Shell Global Solutions

GS.06.51829
RESTRICTED

Determination of the maximum allowable operating temperature of Aliphatic amine/epoxy based GRE pipes for crude oil service

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Determination of the maximum allowable operating temperature of Aliphatic amine/epoxy based GRE pipes for crude oil service

by

F.A.H. Janssen

Summary

Petroleum Development Oman (PDO) would like to increase the maximum operating temperature of Glass fibre Reinforced Epoxy (GRE) pipes installed in the Harweel field to 85 °C. For future projects PDO considers also to apply these aliphatic amine/epoxy based GRE pipes up to a design temperature of 90 °C. Experiments performed by Shell Global Solutions and additional data shows that the supplier provides the pipe material in under-cured condition. Qualification tests performed at the time by the vendor were also performed on under-cured pipe material. The under-cured material qualifies for service up to 80 °C.

Qualification for service up to 90 °C would require testing of fully cured pipe material.

Amsterdam, July 2006

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1. Introduction

Petroleum Development Oman (PDO) would like to increase the maximum operating temperature of glass fibre reinforced epoxy (GRE) pipes installed in the Harweel field to 85 °C. Fibre Glass Systems (FGS) has supplied the GRE pipes.[1] The curing agent used for the epoxy resin was indicated to be an aliphatic amine. For future projects PDO considers also to apply these aliphatic amine/epoxy based GRE pipes up to a design temperature of 90°C. FGS further would like to gain Shell and PDO acceptance of their aliphatic amine/epoxy resin system for design temperatures up to 93.3 °C[2] for which they have full regression data.

The aliphatic amine cured epoxy system as provided by FGS to PDO however does not fulfil the applicable standards DEP 31.40.10.19-Gen./ISO 14692. The glass transition temperature (T_g) of the system is approx. 105 °C and the standards require that the T_g shall be more than 30 °C above the maximum design temperature, in this case therefore resulting in a maximum design temperature of 75 °C. FGS claims[3] that the standards are too stringent for their system because of its special properties.

PDO requested Shell Global Solutions to determine the maximum allowable operating temperature limit for the aliphatic amine/epoxy based GRE pipes for crude oil service.

The T_g and the ring bending stiffness of the aliphatic amine cured epoxy were determined on both as received material and after exposure to hot water. Results were compared with data from literature. This note describes the investigation performed and provides recommendations regarding the maximum allowable operating temperature.

2. Standards and theory

As specified in DEP 31.40.10.19-Gen / ISO 14692, T_g, measured by Differential Scanning Calorimetry (DSC), Modulated Differential Scanning Calorimetry (MDSC) or Dynamic Mechanical Thermal Analysis (DMTA) shall be more than 30 °C above the maximum design temperature[4]. Maximum design temperature is defined as the maximum fluid temperature that can be reached during service.

The rational behind this criterion is the fact that fluids absorbed by epoxy resins during service act as plasticizer and can cause substantial changes of the properties of epoxy resins and their fibre-reinforced composites. Maxwell et Al [3] advises “when using GRP products to ensure that the maximum operating temperature is at least 30 – 40 °C below the T_g of the material (taking into account the moisture effects)”.

The level of the changes depends on the temperature and the type and amount of fluid absorbed. Changes are, amongst others, manifested by reduction in the glass transition temperature[5] T_g.

Of the fluids encountered in crude oil, water is know to be one with significant plasticizing effect on epoxy resins. The interaction of epoxy resins with water and their fibre-reinforced composites and the consequent reduction of glass transition temperature has therefore been subject of many investigations [1][3][4].

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1 The company markets its products under the trade names STAR, SMITH and Fibrecast.

2 200 °F

3 E-mail David Granderson, 18-10-2005 17:39 to Nasser Behlani, NIS PDO-UEC12.

4 ISO 14692:2 section 6.8.2.2.

5 Smaller molecules of plasticizer embed themselves between the polymer chains, increasing the spacing and free volume, and allowing them to move past one another even at lower temperatures. *In polymers, Tg is often expressed as the temperature at which the Gibbs free energy is such that the activation energy for the cooperative movement of 50 or so elements of the polymer is exceeded. This allows molecular chains to slide past each other when a force is applied.*

In Figure 6 the effect of water uptake on the glass transition point of various epoxy systems are presented.

One commonly used empirical equation to calculate the glass transition temperature for a binary (single phase) mixture of polymer and plasticizer is the Fox equation [2];

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (2)$$

Where *w* is the weight fraction and the index *1* is for the polymer and *2* is for the plasticizer and *T* is the temperature in Kelvin. The equation can be used when the glass transition temperature for each pure substance is known[6]. A potential interaction between polymer and plasticizer is in this equation not taken into account.

Elis and Karasz [2] reported for epoxy resins a typical decrease of 20 °C/wt% of water. Based on this figure a weight uptake of 1.5 % water in the resin results in reduction of the T_g of 30 °C. When comparing literature data it is important to verify whether tests were performed on pure resin specimens or composite specimens of glass fibres reinforced resin[7]. Although variations are found between various curing agent/epoxy resin systems the 30 °C criterion appears to cover a general range of systems not being over conservative.

In cases were this criterion is considered over conservative or cases were the criteria might not be conservative enough, the determination of the glass transition temperature or heat distortion temperature on fully saturated GRE specimens at the envisaged operating temperature should be performed. In Appendix 1 a scheme is given how to define the maximum allowable operating temperatures of GRE pipes.

For any engineering application of epoxy resin systems like GRE pipes the main criteria defining the maximum allowable operating temperature should be that the system meets the specifications set, like those for pressure containment and stiffness. A reduction in chemical resistance of the material or even a chemical reaction between crude oil and/or water and the GRE material is not expected although Maxwell et Al [3] do not exclude chemical reactions between GRE material and water and further indicate the potential for leaching of components.

Determination of the glass transition temperature

Typically the softening of epoxies is characterized by means of glass transition temperature (T_g) measurements. The most common method used to determine T_g is to observe the variation of a thermodynamic property with temperature. T_g determined in this manner will vary somewhat depending on the rate of cooling or heating, which reflects the fact that long entangled polymer chains cannot respond instantaneously to changes in temperature. At the glass transition temperature a thermodynamic property will exhibit a discontinuity with temperature.

Appendix 4 discusses the generally used methods to determine the T_g.

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6 For water in general a glass transition temperature of 136 K is used although it should be noted that some conflicting values are reported in the literature. The glass transition temperature of toluene is 117 K.

7 Due to the higher density of glass fibres the percentage weight gain of composite specimens lower than that of neat resin specimens.

3. Experimental

3.1 Sample material

FGS was asked to provide Shell Global Solutions with either ring or pipe samples representative for current Harweel flowlines. FGS provided Shell Global Solutions with two short pipe sections. On the 31 March 2006, FGS informed Shell Global Solutions that the provided material was under cured and that under-cured pipe samples are representative for the state their pipe material is provided to PDO. Expressed in glass transitions temperatures this means:

The undercured material typically has a T_g of 105 °C, confirmed by TMA measurements in Amsterdam. T_g of fully cured material (same resin and curing agent) is typically in the range of 115 – 120 °C.

The water content of the as received material was not determined since drying of the material, typically above 100 °C, would effect its properties due to post curing. Manufacture of under cured GRE seems to have an economical basis i.e. shorter curing schedule, less power consumption and higher production rates with same oven capacity. In Table 1 details of the applied resin systems are giving, together with the curing cycle recommended by the resin manufacturer and the actual curing cycle applied by FGS.

Table 1 *Resin system details*

Epoxy DER 383 Dow Plastics	Epoxide Equiv. Wt. 176-183 Viscosity (cps @ 25 °C) 9,000-10,5000 Specific Gravity 1.16
Aliphatic amine DEH 24 Dow Plastics	triethylene tetramine, TETA Wt. Per Active H 24.4 PHR D.E.R. 331, 12.9
Glass fibres Owens Corning	SE 2348. OC SE 2348 roving was designed for amine epoxy. Single-end roving for epoxy filament winding of small-diameter oil-field pipe and other uses.
Curing cycle of the resin and GRE pipe ”under-cured” system	Radiant Heat applied. Ambient to 85 °C in 4 minutes. Dwell at 85 °C for 6 minutes, then ramp to 141 °C for 5 additional minutes. GRE surface temperature monitored with infrared sensors.
Recommended curing cycle from the supplier based on “fully cured system”	Suggested Cure Schedule by Dow Plastics for D.E.H. 24 Gel at RT plus several days at RT or 1-2 hrs at 100 °C for full cure. Cure schedule for material properties Initial Gel 16 hours at 25 °C Postcure 3 hours at 100 °C
Density of the epoxy	1.15 g/cc
Density of the glass fibres used.	2.624 g/cc Advantex Glass Fibre
Glass content of GRE pipe	77.3 % by weight (TUV AW6/2465-98)
Distilled water uptake [%WT] D.E.R. 383 cured with D.E.H. 24 ASTM D 543 Specimens: 3” x 1” x 0.125” coupons	7 Days 0.38 28 Days 0.76 120 Days 1.40
Heat Deflection Temperature [°C] D.E.R. 383 cured with D.E.H. 24	100

* Dow Liquid Epoxy Resins, Dow Plastics Form No . 296-00224-0199 WC+M

3.2 Glass transition measurements using TMA

For the determination of the glass transition temperature of the GRE material provided by FGS, Shell Global Solutions used a Perkin Elmer Diamond TMA with a high sensitivity that allows measuring sample displacements down to 0.02 microns in the temperature range of minus 150 °C to 600 °C.

The specimen size was:

Diameter = 8 mm
Height = 5-6 mm
Weight = 500 - 600 mg
The heating rate was 5 °C/min.
The maximum temperature was 150 °C.
Measurements were performed heating up from 20 °C to 150 °C.

Sequence:

(a) TMA measurement on as received material two times.
(b) Curing for 20 minutes at 196 °C.
(c) TMA measurement two times.
(d) Curing for 2 hours at 196 °C.
(e) TMA measurement.

Background
The T_g values obtained using TMA showed to increase when measured on the same specimen for a second time. Therefore some exposure tests to elevated temperature were performed to establish the effect of post curing on the TMA results.

Exposure to hot water:
Several as received specimens were exposed to de-mineralized water at 95 °C until saturation. The T_g of the saturated specimens was determined.

3.3 Ring stiffness test

The ring stiffness tests were performed as described in DIN 53769-3, similar as earlier ring tests experiments performed by Shell Global Solutions [OP.99.20168].

Twelve ring specimens were tested, 6 after saturated in de-mineralized H_2O at 95 °C and 6 in as received conditions. Rings were provided with a position mark in order to test the rings in the same position in each compression test. Ring stiffness compression tests were performed at 23 °C, 65 °C, 75 °C, 85 °C, 95 °C, 105 °C and 120 °C.

The H_2O saturated rings were kept in water during the time that the rings were not tested. Table 2 provides the test details.

Table 2 *Ring stiffness test details*

Ring width	mm	16.5 +/- 0.1
Ring outer diameter	mm	112
Wall thickness	mm	6
Max compression force	N	440
Compression		1.5 % = 1.68 mm
Compression loading speed	mm/min	1.68 (or the nearest setting possible)
Period of constant deformation (1.5 %)	min	2
Compression unloading speed	mm/min.	1.68

In accordance with DEP 30.10.02.13, the criterion for the “apparent distortion temperature” was set to 85 % of the initial ring stiffness value retained. To characterize the material the T_g of the ring specimen material was measured, as indicated in Section 3.2.

3.4 Data provided and experiments performed by FGS

To support the investigation, FGS provided results from previous investigations and performed a number of experiments.

(a) Conclusion page of Tüv report AW6/2465-98on the Star 1500 Line.
(b) Velosi America LLC report. Glass fibre, resin and curing agent data. Glass Transition DSC data of 7 pipe specimens.

Experiments

(a) Weight change and heat deflection temperature measurements on GRP specimens exposed to distilled water at 93.3 °C (200 °F) for a period of maximum 7 Days.
(b) Weight measurements on water saturated neat resin specimens to determine effect of DSC measurements on weight, see Appendix 3.

4. Results

4.1 TMA measurements

Figure 1 shows the measured glass transition temperatures on 6 specimens, first measured in as received conditions followed by various exposures to elevated temperature:

(a) TMA measurement on as received material two times.
(b) Curing for 20 minutes at 196 °C.
(c) TMA measurement two times.
(d) Curing for 2 hours at 196 °C.
(e) TMA measurement.

All exposures to elevated temperatures resulted in an increase in the T_g.
Saturation with water at 95 °C resulted in a weight increase of 1.4 %. The T_g of these saturated specimens remained approximately the same as the as received GRE that is 105 °C.

4.2 Weight change measurement after water exposure

Figure 2 shows the weight change of GRE DMA specimens exposed to water at 93.3 °C by FGS versus exposure time. In the same figure the weight change of GRE TMA specimens exposed to 95 °C by Shell Global Solutions versus time are given.

In Figure 3 the weight change of the ring specimens exposed to water at 95 °C are given.

From Appendix 3 provided by FGS it can be derived that the weight change of pure resin exposed to water at 93.3 °C, indicated as saturated[8], is at least 3.5 %. Weight change data of GRE specimens and neat resin specimens can be compared as follows. It is assumed that the water is absorbed by the resin. The resin content of the GRE is approx 25 % by weight see Table 3. Therefore the weight change of the resin is 1/0.25 times the measured weight of the total GRE specimen.

[8] The water content at the start of the exposure tests was not indicated.

Table 3 *Density of resin, glass and water. Glass content and resin content of GRP*

Material	Density (g/cm^3)	
E-glass	2.55	
Epoxy resin	1.15	
Water	1.0	
	[% per weight]	[% per volume]
Glass content	72.5	55.9
Resin content	27.5	44.1

TÜV report data

4.3 Ring stiffness tests

Figure 5 shows the normalized ring stiffness versus Temperature of the Aliphatic Amine cured Epoxy GRP in as received condition and after exposure to water at 95 °C, which resulted in an average weight change 1.2 % w/w.

4.4 Calculated maximum operating temperature values

The maximum operating temperature values calculated on the basis of the obtained test results are provided in Table 4, for further details on the ranking of the obtained values see Appendix 1.

Table 4
Maximum operating temperature values calculated on the basis of the obtained test results

		Method	**Determination Maximum allowable operating temperature**	**Maximum allowable operating temperature** [°C]
1	$T_{g\ dry}$	DSC TMA	$T_{g\ dry}$ – 30 °C	Under cured 105-30 = 75 Fully cured 125- 30 = 95
2	HDT_{dry}	HDT or ring stiffness	HDT_{dry} – 20 °C	115- 20 = 95
3	$T_{g\ wet}$	DSC TMA	$T_{g\ wet}$– 5 °C	105-5 = 100 100-5 = 95
4	HDT_{wet}	HDT or ring stiffness	HDT_{wet}– 5 °C	85 – 5 = 80

5. Discussion of the results

The GRP sample material as provided by FGS has an average T_g of 105°C. The water content of the as received specimens was not determined since this would require drying at a temperature above 100 °C and therefore cause post curing. From literature it is known that GRE can contain moisture even at room temperature. Level of up to 1 % w/w is reported [5].

Measurements confirm that the resin is not fully cured i.e. the T_g increases when the GRP is exposed to elevated temperatures. Already short term exposure to elevated temperatures, such as during TMA measurement result in an increase of the T_g. The T_g of the as received GRP increased with 5 °C as result of one TMA measurement. The T_g of the fully cured resin is approximately 120 °C – 125 °C, see Figure 1.

Exposure of the under cured GRP to water at 93.3 °C or 95 °C is therefore expected also to have a post curing effect on the resin. This complicated the investigation of the effect of water absorption on the T_g since the water absorption causes a decrease in the T_g where the temperature of the water is increasing the T_g. This can be seen in Figure 4, were the specimens exposed to water at 93.3 °C for a period of 24 hours have a lower T_g than the specimens with a higher water uptake exposed for 168 °C, the longer exposure time is expected to have caused post curing. Further exposure of the specimens' causes an increase in water uptake and no or only limited further post curing and as such a drop in the T_g.

To be able to separate the effects of post curing and water absorption when investigating epoxy resins Ellis and Karasz already indicate that it is important that the prepared resins are both completely dry and fully cured.

The provided GRE material is fully saturated with water at 95 °C at 1.4 % w/w see Figures 2 and 3. The 6 mm thick GRE ring specimens were exposed to water at 95 °C for a period of approx. 1000 hours resulting in a weight change of 1.2 %. The size of the specimens determines the time to reach saturation.

The Heat Deflection Temperature (HDT) based on the ring stiffness measurements drops from 115 °C in dry conditions to 85°C in wet condition, based on the knee in the curve.

With the tolerance margin of 5 °C subtracted, the maximum allowable operating temperature for this system is 80 °C.

As response to an earlier note of FGS, we compared results of ring specimens with open ends and one with sealed ends and concluded that this does not make a noticeable difference regarding water uptake.

The data provided by FGS shows that also the pipe samples used for the regression test at 93.3 °C were under cured.

The under cured GRP raises a number of issues:

(a) The required exposure of material specimens to elevated temperatures for quality control procedures, e.g. DSC etc, influences the results of the measurements (as demonstrated in this investigation).
(b) Potential for leaching of uncured resin when GRP is exposed to fluids at temperatures below the level where post curing occurs.
(c) Potential effect of absorbed water on curing and therefore final properties of the GRP material.
(d) During long-term qualification tests the state of the GRE will change over time due to post curing and affect the results.

Data provided by FGS, see Appendix 3, shows that pipe specimens used for the regression testing were also under cured, having an average T_g of 105 °C.

The long-term positive experience using GRP pipe systems within Shell is based on performance-based qualification and the strict application of requirements set. Performance based qualification eliminates the need for in depth, time consuming and costly additional reviews of products offered by suppliers.

Although the results of the investigation seem to indicate that this GRE system might be suitable for long term service at 93.3 °C and sufficient post curing to raise the T_g to the specified level will occur in the field when operating at this temperature, it is strongly advised not to accept the product for a service temperature higher than 80 °C in order to prevent a precedent. In addition Shell Global Solutions does not support the practice of provision of uncured pipes by suppliers since relation to previous product qualification (fully cured) becomes ambiguous. The effect on qualification cannot be quantified and leads to discussion.

6. Conclusions

The pipe material as provided by the supplier is under cured and has an average T_g of 105 °C. As such it qualifies for a maximum allowable operating temperature of 75 °C. Based on heat deflection measurements on almost saturated ring specimens the maximum allowable operating temperature for this system is 80 °C.

The fully cured material has an average T_g of 120 °C and as such could in principle qualify for a maximum allowable operating temperature of 90 °C. Qualification would however require tests on the fully cured GRE pipes.

The pipe material shall be fully cured before it is applied in the field and not anticipated to post cure during operation.

7. Recommendations

Despite the fact that the investigation shows that the GRE material has a potential to post cure under field conditions i.e. elevated temperatures and contact with water, the practice of provision of uncured pipes by suppliers is not acceptable since product qualification becomes ambiguous, material properties change as a result of test conditions, and the principle of performance based qualification, the key to the successful application of GRE within in Shell is violated.

8. References

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3. A.S. Maxwell, W R Broughton, G Dean and G D Sims, Review of Accelerated Ageing Methods and Lifetime Prediction Techniques for Polymeric Materials, NPL Report DEPC MPR 016, March 2005
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5. Collings, Moisture Management and Artificial Ageing of Fibre Reinforced Epoxy resins, Defence Evaluation and Research Agency (United Kingdom), Technical Memo MAT/STR 1093, 1987.

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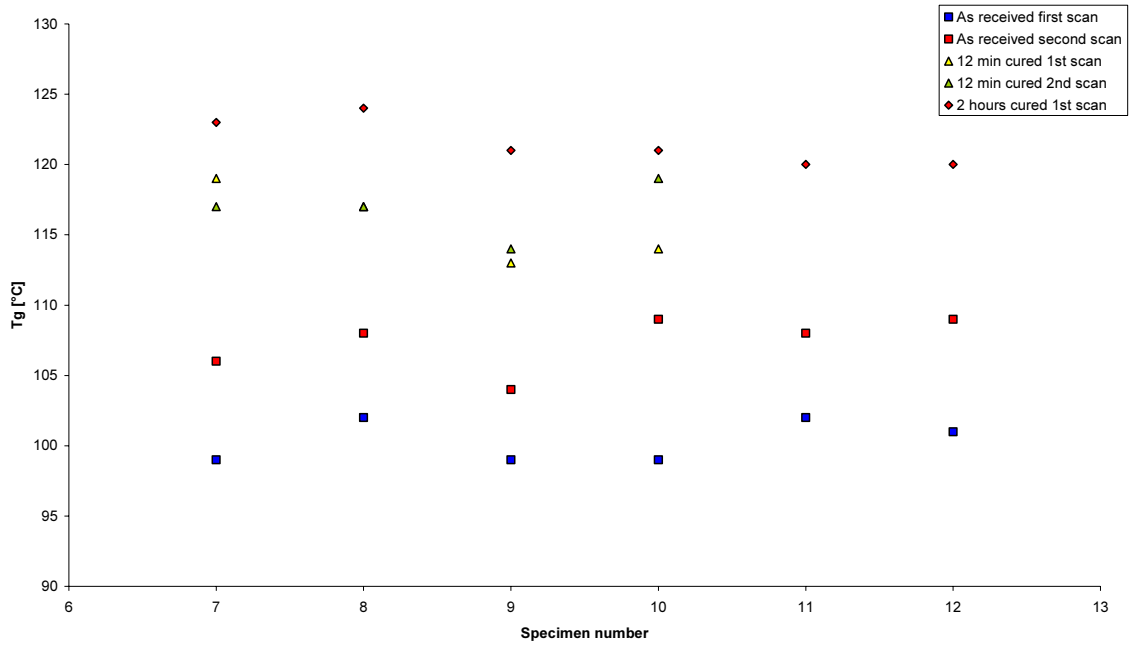

Figure 1
Glass transition temperature measurements using TMA on Fibre Glass Systems Aliphatic Amine cured Epoxy GRP, as received and after various periods of exposure to elevated temperatures.

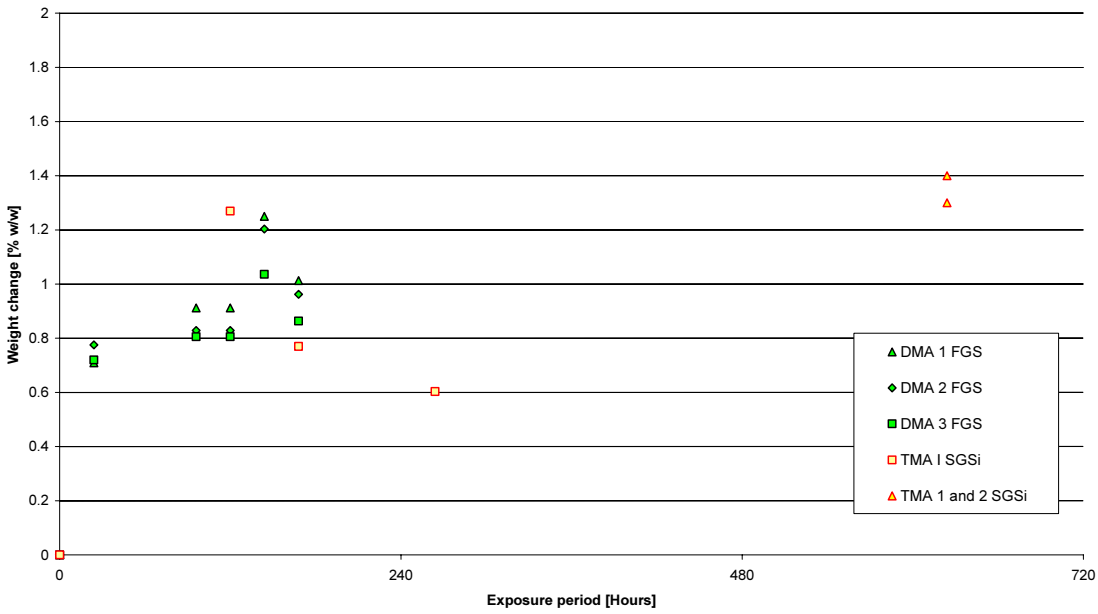

Figure 2
Fibre Glass Systems aliphatic amine cured epoxy GRP, DMA and TMA specimens, weight change after exposure to water at 95 °C

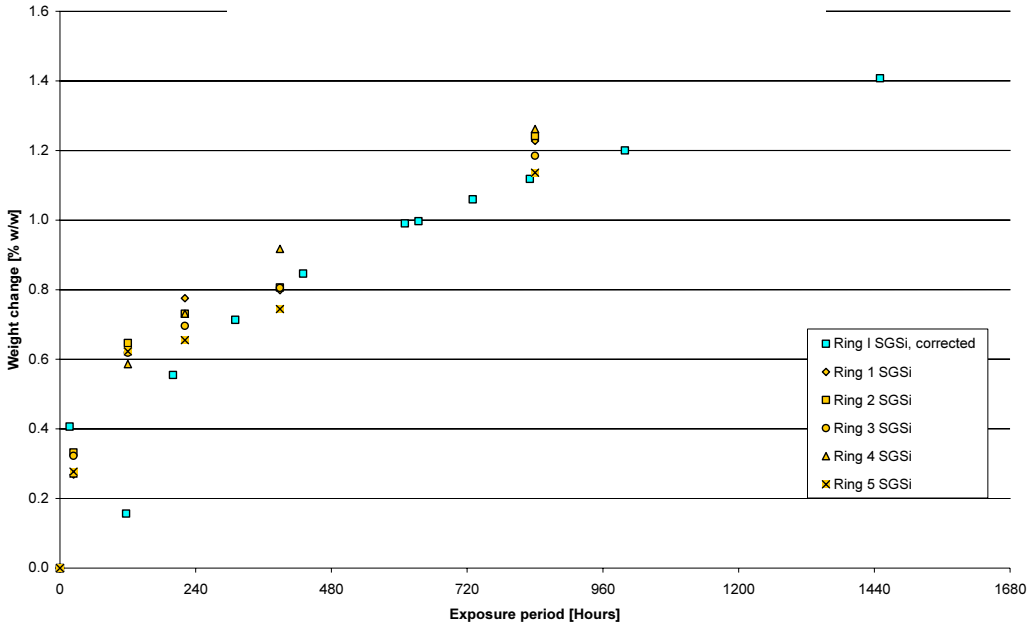

Figure 3
Fibre Glass Systems aliphatic amine cured epoxy GRP, ring specimens, weight change after exposure to water at 95 °C

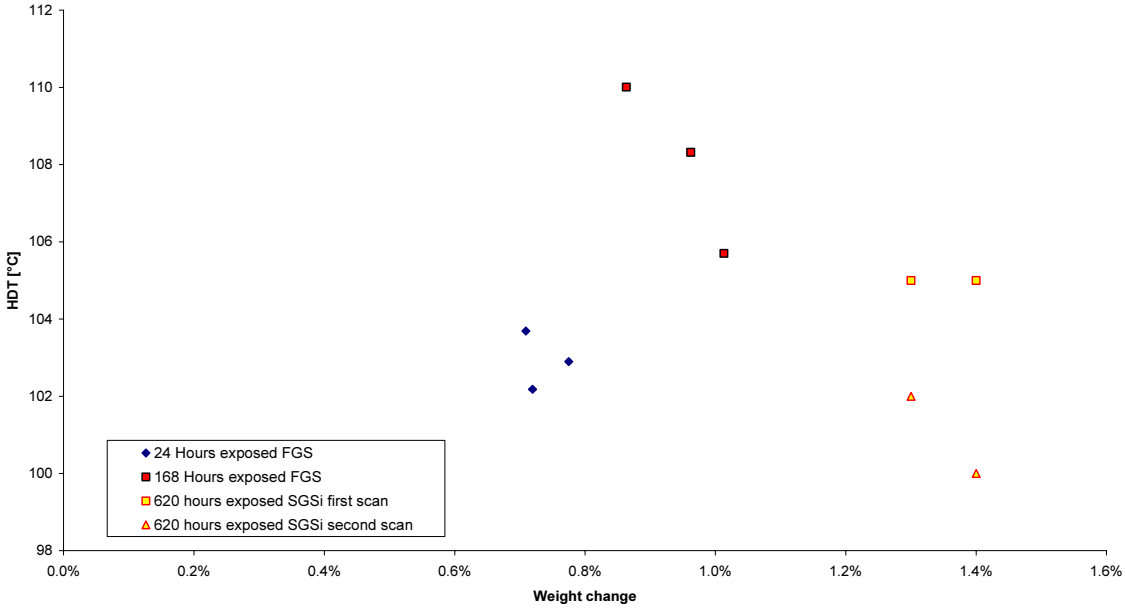

Figure 4
Fibre Glass Systems aliphatic amine cured epoxy GRP, Glass transition temperatures versus weight change after exposure to water at 95 °C for various period of time.

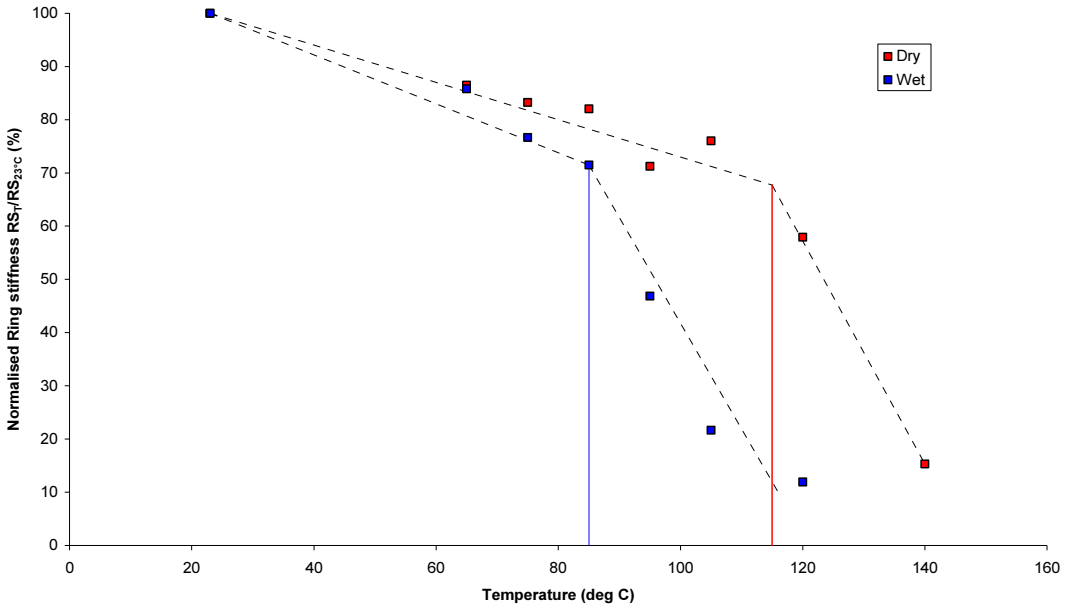

Figure 5
Normalized ring stiffness versus Temperature. Fibre Glass Systems Aliphatic Amine cured Epoxy GRP, Dry and after exposure to water at 95 °C (weight change 1.2 % w/w)

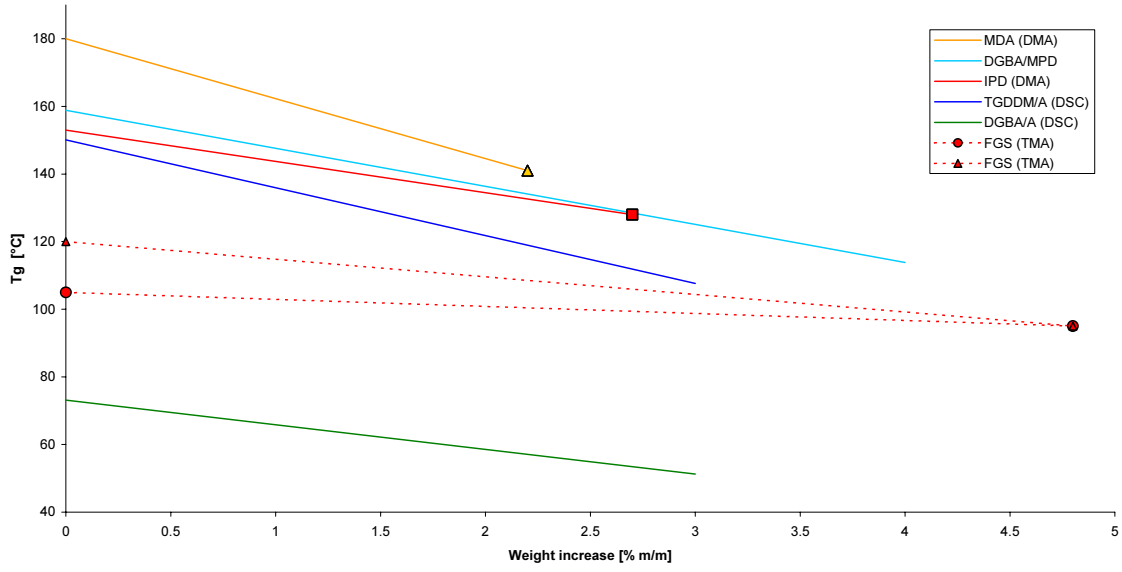

Figure 6
Glass Transition Temperature of various Epoxy resin system versus water uptake

Appendix 1 Defining the maximum operating temperatures of GRE pipes F.A.H. Janssen and P.J.M. van Loon 27.10.2005

		Method	Maximum operating temperature	Reference
1	$T_{g\ dry}$	DSC	$T_{g\ dry}$ – 30 °C	DEP 31.40.10.19-Gen / ISO 14692 Section 6.8.2.1
2	HDT_{dry}	HDT or ring stiffness	HDT_{dry} – 20 °C	DEP 31.40.10.19-Gen / ISO 14692 Section 6.8.2.1
3	$T_{g\ wet}$	DSC	$T_{g\ wet}$ –5 °C	Shell Global Solutions The 5 °C reduction is a measurement tolerance margin
4	HDT_{wet}	HDT or ring stiffness	HDT_{wet} –5 °C	Shell Global Solutions. The 5 °C reduction is a measurement tolerance margin

Ranking:

The maximum operating temperature shall never be higher than HDT_{wet}.

If HDT_{wet} data it not available it shall never be higher than $T_{g\ wet}$.

If $T_{g\ wet}$ data is not available it shall never be higher than HDT_{dry} –20 °C.

If HDT_{dry} data is not available it shall never be higher than $T_{g\ dry}$ – 30 °C.

Wet means saturated with distilled water.
For applications in fluid services not containing water, the resin should be saturated with the actual service fluid or a mixture of fluids similar to the service fluid.

Appendix 2 Thermal history of pipe samples provided by FGS

I did not keep specific records of the thermal history of the pipe sample sent to SGS, but I purposely chose a sample representative of the pipe samples submitted for regression testing at 93.3 °C. T_g = 105 °C. Thermal cure cycles may vary depending on several conditions, mass, mold temperature, etc. The general method is to “gel” the GRE first as to not promote an out of control exothermic reaction, and then apply post cure heat to obtain the required T_g. Gel can be accomplished at room temperature for several hours and anywhere up to 185 °F [85 °C] depending on GRE density, the time desired, and other factors. The pipe sample submitted to you would have a schedule similar to:

Radiant Heat applied such that: Ambient to 185 °F [85 °C] in 4 minutes, dwell at 185 °F [85 °C] for 6 minutes, then ramp to 285 °F [141 °C] for 5 additional minutes. This would be done by monitoring the GRE surface temperature with infrared sensors.

Appendix 3 Glass transition data provided by FGS

4 1/2" 1500 series line pipe TUV samples
ASTM D2992-B Regression Testing at 200 °F (93.3 °C)
T_g's measured by DSC method for samples supplied prior to regression testing.
Sample weight approx 15 mg.
Rate 10 °C/min

Sample #	T_g [°C]
4	104.62
5	106.6
6	106.68
7	107.66
8	107.38
9	102.24
10	106.46
11	102.31
12	104.27
13	106.15
14	104.7
15	97.62
16	106.82
17	102.53
18	102.89
19	104.69
20	107.18
21	110.37
Average T_g	**105.09**

Velosi America report

Sample #	Glass Transition DSC T_g
2	104
3	106.7
7	102.2
1b	116.2
2b	121.9
3b	104.7
4b	107.1

Appendix 4 E-mail FGS to PDO claiming special properties of their aliphatic amine cured resin system

Objective FGS

"….gain full (Shell/PDO) acceptance of our Aliphatic amine/epoxy resin system to 93.3 °C where we have full regression data.

From the recent correspondences with regard to this subject, I am assuming that the amendment within ISO14692 which allows our aliphatic resin system to design temperatures to 93.3 °C is no longer sufficient for your acceptance of our aliphatic amine/epoxy pipe. With that premise in mind, I would offer the following for your and SGS consideration:

6. We have found that prolonged exposure to water at temperatures up to 93 °C, that our aliphatic resin system does not exhibit a reduction in T_g, but actually experiences an increase in the measured T_g. This is a benefit of the aliphatic system over other resin systems, as the epoxy continues to exhibit a rise in T_g at relatively low temperatures where other resin systems do not. I have supplied evidence of this phenomenon previously for your and SGS review. (Pipe samples exposed to 93.3 °C water for over 1000 hours saturation, which did not exhibit a reduction in T_g but a measured increase).
7. Note that Aliphatic amine is the primary curing agent used by most manufacturers (regardless of the resin system used for the pipe manufacture) for adhesive bonded connections because of the relatively low temperature curing required.
8. If further qualification testing is deemed necessary, I would prefer to test all the way to 93 °C instead of stopping short at 85 °C which would again leave a grey area between accepted design temperatures and regression testing qualification temperatures. The cost of the testing should be equal at 85 or 93 °C, but will cover all possible design temperatures for this resin system at 93 °C.
9. We are willing to supply pipe samples for further testing with the agreement that we receive the proposed testing procedure and have an opportunity to review and comment prior to accomplishing the test.

With reference to a different resin system: Star (Fibre Glass Systems) manufactures GRE pipe/fittings at 7 different locations utilizing several processes and different resin systems including (Aliphatic Amine, Aromatic Amine, Anhydride, emitizol, and Cyclo-Aliphatic Amine). Each process is optimized for the resin system processed and the target selling market and cannot easily be modified to incorporate a different resin system (the resin systems are not interchangeable). For the High Pressure Oilfield market where moving salt water, sour crude and gas where H_2S and CO_2 is common place, we have found that our aliphatic amine cured epoxy is best suited (most economical) for this application and maintains a large share of the products supplied by us. The aliphatic amine/epoxy offers higher design stresses than the Aromatic or Anhydride cured epoxy at 93 °C, thus less wall thickness is required and a more economical pipe can be manufactured for this specific application. We will always continue to improve our manufacturing capability, but we see our aliphatic amine curing system remaining the dominant resin system for high-pressure oilfield applications for some time to come.

I look forward to your comments about how we proceed forward from here.

Best regards,

David Granderson

Appendix 5 Test results on pure resin provided by FGS

Date

27-4-2006 13:45

Experiment with 93.3°C water saturated Aliphatic amine cured epoxy samples to determine water loss during T_g measurement and if water is lost from saturated sample prior to 100 °C.

Equipment:

Perkin Elmer DSC-7 calibrated per our ISO 9001 procedures and manufacturers recommendations

Balance: Ohaus adventurer Pro w/ 0.0001 g capability, calibrated per our ISO 9001 procedures and manufacturers recommendations.

The purpose is to compare (2) nearly identical Aliphatic amine cured epoxy samples which have been soaked in water until saturation at 93 °C. Sample 1 to be weighed and have T_g measured, weighed again, T_g2 measured, etc, while monitoring changes in weight as well as changes in measured T_g upon successive runs. Sample 2 was to remain out of the water bath the entire time that sample 1 was being tested, while monitoring weight loss. Upon completion of testing sample 1, sample 2 would be subjected to the same thermal conditions as sample 1 was, but only up to 100 °C to monitor any water loss up to the point of interest. As long as our wet T_g's remain above the maximum design temperature (93.3 °C) this resin system will be acceptable. The idea was to see if there was any appreciable weight loss (water) in sample 2, when subjected to the same thermal cycle as sample 1 (but only up to 100 °C).

(2) DSC disks approximately 0.032" depth and 0.160" diameter, estimated to have at least 3.5% weight gain by water absorption, based on much larger thin epoxy samples being monitored for the last several days. Both samples 1 and 2 were removed from water bath at 1:45 pm.

Sample 1: Consecutive T_g's measured and weights measured

	Initial saturated weight - g	First Scan C T_g1	Second weight after T_g1 -g	2nd Scan C T_g2	3rd weight after T_g2 - g	3rd Scan C T_g3	4th weight after T_g3 - g	4th Scan C T_g4	5th weight after T_g4 - g
#1	0.0183	119.79	0.0180	114.95	0.0180	116.6	0.01800	119.76	0.01800

Sample 2 removed from bath at 13:45 along with sample 1, both surfaces patted dry with paper towel same as absorption samples previously. While sample 1 was having T_g's measured in the DSC-7, and weighed, Sample 2 stayed on dry towel and was re-weighed approximately every 2 minutes and recorded. Weight of Sample 2 remained at 0.0181g for the 54 minutes it was removed from the water bath. Lab temperature was 75 °F, with 36 % relative humidity.

As no weight was found lost in Sample 2 it was decided to place sample 2 in the DSC-7 with a heating program equal to the program used on sample 1, equal start temperatures, equal ramping rates, but only heated to 100 °C. Sample 2 was subjected to the early portion of the DSC program and heated to 100C at 20C/minute then immediately removed from the DSC and weighed again.

Sample 2: contant weighing at near SLT for 54 minutes, then subjected to DSC ramp and 100C, weight loss measured.				
	Initial saturated weight - g	Weight after 54 min -g	Weight after exposure to 100 °C	
#2	0.0181	0.0181	0.0181	No weight loss

Sample 1 then placed back into DSC and isotherm at 95°C for 6 hours, to determine if more moisture can be lost.
Sample 2 placed in desicant with intentions of re-weighing tomorrow.

Conclusion so far: Sample 1 during DSC T_g measurements looses about 1.6 % weight from saturation. 20 °C/min up to 160 °C.
Weight lost in first scan with no more lost on successive scans.
T_g of sample 1 is never found less than 115 °C.
Sample 2, does not loose any weight upon removal from bath for 1 hour and being subjected to same heat ramp as sample 1 up to 100 °C.
When sample 1 is ramped to 100 °C at the same rate as sample 1 was, there is no transition in the curve thus no glass transition below 100 °C.
FGS "wet" T_g's are in excess of 100 °C and should be allowed for operations up to the 93.3 C requested.

Appendix 6 Means to determine the glass transition temperature

Differential Scanning Calorimetry (DSC)
DSC is a technique in which the difference between the heat flux into a test specimen and a reference specimen is measured as a function of temperature and/or time while the specimens are subjected to a controlled temperature programme. There are two types of DSC instruments currently used; "heat flux" and "power compensation" instruments. Although they are fundamentally different in design, the data produced are comparable. DSC is a versatile thermal analysis technique and can be used to study properties such as melting and crystallisation behaviour, glass transition temperature, curing behaviour and specific heat capacity. ISO 11357-2 is relevant to the use of this technique.

Dynamic-Mechanical thermal Analysis (DMA)
DMA equipment applies a sinusoidal load to a sample and the resulting deformation is measured during a controlled temperature programme. The response of the sample is interpreted as the storage (elastic) modulus and loss (viscous) modulus. The ratio of loss and storage modulus, tan d, is also reported. The most common application of DMA is analysis of the glass transition. DMA is more sensitive to the glass transition than DSC. ISO 6721-1 is relevant to the use of this technique.

Thermo Mechanical Analysis (TMA)
TMA measures the change in dimensions of a specimen such as expansion or contraction as a function of temperature, time and force applied on a sample. The main application in the field of polymers is the determination of the coefficient of thermal expansion, the volume swell and the glass transition temperature. The methods are described in the ISO 11359-2:1999 standard.

ASTM 2092, Heat Distortion Temperature (HDT)
This test method describes the determination of the temperature at which the specific modulus of a test specimen is realized by deflection in three-point bending. This temperature is identified as the distortion temperature measured. The distortion temperature is that temperature at which a test specimen of defined geometry deforms to a level of strain under applied stress of 0.455 (Method A) and 1.82 MPa (Method B) (66 and 264 psi) equivalent to those used in Test Method D 648. The test may be performed over the range of temperature from ambient to 300 °C. For the maximum operating temperature limit of epoxies the criteria is set to the distortion temperature minus 20 °C. The distortion temperature is typically measured on small specimens by three point bending. Main limitation with this method is to obtain representative specimens for the actual GRE pipe. To overcome this limitation in this investigation the HDT was determine based on ring bending stiffness measurements according to ASTM D 2412 and/or ISO 53 769.

Bibliographic Information

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Customer Info

Name	:	Petroleum Development Oman LLC	
Address	:	Postal Address:	P.O. Box 81 Postal Code 113 Muscat Sultanate of Oman
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