Accelerated conditioning of plastic packaging by agitation

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Foreword

The following report is a contribution to the knowledge base that is needed for development, amendment and interpretation of the regulations and recommendations concerning the transport of dangerous goods. The report investigates the possibility of further accelerating the compatibility testing of plastics packaging for dangerous goods by agitating the test fluid. The main rationale is that during static storage the fluid close to the packaging wall will be depleted from its active elements and the degradation process will slowly decrease and finally cease. If the fluid is agitated during the test period, the depleted barrier layer will never develop and the packaging wall will constantly be exposed to all active elements. For this purpose a number of tests were performed to study the accelerating effect by agitation.

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Abstract

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The possibility to further accelerate compatibility testing of plastic packaging through agitating the test fluid is investigated in this report. According to the test programme of the UN Recommendations for the Transport of Dangerous Goods plastics packaging may be stored under certain circumstances in an environment with increased temperature, 28 days at +40°C, instead of 6 months in room temperature.

The main objective of this report is to find out if there is a possibility to reduce the storage time by accelerating the degradation process through agitating the test fluid. Agitating the test fluid would reduce any barrier layer containing depleted substance that may develop close to the packaging wall. Tests were carried out with rods made of high-density polyethylene material (HDPE). The rods were tested for swelling and environmental stress cracking using xylene, white spirit and wetting solution as model liquids. The evaluation was made by measuring the weight difference and by tensile testing. The hypothesis was not supported by the tests, i.e. the result shows no accelerated degradation effect when agitating the test specimen.

Keywords: Dangerous goods, compatibility testing, plastics packaging.

Background

Compatibility testing of plastic packaging for dangerous goods can under certain circumstances be done through storage in an environment with increased temperature, 28 days at +40° C instead of 6 months in room temperature. The joint European Chempack project has investigated a number of issues related to compatibility testing. The Chempack study did not investigate the possibility to further accelerate the test method by agitating the test fluid. During static storage the fluid close to the packaging wall will be depleted from its active elements and the degradation process will slowly decrease and finally cease. If the fluid is agitated during the test period the depleted barrier layer will never develop and the packaging wall will constantly be exposed to all active elements.

Objective

The main objective with this project is to find new ways of accelerating the compatibility test procedure for dangerous goods packaging according to RID/ADR. If the statement mentioned above is proven to be correct then agitating the test specimen could reduce the test time. This would also resemble real-life conditions more than the current test method does.

Boundary effects

In a system consisting of a plastic container filled with a liquid, the system can be described as a plane sheet in contact with a solution of limited volume. In a situation where the liquid is not agitated as mentioned above, there can be an additional layer acting as a barrier at the surface of the container, as shown in figure 1. (In order to reduce this layer it is important to agitate the solution/fluid).

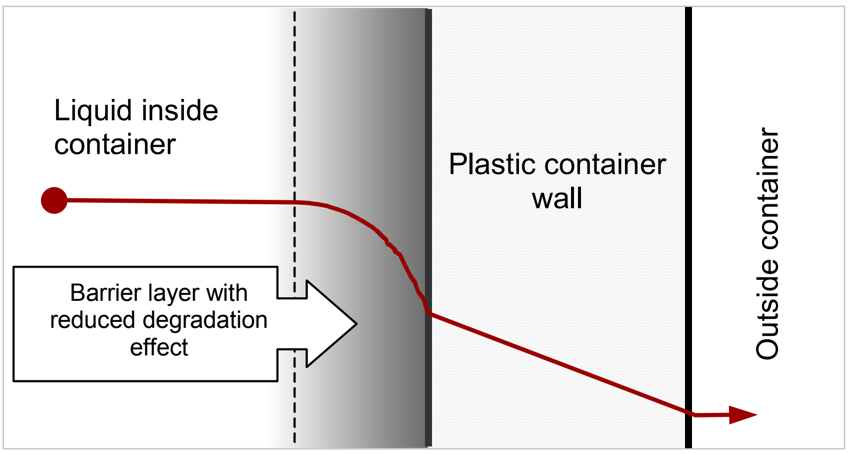

Figure 1. The illustration above shows the barrier layer close to the plastic container cross-section. The line indicates the liquid concentration from fluid to gas form.

Main modes of degradation

Swelling, oxidative degradation and environmental stress cracking (ESC) are commonly known as the three main degradation effects in polyethylene plastics. There are several factors that have influence on the degradation mechanism, e.g. design and production aspects, time, mechanical stress, climate etc. This report only covers swelling and ESC degradation modes.

Swelling

Swelling can be described as a substance being absorbed and retained in the polymer itself. The swelling of a polymer material depends to a large extent on the substance solubility. Swelling affects the amorphous part of the polymer and decreases the strength of the polymer. Aromatic hydrocarbons like xylene, thinner and white spirit are typical chemicals that cause swelling.

Environmental stress cracking (ESC)

Environmental stress cracking is a result of a combination of factors, primarily the influence of a chemical substance and a mechanical load, but also e.g. temperature and packaging material properties are important. ESC is most likely to occur in the amorphous part where the substance is allowed to absorb slowly into the polymer. Surface tension reducing substances like wetting solution could in combination with some of the factors mentioned above cause ESC.

Utilized test methods

Test Specimen

Plastic rods measuring 154 × 20 × 4,2 mm were used throughout the test. The rods were made of material: Borealis BL1521, Semi-HMW High Density Polyethylene.

Methods

Two methods have been used:

- Conditioning method, this method exposes the test specimen (plastic rod) to chemical substances. This is made in order to evoke property changes occurring in the packaging material.
- Evaluation method, this method measures by mechanical means any changes occurring in the test specimen.

Table 1. Table showing method objectives and components.

Test objective	Swelling	Environmental Stress Cracking
Conditioning method	Submerging test rods into white-spirit	Submerging stressed test rods into wetting solution
Evaluation method	Weight comparison	Tensile test

Conditioning method

The test is performed by letting several test rods be submerged into a container with chemical substance (table 1). The container then becomes agitated through a pneumatic cylinder that creates a tilting motion (fig 2). Simultaneously containers with rods are left in a static state for comparison.

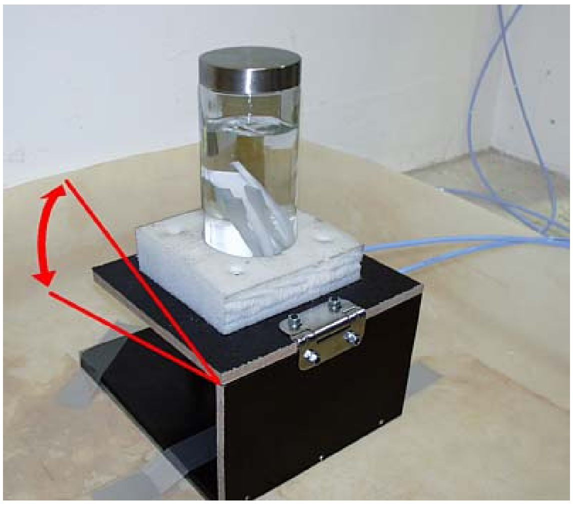

Fig 2. Agitating test performed by a tilting motion.

Model liquids

Xylene

A highly aromatic substance that causes swelling and permeation effect on polyethylene plastics. Xylene is not likely to give an accelerated process by agitation, because it is a pure substance (no depleted barrier layer can occur).

White Spirit

A mixture of substances containing aromatic compounds (17%) that is likely to decrease with time. White spirit is probably therefore a suitable liquid for studying barrier layer effects.

Wetting Solution

This substance can cause severe cracking in polyethylene under stress. Wetting solution is a suitable liquid for studying environmental stress cracking through a tensile test (tables 2 and 4). The concentration of the wetting agent is however not very critical, and thus the process is not expected to become significantly accelerated by agitation.

Table 2. Table showing model liquids, conditioning and evaluation methods.

Model liquid	**Objective**	**Evaluation**
Xylene	Swelling	Weight
White spirit	Swelling	Weight
Wetting solution	Stress cracking	Tensile test

Evaluating Method

General

Each rod included in the test was weighed separately and stamped with a unique number. During the test session a number of test rods were removed for evaluation (only to study swelling effects). This procedure was repeated throughout the test session. As soon as the test rods have been brought up from the model liquid and evaluated they have fulfilled their task and cannot be reused.

Weight Comparison

A comparison between agitated and non-agitated weights was performed. The difference in weight represents the result.

Bent Strip test

Bending a test rod will create a stress field through the test specimen. This stress field ranges from compressing stress at the inside to tensile stress at the outside as shown in figure 3. The stressed (clamped) test rods are submerged into wetting solution and left for a period of two weeks allowing the wetting solution to attack the surface. Thereafter a tensile test is performed (in a tensile test machine) on each rod in order to determine any difference in tensile strength between agitated and non-agitated rods (table 3). There is also a set of rods left in atmosphere for reference testing.

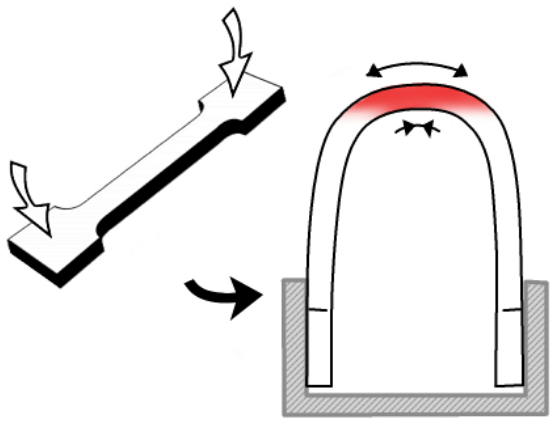

Fig 3. Plastic rod bent in order to illustrate principle for creating tensile (outside) and compression (inside) stress.

As the rods are submerged into wetting solution the damaging process begins. The wetting agent normally creates small microscopic cavities in a plastic surface and due to stress in the plastic material these cavities will grow and interconnect. This behaviour usually results in a larger crack that significantly impairs the construction. The tensile test is performed in a tensile test machine pulling each rod at 100 mm/min until it breaks. The difference in strength between the rods represents the result.

Results

Xylene

This test session was performed using a total of 25 HDPE rods in combination with xylene (stored at +40°C). The results showed no difference in weight increase (about 3 % in both cases). For detailed information see appendix A.

White spirit

24 HDPE rods were tested for swelling effects using white spirit (17 % aromatic stored at +40°C). The test was performed during a six days period and showed no difference in weight increase (1.82 % in both cases). For more information see appendix B.

Wetting solution

A total of nine stressed (fig 5) rods were tested, six of the rods were submerged in wetting solution during a period of two weeks. Three rods were left in atmosphere as reference rods. The test specimens were held at a temperature of 40°C throughout the test. Tensile tests were performed on all rods until rupture. Table 3 describes the lengthening in relation to the conditioning method. In general, the result indicates a very low ESC effect on the rods caused by the wetting solution.

Table 3 Results from the tensile test. Average lengthening expressed in millimeters and in percentages.

Test conditions	Reference rods, 3 pcs	Non-agitated, 3 pcs	Agitated, 3 pcs
Environment	Atmosphere	Submerged	Submerged
Length at rupture	589 mm	507 mm	635 mm
Elongation	+282 % (+435 mm)	+229 % (+353 mm)	+312 % (+481 mm)

Discussion

As expected, the result when testing swelling in xylene showed no significant weight increase. The theory is that the boundary layer of the test liquid at the surface of the plastics material will successively be depleted of active substance if no motion prevents it. However, for xylene the test liquid is pure and there can be no depletion.

For White Spirit, the result indicates a slight acceleration of the process when the liquid is stirred. The difference is small but seems to indicate support for the theory, although not of the magnitude that would necessitate the implementation in the UN test scheme. White Spirit consists of a percentage of aromatic hydrocarbons, which are the active agents in swelling of plastics, dissolved in solvents that are more inert in this respect. The active substances will therefore eventually disappear from the boundary layer if no motion occurs.

When performing the tensile test on rods stored in wetting solution the results are somewhat contradictory. It is a well-known fact that ESC occurs in plastic containers placed under stress in static storage. The result shown in fig 6 nevertheless indicates that agitation in fact would decrease the damaging process and concurrently increases the material plasticity. There are two explanations to this phenomenon:

– The material is in itself resistant to environmental stress cracking (proved by the fact that no cracks occurred in either test)

– There is no depletion of active substance – the wetting agent acts on the plastic surface by reducing surface tension, but does not migrate significantly into it. Furthermore there is a relatively wide range of concentrations (the UN scheme prescribes 1-10 %) that will develop environmental stress cracking in plastics materials that are sensitive to it.

References

CHEMPACK Report, Task 2: New accelerated test methods, SP 99.4304, 1999

UN Recommendations on the Transport of Dangerous Goods (Model Regulations), UN, New York/Geneva

ADR, European Agreement concerning the international carriage of dangerous goods by road, UN/ECE, Geneva

APPENDIX A XYLENE

	Initial start weight (gram)	Start 17/12 13.15	Start 17/12 17.50	Start 19/12 kl. 07.25	Weight # 1 18/12 kl. 8.30	Weight # 2 18/12 kl. 10.30	Weight # 3 18/12 kl.12.30	Stop weight 18/12 kl.14.30		Weight increase in %	Average weight increase (%)	Weight # 1, 19/12 kl.10.25	Weight # 2 19/12 kl.12.25	Weight # 3 19/12 kl.14.30	Weight # 4 19/12 kl.16.30		Increase in %	Average weight increase (%)
Non agitated	8,5	X			8,74													
	8,54	X			8,77													
	8,62	X				8,86	8,87	8,88		2,928								
	8,54	X				8,8	8,8	8,82		3,175								
	8,48	X						8,77		3,307	3,21							
	8,53	X						8,82		3,288								
	8,47	X						8,76		3,311								
	8,56	X						8,85		3,277								
	8,52			X											8,68		1,843	
	8,48			X											8,67		2,191	
	8,6			X										8,74			1,602	
	8,58			X										8,71			1,493	1,49
	8,53			X									8,64				1,273	
	8,53			X									8,63				1,159	
	8,56			X								8,64					0,926	
Agitated	8,59			X								8,68	8,69	8,72	8,74		1,716	
	8,6			X								8,69	8,7	8,72	8,75		1,714	
	8,47			X								8,56	8,58	8,6	8,62		1,74	1,75
	8,47			X								8,57	8,58	8,61	8,62		1,74	
	8,46			X								8,55	8,57	8,59	8,62		1,856	
	8,51		X		8,73	8,76	8,77	8,77		3,055							8,767	
	8,52		X		8,75	8,77	8,78	8,79		3,169								
	8,52		X		8,75	8,77	8,78	8,79		3,169	3,14							
	8,51		X		8,74	8,76	8,78	8,78		3,173								
	8,52		X		8,76	8,77	8,78	8,79		3,169								

APPENDIX B WHITE SPIRIT

	Initial start weight (gr)	Day 1, 10.30h	Day 1, 16.30h	Day 2, 8.30h	Day 2, 16.30h	Day 3, 16.30h	Day 6, 14.30h	Total weight increase (%)	Average weight increase (%)
Agitated	8,4					**8,59**		2,21	1,82%
	8,36				**8,47**			1,30	
	8,37			**8,48**				1,30	
	8,33		**8,38**					0,60	
	8,36			**8,47**				1,30	
	8,39		**8,45**					0,71	
	8,36	**8,38**						0,24	
	8,36						**8,67**	3,58	
	8,36	**8,52**						1,88	
	8,36						**8,67**	3,58	
	8,36				**8,62**			3,02	
	8,36					**8,55**		2,22	
Non agitated	8,36						**8,73**	4,24	1,82%
	8,45						**8,72**	3,10	
	8,36				**8,48**			1,42	
	8,36					**8,5**		1,65	
	8,36		**8,43**					0,83	
	8,36			**8,43**				0,83	
	8,36			**8,53**				1,99	
	8,36					**8,64**		3,24	
	8,36	**8,44**						0,95	
	8,36		**8,44**					0,95	
	8,36				**8,46**			1,18	
	8,36	**8,49**						1,53	