

A joint sealant study

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Joint sealants

- Joint sealants are defined here as polymeric based materials that are applied on a groove between two structures and adheres tightly these components to each other and prevents moisture or gases penetrating through the sealed area.
- Sealing solutions are integral part of each building. The components (e.g. concrete blocks, wall elements, glass structures etc.) of which buildings are constructed are often bonded or sealed to each other by joint sealants.
- Joint sealants are commonly used in various types of structures due to their ease of use, wide range of properties and applicability.
- Such joint sealants are widely applied in nuclear power plants but there is very little information available on their ageing and how to monitor their condition in these nuclear facilities.







Joint sealants

- In the classification of different type of joint sealants several approaches can be used. Joint sealants can be classified based on the material type, elasticity or form.
- Before 1950 traditional caulks based on either oleoresins (e.g. linseed oil), bitumen or tar were used in joints.
- By 1970's the industrially manufactured polymer-based materials had replaced the traditional caulks due to their improved material properties.
- Currently a broad range of different polymer-based materials are applied in joint sealants







Joint sealants

- Several polymer-based sealants available
- Slightly different properties and applications
 - Bonding to substrate
 - Temperature range (flexibility)
 - Resistance to moisture
 - Over painting

Sealant material	Application	General properties	Molecular structure
Acrylic	Wide range of building materials	Retains pliability, cannot be applied at low temperatures, good water resistance	www.cH₂-c─www.c=o
Silicone	Household use (kitchen and bathroom) and construction use (wood, stone, metal bricks)	Flexible, retains pliability, sticks to painted surface but cannot be overpainted	
Polybutene	Wide range of temperatures (e.g. road construction products)	Low cost, excellent durability and water resistance, good package stability and adhesion, will withstand cyclic joint movement, can stain adjacent surfaces and relatively poor recovery from extension	
Latex	Bathroom joints, cracks in plaster, tile, glass and plastic.	Easy to use, water resistant, not very flexible	$ \begin{bmatrix} c_{H_2} \\ d_{H'} \\ c = c_{CH_3} \end{bmatrix}_{n} $
Butyl	Wide range of building and dissimilar materials	Good water resistance, very durable, poor adhesion to painted surfaces	$ \begin{array}{c} CH_3 \\ \\ CH_2 \\ CH_3 \end{array} $
Polysulphide	Basements, glazing frames, ceiling joints, floors, roofs, external walls, cladding, retaining walls, water retaining structures, joints in bridges, roads and aerodomes	Good water and chemical resistance	-S-S- (polymer containing a chain of sulfide atoms
Polyisobutyle nes	Wide range of substrates	Durability, water resistance, may stain surfaces, poor recovery from extension	$\begin{bmatrix} CH_2 & CH_3 \\ I \\ CH_2 & C \\ I \\ CH_3 \end{bmatrix}_n$
Polyurethane	Wide range of building materials, wider and irregular cracks	Retains pliability, good water resistance, overpainting recommended on foam (susceptible to UV- light)	(R NH OR OUNT

- smaller dose rates
 - The effect of water on joint sealants can be thought to be due to moisture and humidity. Moisture can be defined as water or liquid containing traces of water being in contact with a surface while humidity is water vapor.
- It seems that the temperature would be the most significant stressor for joint sealants used inside of nuclear power plants.

Environmental stressors

- Weather related changes, such as exposure to rain, ultraviolet radiation from the Sun and temperature changes during the seasons, are more extreme in outdoor than indoor constructions \rightarrow also indoors, only less extreme
- T inside containments <50°C
- No heavy cycling of temperature is expected to be present during normal operation \rightarrow effect to the thermal expansion of structural elements \rightarrow absence of the cyclic mechanical loading of the sealants.











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Ageing mechanims

Oxidation

- Interaction with matter and formation of radicals R
- Oxygen reaction with radicals and formation of peroxy radicals ROO
- Abstraction of hydrogen from the surrounding molecules
- Formation of hydroperoxide ROOH and additional radicals R
- Decomposition of ROOH and formation non-radical species and radicals R
- Evaporation of plasticizers
 - Evaporation of plasticizers is due to plasticizer migration to the surface and evaporation
 - Complicated phenomena affected by material properties (both polymer and plasticizer), plasticizer concentration and external properties (temperature and atmosphere)
- Water absorption
 - Hygroscopic materials absorb moisture from the air or condensated from the surface
 - Water has an accelerating effect to the ageing due to increased mobility of molecules, decomposition of hydrolysable groups, reversible increase in plasticity and leaching of water-soluble ingredients



Proposed testing methods

Tensile test

- Elongation at break
- Requires sample removal and from a sealant joint, sample removal for a tensile specimen is in practice impossible due to the narrow dimensions of such joints
- · Using tensile test in condition monitoring of joint sealants would require surveillance samples.

Hardness

- Can be considered to be non-destructive if the indentation is not too severe
- Hardness has been shown to correlate well with elongation at break values
- The measurement is sensitive to few factors such as, temperature, clamping of the measurement device around the sealant, applied force and intender tip

Density

- · Ageing increases the amount of oxidation products in the polymer which tend to increase the density of the material
- The evaporation of volatile species from the polymer causes changes in weight, dimensions and density
- · The method requires sample removal but the sample amount is relatively small

Thermo gravimetric analysis

- In TGA the sample is heated in a pre-defined atmosphere and the weight of the remaining ash is measured
- Requires a small amount of sample
- The method is applied in analysing volatile compounds from coatings (ASTM D2369-20), it would be a potential method to be used in evaluation of joint sealants as well

Fourier transform infrared spectroscopy

- The oxidation products have characteristic wavelengths at which they absorb infrared radiation enabling thus identification of these products
- The method requires sample removal.

Dynamic mechanical analysis

- A sinusoidal stress is applied and the strain in the material is measured
- Assessment of material modulus and estimation of elastic modulus



Materials obtained from TVO outage

Outage of 2021

- Both OL1 and OL2 unit reactor buildings
- Two types of sealants
- Original installations
- Temperatures below 30°C
- Air atmosphere
- Dose rates none or very low
 - Max annual dose ca. 0.4 Gy → indicates low effect from radiation to ageing

Näytenumer	o Tiivisteen tiedot (kauppanim yms.)	i Käyttöikä	Käytön aikainen lämpötila °C (myös lämpötilan vaihtelut)	Annosnopeus	Otetun näytteen mitat
1.1	Thiotät	Alkuperäinen	25,8-		170
1.2	Sika?		25,8 -		140
1.3	Thiotät	Alkuperäinen	28,4-		-
1.4	Thiotät	Alkuperäinen	27,2-		-
1.5	Thiotät+Sika?		22,3-		-
1.6	Sika?	• · · · · · · · · · · · · · · · · · · ·	22,3-		-
1.7	Sika?		25,7 -		-
1.8	Sika?	• · · · · · · · · · · · · · · · · · · ·	25,7-		170
1.9	Thiotät	Alkuperäinen	25,6 -		170
1.10	Thiotät	Alkuperäinen	26,5 -		170
1.11	Thiotät	Alkuperäinen	26,5 -		150
1.12	Thiotät	Alkuperäinen	26,2 -		130
1.13	Thiotät	Alkuperäinen	26,5 -		-
1.14	Sika?		26,5 -		100
1.15	Sika? + Thiotät		26,5 -		300
2,1	Thiotät	Alkuperäinen	24,5 -		240
2,2	Sika?		24,5 -		220
2,3	Thiotät	Alkuperäinen	27,8-		93
2,4	Sika?		27,8-		130
2,5	Thiotät	Alkuperäinen	28,1-		100
2,6	Sika?		28,1-		130
2,7	Thiotät+ sika?		26,4 -		110
2,8	Thiotät	Alkuperäinen	26,4-		100
2,9	Thiotät	Alkuperäinen	27,5-		110
2,10	Thiotät	Alkuperäinen	27,5-		100
2,11	Thiotät	Alkuperäinen	27,9-		-
2,12	Thiotät	Alkuperäinen	27,9-		100
2,13	Thiotät	Alkuperäinen	27,8-		130
2,14	Thiotät	Alkuperäinen	27,8-		130
2,16	Sika?		27,1-		-
2,17	Thiotät	Alkuperäinen	- 0.0	250 mSv/h	100
2,18	Thiotät	Alkuperäinen	- 0.0	1250 mSv/h	120
2,19	Thiotät	Alkuperäinen	27,10.0	200 mSv/h	100
2,20	Thiotät	Alkuperäinen	27,10.0	1200 mSv/h	100
2,21	Thiotät	Alkuperäinen	28,10.0	1020 mSv/h	110
2,22	Thiotät	Alkuperäinen	28,10.0	1020 mSv/h	115
2.22	Thisse	All your and in an	00.50.0	500	



Materials testing summary

Test / Sample	TVO 1.5	TVO 1.6	TVO 1.9	TVO 2.1	TVO 2.2	Sikafle x	OKG
Tensile test		Х	Х	X		Х	
DMA	Х	Х	Х		Х	Х	Х
Hardness	Х	Х	Х	X	X	X	X

Sample preparation challenging!





Materials testing EaB vs. E

E seems to be a better ageing indicator





Materials testing DMA and E

- The elastic modulus is known to be a function of G and Poisson's ratio μ : $E = 2(1 + \mu)G \rightarrow \mu \approx 0.5 \rightarrow E \approx 3G$
- The obtained E values from DMA 2-4 times greater than values obtained from tensile tests



Sample	T/°C	G / Mpa	E / Mpa
1.5	20.1	0.4	1.2
1.6	19.4	0.81	2.43
1.9	20.4	2.32	6.96
2.2	20.4	2.36	7.08
Sikaflex	20.4	0.83	2.49
OKG	19.6	0.56	1.68

Materials testing hardness



- Based on the obtained results hardness result seems to be the most promising method to measure joint sealant condition
- Potential to be developed further for a non-destructive method for joint sealants
 - Further development for the Sikaflex sealant e.g. hand-held hardness durometer

Summary

- In modern constructions various types of polymer-based joint sealants are applied
- They are exposed to various environmental stressors of which temperature seems to be the most relevant one
- Ageing mechanisms that joint sealants are exposed in internal use include typically thermally induced oxidation, plasticizer evaporation and water absorption
- Various testing methods are available for joint sealants, but for practical reasons only hardness seems currently a suitable method to evaluate joint sealant condition non-destructively
 - Future work could include development of hardness measurement for newly installed Sikaflex sealant



beyond the obvious

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