REPORT TO THE WATER RESEARCH COMMISSION

EVALUATING THE LONG TERM USE OF POLYPROPYLENE FOR HOT AND COLD WATER PIPING

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EXECUTIVE SUMMARY

Polypropylene pipes are currently used for domestic hot and cold water installations. Polypropylene will also be the system of choice for low cost housing applications. Despite the widespread use of this piping not enough is known about the long term behaviour and ageing of such pipes, especially in hot water applications. This study used laboratory techniques to explore the quality of locally produced pipes in comparison to an imported pipe (from Germany). The objectives of this investigation were to evaluate failure mechanisms experienced in practice; evaluate the long term thermal stability and creep properties of these pipes, and to generate performance data required for quality control or acceptance tests.

Material Characterization

Block copolymer pipe grades (PPH 4122 and PPH 2222) are currently manufactured locally and "pipe grade" material (Tipolene) is imported from Hungary. Analysis of some pipes clearly indicated that convertors have also used non-pipe-grade materials. Also, in many instances insufficient or no stabilizer was added to the polymer. Such pipes can not be expected to provide trouble free service over the required lifetime.

Failure Analysis

Approximately 60 samples of field failures were investigated. The major failure modes, their frequency and proposed remedial actions are given in Table 1. Despite the evidence of defective raw materials being used (18%), the most frequent reason for field failures was incorrect installation procedures (32%). Poor quality processing or incorrect manufacturing procedures caused 21% of the failures investigated. Problems were also encountered with gas or oil pollution of water inside pipes (14%) and failure of fittings (8%). These results indicate that a comprehensive approach will be required to remedy this situation.

Thermal Stability

Many field samples failed by embrittlement due to oxidative degradation. In all these cases it was shown that very little or no stabilizer was present. For well stabilized pipes, extrapolation of Differential Scanning Calorimetry (DSC) data and oven ageing tests indicates that the pipes should have excellent dry heat stability. Predicted service life in air is much higher than specified requirements of >30 years at 25°C and >3 years at 80°C.

Creep Life

The service life of polypropylene pipes is limited by two independent failure modes. Creep rupture is a ductile failure mode occurring at high stresses and short life times while "brittle" craze failure occurs at low stress levels and longer times. According to the literature, the time-to-failure for the latter mechanism is more sensitive to parameters such as molecular weight, molecular weight distribution and crystal morphology than the ductile failure mode. Quality testing should therefore test in the "brittle" fracture regime as this mode limits service life under normal operating conditions.

These trends are summarized in Figure 1 showing the shift in the failure envelopes under unfavourable conditions. Such conditions may involve the following processing and material factors:

- **Surface flaws** (e.g. scratches or notches)
- **Decrease in molecular weight** (Using the wrong grade of polymer, degradation during processing, use of recycled material or oxidative degradation.)
- **Unfavourable morphologies** e.g. orientation effects (e.g. too fast haul-off), large spherulites etc.
- **Stress concentrators** such as contaminants, incompatible filler or pigment particles, use of incompatible carriers in master batches etc.

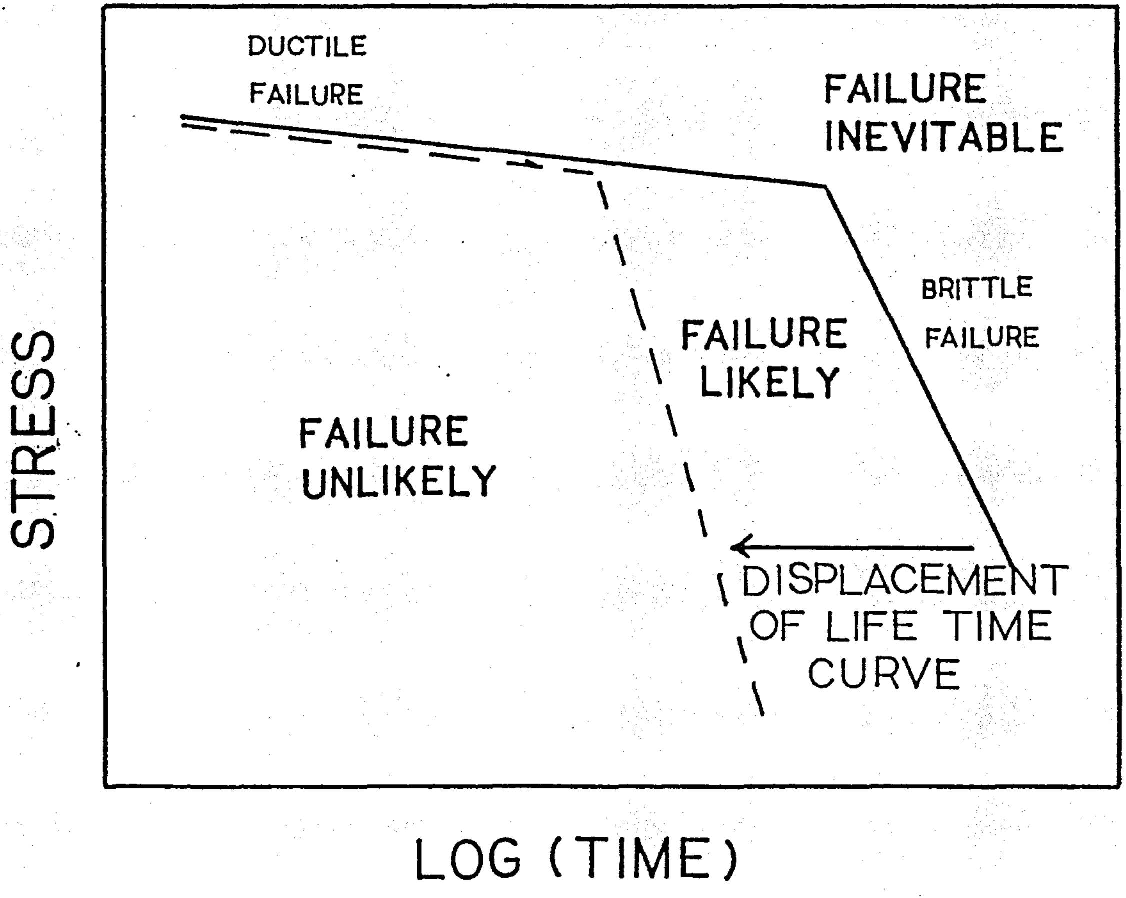

Figure 1: Schematic illustration of changes in the stress time-to-failure envelopes

Actual performance of locally produced pipes was inferior to that of pipes obtained from Germany. With few exceptions, they all fail prematurely relative to the relevant creep curve predictions. The available information suggests that poor processing techniques are responsible for this situation. Locally produced pipes show excessive orientation effects and properties vary anisotropically along the hoop direction in some cases.

Quality Control Testing

To ensure high quality of locally produced pipes as well as adequate service life, the following requirements must be met:

- **Raw Material.** The raw material must be a suitable pipe grade material. This requires a very high molecular weight (Mw ≈ 500 000) and nucleating agents which will ensure a sufficiently fine spherulitic crystal morphology. Under practical conditions the polymer identity may be verified using Infrared (IR) spectroscopy and the molecular weight checked using Melt Flow Index (MFI) measurements.

- **Stabilization of Raw Material.** The raw material must be adequately stabilized against oxidative degradation (exacerbated by elevated temperatures) and UV radiation. The level of antioxidants in the material can be determined by isothermal or dynamic oxidation induction techniques using Dynamic Scanning Calorimetry (DSC). If the identity of the stabilizer is known, IR can also be used to quantify the antioxidant level.

- **Quality of Extruded Pipe.** The pipe should be free from internal ("frozen-in") stresses and conform to the appropriate dimensional requirements. Unfortunately the only way to unambiguously demonstrate acceptable quality requires a long term creep test sampling in the knee region or lower (See Figure 1) of the creep curve (e.g. 95°C with hoop stress of 2,65 MPa). Results obtained to date showed that the failure mechanism in dynamic fatigue tests approximates the creep craze failures expected at long life times for PP pipes. In addition, failure can be induced within days at elevated temperatures. The dynamic fatigue of pipes could therefore provide a quality discriminator for a pipe acceptance test. A large number of such tests need to be conducted to construct a calibration curve.

- **Packaging, Storage and Distribution.** Pipes should not be stored in direct sunlight. Care should be taken that pipes are not mechanically abused during transit and installation. Rolling of pipes into small coils may be sufficient to cause yielding (the yield strain for PP is 5-15%). This nucleates defects which will initiate cracks during service and will ultimately result in premature failure.

TABLE 1.: FAILURE MODES FOR POLYPROPYLENE PIPES

Failure Type (Frequency)	Description	Remedial Action
1. Incorrect Installation (32%)	**Mechanical Damage to pipes during or before installation**	Create awareness that plastic pipes used for pressure applications are not damage tolerant like metal pipes.
	- Sharp rocks dropped on pipes during trench filling.	- Use soft backfill to cover pipes in trenching applications.
	- Sharp rocks deforming pipes during heavy duty compaction or when traffic passes over buried pipes.	- Avoid direct contact between large rocks and pipes.
	- Installation of pipes that were mechanically flattened (probably by a vehicle driving over pipe).	- Do not install pipes that were deformed beyond their yield point. This is detectable by visual inspection: the pipe will show stress whitening at the point of deformation if it has been stressed beyond the yield point. (Apparently one supplier claimed in his advertising blurb that one can drive with a caterpillar across the polypropylene pipes).
	Connection of misaligned pipes - Misalignment resulted in a very small gap at which a water jet was created. This led to severe erosion of the brass olive and eventually a major leak.	- Avoid bending of polypropylene pipes. Use straight sections only.
	Puncturing of pipes with a sharp object - This led to rapid crack growth.	
2. Poor Quality Product/Processing (21%)	- Weld lines from spider die not properly healed.	- Use recommended melt and die temperature profile.
	- Insufficient melting and mixing of material.	- Use longer barrels and appropriate screw design.
	- Pipe deformation by haul-off system.	- Better cooling of extruded pipe.
	- Longitudinal stresses in extruded pipe.	- Reduce haul-off speed, extrude at a slower rate and use correct die size.
	- Wall damage due to severity of embossing process.	- Use correct extrusion die for each pipe size (some manufacturers use the same die to produce pipe diameters for 15, 22 and 54 mm!)
	- Uneven wall thickness. - Incorrect wall thickness.	- JASWIC should specify a fixed minimum wall thickness per nominal pipe diameter.
3. Defective Raw Material (18%)	**Premature pipe failure:**	
	- Mechanical.	- Use only correct and approved pipe grade material.
	- Thermal oxidative.	- Avoid the use of recycled material.
	- Presence of polyethylene in pipe material (use of PE based masterbatch or PE contamination).	- Use PP based masterbatch only.

Failure Type (Frequency)	Description	Remedial Action
4. Pollution (14%)	- Smell of gas in potable water. - Smell and taste of oil/tar in water.	- Choose location of pipes away from gas pipe lines
5. Fittings (8%)	**Mechanical fittings** - Slippage and pull-out of fitting due to: ● Thermal expansion and contraction. ● Pipe shrinkage due to stress relief. - Premature circumferential cracks due to excessive tightening of fittings or oxidative degradation. - Poor sealing. - Olives made by stamping have a sharp edge which cuts pipe. **Welded fittings** - Poor weld bond due to low gas flame. - Blocking of fitting (e.g. T-piece) by plastic melt. - Overheating of fusion fitting causes degradation.	- Mechanical fittings should be regarded as temporary fittings only. - Use stainless steel insert (with a shoulder) and torque limited tools. - Ensure proper pipe alignment. - Use correct fusion time and temperature (work according to procedure DVS 2207 Part II)
6. Other (8%)	- Reason for failure not identified	

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The Steering Committee responsible for this project, consisted of the following persons:

Mr H C Chapman	Water Research Commission (Chairman)
Dr H M Saayman	Water Research Commission
Mr R P Donovan	Cape Town Municipality
Prof R D Sanderson	Stellenbosch University
Mr I Hollander	Sandton Town Council
Mr J J Keuler	SABS
Mr D Huyser	SABS
Mr P Schirmer	Plastomark

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Mr Bohus Zahradnik for various mechanical tests, suggestions and solutions to problems encountered during this study. He also contributed results on water absorbtion, melt flow index (MFI) and the anisotropy in the mechanical properties of ring specimens.

EVALUATING THE LONG TERM USE OF POLYPROPYLENE FOR HOT AND COLD WATER PIPING

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1. INTRODUCTION

Polypropylene pipes are currently used for domestic hot and cold water installations. In South Africa, the annual consumption of polypropylene raw material for this application amounts to approximately 600 tons. Raw material suppliers expect that this volume could increase to 2 000 tons/year should large scale mass housing projects get underway.

Plastic piping for the transportation of potable water potentially offers the following advantages:

- flexibility and the use of long lengths which makes installation easier and reduces the number of fittings;
- low weight with associated ease of transportation and storage, and
- relatively low cost of manufacture and installation.

Potential disadvantages include increased contraction and expansion during temperature cycling, failure modes which differ greatly from those of more conventional piping such as copper and steel, flammability, increased creep under high pressures and temperatures, etc.

Experience in Western Europe has shown that polypropylene piping can be successfully applied for under-floor heating applications. Provided that appropriate guidelines are followed in the choice and selection of the polymer grade during manufacture, acceptable service life should be attainable in practice. However, this raises the cost of manufacture which in today's competitive world leads to the temptation to take short-cuts. Enforcement of appropriate specifications will protect both the consumer and the reputable manufacturer.

Despite widespread use of polypropylene pipes, not enough is known about the long term behaviour and ageing tendencies of such pipes, especially in hot water applications. Because of these uncertainties, many authorities have expressed reservations regarding the use of polypropylene pipes. This implies a need for a sound scientific investigation of the long term performance properties of locally produced polypropylene pipes. The major objectives of this study were:

- the provision of relevant performance data on which criteria for a standard specification could be based;
- to develop or select appropriate test procedures for quality control that will guarantee satisfactory performance over the required service life.

In order to achieve these goals, it was decided to focus on locally produced pipes and to conduct tests which would indicate their long term properties. It was hoped that the data generated would aid the drafting of appropriate specifications as well as routine quality control procedures to be implemented by manufacturers.

In the interest of economy, tests were limited to the most commonly used pipe diameter (OD 22mm). Products from three major suppliers were investigated. A batch of pipes from each supplier was procured from reputable retail suppliers to ensure that a representative sample was obtained and bias excluded. Each supplier subsequently confirmed, in writing, that the product did in fact originate from his factory. In addition, virgin raw material was obtained from Plastomark and served as a reference standard.

The project was executed in four separate phases:

Phase 1: Evaluation of failure mechanisms
The purpose of this phase was to identify the prevalent failure modes experienced in the field and to investigate the root causes of these failures. It was also hoped that guidelines would be generated regarding manufacturing/installation procedures which would help to eliminate these failures.

Phase 2: Material Characterization
The purpose was to quantify all major physical parameters known to affect performance of polypropylene in raw material and pipe form. Also, to develop or select appropriate analytical methods to quantify changes in raw material during processing and to determine the level of additives used.

Phase 3: Thermal Stability
Here the purpose was to estimate the effect of thermal oxidation on the expected service life of each pipe batch. For this a temperature-lifetime curve was developed using thermal scanning and oven ageing techniques. This information was to be used to evaluate the relevance of the Oxidation Induction Time (OIT) requirement of the proposed SABS Standard Specification. It was also hoped to develop a routine quality control test for the stabilizer level in manufactured pipe.

Phase 4: Long term "Creep" properties
The goal in this phase was to determine the effect of mechanical stress and temperature on the service life of existing pipes.

The results of this study are presented below according to the phases of the research project.

2. PHYSICAL AND MATERIAL CHARACTERIZATION

Pipes from manufacturers A, B and C as well as raw material samples from Plastomark were analyzed using the following techniques:

- Optical Microscopy (OM)
- X-ray diffraction (XRD)
- Pyrolysis - Gas chromatography - Mass Spectroscopy (Py-GC-MS)
- Gel Permeation Chromatography (GPC)
- Carbon-13 Nuclear Magnetic Resonance Spectroscopy (^{13}C NMR) and Infrared Spectroscopy (IR)
- Thermal Analysis including Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Thermal Analysis (DMTA)

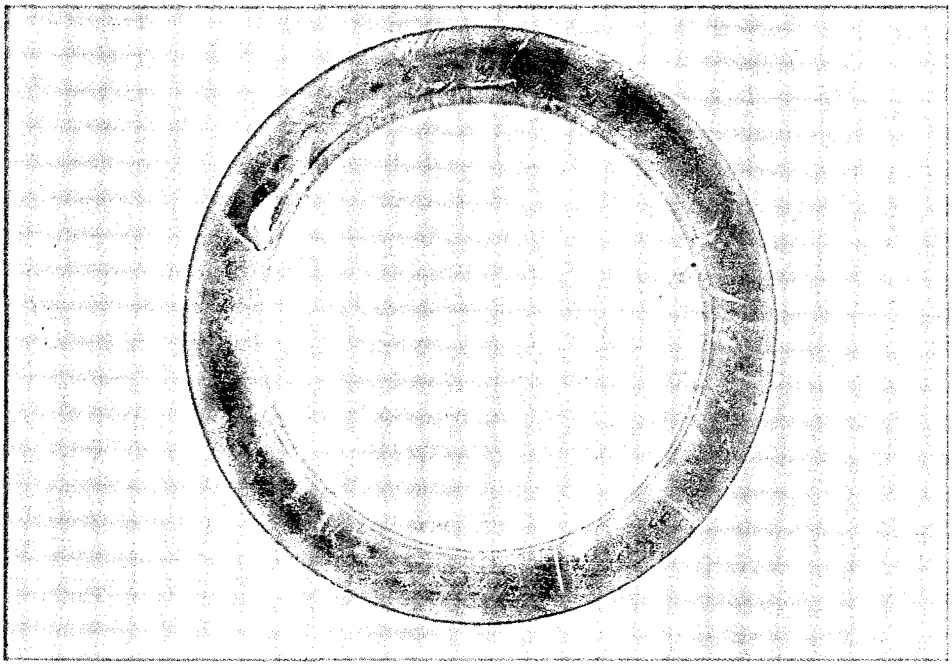
In addition, some samples collected during the failure investigation were characterized.

2.1 Optical Microscopy

Plate 2.1 shows photographs of pipe cross-sections indicating poor pigment distribution in the pipe material. A detailed investigation of the crystal morphologies in the pipe samples was conducted by Reeksting [1] using a polarizing microscope. No major difference in crystal morphology was evident between the pipes investigated. However, surface degradation was discernible in some field samples. This was aggravated by the use of brass fittings. Evidence was found of copper salts migrating into the polymer, catalyzing oxidative degradation.

2.2 X-ray Diffraction

Small rectangular blocks (measuring 3 x 3 x 10 mm) were cut from the pipe walls. Irradiation in the tangential, radial and axial was used to estimate the degree of orientation. An "arbitrary" orientation factor was defined by the area ratio of the second peak (at $2\Theta = 16°$) to the sum of the peaks between $2\Theta = 10$ to 24°. The results are summarized in Table 2.1



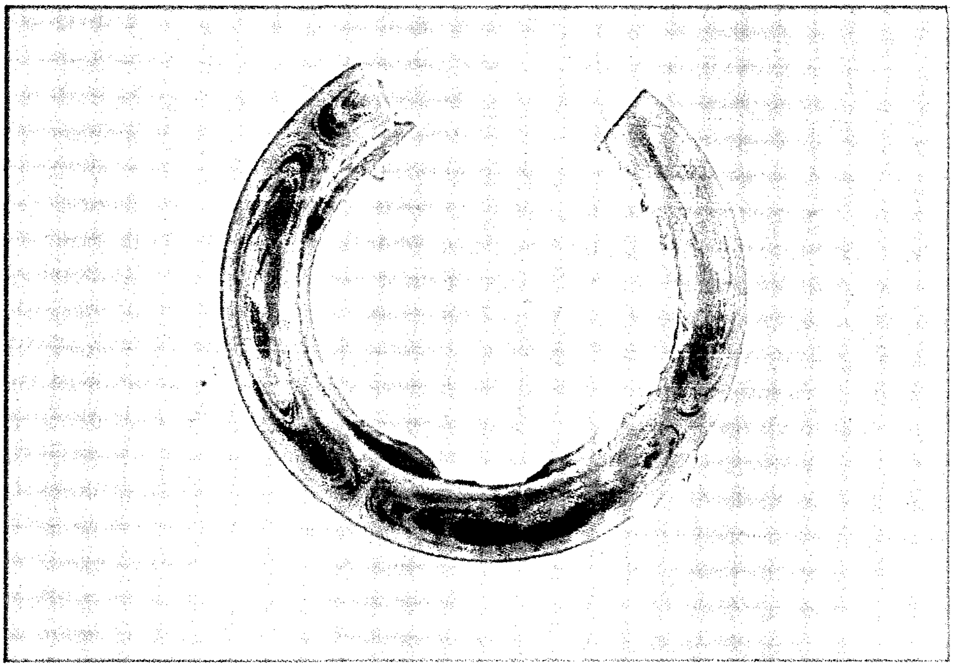


Plate 2.1: Cross-sections of pipes A and C showing poor pigment distribution

Table 2.1 : Orientation Factors

Pipe	X-ray Direction	Orientation Factor
Pipe A	radial	0,9
	tangential	0,5
	axial	0,2
Pipe B	radial	0,5
	tangential	0,4
	axial	0,4
Pipe C	radial	1,0
	tangential	0,5
	axial	0,2

The data indicates similar orientation of crystallites in Pipe A and Pipe C and very little orientation in Pipe B. Typical X-ray diffraction spectra are shown below.

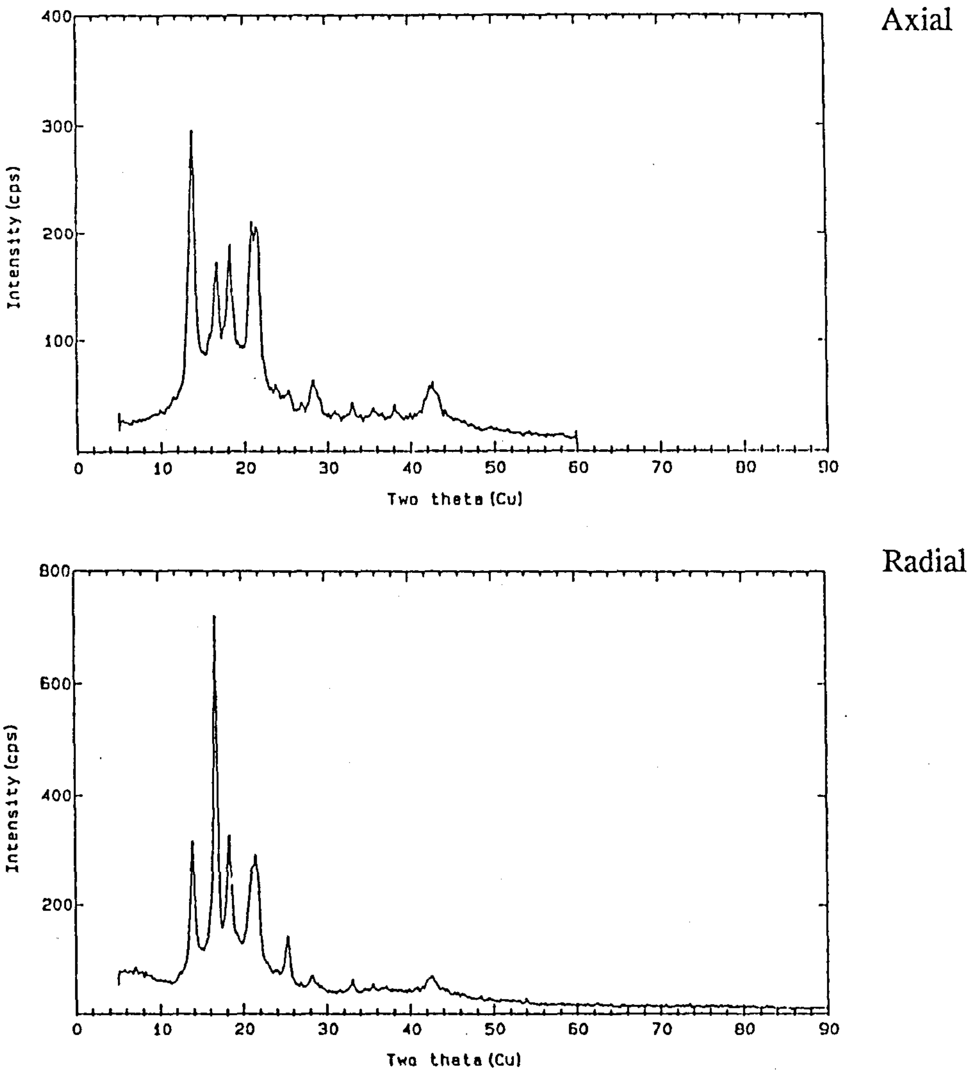


Figure 2.1: X-ray diffraction patterns for Pipe C pipe in radial and axial directions

2.3 Tensile Testing

To check the X-ray diffraction results, thin strips of polymer were removed from the pipes. Results using the radial and axial shavings are reported in Table 2.2 Mechanical tests were conducted at 50 mm/min and both the tensile strength and elongation were evaluated at break.

Table 2.2 : Tensile Properties of Pipe Shavings

Sample	**Direction**	**Tensile Properties**	
		Tensile Strength MPa	**Elongation at break**
Pipe A	Axial	24,2	641
	Radial	21,3	431
Pipe B	Axial	21,7	411
	Radial	24,0	504
Pipe C	Axial	22,1	429
	Radial	17,0	226

The difference between the values for tensile strength and elongation-at-break for the different samples tend to confirm the X-ray diffraction results: The Pipe B sample shows only a small difference indicative of minor orientation effects. However, in the case of the Pipe C sample large differences in elongation-at-break values are observed for the two directions.

Anisotropy of ring specimens

Elongation at break was determined on 8,5 mm wide ring specimens cut from pipe supplied in rolls. They were tested using a cross head speed of 30 mm/min. A reference line (0°) was drawn along the pipe corresponding to the inside diameter of the pipe coil. Pipe rings were tested at angles 0°, 45°, 90°, 135° and 180° with respect to this reference line. Specimens were mounted in such a way that the marked lines were positioned at the centre of the hoop, i.e. elongation or necking started at 90° to the indicated angle.

Results obtained from pipes A and C showed no variation in the elongation-at-break with respect to hoop angle. However, pipe B showed significant differences between 0° and 90°C: the lowest results were obtained at 0° (on the reference line) to the test direction. The average of eight evaluations in each direction were 125% in 0° and 237% in the 90° direction.

After conditioning in hot water (70°C) for several hours it was observed that pipe (B) had lost this anisotropy. The anisotropy possibly derives from post crystallization after coiling or from misalignment of the die and pipe sizing unit during manufacture.

2.4 Melt Flow Index (MFI)

The Melt Flow Index (MFI) of the various samples was as follows:

Table 2.3 : Melt Flow Index

Sample	MFI [g/10 min]		
	5 kg/230°C	2,16 kg/230°C	5kg/190°C
Pipe A	1,7		
Pipe B	2,6		
Pipe C	1,7		
Raw Material	1,4		
Draft Specifications:	SABS 381/50930	CEN/TC155/WG16/N76	SZK HR.10 10.88
a. Compound	-	0,7	≤0,8 (SZK)
b. Pipe Material	2,0	max 40% difference with compound	difference between compound and pipe ≤0,2

These results indicate that the values for Pipe B are on the borderline of the specification. Values for the other pipes are within specification.

During the course of this investigation it was found that the polypropylene pipes absorb a significant amount of moisture (see section 2.10). Theoretically this water could provide a plastization effect during MFI measurements. This was indeed found to be the case for samples tested at SABS in the 80°C (σ_H = 4.4 MPa) creep test:

MFI 5kg/230°C	Sample				
	F	J	K	L	O
Exposed Pipe	2,2	1,7	2,4	2,25	1,7
Dried at 80°C, 6h	1,4	1,4	1,9	1,5	1,7

All the above samples produced a "foamed" extrudate, indicating the presence of water, when MFI was measured before drying. This shows that drying is required before MFI measurements are taken.

2.5 Gel Permeation Chromatography (GPC)

GPC measurements were made using 1,2-dichlorobenzene as solvent at 140°C using polystyrene standards.

Table 2.4: Molecular Weights

Sample	Molecular Weight		Polydispersity
	Mw	Mn	
Pipe A	511×10^3	$86,4 \times 10^3$	5,9
Pipe B	483×10^3	$63,7 \times 10^3$	7,6
Pipe C	539×10^3	87×10^3	6,2
Raw Material (PPH 4122)	567×10^3	81×10^3	7,0
German pipe obtained from Hoechst	558×10^3	101×10^3	5,5

These results confirm the lower molecular weight of Pipe B as indicated by MFI results.

2.6 ^{13}C NMR and IR Spectroscopy

Samples were dissolved in hot trichlorobenzene and ^{1}H and ^{13}C spectra obtained. The information obtained by ^{1}H NMR was not useful for the compositional analysis. The ^{13}C NMR spectra for all samples were very similar. The major component is isotactic polypropylene and the secondary component is a poly(ethylene-co-propylene). This secondary component has a NMR profile resembling a 30% propylene copolymer. It is present in ca 10% concentration. The infrared spectra are consistent with this conclusion.

In the Infrared (IR) spectrum a sharp peak at $\approx$ 700 cm^{-1} is usually visible if more than seven -CH$_2$- units are linked, i.e. indicative of a polyethylene type phase.

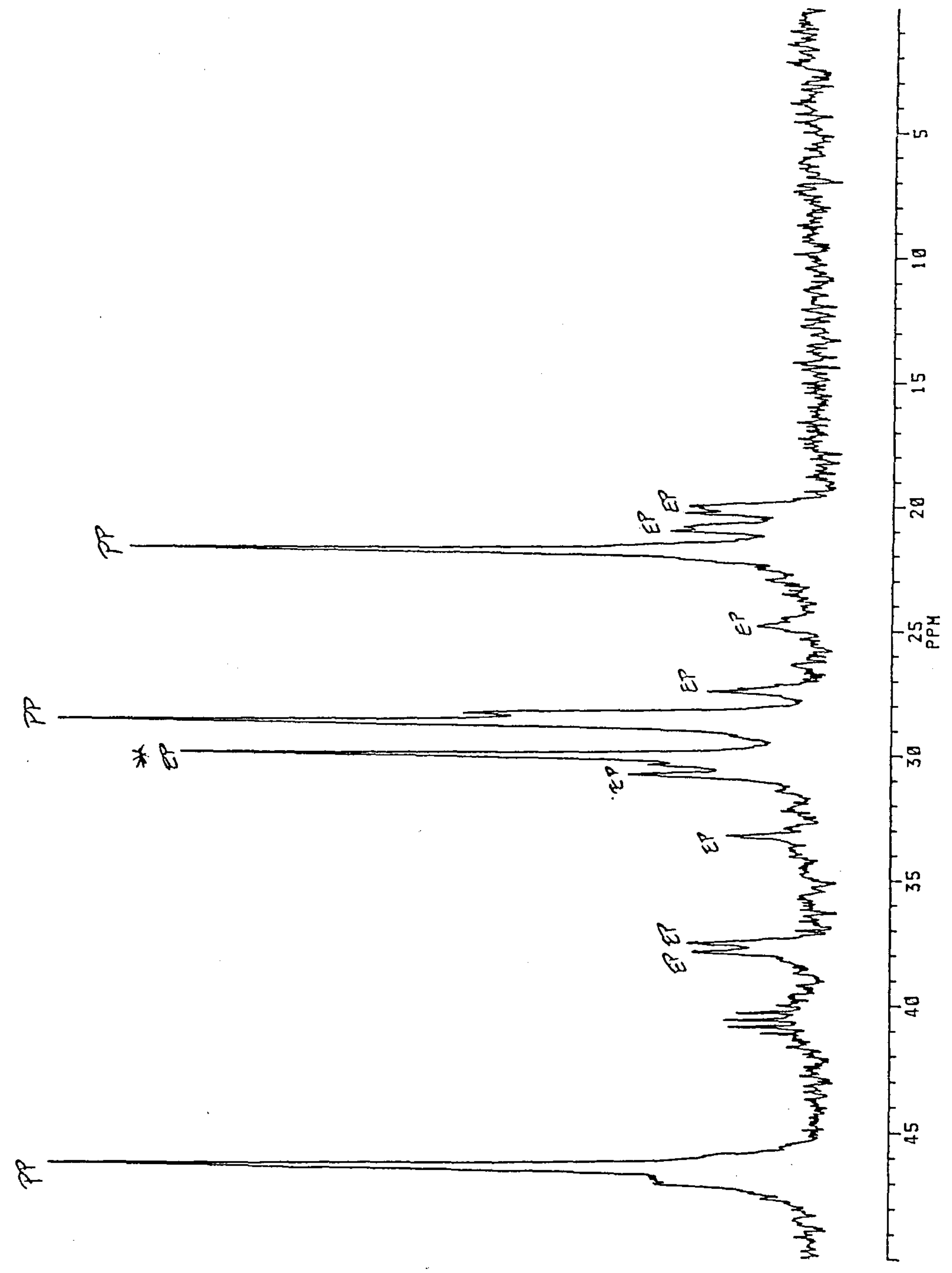


Figure 2.2: Typical ^{13}C NMR Spectrum

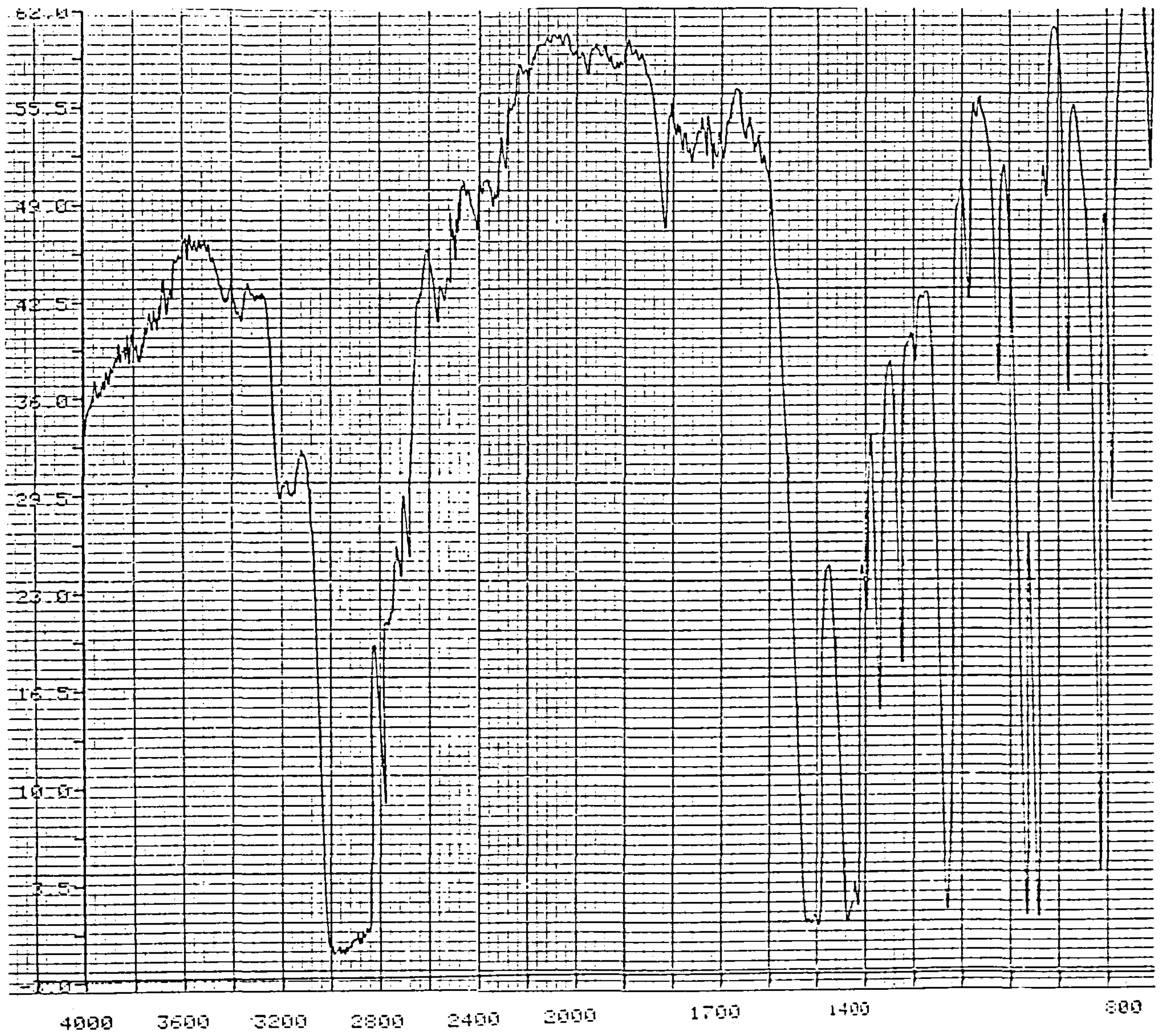
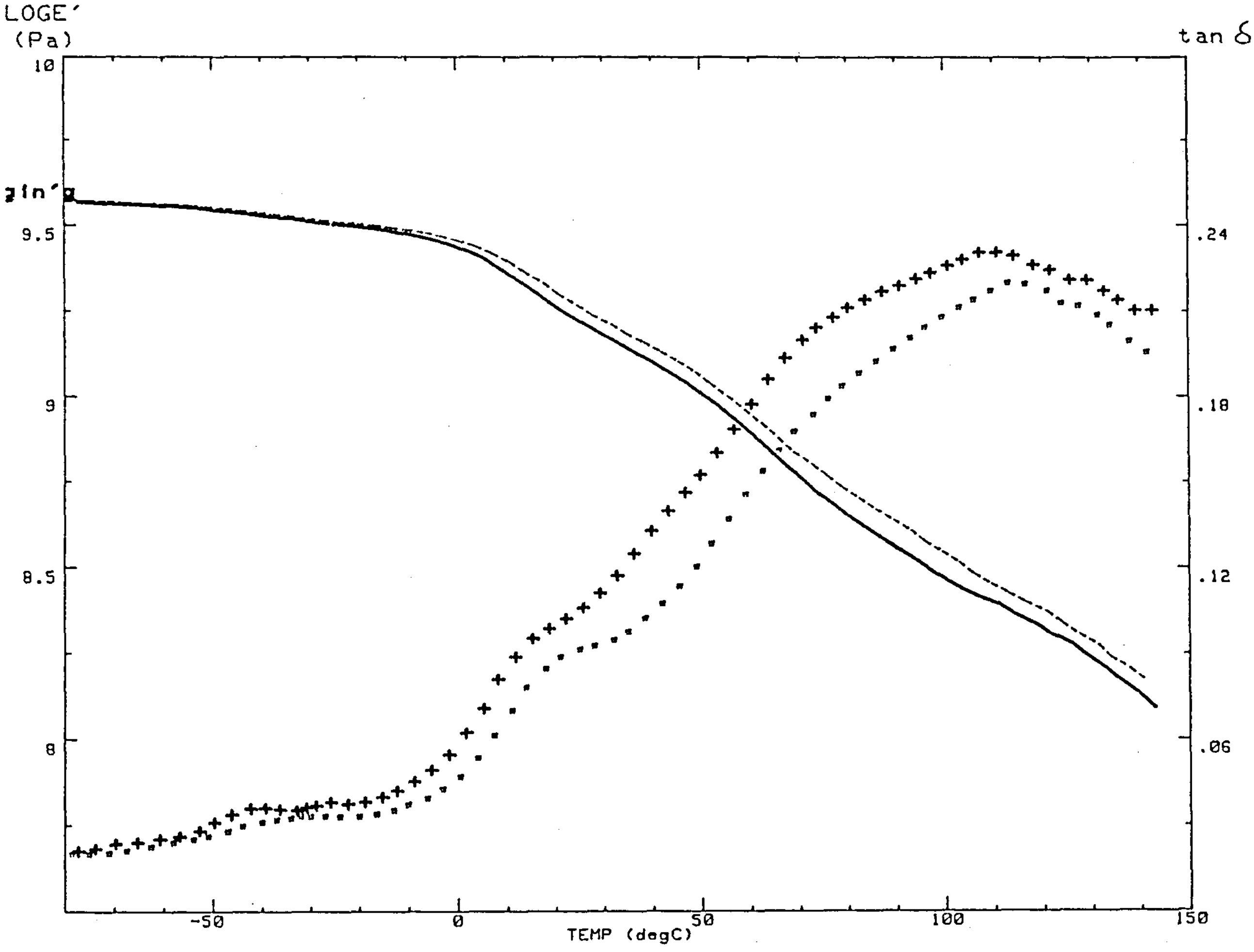


Figure 2.3: Typical IR Spectrum

2.7 Dynamic Mechanical Thermal Analysis (DMTA)

A typical DMTA trace for a pipe sample is shown in Figure 2.4. The traces were again almost identical for all three pipes. Two glass transitions (at -40°C and 20°C) are evident. This indicates the presence of two separate phases. These correspond to the poly(ethylene-co-propylene) and poly(propylene) phase separated components. For a pure polyethylene phase the glass transition is usually below -100°C. The shift to ca -40°C again confirms the copolymer structure.

The other striking feature of the DMTA trace is the decrease in modulus by an order of magnitude when temperature is increased to 100°C.



--- 3 Hz
— .3Hz

Figure 2.4: Typical DMTA Trace for Pipe A Material. The small peak at -40°C indicates a polyethylene-co-polypropylene phase

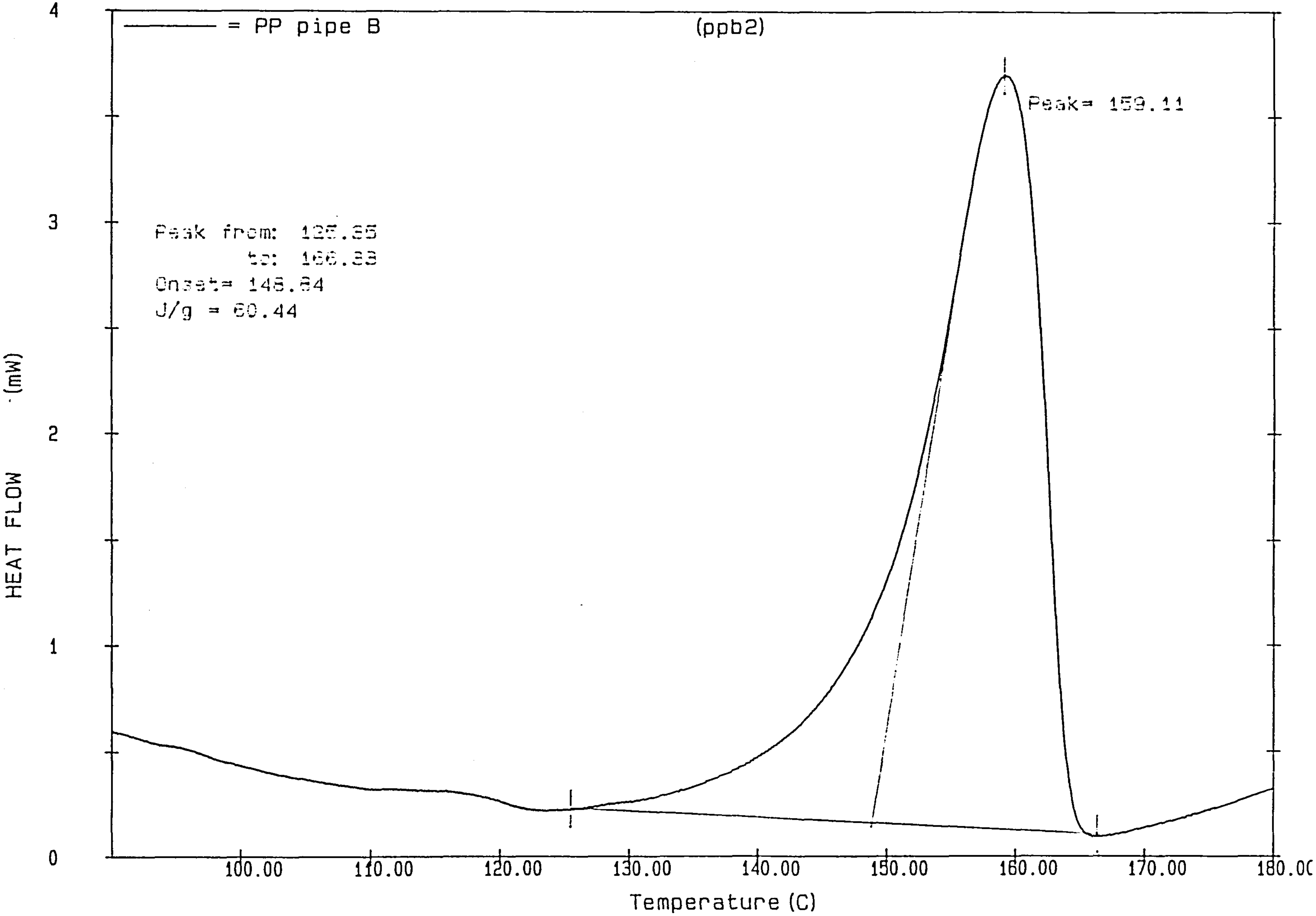


Figure 2.5: Typical DSC trace for Pipe B material. The small peak at 115°C indicates a polyethylene phase

2.8 Differential Scanning Calometry (DSC)

A typical DSC scan is shown in Figure 2.5. It shows the normal polypropylene melting endotherm at ca 160°C. There is only a hint of a polyethylene melting point at ca 115°C. This again confirms the structure interpretation obtained by ^{13}C NMR.

2.9 Ash Analysis

Samples were pyrolyzed at 800°C and the ash content determined in duplicate:

Sample	Ash content (%)
Pipe A	0,55
Pipe B	0,98
Pipe C	0,55
PPH 4122 (raw material)	0,15

These results show a greater degree of impurity in the Pipe B sample.

2.10 Water absorbtion and desorption

Pipe specimens ± 10 cm long were conditioned at various temperatures in distilled water. The moisture content was measured as a function of time. Samples tested for water absorbtion and desorption included two pipes tested at SABS which showed good (>100h) and poor (25h) creep lives when tested at 4,4 MPa and 80°C. Results for these two pipes did not differ significantly except for the room temperature water absorbtion tests. For the standard specimens, Pipe A consistently showed the highest moisture absorbtion followed by pipe C and B. Results are presented in Table 2.5 for the highest and lowest moisture content samples found for each test.

Pre-conditioning	None		24 hrs @ 94°C water		72 hrs @ 94°C water		72 hrs @ 80°C water	
Post conditioning	Water 23°C		Air 23°C		Water 23°C		Water 23°C	
Time (days)	Pipe		Pipe		Pipe		Pipe	
	D	F	D	F	D	B	A	F
1			0,40	0,33	0,67	0,72		
2	0,0098	0,0035	0,36	0,32				
3			0,34	0,30				
4			0,32	0,29				
6	0,033	0,016			0,67	0,36	0,44	0,37
7			0,29	0,27				
10	0,046	0,025			0,68	0,37	0,45	0,38
13	0,056	0,031			0,68	0,38	0,45	0,38

Table 2.5 Water Absorbtion tests (%)

These results are surprising in many respects. Firstly the equilibrium moisture content of pure polypropylene resin is less than 0,01%. Relatively high values are observed (0,01 - 0,68%). This may indicate the presence of hygroscopic fillers or additives but could also indicate the presence of microvoids in the material.

2.11 Discussion and Conclusions

All pipes investigated show a similar chemical composition. They appear to be block copolymers consisting of poly(ethylene-co-propylene) type blocks in polypropylene. The poly(ethylene-co-propylene) blocks contain ca 30% propylene and are present at a ca 10 mole % level. The major difference between the samples is in the molecular weight and its distribution. Pipe B has the lowest molecular weight and the largest polydispersity. These trends are reflected in the MFI values.

All pipes show significant orientation effects induced by processing parameters. Pipes A and C show anisotropy with respect to the axial direction while pipe B shows anisotropy in elongation-at-break with respect to the pipe circumference.

The high water absorbtion of the pipes is remarkable and should be further investigated.

2.12 References

1. O B Reeksting, Technikon Pretoria Report on: "*Investigation: Polypropylene pipes*", September 1992.

3. EVALUATION OF FAILURE MECHANISMS

Altogether 60 failed samples were submitted for analysis from the municipalities of Cape Town, Durban and Port Elizabeth. The fact sheets for each sample are given in Appendix C. A summary of the observed failure categories and possible remedial action is given in Table 3.1

The samples were analyzed by a team of experts from Plastomark, SABS and CSIR. In selected cases additional tests (such as MFI and OIT determinations) were conducted to confirm whether failure was due to incorrect material specification.

From Table 3.1 it is clear that, in the majority of cases, in-service failure was caused by incorrect installation. Plastic pipes are simply not damage tolerant and correct trenching procedures must be followed to achieve the desired service life.

Poor quality manufacturing and selection of incorrect raw materials together accounted for a total of 39% of the failures. These were identified by macroscopic defects in the pipes and incorrect MFI or OIT values for the pipe material respectively. Surprisingly, fittings accounted for only 8% of failures with failures due to both mechanical and fusion bonded fittings.

Plates 3.1 to 3.24 show photographs of selected failures observed in this investigation.

Subsequent to this investigation, a large number of acceptance reports were supplied by Durban Water and Waste. Many of the pipes tested showed insufficient antioxidant levels as measured by IR.

TABLE 3.1: FAILURE MODES FOR POLYPROPYLENE PIPES

Failure Type (Frequency)	Description	Remedial Action
1. Incorrect Installation (32%)	**Mechanical Damage to pipes during or before installation**	Create awareness that plastic pipes used for pressure applications are not damage tolerant like metal pipes.
	- Sharp rocks dropped on pipes during trench filling.	- Use soft backfill to cover pipes in trenching applications.
	- Sharp rocks deforming pipes during heavy duty compaction or when traffic passes over buried pipes.	- Avoid direct contact between large rocks and pipes.
	- Installation of pipes that were mechanically flattened (probably by a vehicle driving over pipe).	- Do not install pipes that were deformed beyond their yield point. This is detectable by visual inspection: the pipe will show stress whitening at the point of deformation if it has been stressed beyond the yield point. (Apparently one supplier claimed in his advertising blurb that one can drive with a caterpillar across the polypropylene pipes).
	Connection of misaligned pipes - Misalignment resulted in a very small gap at which a water jet was created. This led to severe erosion of the brass olive and eventually a major leak.	- Avoid bending of polypropylene pipes. Use straight sections only.
	Puncturing of pipes with a sharp object - This led to rapid crack growth.	
2. Poor Quality Product/Processing (21%)	- Weld lines from spider die not properly healed.	- Use recommended melt and die temperature profile.
	- Insufficient melting and mixing of material.	- Use longer barrels and appropriate screw design.
	- Pipe deformation by haul-off system.	- Better cooling of extruded pipe.
	- Longitudinal stresses in extruded pipe.	- Reduce haul-off speed, extrude at a slower rate and use correct die size.
	- Wall damage due to severity of embossing process.	- Use correct extrusion die for each pipe size (some manufacturers use the same die to produce pipe diameters for 15, 22 and 54 mm!)
	- Uneven wall thickness. - Incorrect wall thickness.	- JASWIC should specify a fixed minimum wall thickness per nominal pipe diameter.

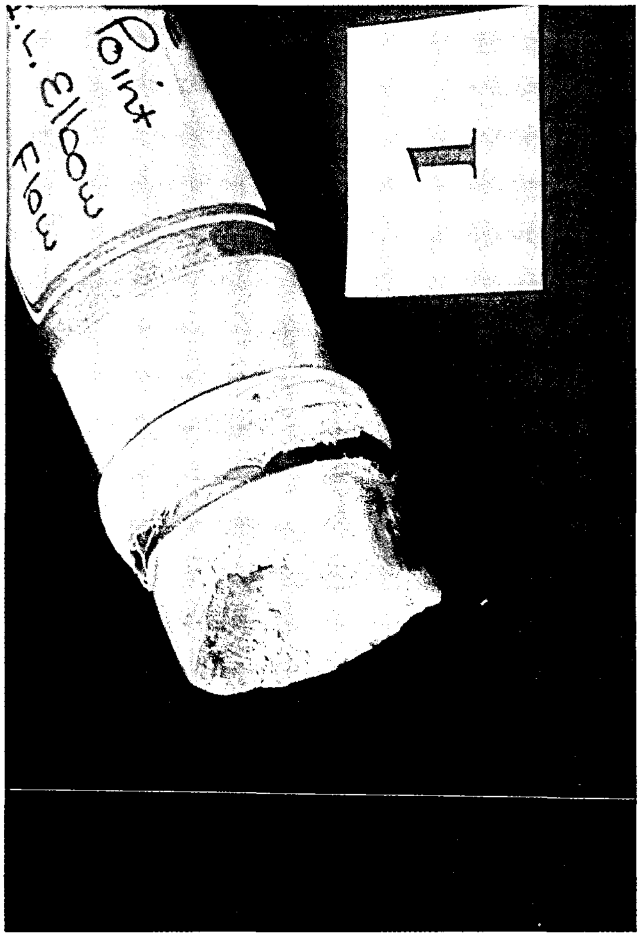
Failure Type (Frequency)	Description	Remedial Action
3. Defective Raw Material (18%)	**Premature pipe failure:** - Mechanical. - Thermal oxidative. - Presence of polyethylene in pipe material (use of PE based masterbatch or PE contamination).	- Use only correct and approved pipe grade material. - Avoid the use of recycled material. - Use PP based masterbatch only.
4. Pollution (14%)	- Smell of gas in potable water. - Smell and taste of oil/tar in water.	- Choose location of pipes away from gas pipe lines
5. Fittings (8%)	**Mechanical fittings** - Slippage and pull-out of fitting due to: ● Thermal expansion and contraction. ● Pipe shrinkage due to stress relief. - Premature circumferential cracks due to excessive tightening of fittings or oxidative degradation. - Poor sealing. - Olives made by stamping have a sharp edge which cuts pipe. **Welded fittings** - Poor weld bond due to low gas flame. - Blocking of fitting (e.g. T-piece) by plastic melt. - Overheating of fusion fitting causes degradation.	- Mechanical fittings should be regarded as temporary fittings only. - Use stainless steel insert (with a shoulder) and torque limited tools. - Ensure proper pipe alignment. - Use correct fusion time and temperature (work according to procedure DVS 2207 Part II)
6. Other (8%)	- Reason for failure not identified	

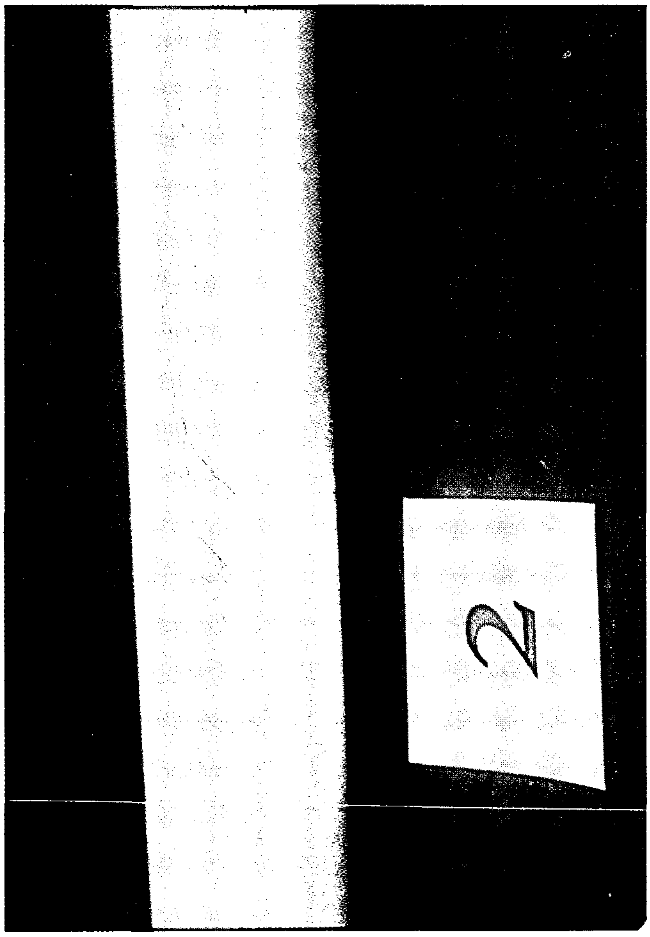
LEGEND FOR PLATES 3.1 TO 3.24

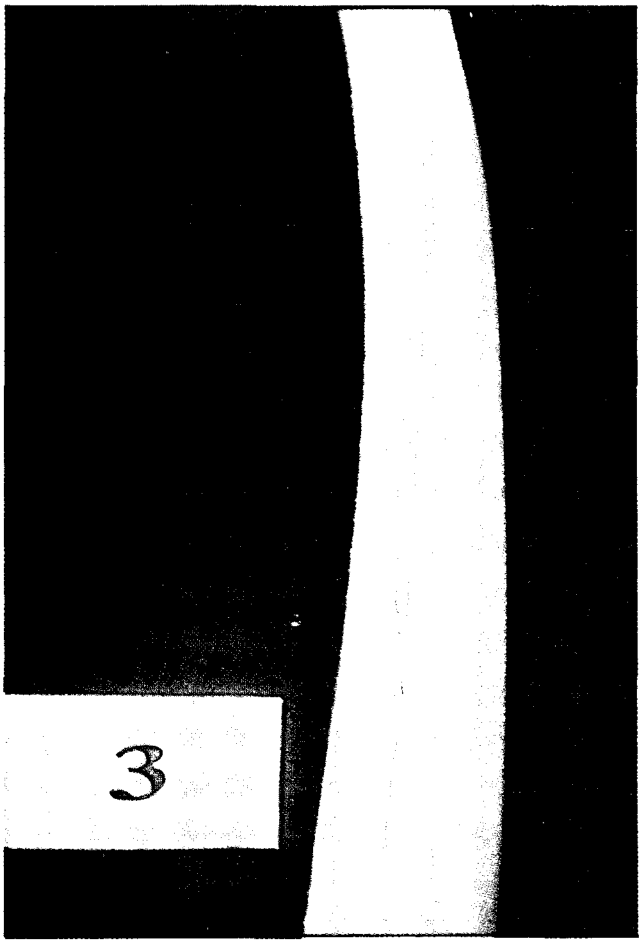
Photograph #	Description
1	Oxidative degradation of a polypropylene pipe connected directly to a geyser outlet.
2	Longitudinal spider lines along pipe surface caused by insufficient pressure during extrusion. This means that the weld lines behind the spider have not "healed" properly resulting in a significantly weakening of the pipe.
3	Brittle failure due to a spiderline defect.
4	Ductile failure due to incorrect material selection and/or excessive operating pressures.
5	Evidence of olive slippage due to: - expansion/contraction caused by thermal cycling. - shrinkage of pipe owing to stress relief.
6	Pipe sample with gas smell.
7	Circumferential crack at brass fitting caused by material embrittlement. The material was not properly stabilized.
8	Defective Pipe. Spider markings and three rows of "dimples" caused by mechanical haul-off system.
9	Embossing too bold. Would cause premature pipe failure.
10	Oxidative degradation similar to photograph 1. This was, in fact, a replacement piece of pipe for pipe 1. Connection too close to geyser.
11	Oily pipe. Extrusion of this pipe was too cold. Extruder probably could not cope with the high molecular weight of the material.
12	Pipe with a gas smell.
13	Pipe marking not acceptable. No rating specified. Identification must contain the name of manufacturer, pressure rating and pipe dimension.
14 - 15	Premature failure of pipe tested at SABS. Typical brittle failure along embossing suggesting that it weakened the pipe.
16	Typical "brittle" failures observed during testing.
17	"Brittle" fracture caused by poor processing

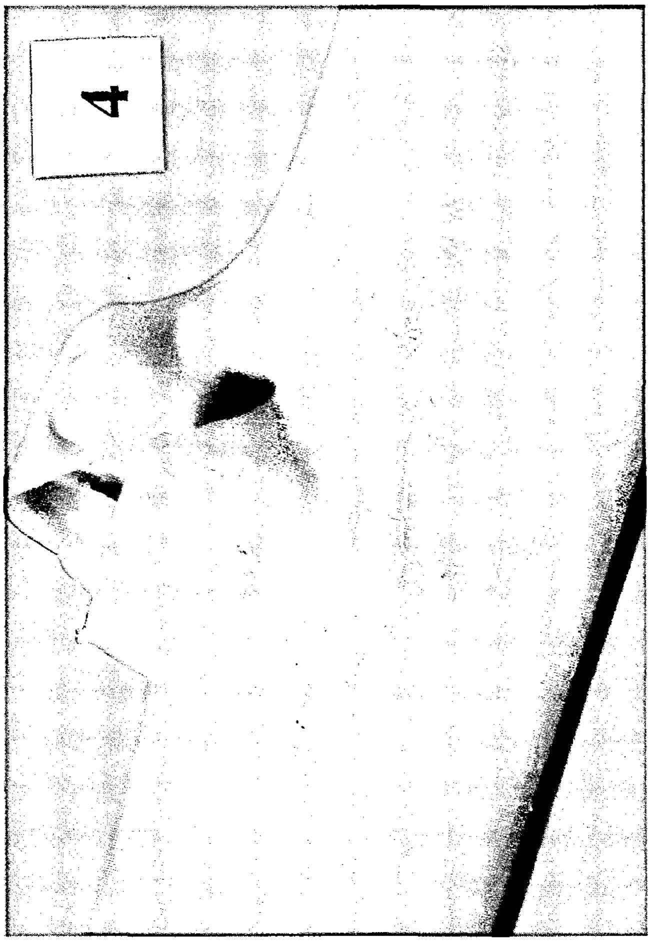
Photograph #	Description
18	Very bad extrusion resulting in a combination of ductile/brittle failure. An angled crack resulted ultimately in a ductile "ballooning". Failure caused by using two different grades in the extrusion and possibly a cooling bath that was too cold.
19	This pipe shows evidence of two brittle cracks inside and an eventual ductile failure on the outside. In this case poor processing was probably the cause of failure. The material was probably not fully molten i.e. the melt temperature was too low. Typical problem with short extruder barrels.
20	Brittle crack failure initiated by an indentation from a sharp rock
21	Typical ductile failure (SABS creep test at 80°C).
22	Typical South African "brittle" craze failure SABS creep test at 80°C.
23	Examples of pipe failure modes observed for locally produced pipes tested at 80°C.
24	Typical crazing failure of pipes manufactured in Germany.

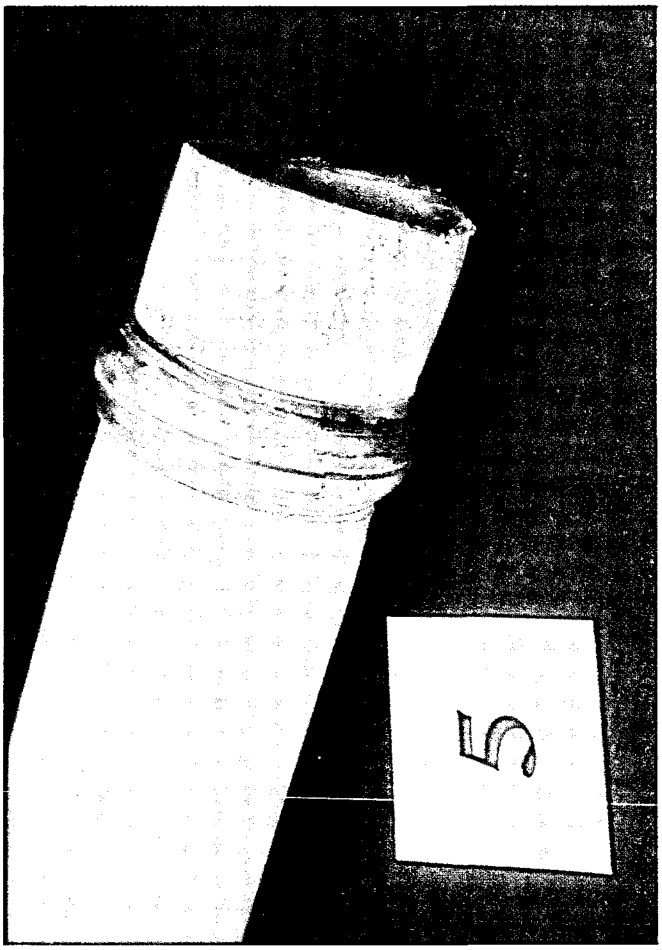
3.6







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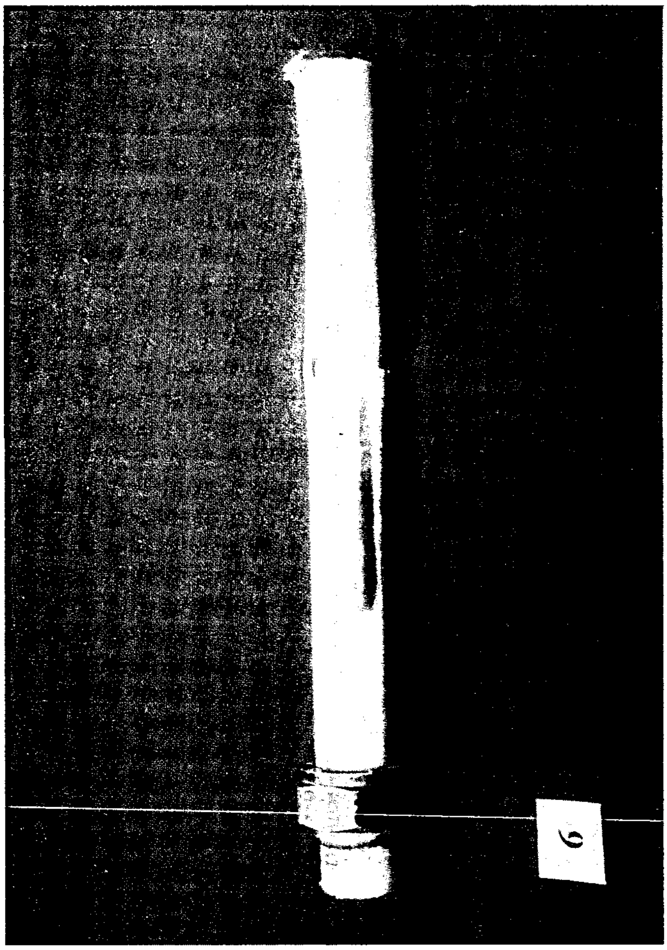
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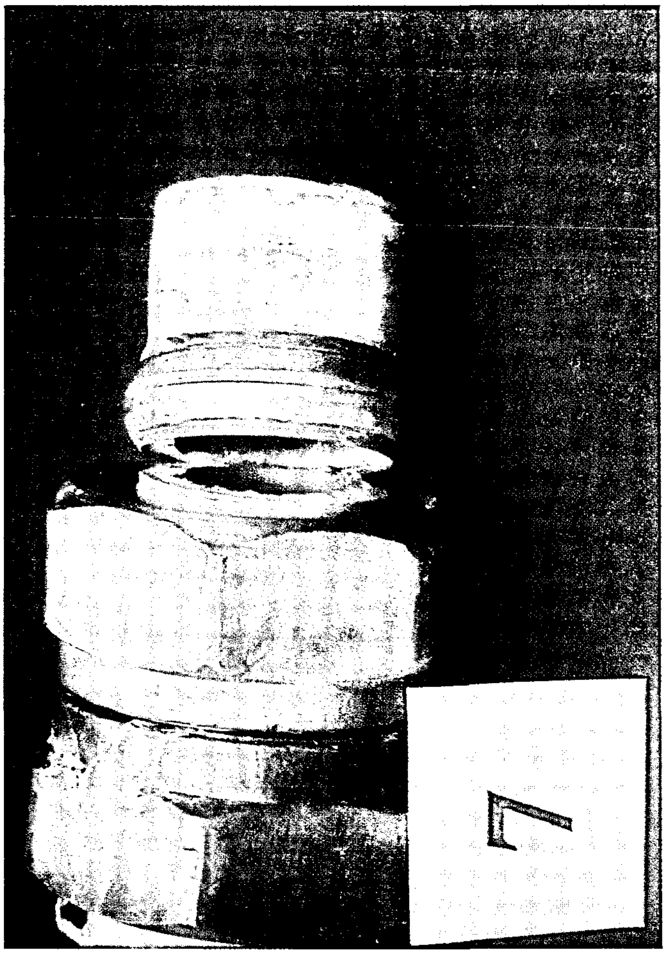
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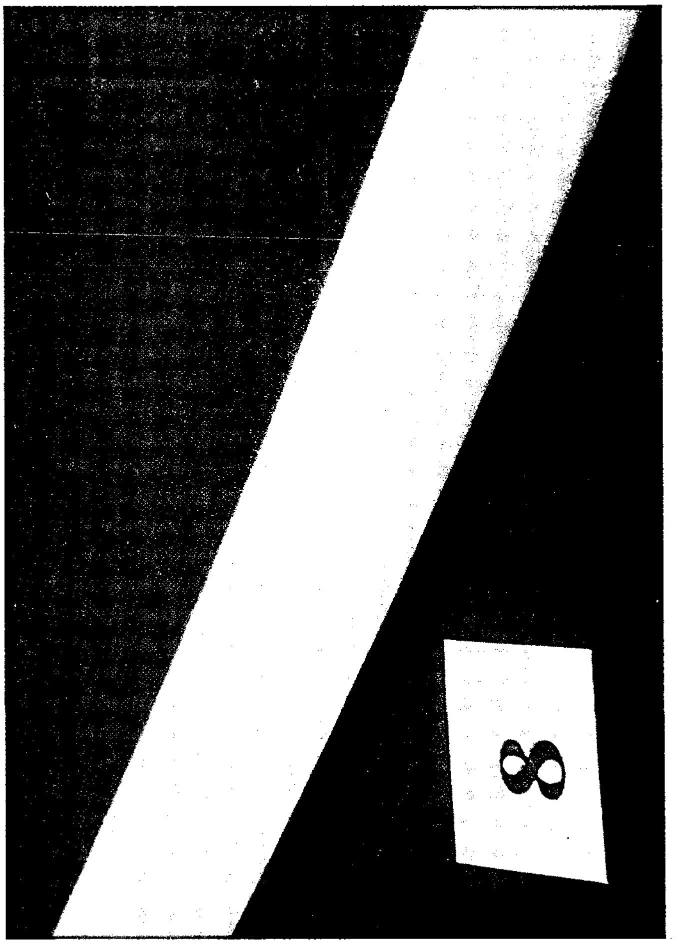
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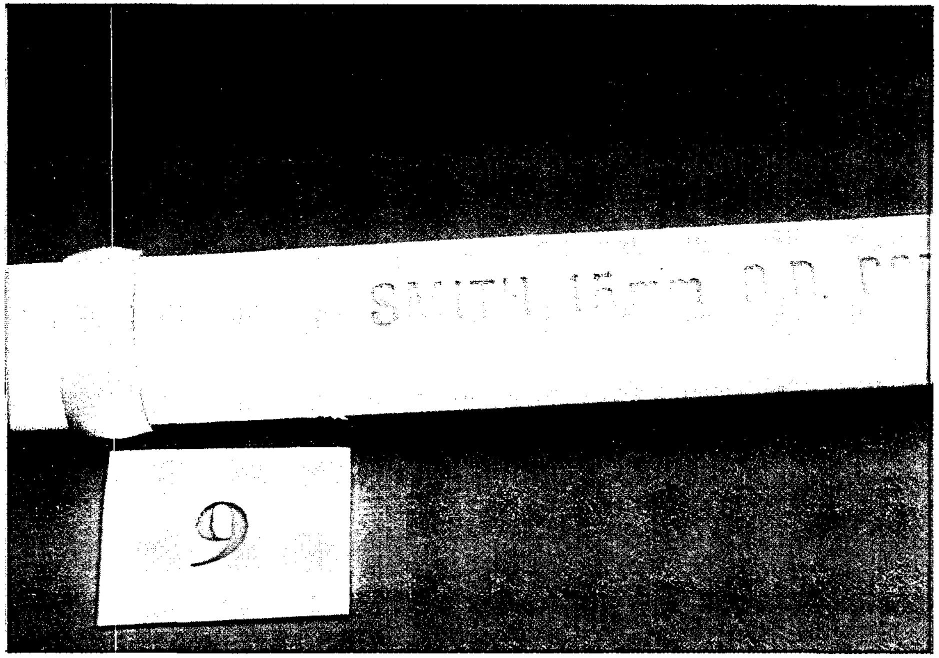
SMITH 15mm O.D.
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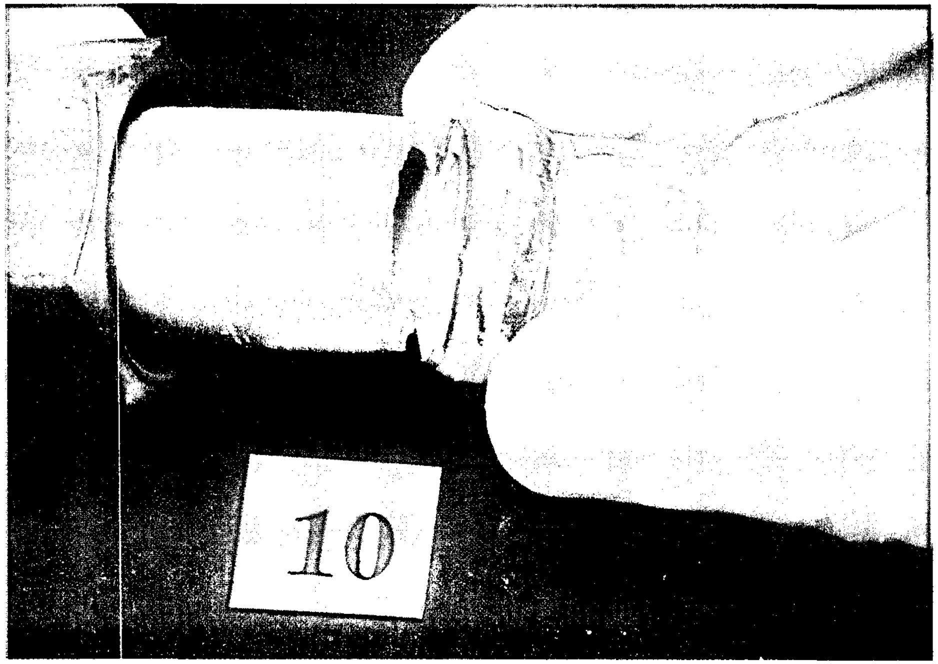
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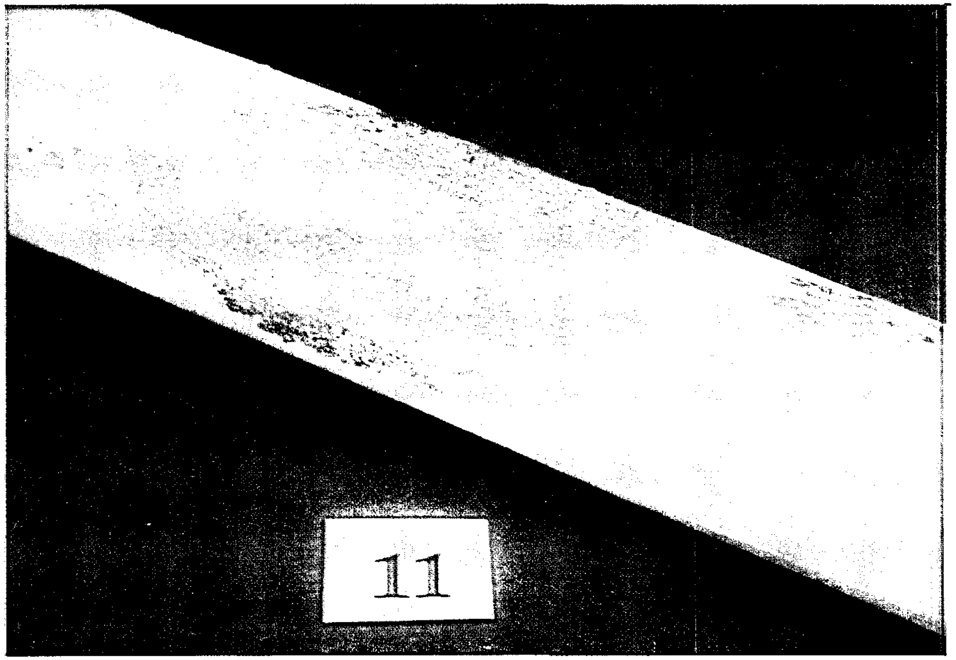
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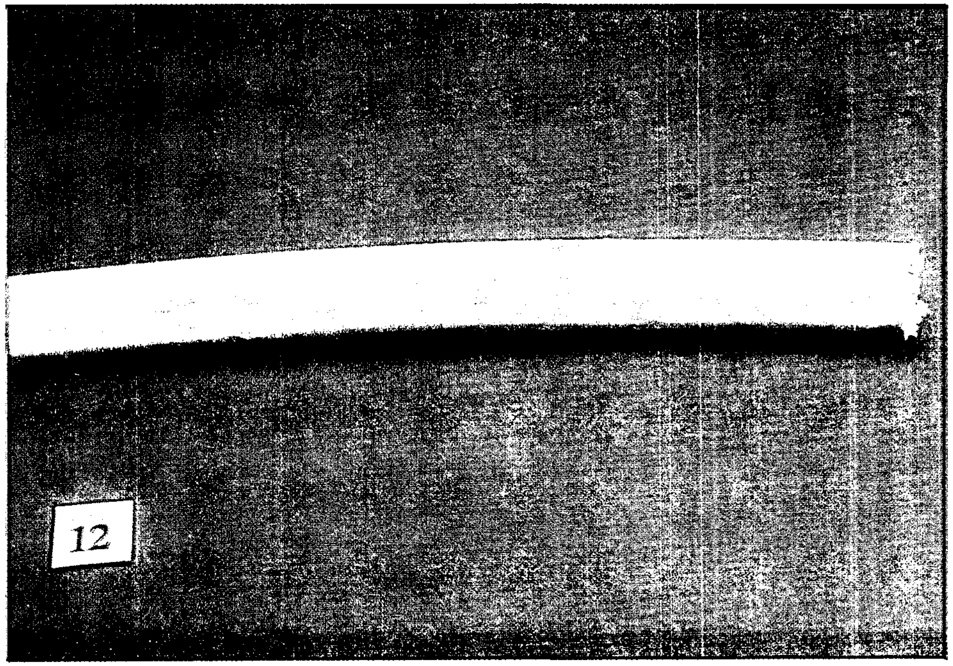
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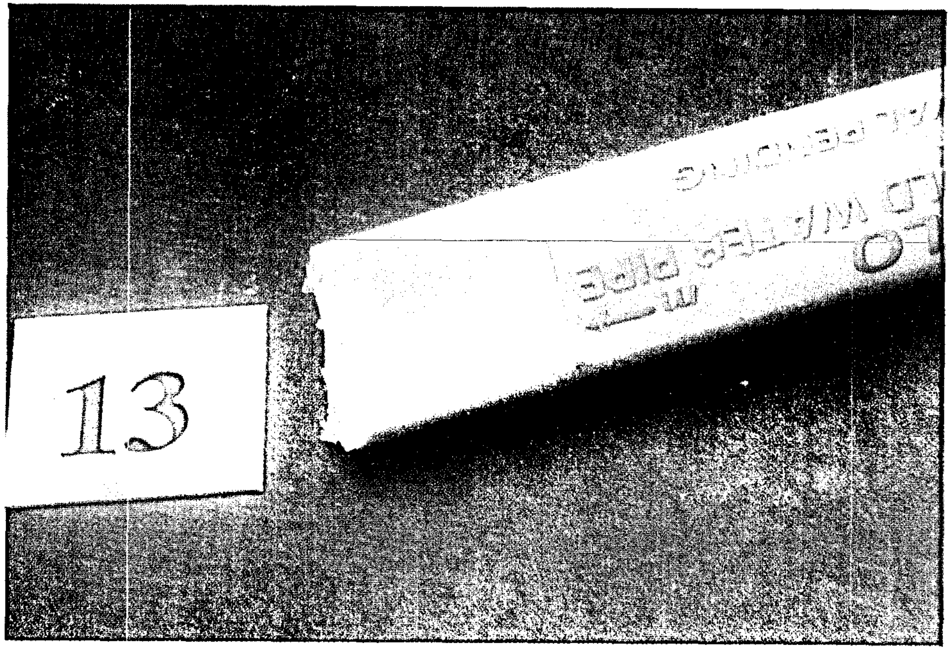
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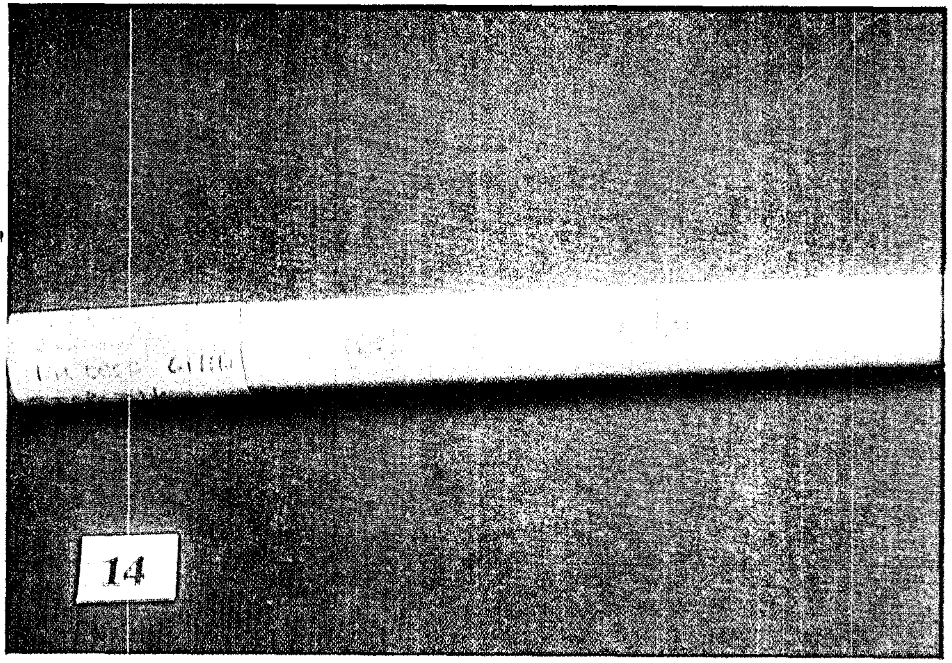
WATER PIPE
PENDING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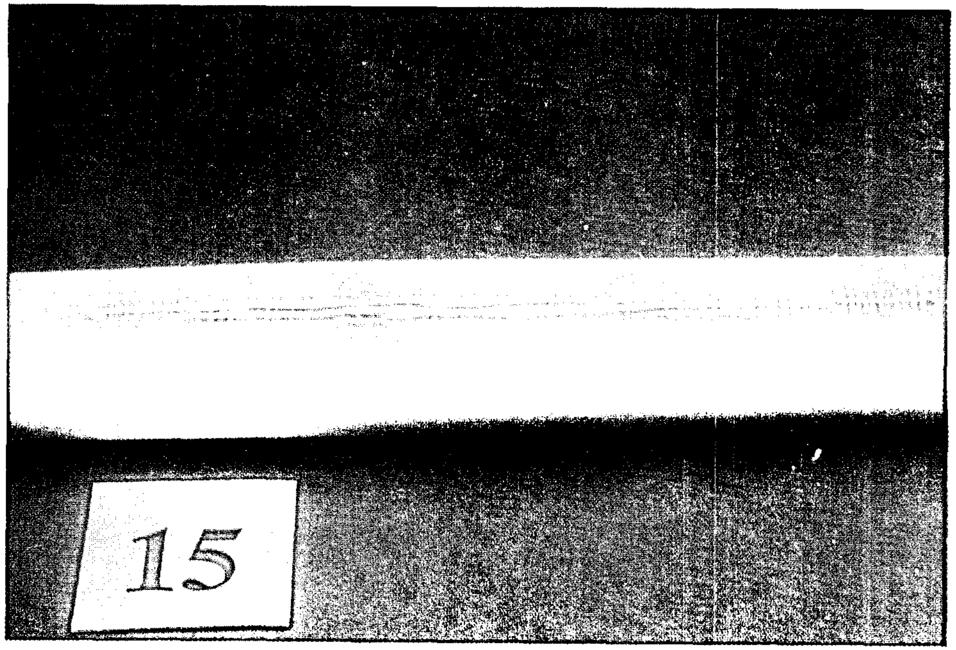
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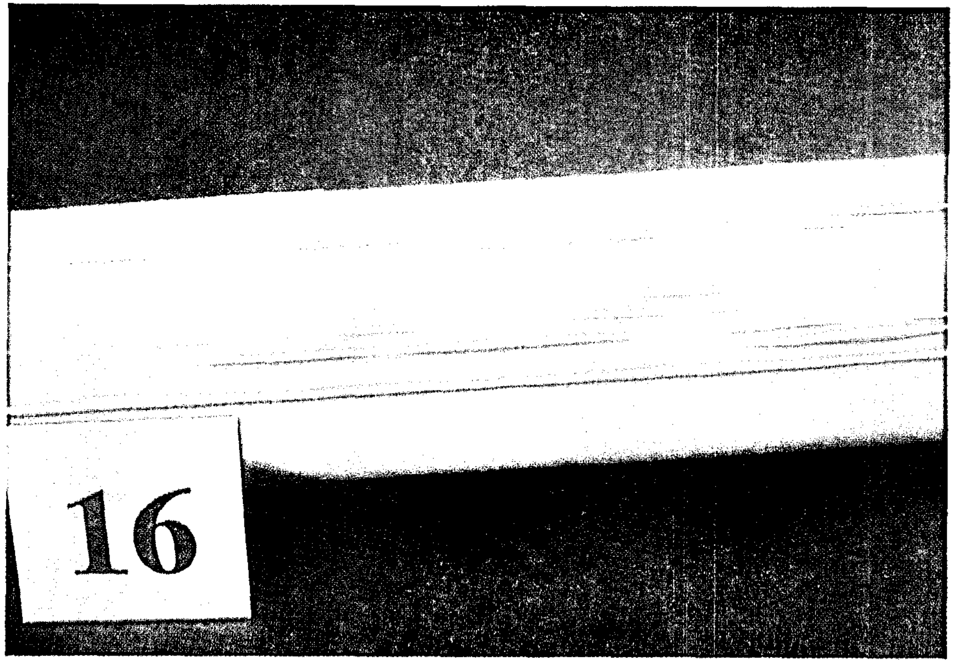
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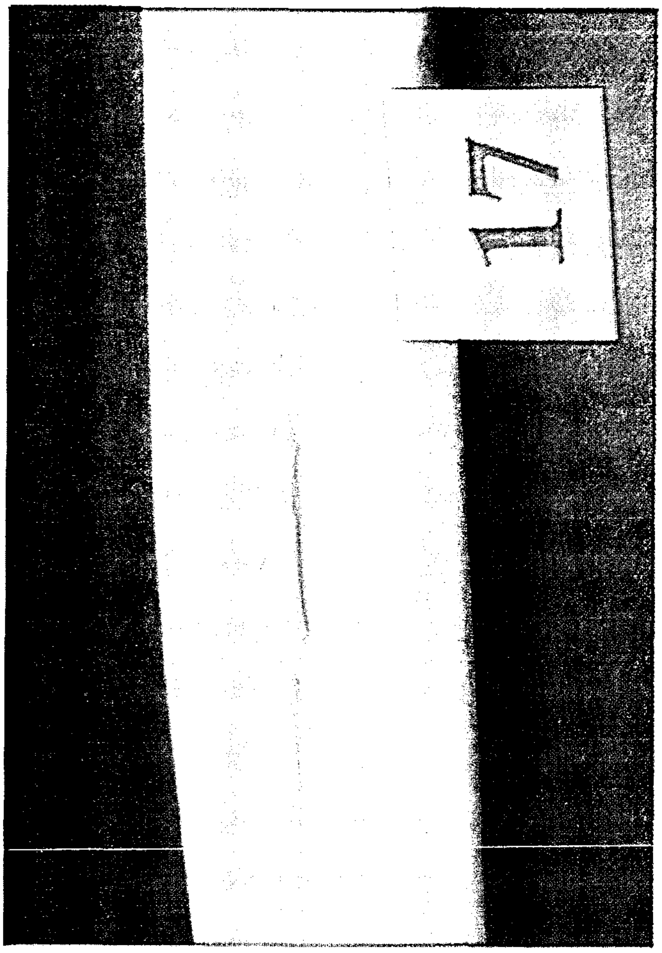
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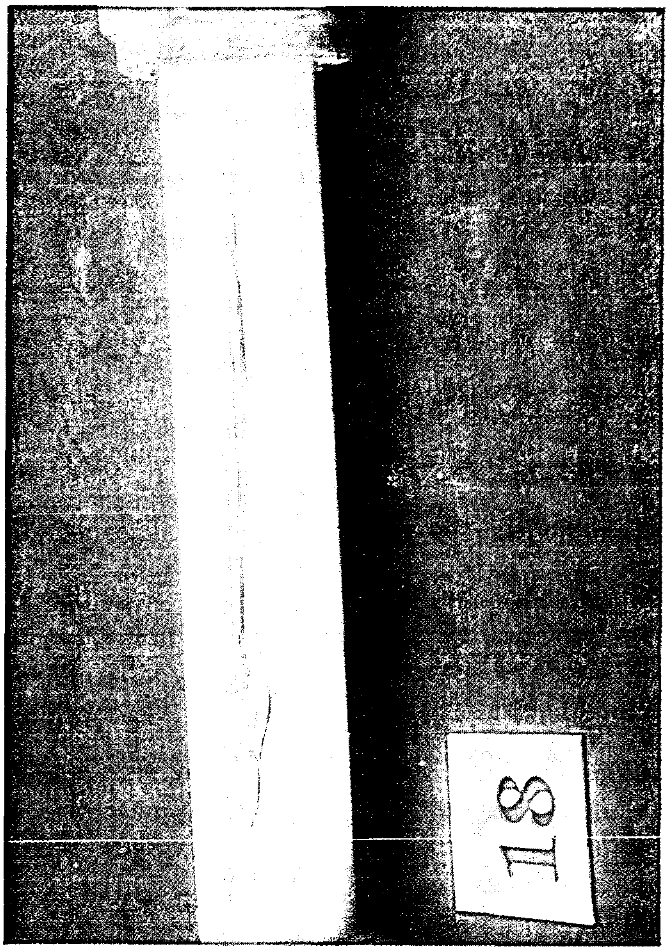
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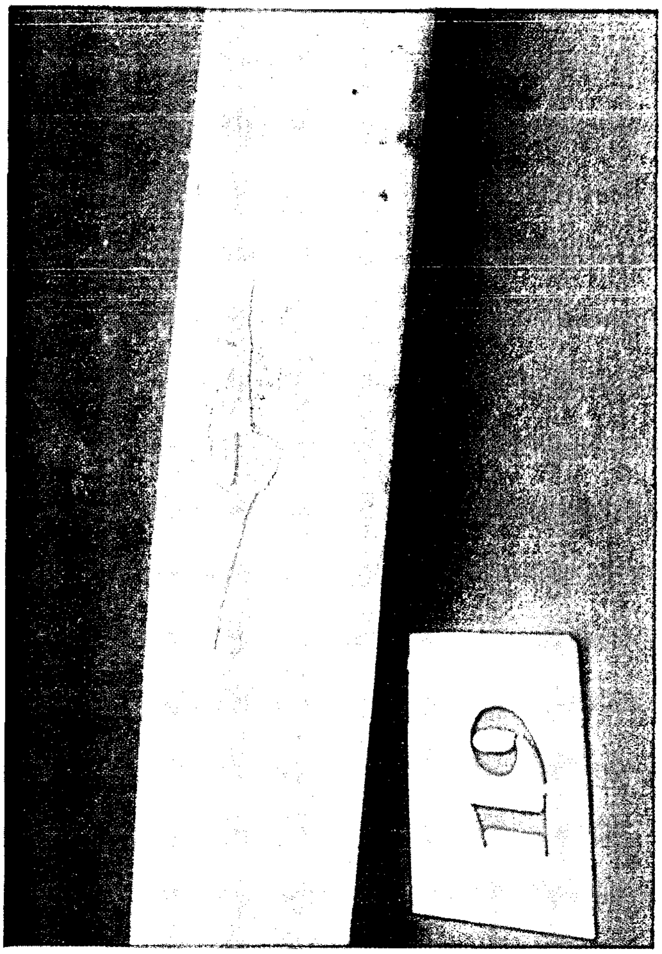
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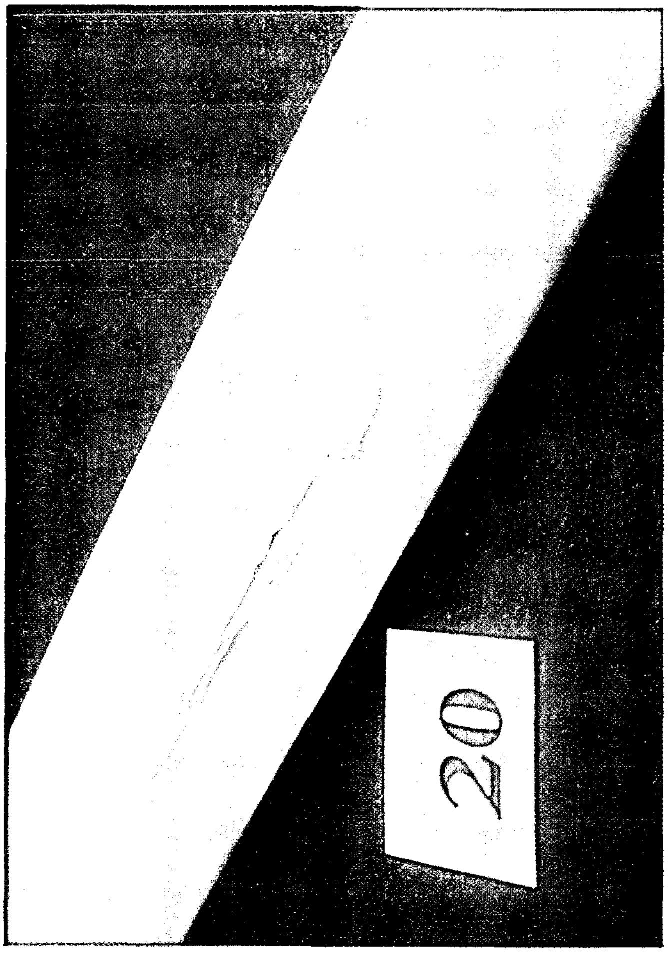
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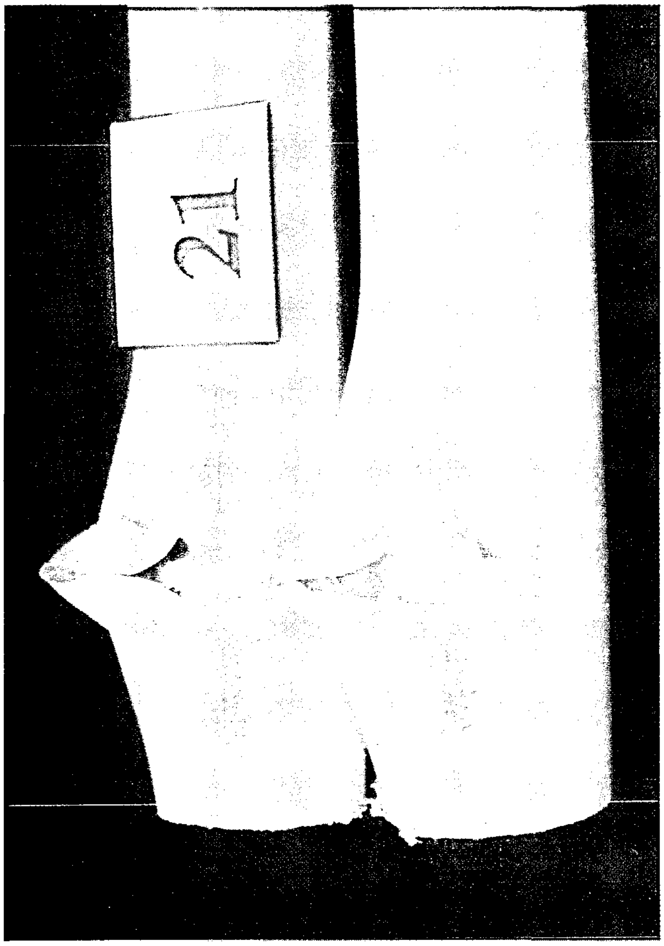
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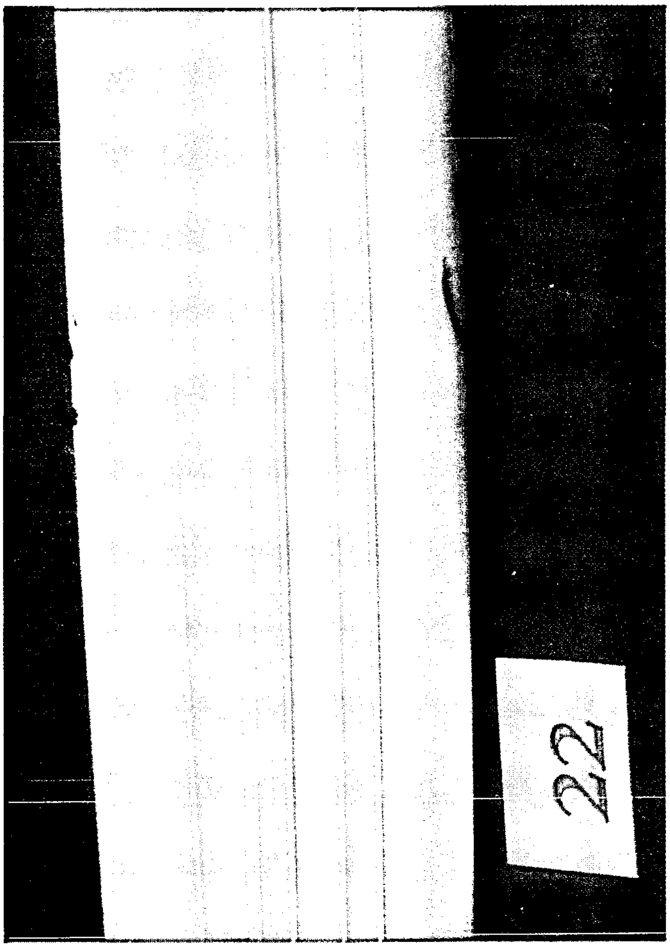
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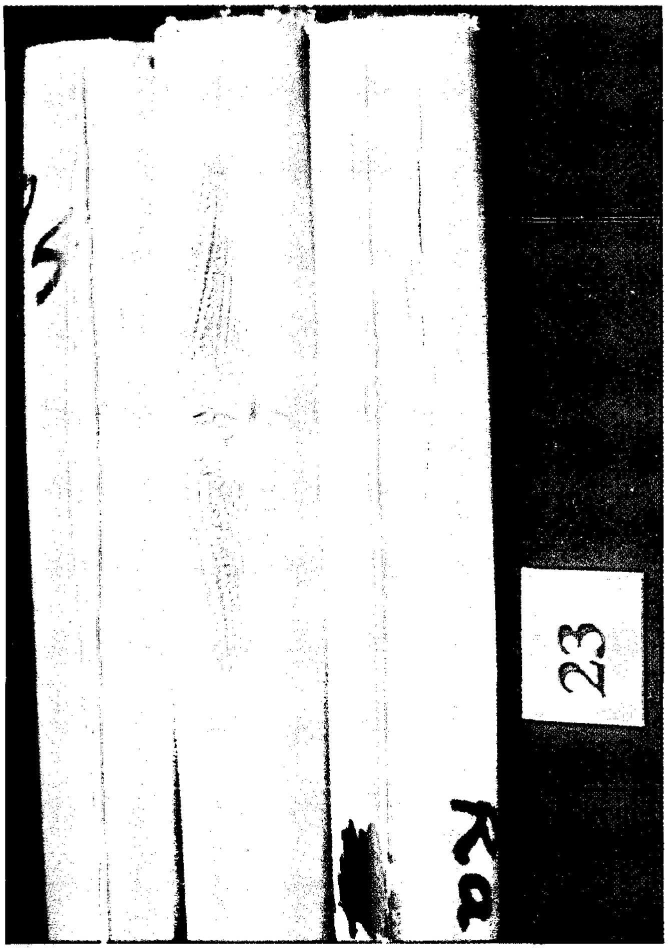
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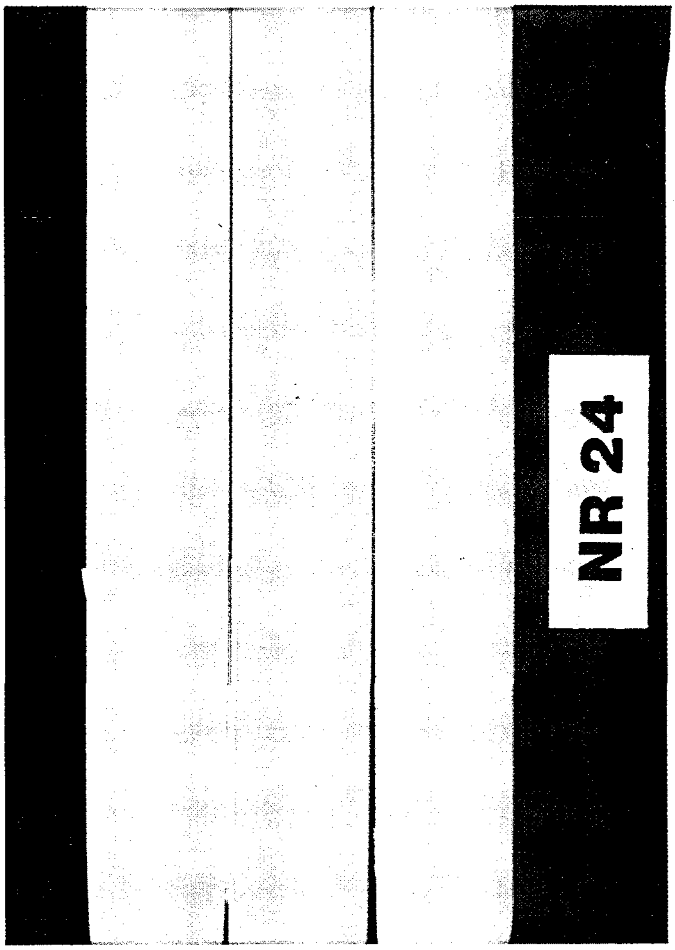

NR 24

4. THERMAL STABILITY

4.1 Introduction

The service life of polymer products (e.g. plastic pipes) depends on environmental factors such as temperature, mechanical stress, exposure to UV radiation etc. Organic polymers are very susceptible to oxidative degradation by molecular oxygen even at ambient temperatures. The degradation process is slowed down by the addition of catalytic amounts (0,1 to 0,5%) of antioxidants and other stabilizers [1 - 3].

4.2 The Mechanism of Oxidative Degradation

An understanding of the mechanism of degradation helps to clarify the role of antioxidants. Plastics degradation usually starts with the formation of free radicals on exposure to heat, UV radiation or mechanical shear. Free radicals have a high affinity for oxygen and react to form unstable peroxy radicals. These in turn form unstable hydroperoxides by hydrogen abstraction from nearby chains [1-4]. This process regenerates a new alkyl radical. At the same time, further free radical species are formed by the decomposition of the hydroperoxides (by heat, shear stresses or UV light etc.). This reaction is often catalysed by impurities such as metal ions or catalyst residues. This leads to a cyclic process resulting in an ever increasing number of reactive free radical species i.e. an autocatalytic degradation process. The cycle can only be broken when inert products are formed from the radical species. The chemical reactions involved in the auto-oxidative degradation cycle process are summarized in Scheme I. The cyclic nature of the process and possible mechanisms for stabilization are given in Scheme II.

SCHEME I: Model for the oxidative degradation of polyolefins [1-4]

1. **Initiation**

$$R \xrightarrow{\Delta,\ h\upsilon,\ \tau} R^\circ$$

(polymer chain) (alkyl radical)

$$R^\circ + O_2 \longrightarrow ROO^\circ$$

(alkyl peroxy radical)

2. **Propagation**

$$ROO^\circ + RH \longrightarrow ROOH + R^\circ$$

(hydroperoxide)

$$ROOH \xrightarrow[M^+/M^{2+}]{\Delta} RO^\circ + ROO^\circ + H_2O$$

$$ROOH \xrightarrow{h\upsilon} RO^\circ + {}^\circ OH$$

$$RO^\circ + RH \longrightarrow ROH + R^\circ$$

etc.

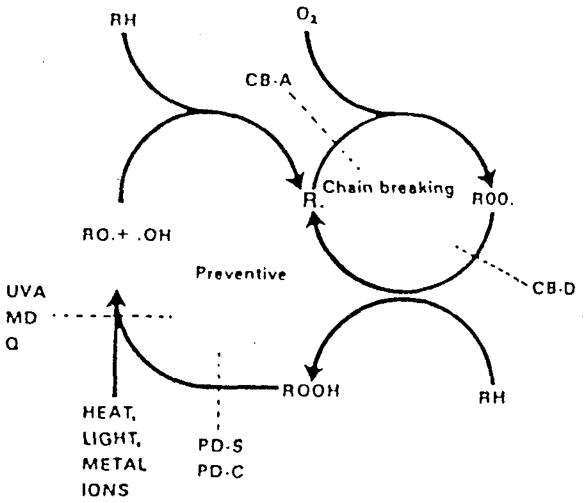
3. **Termination**

$$2\ ROO^\circ \longrightarrow \text{inert products} + O_2$$

$$ROO^\circ + R^\circ \longrightarrow ROOR$$

$$2\ R^\circ \longrightarrow R\text{-}R$$

SCHEME II: **Antioxidant mechanisms in the oxidative degradation processes of polyolefins [1]**



CB-A	Chain breaking by electron acceptors (quinones)
CB-D	Chain breaking by electron donors (hindered phenols and aromatic amine)
PD	Peroxide decomposition (phosphite esters)
UVA	UV absorber (hindered amine light stabilizers)
MD	Metal deactivators
Q	Quencher

4.3 The Stabilization Mechanism of Antioxidants

In the technical literature antioxidants are classified as primary antioxidants and secondary antioxidants [2]. Primary antioxidants interrupt the oxidation cycle by scavenging the free radicals while secondary antioxidants or synergists reduce the hydroperoxides into inert products (see Scheme III). More scientific classifications are based on the auto-oxidative degradation cycle and the mechanism whereby this cycle is broken [1].

The effectiveness of antioxidants depends on additive volatility, solubility, diffusivity, polymer morphology, orientation and the surface-to-volume ratio of the product. The efficiency of stabilizer systems should therefore be evaluated under practical conditions wherever possible. For example, oxidative induction experiments may indicate a high intrinsic activity of an antioxidant system but these tests are conducted with the polymer in a molten state with complete antioxidant solubility and limited loss to the environment. In a practical application antioxidants may be lost through: (a) "blooming" (where the additives migrate to the surface); (b) volatilization due to low solubility of the antioxidant in the solid state; or (c) loss due to harsh environments such as exposure to solvents or hot water. Loss of antioxidants may have a detrimental effect on service life [1]. Also, antioxidants tend to be present in the amorphous regions only as they are excluded from the crystallites.

In practice there is usually a dual need for protection against oxidative degradation. During processing the polymer chains are exposed to high temperatures and shear stresses but usually for relatively short periods only. In these situations free radicals are formed via mechanically induced bond scission and the issue of antioxidant loss and solubility are not that important. In end-use applications, temperatures are much lower but UV exposure is possible and long service life is required.

SCHEME III: Antioxidant mechanisms [2-4]

1. **Inhibition of the Propagation Reaction of ROO°**

$$ROO^{\circ} + AH \longrightarrow ROOH + A^{\circ}$$

Examples of AH include hindered phenols and secondary arylamines. They act as primary antioxidants by donating their reactive hydrogen to the peroxy radicals. In turn a highly stabilized free radical is formed through electron delocalization (resonance) and steric hinderance.

2. **Suppression of the Regeneration of ROOH**

$$ROO^{\circ} + S \longrightarrow RO^{\circ} + SO$$

Synergists reduce ROO° to RO°.

3. **Decomposition of ROOH by Non-Radical Processes**

$$ROOH + A \longrightarrow ROH + AO$$

Phosphites, amines and thioesters decompose hydroperoxides by two electron redox processes or via catalytic pathways.

4. **Metal Deactivators**

$$ROOH + M^{n+} \longrightarrow RO^{\circ} + M^{(n+1)+} + HO^{-}$$

$$ROOH + M^{(n+1)+} \longrightarrow ROO^{\circ} + M^{n+} + H^{+}$$

Chelating agents reduce the catalytic activity of metal ions such as copper ions.

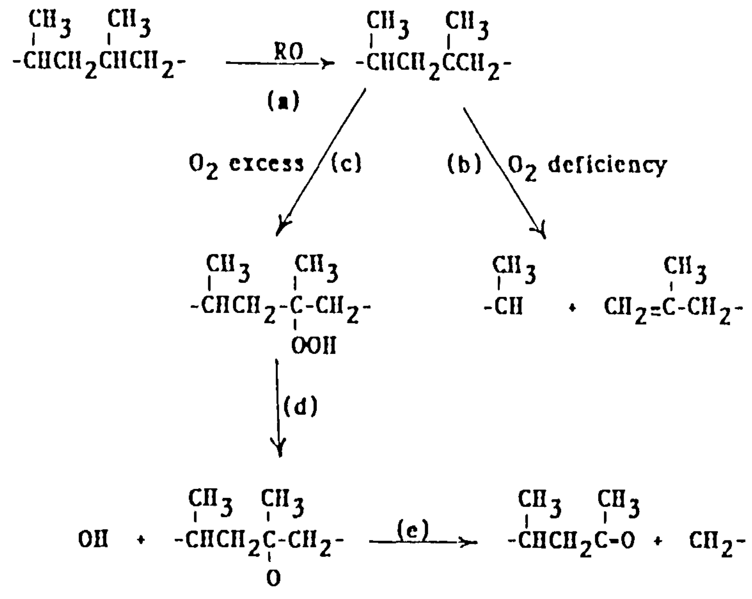
4.4 Oxidative Degradation of Polypropylene

Polypropylene is thermally stable up to approximately 230 °C in the absence of oxygen. In the range 230 °C to 300 °C the molecular weight decreases via a random chain scission process. Degradation rates are strongly affected by residual polymerization catalysts and hydroperoxides formed during storage. Above 300 °C volatilization commences and rapidly increases with temperature.

In general polypropylene is more susceptible to oxidative degradation than other polyolefins such as polyethylenes or polybutylene. This is a direct result of the chain microstructure of this polymer. The hydrogen on the tertiary chain carbons is more labile and therefore easier to abstract by radical attack. In addition, abstraction generally leads to chain scission as shown in Scheme IV. This leads to a rapid decrease in molecular weight and a concomitant loss of mechanical properties such as tensile strength.

Stabilization of polypropylene is commonly achieved using high molecular weight phenolics in combination with a phosphite or thioesters at concentrations of 0,1 - 1%.

SCHEME IV: Chain Scission in Polypropylene [1]



Life expectations may necessitate the use of less volatile antioxidants and UV stabilizers featuring better compatibility with the polymer matrix.

As already indicated, polypropylene suffers oxidative degradation in the presence of oxygen especially at high temperatures [5-7]. Characteristic of this process is a temperature dependent induction period during which the mechanical properties of the material remain virtually unchanged. At the end of this oxidative induction time (OIT) a sharp deterioration of mechanical properties sets in.

The OIT may be taken as a measure of the effective service life at the representative temperature. The oxidative degradation of poly(1-butene) and cross-linked polyethylene pipe extrusion compounds were studied by Kramer [8-11]. Steiner and Koppelman [12] also investigated the thermal degradation of polypropylene at 90 °C. At the OIT, a strong correlation was found in rapid changes of the following physical properties:

- Carbonyl absorbtion in the infra-red spectrum;
- dielectric loss factor (tanδ);
- tensile strength and elongation-at-break; and
- oxidative induction time (OIT) measured by DTA.

While, ideally, the oxidative stability of polypropylene pipes should be measured *in situ*, i.e. in the actual end use application, this is not practical in view of the long service life (>20 years) required. The degradation processes in the solid state are difficult to measure and the kinetics complex. This makes it very difficult to estimate service life from accelerated tests as extrapolations may be unreliable [12].

Steiner [11] has shown that, for polybutylene pipes, pipe failures at 110 °C, low hoop stresses and long testing times were exclusively caused by oxidative degradation due, in the greater part, to leaching of stabilizer by the hot water. Broutman [13] has found that surface embrittlement, due to oxidative degradation, was sufficient to shorten expected service life of polyethylene pipes significantly via brittle failure. Removal of less than 0,03 mm of the pipe surface restored ductile behaviour. It was concluded that surface embrittlement may aid premature crack initiation at relatively low stresses.

4.5 Characterization of Oxidative Degradation

The oxidative degradation of polypropylene can be followed by a wide variety of techniques including:

- **Oven ageing** [5,12,14,15,37]
  Thin samples are aged in recirculating ovens at a pre-set temperature. The effectiveness of residual antioxidants is determined periodically using DSC or DTA. Alternatively the time to mechanical embrittlement is taken as the OIT.

- **Oxygen uptake** [5,16,17]
  The oxygen uptake of polymer samples at a given temperature is followed as a function of time. It was found that the OIT corresponds to an oxygen uptake of less than 10 cm^3/g of polymer.

- **Differential thermal analysis (DTA) and differential scanning calorimetry (DSC)** [8,12,18,25]
  These techniques are commonly used owing to their convenience and ease of automation. Both modes of analysis can use either isothermal or temperature scanning techniques. These techniques report the induction time (temperature) to an autocatalytic degradation exotherm.

- **Thermogravimetric analysis (TGA)** [20,26]
  Both isothermal and temperature scan procedures are used to determine an induction time (temperature). The induction time is usually indicated by a rapid loss of sample mass but this is often preceded by a weight gain due to oxygen uptake.

- **Pyrolysis** [27-31]
  Volatilization of the polymer occurs beyond the oxidative induction time (OIT) and this can be detected by mass spectrometry, infra-red spectroscopy or even a thermal conductivity detector.

- **Decrease in molecular mass** [8,25,32]
  The molecular mass of polypropylene decreases rapidly during oxidative degradation via a variety of chain scission mechanisms. This decrease in molecular weight can be followed by gel permeation chromatography (GPC), viscosity (e.g. MFI measurements) decrease in glass transition temperature (Tg), etc.

4.6 Estimation of Service Life

The specified service life of polypropylene pipes is typically in the order of years to several decades. This implies that oxidative degradation must proceed exceedingly slowly at service temperatures. However, there is a need to estimate expected service life from measurements conducted within reasonable time. This usually necessitates experiments at elevated temperatures, often at temperatures above the melting point of the polymer [16].

Oxidative induction times (OIT's) measured over a range of temperatures often obey Arrhenius kinetics [16]. This means that a plot of log (OIT) versus the reciprocal absolute temperature obtains a straight line with slope proportional to the activation energy. In some studies no change in slope is observed when traversing the melting range e.g. for polyethylene [16,26] and in polypropylene [17]. However, in other investigations a change in slope is observed, e.g. for polybutylene [9], or the data shows two regimes separated roughly by the melting point, e.g. for polypropylene [12,14]. It is therefore clear that extrapolation of results obtained at high temperatures may be misleading if interpreted in terms of oxidative stability under normal conditions [5]. The following factors each play a role in this regard:

- In the solid state the polymer assumes a semi-crystalline morphology. It is usually assumed that oxygen and stabilizers are constrained to amorphous regions.

- Solubility and diffusivity of oxygen is strongly influenced by the degree of crystallinity and the morphology of crystallites.

- Sample thickness plays a role: the oxidation rate becomes diffusion controlled for thicker samples [24,31,33,34]. It has been stated [35] that sample thickness should be less than 120 μm in DSC or DTA studies to ensure kinetic control of degradation.

- Orientation (and therefore built-in stresses) may affect oxidative stability. Surprisingly it has been found that oriented material shows an improved oxidative induction time and maintains a greater proportion of mechanical properties at comparable degrees of degradation [32].

- Some synergistic stabilizers are only effective at higher temperatures (e.g. those experienced during processing or testing) and do not contribute to stabilization at service temperatures [36].

- Volatilization of stabilizers at elevated temperatures and leaching or blooming of antioxidants at services temperatures may also impact estimated and actual service life times [6,11].

- Degradation by mechanical stress during processing results in reduced OIT's compared to virgin material [19]. This has obvious significance for the use of re-grind material.

While accelerated tests such as those described above usually employ testing at elevated temperature, it is also possible to increase the rate of degradation through the use of high oxygen pressures [33]. While this could represent a useful quality control technique, it is difficult to see how this technique could be used in a predictive mode in view of the complex dependence of reaction kinetics on oxygen concentration and the complications of diffusion and solubility limitations.

The residual life of oven aged samples can also be assessed using mechanical testing. In this regard it should be noted that tensile strength does not provide a suitable criterion [7]. However, elongation-at-break does provide a useful indication of the state of ageing. Here it should be mentioned that Underwriters Laboratory regards failure to have occurred when physical property values have dropped below 50% of their initial value.

4.7 Theoretical Model for Antioxidant Consumption

In this approximate analysis we make the following simplifying assumptions:

- Reaction rate controlled - no diffusional limitations.
- Stabilization is essentially due to the level of antioxidant present.
- Antioxidant is consumed during the inhibition reactions.
- The induction time corresponds to the point where complete depletion of the antioxidant has occurred.
- The consumption of antioxidant is dominated by a rate limiting step with an associated Arrhenius temperature dependence.
- Temperature and concentration effects are separable and the antioxidant concentration effect can be modelled in terms of n^{th} order reaction kinetics.
- Concentration refers to an effective lumped concentration of all antioxidants present.

In terms of this model:

$$-\frac{dc}{dt} = k \exp\left(\frac{-B}{T}\right) f(c) \qquad (1)$$

where k = is the pre-exponential factor,
B = E/R is the activation temperature with
E = the activation energy and
R = the gas constant while the function
$f(c)$ = c^n represents the rate dependence on
c = the concentration of antioxidant.

From equation (1) one obtains the integral:

$$F(c_o) = -\int_o^{c_o} \frac{dc}{f(c)}$$

$$= k \int_t^o \exp\left(\frac{-B}{T}\right) dt \qquad (2)$$

For isothermal conditions equation (2) can be integrated directly to yield the following expression for the isothermal induction time:

$$\begin{aligned} OIT &= \frac{F(c_o)}{k} \exp\left(\frac{B}{T}\right) \\ &= A \exp\left(\frac{B}{T}\right) \end{aligned} \tag{3}$$

Taking logarithms obtains:

$$\begin{aligned} \ln\,(OIT) &= \ln\left(\frac{F(c_o)}{k}\right) + \frac{B}{T} \\ &= A + \frac{B}{T} \end{aligned}$$

which shows that a plot of log (OIT) versus the inverse absolute temperature gives a straight line with slope **B** and intercept $\ln\left(\frac{F(c_o)}{k}\right)$.

For dynamic temperature scans at a scan rate of β °C/s the following approximation for $F(c_0)$ can be derived:

$$F(c_0) = \frac{k}{B}\left(\frac{T^2}{\beta}\right) \exp\left(\frac{-B}{T_i}\right) \tag{4}$$

which, on plugging into equation (5) gives:

$$\ln\left(\frac{T_i^2}{\beta}\right) = \ln\left(\frac{BF(c_o)}{k}\right) + \frac{B}{T_i} \tag{5}$$

This shows that a plot of $\ln\left[T_i^2/\beta\right]$ versus the inverse of the induction temperature should give a straight line with slope B and intercept $\ln\left(BF(c_0)/k\right)$.

OIT can conveniently be evaluated using DSC or DTA methods if the OIT falls in the range of several minutes to one hour. For longer times DSC analysis becomes impractical and one has to resort to oven ageing tests.

In oven ageing tests it is not possible to observe the OIT directly as in DSC analysis. Rather it is necessary to remove samples periodically to evaluate their state of oxidation. Assume that the oven is at a temperature T_1, that a sample is removed after time t_1 and subjected to a residual OIT (by DSC) evaluation (t_2) at temperature T_2 (i.e. isothermal conditions). From equations (1) to (3):

$$t_1 = \left(\frac{F(c_o) - F(c)}{k}\right) \exp\left(\frac{B}{T_1}\right)$$

$$t_2 = \frac{F(c)}{k} \exp\left(\frac{B}{T_2}\right) \tag{6}$$

$$= OIT_{residual} \tag{7}$$

$$t_1 = \frac{F(c_o)}{k} \exp\left(\frac{B}{T_1}\right) - t_2 \exp\left[B\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \tag{8}$$

$$= OIT_1 - constant \times OIT_{residual}$$

This shows that a plot of oven time versus residual OIT should give a straight line. The OIT at the oven temperature can be evaluated from the intercept of this straight line.

4.8 Experimental

Three different locally manufactured pipes were evaluated for oxidative stability. Small samples were ground to a fine powder using a laboratory mill. Thin (0,2 mm) shavings were also machined off the end of the pipes. For control purposes thin films of the raw material containing different antioxidant levels were prepared by the raw materials supplier using a laboratory film blowing machine.

The oxidative stability of the different pipe samples were measured as follows:

- **High temperatures (>180 °C)** The OIT was measured in an oxygen atmosphere using DSC and TGA techniques. Both dynamic scanning and isothermal runs were conducted.

- **Low temperatures (150 °C - 90 °C)** Samples were oven aged in air and the stage of ageing assessed using tensile tests with elongation-at-break being used as the failure criterion (50% of initial elongation at break). A set of experiments were also conducted using shavings aged in boiling water to determine the effect of antioxidant leaching.

4.9 Results

4.9.1 High Temperature Results

The isothermal oxidative induction times for the three pipes were measured between 190 and 225 °C in oxygen. The results are shown in Table 4.1. Reproducibility decreased with decreasing temperature. The standard deviation for four determinations varied between ca. 8-15%. The oxidative induction temperature was also evaluated dynamically. The results for scan rates between 1 and 40 °C/min are shown in Table 4.2.

For both isothermal and dynamic evaluations it was found that the results for the pipes B and pipes C showed considerably more scatter than those of pipes A. This is evident in Figures 4.1 to 4.3 in which the data is plotted according to equations (3) and (4). The larger scatter is attributed to the inhomogeneity of the pipe material (this was visually observable). Within experimental error, the slopes of the isothermal and dynamic curves were identical as predicted by equations (3) and (5). In a sense, the dynamic data provides estimates for OIT at higher temperatures than practically possible by the isothermal technique.

TABLE 4.1: ISOTHERMAL OXIDATIVE INDUCTION TIMES MEASURED FOR PIPES

Temperature [°C]	Oxidative induction time [min]		
	Pipe A	**Pipe B**	**Pipe C**
225	2,80 2,08 2,49 2,52 $\bar{x}$ = 2,47 s = 0,30	1,69 1,43 1,72 1,71 $\bar{x}$ = 1,64 s = 0,14	1,17 1,64 1,38 1,39 $\bar{x}$ = 1,53 s = 0,17
215	6,35 6,99 7,45 7,65 $\bar{x}$ = 7,4 s = 0,58	4,46 3,96 3,28 2,35 $\bar{x}$ = 3,51 s = 0,91	3,35 2,92 3,17 2,66 $\bar{x}$ = 2,18 s = 0,31
200	39,2 41,5 40,2 $\bar{x}$ = 40,3 s = 1,1	16,3 13,7 15,5 18,2 $\bar{x}$ = 15,9 s = 1,9	10,4 15,9 12,4 14,5 $\bar{x}$ = 13,3 s = 2,4
195	58,3 59,4 55,2 $\bar{x}$ = 56,7 s = 2,1		
190	111,2 87,0 79,6 64,8 $\bar{x}$ = 85,6 s = 19,4		

TABLE 4.2: DYNAMIC EVALUATION OF OXIDATIVE DEGRADATION

Scan Rate β $\left[\frac{°C}{min}\right]$	ONSET TEMPERATURE [°C] Pipe		
	A	B	C
1	215,7	213,9	209,2
2	223,6	219,1	214,0
5	232,9	223,2	222,3
10	240,2	233,8	230,0
15	243,8	237,5	237,6
25	251,1	246,9	243,2
40	258,3		

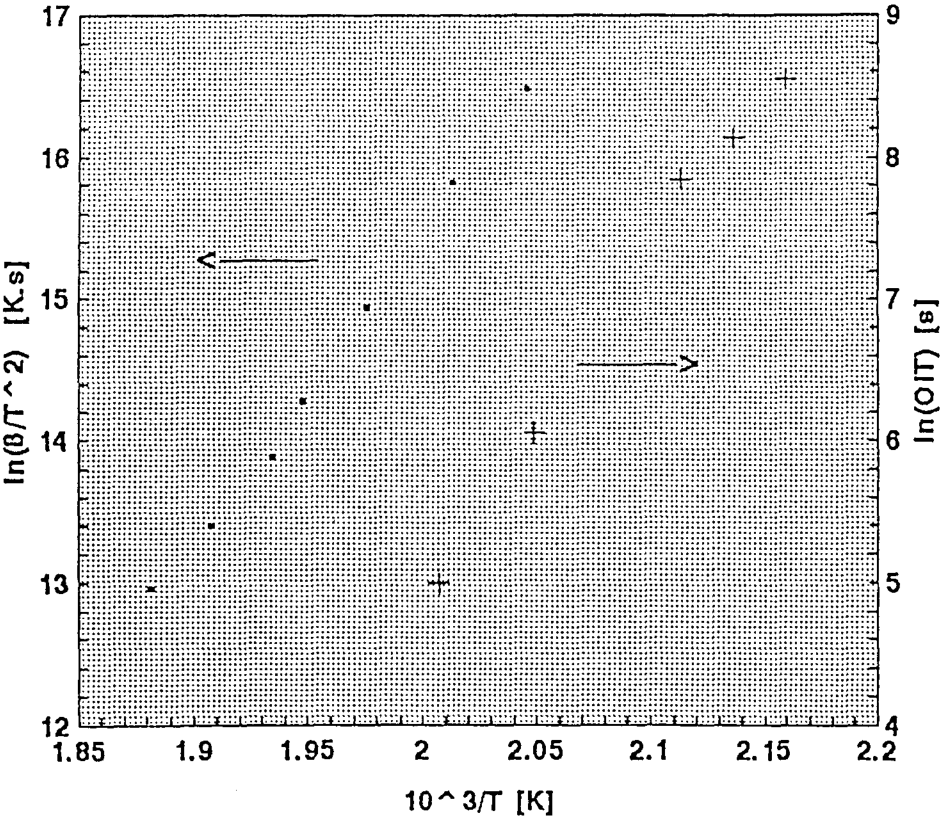


Figure 4.1: OIT measurements by DSC (Pipe A):
■ = Dynamic scanning; + = isothermal scanning

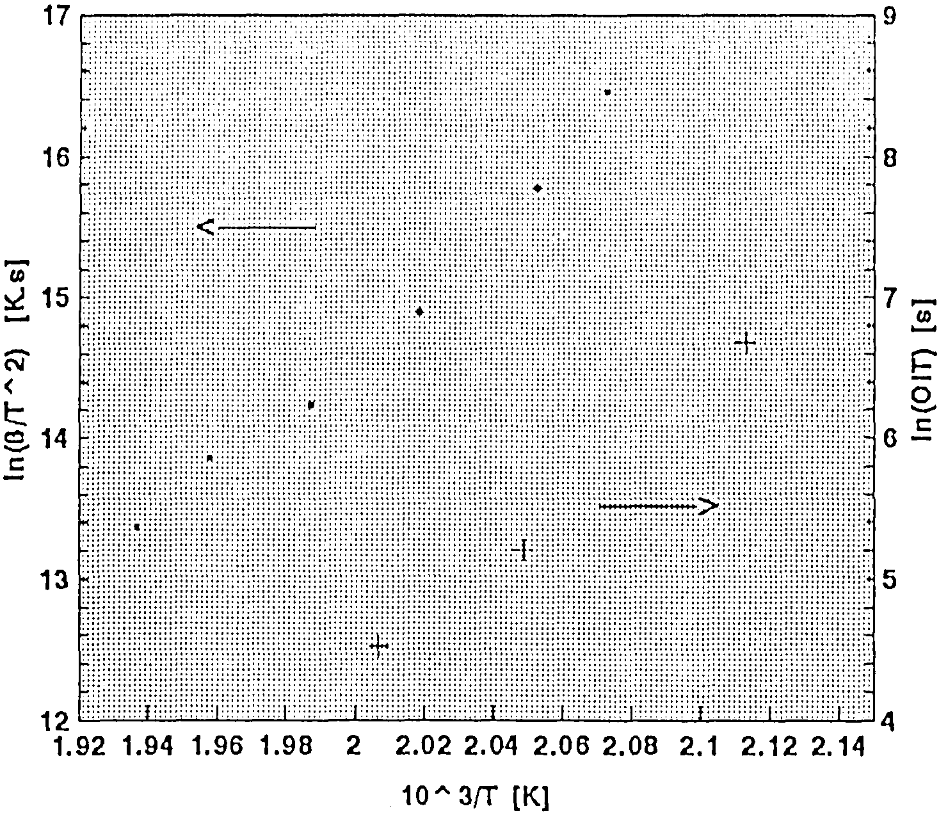


Figure 4.2: OIT measurements by DSC (pipe B):
■ = Dynamic scanning; + = Isothermal scanning

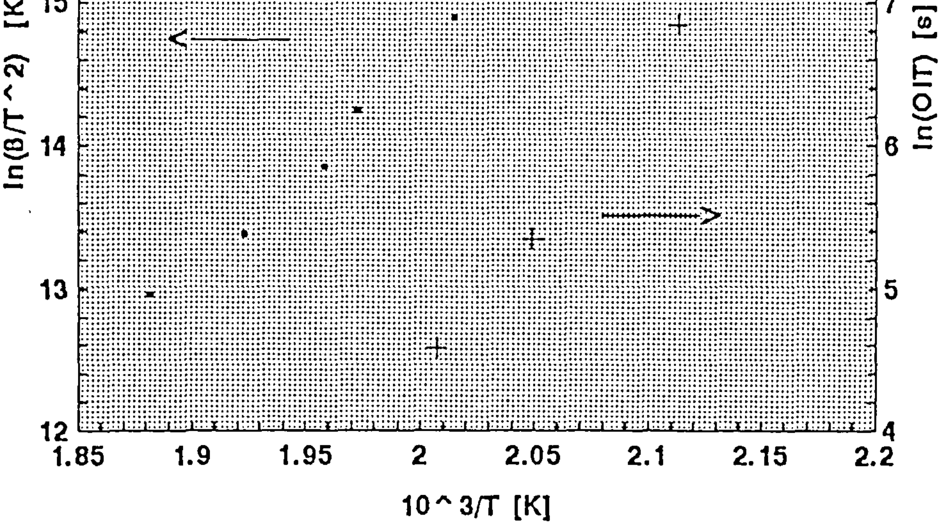


Figure 4.3: OIT measurements by DSC (pipe C):
■ = Dynamic scanning; + = Isothermal scanning

TABLE 4.3: REGRESSION COEFFICIENTS FOR OXIDATIVE INDUCTION TIME: OIT = A EXP (B/T)

	Pipe A		Pipe B		Pipe C	
	A [s]	B [°K]	A [s]	B [°K]	A [s]	B [°K]
Isothermal	255x10^{-21}	23 850	14,3x10^{-18}	21 580	32,9x10^{-18}	21 060
Dynamic Scanning	7,16x10^{-18}	22 150	265x10^{-21}	23 520	5,57x10^{-18}	21 880
Difference at 200 °C [%]	38%		-11%		4%	

Table 4.3 lists regression coefficients for OIT as a function of temperature in terms of an Arrhenius model. The difference in OIT predictions from the isothermal and dynamic measurements are also compared at 200 °C. A very large difference is observed for Pipe A while the other pipes show differences within the experimental scatter of the isothermal measurements.

TABLE 4.4: CHANGE IN MECHANICAL PROPERTIES WITH OVEN AGEING AT 149 °C

Time [Days]	Pipe A		Pipe B		Pipe C	
	TS MPa	EB %	TS MPa	EB %	TS MPa	EB %
0	24,2	641	21,7	459	22,1	454
1	25,5	406	23,2	204	22,4	262
2	24,7	288	21,5	115	25,1	166
3	24,1	266	24,5	128	25,1	121
4	24,5	148	23,8	77	26,2	129
8	25,7	125	23,7	115	25,5	109

TABLE 4.5: CHANGE IN MECHANICAL PROPERTIES WITH OVEN AGEING AT 135 °C

Time [Days]	Pipe A		Pipe B		Pipe C	
	TS MPa	EB %	TS MPa	EB %	TS MPa	EB %
0	24,2	641	21,7	459	22,1	454
1	24,9	395	23,4	202	24,9	279
2	23,2	377	23,8	181	25,2	282
4	27,0	-	24,8	129	25,0	134
7	23,3	256	24,3	-	26,5	-
8	24,4	255	23,6	140	25,4	220
14	25,7	-	23,7	145	20,9	71
28	24,1	218	25,3	105	27,9	82
118		147				

4.9.2 Low Temperatures

Thin, 0,2 mm thick, shavings were used in these oven ageing tests. The tensile strength (TS) and elongation-at-break (EB) were measured at regularly spaced time intervals. Results are presented in Tables 4.4 and 4.5 for oven temperatures of 149 °C and 135 °C respectively. The data are also plotted in Figures 4.4 and 4.5 for 149 °C and 135 °C respectively. The tensile strength remains approximately constant but the elongation-at-break decreases rapidly initially but then levels off at longer times. The data also shows considerable scatter but it would appear that the Pipe A values are more consistent.

It is clear from Figures 4.4 and 4.5 that the tensile stress does not vary significantly with oven age. However, the elongation-at-break decays exponentially. The time to failure was taken as the interval at which the elongation is reduced by 50% of the initial value. This was estimated by a least squares fit to the data.

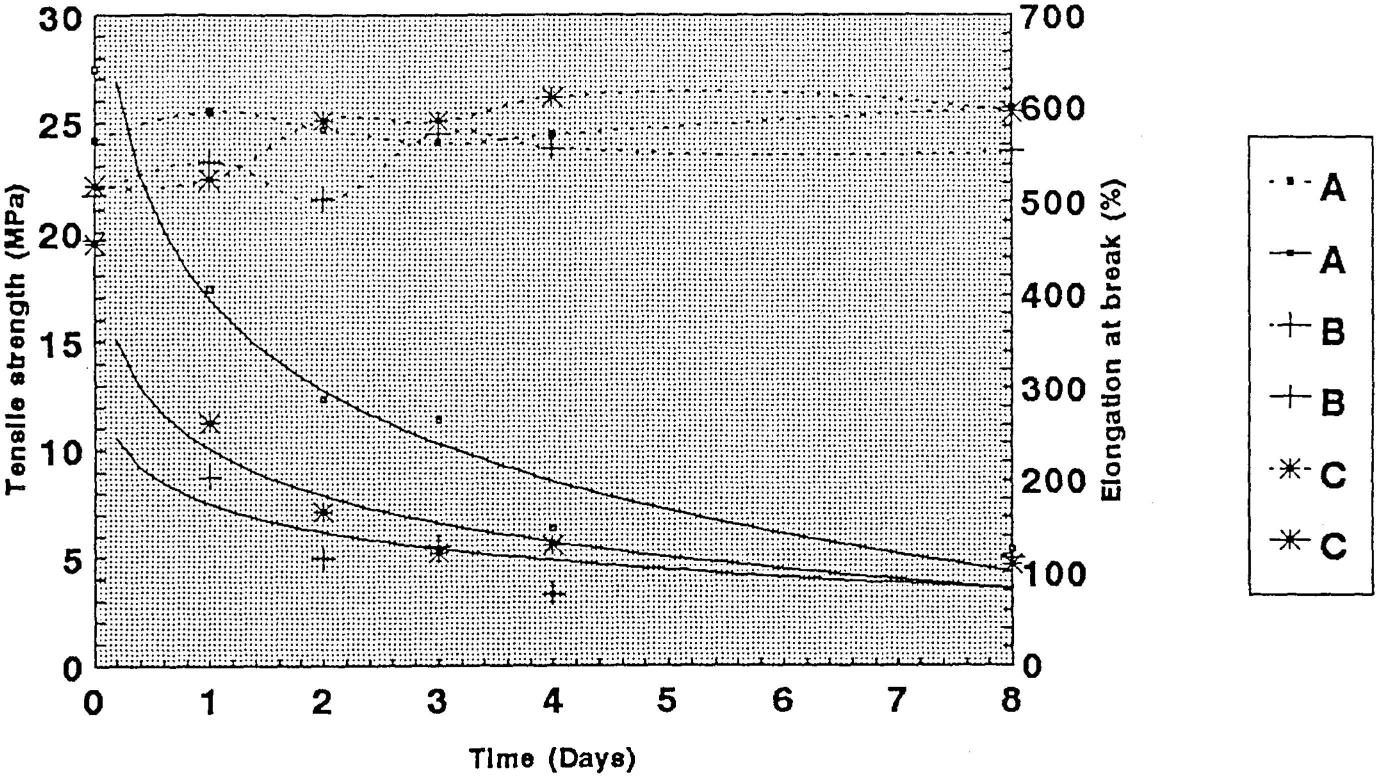


Figure 4.4: Oven ageing at 149°C:
...... = tensile strength;
------ = elongation-at-break

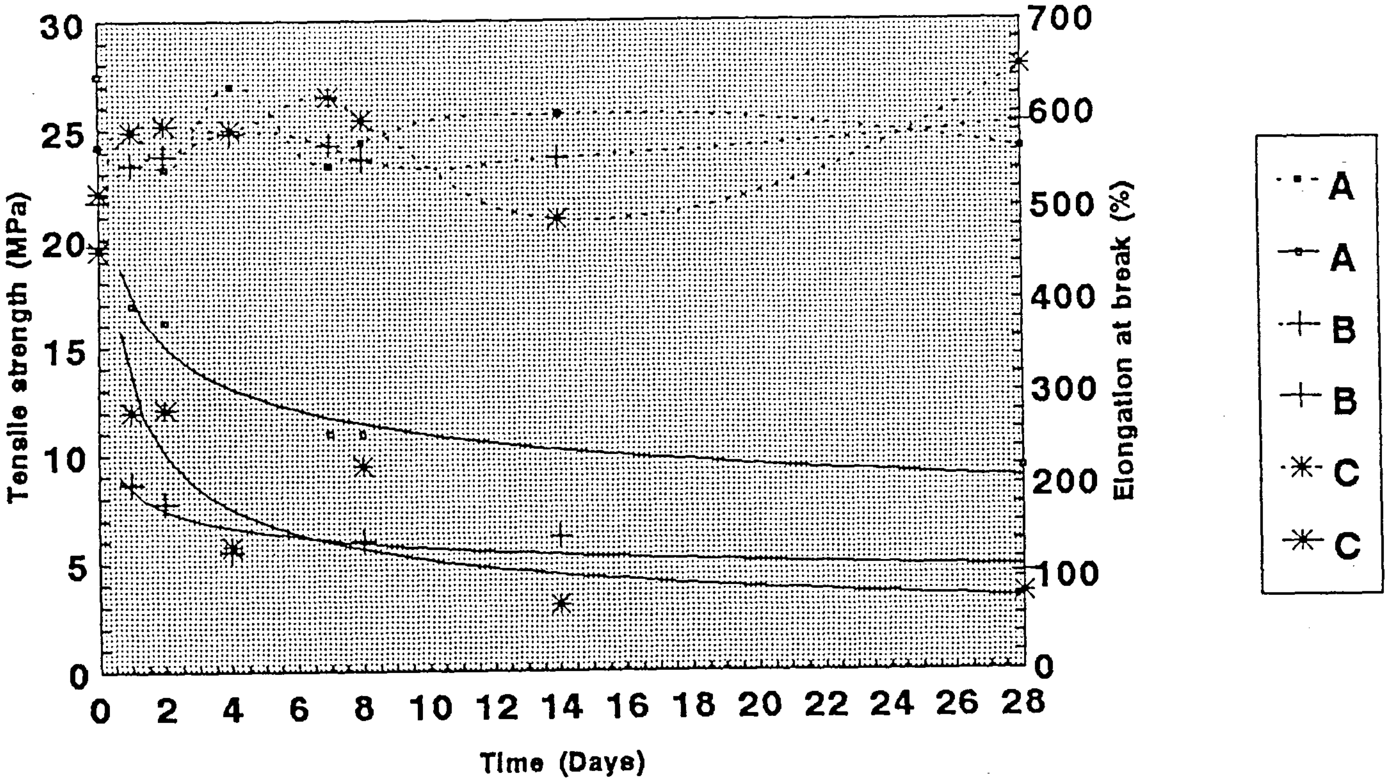


Figure 4.5: Oven ageing at 135°C:
...... = tensile strength;
------ = elongation-at-break

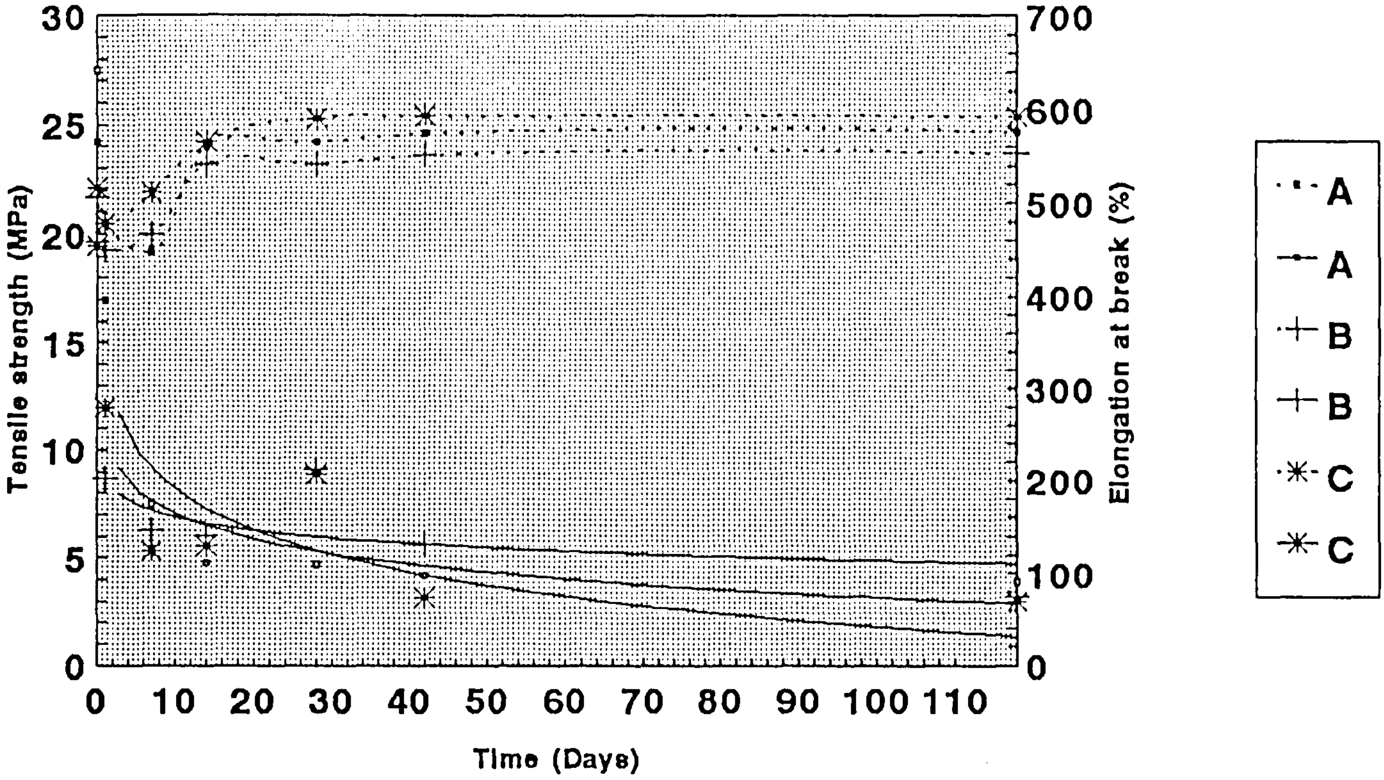


Figure 4.6: Water ageing of pipes at 93°C:
...... = tensile strength;
------ = elongation-at-break

4.9.3 Water Immersion Ageing

Shavings from pipe A were submerged in water kept at 93 °C. Samples were removed periodically and tensile properties determined. The data is plotted in Figure 4.6 and shown in Table 4.6. For all samples the elongation-at-break reduces to 50% of the initial value within ca. four days of submersion.

TABLE 4.6: WATER AGEING OF PIPES

Time [Days]	Pipe A		Pipe B		Pipe C	
	TS [MPa]	EB [%]	TS [MPa]	EB [%]	TS [MPa]	EB [%]
0	24,2	641	21,7	459	22,1	454
1	20,5	396	19,3	202	20,5	279
7	19,2	175	20,0	146	21,9	124
14	24,0	111	23,2	141	24,2	130
28	24,2	109	23,2	212	25,3	207
42	24,6	97	23,6	131	25,4	74
118	24,7	91	23,7	75	25,4	69
224	25,7	73	24,3	66	26,3	72

4.9.4 Prediction of Oxidation Life-Times

Figures 4.7 to 4.9 show life-time curves for oxidative stability based on the DSC OIT and oven ageing tests. The data fall on a reasonably straight line despite the difference in atmospheres used in these experiments (oxygen versus air). The curves can be used to estimate oxidation life limitations at lower temperatures. All pipes will last significantly longer than 3 years at 80°C and much longer than 50 years at 25°C. The data for the water immersion tests fall well below these predictions. It has been reported that the oxidation processes in polyolefins are accelerated in aqueous environments especially in the presence of dissolved salts [38]. Results obtained from these studies indicate that oxidation lifetime can be reduced 50 to 90 percent when thermal oxidation takes place in 0,1 M sodium chloride solutions at 90°C.

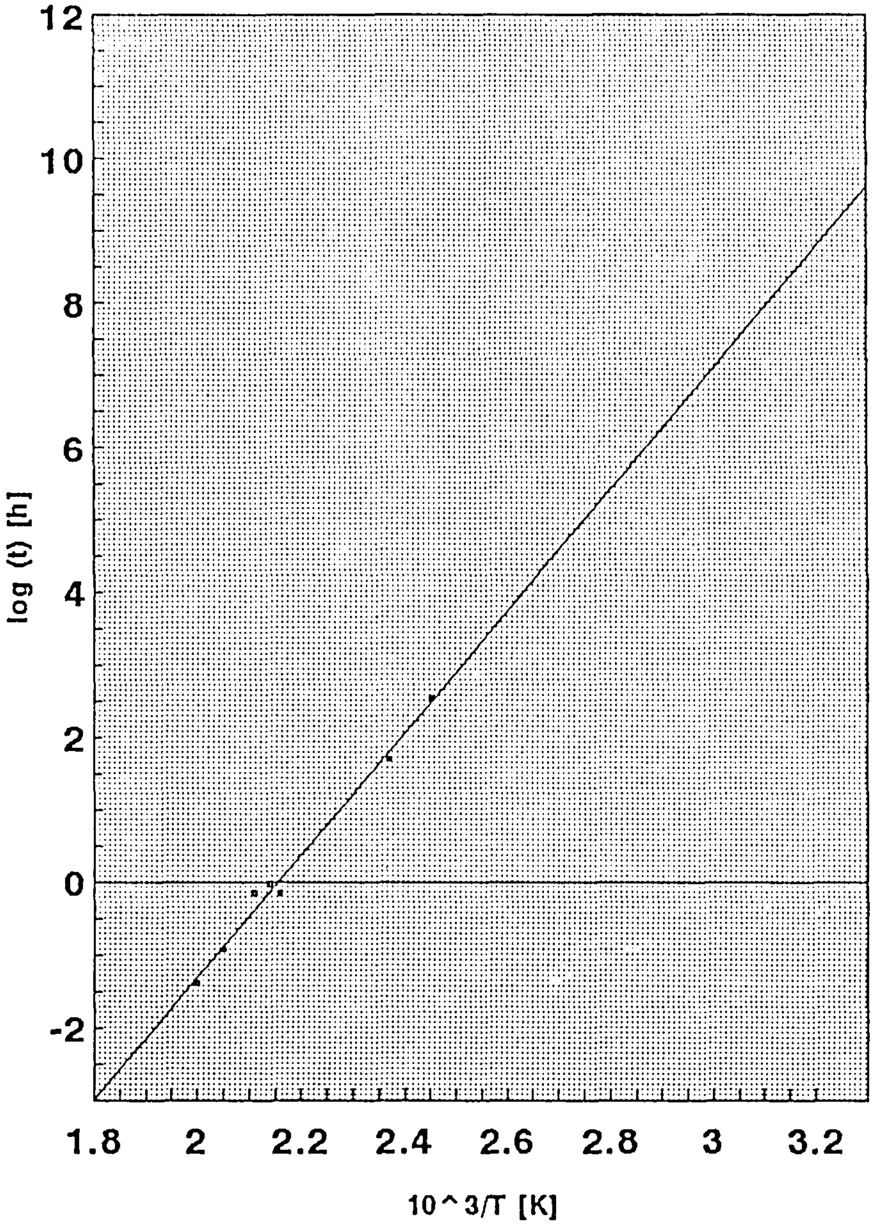


Figure 4.7: Time-temperature lifetime curves for oxidative degradation of Pipe A

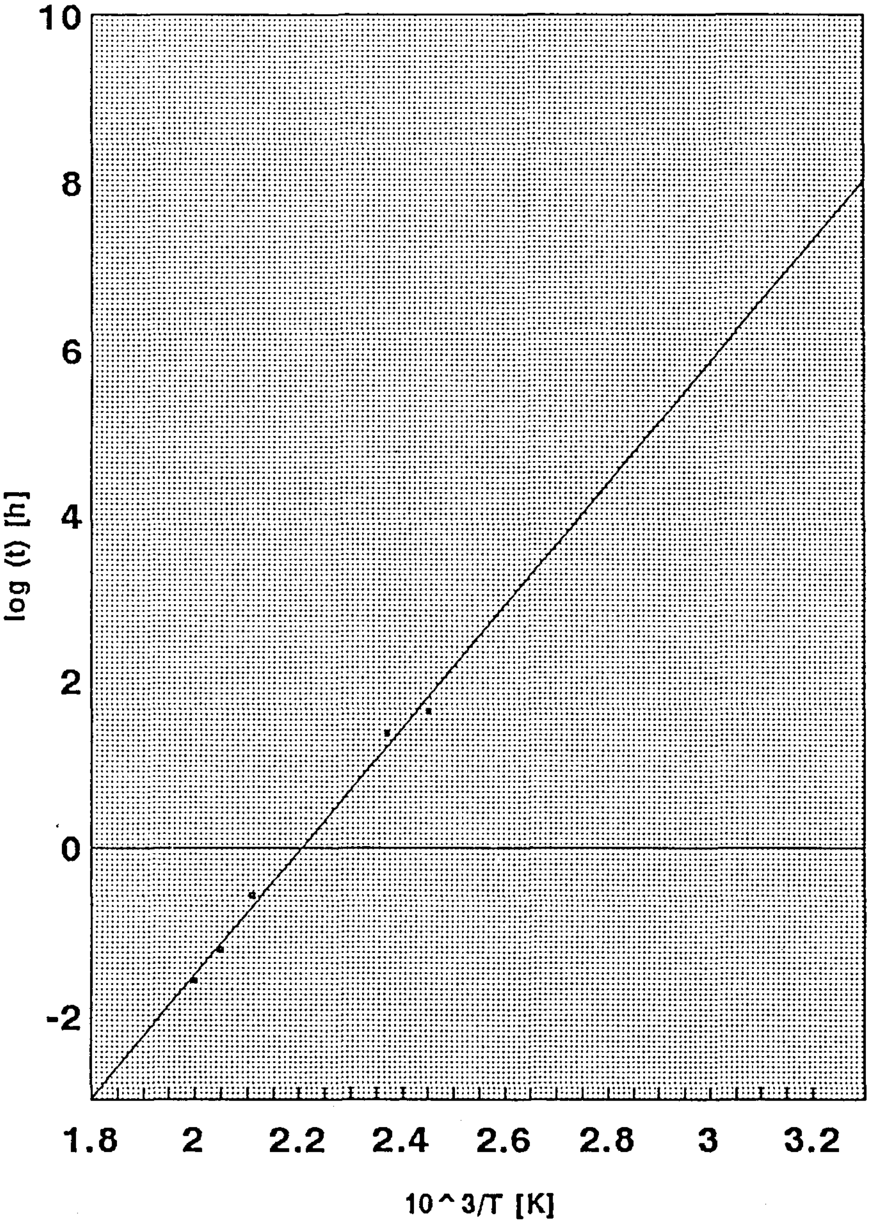


Figure 4.8: Time-temperature lifetime curves for oxidative degradation of Pipe B

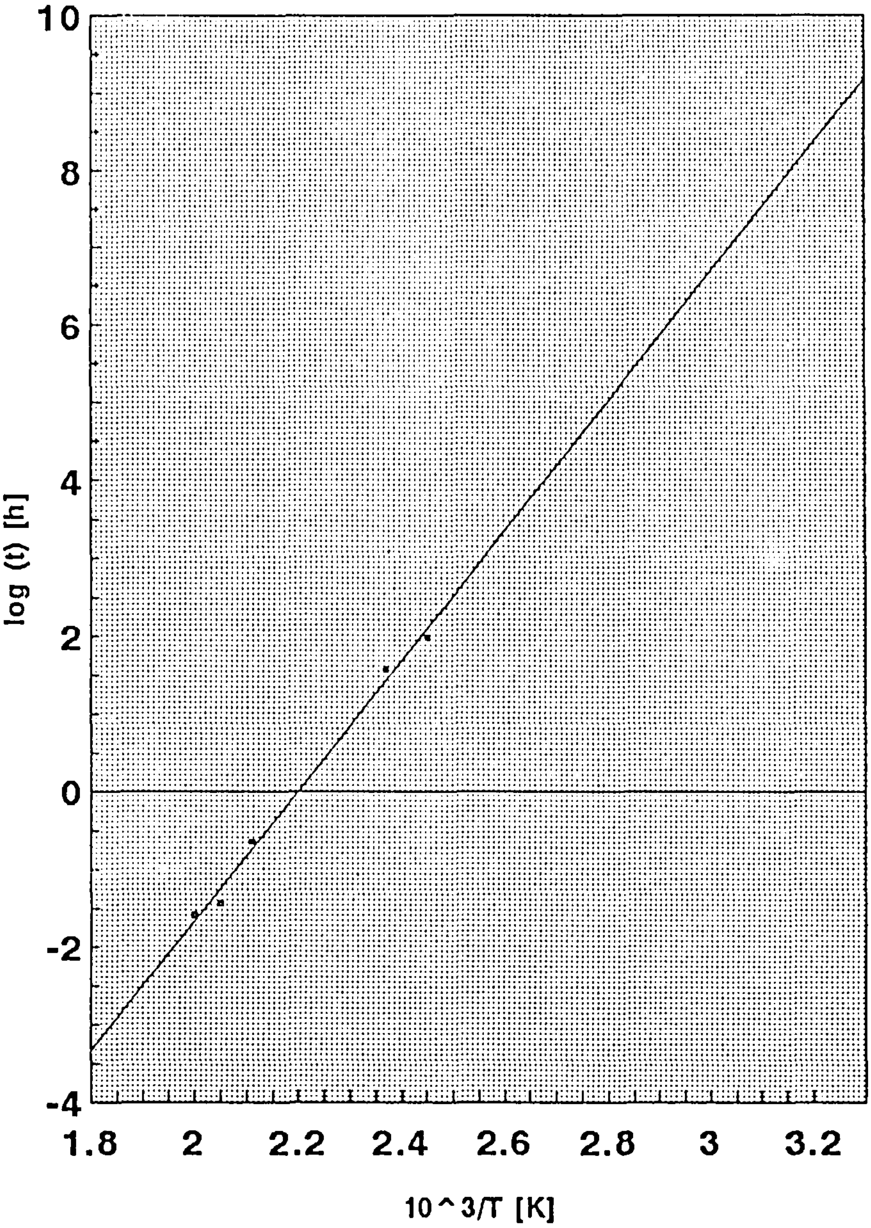


Figure 4.9: Time-temperature lifetime curves for oxidative degradation of Pipe C

4.9.5 Thermal Analysis of Controlled Film Samples

The effect of antioxidant concentrations on both isothermal and dynamic oxidation induction was measured using the polypropylene film samples. Results are presented in Tables 4.7 and 4.8.

TABLE 4.7: INFLUENCE OF ANTIOXIDANT CONCENTRATION ON ISOTHERMAL OXIDATION INDUCTION TIMES AT 200°C

Mixture #	Antioxidant Concentration [%]	OIT [min]
6	0	0,2
4	25	3,23
3	50	8,29
2	75	26,80
1	100	108,00
5	150	219,00

TABLE 4.8: INFLUENCE OF CONCENTRATION ON DYNAMIC OIT

Scan Rate β $\left[\frac{°C}{min}\right]$	Mixture (Antioxidant concentration [%])					
	1 100%	2 75%	3 50%	4 25%	5 150%	6 0%
2	226,2	218,9	212,0	197,5	237,6	166,1
5	235,2	232,0	218,2	205,0	241,7	188,0
10	246,2	240,7	231,2	213,2	250,6	191,8
25	256,2	248,7	242,0	228,8	259,3	206,2

The results are also plotted in Figures 4.10 to 4.11.

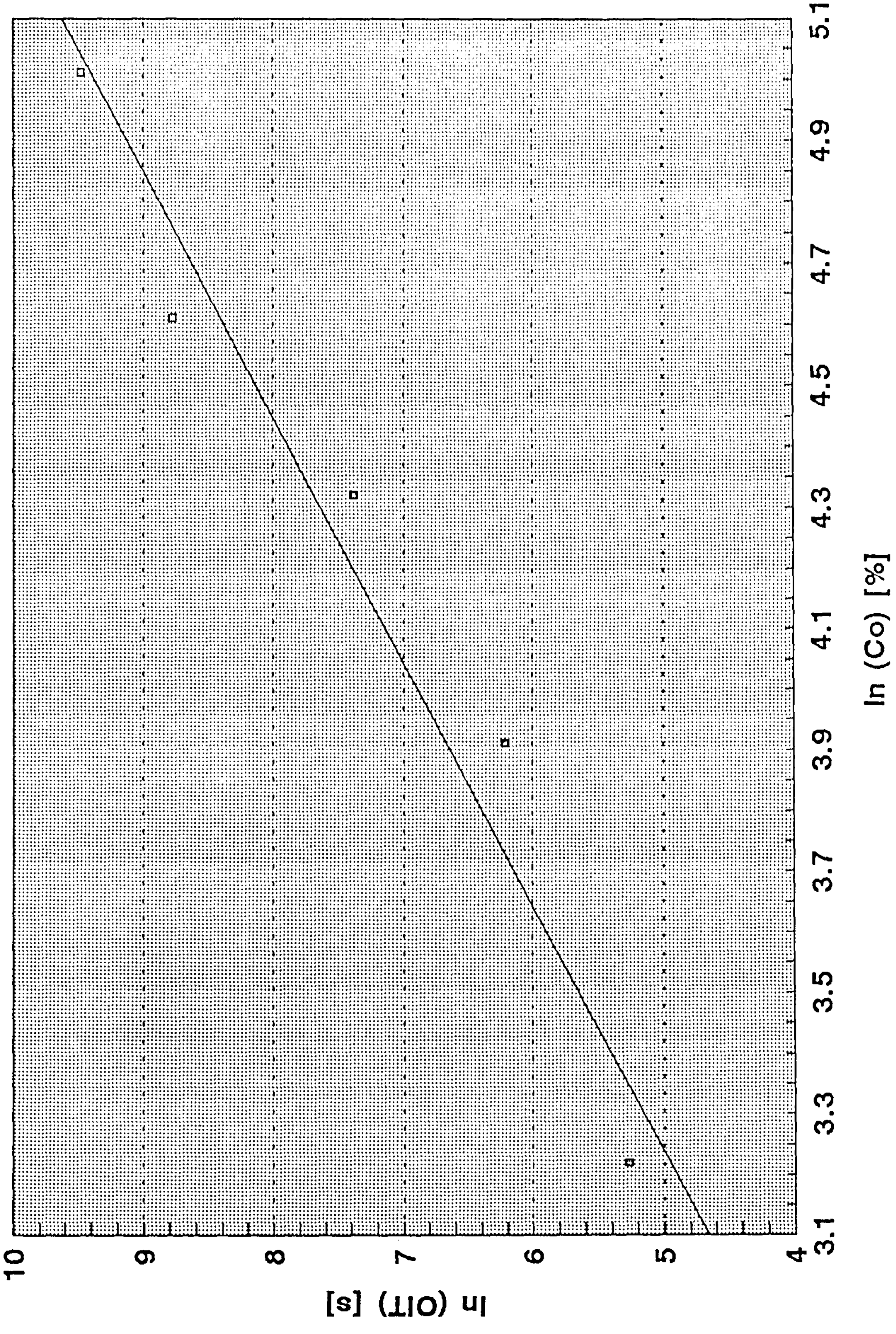


Figure 4.10: Influence of the antioxidant concentration on isothermal oxidative induction time

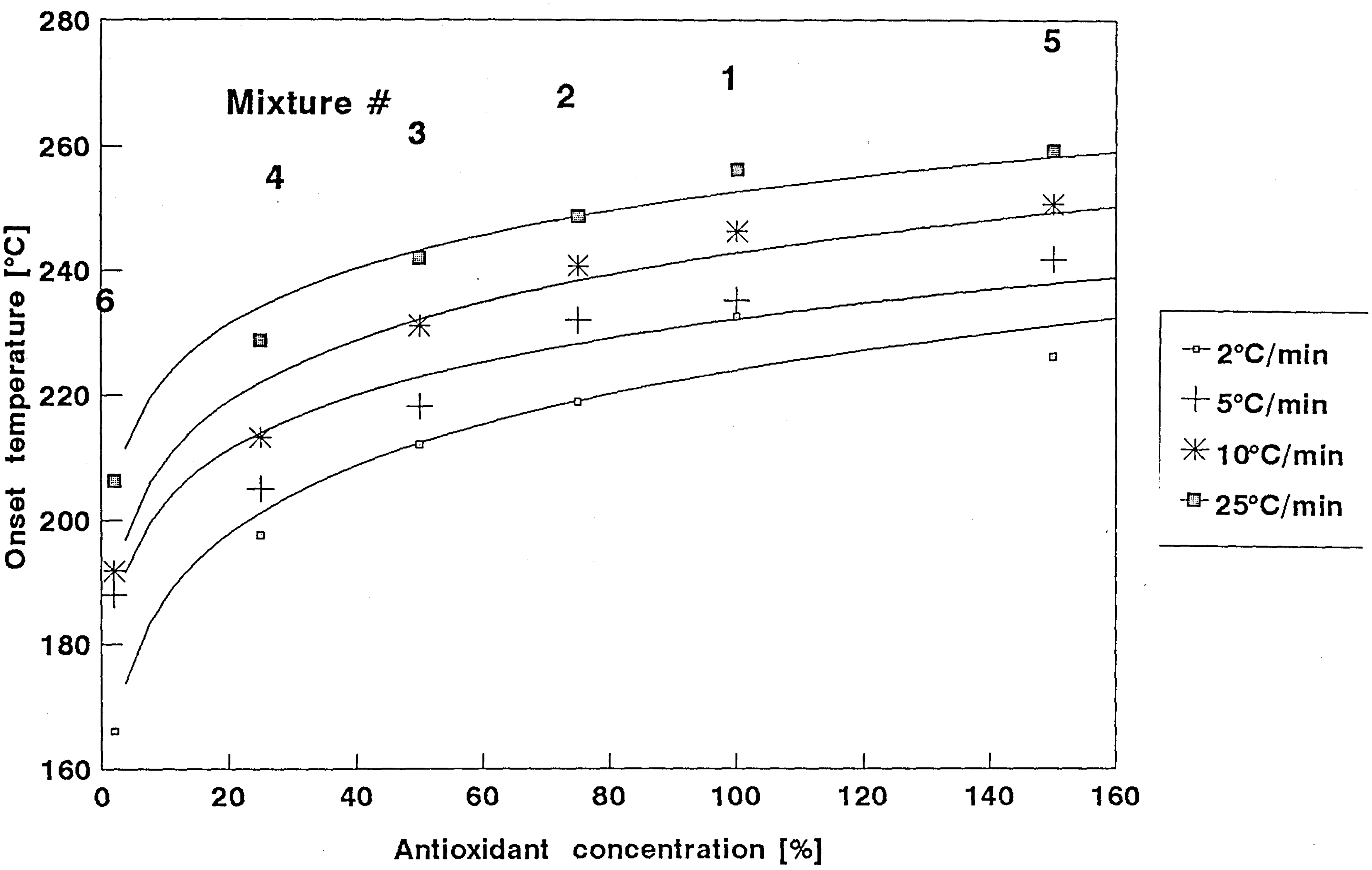


Figure 4.11: Influence of antioxidant concentration and temperature scan rate on the oxidation onset temperature

4.10 Discussion

The oxidative stability of polypropylene can be determined using DSC by two basic techniques:

Oxidation Induction Time (OIT) (ASTM D 3895)

The time from the beginning of exposure to an oxygen containing atmosphere up to the start of auto oxidation is measured in an isothermal mode.

Oxidation Induction Temperature (ASTM D 3350)

The temperature is scanned dynamically and the onset temperature of oxidation determined. Typical heating rates are 10°C and oxygen or air is used.

The dynamic method has the following advantages:

- **Convenience**
  It is not necessary to switch from an inert gas to an oxidizing gas.
- **Speed**
  The OIT can vary tremendously depending on the level of stabilization. This means that the temperature must often be adjusted in order to obtain meaningful results with the isothermal method.
- **Reproducibility**
  Studies by Koski and Saarela [23] have shown that the dynamic method is more reproducible. The current investigation has confirmed this.

Fitting equations (3) and (5) to the data, in Tables 4.7 and 4.8 respectively, resulted in:

$$OIT = 4{,}77 \ x \ 10^{-24} \ C^{2{,}5} \ \exp\left(\frac{2200}{T}\right) \tag{9}$$

for isothermal oxidation; and

$$\left(\frac{Ti^2}{\beta}\right) \exp\left(\frac{-2200}{T}\right) = 1{,}465 \ x \ 10^{-18} \ C^{1{,}89} \tag{10}$$

for dynamic oxidation. The differences in the observed concentration dependences may indicate that the model used for the anti-oxidation, equation (1), is inadequate or, alternatively, the difference results from the data scatter.

Assuming that the pipes contain the same antioxidant, we can estimate the remaining concentration.

TABLE 4.9: ESTIMATION OF RESIDUAL ANTIOXIDANT CONCENTRATION

Pipe	Isothermal OIT @ 200°C in oxygen	Dynamic oxidation at 10°C/min in oxygen
A	78%	85%
B	54%	63%
C	50%	53%

TABLE 4.10: COMPARISON OF INTERLABORATORY RESULTS

Laboratory	Isothermal Oxidation Induction Times [min]					
	Conditions		Sample Pipe			
	T [°C]	Atmosphere	A	B	C	D
Industrial	225	Air	45	13	37	59
	215	Air	167	130	140	145
	200	O_2	141	87	46	>180
Research	200	O_2	42,3	15,9	13,3	-

The Table shows that the dynamic method predicts a slightly higher antioxidant concentration. Inspection of equations (9) and (10) and Figures 10 and 11 shows that the isothermal technique is more sensitive to concentration effects. A 10% increase in concentration results in a 27% increase in OIT.

Comparison of OIT measurements by two different laboratories on the same sample is made in Table 10. These results show poor correlation between tests conducted in air and oxygen on the one hand and between interlaboratory results on the other hand. It is recommended that, in future, OIT measurements should be calibrated using reference standards.

4.11 Estimation of antioxidant concentration from Infrared spectra (IR)

Specific antioxidants will have characteristic absorption bands in the IR. For example Irganox 1010 has a characteristic peak at 3650 cm^{-1} corresponding to an OH group and another at 1748 cm^{-1}. Using the controlled film samples, we estimated the relative concentration of antioxidant using area ratios. The results are shown in Table 4.11. They are very encouraging indicating a good correspondence between IR results and actual concentrations added. This is an in-house technique used by Ciba-Geigy. It is also being used by the Durban Corporation as an accepted test procedure. In using this technique, care should be taken during sample preparation. Excessive heating of the polymer during sample preparation could result in polymer degradation. The resulting carbonyl absorption could be misinterpreted as a characteristic antioxidant peak.

It is recommended that an internal calibration be used and that the 1370 cm^{-1} band be used for this purpose.

However, other effective antioxidants may show different characteristic absorptions. In general, the antioxidants could be extracted using solvents and quantitavely determined using HPLC.

TABLE 4.11: ESTIMATION OF ANTIOXIDANT CONCENTRATION FROM AREA RATIO OF PEAK AT 1740 cm^{-1} IN IR

Sample #	Relative Concentration Antioxidant [%]	Estimated Concentration from IR spectrum [%]
6	0	0
4	25	26
3	50	50
2	75	72
1	100	-
5	150	153

4.12 Conclusions

Both isothermal and dynamic DSC measurements of the auto-oxidative stability of polypropylene are useful quality control methods. The dynamic scanning procedure is more convenient and reproducible and is recommended despite the fact that the isothermal technique is more sensitive to concentration differences. If the antioxidant used is known, IR provides an even more convenient technique for quality control.

The expected service life of three commercial polypropylene pipes were estimated using data obtained by DSC (oxygen atmospheres) and oven ageing tests. Elongation-at-break was chosen as the indicator of residual service life. Failure was defined at the point when the elongation-at-break corresponded to 50% of the initial value. The fact that different atmospheres were used at high and low temperature measurements provides a "safety factor". Predicted service life in air is much higher than specified requirements of >30 years at 25°C and >3 years at 80°C.

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5. CREEP PROPERTIES

5.1 Introduction

Polypropylene (PP), high density polyethylene (HDPE), cross-linked polyethylene (XLPE), polybutylene (PB) and unplasticized polyvinylchloride (u-PVC) piping find widespread use in water-mains and sewerage applications [1-3]. The synthesis of these materials and their processing into pipes was reviewed by Strubel [1] and Kasakevich [2]. Typical material properties are summarized in Table 5.1.

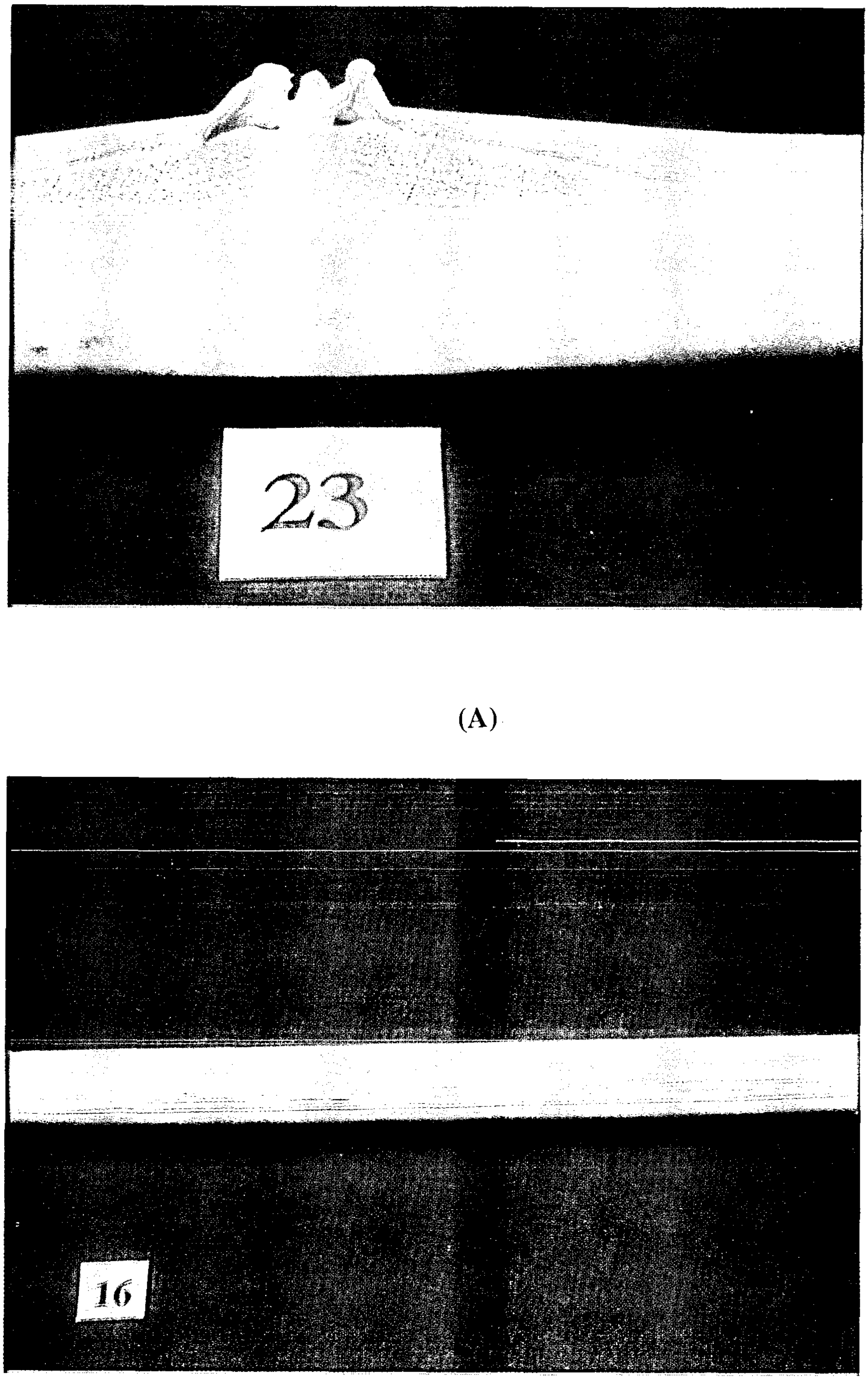
Failures (i.e. leaks) in plastic pipes can usually be traced to either creep rupture (ductile failure) or slow crack growth ("brittle" failure). The time-to-failure depends on the applied stress and temperature. Behaviour typical of plastic pipes is shown in Figure 5.1. Examples of the ductile and brittle failures observed in plastic pipes are shown in Plate 5.1. At high stress, failure tends to occur in the ductile mode within relatively short time intervals. At lower stress levels, a transition to the brittle failure mode occurs and failure occurs only after relatively long time intervals. The observed failure modes are the consequence of the visco-elastic properties of these materials with their associated tendencies to creep and craze.

The tendency to creep under an applied load increases in the series HDPE, XLPE, PP and PB (see Figure 5.2) [5]. These polymers yield at strains between 6 and 12% and ductile failure occurs when the creep strain exceeds a critical value [6]. The time-to-failure for the different materials at 110 °C are shown in Figure 5.3. Polybutylene shows the longest creep rupture life followed by XLPE and PP. The shorter time-to-failure, in a ductile mode, for PP compared to XLPE is the result of a lower critical creep strain for PP. However, Figure 5.3 shows that PP provides for longer service life at low stresses (brittle failure regime). On the other hand environmental factors may also influence the useful service life. At high temperatures polyolefins are subject to oxidative degradation. This results in chain scission and cross-linking reactions which lead to a loss of mechanical properties - specifically ductile yield behaviour. Oxidative degradation may therefore lead to premature brittle failure. The relative resistance to oxidative degradation decreases in the series PB, XLPE, PP, PVC.

TABLE 5.1: TYPICAL PHYSICAL PROPERTIES OF PLASTIC PIPE MATERIALS [2]

PROPERTIES	Units	PB	PP	PP co-polymer	HDPE	XLPE	PVC
1. Density	g/cm^3	0,91	0,90	0,90	0,96	0,93-0,95	1,30
2. Melting range	°C	122-126	165-175	165-175	130-135	121-130	-
3. Heat Distortion Temperature (ASTM D648)	°C	54	45-60	45-60	43-54	-	60-77
4. Tensile modulus (ASTM D936)	MPa	400-450	1 700	1 000	1 400	600	-
5. Bending modulus (DIN790-71)	MPa	340	1 520	1 000	1000-1550	-	40-80
6. Elongation at break (ASTM D1708)	%	340	350	600-700	400-500	250-550	-
7. Bending deformation (ASTM D648)	mm	225	235	200	175	136	48
8. Brittleness temperature	°C	-18	30	-40	-30	-	50
9. Tensile yield strength (ASTM D1708)	MPa	18	33	21	24	13-28	23
10. Tensile strength (ASTM 01708)	MPa	32	36	34	26	21-30	46
11. Thermal expansion coefficient	10^{-4} K^{-1}	1,3	0,9	0,8	1,1	1,4	-
12. Abrasion resistance* (mass loss)	%	1	5,2	-	1,25	-	

* Sand slurry test at 23 °C for 100 h



(A)

(B)

Plate 5.1: Typical ductile creep rupture (A) and brittle craze failure (B) in polypropylene pipes

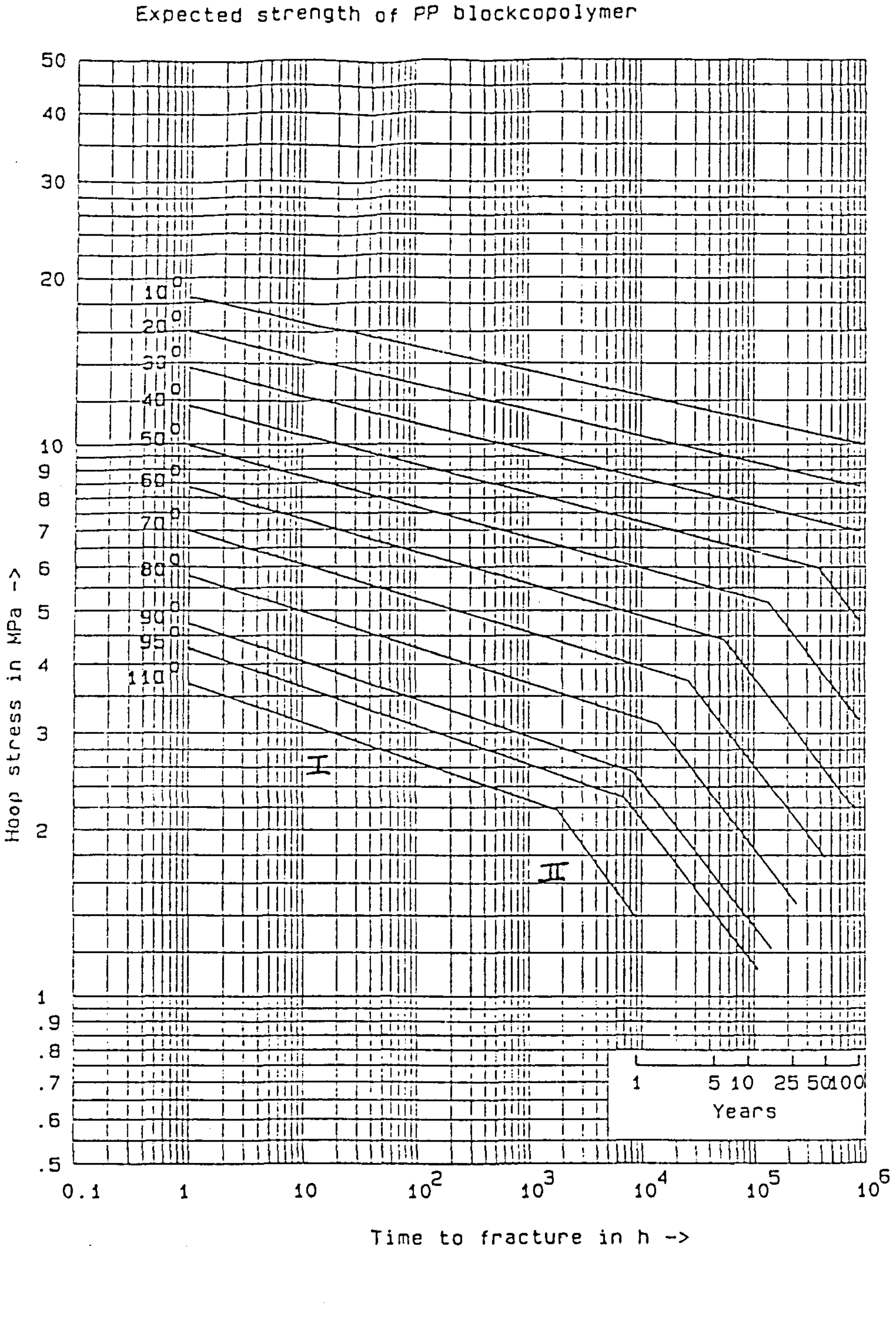


Figure 5.1: Time-to-failure as a function of operating pressure and temperature for a polypropylene pipe.
Curves for ductile (I) and brittle (II) failure modes are indicated

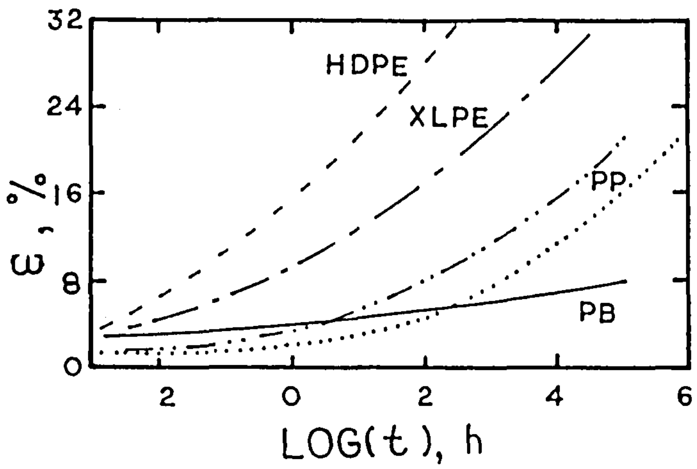


Figure 5.2: Creep curves for polyolefins at 20 °C and an applied stress of 8 MPa [2]. The upper and lower curves for polypropylene are for co-polymer and homopolymer respectively

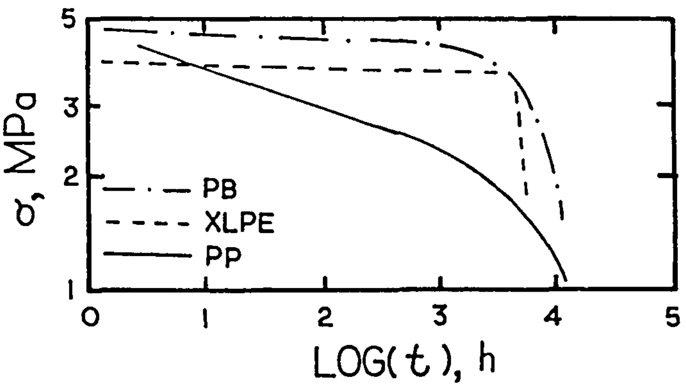


Figure 5.3: Time-to-failure for polyolefin tubes at 110 °C [2]

5.2 Failure Mechanisms

Plastics are visco-elastic materials with behaviour intermediate to viscous fluids and elastic solids. Under the influence of a constant applied stress they show continuous deformation over time (creep or cold flow). Similarly, when a constant strain is applied, a decay in the resultant stress is observed over time (stress relaxation).

5.2.1 Deformation Mechanisms [7-9]

Yielding is a non-recoverable plastic deformation that occurs under the influence of an applied stress. Plastic deformation may take place without significant changes in volume (shear yielding) or may result in an increase in sample volume (crazing). Shear yielding is a bulk phenomenon which occurs homogeneously at low strains but can lead to shear banding at high strains. In addition shear yielding may lead to the initiation of cracks at the intersection of micro-shear bands.

Crazing is a localized deformation that results in cavitation in the form of thin, planar "microcracks". Crazes are not true cracks as they are bridged by arrays of oriented micro-fibrils which make them load bearing. Crazes are initiated at points of stress concentrations (e.g. surface flaws, impurities) in the presence of a negative hydrostatic pressure (tensile stresses). Crazes can also initiate cracks which may lead to brittle failure.

Both crazing and shear yielding provide energy absorbing micromechanisms involving localized visco-elastic and plastic energy dissipation. These processes also occur in the vicinity of crack tips and control the rate of crack propagation. They therefore have a strong influence on the fracture toughness and service life of plastic materials.

5.2.2 Ductile Creep Failure

Eyring and co-workers [10] have developed a theory for non-linear visco-elastic behaviour based on a thermally activated rate process. It assumes that deformation of the polymer requires motion of chain segments across a potential energy barrier. In the absence of stress the chain segments move at a characteristic frequency related to the height of the potential energy barrier:

$$\nu = \nu_o \exp\left(\frac{-\Delta H}{RT}\right) \tag{1}$$

The application of a stress disturbs this dynamic equilibrium. The potential energy barrier becomes skewed resulting in bulk flow (see Figure 5.4). The net flow is given by the difference in jump frequencies across the barrier:

$$\nu = \nu_o \exp\left(\frac{-\Delta H}{RT}\right) \sinh\left(\frac{\upsilon\sigma}{RT}\right) \tag{2}$$

where ν is the frequency, ΔH the activation energy, R the gas constant, T the absolute temperature, υ the activation volume and σ the stress.

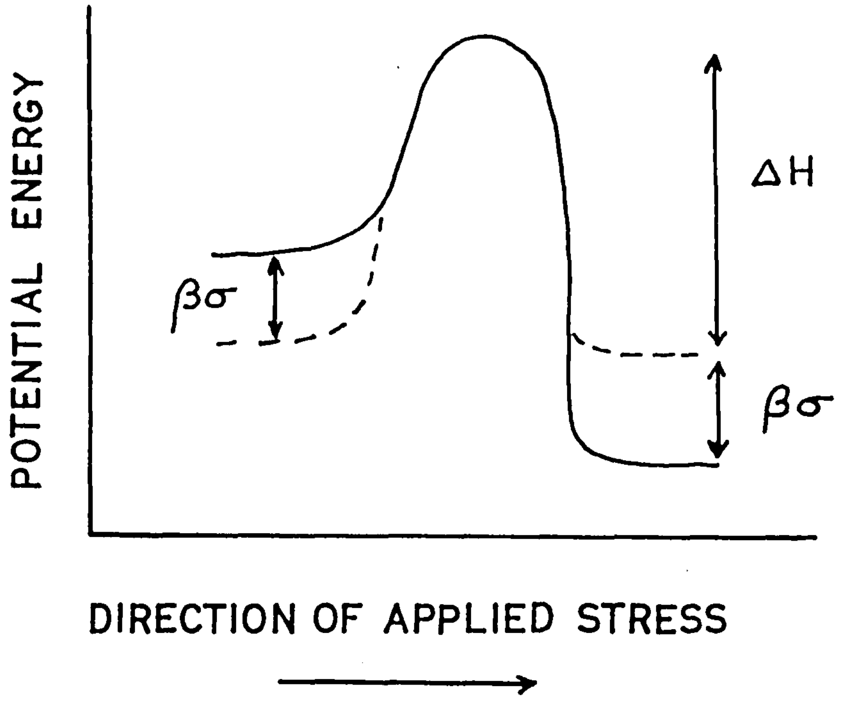


Figure 5.4: Potential energy diagram for bulk deformation (creep) by chain segment mobility [10]

The Eyring theory was developed and expanded by many investigators [8,9]. Zhurkov and co-workers [11] have modelled creep failure in terms of a similar model. They assumed activated breakage of chemical bonds and derived the following model for the time to failure from equation (2):

$$t_f = t_o \exp\left[\frac{\Delta H - \upsilon\sigma}{RT}\right] \tag{3}$$

Zhurkov's [11] model predicts an Arrhenius type temperature dependence for t_f at a constant applied stress, but predicts a linear dependence of $\log(t_f)$ on σ rather than logarithmic dependence.

Brown et al. [6,7] have developed an improved model based on an empirical creep equation:

$$\epsilon = A\,\sigma^m\,t^n\,\exp\left(\frac{\Delta H}{RT}\right) \tag{4}$$

Assuming that the critical creep strain is either constant or varies with stress according to a power law dependence one obtains the following equation for creep life:

$$\log t_{fd} = A + \frac{B}{T} - C\log\sigma \tag{5}$$

where A, B and C are material parameters, with the parameter A also lumping some geometry factors. More detailed models based on shift functions from stress relaxation tests were proposed by Popelar et al. [16]. However, models similar to equation (5) have proved adequate for experimental data presentation [12-17].

5.2.3 Brittle Failure

Static fatigue is the other main failure mechanism. It involves the initiation of a microcrack and its subsequent propagation to the point of macroscopic brittle failure. The time to failure in this case is given by [9]:

$$t_{fb} = t_i + t_p \tag{6}$$

with t_i the initiation time and t_p the time taken for crack propagation.

Crack initiation may be caused by surface defects. These initially lead to crazing and eventually result in the nucleation of cracks [18,19]. Alternatively, high strains may lead to internal nucleation of cracks especially at defects such as impurities or microvoids. Large deformations may open up small voids throughout the bulk in materials such as PVC, PE and PP and give an overall white appearance (stress-whitening).

Figure 5.5 shows a schematic cross-section of a crack tip in a semi-crystalline polymer. The crack tip tends to grow perpendicular to the principal stress direction. At the crack tip the stress field is highly concentrated and this can be described in terms of a stress intensity factor K. For simple geometries the following relationship applies [8,9,20]:

$$K = Y\sigma\sqrt{a} \tag{7}$$

with Y a geometry constant, σ the applied stress and a the crack length. Crack propagation occurs when the stress intensity factor exceeds a critical value corresponding to a material constant [9]:

$$K_{IC} = (E\,G_{IC})^{1/2} \tag{8}$$

where E is the modulus and G_{IC} the work of fracture. In the absence of energy absorbing processes, $G_{IC} = 2\gamma$ where γ is the surface energy of the crack surface. However, as indicated in Figure 5.5, cavitation occurs at the crack tip resulting in crazing and shear deformation. The plastic deformation of the zone around the crack tip and the deformation of craze fibrils constitute large energy absorbtion processes and G_{IC} far exceeds the surface energy estimate.

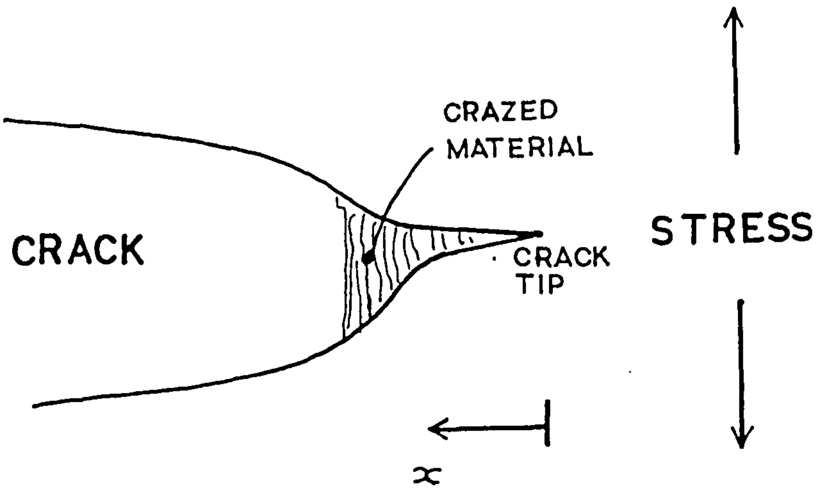


Figure 5.5: Profile of a crack tip showing cohesive zone filled with crazed material

The deformation in the crack tip zone occurs in a visco-elastic fashion. This suggests a time dependence which is material and temperature dependent. Initial crack growth usually proceeds in a stable manner with a power law dependence on K_{IC} [9]:

$$K_{IC} = A_v \dot{a}^n \tag{9}$$

Evans [21,22] has developed an expression for static fatigue life based on the assumption that the crack grows slowly and in a stable manner. He assumed that the above relationship between crack growth rate and K_{IC} applies with a low value of the exponent n:

$$t_f \approx \frac{2nA_v^{1/n} K_{IC}^{(2n-1)/n}}{Y^2 \sigma_c^2 (1-2n)} \tag{10}$$

This expression should allow an estimation of long term static fatigue life from short time fracture mechanics experiments. A quality control method based on these concepts was indeed proposed for polyethylene pipes [20].

Further analysis [6] has shown that the time to brittle fracture should follow similar behaviour to equation (5):

$$\log t_{fb} = R + \frac{S}{T} - Q \ln \sigma \tag{11}$$

where, as before, R contains material and geometry factors while S and Q are material parameters.

Experimental evidence [7,12-16] has confirmed that the failure envelopes in both the ductile and brittle regimes are adequately described by functional dependences of the form of equation (5) or equation (11). However, it should be noted [6] that some interaction between the two mechanisms has been observed in the vicinity of the ductile-brittle transition. In general brittle failure must be viewed as a stochastic process. The time-to-failure is therefore a random variable which depends on parameters such as applied stress, temperature and geometry effects (e.g. flaw sizes and flaw distributions). As a result experimentally determined failure times scatter considerably.

Sometimes the shorter life times are used to construct failure envelopes. Preferably, the experimental data should be treated statistically and envelopes calculated from lower limit curves derived from weighted regression curves [37]. In this regard it should be noted that the following modifications of equations (5) and (11) have been utilized in the literature [12-16]:

$$\log t_f = A + \frac{B}{T} + \frac{C \log \sigma}{T}$$

recommended by ASTM D2837, and

$$\log t_f = A + \frac{B}{T} + C \log \left(\frac{\sigma}{T}\right)$$

The scatter in the available data makes it difficult to distinguish between these models. They all adequately describe the behaviour of polyethylene and polypropylene pipes at elevated temperatures.

5.2.4 Parameters Influencing service Life

While ductile and brittle behaviours show similar functional dependences on stress and temperature, it is important to note that the ductile behaviour is relatively insensitive to the actual morphology of the polymer [17]. In contrast, the brittle fracture mode is strongly affected by parameters such as molecular weight and its distribution, molecular branching and crystal morphology [15,23-26].

a) ***Spherulite size*** [23-26]

The basic morphology of semi-crystalline polymers (e.g. polypropylene) is one of spherulitic domains composed of lamellar crystals. The size, the size distribution and the structure of spherulites have a major influence on the crack paths and the rate of crack propagation [24]. By using PP grades of different molecular weight and utilizing different cooling rates Friedrich [24] was able to produce morphologies ranging from very fine ($<20\ \mu m$) to coarse ($>500\ \mu m$). Cracks were found to propagate most easily along the interfaces of coarse spherulites. Way et al. [23] have also observed that the yield stress and deformation mode of PP are affected by spherulite size. Materials containing large spherulites are more brittle while those consisting of very fine spherulites are highly ductile featuring strains as high as 700%. He also observed a maximum in the tensile strength at a critical value of spherulite size.

This was interpreted in terms of the opposing effects of increased strength and stiffness and the weakening of the interface between spherulites with increase in spherulite size. Fast cooling rates result in small spherulites while slow cooling results in large spherulites. The slower cooling also results in the segregation of impurities and the formation of voids at crystal boundaries with a consequent weakening of the interface. Popli et al. [17] have found instead that the yield stress is dependent on the degree of crystallinity but independent of the superstructure and molecular weight.

It should be noted that in the above studies crystallization was controlled by homogeneous nucleation in the absence of flow induced orientation effects. In the practical situation of pipe manufacturing, the shaping of the polymer melt at the die results in deformation of the random coil molecules. Too rapid cooling will result in internal stress due to "freezing-in" of this orientation effect. It is more convenient to control the spherulite size by heterogeneous nucleation i.e. by the addition of appropriate nucleating agents.

b) Molecular weight

Unless the molecular weight is very low it does not have a direct effect on the yield strength and the ductile failure mode. However, molecular weight has a major influence on the fracture stress. Flory [27] proposed the following relationship between brittle stress and number average molecular weight:

$$\sigma_B = A - B/\bar{M}_n$$

The data for polyethylene in Figure 5.6 shows such a trend [28] at high M_n. The resistance to brittle failure also increases with molecular weight [26]. With higher molecular weight material the chains are longer which leads to a larger number of inter-lamellar and inter-spherulitic tie molecules. This leads to an increase in the extent of plastic deformation in the vicinity of the crack tip and therefore greater fracture toughness. Under these conditions the rate of the fracture process is controlled primarily by crazing [24].

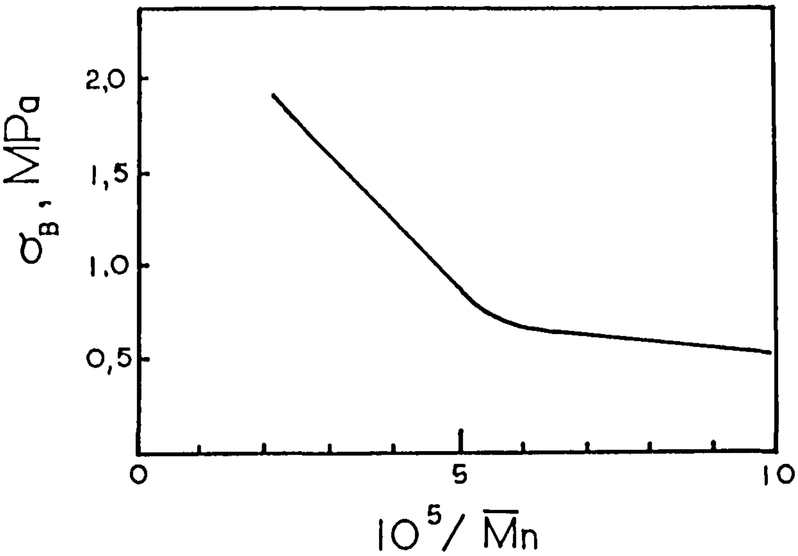


Figure 5.6: Effect of number average molecular weight on the brittle strength of polyethylene [28]

For polyethylenes brittle failure becomes almost impossible to achieve at very high molecular weights (M > 10^6) [29]. This rapid improvement in resistance to brittle failure is illustrated by the data of Gebler [15] for polyethylene and Meinhard [40] for polypropylene on the influence of MFI (a measure of molecular weight) on time-to-failure for pipes. The data for polypropylene is shown in Figure 5.7.

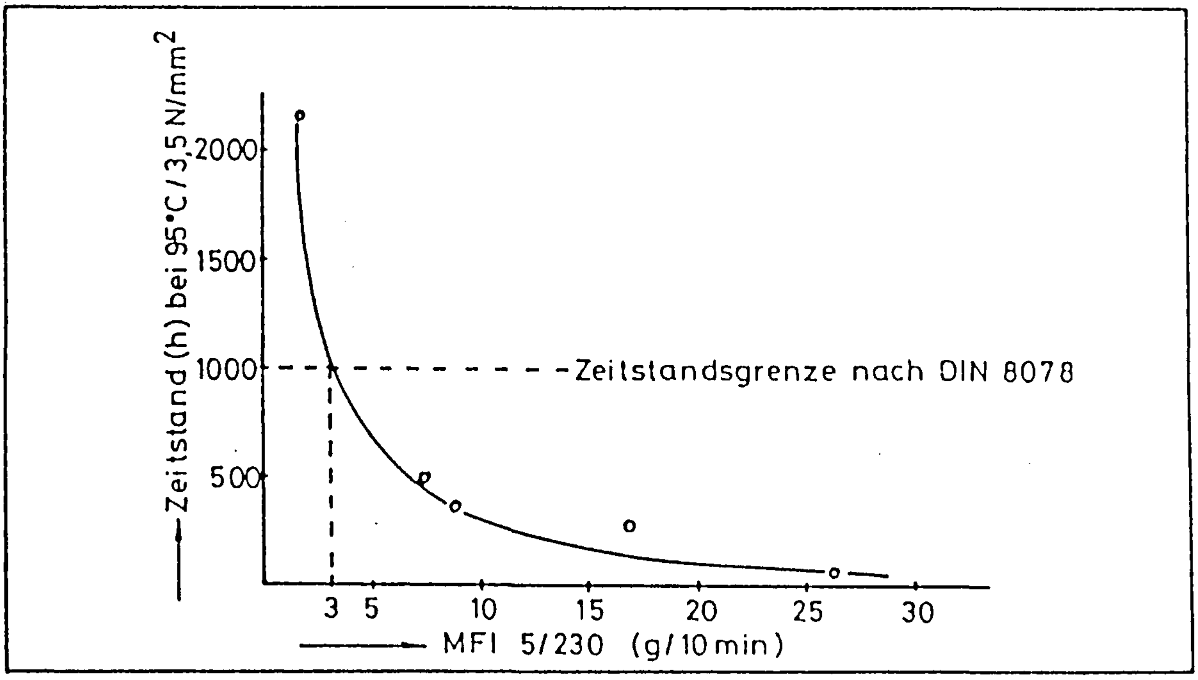


Figure 5.7: Life time dependence on the melt flow index $MFI_{5/230}$ of a polypropylene co-polymer at 95°C and a stress of 3,5 MPa [40]

A reduction in molecular weight during processing and under in-service conditions would have a detrimental effect on service life. Embrittlement by oxidative degradation is of particular concern as it takes place predominantly in the amorphous interstices between crystallites. This leads to a loss of the binding effect contributed by the tie molecules and results in embrittlement and premature failure.

c) Molecular orientation

Brittle strength is more sensitive to alignment effects than the ductile failure process. Material is more likely to fail in a brittle mode when the stress is applied perpendicularly to the orientation direction.

d) Surface flaws

Shrinkage during cooling of extruded parts can already lead to microcracks at spherulite boundaries [25]. In pipes exposed to sunlight or heat, surface embrittlement can trigger premature brittle fracture [30].

5.3 Criteria for residual life assessment

It is clear that plastics do age under service conditions. Prediction of the remaining useful service life could therefore be valuable. However, it is unfortunately very difficult to predict long term performance on the basis of short term tests. The residual service life is affected by a combination of many factors [33-36].

- **Physical ageing** corresponds to a relaxation from a non-equilibrium state towards an equilibrium morphology [8,9]. In glassy polymers such as PVC this usually results in an increase in density and therefore a reduction in "free volume". In the case of polypropylene physical ageing involves decreases in the contour length of tie molecules [32]. Macroscopically this reduces the elongation-at-break and should lead to reduced time-to-failure at low stresses (brittle fracture).

- **Morphological changes** e.g. recrystallization or secondary crystallization. The former is of particular relevance to polybutylene.

- **Thermal degradation** Some polymers are intrinsically unstable at elevated temperatures even in the absence of oxygen. Free radical initiated depolymerization of polypropylene is possible at processing temperatures.

- **Oxidative and photo-oxidative degradation [36]** These are autocatalytic processes taking place in the presence of oxygen. The rate of degradation can be controlled by the addition of suitable stabilizers (anti-oxidants and UV stabilizers).

- **Environmental stress cracking [20]** corresponds to the action of extraneous chemicals in accelerating failure.

- **Physical damage** (usually visible as stress whitening) due to yielding i.e. the history of stresses and strains experienced by the material. This may also be due to mechanical abuse during installation.

A large number of physical tests are available for the characterization of the state of a polymeric material [33]. Here we limit our discussion to "mechanical" measurements:

a) Bending stress

Bending tests are often used to evaluate the embrittlement time e.g. in oven ageing tests. For Pass/Fail evaluations thin samples are usually bent through 180°. For polyethylene the embrittlement correlates well with loss in elongation while for polypropylene a strong correlation is observed with changes in the IR spectrum. However, for thicker samples the bending stress at the point of failure varies only slightly with the state of ageing. Owing to this poor sensitivity this method is not regarded to be of practical utility for thermoplastics such as polypropylene.

b) Impact resistance

Impact resistance correlates well with the state of weathering for HDPE and u-PVC but shows only a weak correlation for PP.

c) Tensile testing

Changes in the stress-strain behaviour of thermoplastics have been used as ageing criteria [39]. Polymers that show plastic deformation initially show an increase in tensile yield strength as the material embrittles. Later the ability to yield is reduced and the yield and tensile strengths converge. At some point failure commences without plastic deformation and tensile strength decreases with age. The variations in yield or tensile strength are, however, insufficient to provide a useful criterion for the degree of ageing [35].

Corresponding to the change in tensile or yield strength, one finds that the elongation at break shows a rapid decrease and this material property therefore provides a useful criterion [35].

d) Fracture testing

It is clear that the "brittle" failure mode controls service life under actual service stresses and temperatures for polyethylene pipes. The time-to-failure in this mode is determined by the fracture toughness which in turn controls the rate of crack growth. Fleissner [20] proposed a quality control procedure based on this principle of fracture mechanics. He found a strong correlation between the time-to-failure of a notched bar in tension with the time-to-failure of polyethylene pipes under pressure. At 80 °C and a stress of 5 MPa the test time was reduced by a factor of 30! The disadvantage of his test procedure is the fact that the tensile test specimens had to be cut from a pressed sheet. It would be advantageous to be able to utilize the pipe geometry directly.

e) *Glass transition temperature*

Ageing can also be followed by the change observed in the glass transition temperature as measured by dynamic mechanical thermal methods [35,36].

5.4 Experimental

5.4.1 Internal Pressurization of Pipes

The resistance of pipes (from manufacturers A, B and C) to internal pressure were measured at 80°C, 95°C and 120°C at SABS, Hoechst (Germany) and at the CSIR. At SABS pressurization occurred in a hot water bath at 80°C using gas pressure and with the pipes filled with water. In the CSIR tests, a convection oven was used and pressurization was achieved by using nitrogen gas. The results of these test are given in Tables 5.2 and 5.3.

Table 5.2 summarizes the results for tests conducted at 80°C. Internal pressure was varied to achieve a given hoop stress in the pipe. The results obtained for the three pipes are compared with JASWIC and DIN specifications. Interestingly, all pipes except pipe B pass the DIN 8078 (1989) requirements, but fail the JASWIC test. All pipes tested at Hoechst also failed prematurely. It is not known why there is a discrepancy between the Hoechst and SABS test results.

TABLE 5.2: CREEP TEST OF POLYPROPYLENE PIPES AT 80°C PERFORMED ON SABS TEST RIG

Test Conditions (Hoop Stress) [MPa]	**Pipe Failure Times [h]**				
	Pipe A	**Pipe B**	**Pipe C**	**JASWIC Specification**	**DIN 8078 (1989) Creep curve for block co-polymers**
6,1	10,7	4,6	10,0	1	0,1
5,2	22,5	11,4	21,5	10	1
4,4	73	22,3	56	100	15
3,8	410	68	155	-	100
(3,6*) (Hoechst Test)	(14,5)	(41)	(46)	-	300
Instant Burst Test MPa	12,9	13,2	13,1	-	-

It should be noted that the current results are compared to the regression lines according to DIN 8078 (1989). These have been revised in 1992 and the requirements have become more stringend! Compare Figure 5.8 (old) with the revised curves in Figure 5.1!

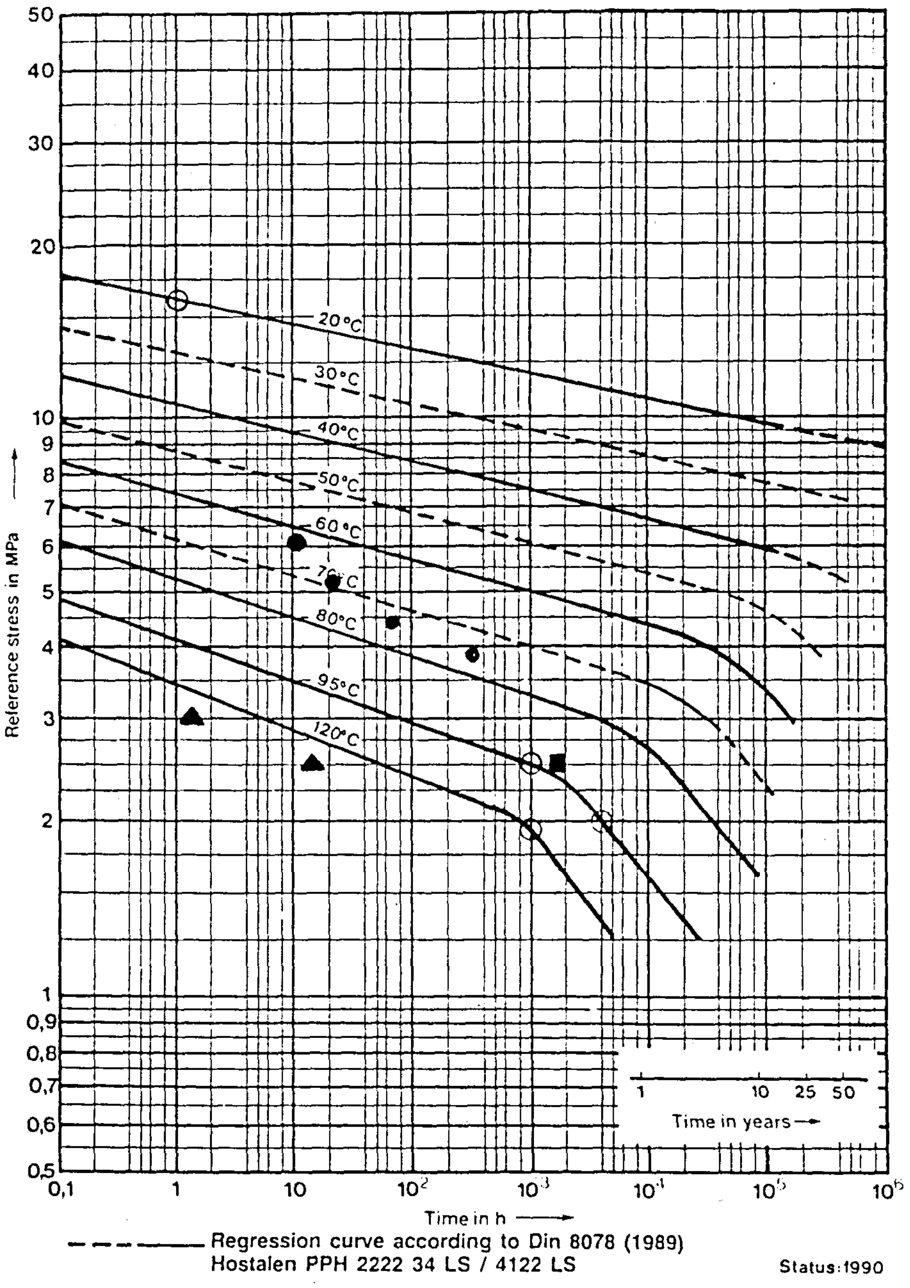


Figure 5.8: Creep data for Pipe A at 80°C (●), 95°C (■) and 120°C (▲). Open circles indicate DIN test conditions.

Table 5.3 summarizes the results for 95°C and 120°C. The data for pipe A is also plotted in Figure 5.8. All pipes fail both DIN and JASWIC specifications at 120°C. However, only Pipe B fails the 95°C DIN 8078 (1989) specification.

Except for the very highest pressures used in the 80°C tests, all the locally produced pipes showed brittle failure despite the fact that the pipes should fail by ductile fracture according to the hydrostatic strength curves of pipes made from Hostalen PPH 2222 34LS/4122 LS. It would appear that the 'knee' of the log *σ* versus the reference (hoop) stress and *t* the lifetime of the pipe for all three locally manufactured pipes is shifted towards the left relative to the curves for Hostalen PPH 2222 34 LS, according to DIN 8078 (1989).

It is believed that the occurrence of brittle fracture in the ductile fracture regime is a qualitative indication that the locally manufactured pipes are of poor quality. This is probably due to poor processing conditions during extrusion or alternatively to the use of non-pipe grade material was used.

TABLE 5.3: HYDROSTATIC STRENGTH OF PIPES AT 120°C AND 95°C

Temperature °C	Hoop Stress MPa	Time to Failure [h]			
		Pipe A	Pipe B	Pipe C	DIN 8078 (1989)
120	3,7 3,0 2,5	- 1,5 11	- 2 11	0,2 5,4 -	0,4 5 50
95	2,5	1 600 1 900	813 1 053	1 104 1 416	1 000

Pipes obtained from Hoechst in Germany lasted in excess of 3 000 hours at 95°C.

5.4.2 Mechanical Testing

Ring specifications with a width of 12,5 mm or 8,5 mm were cut from pipes and mechanical tests performed as follows:

METHOD: 1. Constant tensile loading using cantilever. Specimens were given four notches perpendicular to extrusion direction by using a notching device operated by hand (controlled notching depth; uncontrolled notching speed).

2. Dynamic fatiguing between two constant loads. Specimens were given two notches on the inside of the pipe parallel to extrusion direction using a notching device attached to the Instron machine (controlled notching depth and speed).

3. Constant tensile loading with weight suspended 6 mm from centre of specimen (i.e. non-cantilever loading). Specimens were notched in a controlled fashion using the Instron.

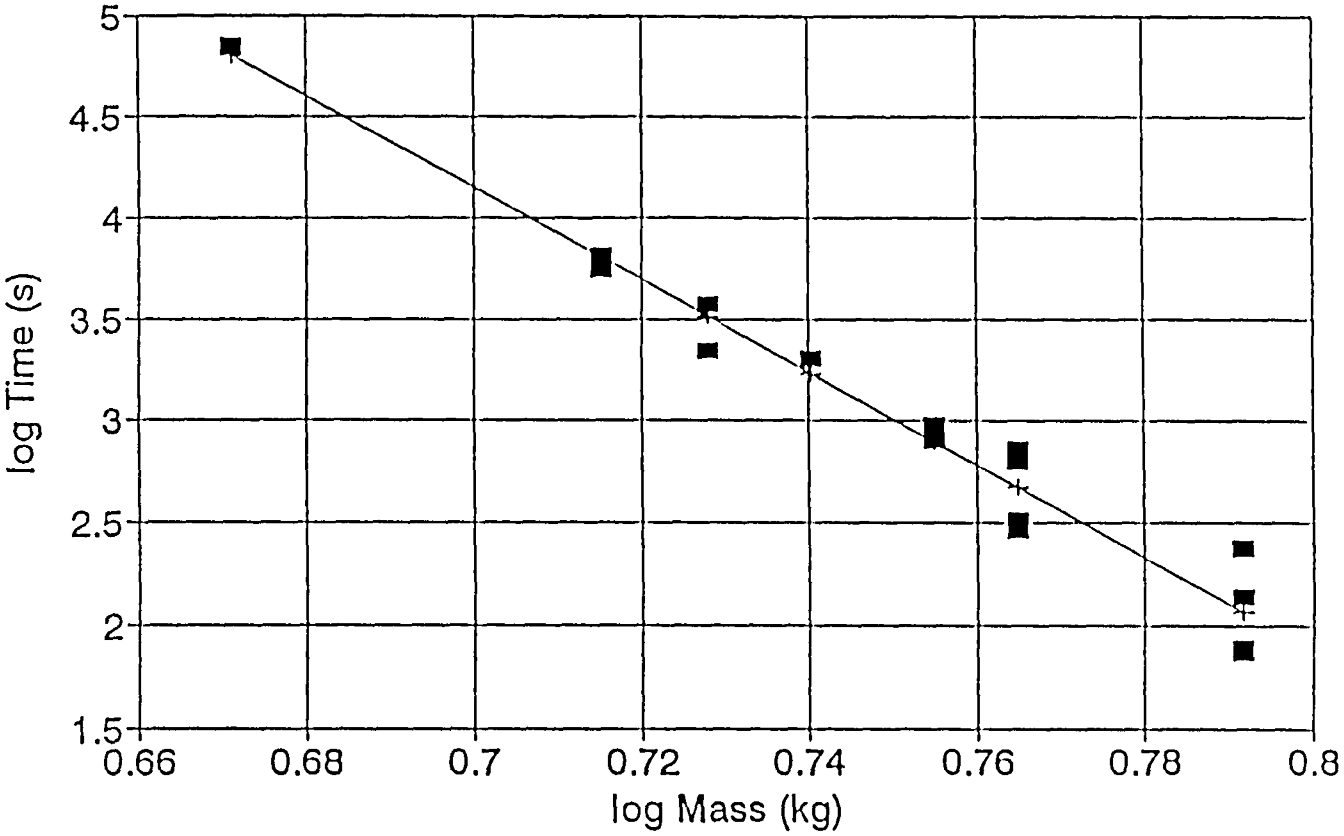
4. Tensile testing of ring specimens at varying crosshead speeds. In addition "dogbone" specimens were cut from axial sections.

A. Constant Tensile Loading

The specimens tested according to test method 1 showed that the procedure is unsatisfactory for the following reasons:

(a) The tests gave high scatter (low repeatability) when measuring time to failure. Although a straight line correlation was obtained for Pipe C type specimens (Figure 5.9), the repeatability using a 5.690 kg weight with other pipe specimens was poor: Failure times varied almost by a factor of six. It was not established whether repeatability was a function of temperature and/or weight or perhaps due to the pipe used. However, according to literature, the **notching method** has a large influence on the specimen lifetime (in particular the speed of notching) [41]. Since notching was performed by hand, there was little control over the speed of notching, and it was therefore decided to design a more accurate method of notching the specimens.

(b) The fracture surfaces of specimens subjected to constant loading did not have the same microstructural features (voids and fibrils) as those observed in the field failures. Plate 5.2 shows the voids formed in the crazing process during brittle crack propagation. It has been shown that the damage mechanism within the root craze of polyethylene or polypropylene is a combination of fibrillation and continuous material yielding, which forms a network of interconnected membranes [41]. The voids which occupy the space between the membranes may be considered as capped tunnels which vary in size and shape and may be connected by holes or tears in the membrane. The fracture surfaces of specimens subjected to constant tensile loading at room temperature show that fibrillation and void formation have been suppressed (Plates 5.3 and 5.4). It has been reported that crazing does not occur at very low temperatures and high deformation rates.



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                 Regression Output:
Constant                          20.05988
Std Err of Y Est                  0.157759
R Squared                         0.962945
No. of Observations                     16
Degrees of Freedom                      14

X Coefficient(s)   -22.7288
Std Err of Coef.   1.191617
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Figure 5.9: Time-to-break as a function of cantilever mass for notched ring specimens (width 12,5 mm) subjected to constant stress (Pipe C)

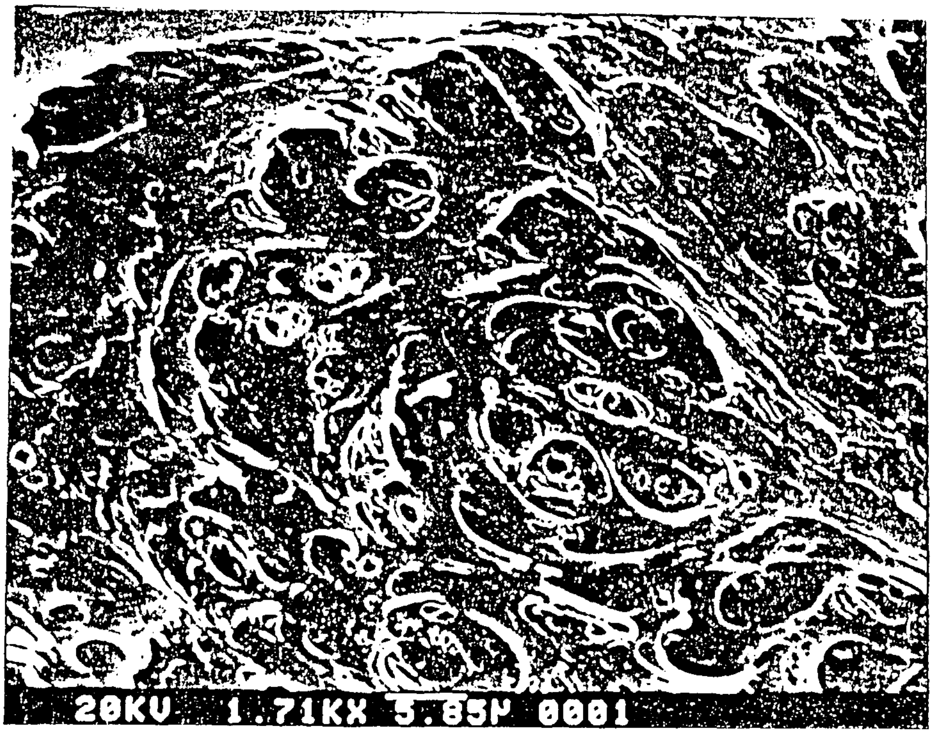

Plate 5.2: Field failure of polypropylene pipe showing void formation due to brittle cracking

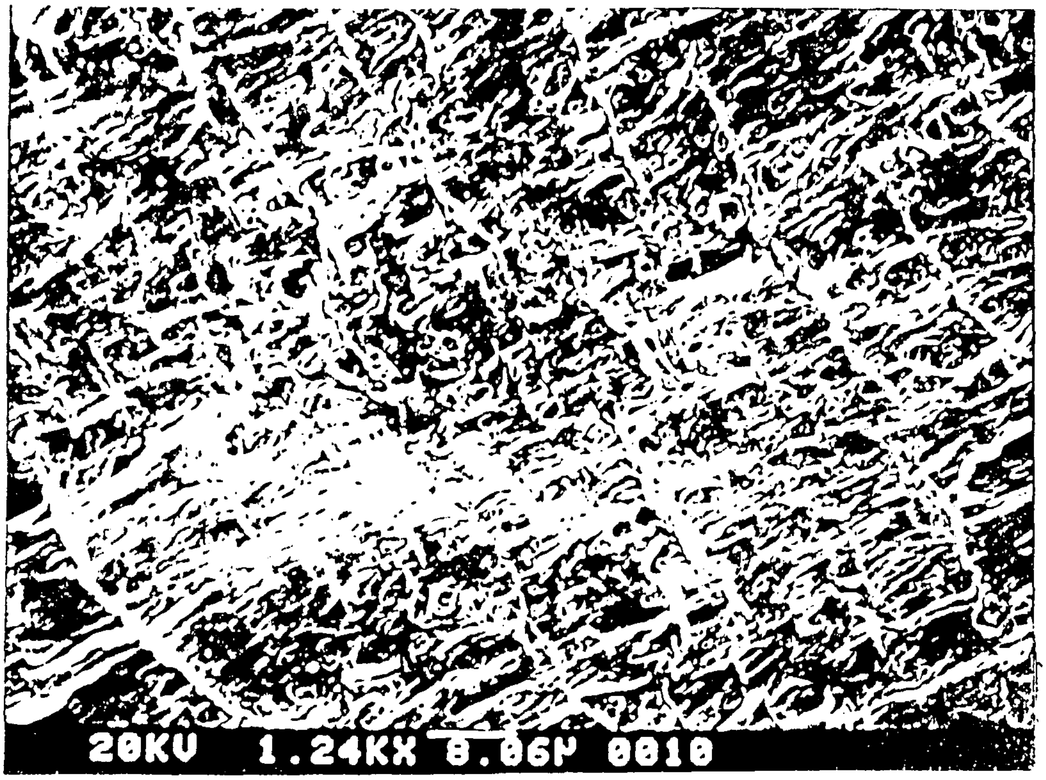

Plate 5.3: Fracture surface of Hostalen polypropylene pipe tested at room temperature. Specimen was notched perpendicularly to extrusion direction.

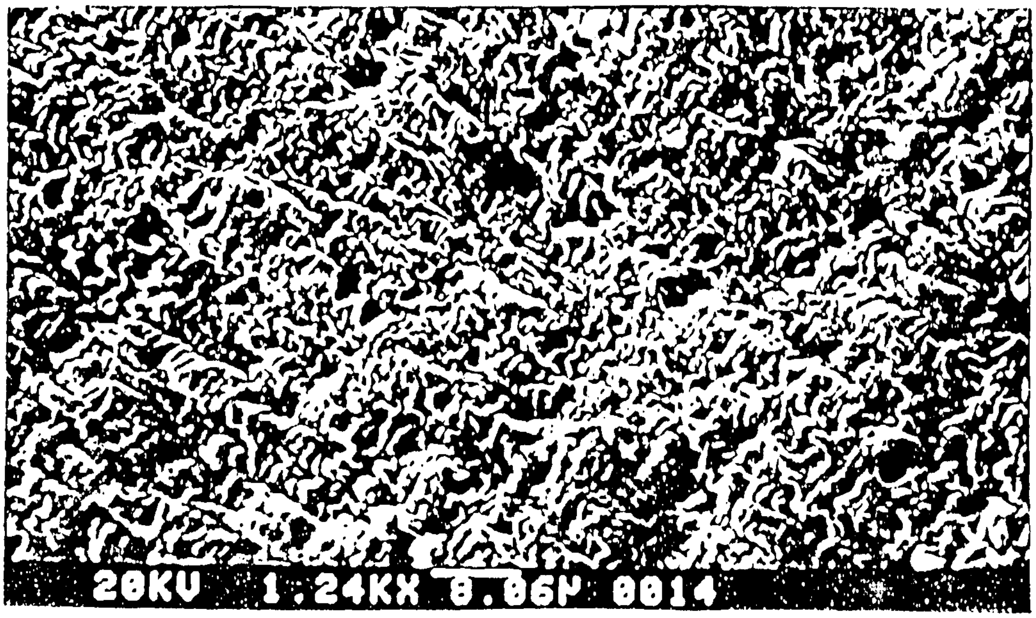

Plate 5.4: Fracture surface of locally produced polypropylene pipe. Specimen was notched perpendicularly to the extrusion direction.

It was therefore decided to perform constant tensile load tests at 120°C, since this would more likely result in crazing. Also, a notching rig was devised which could be attached to the Instron, so as to be able to notch the specimens in a controlled fashion. Furthermore, it was decided to give the specimens two notches on the inside of the pipe parallel to the extrusion direction.

B. Dynamic Fatigue

Specimens were tested according to method 2 at 120°C. Notches were cut to a depth of 22% of the pipe wall thickness, at a speed of 0,05 mm/min (this is the slowest obtainable speed on the Instron). The applied maximum fatigue stress was calculated from σ_{max} = P*(d-e)/(2*e), where d is the nominal external diameter of the pipe and e is the nominal wall thickness.

Pipe B-type specimens (width 8 mm) were fatigued at a frequency of about 0.5 Hz. Failure occurred in a brittle manner after 91 000 cycles (see fatigue tests 1 and 2). The fracture surface is shown in Plates 5.5 to 5.7. Plate 5.7 clearly shows void and fibril formation associated with crazing. Fractographic studies have revealed that creep and fatigue failures have many features in common, and creep and fatigue lifetimes have been found to correlate well in polyethylene pipes. **In fact, it has been considered to adopt fatigue as a quality control method in the production of plastic pipes** [42]. By fatiguing a specially designed specimen, brittle failure resembling that observed under service conditions in polyethylene pipes, was produced in only 3 days. It was determined that the method of loading and crack plane orientation greatly affect the degree and extent of brittle crack propagation [43].

Grey polypropylene specimens from Germany (width 10 mm) were also fatigue tested at 120°C at a maximum applied stress equivalent to 500 kPa. They proved to be much more resistant to brittle crack propagation. After 312 000 cycles crack propagation could not be detected by eye.

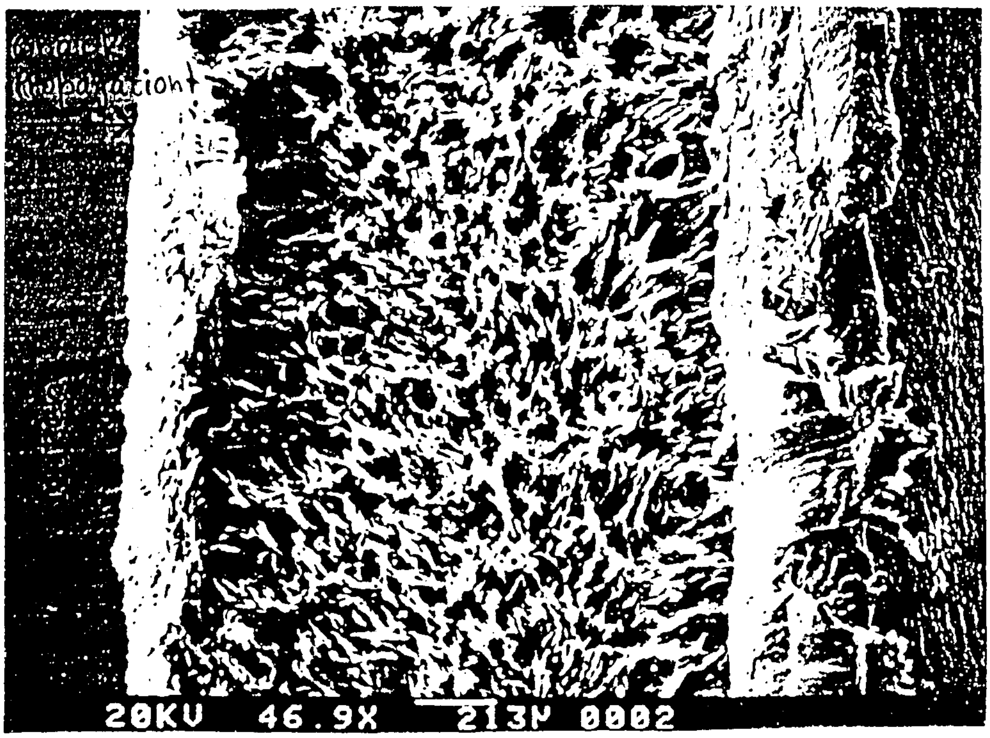

Plate 5.5: Fracture surface of Pipe B specimen fatigue loaded at 120°C between two constant stresses: σ_{min} = 0.18 MPa, σ_{max} = 1.8 MPa. Frequency 0,5 Hz. Brittle crack propagation occurred by void formation and fibrillation.

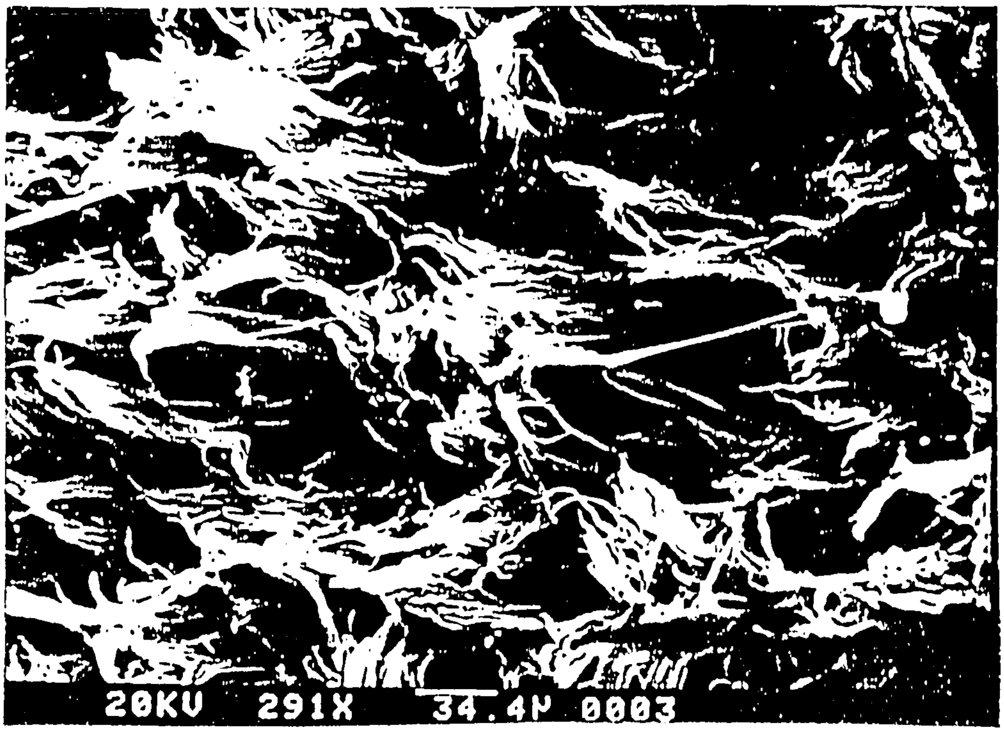

Plate 5.6: Magnified view of fibrillated region in Plate 5.5

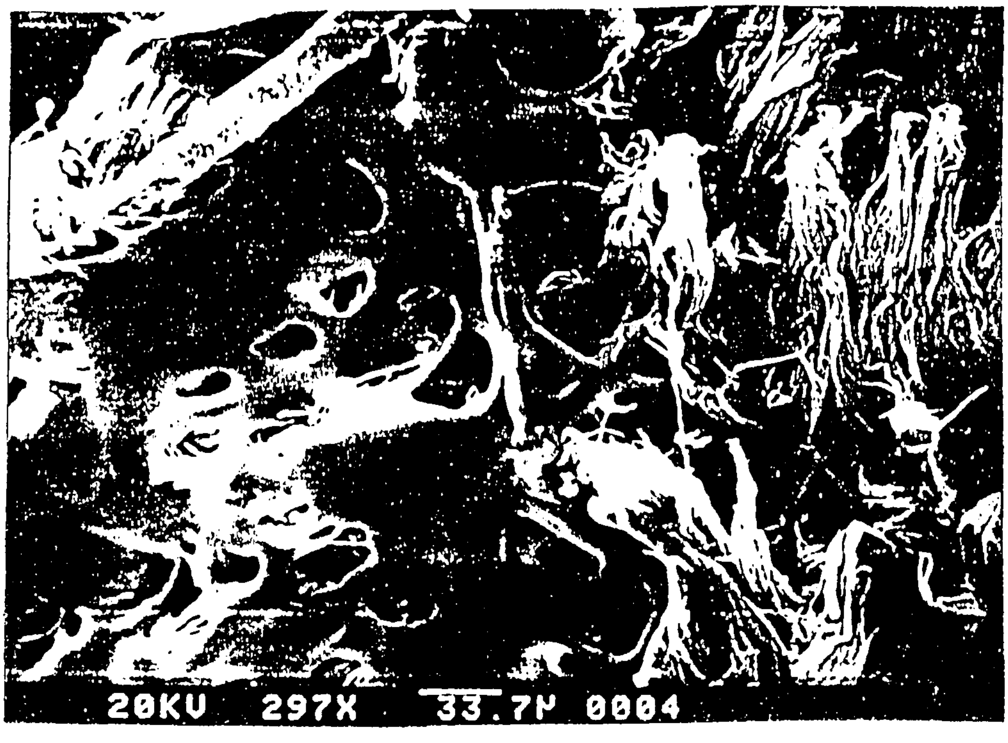

Plate 5.7: Magnified view of void formation and fibrillation in Plate 5.5

A Pipe B-type specimen (width 8 mm) was tested according to method 3 at 120°C. The time to failure was not monitored accurately since it was the mode of failure that was of interest. The specimen failed in a brittle fashion and the fracture surface is shown in Plates 5.8 to 5.9. The time to failure which can be accurately monitored using a computer, is between 101-152 hours. It can be seen that microstructural features do exhibit fibrillation but on a smaller scale compared to the fatigued specimen.

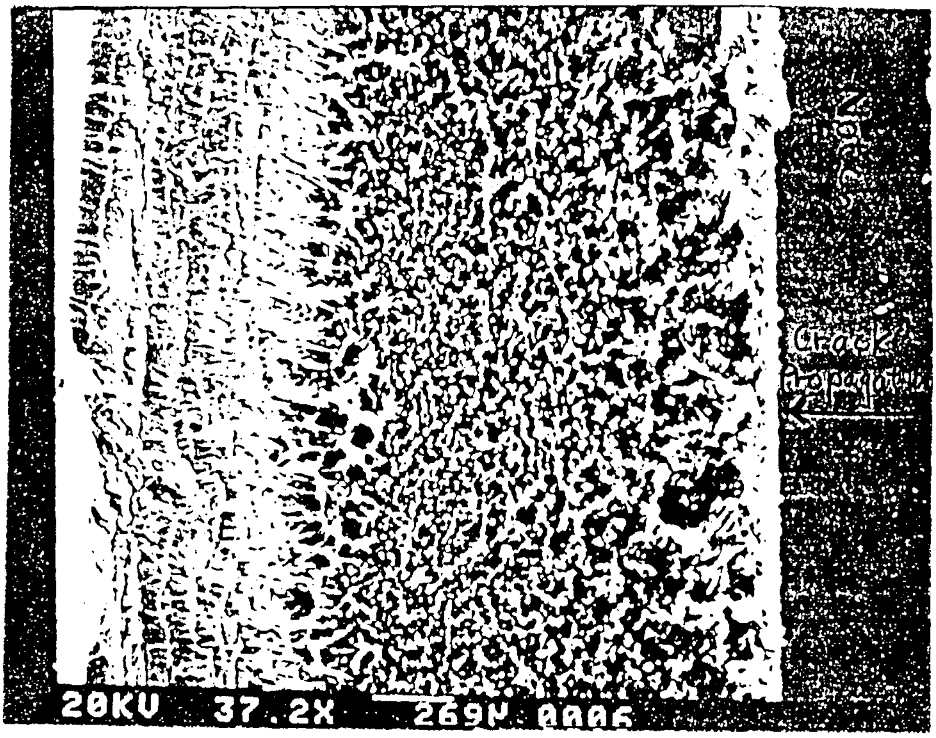

Plate 5.8: Fracture surface of Pipe B-type specimen subjected to constant tensile loading at 120°C: $\sigma = 1.8$ MPa. Fracture occurred due to brittle cracking.

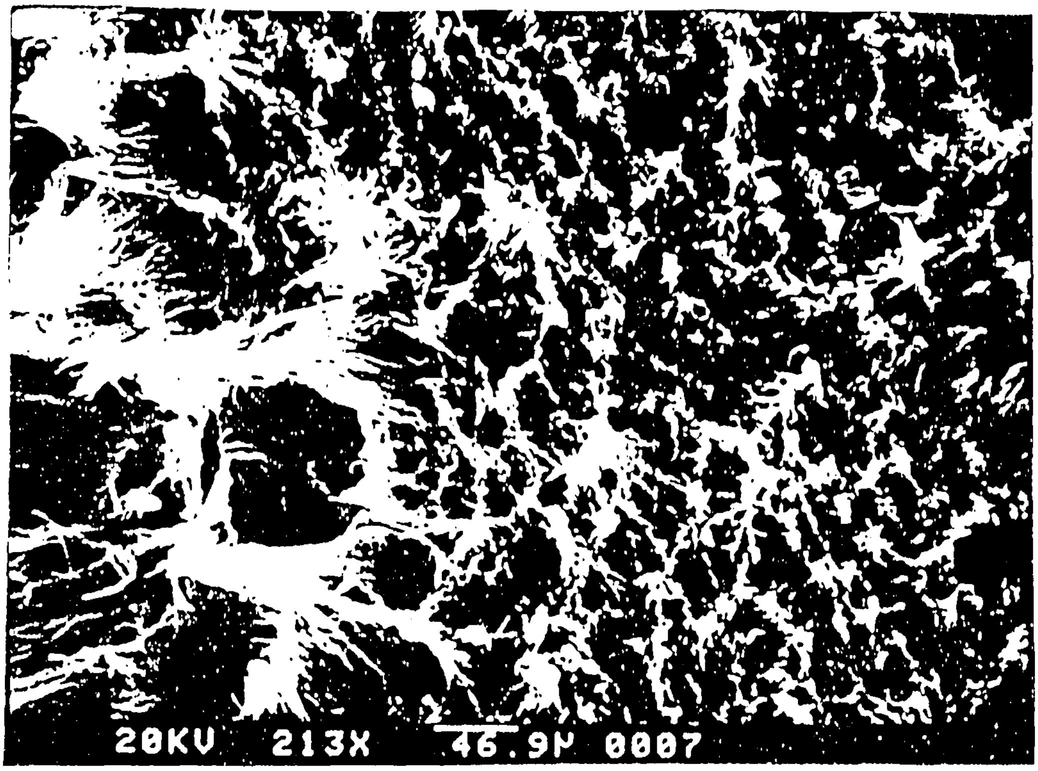

Plate 5.9: Magnified view of fibrillated region in Plate 5.8. Note that voids are considerably smaller than those which formed during fatiguing.

It should be noted that the region of brittle crack propagation is larger in the fatigued than in the constantly loaded specimen, and one would therefore expect the former to have a longer time to failure. However, the fatigued specimen failed after only 40 hours whereas the constantly loaded specimen failed after 100 hours. This evidence therefore suggests that the lifetime of pipes is significantly reduced, if they are subjected to dynamic fatigue cycling instead of simply being subjected to static pressurization.

To summarize: Microstructural examination of the fracture surfaces has shown that fatigue features are similar to those of brittle (craze) field failures. Constant tensile loading fractures resulting from notching the pipe perpendicular to the extrusion direction, did not resemble fatigue failures. In the case of the notches being on the inside of the pipe parallel to the direction of extrusion, constant tensile loading fractures did resemble those caused by fatigue.

The grey Hostalen polypropylene pipe from Germany appears to be considerably more resistant to brittle crack propagation (crazing) during fatigue at 120°C than locally manufactured polypropylene pipes.

TABLE 5.4: TENSILE TESTING OF LONGITUDINAL DOG BONE SAMPLES (29 X 4 mm) CUT FROM PIPES

Crosshead Speed [mm/min]	Elongation-at-break [%]		
	Pipe A	Pipe B	Pipe C
20	-	850	-
50	788	843	784
100	747	808	736
200	260	241	395
300	214	158	247
400	128	112	247

TABLE 5.5: TENSILE TESTING OF 8,5 mm RING SPECIMENS

Crosshead Speed [mm/min]	Elongation-at-break [%]		
	Pipe A	Pipe B	Pipe C
2	922		
5	883		
10	839		
20	823	334	728
50	771	173	748
75	461	107	223
100	254		111
130	211		115

TABLE 5.6: COMPARISON OF TENSILE TESTING AND CREEP LIFE PERFORMANCES FOR A SET OF DIFFERENT PIPES

	Elongation-at-break [%] Crosshead speed [mm/min]			Pipe Creep life at 80°C [h] at indicate stress [MPa]		
Pipe	**50**	**75**	**100**	**5,2**	**4,4**	**3,7**
A	771	461	254	23	66	402
B	173	107	-	11	23	73
C	748	223	111	22	50	155
D	70	36	-		40	
E	102	113	-		88	
F	692	379	258		>100	
G	759	207	179		80	
H	759	553	354		89	
I	732	429	215		34	

C. Tensile testing at constant rate of deformation

Both ring specimens and "dog bone" specimens were tested according to method 4. They reflect mechanical properties in the hoop and axial directions respectively. The results for Pipes A, B and C are presented in Tables 5.4 and 5.5. It is clear that there are differences between the pipes. Pipe B showed the worst performance in terms of loss of extensibility as the draw rate is increased for both ring and "dog bone" specimens. In the creep tests it also did very poorly. It was therefore of interest to investigate the correlation between elongation-at-break at a constant draw rate with creep life performance. Fortunately pipes tested for creep at 80°C were available. The combined results are given in Table 5.6. Unfortunately it turns out that no correlation exists between elongation and creep life: correlation coefficients were typically below 0.5. This result was to be expected in view of the greatly different conditions for these two types of failure.

5.5 Crazing of Polypropylene

Following discussions with Dr Fleissner [44] it was established that Hoechst had already abandoned the mechanical testing route to a quick quality control method for polypropylene pipes. The initial correlation established for polyethylene pipes [20] is still being used successfully for both quality control of existing pipes and for developing improved raw materials at Hoechst. The Hoechst research on this topic [44] showed that no correlation existed between time-to-failure of notched specimens in tensile testing and the creep lifetime of polypropylene pipes under hydrostatic pressure. The reason for this is not clearly understood. It is believed that the crazing ("brittle") failure mode of polypropylene is difficult to simulate in accelerated tensile tests.

During consultations with Dr Fleissner, it was decided that it could be useful to investigate ways to accelerate the crazing of polypropylene. It is well known that polyethylene is subject to solvent stress cracking failures. This failure mode is less of a problem with polypropylene.

The most "promising" media for inducing stress cracking of polypropylene were identified in collaboration with Rapra as follows:

- Igepal detergent at 60°C
- Igepal/Ethylene glycol (50/50) at 115°C
- Chromic acid 20% at 40°C
- Chloroform at 25°C

Samples of polypropylene pipes were tested for environmental stress crack resistance using ASTM F1248-89. In this method ring specimens are notched in the hoop direction. They are then clamped between parallel plates and submerged in the crazing medium. In the present tests the gap between the calming plates adjusted to 4 times the pipe wall thickness. Clamping of Pipe B resulted in craze formation even before immersion. All the other pipes lasted for four weeks or more, the tests being abandoned due to the long times to failure.

5.6 Conclusions

The service life of polypropylene pipes is limited by two independent failure modes. Creep rupture is a ductile failure mode occurring at high stresses and short life times while "brittle" craze failure occurs at low stress levels and longer times. According to the literature, the time-to-failure for the latter mechanism is more sensitive to parameters such as molecular weight, molecular weight distribution and crystal morphology than the ductile failure mode. Quality testing should test in the "brittle" fracture regime as this mode limits service life under normal operating conditions.

These trends are summarized in Figure 5.10 showing the shift in the failure envelopes under unfavourable conditions [31]. Such conditions may involve the following processing and material factors:

- **Surface flaws** (e.g. scratches or notches)
- **Decrease in molecular weight** (Using the wrong grade of polymer, degradation during processing, use of recycled material or oxidative degradation.)
- **Unfavourable morphologies** e.g. orientation effects (e.g. too fast haul-off), large spherulites etc.
- **Stress concentrators** such as contaminants, incompatible filler or pigment particles, use of incompatible carriers in master batches etc.
- **Environmental stress cracking agents** such as hydrocarbons.

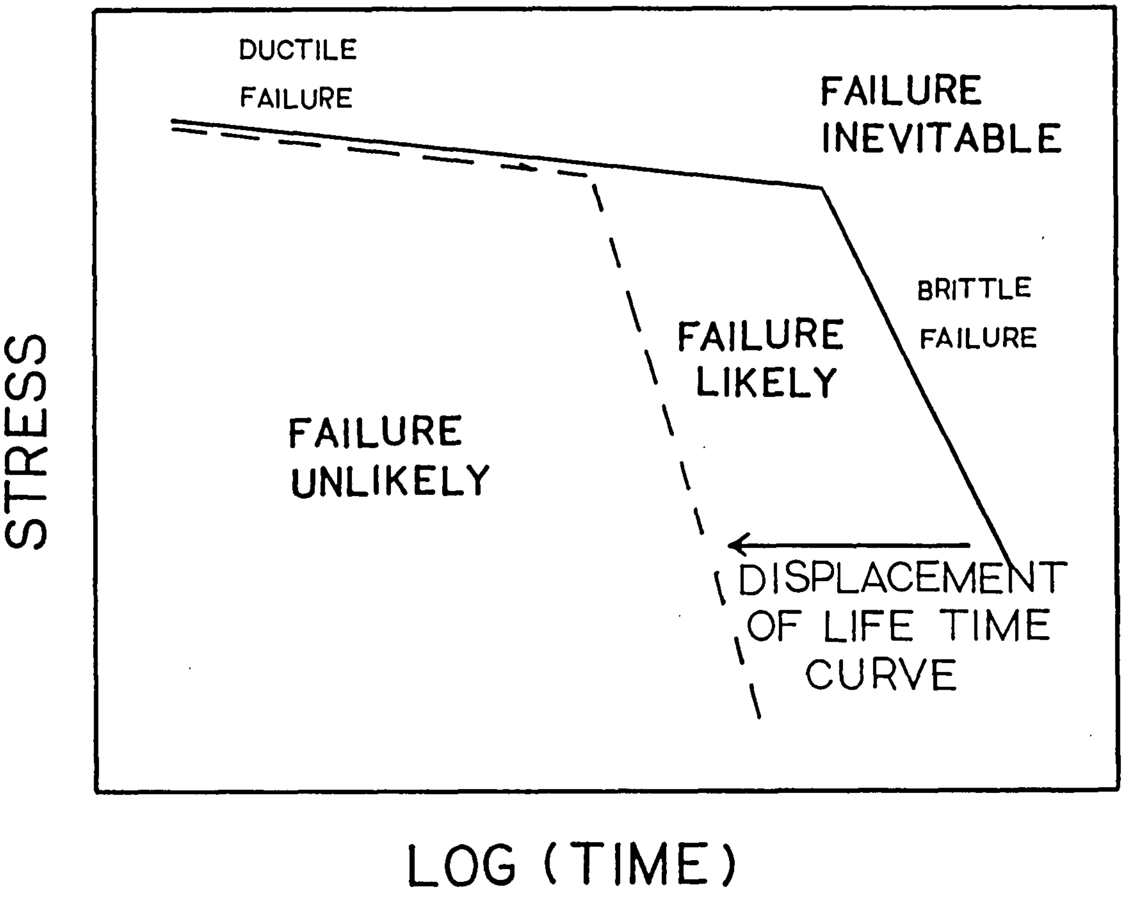

Figure 5.10: Schematic illustration of changes in the stress time-to-failure envelopes [31]

Actual performance of locally produced pipes were inferior to those of pipes obtained from Germany. With few exceptions, they all fail prematurely relative to the relevant creep curve predictions.

Mechanical tests typically did not correlate well with creep life performance. This may well be due to the poor correspondence in the failure process and the difference in morphologies that result. Fatigue testing showed a greater promise in that the morphology of failure surfaces corresponded roughly to the morphologies of craze-cracks generated during creep rupture experiments.

However, further work will be required to demonstrate that a correlation, useful for quality control purposes, actually exists.

Investigations into the possibility of generating solvent crazes using a variety of environmental stress cracking agents proved futile. The high molecular weight pipe grade material apparently has an excellent resistance to this type of failure mode.

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6. CONCLUSIONS

Three batches of locally produced 22 mm polypropylene pipes, manufactured by three different converters, were analyzed in detail to determine their long term ageing characteristics. In addition, approximately sixty failure occurrences of polypropylene pipe installations were investigated.

6.1 Pipe Failure Modes

The three most common causes of pipe failures in the field, in order of frequency, are incorrect installation procedures, use of incorrect material grade and poor processing of pipes:

Incorrect installation
Plastic pipes are generally not damage tolerant, in contrast to metal pipes. Deformation of pipes beyond the yield point, nucleates defects, which, eventually result in failures, long before the expected lifetime. The most common damage of this type, occurs during trenching of pipes when sharp rock are dropped on pipes, or sharp objects dent the pipe during compaction. In addition, pipes are often bent beyond their yield point, which is approximately 12%.

It is recommended that an appropriate trenching procedure be followed, (eg use of sand as a backfill, etc), and that technicians be made aware of the material's sensitivity to gross deformation.

Use of incorrect material grade
In the majority of cases, insufficient stabilizer was present. However, in some instances, the Melt Flow Index (MFI) was also too high. In a specific case, it was proven that pipe was manufactured from non-pipe-grade material.

Poor quality manufacturing of pipes
It was evident in approximately 20% of cases, that failure was caused by poor quality processing. Guidelines for the manufacturing of quality pipes have been published [1-5] and are available from the raw material manufacturers.

6.2 Material Characterization

Spectroscopic, thermal and mechanical characterization of the three standard batch samples, showed that the raw material structure was identical. The identification conforms to a block co-polymer of polypropylene containing segments consisting of an ethylene-propylene co-polymer. This structure is easily confirmed by using ^{13}C NMR, IR, DSC or DMTA techniques.

For routine quality control purposes, DSC or IR should be adequate. Different characteristics were observed when the samples were analysed by Gel permeation chromatography were observed. These are related to differences in molecular weight and its distribution.

6.3 Thermal Stability

Conservative life-time estimates were obtained by combining DSC oxidation induction time data with oven ageing results. These extrapolations indicate that the pipes are highly stabilized with respect to oxidative degradation in air. It is not clear whether this applies to water as well.

Some field samples showed insufficient levels of stabilization.

It is recommended that an OIT test, or an IR spectrum, be incorporated, as part of acceptance testing, to verify the level of stabilization.

It is also recommended that recycling of material be disallowed.

6.4 Creep Life

All locally produced pipes showed poor performance, with respect to creep life at elevated temperatures. All pipes failed at 120°C while only one pipe failed at 95°C. The available evidence suggests that this is the result of poor processing methods. The raw material used, conforms to both manufacturer, ISO and DIN specifications. With apparently identical raw materials, one finds large differences in creep life for pipes from different manufacturers. This suggests that the problem lies with the processing method and/or equipment used.

Unfortunately, the mechanical testing methods explored to date, showed only poor correlation with the quality of pipes. This mandates the use of the creep tests to validate the quality of pipes. It is recommended that both the 1 000 hour specifications for 120°C and 95°C testing, be used for an interim period until the quality of locally produced pipes conform to all ISO (or DIN) Specifications on a consistent basis.

A range of mechanical testing methods were explored as candidate techniques for a rapid acceptance test. Unfortunately most showed only a poor correlation with the long term creep properties of the pipes. This is attributed to the failure mechanisms induced in these tests which differ from the craze failure mechanism observed in long term creep tests. Only dynamic fatigue tests showed similar failure morphologies.

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5. O Lippi, PP Pipe extrusion, 19 April 1994 (Attached as Appendix B)

7. RECOMMENDATIONS

7.1 Recommendations for Further Research

During the course of this investigation the following topics worthy of further research were noted:

- Dynamic fatigue as a predictor for long term life

  Dynamic fatigue tests of ring specimens stressed at levels corresponding to DIN static fatigue levels showed failure morphologies similar to creep failure and resulted in failure times in the order of a few days. It is recommended that a dynamic test rig based on a low cost pneumatic system be devised to allow extensive testing of pipes. These results should be cross-correlated with static fatigue failure times obtained with the 1 000 hour 95°C DIN 8078 (1992) test (hoop stress: 2,65 MPa).

- Validation of the IR test for antioxidant concentration

  It is recommended that this test be conducted in conjunction with standard OIT testing for a period of one year. After this time, an assessment of their respective merits should be made.

- Effect of locally produced iron/oxide based pigments on polymer stabilization

  It is known that some metals catalyze the degradation of antioxidants and polypropylene. Care should be taken that only pure iron oxide pigments be used.

- High moisture absorbtion levels of pipes

  It is not clear whether this phenomenon has an influence on pipe quality.

- Effect of water and dissolved salts on thermal oxidation stability

  Further work could provide an indication of the severity of this effect.

7.2 Suggestions for the Implementation of a Comprehensive Quality Control System

The varied reasons for polypropylene pipe failures indicates that a comprehensive systems approach is required to remedy the situation. It is recommended that a quality control system be implemented as follows:

A. Quality raw material

Lingering doubts remain regarding the effect of the stabilizer system(s) used locally. It is recommended that pipe be manufactured both locally and abroad using both locally and overseas raw materials under identical processing conditions. These pipes should then be qualified using the DIN 8078 (1992) quality control tests. The results from these tests should provide a good indication of the raw material suitability *vis-a-vis* the adequacy of local manufacturing techniques.

In addition, it is recommended that the replacement of the current block-copolymer grade with the more suitable random copolymer pipe grade be investigated. The latter provides better long term creep life at comparable hoop stress levels and is apparently also easier to process into pipes.

B. Implementation of Quality Manufacturing Techniques [1-5]

Locally produced pipes are often made using unsuitable machinery and/or inappropriate processing conditions. It is recommended that a complete quality control system be implemented by manufacturers in terms of the ISO 9000 system. This should include a raw material acceptance test as well as quality control tests on the final product. It is suggested that such a system be phased in over a two year period after which time all pipes should conform to ISO or DIN specifications. Also, it would be advantageous to make use of pipe manufacturing specialists from Europe to assist with the qualification of machinery and processing techniques. It is recommended that the ISO/DIN quality tests be implemented to monitor quality improvements during this period.

C. Implementation of a revised Pipe Acceptance Specification

It is recommended that the dynamic fatigue test be validated as a quick test for creep resistance in the pipe acceptance test. This will require long term testing of a large number of pipes with differing diameters and properties. In addition this test should include revised procedures to evaluate:

- the level of antioxidants;
- the degree of temperature inversion as a measure of built-in stresses.

A draft acceptance specification is given in Appendix A.

D. Implementation of Codes of Practice for Installation (e.g. trenching) of Pipes [6,7]

It is recommended that appropriate installation procedures (inclusive of approved weld bonding techniques) be drafted or selected for implementation by plumbers. This will also require drafting of a suitable course and of training of operators over a period of time.

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7. SABS 1200 LD.

APPENDIX A : DRAFT MODIFICATIONS TO ACCEPTANCE TEST FOR RAW MATERIAL AND PIPE MADE FROM POLYPROPYLENE BLOCK COPOLYMER

Definition of Acceptance Test:

Fast verification of the conformity of a batch of pipes (or raw material) to a specific type.

1. ACCEPTANCE TEST FOR RAW MATERIAL (Minimum requirements)

1.0 Molecular Weight

The melt flow index (MFI) will be used to control the molecular weight of the raw material and the material in its converted form.

Test Conditions (ISO 1133)	MFI Values	
	Raw Material	Pipe
a. 230°C/5kg	$\leq$ 1,5	$\leq$ 2,0
b. 230°C/2,16kg (ISO 1133 Condition 12)	$\leq$ 0,7	$\leq$ 1,0

The use or addition of recycled materials shall not be permitted.

2.0 Antioxidant Concentration

The level of antioxidants will be determined using one of the following techniques:

2.1 Isothermal (or dynamic) Oxidation Induction Time (Temperature)

Sample thickness shall be < 200μm. Tests shall be conducted in comparison to standard film samples containing known quantities of stabilizer.

Method	**Atmosphere/ Temperature**	**Provisional Requirements**
Isothermal (ASTM 3895)	225°C in Air or 200°C in O_2	$\geq$ 30 minutes $\geq$ 20 minutes
Dynamic (ASTM D 3350)	Scan rate of 10°C/min in O_2 Start temperature 30°C or lower	$\geq$ 235°C

2.2 Infrared (IR) Test

This test is only valid if the identity of the stabilizer(s) is exactly known and therefore also the specific corresponding wave length.

In some instances interference between different stabilizes may occur.

A sample of the polymer to be tested is pressed into a film of ca 250μm thickness at a temperature of $\leq$ 230°C. Care should be taken to limit the time during which the polymer will be exposed to high temperatures as this may result in degradation.

Procedure:

The net absorbency at the appropriate wavelength is determined taking the absorbency of the polymer matrix into account. To correct for the thickness a polymer sample containing no additives is used as a reference. Preferably a FTIR machine with a high resolution should be used.

For the Hoechst raw material a calibration curve based on the following nominal stabilizer concentrations is used: 25, 50, 75, 100 and 150%. The absorbtion from the unknown is used to determine an equivalent antioxidant concentration using this technique.

3.0 Longitudinal Thermal Reversion

Using test methods according to the following specifications, the change in pipe length after heat treatment at 150°C for 150 minutes should not exceed 2%:

DIN8078 (1992)
ISO 3478 Method B

4.0 Impact Resistance (optional)

The impact resistance shall have a value not exceeding 10% according to draft specifications of ISO DIS 3127 conducted at 0°C.

5.0 Time-to-Failure of Polypropylene Block Copolymer Pipes under Constant Internal Pressure

The time-to-failure of pipes are determined using DIN 8078 (1992) with the following conditions:

Temperature °C	Medium	Test Stress MPa	Minimum Life Time (h)
20	Air or Water	16	1
95	Air or Water	2,65	1 000

APPENDIX B : EXTRUSION OF POLYPROPYLENE PIPES

PP PIPE EXTRUSION

by O Lippi

PLASTOMARK (PTY) LIMITED
TECH CENTRE

INFLUENCE OF COOLING

The heat dissipation of an extruded PP pipe is poor owing to the materials low thermal conductivity. As a result, the post cooling process of the pipe, after exiting from the die, takes longer (compared with PE-HD) and therefore requires a longer residence time in the cooling medium. This does not necessarily relate to reduced outputs, but necessitates stretched cooling baths and an overall lengthened production lane, when recommended cooling conditions are employed. In practice this problem is often overcome by the application of severe post cooling of the pipe, which allows for shorter cooling lanes and extruder outputs to be increased. This objective, however, is achieved at the expense of pipe quality, as a result of internal stress being frozen into the pipe. The life expectancy of such a pipe will be substantially reduced and evidence thereof will clearly be indicated in comparative hydrostatic pressure test results. Another important physical characteristic which will be negatively affected is the pipe's resistance to impact which will be markedly lower than a stress relieved pipe.

COOLING RECOMMENDATIONS

The cooling intensity of the water in the calibration and cooling baths should be accurately monitored to allow a degree of stress relaxation to occur after exiting of the pipe from the die. This objective is achieved by regulation of the cooling medium at approximately 50°C in both calibration and first cooling baths. Temperatures of subsequent cooling baths may be reduced ideally to 30°C, but not lower than 20°C. This profile for the cooling medium is of particular importance when producing small diameter, thin walled pipe at high output rates, allowing a degree of stress relaxation to occur before the pipe wall solidifies. Molecular orientation is the prime cause of stress formation in a pipe during the extrusion process. Tests have shown that pipe exhibiting high levels of stress are generally produced under compromised conditions of high extrusion speed coupled with excessively high haul-off rates and severe post cooling.

It is also recommended practice to make use of intermittent cooling. This is achieved by intercepting the cooling by spacing water baths (allow 1,5 - 4,0m distance between baths, depending on pipe size and extrusion rate). In the uncooled sections the pipe is partly annealed by its own remaining internal heat which is given the opportunity to be conducted to the cooled outer surface. In this way internal stresses are considerably reduced. The importance of intermittent cooling increases with increasing wall thickness and large diameter pipe should be given two or three such tempering steps. It has been established that the ideal temperature of an extruded pipe as measured on the inside wall of an extruded pipe after the haul-off, should be approximately 85°C. This temperature provides the guide for the length of the entire production lane for a specific pipe type/class, when the recommended cooling conditions are employed.