Thirty Year Ageing of Plastics

K. C. Brady & W. McMahon
Transport Research Laboratory, Berkshire, UK

G. Lamming
Rapra Technology Ltd, Shropshire, UK

ABSTRACT: The report provides details of a 30-year programme to investigate the ageing of six plastics under various climatic conditions. The plastics comprised three types of polyvinyl chloride (PVC); a styrene-butadiene copolymer; and both low and high density polyethylenes. Specimens of each plastic were stored at sites with temperate, hot and wet, and hot and dry environments. At intervals throughout the programme, tests were performed to determine any changes in the physical properties of the plastics. There was little change in the properties of the polyethylenes and a PVC plasticised with dioctyl phthalate. However, the properties of the other plastics changed over the 30-year period due to a reduction in the effectiveness of the plasticisers or stabilisers.

1 INTRODUCTION

A long-term test programme to investigate the ageing of six plastics under various climatic conditions was initiated in 1958 by the Rubber and Plastics Research Association (now RAPRA Technology Ltd). The plastics were chosen from those available in the early 1950's and, although some may no longer be in general use, the test data and resulting conclusions may be relevant to predicting the performance of contemporary products.

Specimens of the plastics were stored at sites with temperate, hot and dry, and hot and wet environments: tests were performed on specimens recovered from each site at intervals throughout the 30-year programme. This paper presents details of the sites and materials, and provides an interpretation of the results of the tests.

2 DETAILS OF THE TEST PROGRAMME

The materials used, and the designation adopted in this report, are as follows:

(i) PVCD - PVC plasticised with dioctyl phthalate (DOP) - a standard cable covering
(ii) PVCP - PVC plasticised with polypropylene adipate
(iii) UPVC - a high-impact unplasticised PVC
(iv) SB - a styrene-butadiene copolymer (Styron 475)
(v) LDPE - a low density polyethylene
(vi) HDPE - a high density polyethylene

Specimens of each material were placed in ventilated aluminium boxes and stored in conditions as described in Table 1. The following tests were performed on the recovered specimens:

(i) appearance, weight and dimensions: BS2571(1955)
(ii) water absorption and water extractable matter content: BS2782: Part 5, method 502C (1958)
(iii) impact strength (for UPVC, HDPE and SB only): BS2782: method 306A (1957)
(iv) softness: BS2782: Part 3, method 307A (1957)
(v) tensile strength and strain at rupture: BS903: Part A2 (1971) for PVCD and PVCP; ASTM D638-56T (type 1) for the other materials

Many of the test methods were superseded in the course of the investigation but for consistency the same methods

Table 1. Climatic characteristics of storage sites

Climate	Location	Daily mean and range of temperature (°C)	Mean annual rainfall (mm)	Average daily mean relative humidity (%)
Temperate	RAPRA Laboratory UK	22 21 - 25	-	60
Hot and dry	Cloncurry Australia	26 16 - 32	450	40
Hot and wet	Cairns Australia	24 20 - 29	3550	80

were used throughout. Some of these tests were also performed on specimens that had been stored for up to six months at temperatures of 70°C or 100°C, either in a dry atmosphere or at a relative humidity of 100 per cent. The results of these accelerated ageing tests have been reported by Moakes (1976).

A number of specialised tests were also undertaken on the 30-year old specimens to investigate aspects of particular interest: the techniques used were differential scanning calorimetry (DSC) and infra-red spectroscopy (IR).

3 RESULTS OF TESTS

3.1 PVCD

The relative density, softness and water extractable matter content did not change during storage. The data from the tensile tests, summarized in Table 2, show that the strength properties of the material did not change substantially over the 30-year period.

3.2 PVCP

The appearance of the specimens changed with age. The 30-year old specimens had a pitted, crusty appearance and those from the temperate and hot dry sites also had a moist surface deposit. This deposit was primarily adipic acid, formed by the hydrolysis of the propylene adipate plasticiser. The data provided in Table 3 show that there were substantial changes in the water absorption value and the water extractable matter content over the 30-year period.

A summary of the results of the tensile tests is provided in Table 4. Whereas the tensile strength of the specimens stored at the temperate site did not vary substantially, the data for the hot sites show an increase in strength of about 40 per cent over the 30-year period. The strain to rupture of the material reduced with age, particularly in the hot environments: this embrittlement is consistent with the loss of plasticiser. Stress-strain relations for some of the 30-year old specimens stored at the temperate and hot wet sites are shown in Figure 1. The peak tensile strength of the aged specimens was achieved at strains of about 5 per

Table 2. Summary of results of tensile tests on PVCD

Age of specimens (years)	Temperate		Hot wet		Hot dry	
	σ_r	ϵ_r	σ_r	ϵ_r	σ_r	ϵ_r
Initial	20.0	290	20.0	290	20.0	290
1	19.6	300	20.0	310	19.7	310
2.5	20.0	300	20.2	300	19.3	290
3.5	20.2	320	20.6	330	18.3	320
5.5	17.3	300	18.2	290	20.6	300
7.5	20.2	310	19.8	320	19.5	330
11.5	22.3	300	23.4	240	23.0	240
15.5	20.2	320	20.6	300	19.5	310
20	20.0	320	20.5	310	20.0	310
30	21.2	300	20.0	300	21.4	280

σ_r Mean strength at rupture (MN/m^2)
ϵ_r Mean strain at rupture (%)

Table 3. Physical properties of PVCP

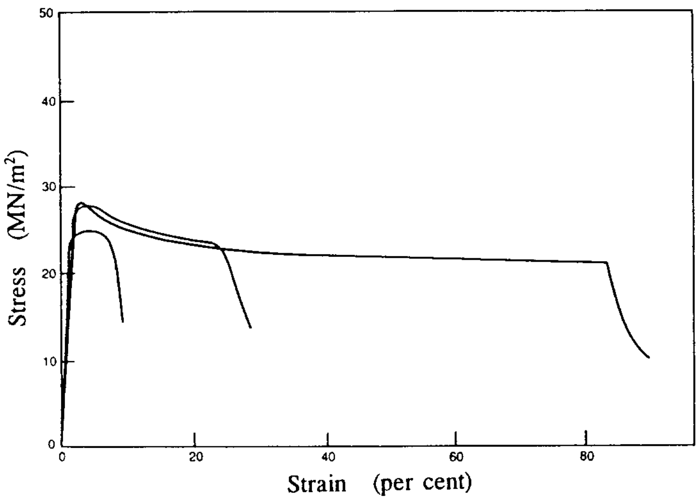
	Initial values	30-year aged values		
		Temperate	Hot dry	Hot wet
Relative density	1.370	1.368	1.383	1.371
Water absorption (%)	1.90	0.17	0.15	0.37
Water extractable matter (%)	0.30	0.20	0.11	0.44
Softness (mm/100 indentation)	4	2	3	4

Table 4. Summary of results of tensile tests on PVCP

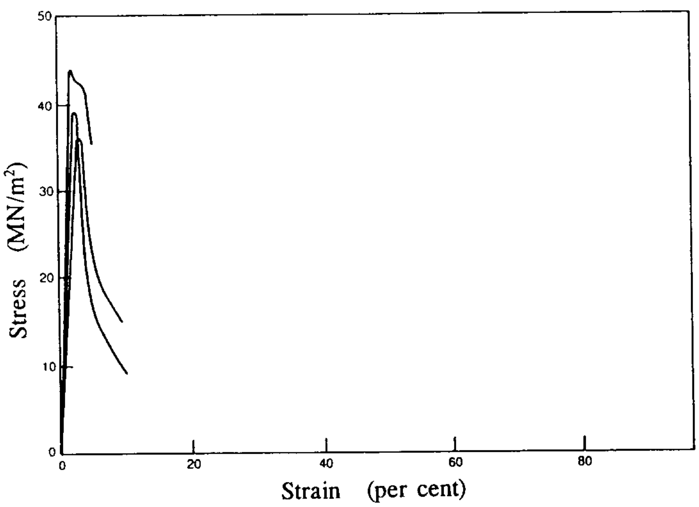
Age of specimens (years)	Temperate			Hot wet		Hot dry		
	σ_{max}	ϵ_{max} +	ϵ_r +	σ_{max}	ϵ_{max}	σ_{max}	ϵ_{max} +	ϵ_r +
Initial	27.6	170		27.6	70	27.6	70	
1	27.7	170		28.1	110	27.5	110	
2.5	28.0	140		27.6	110	26.6	150	
3.5	24.8	150		-	-	23.8	90	
5.5	23.1	120		28.4	80	24.6	30	100
7.5	23.9	120		31.9	70	25.1	-	160
11.5	25.1	140		-	-	25.9	-	170
15.5	23.5	5	170	41.1	5	31.8	3	
20	22.0	-	100	44.0	5	24.4	-	35
30	27.6	5	90	41.9	5	38.7	3	10

σ_{max} Mean peak strength (MN/m^2)
ϵ_{max} Mean strain at peak strength (%)
ϵ_r Strain at rupture (%)
\- Data not available
\+ Strains at peak and rupture are only given when peak is evident in stress-strain relations

cent, and there was wide variation in the post-peak behaviour of the specimens stored at the temperate site. The variability of stress-strain relations shown in Figure 1(a), was probably due to variations in the loss of plasticiser from the individual specimens.



(a) Results for 30-year old specimens stored in temperate environment.



(b) Results for 30-year old specimens stored in hot wet environment

Fig. 1 Stress-strain relations from tests on specimens of PVCP

3.3 UPVC

After 30-year storage, the specimens at the temperate site had turned grey and those in the hot environments were amber with white striations; some were also distorted. A comparison of some of the tests on unaged and 30-year old specimens is provided in Table 5. The water absorption value and the water extractable matter content had both reduced considerably and the impact strength of the plastic had reduced by 75 per cent. Infra-red spectroscopy showed that the metal soap stabilisers had been lost or rendered inactive, particularly at the hot sites.

A summary of the results of the tensile tests is given in Table 6. It would appear that the results of the tests had not been reported consistently: nonetheless the data show an increase in strength and a loss of ductility with time. Stress-strain relations for specimens stored for 2.5 years and for 30 years at the temperate site are given in Figure 2: this shows that the shape of the stress-strain relation for the material had changed with ageing.

3.4 SB

The appearance of the specimens changed during their time in storage, particularly in the hot environments. The specimens became amber-yellow with age and those in the hot sites developed white striations. The impact strength of the material reduced with time at all three sites: the reductions after 3.5, 15.5 and 30 years were 15, 70 and 94 per cent respectively. However, there were no

Table 5. Physical properties of UPVC

	Initial values	30-year aged values		
		Temperate	Hot dry	Hot wet
Relative density	1.338	1.336	1.337	1.330
Water absorption (%)	0.40	0.03	0.03	0.03
Water extractable matter (%)	1	0	0	0
Impact strength (Joules)	12.5	3.2	3.0	3.1

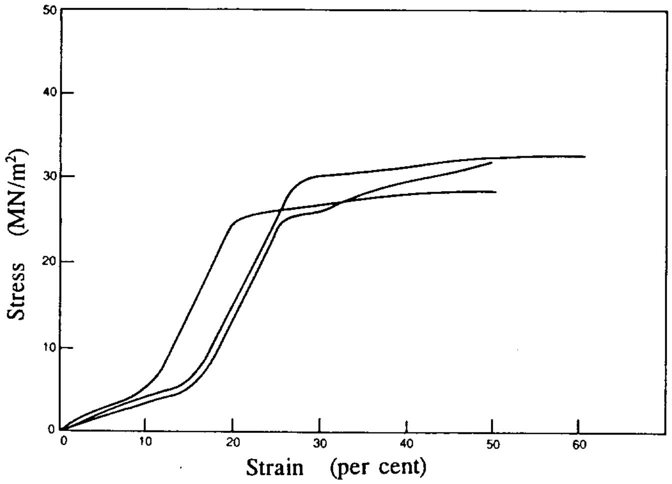
Table 6. Summary of results of tensile tests on UPVC.

Age of specimens (years)	Temperate				Hot wet				Hot dry			
	σ_{max}	ϵ_{max}	σ_r	ϵ_r	σ_{max}	ϵ_{max}	σ_r	ϵ_r	σ_{max}	ϵ_{max}	σ_r	ϵ_r
Initial	-	-	31.9	70	-	-	31.9	70	-	-	31.9	70
1	R	R	30.6	55	R	R	33.2	60	R	R	30.4	50
2.5	R	R	30.1	45	R	R	31.1	60	29.4	25	29.0	50
3.5	-	-	29.1	-	-	-	27.2	-	-	-	28.4	-
5.5	-	-	-	-	33.3	5	29.3	55	35.5	-	30.6	80
7.5	R	R	33.1	60	34.5	8	34.2	70	R	R	34.2	50
11.5	-	-	35.9	65	-	-	35.7	75	-	-	34.4	25
15.5	38.5	4	34.6	65	38.4	2	35.3	40	39.0	3	36.2	30
20	-	-	37.4	50	-	-	37.4	50	-	-	34.1	30
30	38.0	4	33.7	35	46.7	2	43.6	14	41.6	3	35.0	25

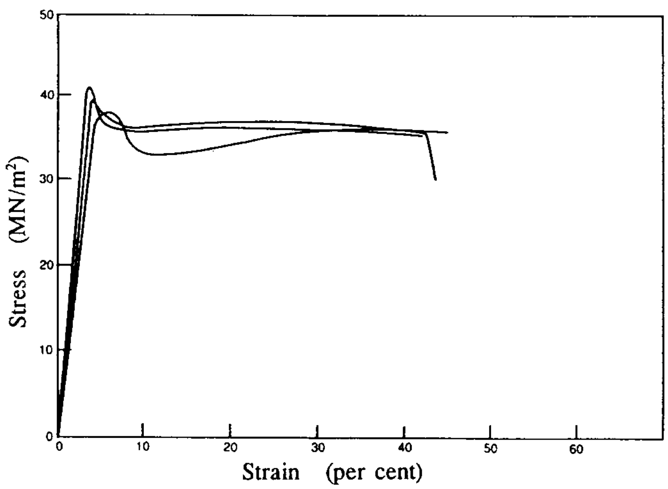
σ_{max} Mean peak strength (MN/m²) σ_r Mean strength at rupture (MN/m²) - Data not available

ϵ_{max} Mean strain at peak strength (%) ϵ_r Mean strain at rupture (%) R No peak observed prior to rupture significant changes in the relative density, water absorption value, or water extractable matter content.

A summary of the results from the tensile tests is provided in Table 7. The data from all the sites show an increase in strength with time accompanied by a reduction in the strain to rupture.



(a) Results for 2.5-year old specimens stored in temperate environment.



(b) Results for 30-year old specimens stored in temperate environment

Fig. 2 Stress-strain relations from tests on specimens of UPVC

Table 7. Summary of results of tensile tests on SB

Age of specimens (years)	Temperate		Hot wet		Hot dry	
	σ_r	ϵ_r	σ_r	ϵ_r	σ_r	ϵ_r
Initial	29.8	25	29.8	25	29.8	25
1	29.7	25	29.7	25	30.0	20
2.5	30.2	20	33.4	20	33.4	20
3.5	31.6	20	31.6	20	30.7	20
5.5	38.3	10	37.9	15	36.4	10
7.5	38.9	10	39.5	10	38.0	10
11.5	39.2	10	40.4	10	39.1	6
15.5	42.9	10	36.5	10	36.9	10
30	35.7	10	37.9	10	37.0	7

σ_r Mean strength at rupture (MN/m^2)
ϵ_r Mean strain at rupture (%)

3.5 LDPE

The appearance of the specimens did not change much during storage. The density, water absorption value and water extractable matter content were reasonably constant over the 30-year period. A summary of the results of the tensile tests is provided in Table 8: these data indicate a modest increase in tensile strength and a reduction in the strain to rupture with time.

Table 8. Summary of results of tensile tests on LDPE

Age of specimens (years)	Temperate		Hot wet		Hot dry	
	σ_r	ϵ_r	σ_r	ϵ_r	σ_r	ϵ_r
Initial	11.9	200	11.9	200	11.9	200
1	12.5	195	12.6	195	12.4	175
2.5	12.5	180	12.6	165	12.5	190
3.5	12.7	225	12.7	120	12.8	135
5.5	12.9	155	12.6	180	12.9	180
7.5	12.6	175	13.0	170	13.1	170
15.5	13.4	185	13.2	165	13.4	150
30	13.3	175	13.4	180	13.5	155

σ_r Mean strength at rupture (MN/m^2)
ϵ_r Mean strain at rupture (%)

3.6 HDPE

The appearance of the specimens hardly changed during storage. There were no substantial changes in the density, water absorption value, or water extractable matter content. However there was a reduction of about 50 per cent in the impact strength over the 30-year period. To investigate differences in the morphology of the material and to provide data for comparative purposes with contemporary HDPE products, DSC techniques were used to determine the melt temperature, crystallinity, and oxidation induction temperature for the 30-year old specimens: the data are summarised in Table 9. There was no substantial difference in the morphology of the specimens stored at the three sites.

A summary of the results of the tensile tests is provided in Table 10. The peak strength of the material was developed at between 10 and 20 per cent strain, but rupture of some of the specimens occurred at strains of 60 per cent or more: unfortunately not all the tests were continued to rupture. The data show that over the 30-year period the tensile strength of the material remained sensibly constant, but there was a modest reduction in the strain at which the peak strength was achieved.

Table 9. Results of DSC tests on specimens of HDPE

Environment and test number		Melt temperature (°C) Onset	Melt temperature (°C) Peak	Crystallinity (%)	Oxidation Induction Temperature (°C)
Temperate	a	126.3	134.0	79.0	220
	r	125.5	133.3	78.4	-
Hot and dry	a	126.0	133.9	78.7	216
	r	125.0	132.7	77.1	-
Hot and wet	a	126.6	133.6	79.6	220
	r	124.8	133.1	78.7	-

a - as received
r - reheated specimens

3.7 Accelerated ageing programme

The effects on the material properties of natural ageing were not replicated by the accelerated ageing environment. Of the six materials, only the properties of PVCP and LDPE showed similar trends in both the natural and artificial environments, but due to the limited test data it was not possible to establish the rate at which ageing was accelerated in the artificial environment. A fuller comparison of the results is provided by Brady et al (1994).

4 DISCUSSION

A comparison of the data obtained from the hot dry and the hot wet environments only shows differences for the PVCP material. It can be inferred that the rate of migration or reaction of the polypropylene adipate plasticiser was affected by the level of humidity.

Similarly, a comparison of the sets of data obtained from the temperate and the hot sites shows no substantial differences for the PVCD, SB, LDPE and HDPE materials. The data for the PVCP and UPVC materials show that the increase in tensile strength and the decrease in strain to rupture were more pronounced in the hot environments. It seems probable therefore that the difference in performance was due to a higher rate of reaction of the additives (plasticiser and stabiliser) at the higher prevailing temperatures.

The environments used in this study are unlikely to model exactly the in-service conditions for many products. It should be appreciated that the test specimens were unstressed and shielded from direct sunlight. Moreover, although the 30-year test period may be equivalent to the anticipated lifetime of many building or architectural products, it is only 25 per cent of the lifetime required by the UK Department of Transport for permanent structures. Nonetheless, the performance of the PVC plasticised with dioctyl phthalate and the polyethylenes provides some assurance that products manufactured from these materials can function effectively for long lifetimes. The relatively small changes in the properties of these plastics in the hot environments are particularly encouraging, as these suggest that the working lifetimes of products used in temperate zones, or below ground, could substantially exceed 30 years. However it may be necessary to take account of the reduction in the ductility of these plastics when they are used for long-term structural applications.

Although the performance of the other plastics (PVCP, UPVC and SB) was perhaps not as good, products manufactured from these may still be suitable for many short and medium term applications. It seems probable, however, that the rates of deterioration of these plastics would be higher when exposed to outdoor weathering than were recorded in this study.

In the design of permanent structures, the use of data from accelerated ageing programmes may seem attractive as there is a paucity of data from long-term natural ageing

Table 10. Summary of results of tensile tests on HDPE.

Age of specimens (years)	Temperate			Hot wet			Hot dry		
	σ_{max}	ϵ_{max}^{+}	ϵ_r^{+}	σ_{max}	ϵ_{max}^{+}	ϵ_r^{+}	σ_{max}	ϵ_{max}^{+}	ϵ_r^{+}
Initial	25.9	15	-	25.9	15	-	25.9	15	-
1	26.4	20	40	26.4	15	-	25.4	15	45
2.5	25.8	15	50	25.8	15	50	25.5	15	45
3.5	21.3	15	120	21.7	15	>100	21.5	15	>100
5.5	28.2	-	-	25.9	-	-	25.1	15	220
7.5	24.6	15	170	25.7	20	150	24.6	15	-
15.5	27.4	10	-	25.6	10	-	25.4	10	35
30	25.6	10	27	26.0	-	-	27.0	10	210

σ_{max} Mean peak strength (MN/m^2) — - Data not available
ϵ_{max} Mean strain at peak strength (%) — + Strains at peak and rupture strength are only given when peak evident in stress-strain relations
ϵ_r Strain at rupture (%)

of plastics. However, this study has shown that the changes in material properties due to accelerated ageing do not always replicate those produced by natural ageing.

The data show that the long-term performance of a plastic can be dependent upon the types of additive used to impart plasticity and long-term stability. This suggests that data from durability trials may be product specific, and data published for 'generic' base polymers must therefore be used with caution.

5 CONCLUSIONS

This report presents data obtained from tests on specimens of six plastics stored for a 30-year period in temperate, hot dry, and hot wet environments. The performance of the plastics was variable, but there tended to be an increase in tensile strength and a reduction in ductility with time.

(i) Little, if any, change was recorded in the physical properties of a PVC plasticised with dioctyl phthalate and both low density and high density polyethylenes.

(ii) The appearance and properties of a PVC plasticised with polypropylene adipate changed substantially with time. The surfaces of the 30-year old specimens were covered with a crust formed by the hydrolysis of the polypropylene adipate plasticiser.

(iii) The appearance of the specimens of the unplasticised PVC changed over the 30-year period. Infra-red spectroscopy showed that there was a loss of the metal soap stabiliser from the surface of the specimens stored in the hot environments.

(iv) The appearance of the specimens of the styrene-butadiene copolymer also changed with time: the change was more pronounced in the hot environments. The impact strength of the material was substantially reduced over the 30-year period.

The performance of the PVC plasticised with dioctyl phthalate, and both the low and high density polyethylenes, provides some assurance that products manufactured from these can be designed for long-life applications.

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