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**Investigation of
Degradation of LD-
Polyethylene in Contact
with Wet Concrete and
in Moist Air under
Accelerated Conditions**

Abstract

LDPE, unstabilized and stabilized with phenolic antioxidant or HALS, was subjected to accelerated ageing at 70, 80 and 90 °C in the environment of wet concrete and in moist air. The degradation was studied with the aid of elongation at break measurements, carbonyl index and induction temperature. The activation energies depend not only on the stabilization system but also on the environment. The rate of degradation in wet concrete environment at ambient temperatures was much higher than in moist air. Even unstabilized film was degraded faster in contact with wet concrete, probably due to the catalytic action of metal ions in the concrete. The carbonyl index measurements showed a poor correlation with elongation at break measurements. A good correlation has been achieved by induction temperature measurements. The degraded materials having their elongation at break decreased by 50 %, showed an induction temperature which corresponds to the value of the unstabilized polyethylene.

Key words: polyethylene, activation energy, accelerated ageing, wet concrete environment.

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1 Introduction

The cost-effective use of polymeric materials such as for example polyethylene (PE) in construction products, depends on the ability of these materials to resist deterioration of their mechanical and physical properties over long periods of time, often 50 years or more. For this reason, it is important to have test methods for a reliable prediction of service life. It is, of course, essential that the test designer do not induce any other degradation mechanisms than those occurring under in-use conditions. Each of the most important degradation factors must be considered to generate service life data, since the service life of a material is a function of the degradation factors acting on it during the different stages of its life cycle. In actual service, these degradation factors may also interact to increase the rate of degradation (synergistic effects) or less often to decrease the rate (antagonistic effects).

Polymer materials are oxidized by atmospheric oxygen like most other organic compounds. This process is called autooxidation. Antioxidants are used to minimize the rate of oxidation. The term polymer degradation denotes, in the case of PE, changes in physical and mechanical properties caused by autooxidation and other processes involving bond scission in the backbone of the macromolecules as well as crosslinking. PE-materials undergo oxidation reactions with atmospheric oxygen which is the main reason for the degradation in service. To prevent the oxidation, the addition of antioxidants such as hindered phenols and amines is widely used, which retards oxidation and thus the ageing. The main mechanism of the oxidation reactions and stabilization is well known and described [1,2,3]. The problem with physical depletion of the stabilizers by migration, extraction, etc. has also been investigated [4,5,6].

PE-films, foils and sheets are commonly used in buildings as construction films, vapour barriers, damp-proof membranes, safety sheets, parquet floor underlay, ground sill insulation, etc. In certain constructions, these products are in contact with wet concrete during their service life. The alkaline environment created by wet concrete may accelerate the degradation due to chemical or physical depletion of stabilizers which leave the material unprotected against autooxidation. Some components in concrete, e. g. chromium and iron ions, may also accelerate the degradation. It is known that metals which form two ions of similar stability and whose oxidation numbers differ by one (e. g. $\text{Fe}^{2+}/\text{Fe}^{3+}$) are the most active catalysts for autooxidation due to the increased rate of hydroperoxide decomposition [2].

In this investigation it is demonstrated how low-density polyethylene (LDPE) film, stabilized with common stabilizers is affected by prolonged action of wet concrete. A comparison is made to films exposed only to moist air. The possibility of life time prediction using the accelerated ageing method presented is also shown, as well as evaluation of activation energies and acceleration indexes.

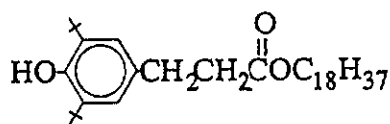
2 Experimental

2.1 Materials - PE-films

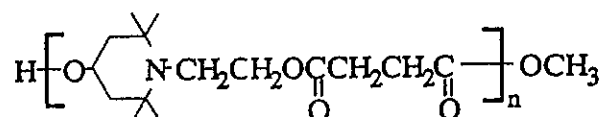
The material used in this study was low density polyethylene (LDPE) from Neste Oy - NCPE 6600 with melt flow rate $MFR_2 = 0,3 \text{ g/min}$ and density 922 kg/m^3 . The films were manufactured by Neste Oy in Finland.

All films were approx. $200 \mu\text{m}$ thick and contained a process stabilizer. The films were additionally stabilized as follows:

- Film 1 contained no other stabilizer.
- Film 2 contained 0.1 % Irganox 1076 from Ciba-Geigy. Antioxidant of the phenolic type.
- Film 3 contained 0.1 % Tinuvin 622 LD from Ciba-Geigy. Polymeric light stabilizer of the hindered amine type (HALS).
- Film 4 contained 0.1 % Irganox 1076 and 0.1 % Tinuvin 622 LD.



IRGANOX 1076

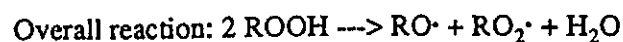
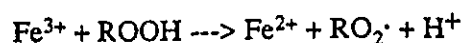
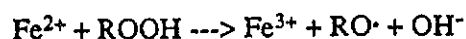


TINUVIN 622 LD

2.2 Materials - Concrete

The concrete material used in the experiments was of the quality K 25 with compression strength 25 MPa. Only fresh concrete was used. This was checked using phenolophtalein as alkali indicator.

The raw materials used in manufacturing of concrete (stones, sand, gravel and water) contain varying amounts of metal ions. It is known that transition metal ions and many metal complexes increase the rate of both thermal and photo-oxidation by catalytic action. The most active catalysts are such metals which form two ions of similar stability and whose oxidation numbers differ by one (e.g. ions of Fe, Co, Mn, Cu, Cr, Al, Ni, Ti). The ions catalyse the decomposition of hydroperoxides to free radicals according to:



The deleterious overall effect of metal ions lies in their ability to decompose otherwise stable hydroperoxides, resulting in the formation of reactive free radicals able to start new radical chain reactions [2,14,16,17,18,19].

The cement used in our tests contained about two weight percent iron oxide, Fe_2O_3 which is included in the mineral tetra-calcium-aluminium-ferrit. The material also contained between 0.3 and 0.4 weight percent iron sulphate, $\text{FeSO}_4 \cdot 2\text{H}_2\text{O}$ which is normally used in order to reduce Cr^{6+} (allergyforming) to Cr^{3+} . The qualitative X-ray analysis showed that besides iron, small amounts of Al, Ti and Mn could also be identified. The influence of iron in concrete on the degradation of PE will be investigated in forthcoming work.

2.3 Accelerated Ageing

Concrete cubes with dimensions 130x110x50mm were placed in a glass container with the dimensions 350x200x150mm. The container was filled with deionized water to a level of roughly 15 mm under the upper edge of the concrete cubes. Test pieces of the PE-films, size 170x125mm, were placed on the top of each of the submerged cubes and another cube was placed over the film in order to create a good contact between the wet concrete and the PE-film. An additional test piece of PE-film was placed on the top of each of the uppermost concrete cubes. The glass containers were covered with cover sheets of glass and placed in the heating cabinets at 70, 80, and 90°C. Throughout the tests, the water level was adjusted by refilling with deionized water.

2.4 Elongation at Break

A tensile test was carried out in accordance with Swedish standard SS 24 10 20 with the aid of an Instron 1122 Universal Testing Machine. Five strips of 15 mm width were taken out of each test piece. The speed of elongation was 500 mm/min and the clamping length was 100 mm. The elongation at break values presented are the arithmetic mean value of five measurements.

2.5 Thermal Analysis

A common way of quantitatively determining the concentration of the effective stabilizer in polyolefins is the isothermal oxidative induction time (OIT) test. Here, the DSC instrument is used to determine the time of a "thermal titration" of a stabilizer in oxygen at constant temperature. Unfortunately, this method gives no relevant information on the HALS stabilizer concentration. The method we used for the quantitative determination of the remaining amount of active stabilizer in the polymer was therefore based on the kinetic thermal analysis. This method, which exists as a Swedish standard method for plastics pipes (SS 3579, Method A), is based on the determination of the oxidative induction temperature (T_i), i.e. determination of initial temperature of the exothermic oxidation reaction (see figure 0). It has been shown [24] that for many stabilizers, the induction temperature increases approximately as a linear function of the stabilizer content up to about 0.1 % by weight.

Samples were analysed by DSC (Differential Scanning Calorimetry) using a Mettler DSC 30 TA 3000 instrument. The scanning parameters were: temperature range 50-250 °C, heating rate 10 K/min and the oxygen flow rate 50 ml/min.

2.6 IR Measurements

The IR measurements were carried out on a Cygnus 100 Mattson FTIR spectrophotometer. The absorption spectra were recorded on fourfolded films (0.8 mm total film thickness) with a resolution of 4.0 cm^{-1} .

The oxidative degradation of polyethylene is often determined by recording the intensity increase of the carbonyl absorption band at $1710 - 1720\text{ cm}^{-1}$ in the IR-spectrum [7-13,15,19,20].

A quantitative method to measure the degree of degradation is to relate the carbonyl absorbency to the absorbency of a reference band. For polyethylene, the overtone or combination band at 2019 cm^{-1} is usually used as reference band [20,21]. In our investigation, carbonyl index (CI) was calculated using

$$CI = A(1719\text{ cm}^{-1}) / A(2019\text{ cm}^{-1})$$

where A is the absorbency at a given wave number.

The phenolic antioxidant Irganox 1076 and the hindered amine light stabilizer (HALS) Tinuvin 622 also show characteristic absorption bands at 1740 respectively 1735 cm^{-1} in the IR-spectrum of the stabilized polyethylene.

2.7 Prediction of Service Life

Semiempirical prediction of the service life is usually based on the assumption that the degradation mechanism can be described by a simple model such as the Arrhenius equation. However, a complex reaction, involving a number of successive and parallel elementary reactions may not follow the Arrhenius equation strictly. An extrapolation of the rate of changes in some property, made on the basis of this equation may lead to a great error in life time prediction. Another source of error can arise during accelerated test conditions, e.g. if an antioxidant disappears through chemical reactions during the test, while under service the antioxidant depletes via migration or extraction.

Most studies have been carried out under single stress conditions. However, it has been shown [22] that conducting single stresses consecutively does not give the same results as tests with applied stresses simultaneously. In this study we have tried to take into account most of the factors which can be responsible for the material degradation under service life conditions and applied them simultaneously. The acceleration was achieved by a moderate increase of temperature and a constant influence of wet concrete.

In our system the materials had the possibility to undergo more than one process in parallel. The ageing processes in such a system consist of many reactions, both chemical and physical. We considered, however, a simplified model where antioxidants were consumed in two main streams of concurrent reactions: one related to reactions depending on atmospheric oxygen and the second one depending on reactions caused by wet concrete. As such reactions involve nonequilibrium processes, the following equations may not be self consistent in a thermodynamic sense. The equations can, however, be used as a first approximation.

The experiments which were run at three controlled temperatures gave the information about the time needed for the materials to reach 50 % retention of the elongation at break (t_{50}). The logarithm of time was then plotted versus $1/T$ according to the equation:

$$\ln t = A + E_a/RT$$

t stands for time, A is the frequency factor, R is the universal gas constant, T denotes the temperature in Kelvin and E_a is the activation energy. From the slope of the curves the activation energies for the materials were determined. The prediction of the life times at the "in use" temperature were calculated using the equation:

$$t_w = t_e * \exp \{ E_a/RT * (T_e - T_w)/T_e T_w \}$$

t_w and t_e stands for the time (t_{50}) at working resp. elevated temperature, T_w and T_e are working resp. elevated temperature and E_a is activation energy.

3 Results and Discussion

The samples have been characterized using the following techniques: tensile test, thermal analysis and infrared spectroscopy. A significant feature of our measurements has been that the test results showed an increasing scattering and an increasing standard deviation with the increased degree of degradation of the samples. We have also observed distinct marks for the non-uniform degradation of the aged materials by occurrence of spots of discoloured material.

It is known that below the melting point of a semicrystalline polymer, the nature of the polymer offers great opportunity for inhomogeneous antioxidant distribution. Billingham et al. [23] presents a couple of investigations dealing with problems of non-uniform degradation in polyolefines. It is shown e.g. that oxidation in polypropylene can be localised at "trigger-spots" which are associated with iron particles introduced during processing. Existence of localised regions, much more sensitive than the average to degradation, is also demonstrated. The existence of such regions are explained by inhomogeneous antioxidant distribution or by localised concentration of impurities. In our experiments, an additional source of non-uniform degradation was present, viz. the influence of such inhomogeneous material as concrete.

3.1 Ageing of Film 1.

A relatively long ageing time and a high induction temperature (T_i) of film 1 indicate a good efficiency of the process stabilizer used. A comparison with an unstabilized film (see fig. 1) shows the magnitude of the durability improvement by the addition of this process stabilizer. At 90 °C the time to 50 % retention of elongation at break (t_{50}) for film 1 increases sixfold in the environment of wet concrete and more than fourfold in moist air compared with the unstabilized films.

It is also interesting to note that t_{50} of the non-stabilized films in moist air at 90 °C is about three times longer than the corresponding value for the films in the wet concrete environment. As the materials contain no additives this result indicates that components originating from the concrete, probably metal ions, significantly accelerate the degradation.

The change of the elongation at break of film 1 versus the ageing time at various temperatures is presented in figures 2a and 2b. From the figures the ageing time to 50 % loss of elongation at break (t_{50}) was evaluated and plotted versus $1/T$ in an Arrhenius plot (fig. 8). Linear relationships were obtained. The calculated activation energy (E_a) was 142 kJ/mole for film 1 under the influence of wet concrete and 120 kJ/mole for the same film under the influence of moist air only.

The degradation of the films has also been followed by measurements of the carbonyl index. The results, presented in figures 3a and 3b, indicate that monitoring the degree of degradation by measuring the formation of the non-volatile carbonyl oxidation products does not correspond to the results from elongation at break measurements. The materials with only 50 % retention of the elongation at break show an insignificant increase of the carbonyl index. Even completely degraded materials with no mechanical strength show carbonyl indexes less than 2.

The depletion of stabilizers and the degradation of the materials have also been monitored by induction temperature (T_i) measurements. The measurements showed that various stabilizers gave different T_i values at the same concentration level and that T_i decreases during the ageing process. T_i continues to decrease even when the stabilizer is completely used up. In order to establish a T_i value for LDPE without stabilizers the measurements have been performed on various non-stabilized materials as well as on materials where all additives have been removed by dissolution and precipitation procedure. This value has been established to 206 ± 1 °C.

The results of T_i measurements on film 1 are shown in figures 4a and 4b. It is interesting to point out that when a material has reached the degradation level corresponding to 50 % retention of elongation at break, the respective T_i value is on the level of non-stabilized material which indicates that all stabilizer has been used up. The remaining time to complete loss of mechanical strength is then very short.

3.2 Ageing of Film 3

The change of elongation at break of film 3 (containing 0.1 % Tinuvin 622) as a function of ageing time is presented in figures 5a and 5b. From the figures, the t_{50} 's were evaluated and plotted in the Arrhenius diagram (fig. 8). The calculated activation energies were 115 kJ/mole in wet concrete environment and 110 kJ/mole in moist air.

The results of the carbonyl index measurements are presented in figures 6a and 6b. Also in this case the carbonyl index increased only slightly for the degraded materials with only 50 % retention of the elongation at break. The formation of carbonyl oxidation products is different in wet concrete environment, compared with moist air, for film 3. In wet concrete environment the carbonyl index, which is a measure of the intensity of the peak at 1719 cm^{-1} , increases up to a max. value which is less than 2 and declines thereafter. At the same time, many other peaks corresponding to the various oxidation products can be distinguished namely : 1720 cm^{-1} (keton RCOR), 1702 cm^{-1} (carboxylic acid RCOOH), 1738 cm^{-1} (ester RCOOR), 1763 cm^{-1} (peroxy ester RCOOOR), 1787 cm^{-1} (peroxy acid RCOOOH) and 1570 cm^{-1} (carboxylate COO-) [25,26]. Some of these bands occur even in the material aged in moist air.

The results of the T_i measurements of film 3 are presented in figures 7a and 7b. The T_i values decrease with increased ageing time and in a similar way as film 1 the values reach the level of an unstabilized film after the ageing time corresponding to 50 % retention of elongation at break.

3.3 Ageing of Films 2 and 4

Thermooxidative stability of polyethylene can be increased considerably by addition of high molecular weight HALS to the base of stabilization [27,28], However, both synergistic and antagonistic effects have been reported.

Film 2 in our investigation was stabilized with a process stabilizer and 0.1 % Irganox 1076 which is an antioxidant of the phenolic type. Film 4 was stabilized as film 2, but contained in addition 0.1 % Tinuvin 622 (HALS). The results of the elongation at break measurements as a function of ageing time in wet concrete environment, at 90 °C, are presented in figure 9a. For comparison, curves corresponding to unstabilized film (film A), film stabilized with a process stabilizer (film 1), and film stabilized as film 1 + 0.1 % Tinuvin 622 (film 3) are included. The t_{50} values for the films in wet concrete environment at 90 °C are the following:

Film A	> 3 days
Film 1	18 days
Film 3	58 days
Film 2	300 days
Film 4	300 days

These results show the magnitude of the durability improvement of PE-film by the use of various stabilizers and especially the contribution of the HALS. It is shown that the addition of Tinuvin 622 improves the stability of the film containing process stabilizer only. However, the addition of Tinuvin 622 to the film stabilized with Irganox 1076 does not significantly influence the durability of the film in wet concrete environment.

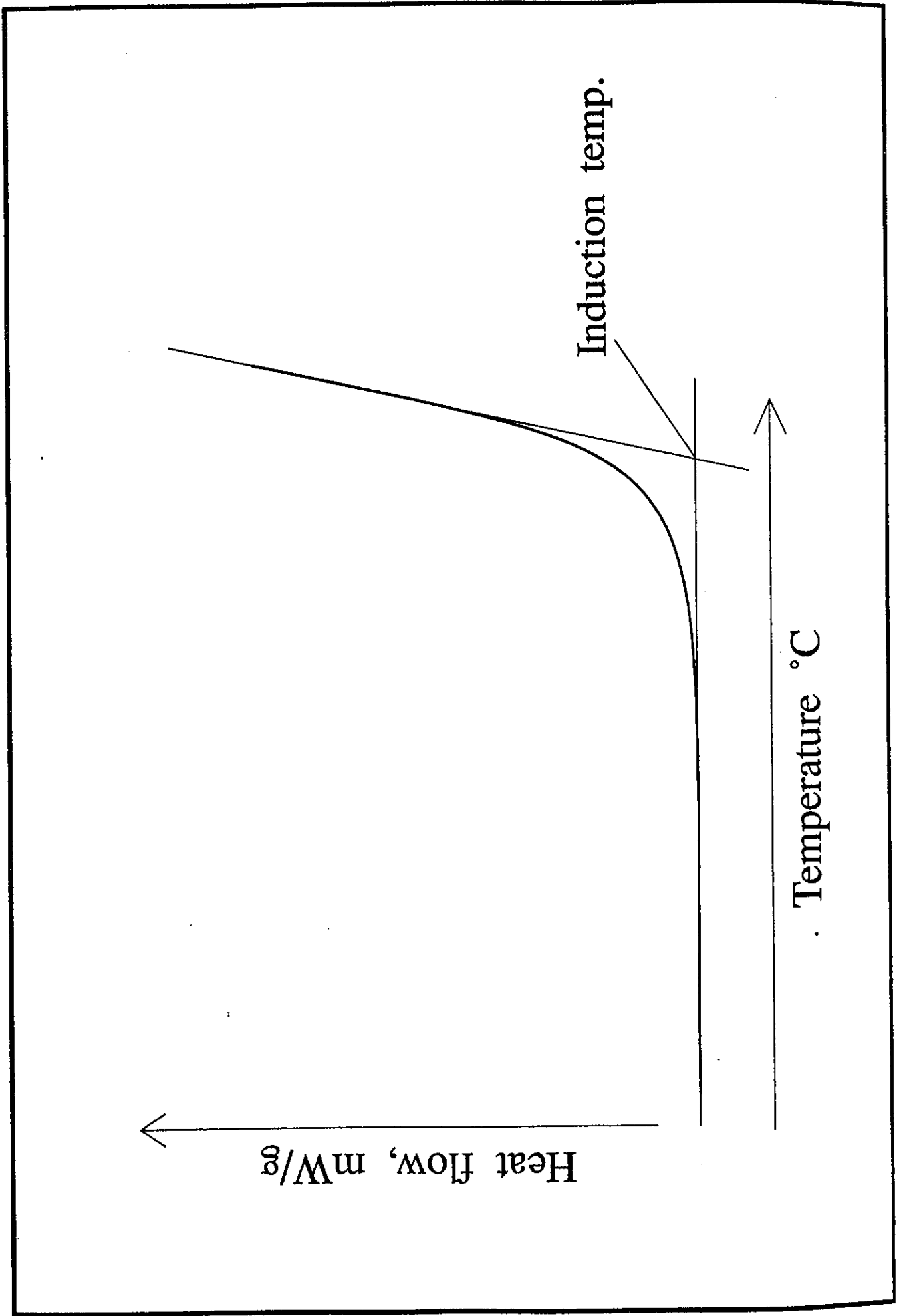
The results of the T_i measurements of film 2 and 4 are shown in figure 9b. The T_i values decrease with increased ageing time and reach the level of an unstabilized film after an ageing time corresponding to 50 % retention of elongation at break.

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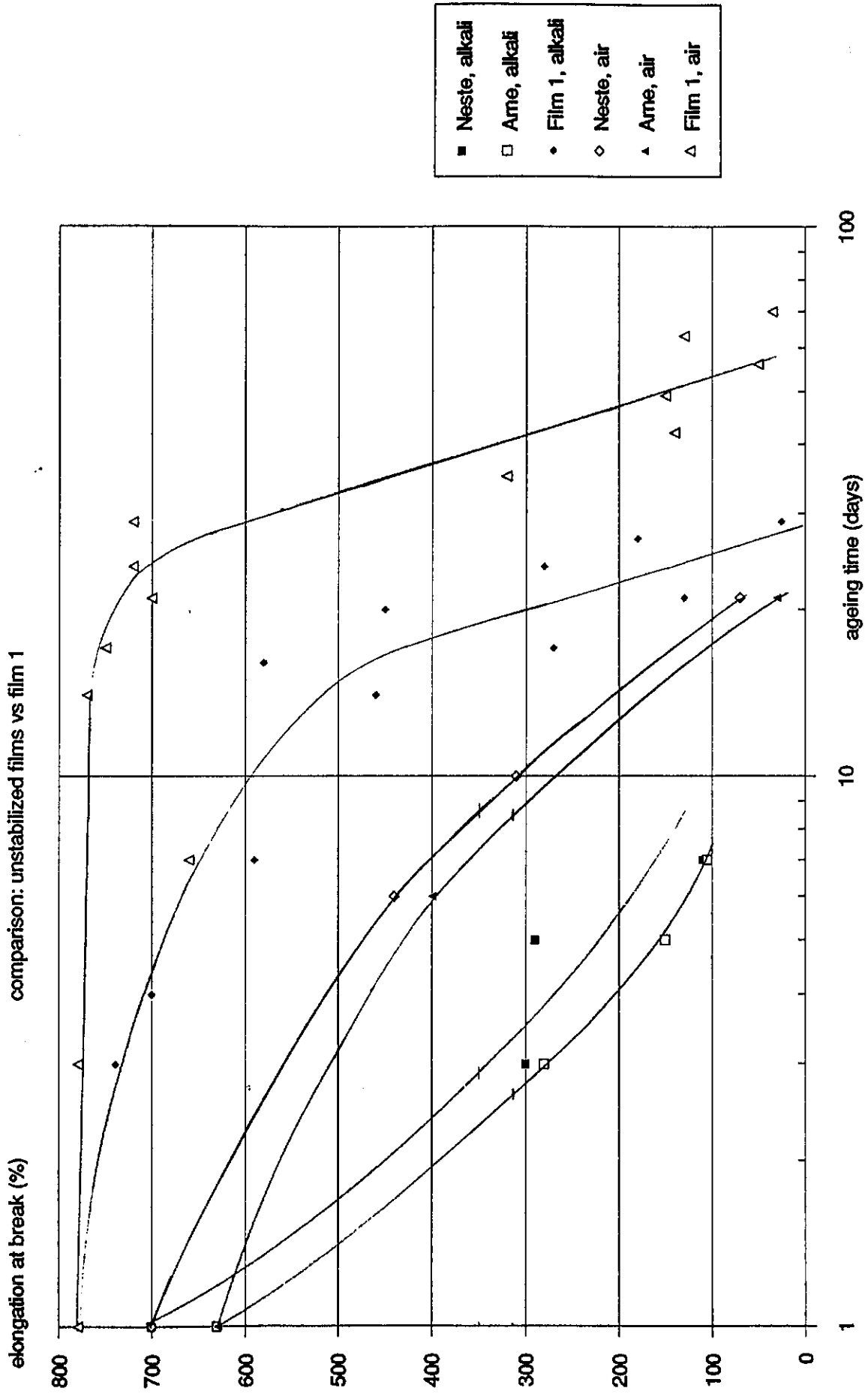
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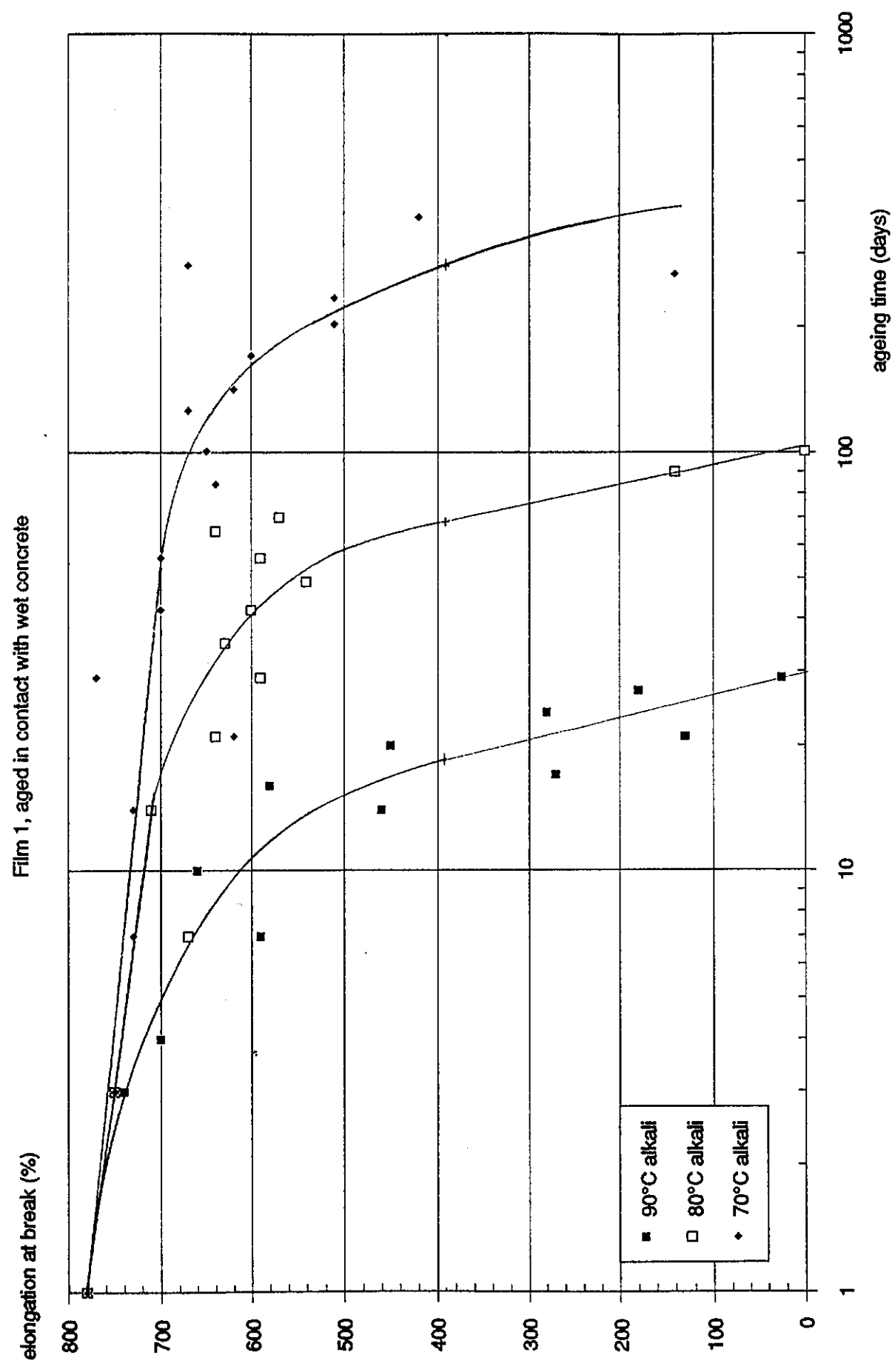
Figur 0



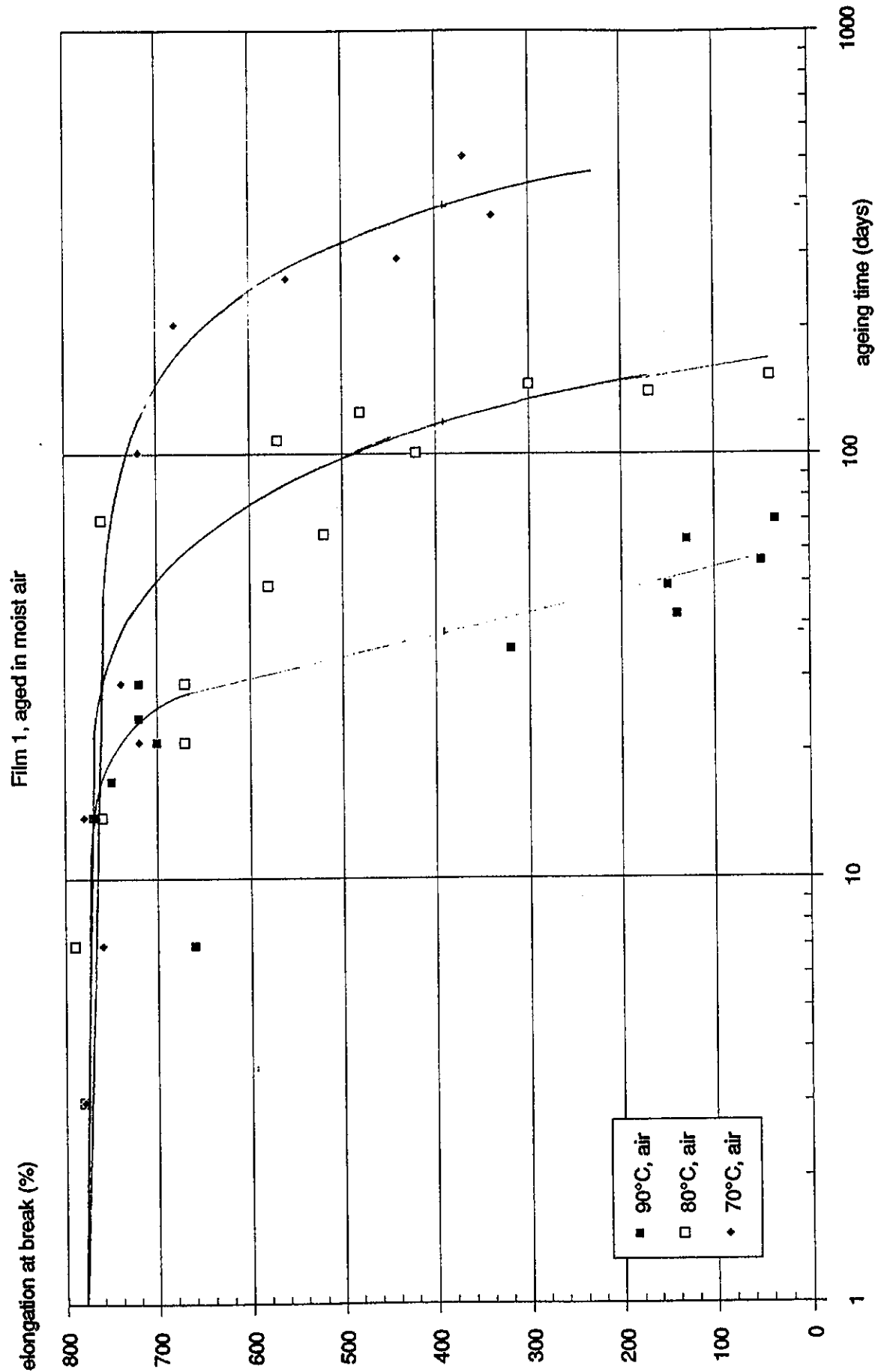
Figur 1



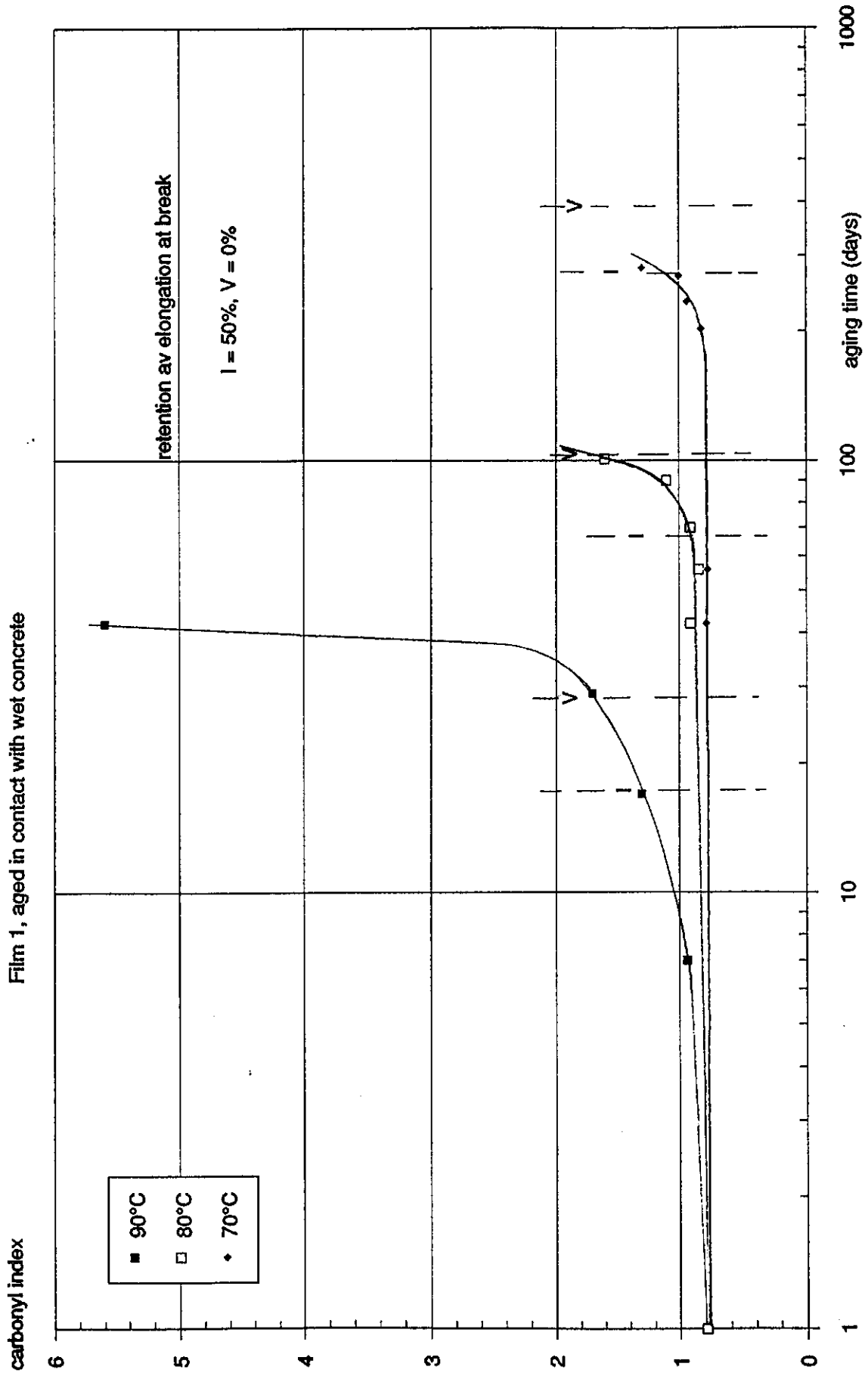
Figur 2a



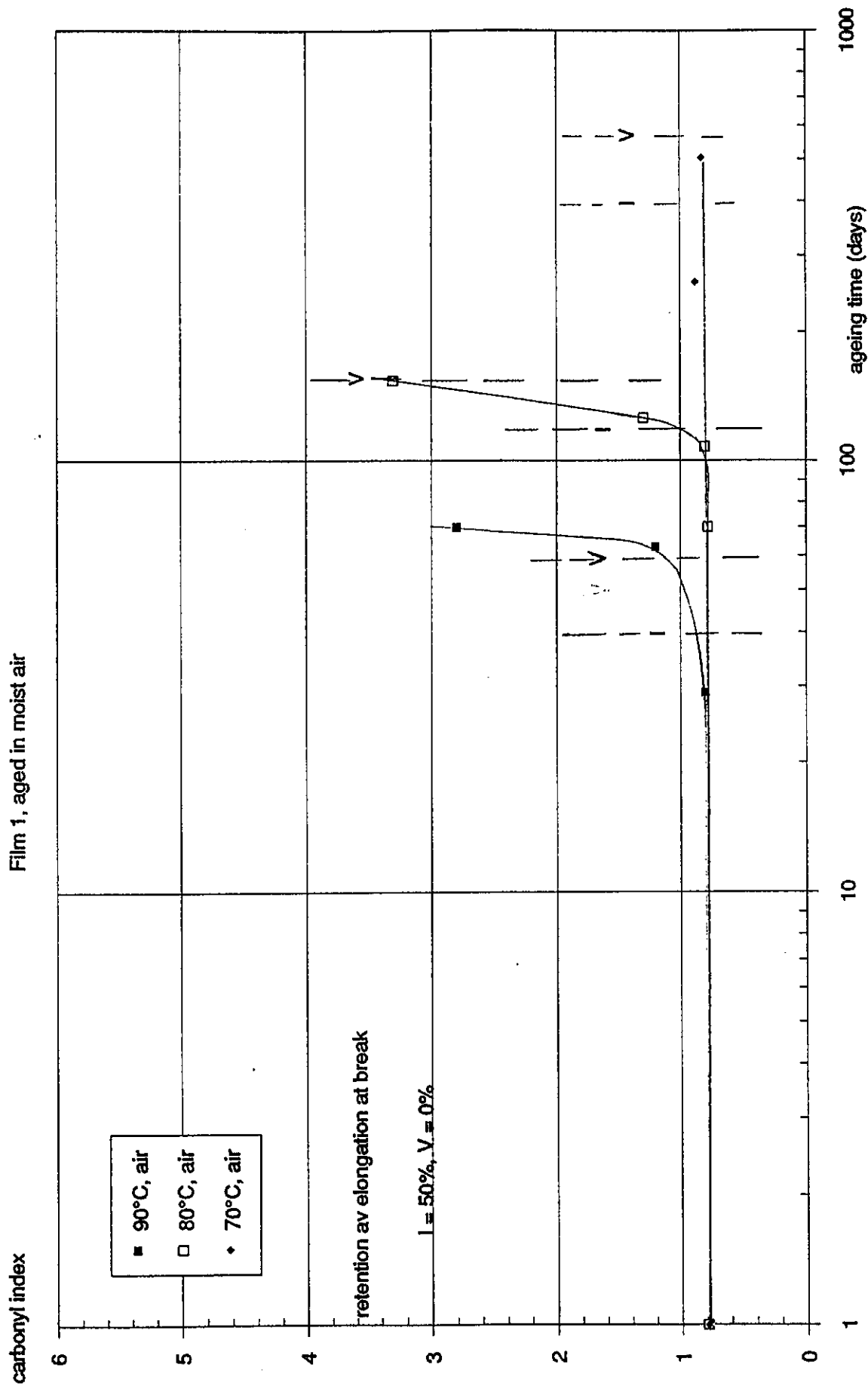
Figur 2b



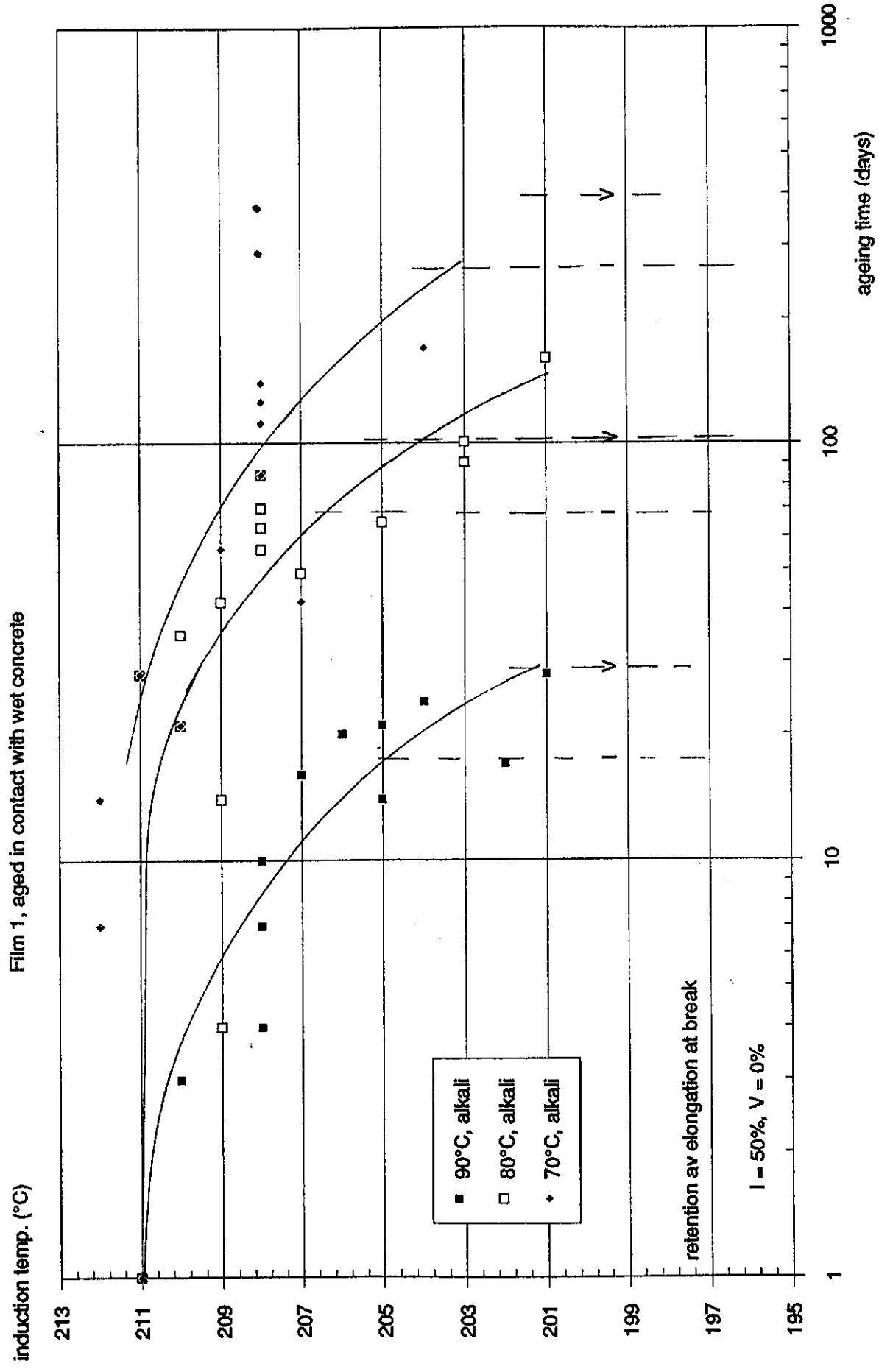
Figur 3a



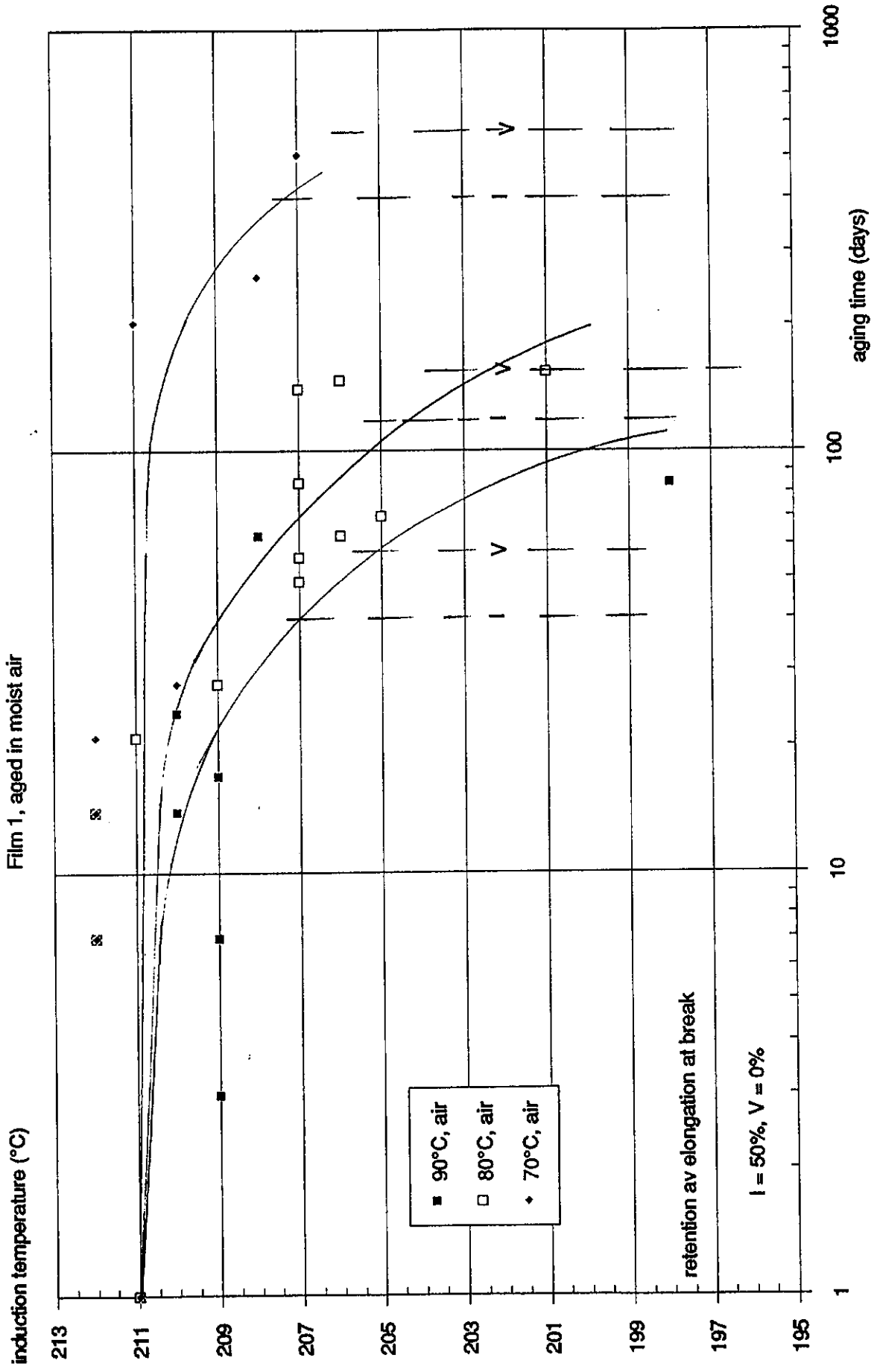
Figur 3b



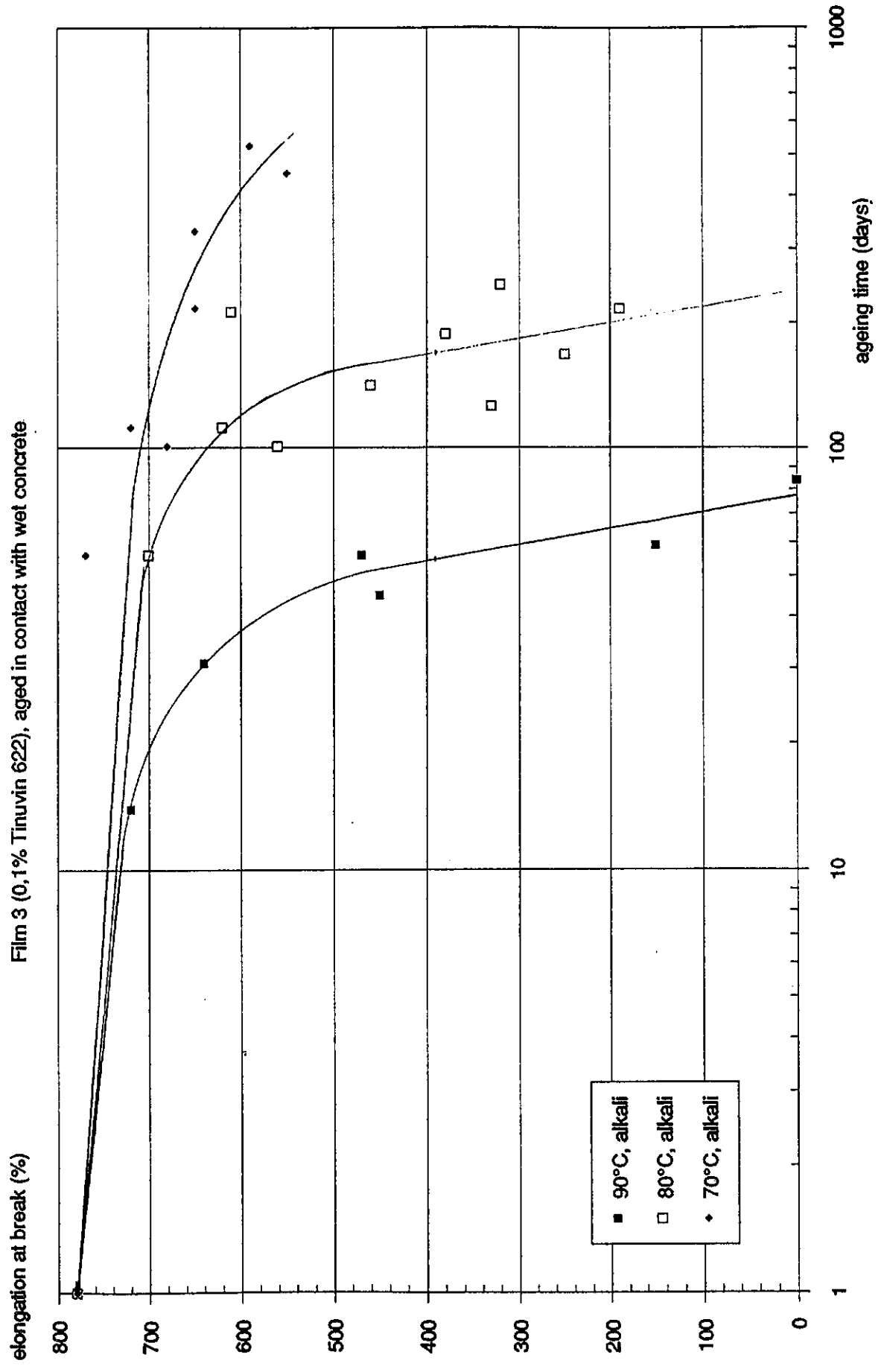
Figur 4a



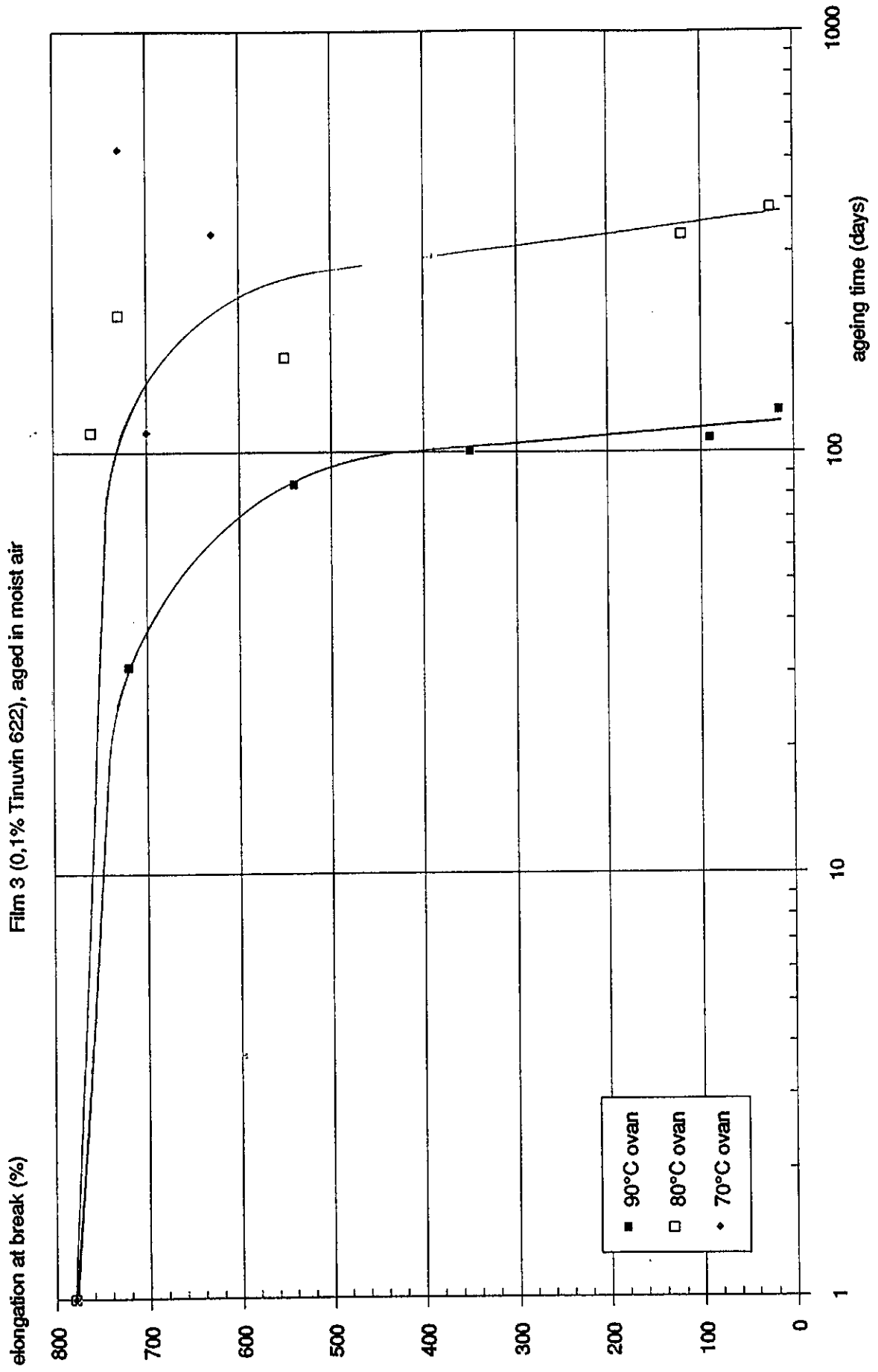
Figur 4b



Figur 5a

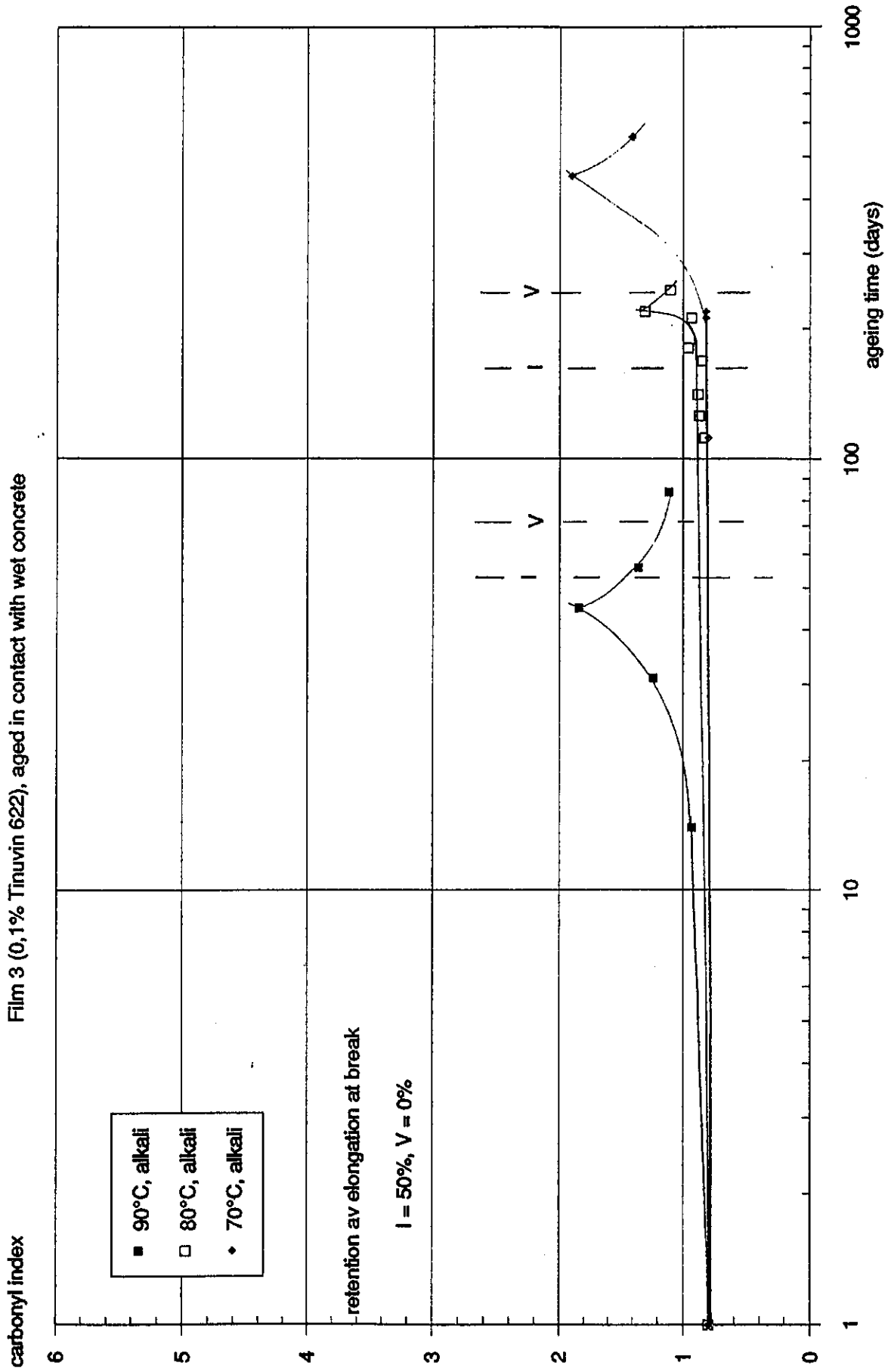


Figur 5b



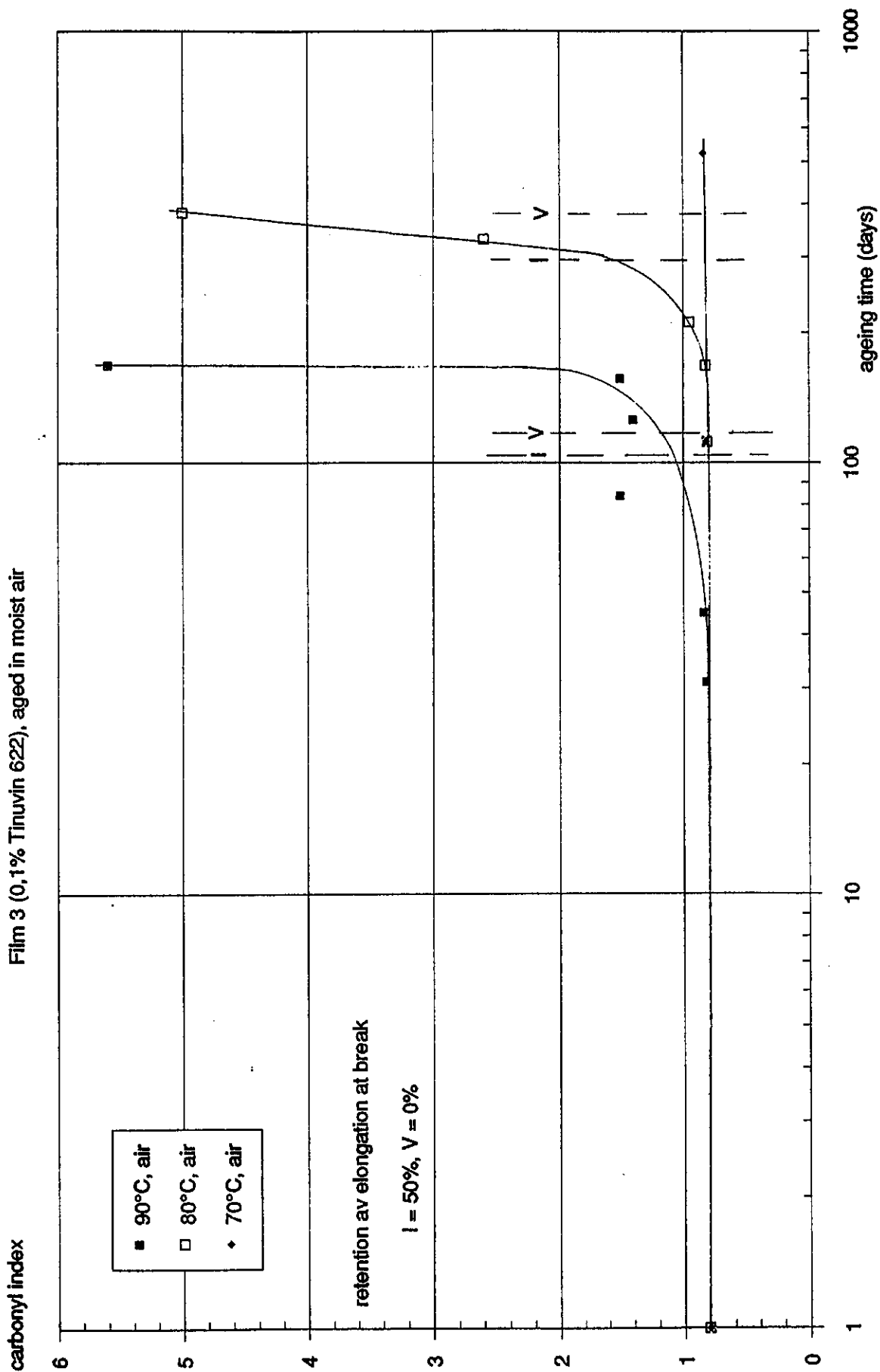
Figur 6a

Film 3 (0,1% Tinuvin 622), aged in contact with wet concrete



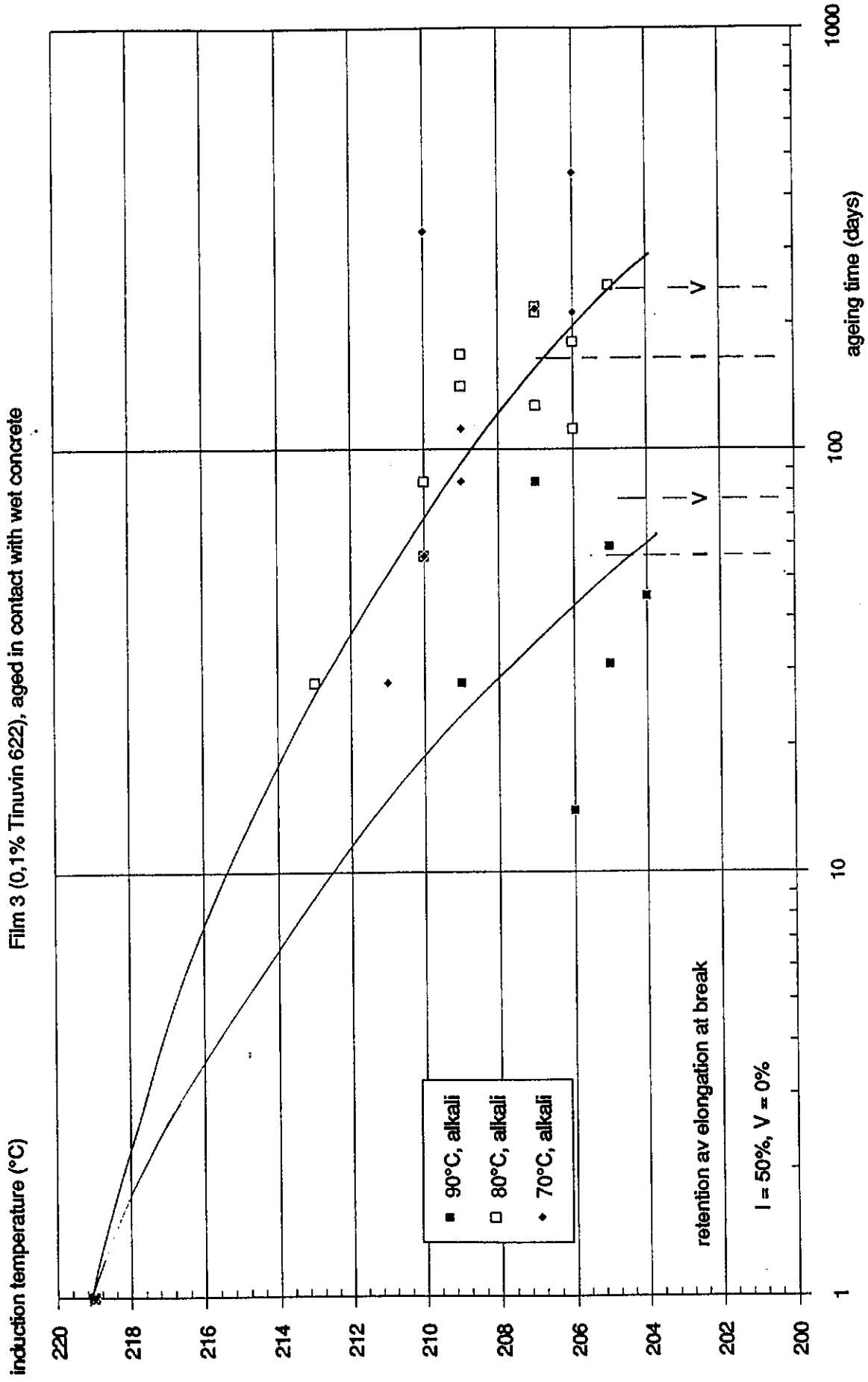
Figur 6b

Film 3 (0,1% Tinuvin 622), aged in moist air

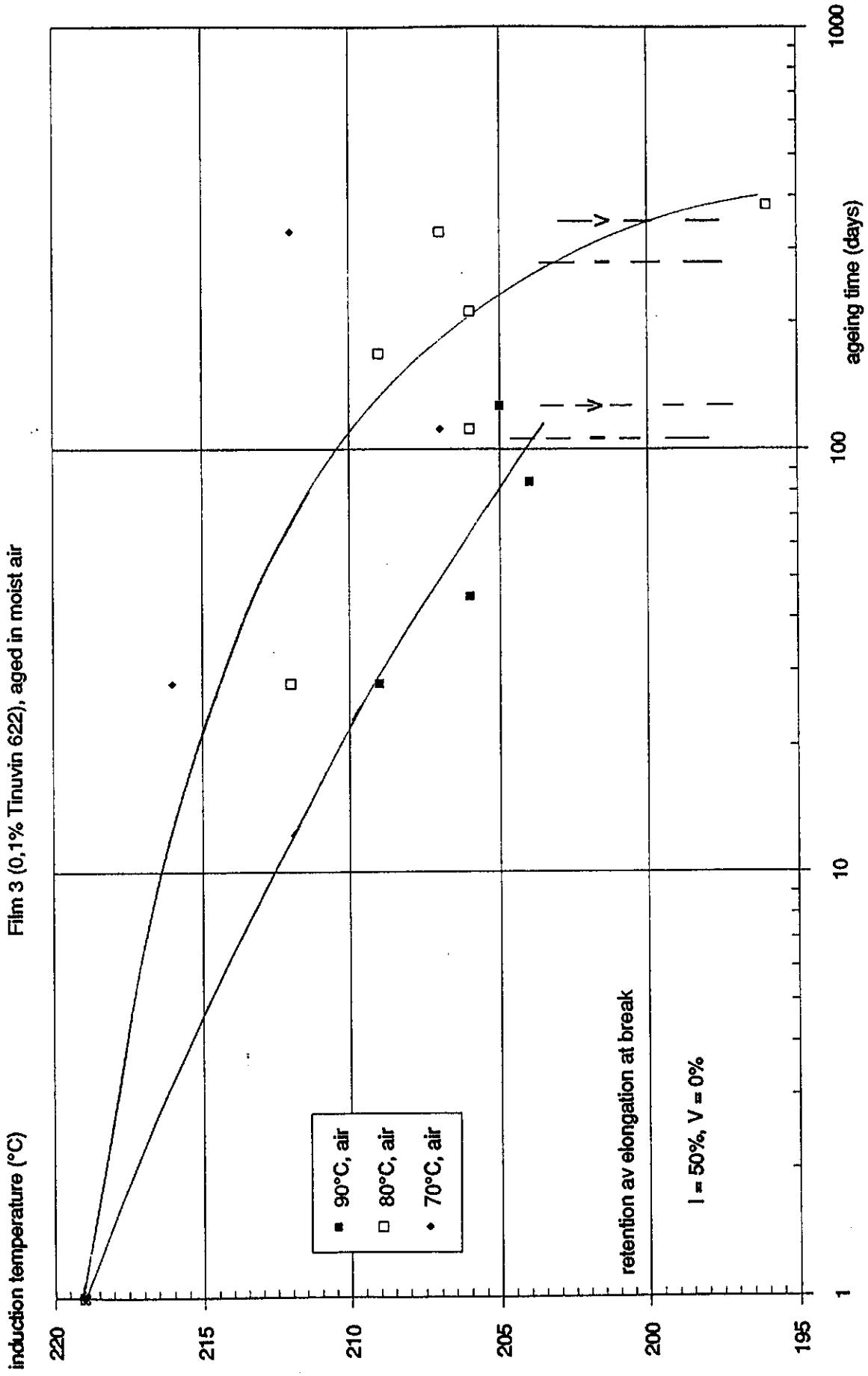


Figur 7a

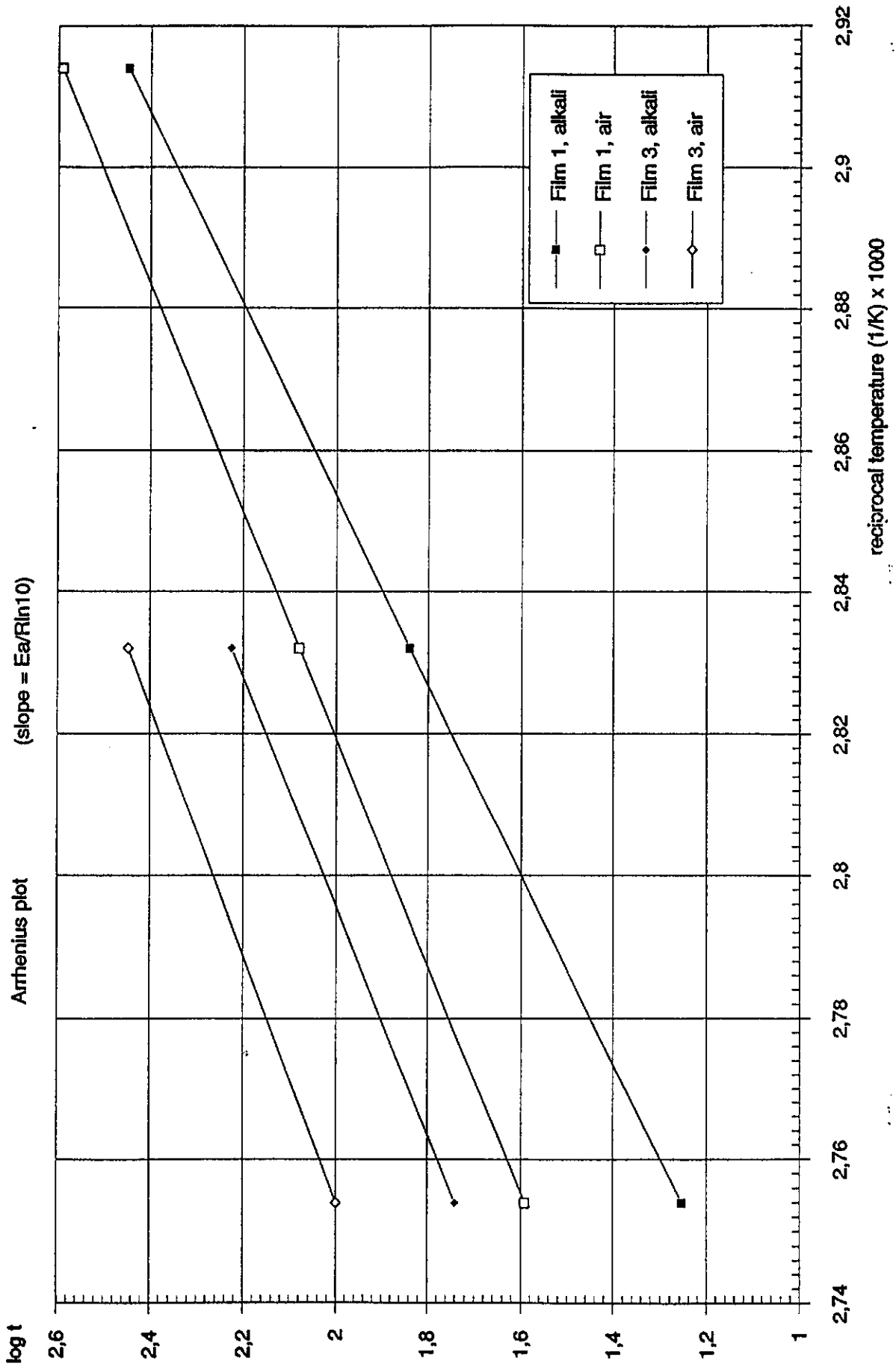
Film 3 (0,1% Tinuvin 622), aged in contact with wet concrete



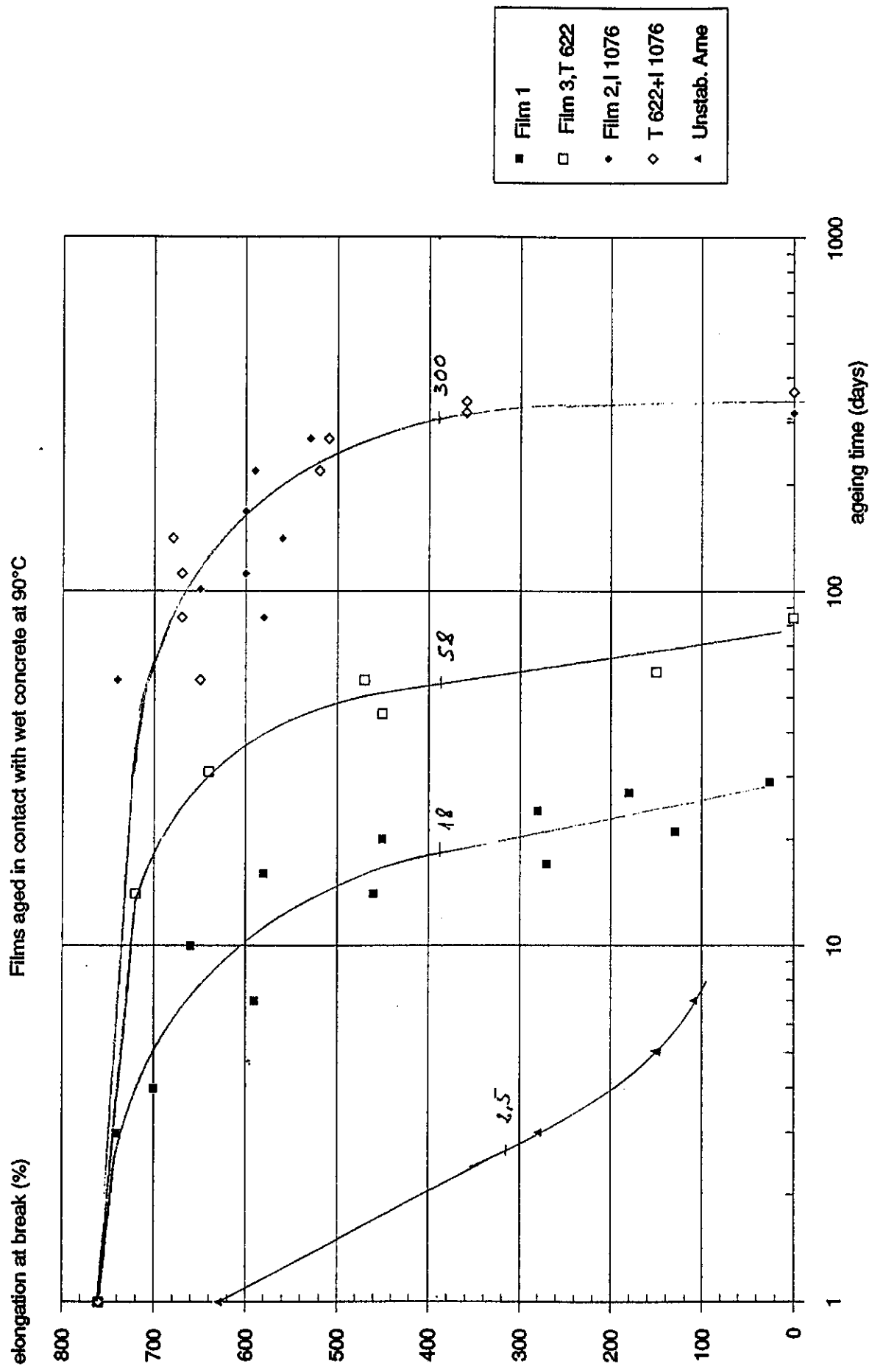
Figur 7b



Figur 8



Figur 9a



Figur 9b

