„Labormethode zum Nachweis der chemischen Verträglichkeit von Behälterwerkstoffen aus Polyethylen gegenüber Pflanzenschutzformulierungen“

Laboratory method for the evaluation of the chemical compatibility of container materials based on polyethylene against crop protection formulations“

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Introduction

Damage due to slow crack growth (SGC) is a typical mode of failure for components and packaging made from polyethylene (PE). Usually, this crack growth originates from a local stress concentration caused by an external load, local defect or notches, or a combination of those. The crack propagation can be accelerated by contact with liquid media – this is then termed *environmental stress cracking* (ESC). Therefore, a proof of sufficient chemical compatibility is required for materials based on high-density polyethylene (PE-HD) in applications as packaging for liquid dangerous goods, which essentially also comprises resistance against ESC. This proof may either be provided by type testing of containers, or - especially for only minor changes in the polymeric material – complementary by approved laboratory methods.

In the field of crop protection formulations, the so called “*bottle test*” has been developed to address this issue, which is specified in the BAM Dangerous Goods Procedural Rules GGR 015 as well as the national standard DIN 2002. In contrast to other established ESC testing methods which are based on complete immersion of the test specimen in the liquid medium, this test also allows the evaluation of materials with a multilayer structure or surface modification as they will be exposed only from one side. For the *bottle test* special test bottles and a device for their defined deformation were developed as well as specific test liquids, in order to be considered representative for the typical damaging effect of crop protection agents. However, this concept is up to now only established in Germany, and the research project is intended to provide foundation and results to support the introduction in European and international regulations.

Topics

In this research project the testing procedure *bottle test* as well as the corresponding test liquids have been addressed and comprehensively investigated in comparison with other established methods for ESC testing of PE-HD.

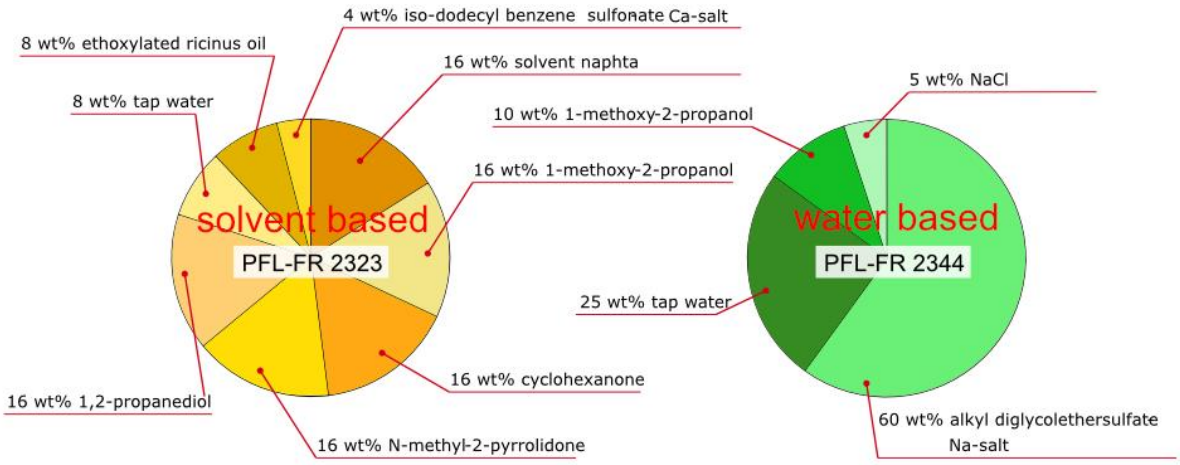
To this aim, the following topics were considered:

- comparison of bottle test with pin impression test and full notch creep test (FNCT)
- evaluation of up to five typical PE-HD container materials
- implementation of the test liquids PFL-FR 2323 and PFL-FR 2344 for all test methods
- comparison of the PFL with their constituent components regarding the damaging effect
- comparative evaluation of the damaging effect of a binary mixture of relevant components, including variation of composition
- comparison of the damaging effect of mixtures of relevant PFL components
- investigation of the sorption behavior of the considered media and components regarding saturation concentration and diffusivity
- Variation of mechanical load levels (FNCT) – characterization of the transition from crack propagation to ductile shear deformation
- Characterization of the damaging mechanisms by detailed microscopic fracture surface analysis (LM - light microscopy, LSM - laser scanning microscopy, SEM - scanning electron microscopy)
- Optical monitoring of crack opening displacement (COD) and crack propagation
- Quantitative evaluation of optical monitoring by digital image correlation (DIC)

In the following, some topics and results are exemplary outlined:

Test liquids for crop protection formulations

For the *bottle test* as well as for the testing methods considered in comparison, i.e. the *pin impression test* and the *FNCT*, the test liquids specified (Fig. 1) in DIN 2002 were applied, which are considered representative for the damaging effect of crop protection formulations.



Fig, 1: Composition of the test liquids PFL-FR 2323 und PFL-FR 2344

Bottle test

The test bottles filled with the respective test liquid are to be deformed in a standardized device (Fig. 2) and stored under well-defined conditions at 40 C, by default for 28 days.

Fig. 2: Deformation device with PE-HD test bottles

After the exposing storage, the specimens for the tensile impact test are prepared from the deformation zone of the bottles. The obtained tensile-impact strength allows to draw conclusions with respect to the damage occurred during exposure.

The observed damage in the deformation zone has been analyzed by SEM (Fig. 3) to reveal indications of crack formation and propagation.

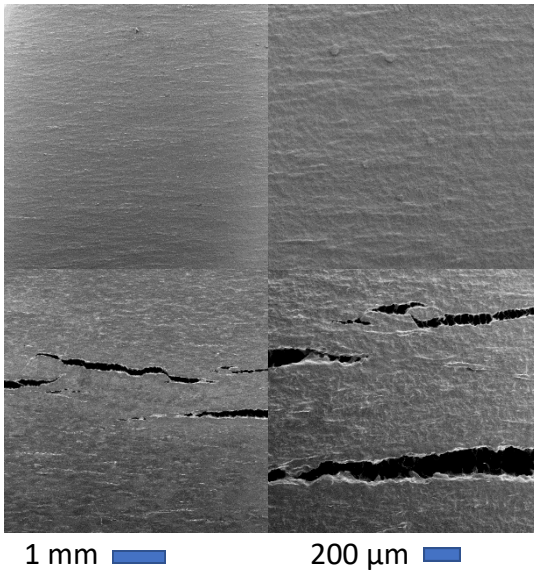


Fig. 3: Specimen surface in the deformation zone after exposure at 40 °C to PFL-FR2323 (top) and PFL-FR2344 (bottom), analyzed with SEM

Pin impression test

The specimens are deformed by impressing a metallic pin of 4 mm diameter into a 3 m bore hole (Fig. 4) inducing mechanical stress on a opposite notch. Multiple specimens can be mounted on a single pin to be exposed by immersion in the respective test liquid at 40 °C.

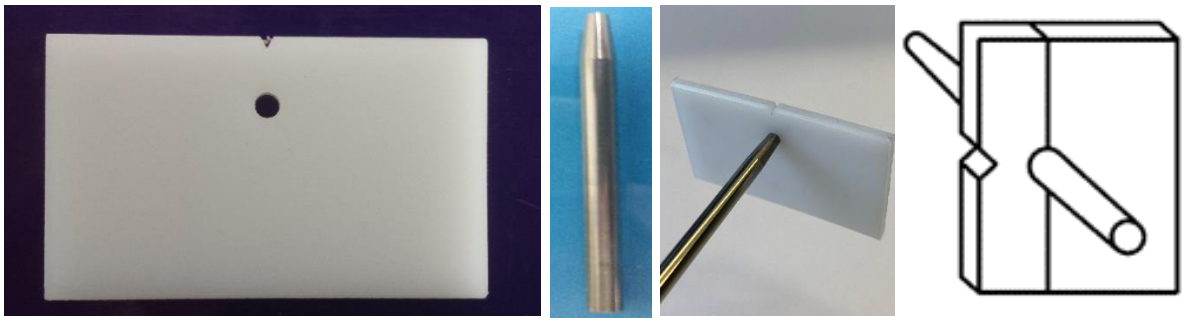


Fig. 4: Specimen before pin impression and immersion (left), metal pin (center) and scheme of specimen with impressed pin – left part to be cut for tensile test (right)

After sequential removal of the specimens, the notched part is cut at the bore hole and subjected to a tensile test. The remaining tensile strength is determined in comparison to a virgin specimen. The interpolated time duration to 50% of the initial tensile strength defines the characteristic value for the assessment of the ESC-resistance (Fig. 5).

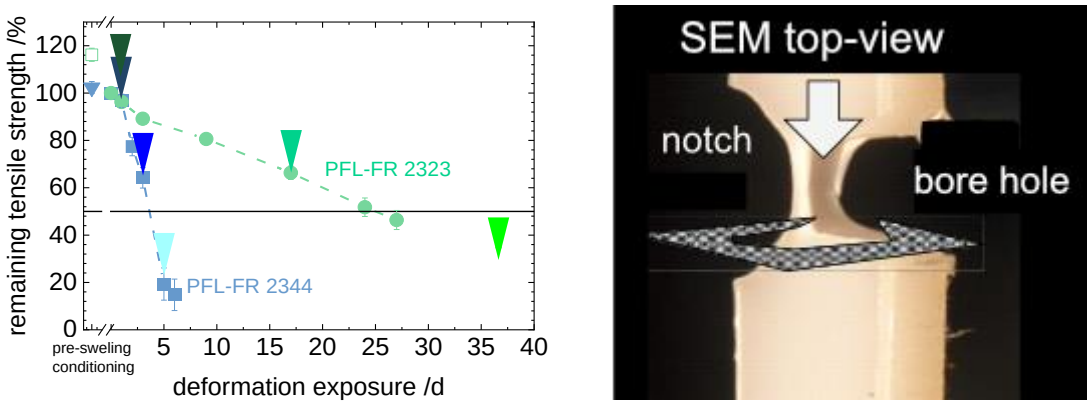


Fig. 5: Remaining tensile strength after immersion with pin in test liquid PFL-FR 2323 (green) und PFL-FR 2344 (blue) (left). Image of a specimen during tensile test (right) with sketched plane of subsequent fracture surface analysis by SEM.

To verify the occurred damage mechanism the fracture surfaces have been analyzed by SEM (Fig. &).

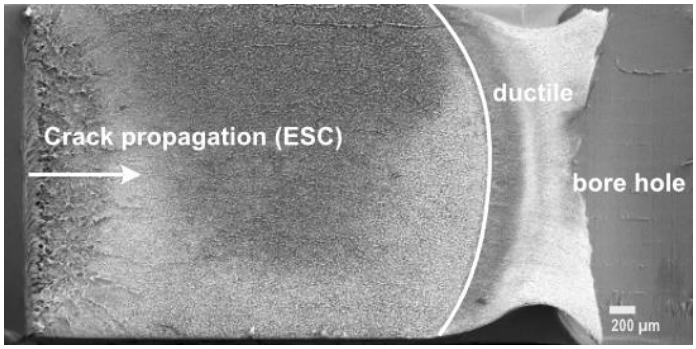


Fig. 6: SEM micrograph of a specimen after pin impression test

Emerging from the notch (left side) the fracture surface shows the characteristic pattern resulting from ESC crack propagation, formed by damaging during immersion with impressed pin, center: zone of ductile deformation by tensile test; right side: bore hole for the metal pin.

Full Notch Creep Test

The Full Notch Creep Test (Fig. 7) is a well-established method for testing and investigating environmental stress cracking of PE-HD. A circumferentially notched specimen is fixed between two clamps, immersed in the liquid test medium and subjected to a constant mechanical load. The time duration to complete failure under well-defined conditions (here: 40 °C) defines the characteristic value for the assessment of the resistance against ESC.

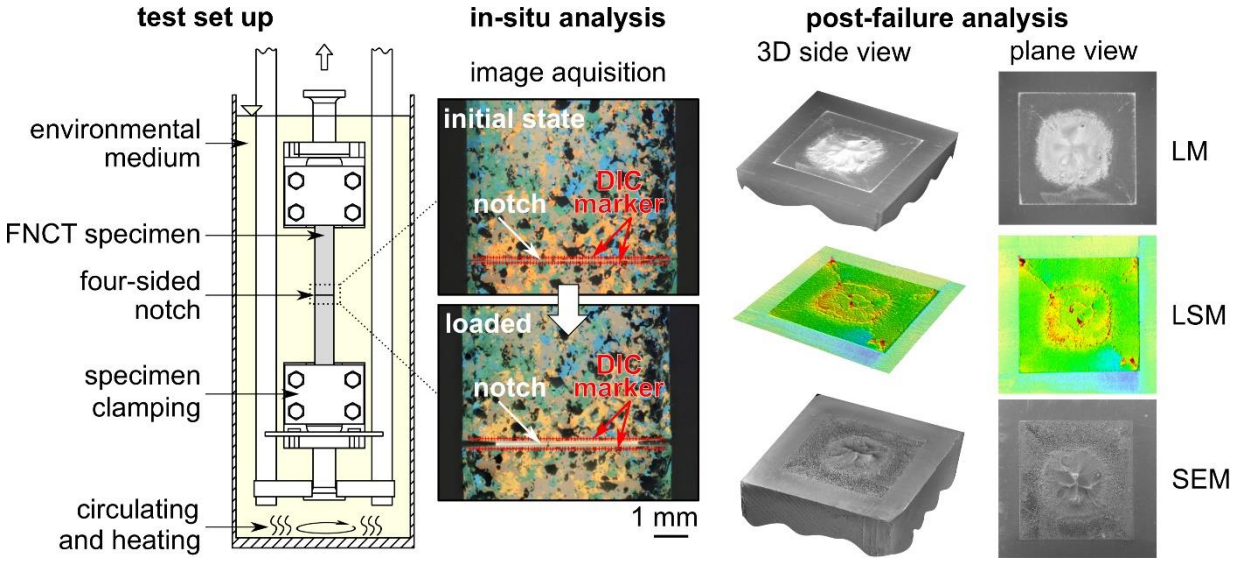


Fig. 7: Schematic representation of clamping and media vessel (left); notched FNCT-specimen with arbitrary color pattern for digital image correlation (center); ex-post fracture surface analysis by LM - light microscopy, LSM – laser scanning microscopy and SEM – scanning electron microscopy

In the current research project, the FNCT testing was complemented with an optical in-situ monitoring using a digital camera system (Fig. 8).

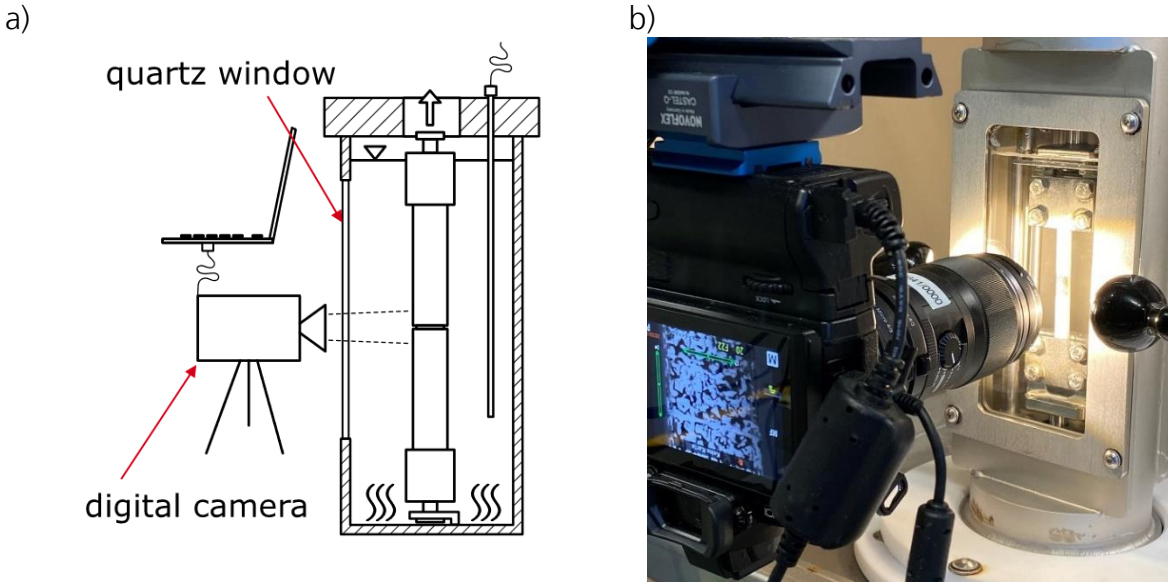


Fig. 8: a) Scheme of the optical monitoring of notch and crack opening displacement (COD); b) image of the experimental arrangement with digital camera and medium vessel including immersed clamping device and specimen

The camera arrangement allows for a time-resolved in-situ monitoring of the notch and the crack opening displacement (COD) which is correlated with the actual crack length. A digital image correlation using an arbitrary color pattern on the specimen enables a quantitative analysis of the crack propagation. As shown in Fig. 9 the optical monitoring also improves the fracture surface analysis, enabling a direct assignment of different zones of the fracture.

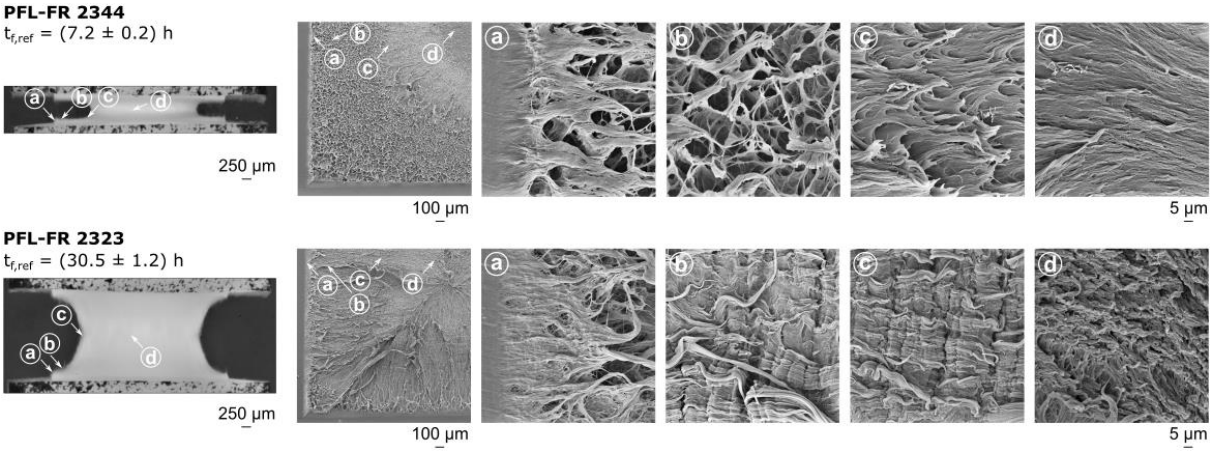


Fig. 9: Assignment of specific structures (right) of the fracture surface to the respective position in the final notch opening (side-view, left) directly preceding the failure (break) [4]

Comparison of the test methods

The general suitability of the two test liquids, PFL-FR 2344 und PFL-FR 2323, for the assessment of ESC was confirmed. Based on the comparison of the three employed testing methods (Fig. 10), individual advantages and limitations were identified with respect to the method-related applicability.

Due to full control of notch and mechanical load in combination with the detailed ex-post fracture analysis the *Full Notch Creep Test (FNCT)* provides the best preconditions for in-depth scientific investigations. The possibilities are further extended by the implemented optical in-situ monitoring.

In contrast to this, the *pin impression test* has proven to be an extremely versatile and practicable method in the field of crop protection agents, as the specimen and test conditions result for PE-HD in most cases unambiguously in damage by crack growth (ESC) allowing for a useful ranking of materials. At the same time the procedure is very efficient and provides good reproducibility.

The *bottle test* is the only method of the evaluated testing procedures enabling the necessary one-sided exposure of the container walls to the liquid test medium, required for the assessment of materials with multilayer structures or surface modifications with respect to ESC resistance. This is especially relevant for crop protection agents where the solvent-containing formulations require additional permeation barriers. Also, for this testing method

the general suitability was confirmed. However, also some details for possible improvements were identified.

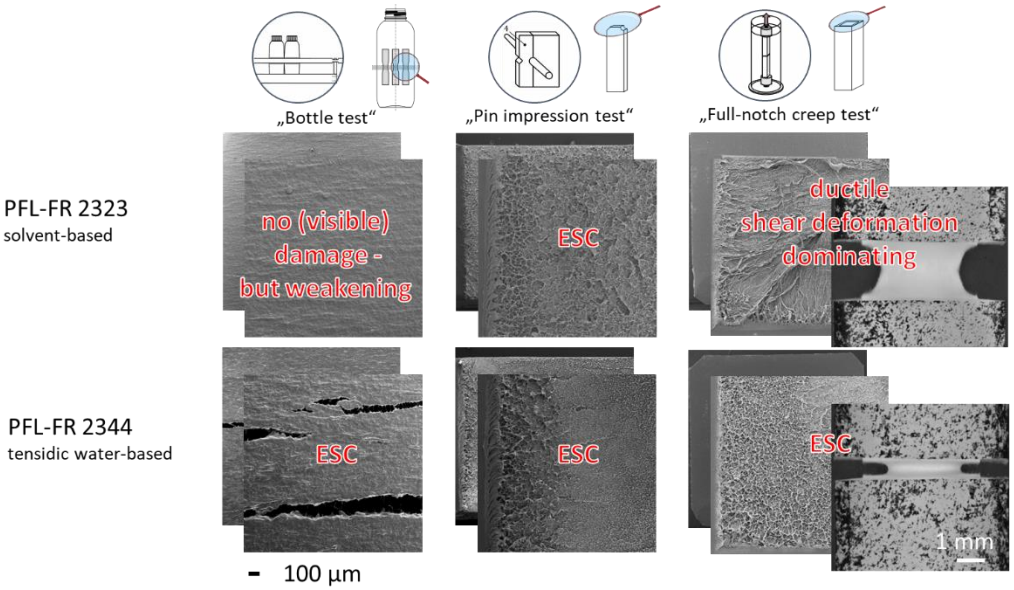


Fig. 10: Comparison of the evaluated test methods for ESC of container materials based on PE-HD

Results from this research project have been already published in several scientific papers.

Published or accepted until now:

[1] M. Thuy, U. Niebergall, H. Oehler, I. Alig, M. Böhning
Evaluation of the damaging effect of crop protection formulations on high density polyethylene using the Full Notch Creep Test
Polymer, 228 (2021) 123853.
DOI: 10.1016/j.polymer.2021.123853
https://doi.org/10.1016/j.polymer.2021.123853

[2] M. Thuy, U. Niebergall, H. Oehler, I. Alig, M. Böhning
Damaging effect of admixtures used in crop protection products on high density polyethylene packaging material
Polym. Test., 114 (2022).
DOI: 10.1016/j.polymertesting.2022.107672 [OPEN ACCESS]
https://doi.org/10.1016/j.polymertesting.2022.107672

[3] M. Thuy, M. Pedragosa-Rincon, U. Niebergall, H. Oehler, I. Alig, M. Böhning
Environmental Stress Cracking of High-Density Polyethylene Applying Linear Elastic Fracture Mechanics
Polymers (Basel), 14 (2022).
DOI: 10.3390/polym14122415 [OPEN ACCESS]
https://doi.org/10.3390/polym14122415

[4] M. Thuy, N. Brauch, U. Niebergall, I. Alig, H. Oehler, M. Böhning
Environmental stress cracking of PE-HD induced by liquid test media representing crop protection formulations in: ASTM STP1643 on Symposium on Advances in Accelerated Testing and Predictive Methods in Creep, Fatigue, and Environmental Cracking (accepted, in press)

Benefit for small and medium enterprises (SME)

The economic and societal importance of the obtained research results arises from the extensive use of plastic containers, especially in the field of crop protection and pest management in agriculture and forestry, which are predominantly mastered by smaller businesses. In addition, the safety relevance regarding transport and use of such products as well as the prevention of damage or accident with significant potential of hazardous risks for humans and environment is evident

The findings are supportive for such SME to appraise the bottle test and the alternative methods with respect to their ability to make reliable and robust assessments of the susceptibility to environmental stress cracking (ESC). In this context also the direct comparison of different test methods addressing ESC facilitates the choice of suitable test scenarios for different applications and products. This attains additional relevance in conjunction with future requirements regarding the use of recycled materials which is more and more demanded by legislation and regulations.

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URL:
https://www.lbf.fraunhofer.de/content/dam/lbf/de/documents/AiF-Veröffentlichungen/container-materials-polyethylene-IGF20673N_EN.pdf