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for enteral pump applications

Developments in SEBS
for medical and other valuable applications

Simulated service testing
of liquid silicone rubber based thermal insulation coatings

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Simulated service test: The way to predict the expectation of thermal insulation coatings based on liquid silicone rubber

by Roman Vanecek, Dow

Rising global energy demand is driving oil and gas producers to maximize existing assets and tap the potential of deeper, hotter and more remote reserves. Innovative flow assurance technologies are more critical than ever to help access these valuable resources from more extreme environments, safely and responsibly. Subsea production and tie-back systems must be able to handle higher material temperatures and pressures, as well as meet critical performance specifications for deep water equipment. Innovative technology for subsea systems is critical to avoid issues and failures caused by joint separation, cracking, degradation, hydrostatic crushing and/or improper application. Applicators are seeking resilient, convenient insulation for high pressure, high temperature (HPHT) environments with dependable processing and quality control for the expected two to three decades lifespan of oilfields. Operators now require effective thermal insulation to maintain flow above hydrate formation temperatures to reduce blockages.

Figure 1 - ETS pipe after removal from the SST pressure vessel

Table 1 - simulated service test conditions

Conditions of simulated service test				Analytical testing performed by
Temperature (°C)	Pressure (bar)	Duration (days)	Test facility	
180	300	90	Doosan	Dow
180	300	365	Doosan	Dow
115	300	11	SWRI	SWRI
135	300	11	SWRI	SWRI
150	300	365	Doosan	Element
160	300	11	SWRI	SWRI

While the oil and gas industry is moving "deeper," the challenges on wet thermal insulation material are increasing. The insulation system needs to withstand the combination of high hydrostatic pressure and extreme thermal gradient over 160°C or more, created by high fluid temperature in the core and cold seawater on the other side (refs. 1 and 2) of the structure. Wet subsea insulation materials, those exposed to a seawater environment, can be typically represented by polypropylene, epoxy/phenolic foams, polyurethane and rubber (ref. 3).

Silicone rubber has decades of field history in high temperature automotive uses, exterior glazing and fenestration, and other demanding applications, but is only recently being used for passive thermal insulation coatings on various subsea structures in oil and gas production. Due to its excellent thermal resistance, this material shows benefits specifically for high temperature/high pressure subsea environments. Silicone rubber used as thermal insulation is based on polydimethylsiloxane technology; "hybrid" material combining the benefits of inorganic characteristics with organic functionality. The Si-O bond strength is the basis of the high thermal resistance of the silicone rubber. Today, silicone insulating materials used on subsea structures are typically two-part systems applied in a cast-in-place process using dispensing systems mixing and pumping the material into pre-installed molds. Once mixed, the individual components start to react to build up a three-dimensional silicone network. After being cured to the desired hardness, the molds can be removed.

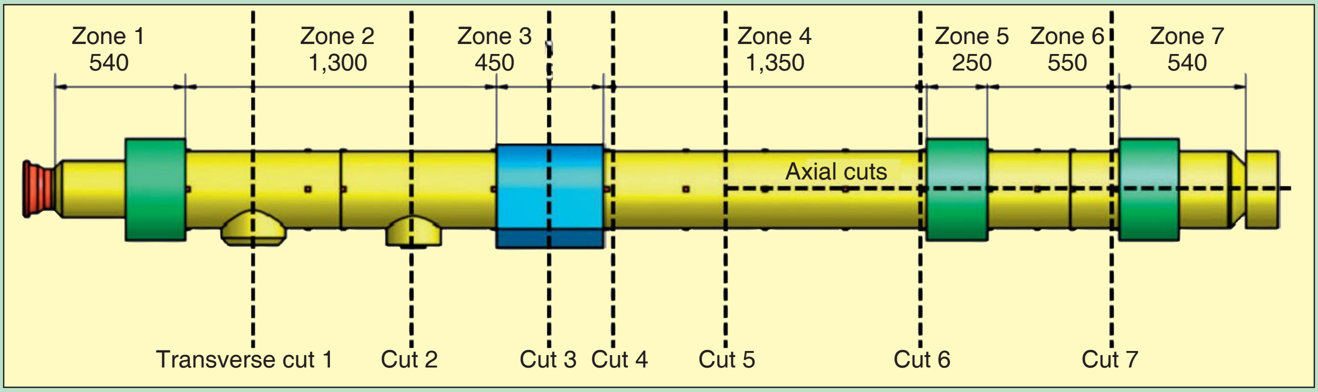
The combination of long term, small scale aging tests and short, full scale simulated service tests was traditionally used as the basis for wet insulation system qualification (ref. 4). The question is how to use such generated data to predict the lifetime expectations of the insulation (refs. 5 and 6). Specifically, for silicone rubber insulation, the information based on the small scale aging test can be contradictory to what is received testing the material aged in a full scale simulated service test. This discrepancy is even larger undergoing the long term (full year) simulated service test.

This study presents the findings obtained by evaluating DowSil XTI-1003 RTV silicone rubber insulation in multiple simulated service tests at different aging conditions and test durations. The comparison between unaged material and the SST aged one is shown. Test re-

Table 2 - test program with sample origin and cross-section insulation thickness location

	Zone					Radial location			Insulation thickness location		
Test piece	2	3	4	5	6	0°	120°	240°	Inner	Middle	Outer
Density	Y	-	Y	-	Y	-	-	-	-	Y	-
Thermal conductivity	Y	-	Y	-	Y	Y	Y	Y	Y	-	Y
Heat capacity	Y	-	Y	-	Y	Y	Y	Y	Y	-	Y
Durometer hardness	Y	-	Y	-	Y	-	-	-	-	Y	-
Compressive strength	Y	-	Y	-	Y	-	-	-	-	Y	-
Tensile strength/ tensile elongation	Y	-	Y	-	Y	Y	Y	Y	Y	-	Y
Tear strength	Y	-	Y	-	Y	Y	Y	Y	-	Y	-
FTIR	Y	Y	Y	Y	Y	-	-	-	-	-	-

Figure 2 - schematic picture of ETS pipe with corresponding locations of cuts during sectioning



sults are used to establish new methodology for lifetime prediction of silicone rubber insulation material. A comparison between small scale aging testing and system testing is also discussed.

Results and discussion

Simulated service tests and experimental test specimen

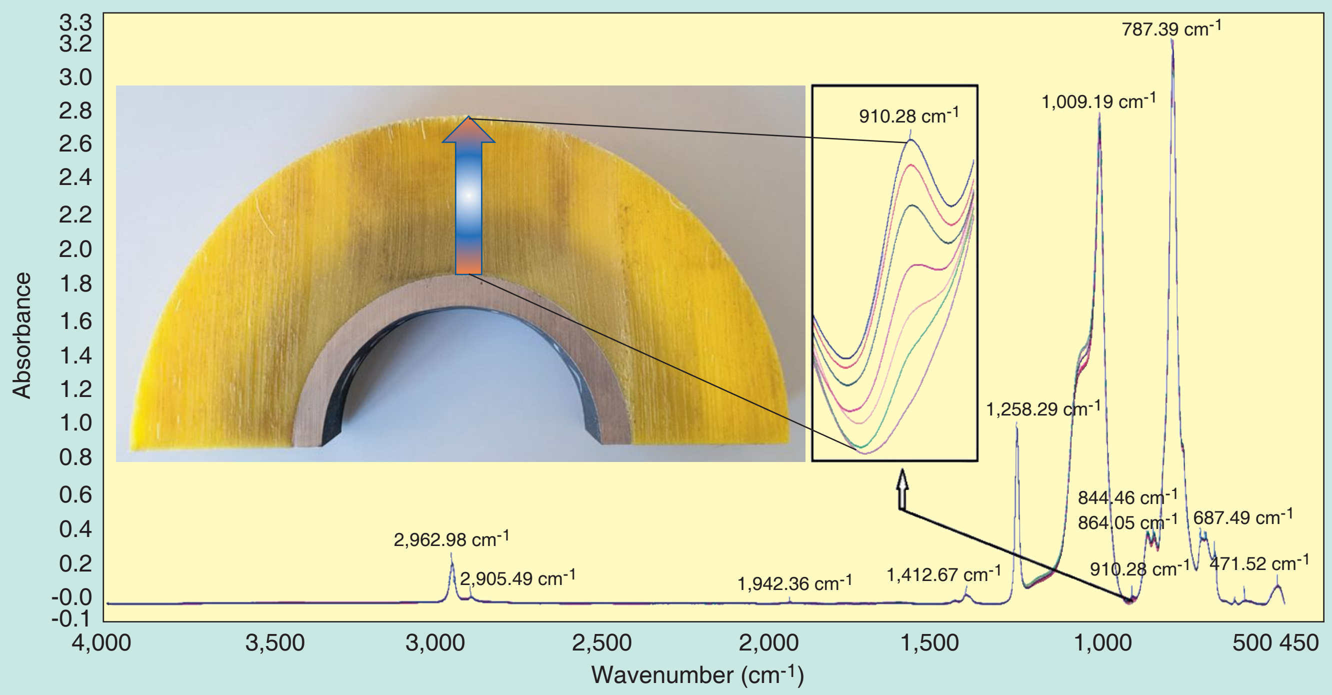
DowSil XTI-1003 RTV silicone rubber insulation was applied in three-inch thickness by various applicators on an industry defined equipment test specimen (ETS), and specific simulated service tests were conducted. The test piece was prepared in accordance with ISO 12734 Annex H. Table 1 shows an overview of selected insulation applicators and test condition details, as well as the analytical laboratory involved in post-mortal testing. Results are discussed in two steps. First, the impact on long term (three and 12 months) high temperature (180°C) SST aging on material characteristics is presented. Second, the impact of all the various SST aging conditions on insulation properties is summarized and compared with small scale test results generated during GP 65-08-01 Rev. 3 qualification of DowSil XTI-1003 RTV silicone rubber insulation performed by Element Material Technology, U.K.

For both 180°C SSTs, the insulation material was applied on an equipment test specimen by Lindberg and Lund in Norway, and exposed to aging conditions in large pressure vessels at Doosan Babcock, Scotland. The ETS specimen consisted of a representative insulated pipe with simulated equipment additions divided into seven distinct zones. The ETS included a representative straight section of pipe, two joints, a valve with two stems, nozzle, sensor, three flanges and a propagation damage stop. The test set-up consisted of a six meter long pressure vessel where the test specimen was installed. The annulus between the insulated pipe and the vessel was filled with water, which was pressurized to simulate the maximum depth of seawater in which the insulation would operate. Around the outer wall of the pressure vessel, there was a cooling jacket that maintained the water inside the vessel at a subsea water temperature of 4°C. In the pipe bore of the test specimen, a heating mandrel was installed which provided the required process temperature inside the pipe. The test specimen was open at one end and blank at the

Table 3 - summary of test results measured after three and 12 months of SST aging at 180°C compared with unaged reference

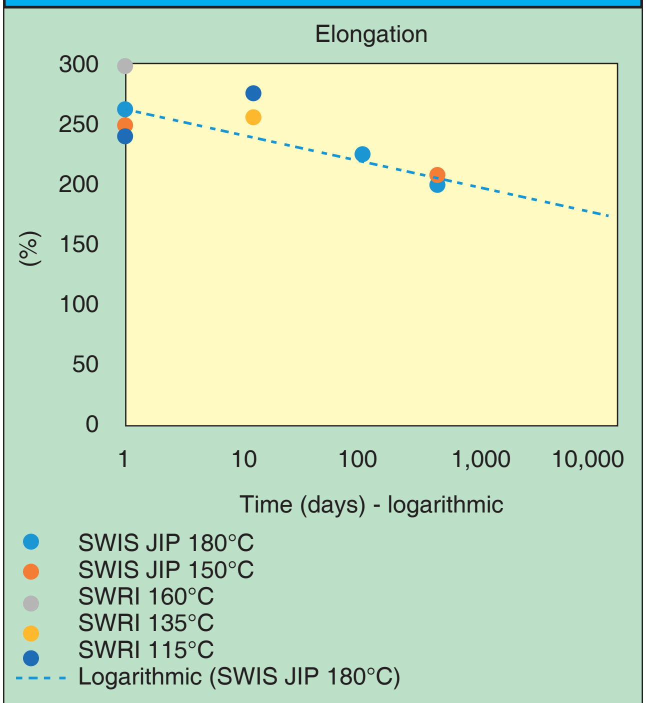
Test method	*Unaged reference*	*Zone*	*ETS 16 (3 month)*	*ETS 13 (12 month)*
Density (g/cm^3)	1.07	2	1.08	1.08
		4	1.08	1.08
		6	1.08	1.08
Hardness (durometer A)	45.3	2	51.5	54.6
		4	51.4	55.6
		6	51.5	55.5
Compressive strength at 50% strain (MPa)	3.5	2	4.29	5.62
		4	4.26	5.71
		6	4.09	5.34
Tear strength (N/mm)	18.1	2	18.8	18.8
		4	19.1	12.4
		6	19.5	14.5
Tensile strength (MPa)	4.8	2	6.2 - inner 5.7 - outer	6.7 - inner 6.9 - outer
		4	6.2 - inner 5.7 - outer	7.4 - inner 6.7 - outer
		6	6.2 - inner 5.7 - outer	7.5 - inner 6.7 - outer
Tensile elongation (%)	261	2	211 - inner 229 - outer	178 - inner 244 - outer
		4	203 - inner 244 - outer	185 - inner 202 - outer
		6	218 - inner 253 - outer	190 - inner 206 - outer
Heat capacity (J/gK) at 80°C	1.42	2	1.43	1.52
		4	1.42	1.52
		6	1.45	1.57
Thermal conductivity (W/mK)	0.186	2	0.189	0.189
		4	0.188	0.188
		6	0.186	0.189

Figure 3 - DowSil XTI-1003 silicone rubber insulation FTIR, absorption spectra of 90 days aged material performed across the insulation thickness



other end. The pipe bore was heated to 180°C before pressurizing the pressure vessel to 300 bar. The test conditions were held for a period of 90 and 365 days, respectively. Figure 1 shows the ETS pipe once removed from the pressure vessel after a 90-day aging test.

Figure 4 - summary of mechanical properties tested after various SST aging programs



Experimental test piece sectioning

Following aging testing, the ETS was sectioned by seven transverse cuts and several axial cuts (figure 2) using a water cooled and lubricated bandsaw. For later characterization, the aged samples from various zones were rough cut manually to a manageable size from which the sheets for different tests were sliced using the rotational meat slicer machine. Due to the high friction between the silicone rubber and the rotating slicer blade, soap water was used as lubricating media. To compare the unaged sample (cast as thin sheets) with aged material, the sample surface finishing should be as good as possible without any mechanical defects, cuts, metal debris, etc.

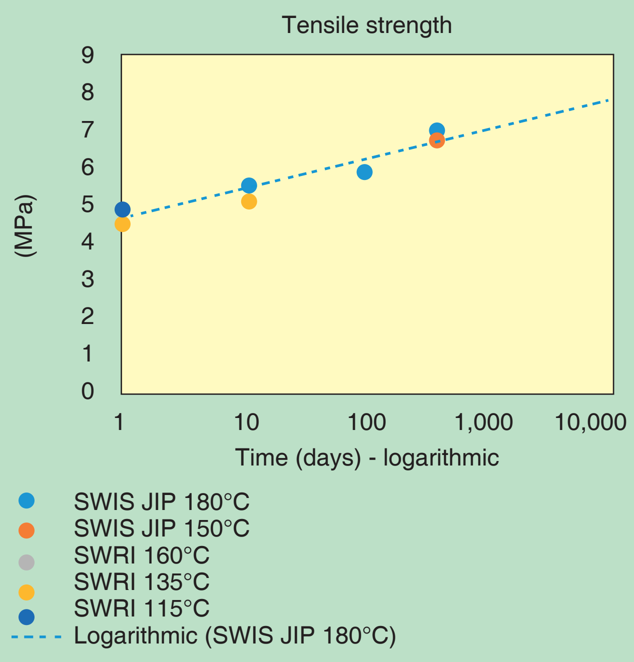
Characterization after SST aging

The proposed test program is summarized in table 2. Testing was conducted in accordance with specific standards which are those agreed to by the Subsea Wet Insulation System Joint Industry Project (SWIS JIP) for similar materials, and which can be used for comparative purposes. Post SST samples were taken from zones 2, 4 and 6 for each type of test. FTIR testing was done for all six zones. Test sample orientation and origin are indicated in table 2, as well.

SST aging at 180°C for three and 12 months

The results of 180°C SST testing for two different durations are summarized in table 3. There were few to no changes in density, heat capacity and thermal conductivity between aged versus unaged materials observed. Results of mechanical tests matched expectations and showed typical behavior (ref. 7) for room temperature curing liquid silicone rubber materials which had been exposed to elevated temperature (post-cure) conditions. Specifi-

Figure 5 - summary of mechanical properties tested after various SST aging programs



cally, durometer A hardness increased by approximately 10 points. Tensile strength showed an increase with a corresponding decrease in elongation at break. Compressive strength increased when compared to unaged material. As a result of higher thermal stress, the inner section showed slightly higher tensile and lower elongation at break values than the samples from the outer section of the insulation.

General trends show that, as thermal exposure increases, increased residual crosslinking occurs, resulting in higher crosslink density of the silicone rubber. The thermal performance of DowSil XTI-1003 RTV silicone rubber insulation remains unaffected by long term exposure under these conditions.

Fourier transform infrared spectroscopy (FTIR) analysis showed a typical pattern of silicone material. Minor differences in some additional peaks are related to unreacted Si-H detected in the unaged reference sample. Initially, unreacted Si-H has an impact on the post-curing effect happening over time. Some of the increase in mechanical properties is linked to this effect. CH3/CH2 groups are detected in some samples when aged. This is matching the expectations and is related to some minor rearrangements within the rubber network. The level of post-cure effect can be seen on intensity of the peak linked to Si-H, as shown in figure 3. In total, seven different samples were cut across the insulation thickness in different distances from the hot pipe core. The increasing intensity of the ~910 cm^{-1} peak corresponding to Si-H species can be observed. Obviously, samples taken closer to the hot pipe area show lower intensity of this specific peak. For the samples close to the cold water environment, higher peak intensity is typical.

Summary of multiple SST tests

Figures 4, 5 and 6 summarize tensile elongation, tensile strength and hardness of all simulated service tests performed on DowSil XTI-1003 RTV silicone rubber insulation at various test houses. A logarithmical trend line based on 180°C SSTs shows the expected progress up to more than 25 years of aging.

In various SST programs, it was shown that most of the change of initial particular mechanical properties is happening during the first couple months of exposure. An example of elon-

Figure 6 - summary of mechanical properties tested after various SST aging programs

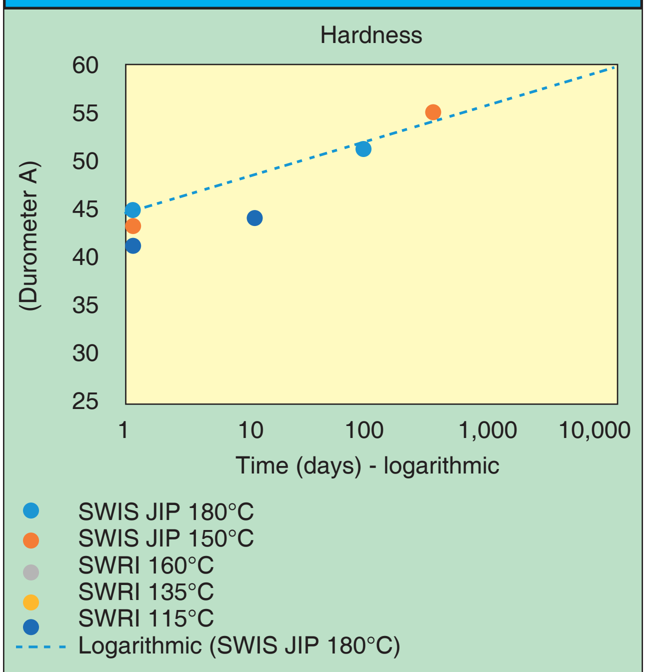


Figure 7 - elongation measurements performed on various SSTs

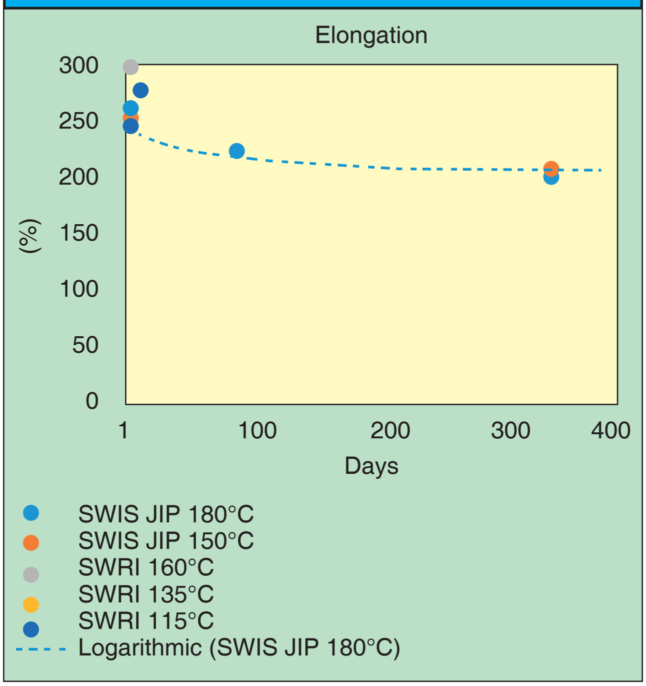


Figure 8 - comparison of full scale SST and small scale testing

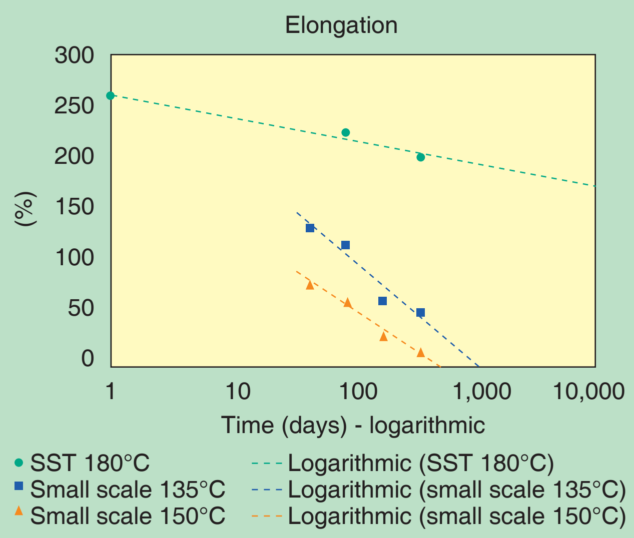
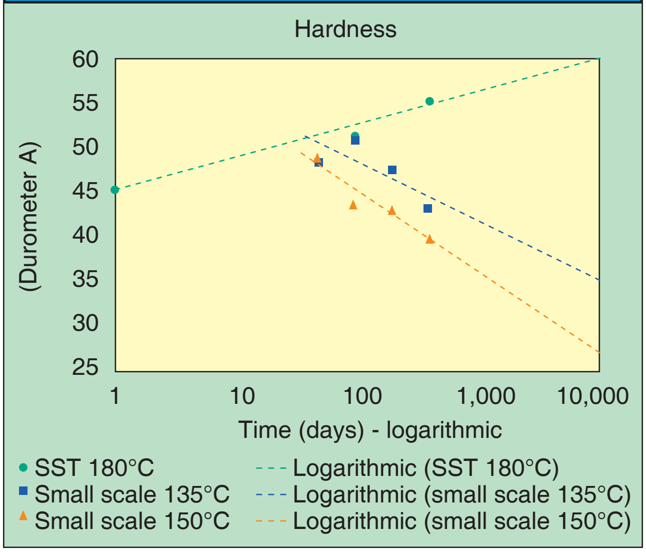


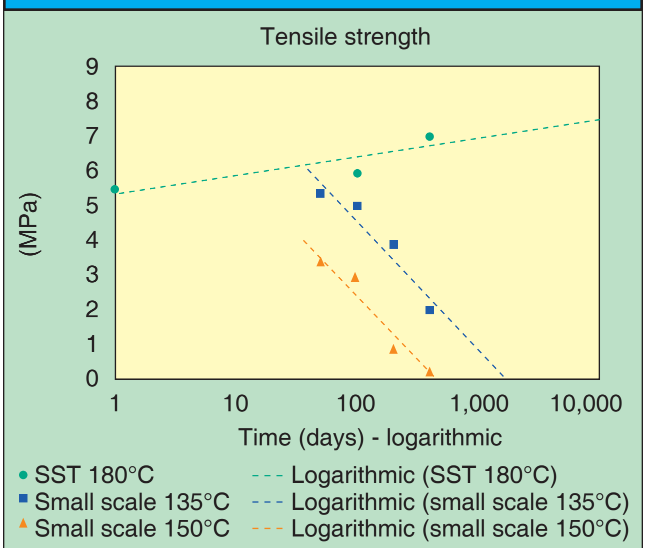
Figure 10 - comparison of full scale SST and small scale testing



gation for the SWIS JIP performed at 180°C is demonstrated in figure 7. Based on values presented in table 3, it can be calculated that the drop in elongation over the first three months (zero to three months, drop of elongation by 13.4% from initial value) of aging is approximately the same as the change during the next nine months (three to 12 months, drop of elongation by 11.1%).

This change is again an expected behavior related to *in situ* post-curing effects typical for room temperature curing silicone elastomers. During the post-cure exposure to elevated temperature, the crosslinking reaction drives the curing of material to a further state of completion. As a result of that, the material stabilizes its physical characteristics and exhibits the following changes: The hardness of the material will increase, compressive strength will increase, tensile strength will typically increase and the elongation will decrease.

Figure 9 - comparison of full scale SST and small scale testing



Comparison of full scale SSTs and small scale testing

Figures 8-10 summarize the results of mechanical tests performed on small scale samples (2 mm thick tensile dumbbells and hardness blocks) compared to observation based on 180°C SST tests (three and 12 months). The exposure of small scale samples in synthetic seawater at either 135°C or 150°C at 350 bar pressure was conducted for a period of 360 days, and included interim inspections after 45, 90 and 180 days in which a series of mechanical tests was conducted to quantify any aging of the material by the exposures.

The results generated on small scale samples and those which passed full simulated service tests can be seen as contradictory. Presented small scale results (figures 8-10) focus only on the changes happening after the *in situ* post cure of silicone rubber was complete. Small scale aging tests performed at 135°C and 150°C show a strong drop of elongation and tensile strength, as well as hardness over the year of aging. Based on this, silicone rubber would probably not be chosen as an insulation material for projects dealing with temperatures higher than ~120°C. Small scale aging delivers valuable information, e.g., for fast screening of different technologies, but does not simulate the real environment subsea structures are typically facing.

Comparing small scale observations with post-mortal tests performed on samples cut from the full scale SST aged at an even higher temperature (180°C), the mechanical properties show quite different behaviors. Even after more than 25 years of extrapolated aging, the elongation from SST samples is expected to be higher than 50% of the initial value. Tensile strength, as well as hardness, are even increasing. Silicone rubber post-curing in a full scale SST environment was, even after one year of aging, not yet fully concluded. This correlates quite well with the observations from the FTIR measurements (figure 3), where the outer sections of the insulation are still showing an increased level of Si-H species. SST is designed to simulate real conditions with high heat inside the system, surrounded with permanently cold water outside. Such created thermal gradient is significantly reducing, compared to small scale tests, the heat impact on the silicone rubber insulation.

Conclusions

Multiple simulated service tests using the DowSil XTI-1003 RTV silicone rubber insulation material were performed. Key findings of this study show that, even after a full year of 180°C/300 bar aging, the silicone rubber maintains its elastomeric behavior. The expected changes in mechanical properties are related to post-cure effects typical for room temperature curing silicone elastomers. Thermal performance of the silicone rubber remains unchanged. Comparing the SST system test results with the small scale tests, it becomes obvious how contradictory the obtained information can be. While the SST is best at reflecting the real subsea conditions, the generated test results on aged rubber can be used to predict the lifetime expectation on insulation systems.

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SEBS for medical applications

(continued from page 34)

New radial SEBS compounds having high vinyl content and combined with polypropylene are suitable to prepare medical stoppers with properties as good as other SEBS products available on the market.

Nonwovens containing SEBS show a much lower set and a higher recovered energy versus standard existing nonwovens.

The new SEBS nonwovens presented in this article exhibit excellent strength, elasticity and high elongation at break, and are also biaxial, exhibiting similar stretch values in machine and cross machine directions.

This article is based on a paper presented at the 196th Technical Meeting of the Rubber Division, ACS, October 2019.

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