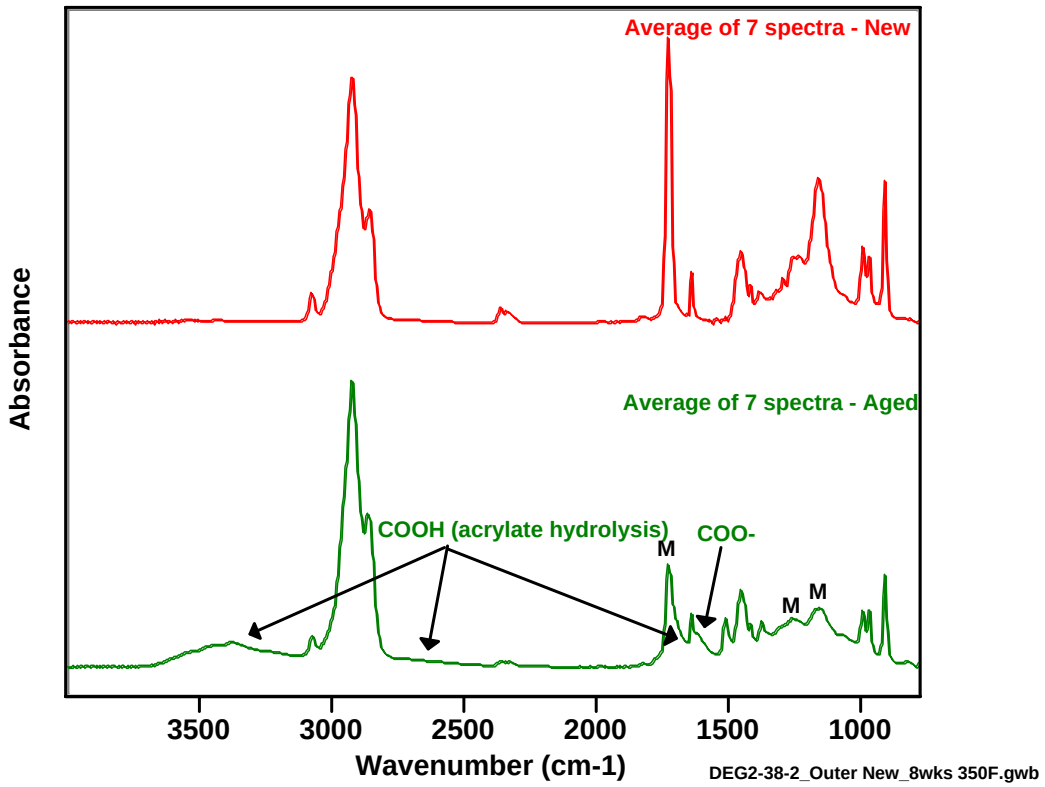


Figure 8. IR Spectra of DEG2-38-2 (outer material) - New and Aged at 350°F for 8 weeks ("M" labels bands of the methacrylate component)

New and Aged DEG 2-36-3

The average spectrum from the bulk of the New DEG 2-36-3 sample is shown in Figure 9. The DEG 2-36-3 formulation has a urethane component in addition to the butadiene and methacrylate components. IR bands due to the butadiene and methacrylate components are labeled on this spectrum. Additional bands are due to the urethane component. Figure 9 also includes a spectrum from what is apparently a urethane-rich region of New DEG 2-36-3. IR bands due to the urethane component are labeled in this spectrum. The band peaking near 2275 cm^{-1} is due to unreacted nitrile (-C≡N) groups.

Spectra of New DEG 2-36-3 and DEG 2-36-3 aged at 325°F for eight weeks are shown in Figure 10. The second spectrum from the top of Figure 10 is an average spectrum from the bulk of the aged material. This spectrum shows a loss of about 1/3 of the relative intensity of methacrylate bands compared to the spectrum of New DEG 2-36-3. It also shows aging trends more apparent in the spectrum of the "Translucent amber material" (bottom, Figure 10). The spectrum from the "Liquid Drop" in the aged material (second from bottom, Figure 10) is due to the butadiene component. The spectrum of the Translucent, amber, material is from a region relatively rich in the urethane component. The labeled bands in this spectrum are due to aromatic, primary amines and carboxylic acids, whose presence is believed to result from the hydrolysis of urethane groups.

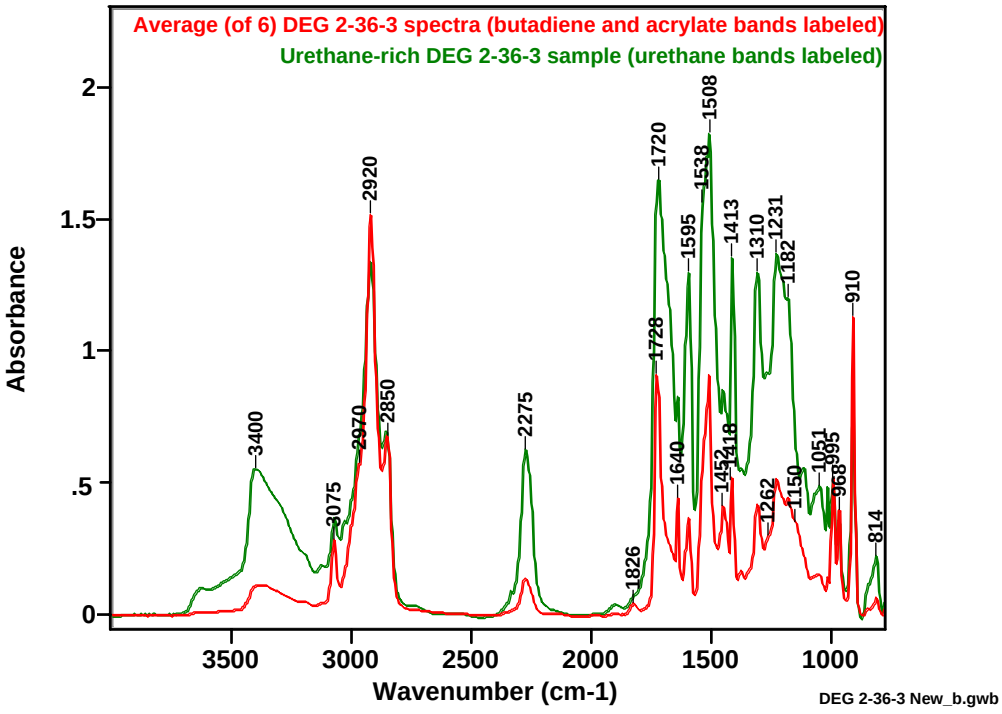


Figure 9. IR Spectra of DEG2-36-3 (New)

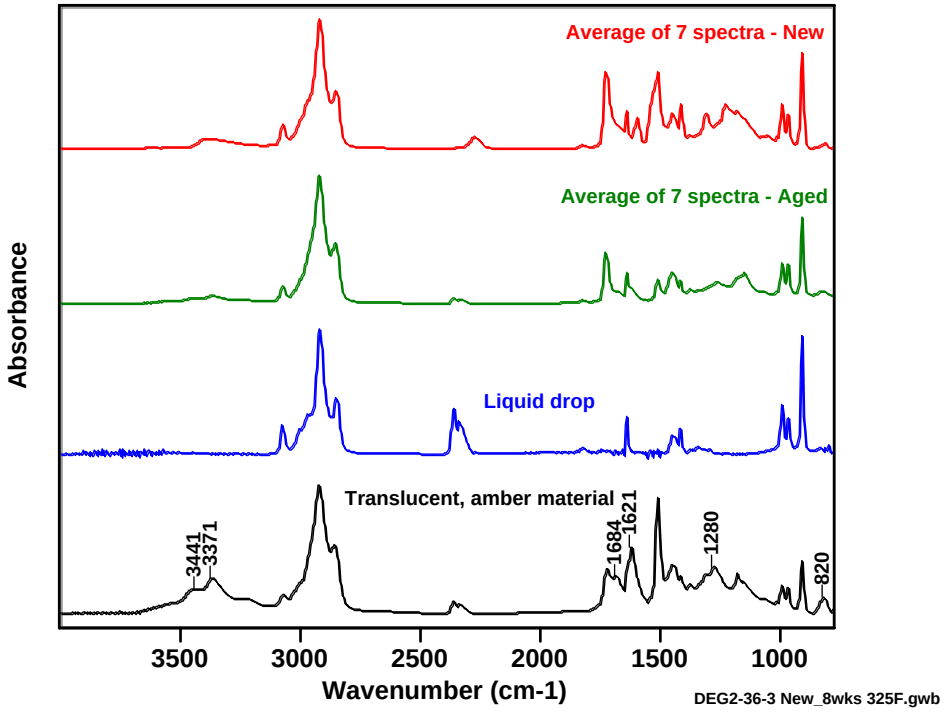


Figure 10. IR Spectra of DEG2-36-3 - New and Aged at 325°F for 8 weeks

Figure 11 shows spectra of New DEG 2-36-3 and DEG 2-36-3 aged at 350°F for eight weeks. Bands due to the butadiene in the aged DEG 2-36-3 spectrum are less than half their relative intensity the spectrum of New DEG 2-36-3, indicating loss of the butadiene component. Labeled bands in the spectrum of aged DEG 2-36-3 indicate the formation of aromatic, primary amines and carboxylic acids, as occurred with the DEG 2-36-3 aged at 325°F. The amines and carboxylic acids are believed to be the hydrolysis products of urethane groups. Note that none of the spectra of DEG 2-36-3 aged at 325°F and 350°F show nitrile bands (the features occurring between 2000 and 2500 cm^{-1} in the aged spectra peak higher in frequency than the nitrile bands – these features are due to uncompensated, atmospheric carbon dioxide). The nitrile groups present in New DEG 2-36-3 (Figure 9) have reacted in the hot, aqueous, aging environment.

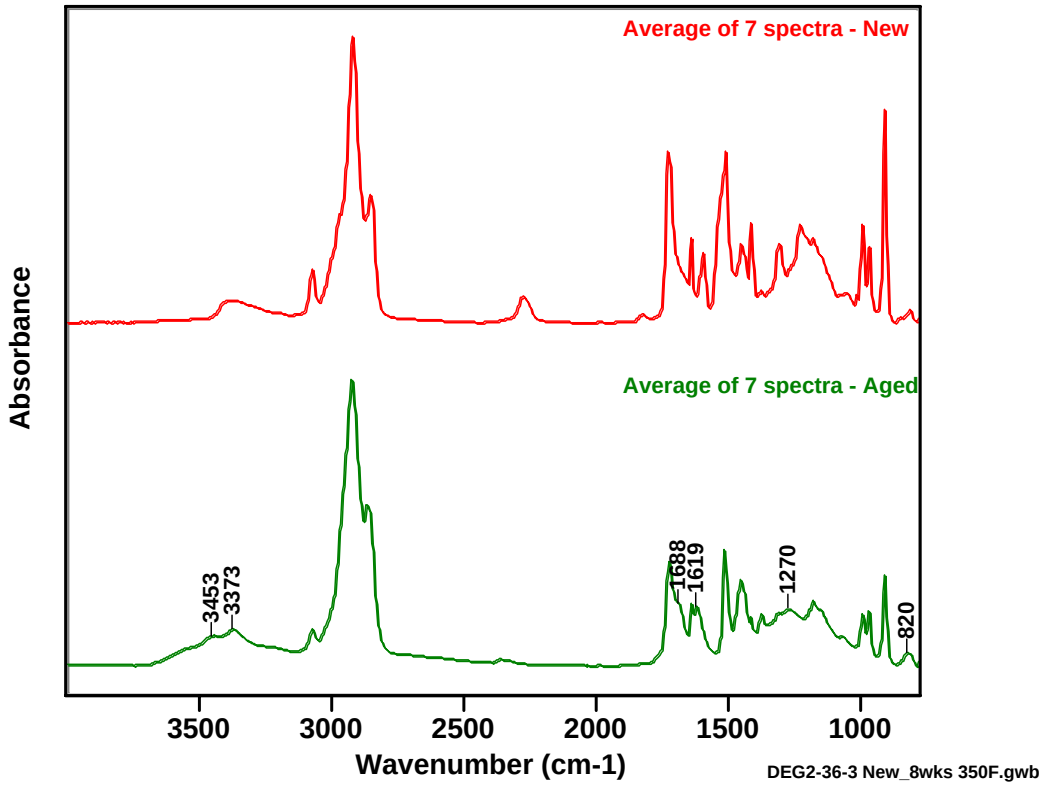


Figure 11. IR Spectra of DEG2-36-3 - New and Aged at 350°F for 8 weeks

Liquid in Contact with the Geothermal Plug.

IR spectra of the residues from the contact liquid yield IR spectra from a number of different chemical species. The major components of the residue include alkanolamines, amides, carboxylic acids and carboxylates. These chemicals are most likely reaction products of materials leached from the butadiene, methacrylate and urethane components.

Summary

Although the geothermal plugs retain much of their physical properties, a lot of chemistry is occurring during aging, including hydrolysis of ester linkages in the methacrylate component and hydrolysis of urethane groups in the urethane component. In addition there is apparent loss of the butadiene component in aged DEG 2-38-1, of the methacrylate component in DEG 2-38-2, and of both the methacrylate (325°F) and butadiene (350°F) components in DEG 2-36-3. The higher aging temperature tends to enhance the aging effects.

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