
Accelerated ageing of polyurethanes for marine applications

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Abstract:

Polyurethanes are frequently used in underwater applications. They are required to resist the marine environment over long periods of immersion but the multiplicity of resin formulations makes material selection difficult. Accelerated tests are essential to guarantee long term integrity. This paper presents results from an experimental study in which polyurethane samples of two hardnesses, 40 and 90 Shore A, have been subjected to immersion in artificial sea water for periods up to two years at temperatures from 50 to 100 °C. In parallel samples have been immersed at sea in the Brest Estuary for up to five years. Mechanical properties have been measured on tensile specimens after ageing. The accelerated test results and FTIR analysis indicate that hydrolysis can occur. However, an estimation based on a linear Arrhenius extrapolation indicates that the timescale for 50% property loss at sea temperatures is in excess of 100 years. The results from sea ageing confirm that these materials retain 100% of their initial tensile properties after five years of immersion.

Keywords: Polyurethane; Marine; Ageing; Sea water; Accelerated test

Introduction

Polyurethanes are a remarkable class of polymers which exhibit a wide range of mechanical properties, and several reference texts describe their chemistry and physical behaviour, e.g [1]. These materials are currently finding increasing applications at sea. For the offshore industry this includes seals, protection and deepwater flow line coatings [2]. In the fishing industry selectivity grids are now being proposed in polyurethane [3], while oceanographic applications include fenders and tubing on underwater vehicles and underwater antenna protection. All these structures can spend several years underwater, either continuously or intermittently, and the material selected must be shown to retain its mechanical properties. Such data are not readily available and the aims of the present study were twofold: first, to examine the use of an accelerated test method for this type of application, based on the ISO 11346 standard for accelerated ageing of rubber [4], and second to determine whether such materials are suited for marine structures of this type which are immersed for long periods.

There have been many previous studies of the long term durability of polymers in marine environments. For example, the proceedings of an ASTM symposium on materials for deep sea applications in 1969 include some data on the behaviour of common polymers [5]. Bowditch described the various mechanisms which contribute to the durability of polymer adhesives in the presence of water [6]. These include plasticisation, swelling, hydrolysis and debonding of fillers. Fibre reinforced composites, widely used in marine structures, have received particular attention. A recent review of durability of marine laminates indicates the extent of experience for these filled thermoset materials [7]. Data from samples both removed from ship structures and immersed at sea for over 20 years have been correlated with accelerated laboratory test results [8]. Damage parameters have been used to evaluate the influence of seawater ageing on polymers and their composites [9]. Master curves based on time-temperature equivalence have also been used to evaluate the long term evolution of both stiffness and strength properties of composites in water [10].

Previous studies on elastomers include discussions on lifetime affecting factors [11]. Many studies have examined ageing in air, where photo-oxidation is the main concern, but fewer authors have published results for ageing in sea water. Burns et al. followed the bulk modulus of natural rubbers, neoprenes and polyurethanes after ageing for up to two years in artificial sea water [12]. The stiffness properties of the urethane materials were quite stable over that period. Murata et al. discuss the hydrolysis resistance of polyurethanes and show the importance of the diol chemistry on molecular weight stability in water [13]. Rutkowska et al examined the degradation of polyester- and polyether-based polyurethanes in sea water for periods up to 12 months and showed the significantly higher strength retention of the latter [14]. A recent review of elastomers used in the

offshore industry described different modes of deterioration, including mechanical degradation, chemical changes and cracking due to UV and ozone attack [15].

The most common approach to accelerate ageing uses elevated temperature tests combined with the Arrhenius expression to relate the resulting evolution to behaviour at lower temperatures or longer times. This is embodied in the ISO standard test method 11346 [4], but there is considerable discussion over the validity of this approach. The use of tests at elevated temperature is based on the assumption that only the kinetics of the ageing mechanisms are modified in the temperature range employed, not the mechanisms themselves. Celina et al examined the Arrhenius approach for a range of materials exposed to thermal ageing [16]. They highlighted the need to establish whether a linear extrapolation is valid, and showed that competing mechanisms may result in non-Arrhenius behaviour. Another study of polychloroprene aged for 24 years in service also showed evidence that the linear Arrhenius extrapolation was not valid [17]. In the case of thermal ageing the use of oxygen consumption measurements may be used to check the validity of lifetime predictions [18], but these cannot be applied to marine ageing.

The influence of ageing is often followed by measurement of tensile properties, as this is one of the easiest tests to perform. Compression set and sealing force measurements have also been employed, for joint life applications [19]. Various other methods have been applied in parallel with mechanical tests, including FTIR (Fourier Transform Infrared) spectroscopy, weight change and permeability measurements, and GPC (gel permeation chromatography) and NMR (nuclear magnetic resonance) analyses. In the current work tensile testing was the main technique employed, supported by hardness measurement and FTIR analysis.

Materials

The samples studied here are polyether-based polyurethanes. They were manufactured by casting commercially-available components between plates in the form of 18 panels (8 of flexible and 10 of rigid PU) of dimensions 300 by 300 mm². The resulting plaques were nominally 4 mm thick. At the time this study started this range of products was marketed as *Ureol*. It is a product used for moulds, but also for prototype parts, particularly where abrasion resistance is required. Two materials have been studied, produced by mixing three components. The material subsequently described as “flexible PU” is nominally of hardness 40 Shore A and is based on two isocyanates (75 parts *XB5073* and 25 parts *XB5075*). The material designated as “rigid PU” is of nominal hardness 90 Shore A and the isocyanate mix is 50 parts *XB5075* with 50 parts *6414A*. Both use an aromatic amine hardener (*6414B*), 22 parts for the flexible, 48 parts for the rigid material. Sample sheets were cast

between metal plates at room temperature in a temperature and humidity controlled laboratory. All were then post-cured at 40°C for 16 hours to stabilize their properties.

Testing

The main technique employed to follow material properties was tensile testing of H2 dumbbell specimens according to test methods ISO 37 [20]. The standard Figure 1 shows the specimen geometry. These were cut from plates using a die set before ageing. Tensile tests were performed at a cross-head displacement rate of 50 mm/minute for the rigid material and 100 mm/minute for the more flexible elastomer. The strain was determined from the crosshead displacement as extension divided by initial gauge length. Gauge length was taken as 20 mm throughout, as recommended in the standard. More reliable values can be obtained by clipping an extensometer onto the specimen, but preliminary trials showed that the knife edge of the extensometer caused premature failures. The extensometer was therefore not used to follow ageing effects. Stress was defined as applied load divided by initial cross-sectional area. Tests were performed in a laboratory at controlled temperature and humidity (23 ±2°C, 50±5% RH). Over 1000 tensile specimens were tested in the study. Annual machine calibration by a certified organisation over the 5 year period ensured that variation in measured values was not caused by changes in load cell characteristics.

Figure 2 shows examples of tensile plots for both materials. Several values can be taken to characterise the materials, in this study the values analysed were:

For the flexible (Shore 40A) material:

- Stresses at 50%, 100%, 200%, 300% strain
- Failure stress and strain

For the rigid (Shore 90A) material:

- Initial slope, yield point, (ISO 527, [21]), stresses at 50%, 100%, strain
- Failure stress and strain.

Shore A hardness was also measured, the median value of five measurements on two 25 x 25 mm² samples, after 15 seconds indentation. For the laboratory aged samples weight change was also noted. IR spectroscopy was performed on certain samples. The spectra were collected using a *Thermo Nicolet Nexus* spectrometer in the ATR mode with the specimen surface in contact with a germanium crystal. Two hundred scans were added to obtain the final spectrum.

Ageing Conditions

The ageing test conditions are summarized in Table 1.

- Laboratory ageing

Laboratory ageing was performed in sealed vessels containing artificial sea water prepared according to ASTM D1141 [22], and maintained at different temperatures. Ten specimens were removed periodically and tested, five immediately after stabilising at room temperature (referred to as the “wet” condition), and five after drying in a vacuum oven at 40°C until constant weight was achieved (“dry”). As discussed below, the plate from which each sample was cut was carefully noted so that changes in properties could be related to the initial value for reference specimens from the same plate.

- Testing at sea

The IFREMER natural test site in the Brest Estuary in Brittany was used. Ten tensile specimens of each material and three rectangular coupons for weight gain and other analyses, were fixed to each of eight glass reinforced composite frames, Figure 3, which were in turn mounted on a metal frame. The latter was fully immersed at a water depth between 2 metres at low tide and up to 8 metres at high tide. The water temperature at this site varies annually in the range between 9 and 20°C. Specimens were recovered by divers and either kept in natural seawater tanks until testing wet or dried until a constant weight was recorded and then tested.

Results

a) Initial properties

The materials were produced manually, as this is the technique used in practice, and this leads to differences in quality and thickness. A first series of tests was performed to investigate the variability of results, as this information is essential to be able to evaluate the effect of ageing. One sample was cut from each of the 18 panels and tested to failure. Figure 4 shows examples of results for the two materials. There is a quite significant variation in strength and failure strain. Such a large variation would make it very difficult to quantify changes, so for all the subsequent ageing tests the reference values used to evaluate changes are those for samples cut from the same panel.

b) Laboratory ageing

In this section the results from tests after laboratory ageing will be presented, for the flexible elastomer then for the rigid PU. However, first a set of raw failure stress data from tests at 50°C on both materials after drying are shown, which indicate the scatter in results, Figure 5. Note that this plot does not reflect the trend in material behaviour with ageing exactly however, as all specimens were not taken from the same panel. To obtain the trend with ageing these values must be expressed as a percentage of the reference value of the panel from which they were taken, as explained in the previous section (Figure 4). Mean values are shown in Figure 5, with error bars indicating \pm one standard deviation, and these indicate that the coefficients of variation within each set of tests are in the range from 6 to 18% for the flexible PU and 5 to 13% for the rigid material. While not negligible they are sufficiently small to allow trends in the material response with ageing to be evaluated. For clarity only the mean values will be shown in the following sections.

- Flexible PU

Figure 6 shows the influence of a 50°C wet ageing for periods up to two years on the failure stress of wet and dried samples. These results show a drop in stiffness and strength of wet samples from the shortest ageing periods. Hardness of wet specimens also drops, values as low as 25 Shore A are recorded after one month. After drying this drop is recovered, suggesting that it is due to plasticization by water. This is supported by the failure strain values, which increase with immersion initially but are subsequently not further affected. For the shortest immersions all the properties after drying are higher than initial values, but for immersions exceeding 2 months the dried specimens show very similar stiffness and strength to the unaged specimens. One hypothesis is that ageing at 50°C may initially complete cross-linking, and small increases in hardness are noted (from 38 to 41 Shore A), but there is no other data to support this. Another possibility is that leaching out of plasticizers is the cause of the initial increase in stiffness after drying, but in this case one would expect a net reduction in weight after drying. A weight decrease was recorded after 30 days but it was very small and probably not significant, Figure 7.

Figures 8 and 9 show examples of the data from tests on wet and dry samples for the same stiffness and failure stress properties after tests at all temperatures. The effect of temperature is to shift the property degradation to shorter ageing periods as expected. This is particularly effective for the specimens after drying, for which property losses up to 60% are measured. It is apparent that the use of elevated ageing temperatures (70°C and

above) results in significant irreversible material degradation, whereas for ageing up to two years at 50°C the changes appear fully reversible. At the highest temperatures stiffness drops by 50 to 60% and reaches a plateau value, whereas failure stresses are still decreasing even after the longest immersion periods. The influence of temperature on results for the materials in the wet state is more difficult to analyse, as reversible (plasticization) effects are combined with permanent degradation. FTIR analysis of samples clarified these results. Analysis of samples removed after 60 and 183 days at 50°C showed no change compared to reference (unaged) specimen spectra. However, the analysis of a specimen removed after 90 days at 90°C indicated a strong increase in the band at 1014 cm⁻¹, Figure 10, corresponding to the C-O of alcohol formation, indicating the presence of hydrolysis.

- Rigid PU

Figure 11 shows the results for the rigid PU aged at 50°C for up to 2 years. The trends are similar to those for the flexible PU, with a drop in stiffness and strength in the wet state but after drying the specimens show improved properties for all ageing conditions. Once again there is an initial increase over the first two months then a levelling off. The trend in failure strain is again less clear-cut, measured values being similar to the unaged specimen values. In this case the weight change plots show a significant drop in weight after drying suggesting that plasticizer extraction occurs soon after immersion, Figure 12.

Figures 13 and 14 show examples of the influence of higher ageing temperatures. Here temperatures of 80°C and above are required to produce permanent drop in stiffness and 90°C to produce a permanent strength loss. This indicates that the degradation kinetics are significantly slower for the rigid material compared to the flexible PU. Once again FTIR analysis was used and indicated very similar results to those for the flexible PU shown in Figure 10, with no change after 60 and 183 days at 50°C but a strong increase in the 1014 cm⁻¹ band indicating hydrolysis after 90 days at 90°C.

c) Ageing at sea

Samples immersed at sea were removed periodically. The sample holders were covered with a layer of biofilm after 3 months, Figure 15a, which increased as marine fouling then attached to it, Figure 15b, and developed into a thick marine fouling layer after longer periods, Figure 15c. After 5 years three of the ten flexible specimens had detached from the frame, all the rigid specimens were still in place. The specimens were cleaned manually before testing, the fouling layer could be removed quite easily when wet though some hard fouling (barnacles),

adhered more strongly. Their removal resulted in notches on the specimen surface and these were monitored closely during tests, but did not appear to promote early failure.

Results from both series of tests are shown on Figure 16. The properties of both materials improve with ageing time. This suggests that the sea ageing period at low temperature (9-20°C) corresponds to the initial laboratory ageing period at 50°C, period during which tensile properties tend to improve after drying. Weight decreased after drying, indicating that the same plasticizer extraction may be responsible for the stiffness increase. A set of three flexible specimens was kept in a dry environment for 7 years in parallel with the aging tests. These were then tested and the failure stress had increased by about 35% compared to the initial test results for the same panel. This indicates that while some material improvement occurs with time the majority of the change noted is caused by exposure to water. This will be discussed further below, but the important practical conclusion from the sea ageing tests is that no significant degradation of either material was noted after 5 years at sea. Even in the wet state the material retains stiffness and strength properties. FTIR analysis was performed on both the external surface and the interior of specimens aged for 5 years. Results are shown in Figure 17 and suggest that hydrolysis occurs but is superficial, the majority of the specimen is not degraded. There is also a significant decrease in the response at 1725 cm⁻¹, which is the ester band of phthalate plasticizers. This suggests that at long periods extraction of plasticizers (di-butyl phthalate) occurs.

Discussion

The aims of the present study were to examine the use of an accelerated test method for this type of application, and to determine whether these PU materials are suited for marine structures. The validation of accelerated tests is essential if new formulations are to be evaluated in a reasonable time period. The risk with increasing temperature to accelerate tests is that the failure mechanisms which are induced are not those which would occur naturally when ageing is performed at temperatures more representative of the service environment. In the present case the environment of interest is sea water at temperatures of 20°C or less. The results shown above, notably Figure 6, clearly indicate that even at 50°C, while water uptake does cause a reduction in properties, no significant permanent degradation occurs even after 2 years. The only change noted is some loss of plasticizer. In order to apply the standard ISO test method and degrade these materials it was therefore necessary to further increase the ageing temperature. This results in secondary effects such as post-curing, which modify the material, but it does enable permanent degradation to be induced. It is then possible to use the Arrhenius construction to quantify degradation kinetics. To apply this a straight horizontal line is plotted from the property

loss of interest on the graph of property loss versus ageing time and the times are read off. These are then plotted versus reciprocal of absolute temperature. This is only possible over a small range here and Figure 18 shows an example of the results but only for the flexible PU stiffness. The changes for the rigid material even over this large range of temperatures do not allow more than two points to be extracted. For the flexible PU this then allows predictions to be extended to lower temperatures, (assuming that this linear extrapolation is valid over the whole temperature range). For a sea temperature of 15°C for example, the time predicted for a 20% drop in stiffness is over 200 years. The acceleration factors in using elevated temperatures to predict change in properties for 15°C are large, aging times are reduced by a factor of around 60 by raising water temperature from 50 to 90°C for example.

Figure 19 shows the only failure stress data that could be used for Arrhenius plots for the two materials. This indicates the difference between the rigid and flexible materials which do not show the same activation energy. The small number of values make quantitative predictions of strength impossible but extrapolation of these plots suggest that at least 20 years immersion at 50°C would be necessary to reach a 20% loss in strength.

There is some additional uncertainty in these values due to the existence of two values in some cases, for example there are two aging durations corresponding to the 20% strength loss of flexible PU at 80°C.

A set of values corresponding to a 10% drop in yield stress of the rigid PU is also shown on Figure 19, and indicates a similar slope to those corresponding to the failure stress values for this material.

Concerning the suitability of these materials for long term marine applications the results presented above clearly indicate that both formulations tested retain their properties after 5 years' immersion at sea. There may of course be other factors to consider when selecting a material for long term use at sea, including damage resistance, low temperature transitions or stress/water interactions, but from an ageing standpoint these results suggests that both are well suited to prolonged seawater exposure.

Conclusions

This paper presents data from an extensive experimental study of the wet ageing of two polyurethane polymers. Over 1000 tensile tests have been employed to quantify the change in mechanical properties and these reveal that ageing temperatures of 70°C or more are required to be able to apply the Arrhenius construction of ISO 11346 to estimate lifetime. Based on this approach lifetimes in excess of 20 years, before a 20% permanent drop in failure stress, are predicted for structures at 50°C. A reversible drop in properties may occur for materials in the wet condition however, due to plasticization, and this should be taken into account in design

Tests at sea confirm that no loss of properties occurs after 5 years' immersion. Detection of hydrolysis on the surface of sea aged samples by FTIR analysis and extraction of plasticizer revealed by weight changes suggest that at least two of the failure mechanisms induced by elevated temperature laboratory ageing are representative of degradation which might be encountered in service. Given the very slow degradation kinetics measured it appears that these polyurethanes are suitable for long term underwater applications. Mechanical rather than physico-chemical damage is likely to determine their effective lifetime.

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Figure headings

Figure 1. Tensile specimen geometry

Figure 2. Tensile test values used to quantify the influence of ageing, a) flexible PU, b) rigid PU.

Figure 3. Ten tensile specimens and three weight gain squares on glass/epoxy composite mounting frame, rigid PU. Frame dimensions 125 by 250 mm².

Figure 4. Variability of initial tensile properties between plaques.

a) failure stress, b) failure strain

Figure 5. Scatter in measured values. Influence of ageing at 50°C on failure strength of flexible and rigid PU after drying, mean values (error bars show \pm one standard deviation). Note that specimens were taken from different panels.

Figure 6. Influence of ageing in water at 50°C on wet and dry properties, flexible PU.

a) Stress at 50% strain, b) Failure stress, c) Failure strain

Figure 7. Weight change before and after drying versus immersion time at 50°C, flexible PU.

Figure 8. Results from ageing at all temperatures, flexible PU

a) Stress at 50% strain, wet

b) Stress at 50% strain, dry

Figure 9. Results from ageing at all temperatures, flexible PU

a) Failure stress, wet

b) Failure stress, dry

Figure 10. FTIR flexible PU, laboratory ageing 90 days 90°C

Figure 11. Influence of ageing in water at 50°C on wet and dry properties, rigid PU.

a) Stress at 50% strain, b) Failure stress, c) Failure strain

Figure 12. Weight change before and after drying versus immersion time at 50°C, rigid PU.

Figure 13. Results from ageing at all temperatures, rigid PU

a) Stress at 50% strain, wet

b) Stress at 50% strain, dry

Figure 14. Results from ageing at all temperatures, rigid PU

- a) Failure stress, wet
- b) Failure stress, dry

Figure 15. Samples after sea ageing

- a) 3 months, flexible PU
- b) 7 months, flexible PU
- c) 5 years flexible and rigid PU

Figure 16. Results from sea ageing tests.

Figure 17. FTIR results from samples aged at sea for 5 years, surface and interior of specimens.

Figure 18. Arrhenius plots, flexible PU after drying, stress at 50% strain for different % reductions and extrapolation to 15°C.

Figure 19. Arrhenius plots, flexible and rigid PU, for 5, 10 and 20% reduction in failure stress

Tables Headings

Table 1. Aging test conditions

Temperature °C	Ageing period, days						
Reference specimens, unaged							
20	0						1850
Laboratory ageing, artificial sea water							
50	30	60	120	186	365	745	
70	7	30	60	120	270		
80	10	30	60	120			
90	2	10	20	40	90		
100	5	10					
Ageing at sea							
9-20			106	210		1200	1830

Table 1. Ageing test conditions

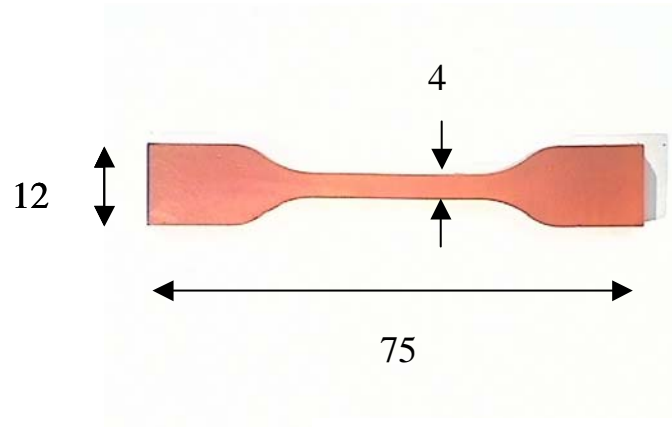


Figure 1. Tensile specimen geometry

PU flexible 40 Shore A

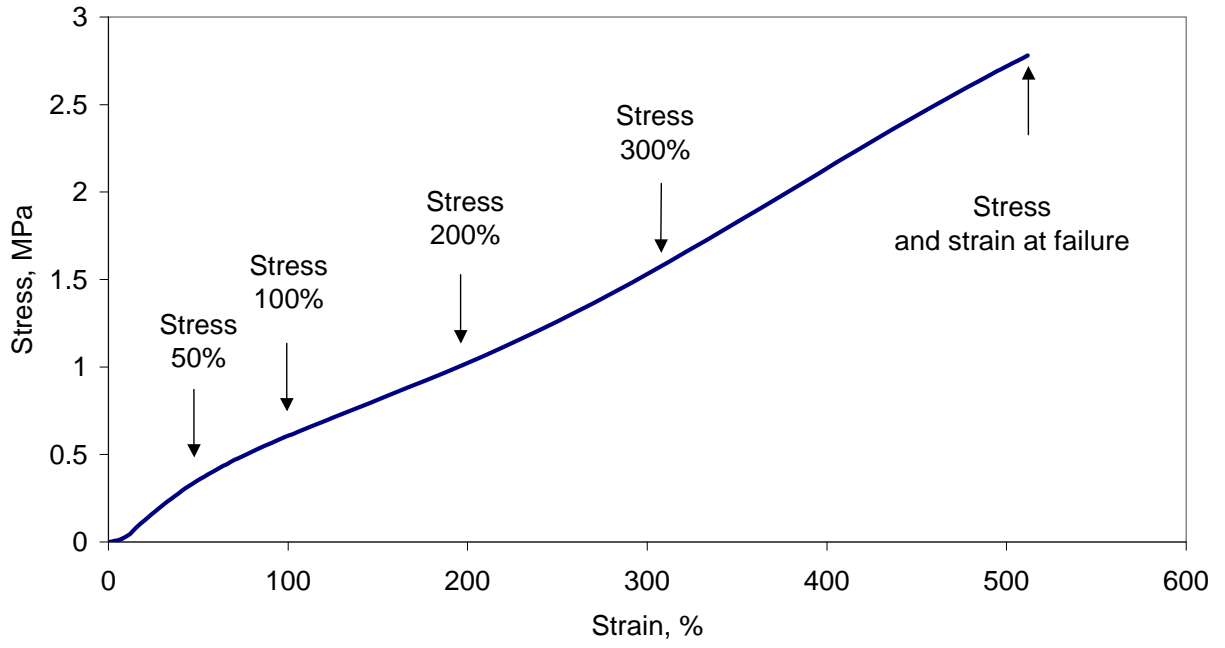


Figure 2a. Tensile test values used to quantify the influence of ageing, flexible PU.

PU rigid 90 Shore A

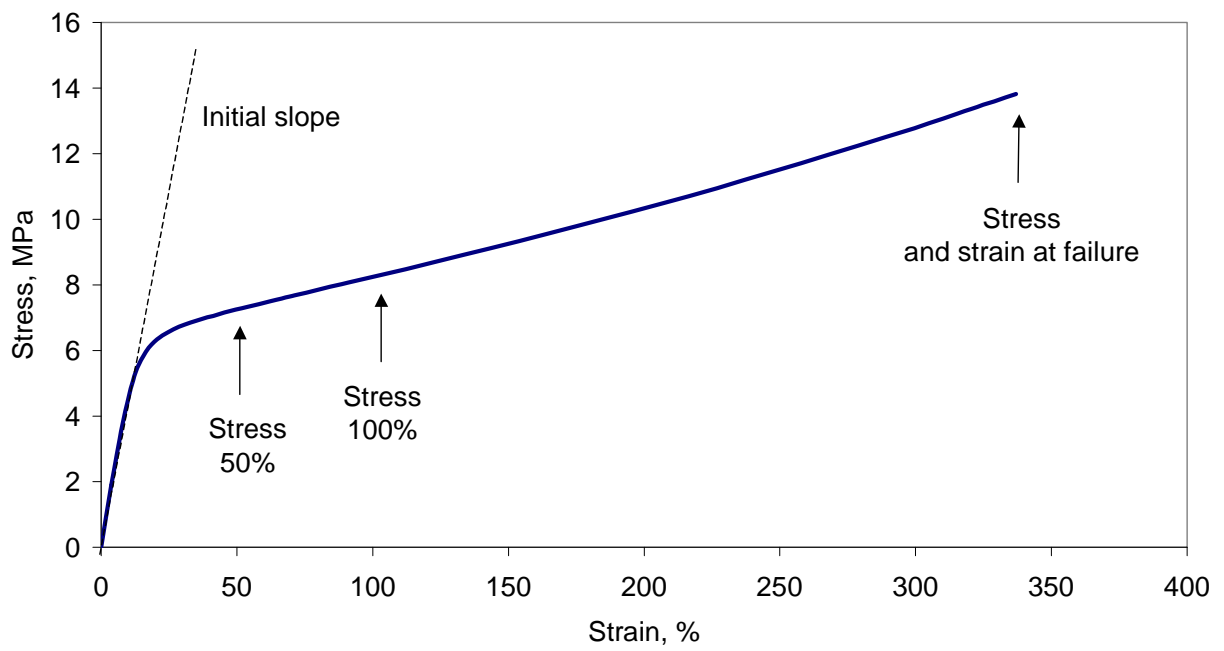


Figure 2b. Tensile test values used to quantify the influence of ageing, rigid PU.

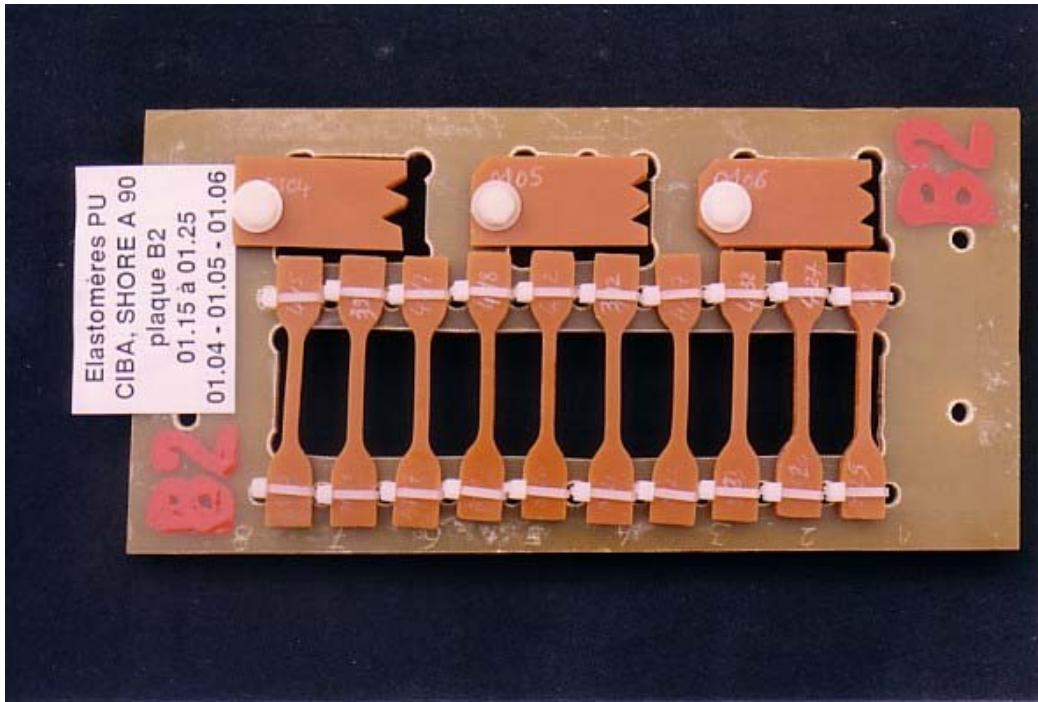


Figure 3. Ten tensile specimens and three weight gain coupons on glass/epoxy composite mounting frame before immersion, rigid PU. Frame dimensions 125 by 250 mm².

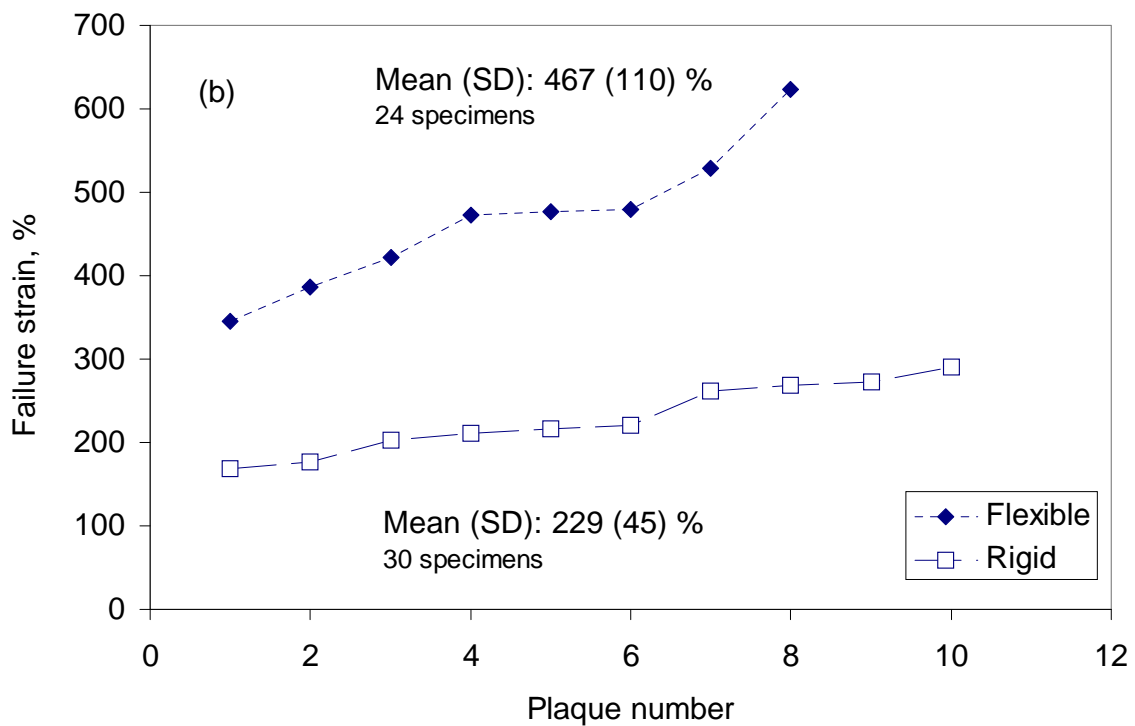
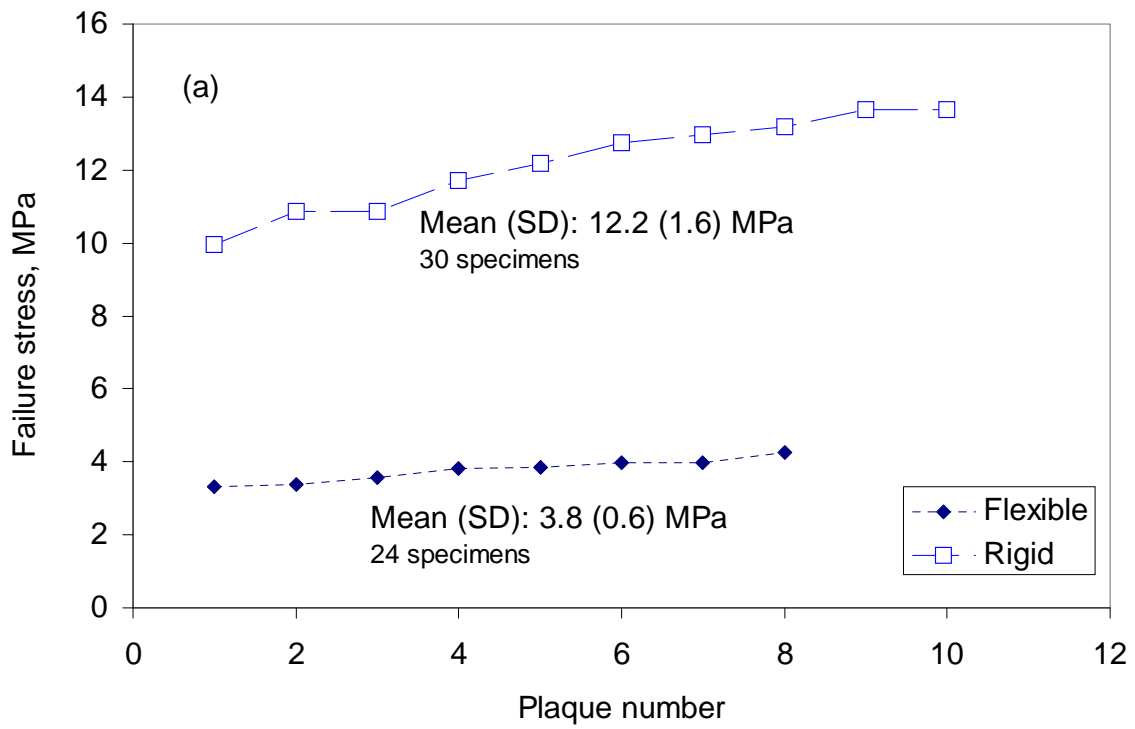


Figure 4. Variability of initial tensile properties between plaques.

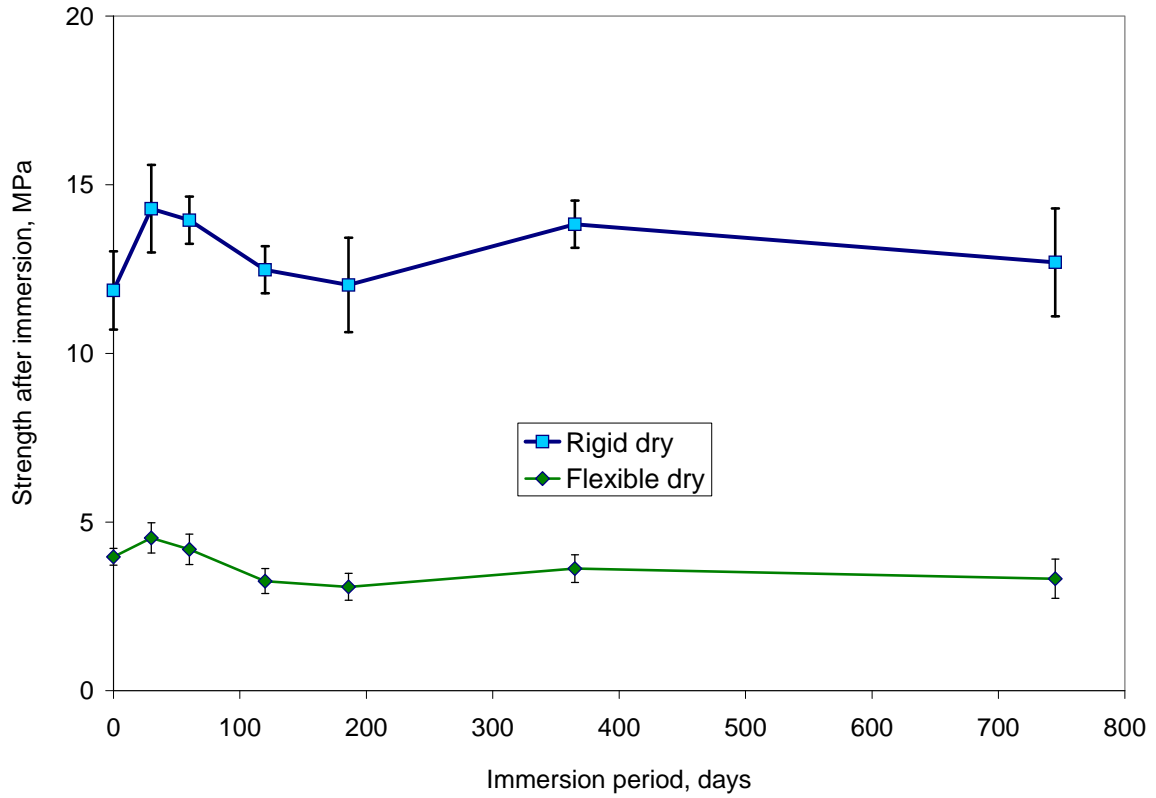


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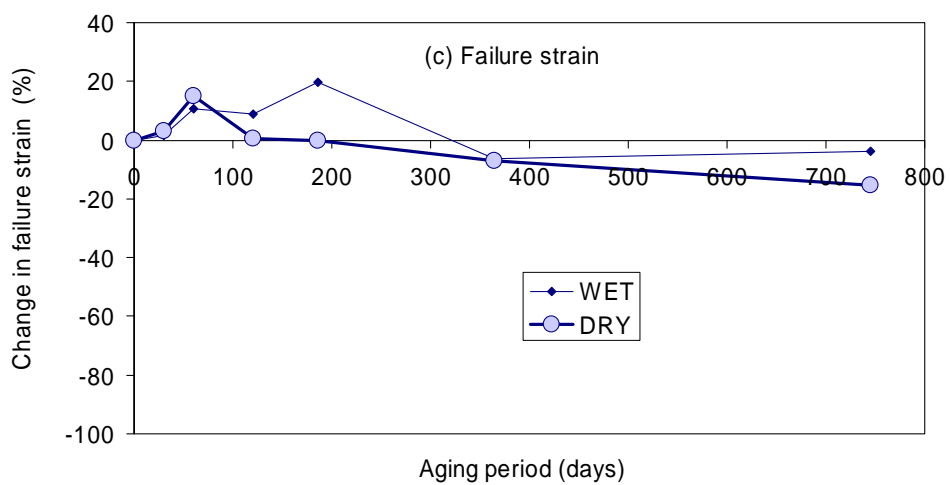
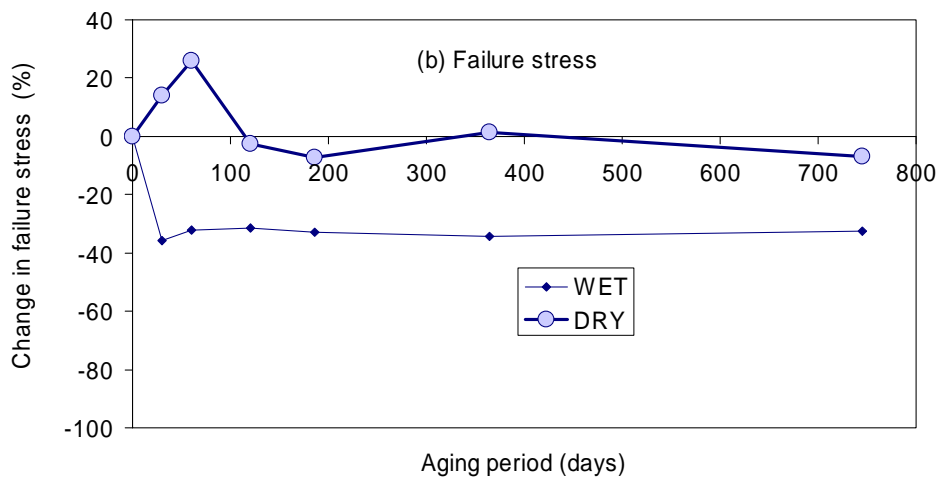
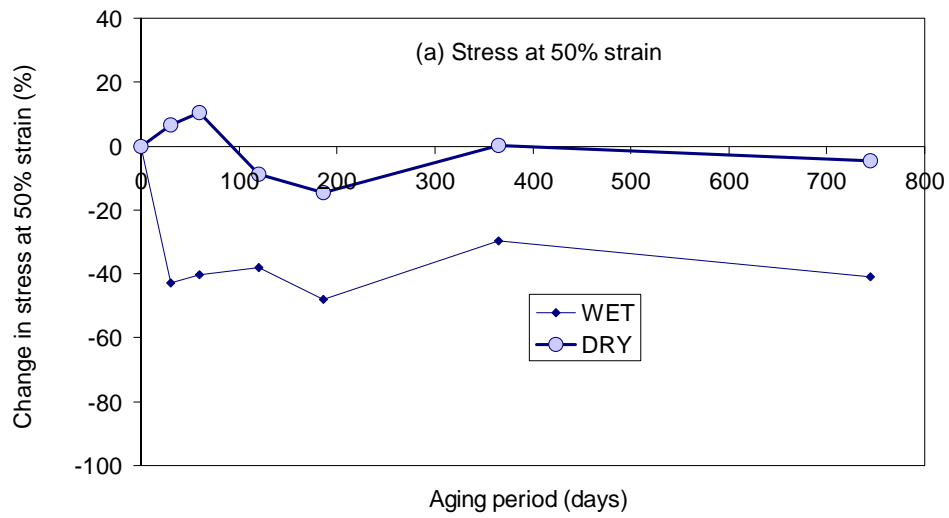


Figure 6. Influence of ageing in water at 50°C on wet and dry properties, flexible PU.

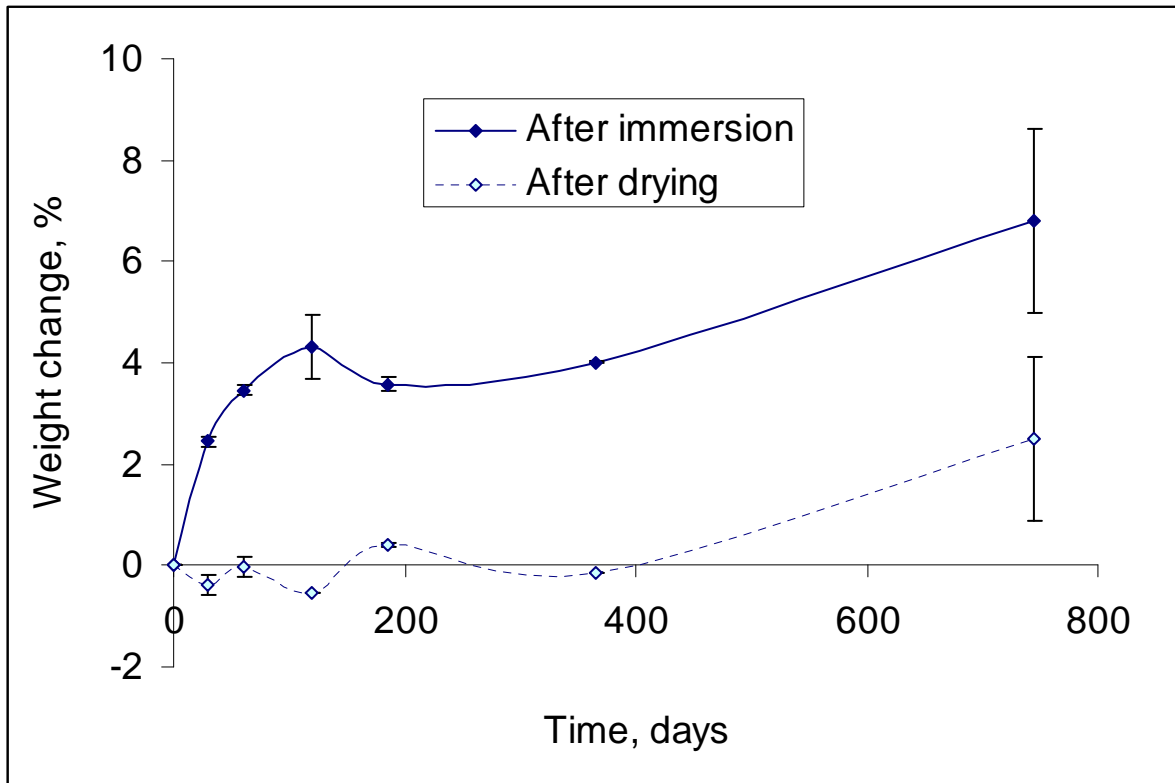


Figure 7. Weight change before and after drying versus immersion time at 50°C, flexible PU.

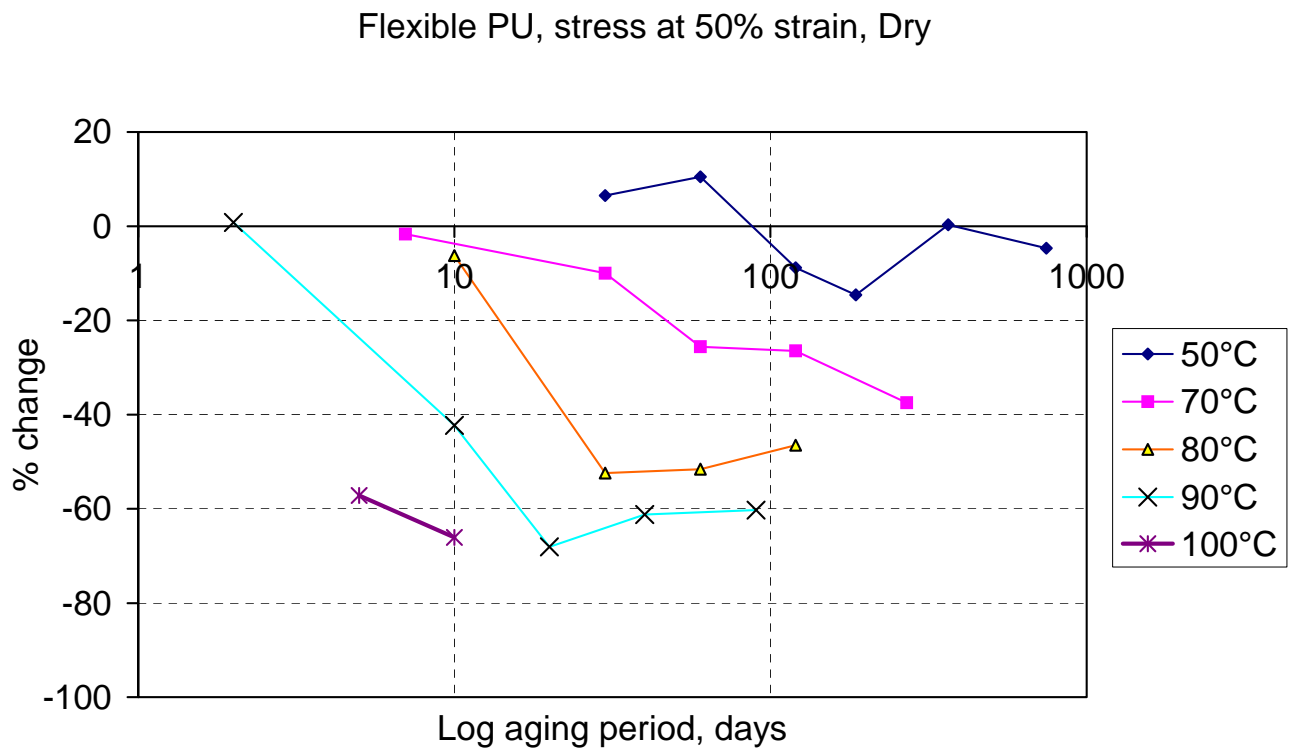
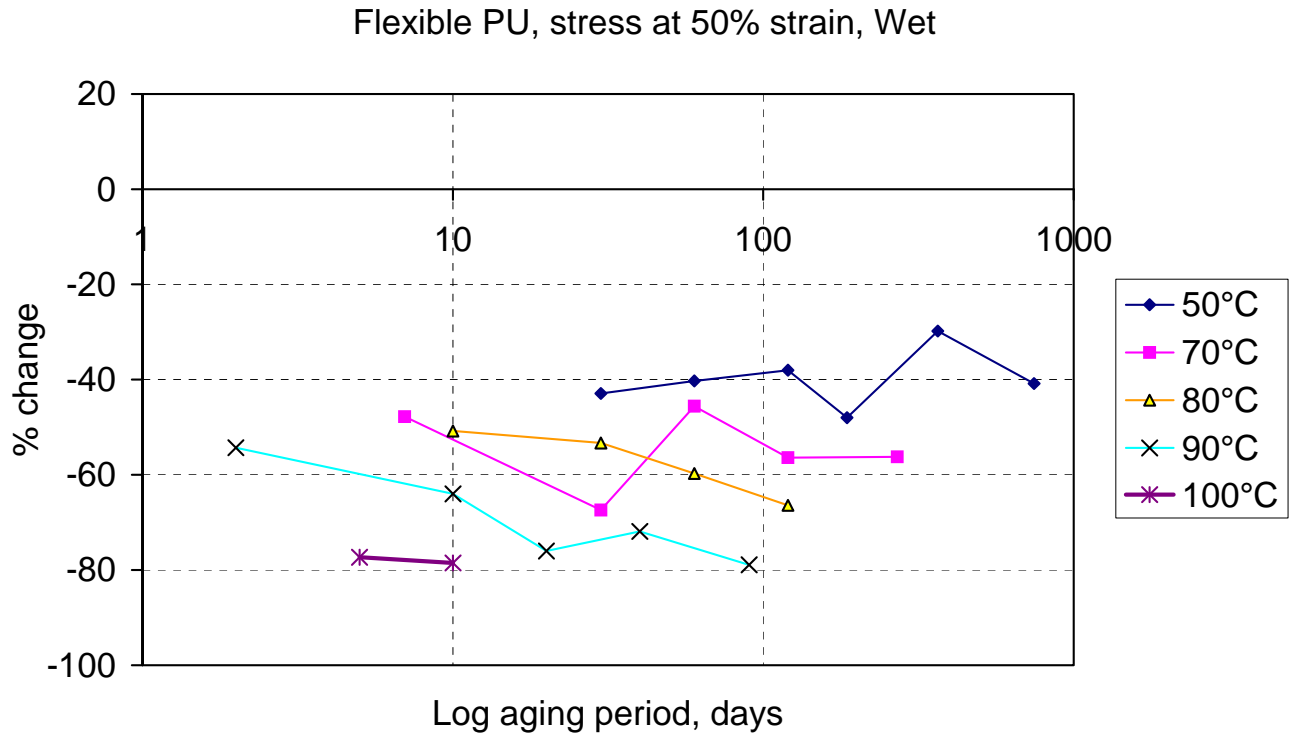


Figure 8. Influence of temperature on stiffness loss, stress at 50% elongation, flexible PU wet and dry, compared to reference values.

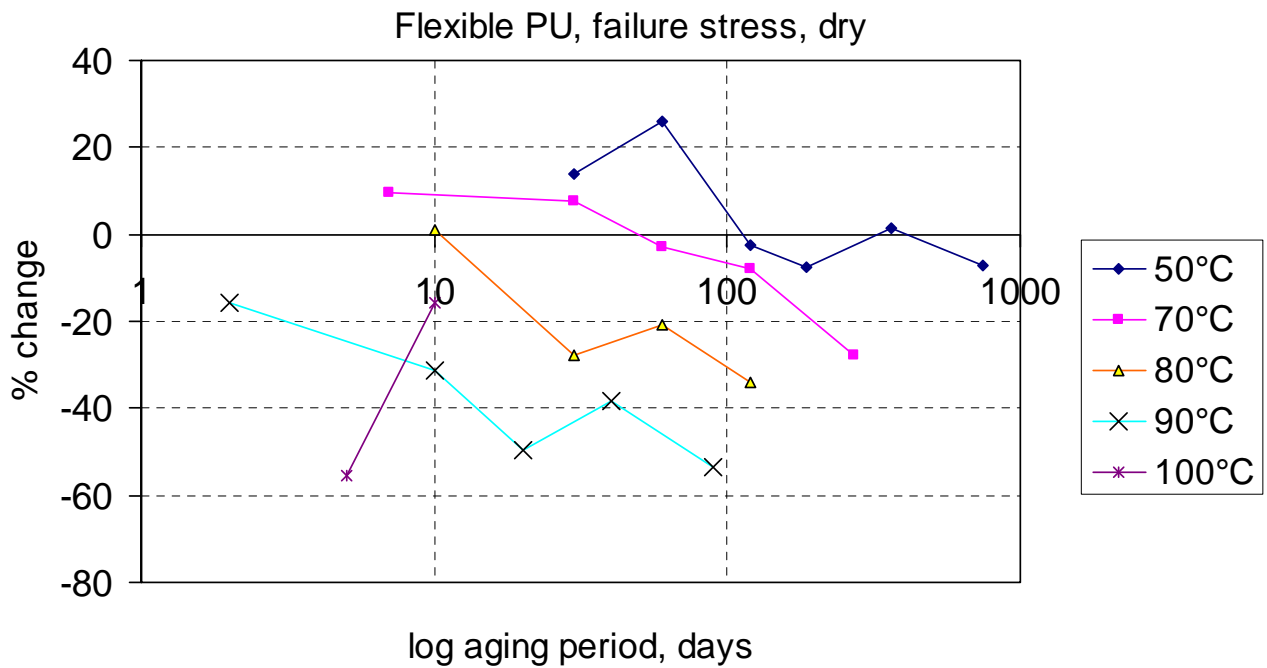
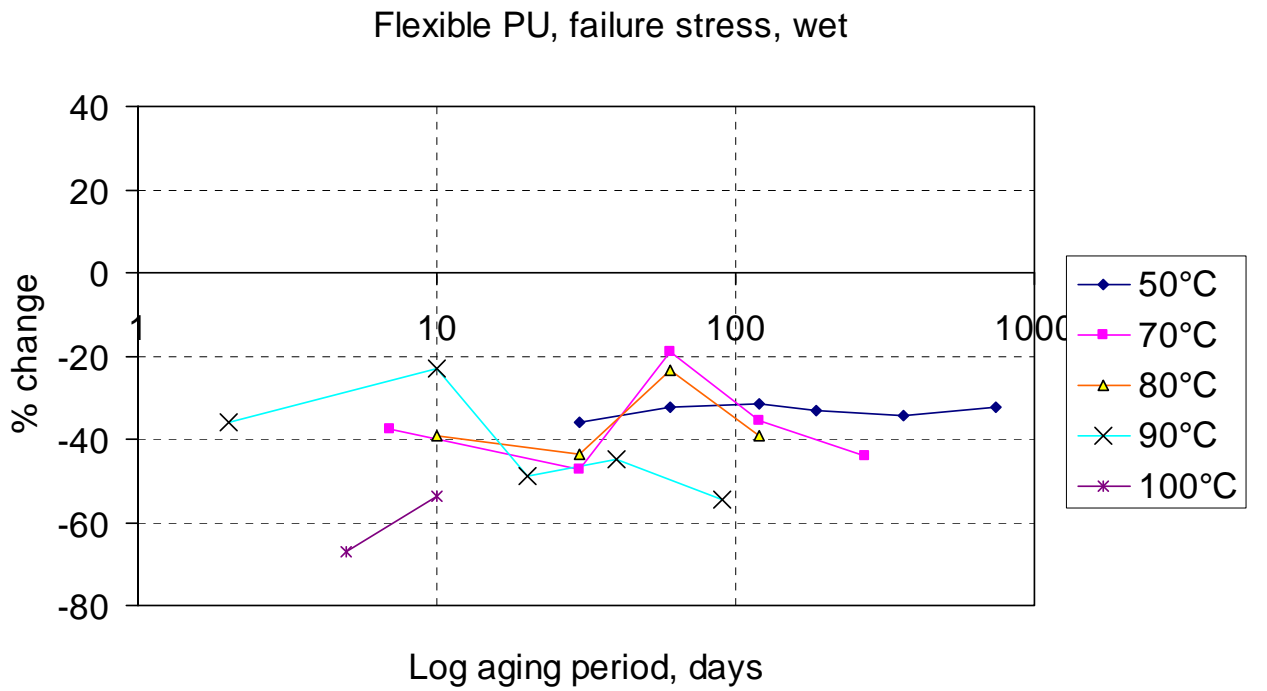


Figure 9. Influence of ageing temperature on strength loss, flexible PU, wet and dry, compared to reference values.

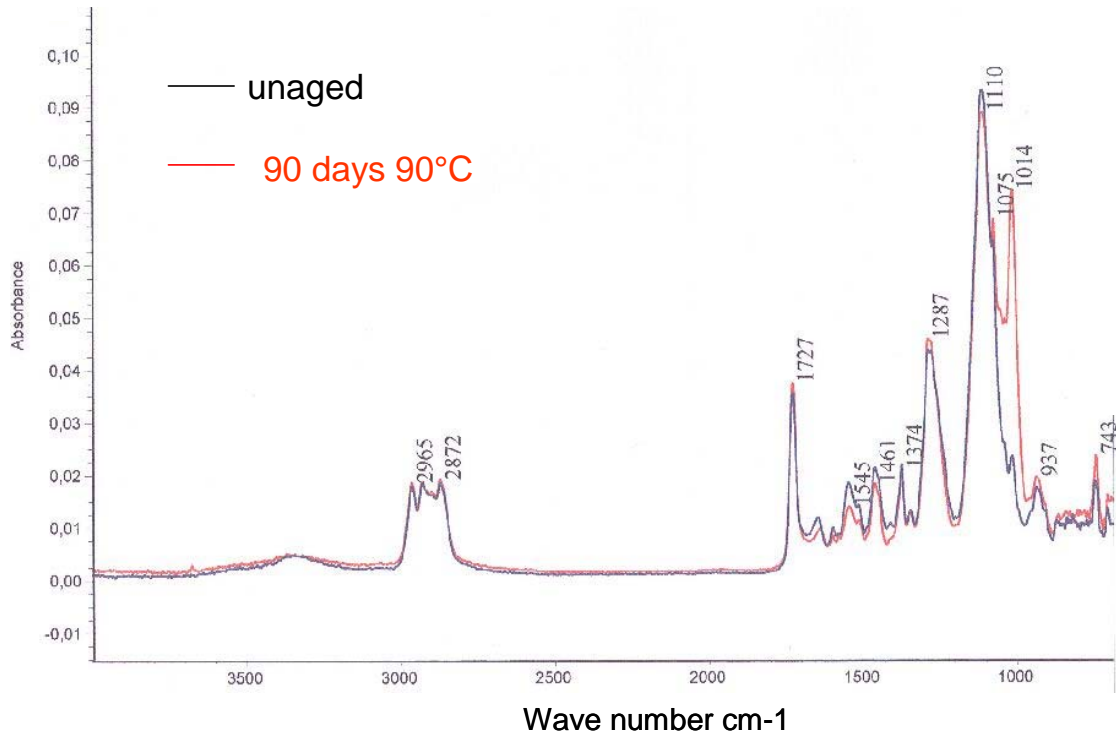


Figure 10. FTIR, Flexible PU, laboratory ageing 90 days 90°C.

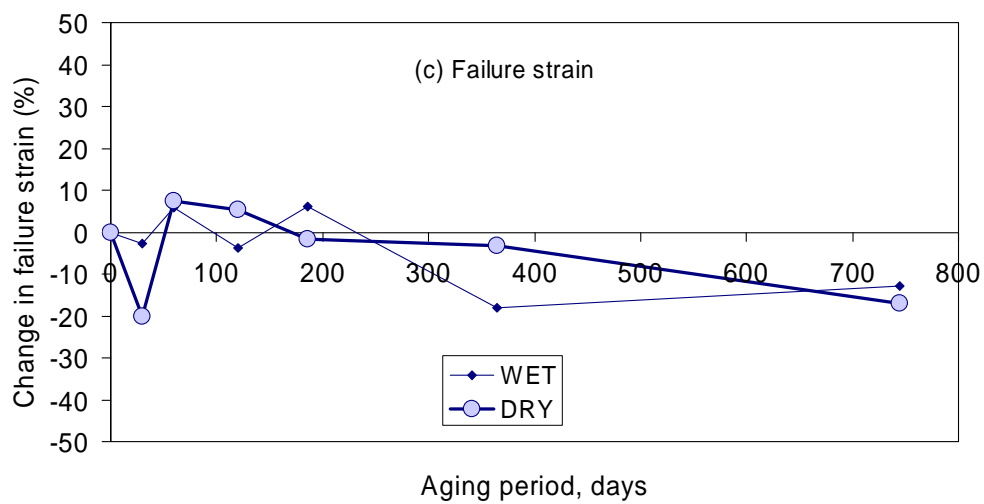
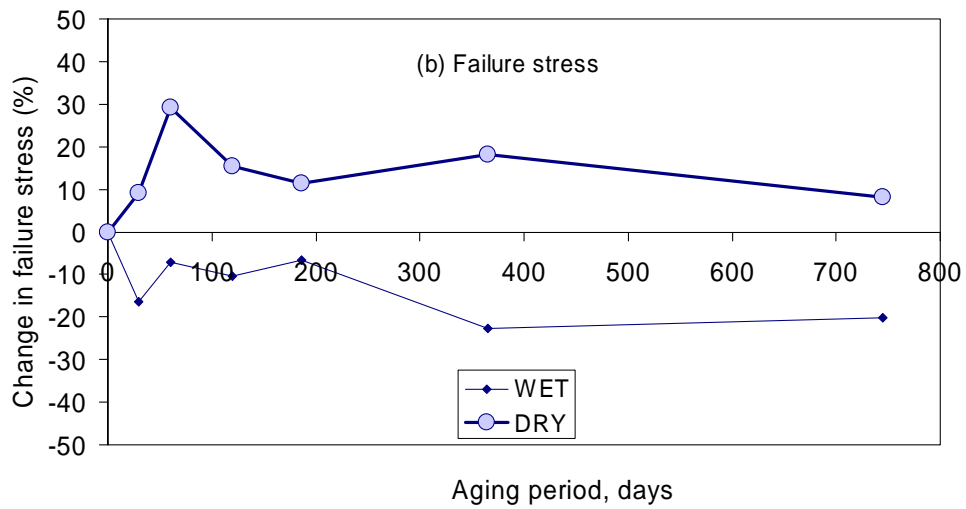
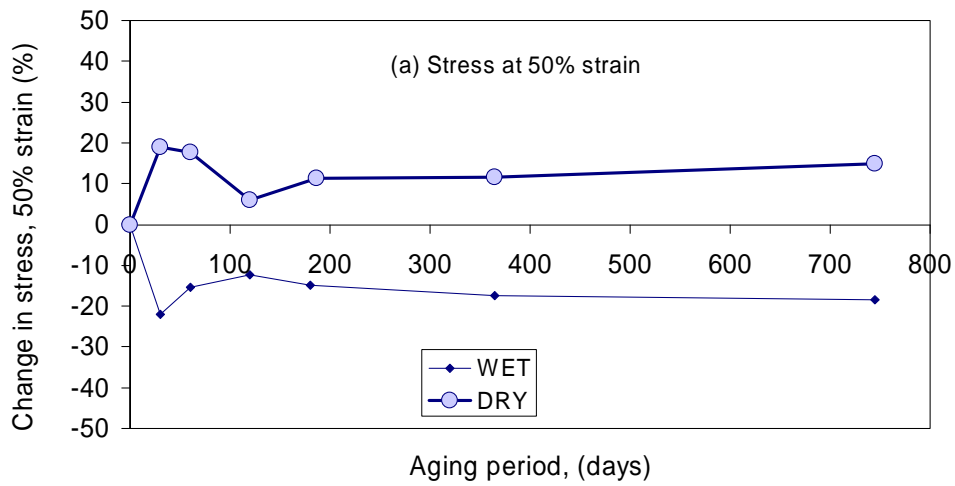


Figure 11. Influence of ageing in water at 50°C on wet and dry properties, rigid PU, compared to reference values.

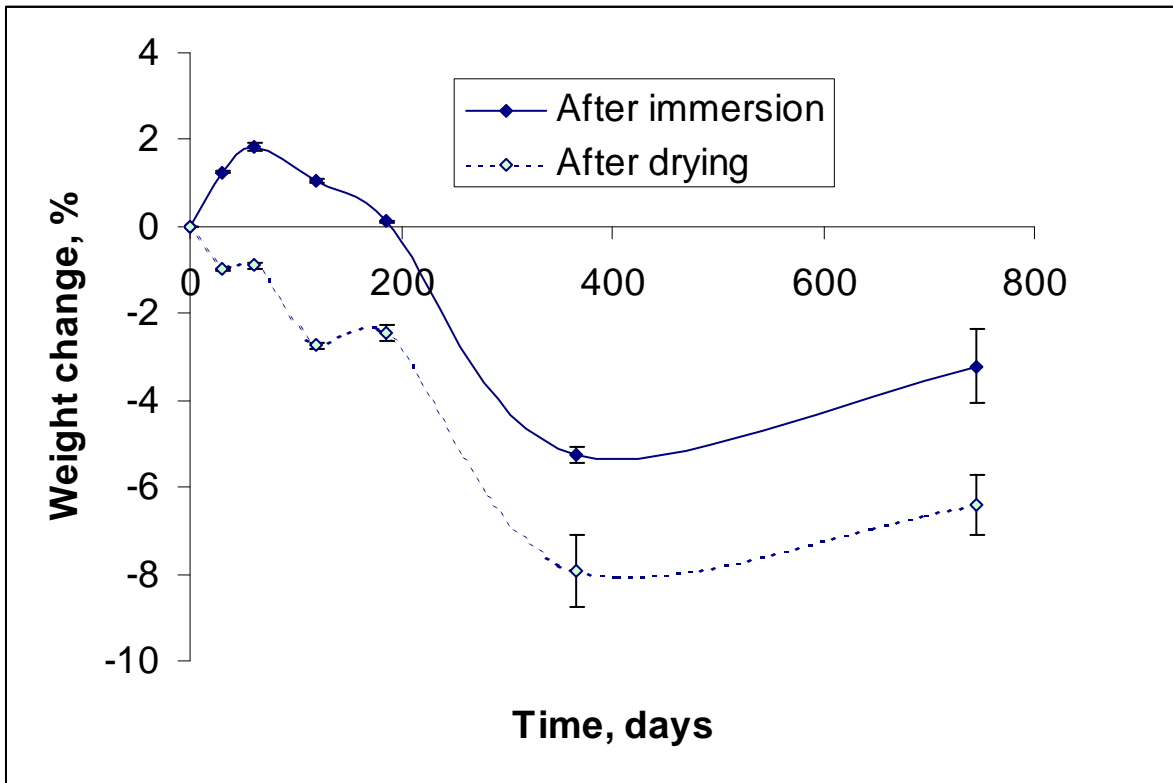


Figure 12. Weight change before and after drying versus immersion time at 50°C, rigid PU.

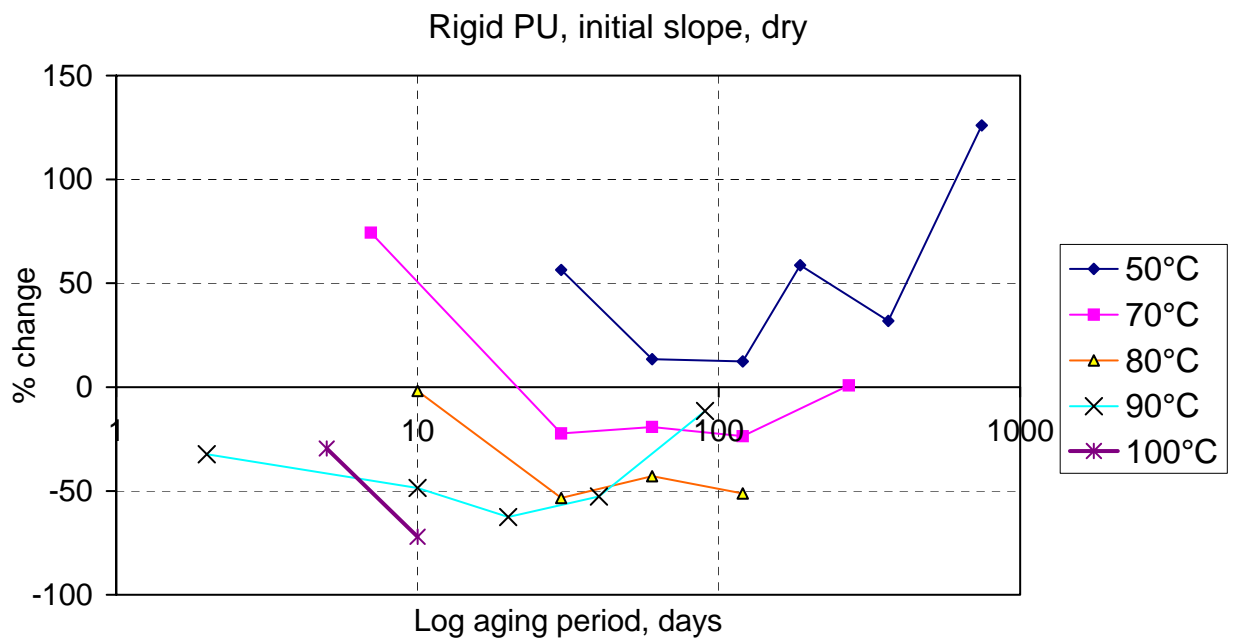
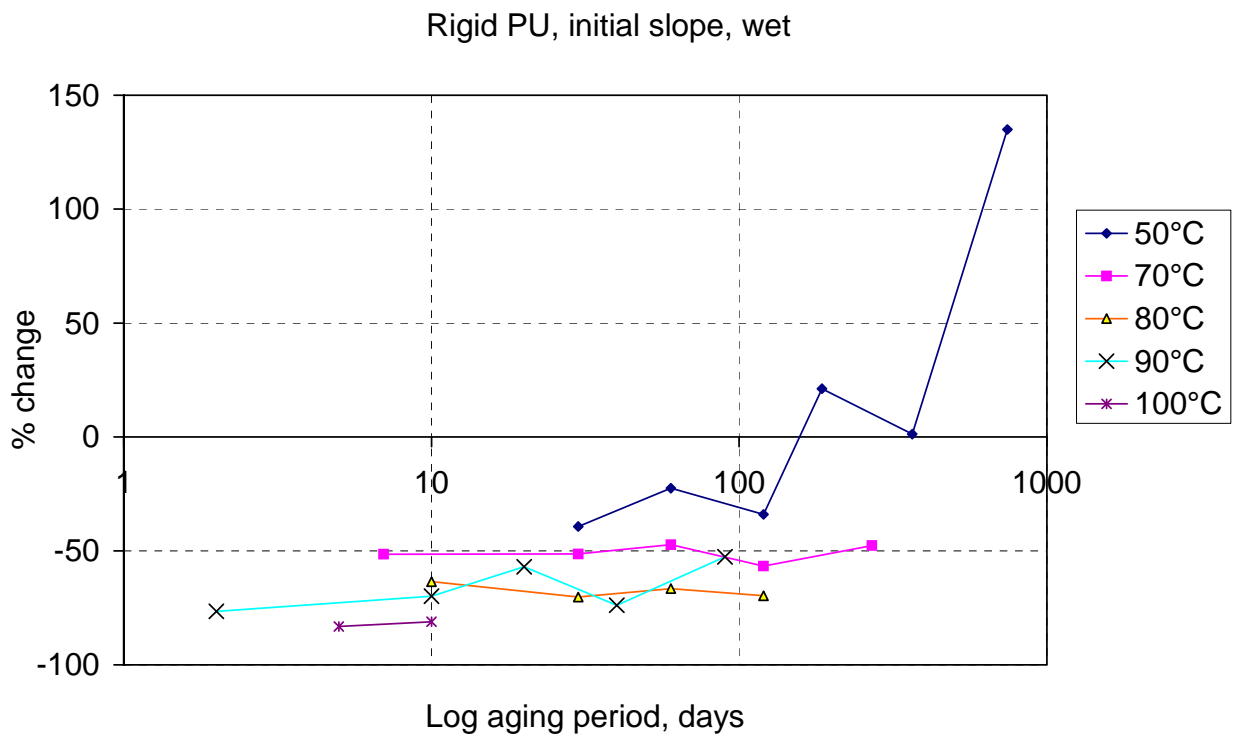


Figure 13. Influence of temperature on initial slope, rigid PU wet and dry, compared to reference values.

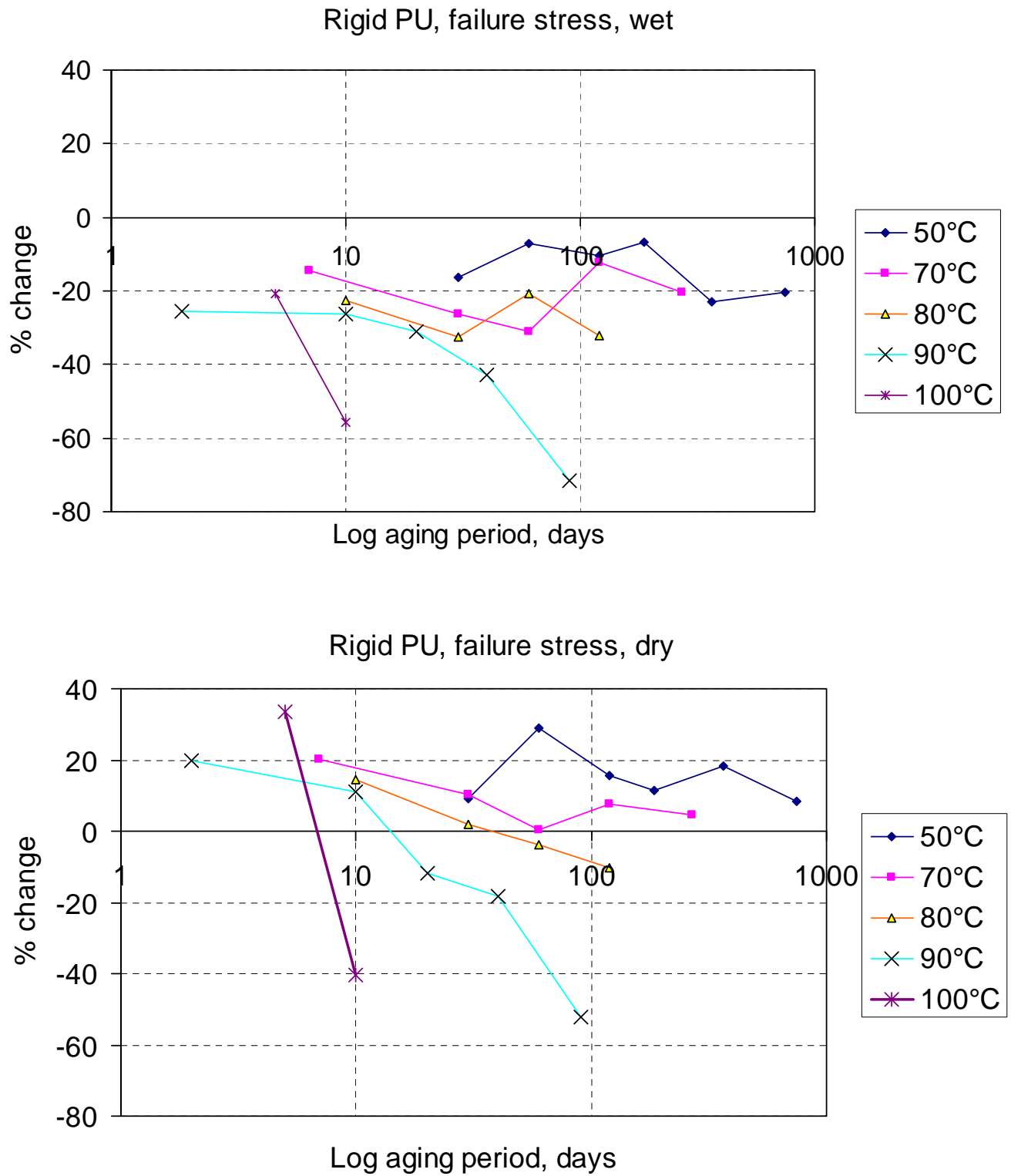
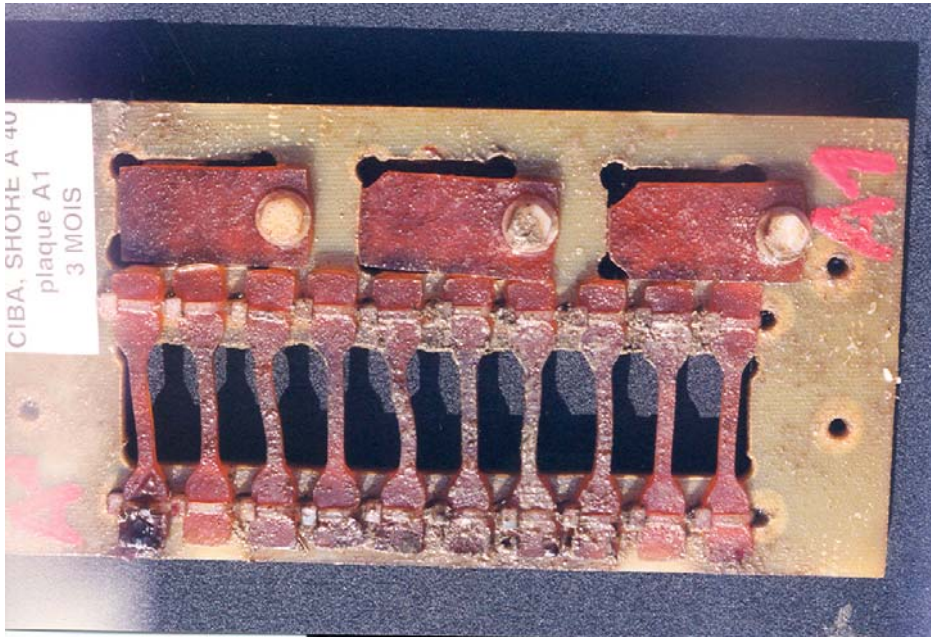
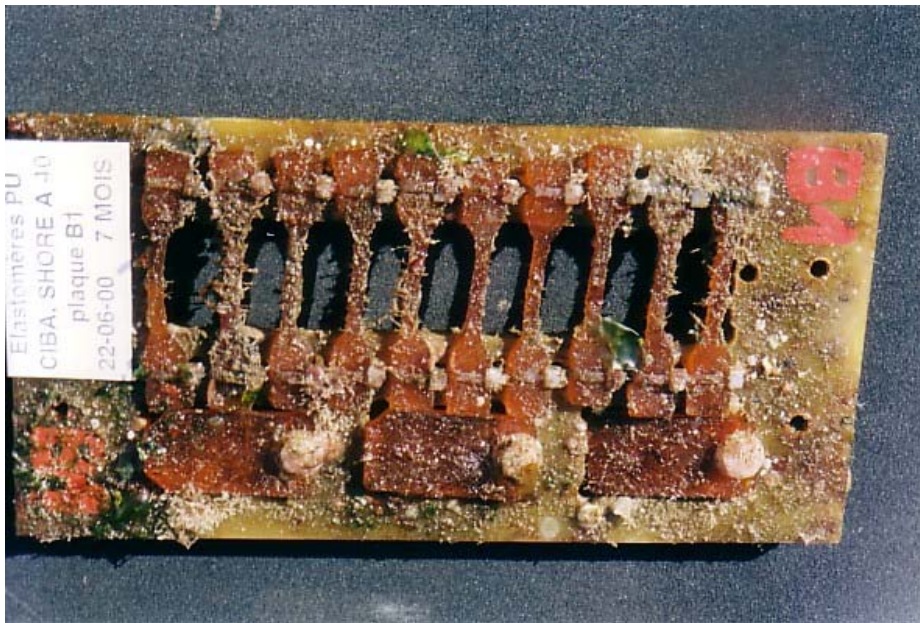


Figure 14. Influence of ageing temperature on failure stress, rigid PU, wet and dry, compared to reference values.



a)



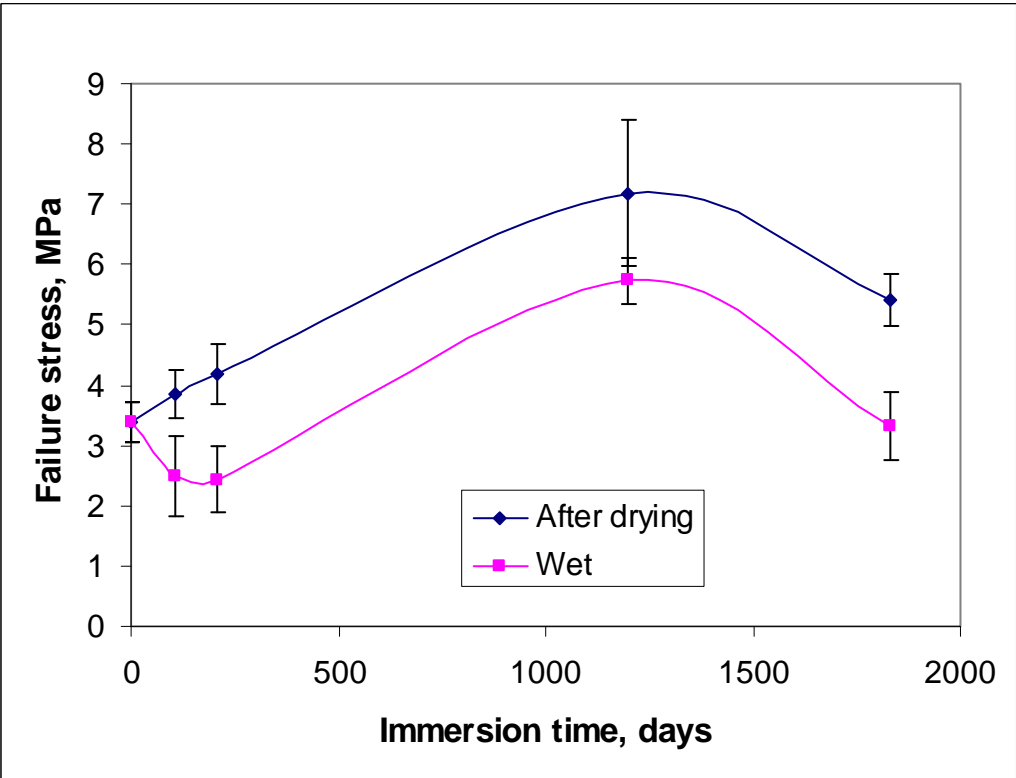
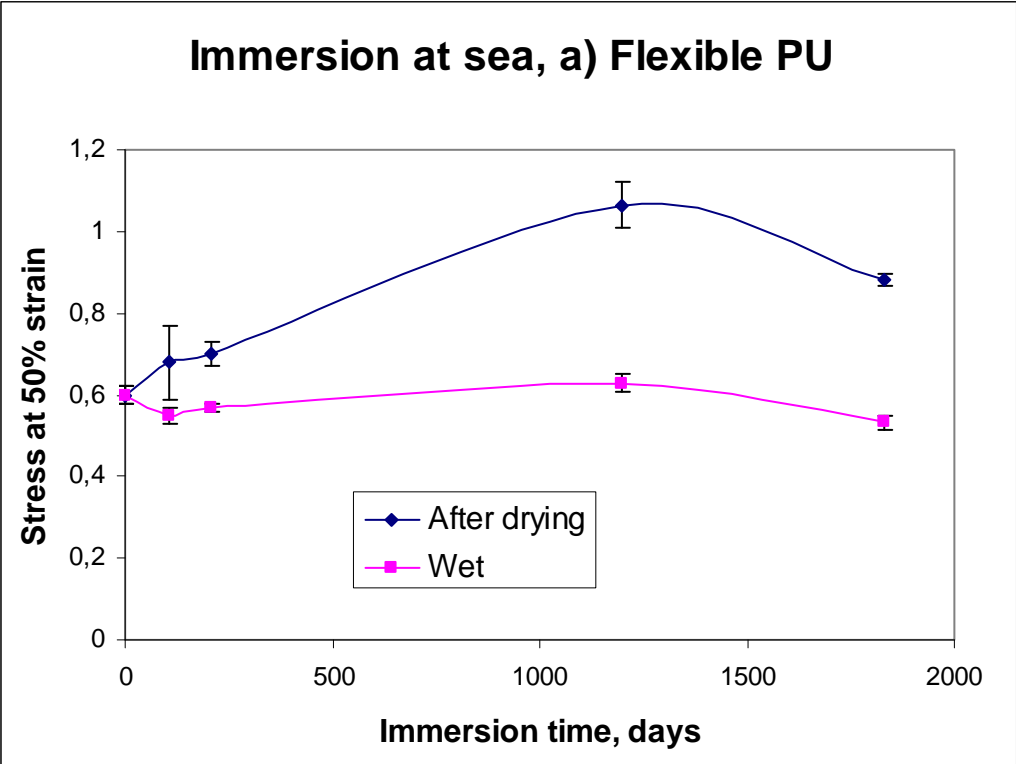
b)



c)

Figure 15. Samples after sea ageing

- a) 3 months, flexible PU
- b) 7 months, flexible PU
- c) 5 years flexible and rigid PU



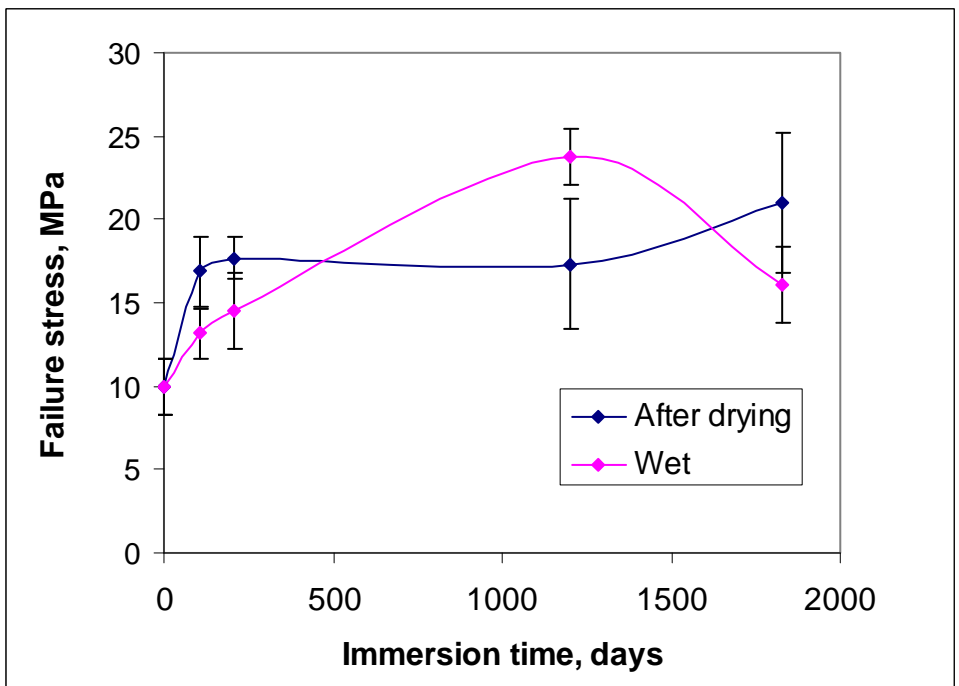
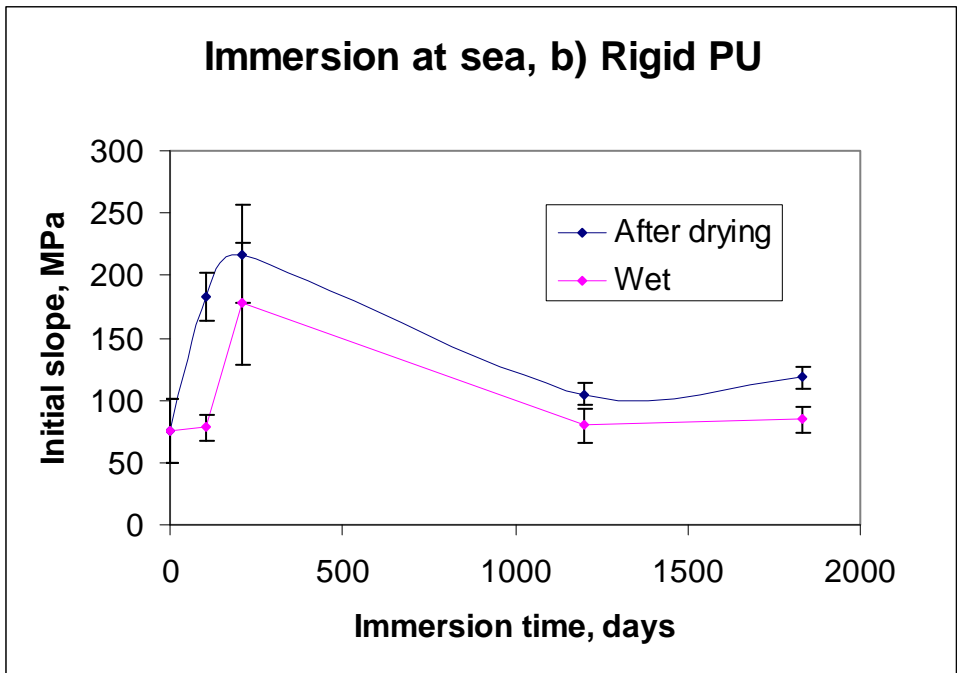
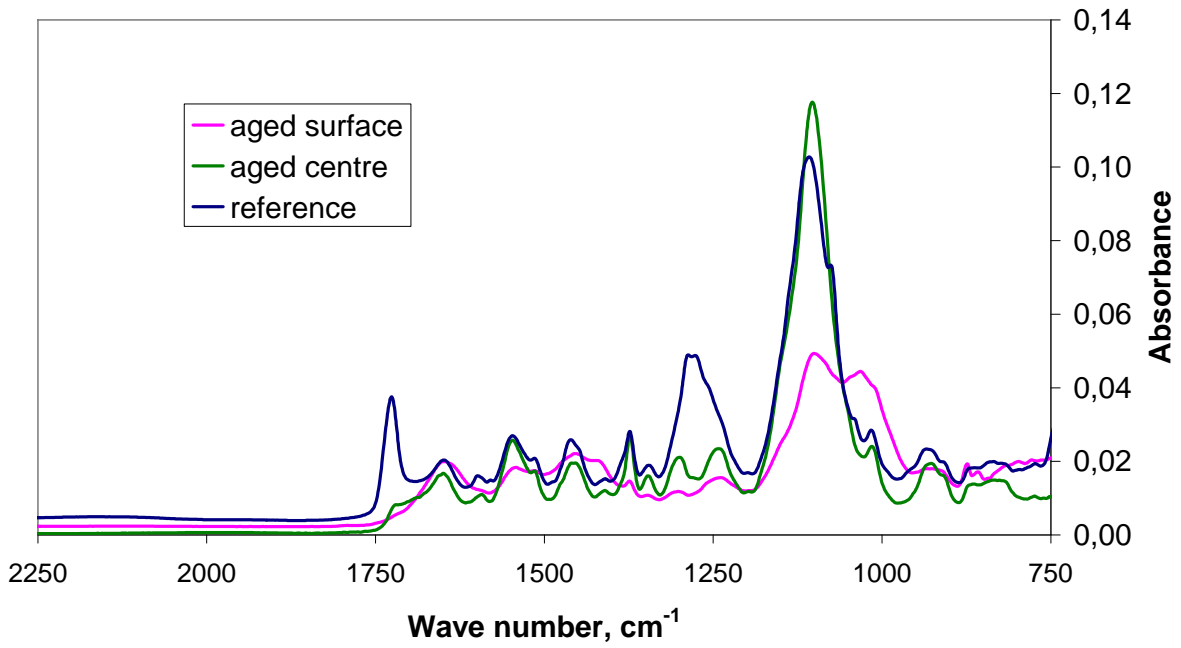


Figure 16. Results from sea ageing tests.

Flexible PU



Rigid PU

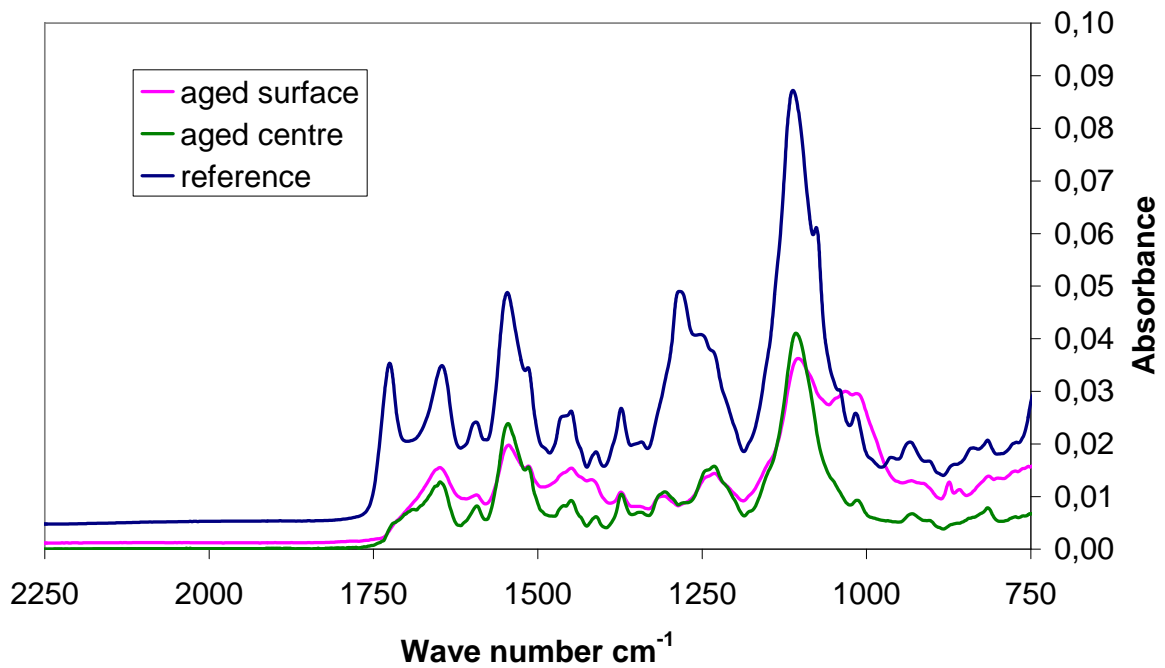


Figure 17. FTIR results from sample aged at sea for 5 years, surface and interior of specimens.

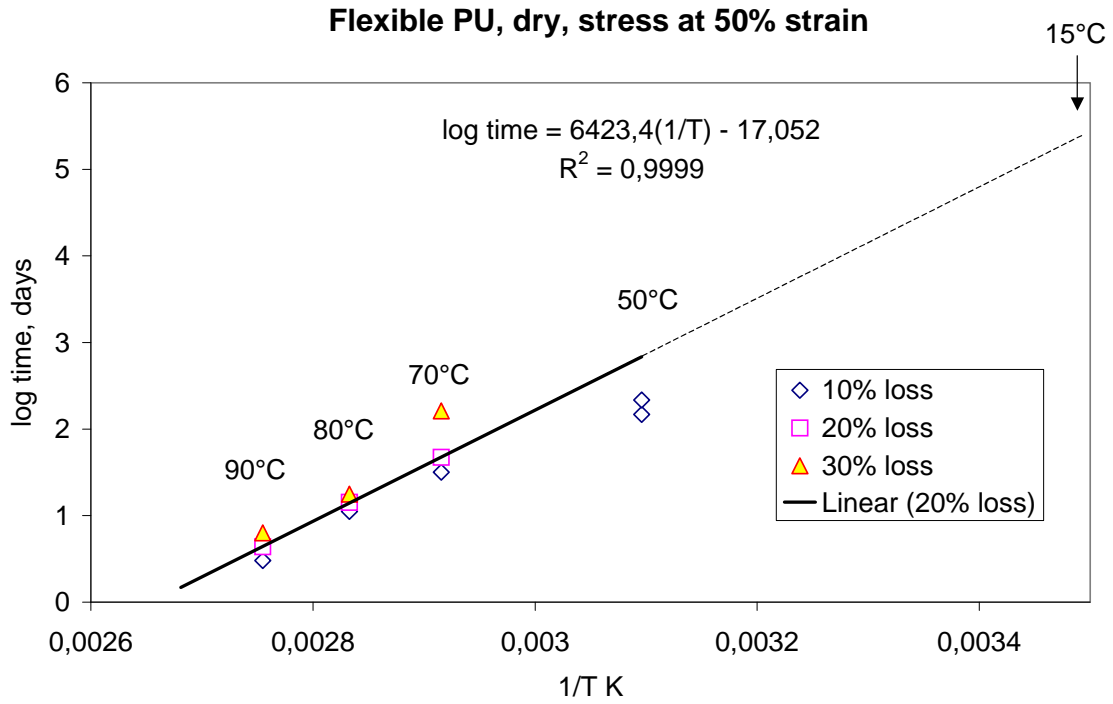


Figure 18. Arrhenius plots, flexible PU after drying, stress at 50% strain for different % reductions and extrapolation to 15°C.

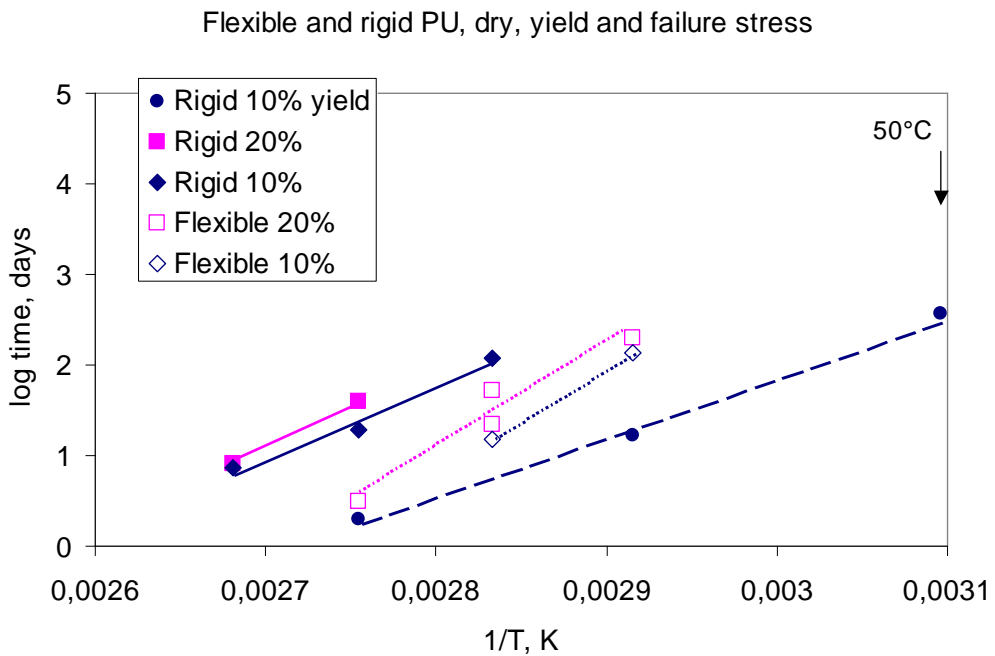


Figure 19. Arrhenius plots, flexible and rigid PU after drying, for 10 and 20% reduction in failure stress.