

Compatibility of liquid and Solid Insulation Materials for High Voltage Subsea Connectors

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ABSTRACT

The main objective of this study is to identify reliable insulation materials and systems for novel AC and DC subsea power connectors for oil and gas exploitation. A combined solid-liquid insulation system might be radically altered if the materials are not compatible. Different combinations of relevant solid and liquid insulation materials were exposed to well defined and realistic subsea (and atmospheric) conditions, and potential material alterations were thoroughly examined with respect to ageing for up to three years. Mechanical and thermal properties have been characterized for poly(ether ether ketone) (PEEK), silicone rubber and epoxy aged in a synthetic ester. No profound effect of hydrostatic pressure was found, however the effect of increased humidity in the ester in combination with elevated temperature is dramatic for epoxy and silicon rubber.

Index Terms — subsea connectors, ester, silicone, epoxy, plastic insulation

1 INTRODUCTION

THE major challenge for subsea-only production is how to provide electrical power to the submerged installations. The future resources are farther from land, at greater depths and in colder and harsher environments, making maintenance and repair procedures even more critical. Subsea high-power connectors are considered as one of the most critical components in the offshore power delivery systems for subsea boosting and processing. In a pressure compensated component like a wet-mate connector, dielectric liquids will always be in contact with different polymer sealing and electrical insulation materials. Establishing competence on material compatibility for high voltage subsea components like capacitors, cable terminations and power transformers is therefore essential [1]. If oil is allowed to diffuse into a solid material, the result can be swelling (volume expansion), reduced mechanical strength, delamination of composite structures, and reduced electric breakdown strength. Chemical components in a solid material like plasticizers, hardening agents and stabilizers may desorb and diffuse into the liquid as dissolved additives and reduce the intrinsic breakdown strength of the oil. The compatibility of solids and liquids is usually graded on a compatibility scale [2].

The thermoplastic polymer poly(ether ether ketone) (PEEK), is a typical engineering polymer with excellent

mechanical strength, high chemical and biological stability, and superior anti-radiation and heat-resistant properties [3-5]. Although much research has been conducted on thermal decomposition of PEEK [6], long-term degradation mechanisms have scarcely been studied. The same can be said about thermoset polymer epoxy or silicone rubber subjected to insulating liquids, two other potential solid insulator materials. According to international test standards [7], compatibility tests are typically performed for 168 hours (1 week) under atmospheric pressure. This might not be satisfactory to screen materials for high voltage subsea connectors aiming for 25 years design life. In the literature, various compatibility tests between solid and liquid electrical insulation materials can be found using various techniques [8]. However, to the best of our knowledge, there are no available studies that investigate the effect of elevated hydrostatic pressure.

In the present paper the effect of long-terms ageing of PEEK, silicone rubber and an epoxy composite in contact with a synthetic ester is discussed based on subsequent material characterization. Ageing was performed at elevated temperatures, at atmospheric and elevated pressure (300 bar).

2 EXPERIMENTAL

2.1 PREPARATION OF THE MATERIALS

Three solid materials are tested for their compatibility with a synthetic ester: Poly(ether ether ketone) Vestakeep 3300G (PEEK), silicone rubber elastosil LR3003/60 (SiR) and epoxy (Araldite XB5950/XB5951).

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2.1.1 SETUP FOR AGEING UNDER ATMOSPHERIC CONDITIONS

The standard NORSOK M-710 [9] specifies that the solid to oil ratio during qualification of solid materials for permanent use subsea should be 1:25. This is therefore one of the chosen test conditions. In addition, for PEEK and silicone, a lower solid to oil ratio (1:2) was included to investigate how a small oil volume eventually can change the rate of degradation process of both the solid insulation and the oil itself. All the materials were aged at two temperatures.

PEEK was aged at 130 and 160 °C, respectively below and above the glass transition temperature of PEEK (measured to be 146.5 °C). Silicone is an amorphous material and was aged at the same temperatures. Epoxy was aged at 90 and 160 °C, respectively below and above its glass transition temperature (measured to be 122 °C). The effect of humidity in the oil was also investigated and all the solid materials were aged in a synthetic ester with two different initial relative humidity (% RH): 10% RH (dry) and 90% RH (humid) with 200 and 1900 ppm, respectively. Preparation of the synthetic ester (ester) with these two levels of controlled relative humidity was done as follows; the ester from the barrel was dried in a vacuum chamber for 48 hours at 90 °C leading to a relative humidity of approximately 10%. An aliquot of this oil was then humidified in a climate chamber for several days until a relative humidity of 90% was reached. Before ageing, all the bottles were flushed with nitrogen and the inside of the lid of the bottles was sealed with a lead gasket to prevent potential oxidation and water leakage. Reference samples of solid materials aged in nitrogen (without the ester) were prepared under the same conditions and in identical containers as described above. An example of a set of bottles containing PEEK before ageing is shown Figure 1.



Figure 1. Bottles used for ageing of PEEK with a solid to oil ratio 1:25.

Samples were removed for testing after 1, 2, 4, 12, 26 and 52 weeks, except for epoxy where the first outtake was done after 4 weeks.

2.1.2 SETUP FOR AGEING UNDER PRESSURE

Pressure vessels with a 1-liter volume were used for compatibility studies of PEEK and silicone rubber in the dry ester. The pressure was kept constant at ~300 bars and the temperature at 90 °C. Samples were removed for testing after 1, 3, 6, 12, 18, 24, 30 and 36 months.

2.2 INSTRUMENTATION

After each sampling point, the materials were characterized by tensile strength and differential scanning calorimetry to investigate their mechanical and thermal properties, respectively. The variation of humidity of the oil was determined by Karl Fischer titration.

2.2.1 TENSILE TESTING

Tensile testing of the solid materials was performed according to the standard D638-10 "Standard Test Method for Tensile Properties of Plastics" [10] and ISO 527-2:1993 "Plastics - Determination of tensile Properties – Part 2: Test conditions for moulding and extrusion plastics" [11].

Measurements were performed with a mechanical test bench from Lloyd (LR5K with Laserscan 200). The gauge length was marked by reflective tape and the strain measured by use of a laser. Five parallel tensile strength measurements were performed for each material at all ageing conditions. Dumbbell test specimens of the three materials were cut from 0.5 mm thick tape of material, with geometry as specified in the standard ISO 527-2 [11] as shown Figure 2. For practical reasons, the dog bones aged in a solid to oil ratio 1:2 were smaller than in 1:25.



Figure 2. Sample geometry for tensile strength experiments for the three-different studied materials epoxy, silicone and PEEK from top to bottom (solid to oil ratio 1:25).

2.2.2 DIFFERENTIAL SCANNING CALORIMETER

A Differential Scanning Calorimeter (DSC) from Mettler Toledo (HP DSC827e) was used to characterize the thermal properties of the materials. Characteristic temperatures which were investigated include the glass transition and melting temperature.

PEEK and silicone rubber were characterized by measurements in the interval 25 – 400 °C with a heating rate of 10 °C/min. Epoxy was characterized by measurements in the interval 25 – 200 °C with a heating rate of 10 °C/min.

The crystallinity of PEEK samples was estimated based on the area between a baseline curve, drawn from above the glass transition temperature to above the melting point, and the measured curve. The weight degree of crystallinity W_c is proportional to the melting enthalpy ΔH_m through the relation

$$W_c = \frac{100 \Delta H_m}{\Delta H_c} \quad (1)$$

where ΔH_c is the melting enthalpy of 100% crystalline material. For PEEK, $\Delta H_c = 130 \text{ J/g}$ [12].

2.2.3 HUMIDITY DETERMINATION

The variation in humidity of the oil as a function of time was measured using volumetric Karl-Fisher titration (Metrohm 737 KF Coulometer with a 703 Ti stand). 1 ml samples were used with three parallel measurements for each ageing condition.

2.2.4 SCANNING ELECTRON MICROSCOPY

The structure of aged epoxy samples was studied by scanning electron microscopy (SEM) using a Teneo V5TM SEM from Thermo Fisher Scientific. Prior to the measurement, the samples were coated with palladium using a sputter coater, Polaron collating unit E5100.

3 RESULTS AND DISCUSSION

3.1 ATMOSPHERIC PRESSURE

3.1.1 MECHANICAL PROPERTIES

3.1.1.1 PEEK

The measured stress at break of PEEK aged in the ester with a solid to oil ratio 1:2 is shown in Figure 3.

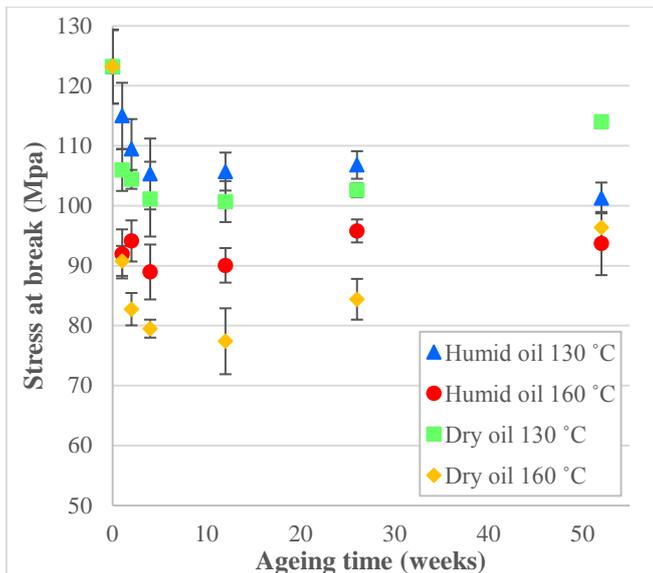


Figure 3. Stress at break measured for PEEK after ageing at 130 and 160 °C in humid and dry oil at atmospheric pressure for 1 year with a solid to oil ratio 1:2.

At all ageing conditions, one can observe a drastic reduction of the stress at break in the first weeks of ageing due to the high temperature, followed by a plateau and a weak increase the following months. The temperature seems to be the governing factor, as PEEK aged at 160 °C either in dry or

humid oil show a loss of ca. 40 % of its initial mechanical strength after a month while the samples aged at 130 °C lost 25 % of its mechanical strength. Elevated temperature will promote chain reorganization and accelerate degradation of the polymeric network, especially in the amorphous regions, leaving the material with reduced mechanical strength. The moderate increase of the stress at break towards the end of the ageing period might be explained by internal reorganization in the polymeric material, see also discussion in section 3.1.2.1 where the thermal properties of the PEEK is presented.

The plots of stress at break for PEEK aged in the ester with a solid to oil ratio 1:25 are shown in Figure 4 and follow the same trend as seen for the solid to oil ratio 1:2, except for a less pronounced increase towards the end of the ageing period. PEEK aged at 160 °C either in dry or humid oil lose 25 % of the mechanical strength after a month, while the loss for the material aged at 130 °C is 15 %.

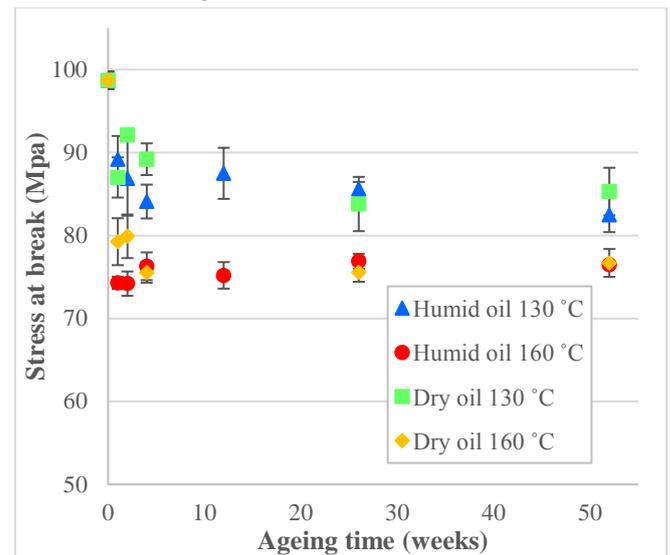


Figure 4. Stress at break measured for PEEK after ageing at 130 and 160 °C in humid and dry oil at atmospheric pressure for 1 year with a solid to oil ratio 1:25.

The differences in absolute stress at break values prior to ageing between the two different conditions is likely due to the difference in size for the dog bones aged solid to oil ratios 1:25 and 1:2.

Nevertheless, based on these results, one can conclude that the effect of ageing in the ester on the mechanical properties of PEEK occurs during the first month and does not vary significantly during the remaining of the ageing period studied here. Moreover, the difference between ageing in dry and humid oil is not considered significant. An observation that implies that hydrolysis is not a significant factor here, rather, partial solvatisation from absorption of oil causes attenuation of mechanical properties

3.1.1.2 Silicone rubber

Silicone rubber was aged in a dry and humid ester with a solid to oil ratio 1:25 at 160 °C and at atmospheric pressure. Ageing was initially scheduled to last for a year but was

terminated in dry and humid oil after 12 weeks because it was observed that the silicone rubber was almost completely dissolved, as can be seen Figure 5. The tensile strength measurements of the samples aged in the ester were partly impossible as the samples were already too degraded to be analyzed after four weeks of ageing. This could be explained by a hydrolysis phenomenon. Silicone is generally a very stable polymer; therefore, it is used in a wide variety of adverse environments such as high temperature or elevated electrical stress. However, a great deal of this stability derives from the fact that hydrolysis reactions which occur are reversible and the polymer essentially heals itself [13]. It is likely that such reversibility would not occur in the surface region where high concentrations of other components, such as water, can exist. In other words, silicone degrades when you have an external phase which acts both as degradation medium and transport medium.

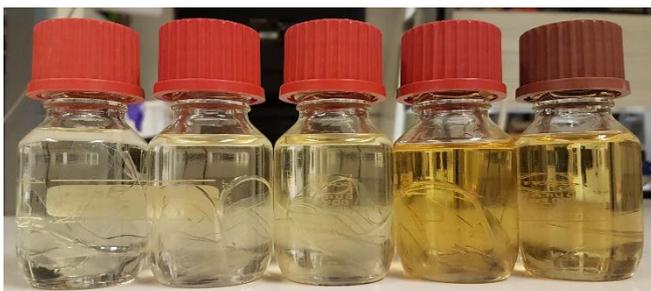


Figure 5. Silicone rubber in humid ester after, from left to right, 0, 1, 2, 4, 12 weeks of ageing at 160 °C. One can observe the progressive degradation of the silicone rubber as a function of time.

3.1.1.3 Epoxy

Tensile strength measurements of epoxy aged in the ester with a solid to oil ratio 1:25 are shown in Figure 6 showing stress at break.

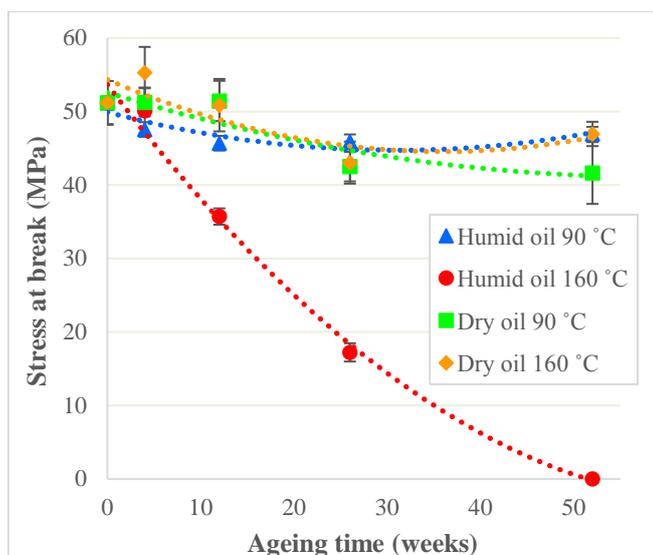


Figure 6. Stress at break measured for epoxy after ageing at 90 and 160 °C in humid and dry oil at atmospheric pressure for 1 year.

Contrary to what was observed with PEEK, most of the tensile strength loss did not occur within the first weeks but the material seems to constantly lose part of its tensile strength over time.

For all the samples aged at 90 °C in a dry or humid ester and for the samples aged in the dry ester at 160 °C, a small decrease in stress at break – ca 10 % - can be observed over the time frame of the experiment (one year). For the samples aged at 160 °C in humid oil, the results are completely different. One can observe a dramatic decrease of stress at break over time up to a point, after one year of ageing, where tensile strength measurements become impossible. A visual inspection of the sample aged for a year in humid oil at 160 °C shows that this sample is not dissolved like what was observed with silicone rubber, but has completely lost its rigid behavior, becoming soft and flexible.

The structure of epoxy aged in dry and humid ester at 160 °C for a year was studied with SEM, and some examples are shown in Figure 7.

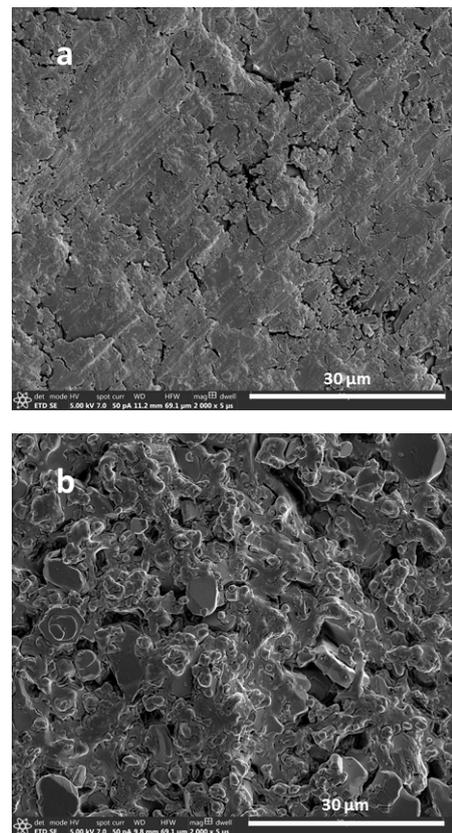


Figure 7. Scanning electron microscopy pictures of epoxy samples aged for one year at 160 °C in (a) dry and (b) humid ester.

Epoxy aged in dry ester has a quite regular structure, while ageing of epoxy in a humid ester has provoked a partial degradation or a rearrangement of the structure. This structural change seems to have caused a loss of mechanical strength and rigidity. Since the humidity level in the oil is the only factor that differs between the two samples, one can

easily conclude that, contrary to what we observed with PEEK, humidity clearly affected the structural properties of the material at high temperatures. The water in the oil will interact with and hydrolyze the material. Hydrolysis of the polymer network and fillers in the epoxy, will lead to a compromised chain structure and a higher free volume, hence the mechanical strength is severely diminished. See further discussion of this phenomenon in Section 3.1.2.2

3.1.2 THERMAL PROPERTIES

3.1.2.1 PEEK

In this section, results from ageing of PEEK in the ester, at 130 and 160 °C at atmospheric pressure are presented for both solid to oil ratios. The measured Tg of PEEK aged in humid and dry esters are shown in Figures 8 and 9, respectively. The original PEEK as delivered from the factory has a measured glass transition temperature (Tg) at 146.5 °C and an estimated crystalline content of 32.8%.

One can observe an increase of Tg after ageing at 130 °C for a solid to oil ratio 1:2 while the Tg onsets remain constant for the solids aged at 160 °C and at 130 °C with a solid to oil ratio 1:25. After ageing of PEEK in the dry ester with solid to oil ratios 1:2 and 1:25 at 130 and 160 °C, one can observe an increase of Tg after ageing at 130 °C and an opposite development after ageing at 160 °C.

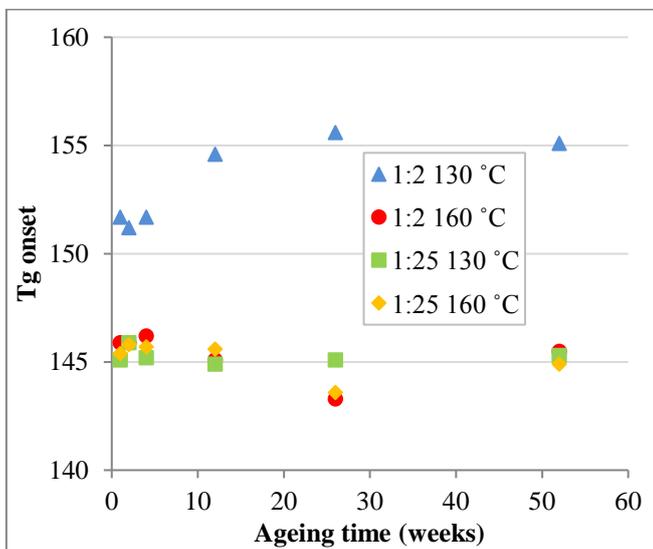


Figure 8. Tg onset measured for PEEK after ageing at 130 and 160 °C in humid oil at atmospheric pressure for 1 year.

PEEK is a semi-crystalline polymer composed both by crystalline and amorphous regions. This might indicate the existence of an intermediate phase between the two regions to facilitate the transition. This region may have a lower activation energy for movement than the bulk amorphous phase. Therefore, nucleation may occur below the measured glass transition temperature. If this happens the transition between the phases is not as smooth anymore, thus building

strain in the material and this might explain the reduced tensile properties and the increased Tg.

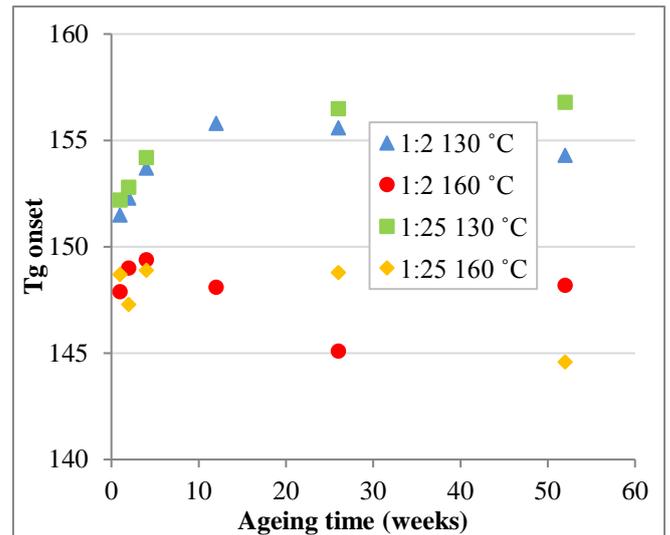


Figure 9. Tg onset measured for PEEK after ageing at 130 and 160 °C in dry oil at atmospheric pressure for 1 year.

At 160 °C the ageing temperature is higher than the glass transition temperature, and therefore movement in the bulk phase is expected, but also secondary crystallization. This might result in a more brittle material, hence reducing its mechanical strength as observed here.

3.1.2.2 Epoxy

The measured Tg of epoxy aged in dry and humid esters are shown in Figure 10.

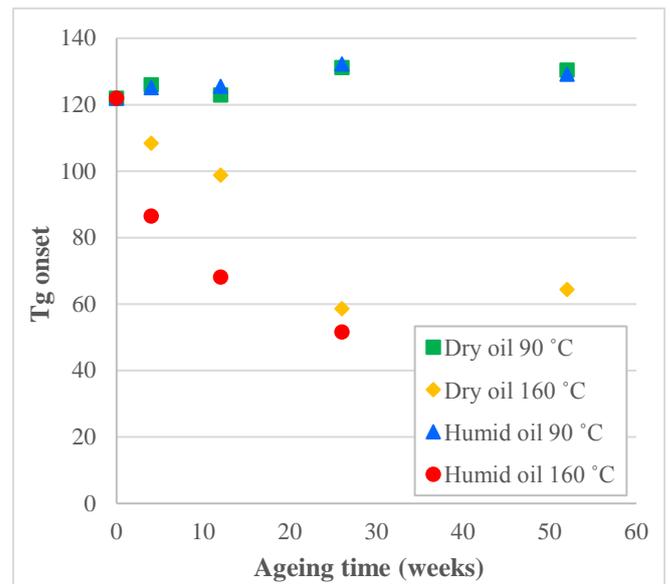


Figure 10. Tg onset measured for epoxy after ageing at 90 and 160 °C in humid and dry oil at atmospheric pressure for 1 year.

For unaged epoxy Tg was measured to be 122 °C. After ageing at 90 °C in both dry and humid esters, Tg of epoxy slightly increases with time. For a cross-linked material as

epoxy, it is likely that exposure to high temperature will increase the degree of cross-linking which also increases Tg [14], as observed here.

At 160 °C, for epoxy aged in both dry and humid esters, Tg decreased significantly after only 4 weeks of ageing. For epoxy in humid oil Tg continued to decrease until no observable glass transition was found after 52 weeks, and the material seemed to be totally amorphous. Long-term exposure of epoxy to water leads to both reversible (physical) and irreversible (chemical) degradation of the material [15]. Hydrolysis will lead to chain scission



where X and Y represent chemical groups in the epoxy main chain. Initially, when a water molecule causes chain scission between two crosslinked molecules, it will combine chemically to the polymer leading to an overall weight increase. This will be the predominant process for a relatively small amount of water diffusing into the polymer. This is most likely the cause for the observed decrease of Tg of epoxy aged in dry oil at 160 °C. However, for epoxy aged in humid conditions the probability of a crosslink polymeric chain being cut by hydrolysis in two places will increase. When this occurs, the central polymeric segment will become detached from the network and be free to diffuse out of the bulk material by leaching altering the material in an irreversible way.

3.2 ELEVATED PRESSURE

PEEK and silicone rubber were aged in a dry ester at 300 bar and 90 °C for three years. The measured stress at break is shown in Figures 11 and 12 for PEEK and silicone rubber, respectively.

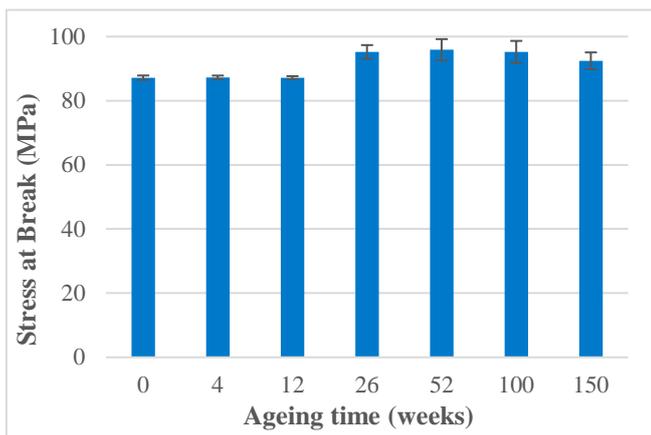


Figure 11. Stress at break measured for PEEK after ageing at 90 °C and 300 bars for 3 years.

The tensile strength of neither material is significantly affected by ageing at such a low temperature. The same trend was observed during aging of both materials in the ester at atmospheric pressure below their glass transition temperatures. As observed for the samples aged at atmospheric pressure (not shown), the mechanical properties

of both materials are not significantly affected by ageing at this low temperature. Elevated pressure does not modify the stress at break measured indicating no structural modifications of the materials. This is confirmed by DSC (not shown) where the heat flow curves showed no change compared to the original materials.

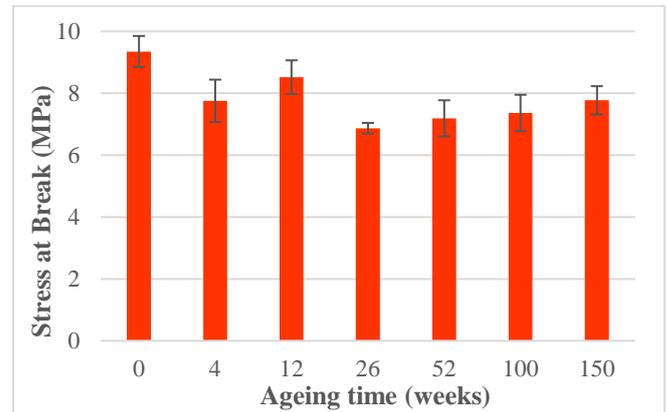


Figure 12. Stress at break measured for silicone rubber after ageing at 90 °C and 300 bars for 3 years.

4 CONCLUSION

Three different commercial available materials, PEEK, silicon rubber and epoxy have been aged in a synthetic ester under various conditions in order to test their chemical compatibility. The mechanical properties of PEEK were reduced while the morphology of the material was moderately altered, especially at 160 °C. All changes reached a plateau after approximately 10 weeks of ageing, indicating a stable system after initial degradation of the polymeric material mainly due to exposure to enhanced temperature. Ageing of silicone rubber in the ester at 160 °C led to a severe degradation of the material, especially in humid oil. This was explained by a hydrolysis phenomenon leading to an irreversible destruction of the material. Ageing of epoxy in the humid (90 % RH) ester at high temperatures substantially altered and weakened the material without leading to its complete destruction as observed with silicone. Nevertheless, hydrolysis is again the governing mechanism. The presence of water vapor is most likely responsible for the scission of the cross-linked polymer network, substantially weakening the material.

On the other hand, it was observed that hydrostatic pressure had little influence on ageing of PEEK and silicone rubber in the dry ester at 90 °C.

Based on the findings in this study, the importance of increased relative humidity in the liquid of a hybrid electrical insulation system for subsea application should be emphasized. Even though the results in this investigation is based on studies performed at quite high temperatures, it is likely that a solid/liquid-system that appear compatible under dry conditions at lower temperatures might be vulnerable if water makes its way into the system.

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