Durability of elastomeric building sealants — results from a five year programme

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Abstract

An extensive and comprehensive multi-year durability study was undertaken in which a series of high-performance sealant products were artificially and naturally aged in an effort to determine test methods and test regimes most likely to simulate in-service conditions. Sixteen elastomeric products were evaluated of which fourteen were sealants based on either polysulphide, polyurethane or silicone compounds. The remaining products, an ethylene-propylene-diene-monomer and a polychloroprene, were used as a basis of comparison to the ageing effects on rubbery compounds subjected to both artificial and natural ageing. Both free-film and model joint compounds were tested. Artificial ageing was conducted using different weathering apparatus and consisted of various combinations of exposure to fluorescent or Xenon lamp Ultra violet radiation, simultaneous heat ageing at temperatures ranging from 60 to 140°C and, water condensation or spray. Natural ageing took place on a site located near the test laboratories and characterised by its temperate climate and industrial setting. The change in materials properties was characterised through mechanical tests (tensile strength and elongation at break), thermo-analytical methods and chemical spectroscopy including attenuated total reflectance and photo-acoustic Fourier transform infrared spectroscopy. Results from specimens aged artificially are compared with those aged from 5 years open air weathering in Leipzig. As well, results on model joints are compared with those obtained from testing free-films. These preliminary results strongly suggest that the research should continue such that a comprehensive assessment of different ageing regimes and their effects on various sealant products can be ascertained. This work would then provide a fundamental basis for developing useful and predictive assessment tests for sealant products currently in use.
Keywords: accelerated ageing, chemical spectroscopy, correlation, cyclic movement, elastomeric sealants, free films, joint models, natural weathering, thermo-analytical, time compression factor.

1 Introduction

There exist a number of problems associated with developing useful tests to assess the long-term performance of sealants. To adequately assess their long-term performance, a great deal of testing and time is required in relation to the actual time in-service. Typically, the long-term performance of sealant products is assessed on the basis of practical experience derived from field studies [8]. Field studies undertaken to the evaluate products tested in present study will be reported in a subsequent conference to be held in Berlin this June [2]. The present work focuses on the results of laboratory studies using artificial and natural ageing conditions as a basis for developing standard test methods. To yield useful and reproducible results, standard test methods require simplified test conditions, reduced testing periods and test conditions in which the number of factors causing ageing are minimised. An understanding of factors that influence the long-term testing of building sealants is critical to the development of suitable test methods

2 Experimental

2.1 Materials

The elastomeric sealants evaluated in this study are given in Table 1 below. The products are representative of the most widely used high-performance products, namely, silicone, polysulphide and polyurethane based sealants. In order to offer some comparison to the properties of other rubbery compounds used in building construction, the sealant products were compared to both polychloroprene an EPDM rubber compounds. The colour and curing system are provided for each of the 16 products tested. Two types of joint specimen were prepared: free-film specimens having dimensions of 900 mm x 80 mm x 2-3 mm, and model joint specimens conforming to ISO 8339 [10].

Table 1 — Material types, curing systems and colours

No.	Material type	Curing system	Colour
A5	Silicone rubber	1 part neutral cure, Oxime based	Grey
A6		1 part basic cure, Amine-Oxime based	Grey
A7		1 part neutral cure, Oxime based	White
A8		1 part neutral cure, Oxime based	White
A17		1 part neutral cure, Alkoxy-Titanium based	White
A18		1 part neutral cure, Benzamido-Titanium based	Grey
A19		1 part neutral cure, Benzamide based	White
A21		1 part acid cure, Acetate based	White
B9	Polysulphide rubber	2-part Manganese dioxide cure	Grey
B10		2-part Manganese dioxide cure	Grey
B12		2-part Manganese dioxide cure	Black
B22		2-part Lead dioxide cure	Grey
B28		Prefabricated	Grey
C23	Polyurethane	1-part	Grey
D24	Polychloroprene	vulcanised	Black
E25	EPDM rubber	vulcanised	Black

2.2 Test series

Six different series of tests samples were prepared such that the effects of weathering using different accelerated ageing techniques could be compared to that of natural ageing (Table 2). The majority of tests were conducted on free films; however, results of tests were compared to those obtained on model joints.

Table 2 — Description of test series and related apparatus for conducting ageing studies

Test series No.	Description	Apparatus
1	Fluorescent UV radiation and heat ageing at + 50°C	UVCON (Atlas); UVA 340 lamps
2	Xenon arc UV radiation and heat ageing at + 50°C	Suntest CPS (Heraeus); NXE 1500 lamps
3	Thermal ageing at different temperatures up to + 90°C	Heat ageing ovens
4	Test Series No. 1 combined with extension and compression of model joints	UVCON (Atlas); UVA 340 lamps
5	Natural weathering at an outdoor site in Leipzig	Nil
6	Control specimens stored in laboratory conditions (DIN 53386-A [4])	Nil

Details regarding the test conditions and specimen exposure regimes are given below for each of the test series.

2.2.1 Ageing using fluorescent UV radiation and heat

Free-film specimens were evaluated for changes in mechanical properties and variations in chemical structure after every 1000 hours exposure for up to a total 6000 hours exposure in the accelerated weathering apparatus given in Table 1 above. Four different cycles were used to assess variations in the ageing regimes, including:

i.) 8hrs UV at + 60°C; 4 hrs heat ageing at + 50°C
ii.) 8hrs UV at + 70°C; 4 hrs heat ageing at + 50°C
iii.) 8hrs UV at + 80°C; 4 hrs heat ageing at + 50°C
iv.) 8hrs UV at + 90°C; 4 hrs heat ageing at + 50°C

2.2.2 Ageing using Xenon-arc radiation, heat and water spray

Specimens were likewise subjected to exposure intervals of 1000 hours for up to 6000 hours of total exposure. Mechanical properties were determined and chemical analysis was performed on free-film specimens after each ageing interval. Over a 21-day period, the ageing cycle consisted of 3 consecutive cycles of:

- 3 days at + 80°C; 1 day of H_2O; 2 days at + 80°C; 1 day of H_2O.

2.2.3 Thermal ageing

Thermal ageing was conducted on free-film specimens over a 6000-hour period with ageing intervals of 1000 hours respectively. Two sets of heat ageing tests were carried out: the first subjected specimens to temperatures ranging from + 60°C to + 90°C over extended periods of time; the second set was used to subject specimens to heat ageing at higher temperatures (i.e., + 100°C, +110°C, +120°C, +140°C) but for shorter intervals (i.e., up to 3500 hours total exposure with intervals of 500 hours)

2.2.4 Artificial ageing combined with extension and compression

Model joints prepared in accordance with ISO 8339 [10] were subjected to artificial ageing conditions for periods of up to 6000 hours. Strains were applied (± 7.5% and ± 12.5% of joint width) to these joints (ISO 9047 [11]) prior to the start of each ageing interval of 1000 hours. The ageing regime consisted of:

- 8hrs UV at + 60°C; 4 hrs heat ageing at + 50°C
- 8hrs UV at + 70°C; 4 hrs heat ageing at + 50°C
- 8hrs UV at + 80°C; 4 hrs heat ageing at + 50°C

During the ageing process, strains were altered from the extended state to the compressed state every two weeks.

2.2.5 Natural ageing

Free-film and model joint compounds (ISO 8339 [10]) were exposed to natural ageing at an outdoor test site located in Leipzig, that has a temperature climate and local conditions suggest and industrial setting. This ageing regime started in January 1993. The model joint compounds were also subjected to two strain levels: ± 7.5% and ± 12.5% of joint width. Changes in extension and compression were made at the same intervals as was previously given above in 2.2.4.

2.3 Test methods

2.3.1 Mechanical tests

Prior to testing, all samples were stored in standard conditions of 23°C and 50% RH in accordance with DIN 50014 [3]. Following this, three strips were cut from specimens of 45-mm length and tested in tension according to both DIN 53504 [5] and ISO 33 [9] respectively. Both tensile strength and elongation at break were recorded for each of the specimens. Tensile tests on thin strips potentially eliminate the effect of substrate since for the majority of sealant products this does not have a negative effect [1].

Tensile tests on model joint compounds was carried out using ISO 8339 [10] and provided information regarding the tensile strength and elongation at break and the tensile modulus.

2.3.2 Physical-chemical tests

The glass transition temperature of weathered samples was determined using a dynamic differential scanning calorimeter (DSC), model DSC 200 (Netzsch Geraeteban). Chemical changes at the surface of the weathered samples were examined using attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy (IMPACT 400, Nicolet). As well, photo acoustic (PAS) FTIR spectroscopy was used to examine the surface of samples that had a severely degraded surface since this technique readily lends itself to chemical analysis in instances where surfaces are sufficiently deteriorated as to render the ATR method useless. For the PAS technique, a MTEC model 300 photoacoustic cell was used to collect the requisite data.

3 Results

The results from these ageing tests indicated that almost all of the materials survived artificial ageing at temperatures between + 60 and + 120°C. Specific results of tensile testing of artificially and naturally aged free-film specimens is provided in the first two parts of this section and results regarding model joints are discussed in subsequent parts. No detailed description of the results obtained from the chemical analysis is provided in this paper although a summary statement is given in the final part of this section.

3.1 Tensile tests on free-films

3.1.1 Artificial ageing

Based on the results obtained from these tests, the 16 products evaluated in this study can be classified in essentially three (3) different materials "types", corresponding to their response to artificial ageing and related physical characteristics. These are:

i.) Type 1 materials have elongation at break (ε_r) that change as a function of temperature in accordance with the Arrhenius equation whilst not having any evident nor significant effect on the strength at break. An example of a Type 1 material is provided in Figures 1-4 that depict changes in properties of product B28. Type 1 materials include products: B9, B10, B22, B28, C23, D24 and E25

ii.) Materials characteristic of Type 2 suggest that the tensile strength at break (σ_r) follow the Arrhenius relationship whereas the strain at break is not coupled to changes in temperature. An example of this relationship is given in Figures 5-8 showing changes in σ_r over different exposure times for product A17. Materials in this category include products A17 and B12.

iii.) Type 3 materials are characterised by little or no aged-induced changes in a given ageing regime. Essentially, the materials are only slightly or completely insensitive to the effects of heat, UV and water in the exposure regimes and over the time intervals over which they were tested. This is evident in instances where the ageing effects act alone or indeed where the ageing period was prolonged from 6000 hours to 12000 hours. Representative of this material type is product A19, whose results are provided in Figures 9-12 respectively. Materials of this type include products: A5, A6, A7, A8, A18, A19 and A21.

3.1.2 Comparison of artificial ageing and natural weathering

At this stage, data for specimens exposed to natural weathering over a 5 year period is available for the 16 products evaluated. An important result from these tests

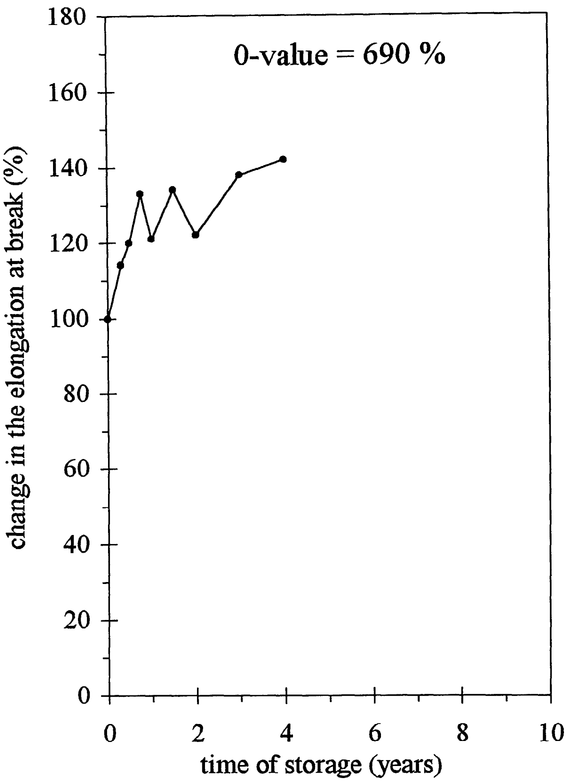

Fig. 1: Material B 28 - natural weathering

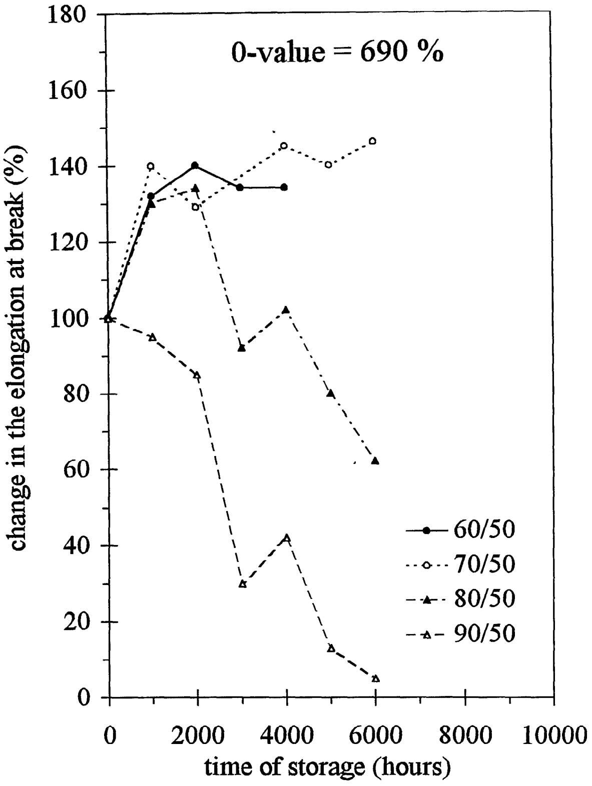

Fig. 2: Material B 28 - accelerated ageing UVCON

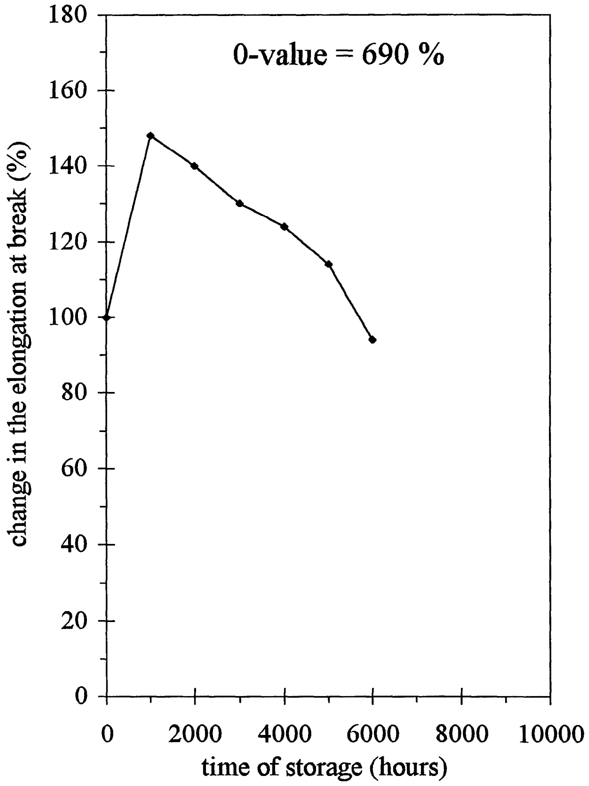

Fig. 3: Material B 28 - accelerated ageing SUNTEST

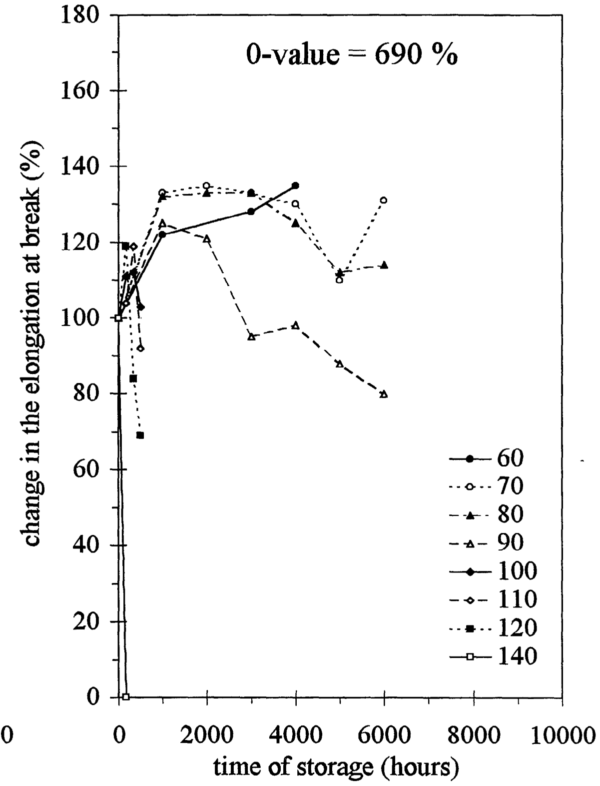

Fig. 4: Material B 28 - accelerated ageing OVEN

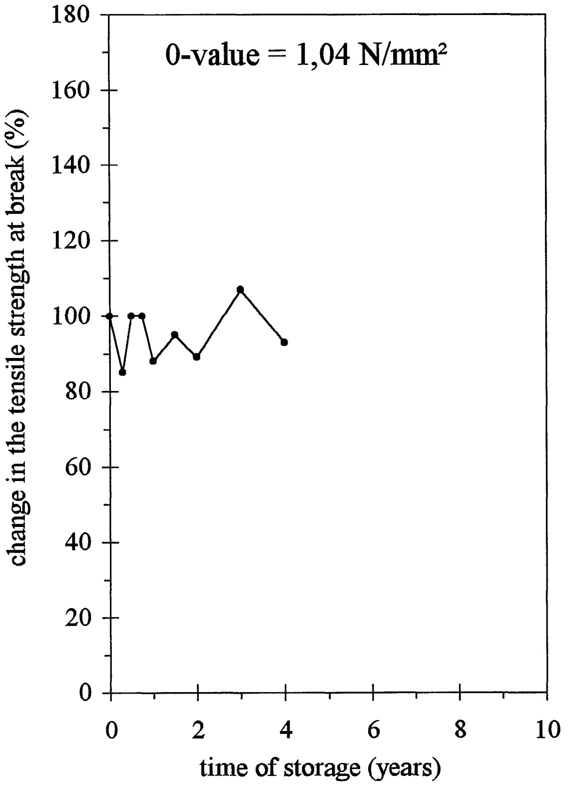

Fig. 5: Material A 17 - natural weathering

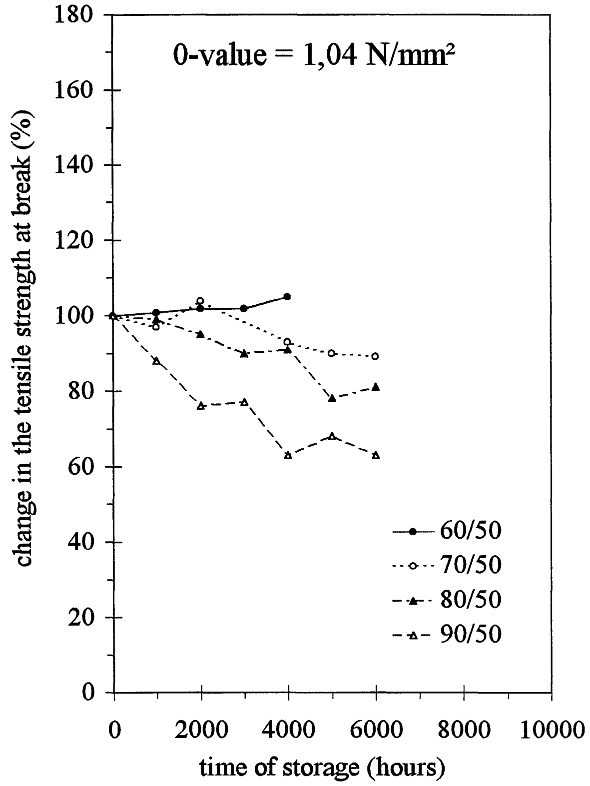

Fig. 6: Material A 17 - accelerated ageing UVCON

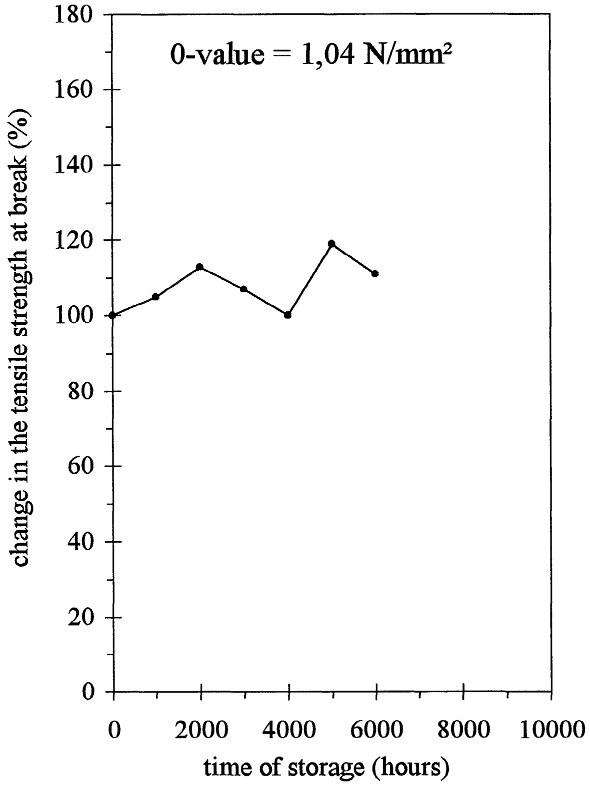

Fig. 7: Material A 17 - accelerated ageing SUNTEST

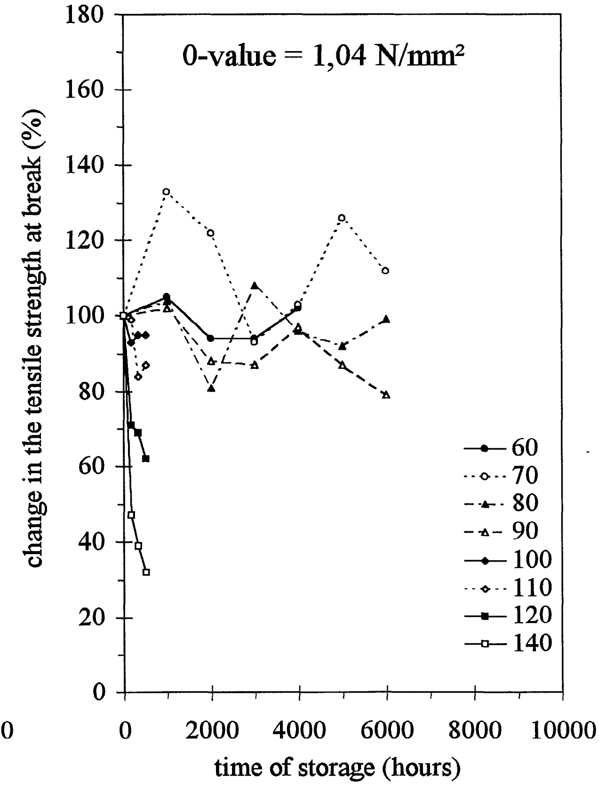

Fig. 8: Material A 17 - accelerated ageing OVEN

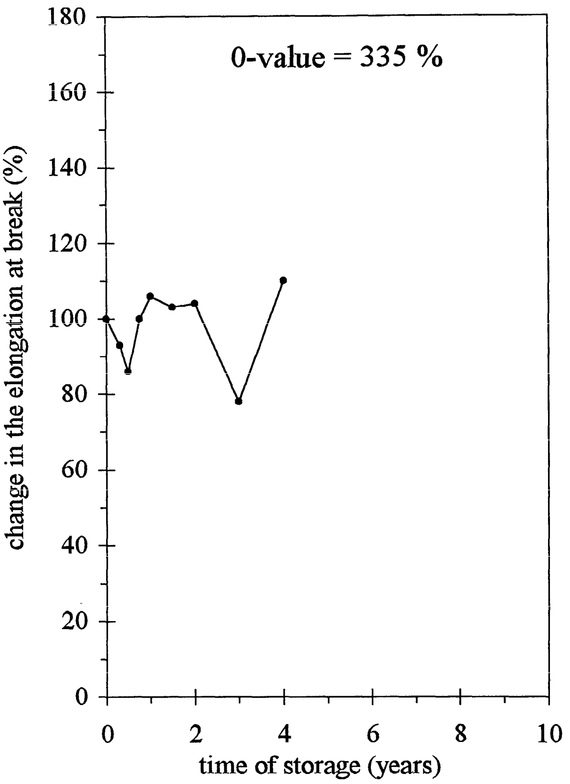

Fig. 9: Material A 19 - natural weathering

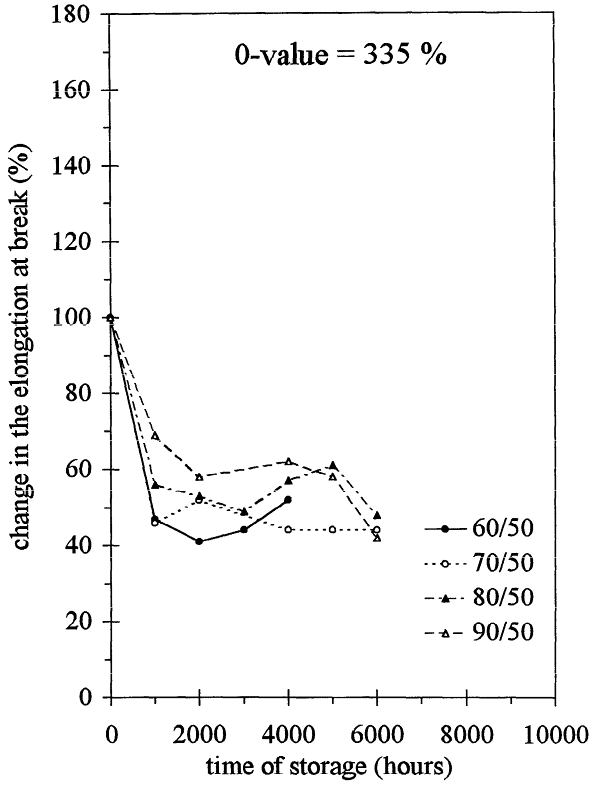

Fig. 10 Material A 19 - accelerated ageing UVCON

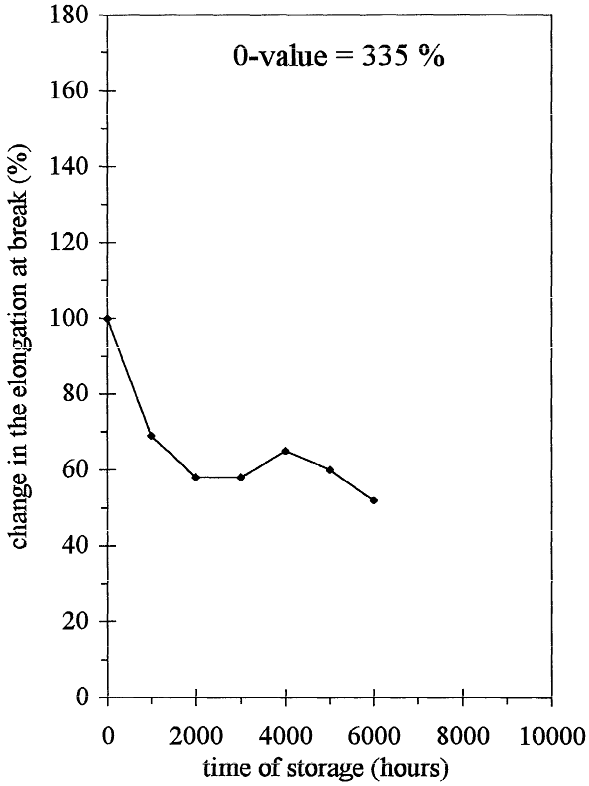

Fig. 11: Material A 19 - accelerated ageing SUNTEST

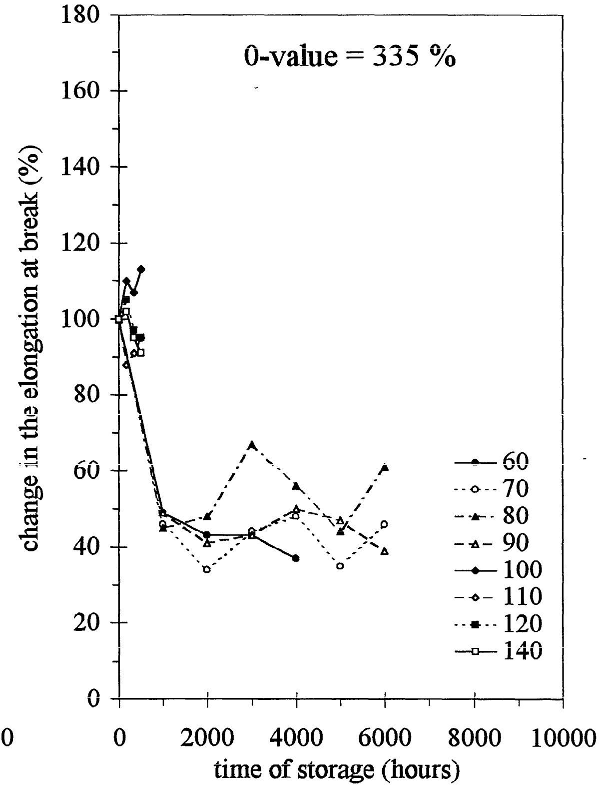

Fig. 12: Material A 19 - accelerated ageing OVEN

showed that post-curing can take place over one year in certain materials and actual ageing appears to only take place thereafter.

For civil engineering applications in-service temperature for sealants are not expected to exceed 70°C and typically, higher test temperature are likewise not used. Assuming results between natural ageing over 4 years and artificial ageing over 36 weeks (6000 hours) correlate reasonable well, one can then postulate that there exists a time-compression factor of 1:6 (32 weeks: 4 x 52 weeks). The current results indicate that virtually all sealants can be tested to temperatures of at least 90°C without adverse effects. Assuming that this can be extended to higher temperatures as wee, time-compression factors for different test temperatures can be calculated from the Arrhenius equation as provided in Table 3 below.

Table 3 — Estimated time-compression factors at given temperatures

Test temperature °C	Time-compression factor
70	1:6
80	1:12
90	1:24
100	1:48
110	1:96
120	1:192

It is to be noted that each 10°C increase in test temperature doubles the time-compression factor. The implications regarding this proposal suggest that considerable savings in time and costs can accrue provided the applicability of test temperatures in excess of 70°C can be substantiated by additional work. Based on these promising initial results, the current test series is being extended. As well, the degree of correlation declines only slightly with increases in test temperature within the range of temperatures examined in this study.

3.2 Tests on model joints in comparison to free-films

Model joints were tested on 10 of the 16 products evaluated in this study. Changes in tensile strength and elongation at break for specimens exposed to 4 years natural weathering were similar to results obtained from free-films with the exception of material A5. In this case, results obtained for the elongation at break from the free-film specimen did not correspond to that of the model joint compound; it is not possible at this time to offer an explanation for this occurrence. In the case of materials A5, A6, A7, A8 and C23, it was possible to obtain values for both the tensile strength and elongation at break whereas for the remaining materials, adhesion was lost prior to being obtaining useful results.

Model joints subjected to artificial ageing series No. 1 provided similar results to those aged in natural conditions based on results of tensile tests on products A5 and A6. It must also be noted that post-curing occurs more slowly in model joints as compared to free-films and as well, the effect of UV radiation is less pronounced in model joint specimens. Ultra violet radiation essentially produces only surface effects. Results for values of modulus at 50 and 100% extension did not provide as clear an indication of changes in performance as was evident for either the tensile strength or elongation at break and hence, these values have not been reported here.

3.3 Comparison of Ageing with movement cycles

The results of this section as based on three products namely, A5, A6 and C23. Products A5 and A6 were chosen as being representative because they were found to be particularly resistant to artificial ageing, as was seen in previous test results. As well, all these products preferentially had excellent adhesion to the concrete substrate and consequently failed in cohesion. Product C23 is the weakest material despite its' excellent adhesion to concrete.

The remaining tests have not yet been completed however the status of the various test series is provided below in Table 4.

Table 4 — Description and status of Natural and Artificial weathering test series for elastomeric sealant products

Series description	Status
NW[1] with and without extension of +25%[†]	5 years natural exposure
NW with 1 extension/compression cycle /yr.: 6 months at +12% (winter); 6 months at -12% (summer)	1 year natural exposure
NW with 6 extension/compression cycles /yr.: 1 month at +12%; 1 month at –12%	1 year natural exposure
AW[2] using UV CON at 80°C /50°C and extension/compression cycling, alternating every 1000 hrs between +12.5% (at –20 °C) and –12.5% (at 80°C)	Complete after 6000 hours exposure
AW using UV CON at 70°C /50°C with extension/compression cycling, alternating every 2 wk. between +12.5% (at –20 °C) and –12.5% (at 70°C)	Complete after 6000 hours exposure
AW using UV CON at 60°C /50°C with extension/compression cycling, alternating every 2 wk. between +12.5% (at –20 °C) and –12.5% (at 60°C)	4000 (of 6000) hours completed

1. NW – Natural weathering
2. AW – Artificial weathering

[†] + Indicates extension and - compression

Preliminary results from this test series suggest that continuos extension alone has only a very slight effect whilst artificial ageing with simultaneous extension-compression cycling has a significant negative effect. Work in the area of artificial ageing should continue with emphasis on separate extension-compression cycles having lesser effects than those previously undertaken. It is likely that these would more closely resemble in-service conditions.

3.4 Physical-chemical test methods

Based on results obtained to date, the use of DSC appears to be the most suitable method for investigating changes in glass transition temperature (T_g) for elastomeric sealants. In many instances, a loose correlation between mechanical properties and T_g has been observed.

With respect to the use of ATR-FTIR, it has been observed that this method does not provide useful results since it requires a near perfect contact between the ATR crystal and the surface of the sealant sample. This condition very often is not met because the surface of the degraded polymer is comparatively rough and uneven in relation to the un-degraded specimen. On the other hand, PAS is the technique of choice for sealant materials since surface roughness is not important in this technique and changes in chemical spectrum can readily be obtained using this method.

4 Proposal for standard test methods

4.1 Free-film and model joints

Free-film specimens should be used where adhesion to the substrate is not critical to evaluating the product. Specifically, this applies to those materials that are used as a jointing tape or 'Band-Aid' jointing product. Where previous trials have shown that the sealant adhesion to the substrate is likely to remain, or indeed, increase over the long-term, then the use of free-film testing is considered adequate. In all other cases, tests on model joints are preferred.

4.2 Thermal or combined ageing

Thermal ageing alone is suitable for those elastomeric sealants that have at least some sensitivity to UV radiation. Of the 16 materials evaluated in this study, the products that could be tested in this fashion include A5, A6, A7, A8, A19, A21, D24 and E25. The simplicity of thermal; ageing lends itself very well to accelerated ageing, e.g., it is possible to test these products at 120°C as opposed to the typical test temperature of 70°C. Testing at 120°C would provide a time-compression factor of 1:192 and this would permit estimating the effects of ageing over 11 years with a test conducted in 500 hours (3 weeks). The results could potentially be extrapolated to 22 years.

Combined ageing should be used for all products that have a certain higher degree of UV sensitivity. These materials include A17, A18, B9, B10, B12, B22, B28 and C23. The time-compression factor is 1:24 for tests conducted at 90°C and this implies a test time of 3000 hours (18 weeks) that would simulate ageing over about 8 years. Other possible suggestions include conducting the test over 500 hours (3 weeks) such that 2.5 years of ageing is simulated.

5 Conclusions

Considerable work has been undertaken to artificially and natural age a series of high-performance sealant products in an effort to determine test methods and test regimes most likely to simulate in-service conditions. This substantial set of result remains to be fully reviewed, however, in this report the following is apparent:

- Post-curing can take place over one year in certain materials and actual ageing appears to only take place thereafter.
- Virtually all sealants can be tested to temperatures of at least 90°C without adverse effects.

- Changes in tensile strength and elongation at break for specimens exposed to 4 years natural weathering were similar to results obtained from free-films (with the exception of 1 of 8 silicone-based materials).
- Continuous extension alone has only a very slight effect whilst artificial ageing with simultaneous extension-compression cycling has a significant and negative effect on performance indicators.
- The use of DSC appears to be the most suitable method for investigating changes in glass transition temperature (T_g) for elastomeric sealants.
- Photoacoustic FTIR spectroscopy is the technique of choice for sealant materials since surface roughness is not important in this technique and changes in chemical spectrum can readily be obtained using this method.

The research should continue such that a comprehensive assessment of different ageing regimes and their effects on various sealant products can be ascertained. This work would then provide a fundamental basis for developing useful and predictive assessment tests for sealant products currently in use.

6 References

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