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The development of test procedures for the investigation of the chemical/physical compatibility of PE packagings for the transport of dangerous goods (CHEMPACK)[1]

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Introduction

The regulations for the transport of dangerous goods give requirements for packagings and IBCs (Intermediate Bulk Containers) which are to be used for transport. These requirements are basically mechanical requirements and a test program for testing each type of packaging/IBC consisting of tests like drop test, stacking test and internal hydraulic pressure test has to be performed in order to obtain an approval.

For plastic packagings the investigation of the chemical/physical compatibility is part of the test procedure. The UN Recommendations on the Transport of Dangerous Goods (1) state that a storage of each substance to be transported for a period of e.g. 6 months before carrying out the mechanical performance tests is a way for this investigation.

The European regulations for the transport of dangerous goods (RID/ADR) (2) have further developed this procedure by making this 6 months storage a compulsary requirement. It will be clear, however, that storage of each substance to be transported for each packaging type to be approved is a lengthy, costly and elaborate procedure. For this reason a method was developed for the plastic material most commonly used (HMW-HDPE = high molecular weight high density polyethylene) with standard liquids with each standard liquid being representative for a specific kind of interaction (swelling, stress cracking and chemical degradation). In this way testing on packagings could be restricted to these standard liquids and chemicals to be transported could be assimilated to 1 or more of the standard liquids by assimilation either through a published list or by comparing the effect in laboratory test methods. Moreover the storage time was diminished by performing the storage at

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increased temperature (40°C) leading to acceleration of the procedure (3 weeks storage time instead of 6 months).

Because of the developments in technology both in packaging and materials the need was felt to be able to apply the standard liquid system also to other types of PE than the HMW-HDPE. Further is was found necessary to evaluate the present system of standard liquids with the aim of simplification and maybe introduction of other test procedures.

For this reason a European project CHEMPACK (3) was carried out in the time period 1 November 1997 - 1 November 2000 with a budget of 1.1 MEURO and a participation of 5 material manufacturers, 4 packaging/IBC manufacturers and 4 test institutes and coordinated by TNO. This paper gives a summary of the results of the project CHEMPACK with contributions of the partners as mentioned in (3).

Selection of packagings and materials

The selection of packagings and materials to be investigated in the project CHEMPACK was done in consultation with the participants. Packagings and materials were selected which were both representative for what was applied in practice and also had varying properties, volumes and methods of processing, so that the conclusions would be relevant for the general application of PE materials as much as possible.

The material-packaging combinations, which were selected, are given in Table 1.

Type of packaging	Nominal volume of packaging (litre)	Type of material	Method of processing
IBC	1000	LLDPE	RM
IBC	1000	HDPE	BM
Drum	220	HMW-HDPE	EX/IM
Drum	220	HMW-HDPE	BM
Jerrican	20	HMW-HDPE	BM
Jerrican	20	HMW-HDPE	BM
Jerrican	10	MMW-HDPE	BM
Bag in box	5	LLDPE	EX

LLDPE = linear low density PE
HDPE = high density PE
HMW-HDPE = high molecular weight high density PE
MMW-HDPE = medium molecular weight high density PE
RM = rotational moulding
BM = blow moulding
EX = extrusion (body)
IM = injection moulding (head)

Table 1 Selected packagings and IBCs with PE materials for the project CHEMPACK

Interaction of chemicals with PE

The aim of the project CHEMPACK was that it should lead to a testing procedure with standard liquids, which would cover at least 90% of the chemicals, which are transported as dangerous goods in plastic packagings/IBCs.

An inventory was thus made of the relevant chemicals which are mostly found in the classes 3, 6.1 and 8 (flammable, toxic and corrosive liquids). Examples of types of chemicals are hydrocarbons, alcohols, esters, hydrogen peroxide, sulphuric acid and nitric acid.

An investigation was made into the possible interaction mechanisms of the relevant chemicals and the PE material. The following interactions were identified: chemical interaction (degradation) and physical interaction (swelling and stress cracking). Taking factors as oxidizing strength and penetration depth into account it was established that the strongest effect of chemical degradation is to be expected from nitric acid. Nitric acid is thus proposed as a standard liquid for the degradation interaction type.

For physical interaction four categories of chemicals were considered: aqueous solutions of inorganic chemicals, aqueous solutions of surfactants (detergents), polar organic chemicals and non-polar organic chemicals. For aqueous solutions of inorganic chemicals a similar interaction as compared to water is expected, though for some of these liquids (e.g. sodium hydroxide solution) the effect can be higher than for water. For aqueous solutions of surfactants stress cracking is to be expected and as standard liquid an aqueous surfactant solution (ionic alkyl benzene sulphonate is preferred to nonionic ethoxylated alkylphenol compounds) is proposed. For polar organic chemicals environmental stress cracking is to be expected as well but less than for the surfactant solution. Acetic acid and butyl acetate (when also swelling is involved) are appropiate standard liquids, although acetic acid should be adequate to cover the effect of both environmental stress cracking and swelling as represented by butylacetate. For non-polar organic chemicals swelling is the main interaction. It is proposed to use a standard liquid which is defined as good as possible (xylene mixture or aliphatic mixture but not a combination of both as is used presently).

Based on the considerations as given (type of chemicals to be considered and type of interactions with PE) the following standard liquids as given in table 2 are proposed for further study.

Standard liquid	Type of interaction	Category of chemicals
Nitric acid 55%	Oxidation	Oxidizing chemicals
Water	Swelling by aqeous solutions with non or moderate chemical or physical interaction	Aqueous solutions of salts, inorganic acids, alkalis
Aqueous solution of alkyl benzene sulphonate surfactant	Environmental stress cracking	Aqueous solutions of detergents and cleaning agents
Acetic acid	Environmental stress cracking	Organic alcohols, ketones, etc
Butylacetate	Environmental stress cracking and moderate swelling	Larger organic molecules with polar groups
Mixture of aliphates	Swelling	Aliphatic chemicals
Mixture of xylenes	Swelling	Aromatic chemicals

Table 2. Proposed standard liquids

The verification of the proposed standard liquids was done in the next phase of the CHEMPACK project. Further substances were selected for consideration where uncertainty existed of its effects and what standard liquids would be applicable: solution of sodium hydroxide, sulphuric acid and hydrochloric acid.

Verification of standard liquids

The use of standard liquids serve 2 purposes: the interaction should be representative for a group of chemicals with similar interaction mechanisms and by increasing the temperature the speed of interaction can be increased such that the storage period of 6 months can be decreased by a factor of 5-10.

In order to verify the selection of the standard liquids as proposed for the type of PE materials as selected, an experimental program was executed both on packagings/IBCs and on material samples.

First an inventory was made of available test methods for testing materials on oxidation, environmental stress cracking and swelling and methods for the detection of the degree of interaction. From the results of this inventory a selection was made of suitable test and detection methods which were used in the experimental program.

The experimental program on packagings was performed with liquids which were supposed to have an oxidation and swelling effect. It was not possible to study the environmental stress cracking effect on packagings which had been stored with a stress cracking agent as no detection method was available to detect small cracks which are expected to occur in the packaging specifically on certain locations with stress concentrations.

For the investigation of the oxidation the effect of 6 months storage at ambient temperature was compared to storage at higher temperature (40°C) at different storage time periods. Detection methods used included melt flow rate, tensile strength and infrared.

A typical result can be seen in table 3.

Storage medium	Storage time (days)	Storage temperature (°C)	Tensile strength at yield (MPa)	Elongation at break (%)	MFR (g/600 s)	MFR increase (%)
None (control sample)	0		21.9	670	1.58	
Water	180	15	21.1	690	1.59	0
Nitric acid	180	15	21.7	700	1.95	23
Nitric acid	14	40			2.08	32
Nitric acid	21	40	22.0	660	2.21	39
Nitric acid	28	40	21.7	680	2.23	41
Suphuric acid	180	15	21.4	700	1.69	7
Sulphuric acid	14	40			1.57	0
Sulphuric acid	21	40	21.4	660	1.65	4
Sulphuric acid	28	40	22.1	660	1.68	6

Table 3 Results of tests after storage of 220 litre drum with nitric acid (55%) and sulphuric acid (96%)

It can be concluded from the results that for nitric acid acceleration by temperature increase is possible and that 6 months storage at 15°C can be accelerated to 3 weeks at 40°C. Degradation was detected on the melt flow rate, but no effect of the degradation could be observed on tensile strength at yield or elongation at break. In other experiments no effect with the notched tensile impact test was observed either. Further the effect of sulphuric acid is negligible.
The results for the other packaging types and materials are comparable.

The swelling was determined by measuring the mass increase as a function of time in both a xylene mixture and an aliphatic mixture. Also the yield strength, elongation at yield, force at break and elongation at break were determined. All measurements were done on the 10 litre packaging.
Typical results are given in Fig 1.

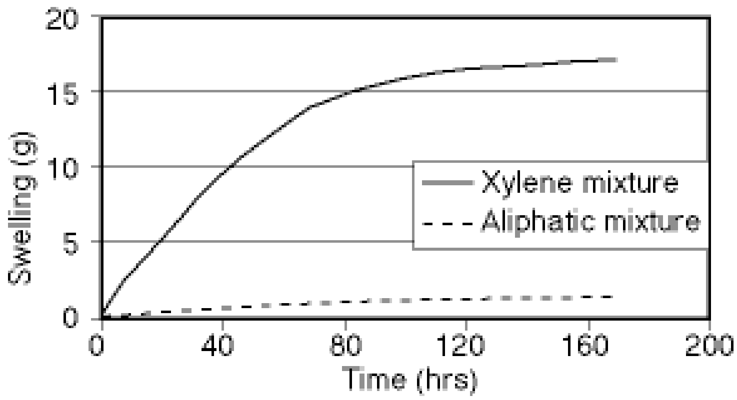

Fig 1 Swelling of 10 litre jerrican after storage with xylene mixture and aliphatic mixture as function of time at 23°C

It can be concluded that the rate of absorption is much higher for the xylene mixture compared to the aliphatic mixture (saturation is reached after about 5 days for xylene mixture at a temperature of 23°C, while for the aliphatic mixture equilibrium is not reached after 7 days).
No effect was observed on the mechanical properties with the aliphatic mixture, while for the xylene mixture the mechanical properties changed with the degree of swelling (decrease of yield strength of 16%, increase of elongation at yield of 40%).

The swelling effect was studied in more detail on material samples.

The experimental program on material samples consisted in exposing test samples at different temperatures to chemical substances using test methods for environemntal stress cracking, oxidation and swelling.

Environmental stress cracking

A method, that was developed recently, was applied, namely the FNCT (full notch creep test). Typical results for the FNCT test are shown in table 4.

Material	Temperature (°C)	Stress (MPa)	Failure time (hrs)
HMW HDPE (1)	50	9	12.5
HMW HDPE (2)	50	9	13.5
LLDPE	50	5.5/9	15.0/2.5
HMW HDPE (1)	70	9	1.3
HMW HDPE (2)	70	9	1.4
LLDPE	70	5.5/9	1.2/0.2

Table 4 Results for FNCT test for 3 materials as a function of temperature after storage in a stress cracking agent (2% Marlon A in water). For LLDPE also a stress level of 5.5 MPa was selected because of the lower yield stress of this material

It can be concluded that there is an acceleration factor of about 10 at a temperature increase of 20°C.

Experiments with the Bell Test and the Pin Impression Test were also performed on several materials, but often no failures were observed within the time periods as studied. For LLDPE these methods are not suitable, because of the lower stress levels occurring in these tests.

For the oxidation experiments typical results with the tensile impact test as detection method are shown in table 5 and table 6.

Storage time (days)	Storage temperature (°C)	Tensile impact strength (kJ/m^2)	Standard deviation (kJ/m^2)
0	23	583	32
42	23	627	26
10	40	609	22
42	40	564	14
5	50	570	17
10	50	548	36
3	60	635	26
5	60	568	20

Table 5 Tensile impact strength of HMW-HDPE after storage in nitric acid 55% at several temperatures

Storage time (days)	Storage temperature (°C)	Tensile impact strength (kJ/m^2)
0	23	114
42	23	109
181	23	112
385	23	99
10	40	110
15	40	107
22	40	100
29	40	99
43	40	87
67	40	17
3	60	102
5	60	4

Table 6 Tensile impact strength of LLDPE after storage in nitric acid 55% at several temperatures

Only for the LLDPE material a noticable effect can be observed for the temperatures and time periods investigated. The acceleration factor is of the order of 10.

It is of interest to note that both the tensile test method and the tensile impact strength method do not show much effect for a certain time period after which a rapid drop in mechanical properties is noticed. This effect is shown in fig 2.

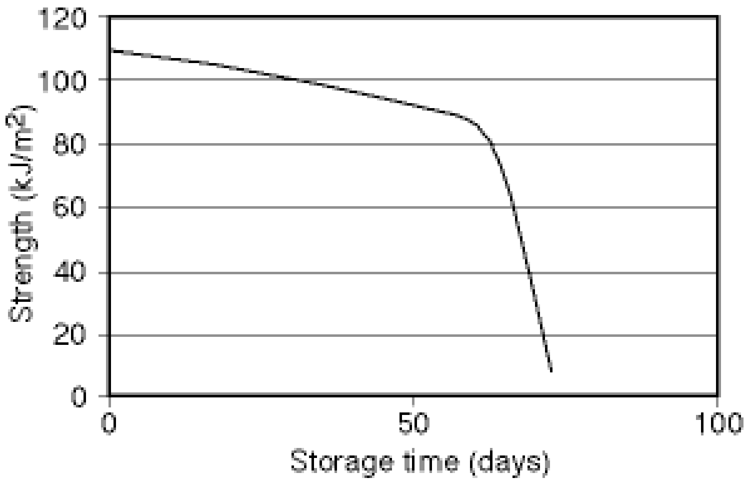

Fig 2 Tensile impact strength of LLDPE as a function of storage time in nitric acid 55% at 40°C

Fig 3 shows an infrared scan of a PE sample. The amount of carbonyl (C=O) as a function of cross-section depth of the sample at different storage temperatures and times is presented. This clearly shows the penetration of the nitric acid into the PE and the corresponding degradation.

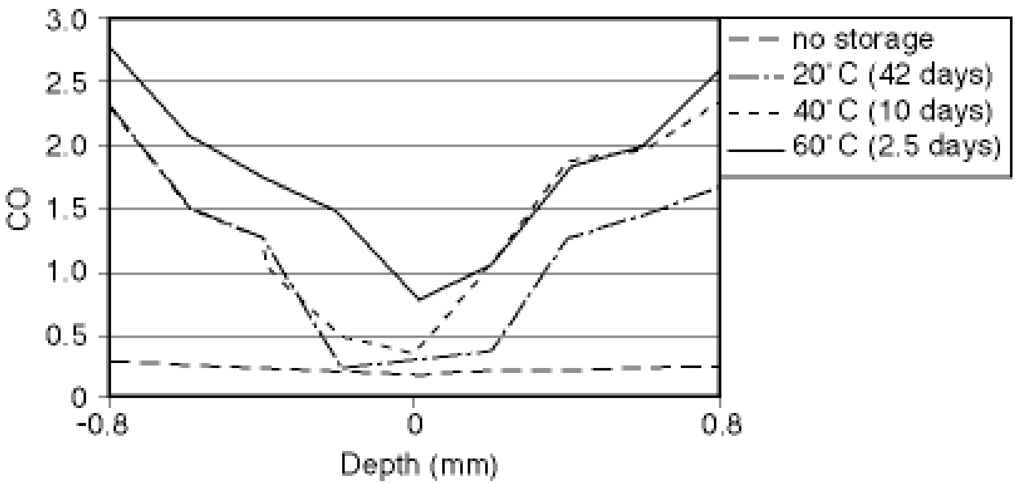

Fig 3 Amount of carbonyl (C=O) as a function of cross-section depth

For the liquids sulphuric acid 96%, hydrochloric acid 36% and sodium hydroxide solution 15% no effects could be detected.

Swelling

Typical results for the swelling test experiments are shown in Figs 4 - 7. In these figures the absorption at different temperatures and thicknesses for xylene and aliphatic mixtures are shown for two materials. For the other materials the results are comparable.

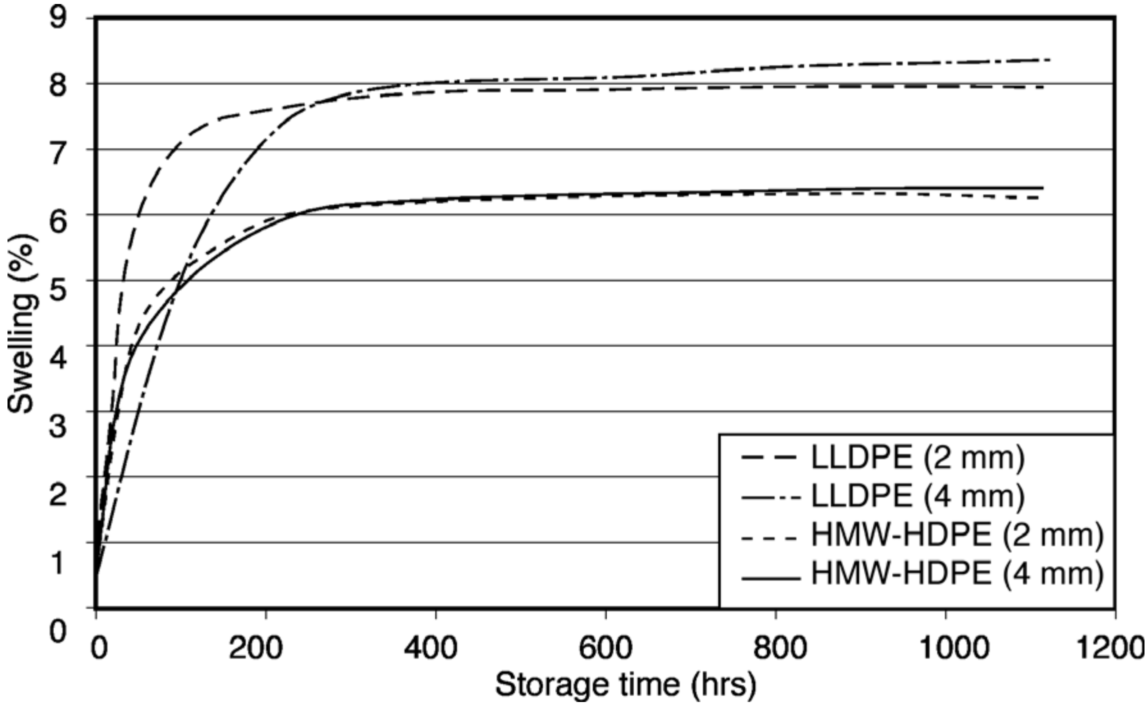

Fig 4 Swelling of HMW-HDPE and LLDPE material as a function of storage time for 2 thicknesses in xylene mixture at 23°C

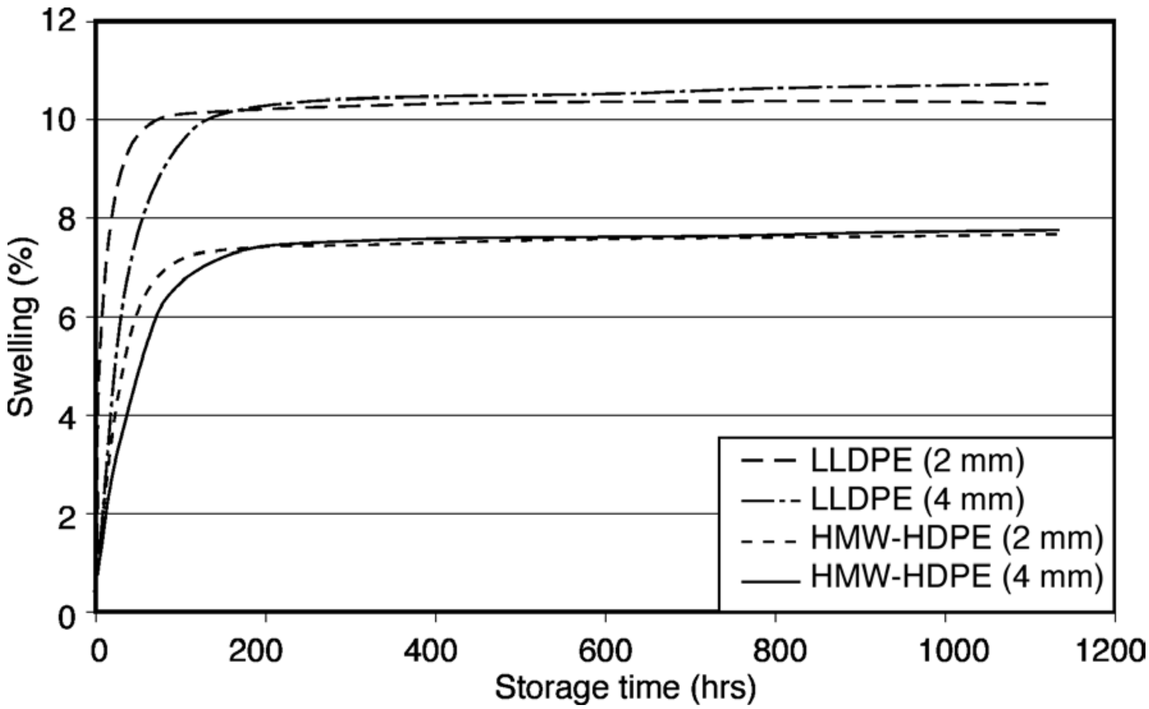

Fig 5 Swelling of HMW-HDPE and LLDPE material as a function of storage time for 2 thicknesses in xylene mixture at 40°C

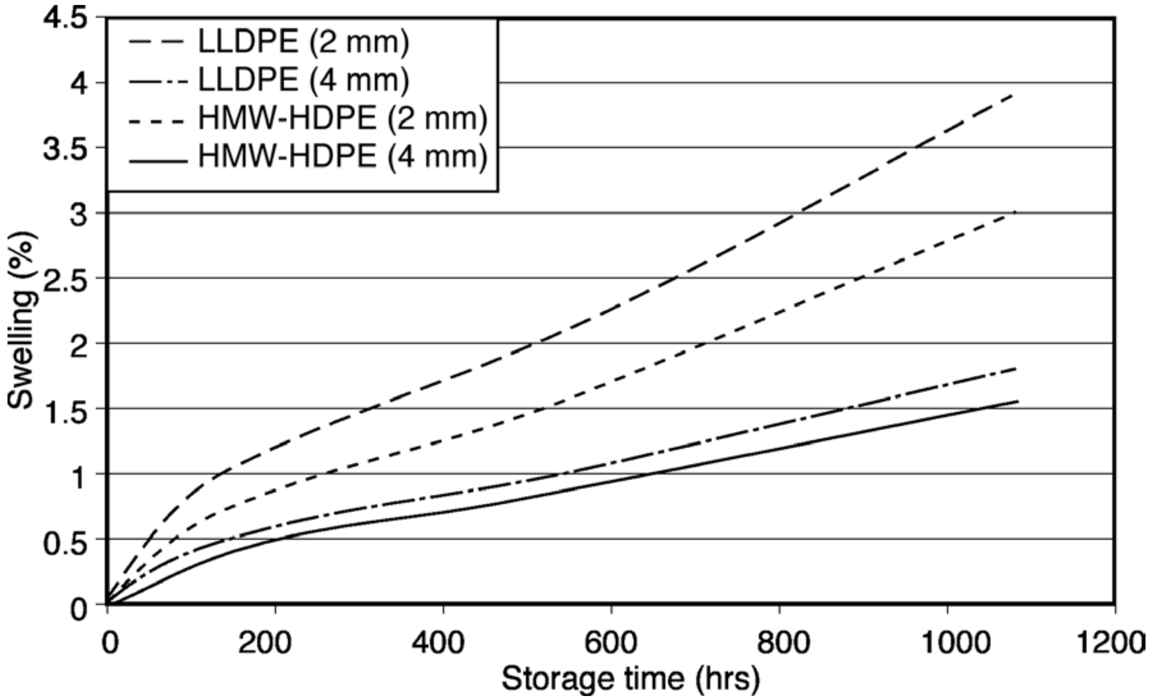

Fig 6 Swelling of HMW-HDPE and LLDPE material as a function of storage time for 2 thicknesses in aliphatic mixture at 23°C

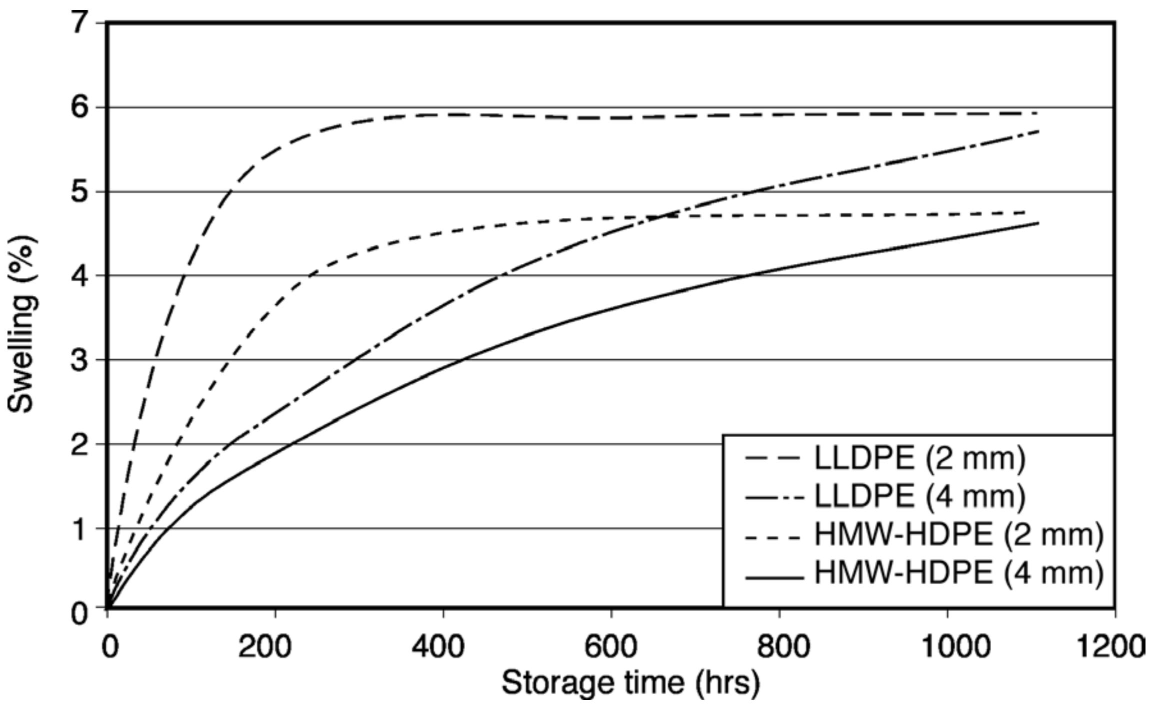

Fig 7 Swelling of HMW-HDPE and LLDPE material as a function of storage time for 2 thicknesses in aliphatic mixture at 40°C

It can be concluded that the time to saturation for the xylene mixture is much shorter than for the aliphatic mixture. Also the degree of swelling is larger for the xylene mixture. Increase of temperature decreases the time to saturation and increases the degree of swelling. As expected, the time to saturation increases with the thickness of the specimen.

Discussion and conclusions

It has been shown in the CHEMPACK project that the standard liquid system which is part of the European regulations for the transport of dangerous goods (ADR/RID) and is applied to HMW-HDPE can also be applied to other types of PE. This includes types of PE which are used in packagings and IBCs varying in volume from 5 - 1000 litre (MMW-HDPE, LLDPE).

The kinds of interaction which can occur were identified as oxidative degradation, environmental stress cracking and swelling.

The appropiate standard liquid for oxidative degradation is nitric acid 55%. It has been shown that acceleration of the process of degradation is possible by temperature increase, leading to a storage period of 3 weeks at 40 °C instead of 6 months at ambient temperature. It has been shown that mechanical testing of samples stored in nitric acid does not give noticable effects for some time period, after which a sharp decrease in mechanical properties is observed. Other methods, like melt index and infrared show degradation and penetration of nitric acid as a function of storage time. These observations could also have important implications for the practice of transport of nitric acid in plastic packagings and IBCs: breakdown of the mechanical properties and thus failure could occur in a short time period.

The appropiate standard liquid for environmental stress cracking is an aqueous solution of alkyl benzene sulphonate. Accelaration of the stress cracking process is possible in such a a way that 6 months storage can be replaced by 3 weeks at 40 °C. However, this storage has no meaning when after this period a stacking test which loads the packaging is performed, as the stresses in such a test are much higher than in a storage without loading. There are several possibilities for assimilation test methods, but existing methods like the Bell test or the Pin Impression Test lead not to failure in many cases for HDPE or are unsuited for stress relaxing materials like LLDPE. Therefore the test which was recently proposed and also used in the CHEMPACK project, the FNCT test, is preferred. However, more experience has still to be gained with this method, e.g. in relation to the value of the stress to be selected in order to be sure that only brittle fracture occurs.

For lower degree of environmental stress cracking or when there is environmental stress cracking together with swelling, other standard liquids can be used: acetic acid and butyl acetate.
The appropiate standard liquid for swelling is a xylene mixture or an aliphatic mixture. The advantage of using a xylene mixture is that the equilibrium is reached in a much shorter time than with an aliphatic mixture. The disadvantage is that the degree of swelling is higher. It has been shown, that increase of temperature to 40°C is not necessary for xylene mixture (except for very thick walls). Temperature increase is necessary for aliphatic mixture, leading to a higher degree of swelling than would have occurred at ambient temperature. It has been shown that mechanical properties like yield stress decrease with the swelling.

When no oxidative degradation, environmental stress cracking or swelling occurs, the standard liquid is water. It has been shown, that substances like sulphuric acid, hydrochloric acid and sodium hydroxide solutions have no noticable effect on PE and can thus be assimilated to water.

References

1. Recommendations on the transport of dangerous goods, 11th edition, United Nations (1999)
2. RID/ADR Regulations for the European transport of dangerous goods by rail and road (1998)
3. The CHEMPACK project was carried out with support of the SMT (Standards, Measurements and Testing) programme under contract no. SMT 4-CT97-2175).
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