Novel Comparative Exudation Test Method

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ABSTRACT

Following the global trend of the continued technological pursuit for sustainable solutions, a significant number of new PVC plasticisers and additives have been offered to the market. Flexible PVC formulators have been constantly faced with the challenge of evaluating and certifying new materials for use in various applications.

Many physical characteristics of the compounds can be evaluated with established and reliable test methods that allow fairly precise comparisons between different raw materials. These tests can indicate with a high degree of confidence how the different formulations will compare in real life processes and applications, including tensile strength, elongation, weight loss, fusion temperature, gelation temperature and so on.

However, the tests for compatibility, one of the most common concerns with new products, are not nearly as reliable or significant in determining final product performance. Many formulators use existing exudation tests, such as the loop test or the vegetable paper test, but the results are often not appropriate to answer their questions about product long term compatibility. Others use in-house tests that are specific to their application, but are not standardized across the industry.

This paper proposes a novel, simple method to determine exudation over time. This method could bring an additional approach to exudation assessment, allowing a direct comparison of samples to evaluate differences between raw materials, with the advantage of obtaining a quantitative result that can be observed over time, using a simple methodology that requires simple equipment and that is sensitive enough to present reliable data without the need of forced ageing or extreme conditions.

The method has been extensively used in the past years with various formulations and the present paper will cover examples of different materials tested under several different conditions to illustrate results. Although more data should be gathered to improve statistical significance it is possible to conclude that the proposed test is an improvement over existing tests and could represent an interesting method to compare various formulations under known conditions.

KEY WORDS

Exudation; Test method; PVC; Plasticisers; Additives
1 INTRODUCTION

1.1 RELEVANCE AND PRIOR STUDIES

The increased regulatory pressure over traditional plasticisers has been motivating formulators of flexible poly vinyl chloride (PVC) to search with greater urgency for alternative materials. This pursuit poses several challenges, including a comprehensive evaluation of the new products in comparison with traditional general purpose plasticisers, such as DEHP (di-ethyl hexyl phthalate) or DINP (di-isononyl phthalate). This evaluation includes the study of the performance of the final compounds in the processing stages as well as in the final applications.

The areas of attention for a formulator trying a new product include several characteristics, such as elongation, rupture, transparency, colour, thermal stability, light stability, etc. Exudation figures among one of the main concerns. Several studies address this concern, especially for the introduction of new products in substitution for well established plasticizers, considering damaging effects such as adhesion problems\(^1\), surface degradation\(^2\), compatibility concerns\(^3\) and surface chemical characteristics\(^4\). For some applications, many times with high value-added articles, such as shoes and apparel, exudation may represent significant quality risks, affecting mainly the appearance of the final article. In other cases, exudation may cause indirect problems, such as printed patterns peeling off or dirt accumulation.

The immediate or short term performance of different formulations can be tested with a high degree of confidence, as many well established international standard test methods have been developed. For longer term performance (ageing, mass loss, etc.), although the degree of confidence diminishes, there are many tests that are quite useful for comparison between various formulations.

However, in spite of its relevance to the formulator, exudation has been for a while tested mostly qualitatively, such as the loop test\(^5\) (ASTM D 3291). Although it is possible to determine high and low exudation from observation, the method is considered a subjective\(^6\) measure of comparison. Also, due to its nature of creating an extreme condition (stress at the loop region), the test does not always correlate with field observations. Another common test in the industry is the use of vegetable paper rolled with the PVC sheet, and then observing whether the paper was stained. This test included the additional factor of vegetable paper affinity with the exudates, which can accelerate the effect and not represent actual performance in normal conditions.

Some studies\(^7,8\) demonstrate correlations between compatibility of plasticiser and physical chemical parameters, which are very useful as predictors, but are not direct evaluations of observed exudation under known conditions.

1.2 DEFINITIONS

Exudation has been used in the literature to signify different phenomena. It can be used to refer to: the total migration of the plasticiser and other additives into a medium (water, solvents, oils);
the amount of material that has been removed from the PVC matrix measured by weight loss; or as a surface effect.

In the present paper, the term exudation refers to the surface phenomenon. It can be described as the presence of an accumulation of the plasticizer or other additive on the surface of the final product, causing several problems such as adhesion failures, poor aesthetics, greasy or sticky areas. Such definition was used in investigations of polymeric plasticiser behaviour\(^9\), or in general formulation handbooks\(^\text{10}\).

Fig. 1: Migration and evaporation mechanisms

The undesirable presence of plasticiser or other additives can be explained as a combination of two physical mechanisms, resulting in the accumulation of material on the surface. One is the migration of the plasticiser and other liquid additives through the PVC matrix, where these molecules move inside the polymeric medium until they reach the surface. The other is the evaporation of those materials after they’ve reached the surface. Fig. 1 illustrates both mechanisms, as they happen simultaneously after the compounded flexible PVC is prepared.

If the rate of migration to the surface is greater than the rate of evaporation, an accumulation of material is observed on the surface. This accumulation is, for the purpose of this paper, defined as exudation (indicated as “exudate” in Fig. 1). It is important to keep in mind that such mechanisms may have varied rates and a compound that does not exhibit exudation in a certain test condition may present exudation under different conditions. This paper will not discuss the details and theory of these mechanisms, but it is expected that several factors should influence differently rates of migration and evaporation, such as temperature, air flow, light, compatibility, viscosity, molecular weight, surface tension and humidity.

1.3 OBJECTIVE

The objective of this paper is to present a novel test method to measure exudation under real life conditions, with simple laboratory equipment, to evaluate by comparison different flexible PVC formulations. The method is intended to provide an additional approach to existing methods for exudation assessment. It allows quantitative and temporal analysis of exudation of various materials, including plasticisers and other additives. The controlled tests were not sufficient to provide enough data for a thorough statistical analysis, but they offer enough evidence to have the method be considered as a future useful standard.
2 EXPERIMENTAL METHODS AND MATERIALS

2.1 EXPERIMENTAL SUMMARY

Three laboratories were involved in the controlled tests: Nexoleum (NEX); Elekeiroz (ELE); and Braskem (BRA). The production of test samples was done at once in the same laboratory, to reduce variability due to samples preparation. All laboratories received the samples simultaneously and were in charge of weekly evaluations. All lab technicians were properly briefed to reduce potential procedure differences among labs. The tests included visual evaluations, surface weight loss, surface tension and gloss, to compare different measurement methods and their efficacy.

2.2 MATERIALS

Formulation raw materials:

- Resins (emulsion and suspension)
- Pigment (black only)
- Plasticisers
- Stabiliser
- High gloss paper (Ultracast PVC Patent, from Warren; Superlak, from Favini)
- Cleaning cloths
- Anhydrous Ethanol

2.3 TEST EQUIPMENT

- Plastisol mixer
- Compound mixer
- Laboratory calender
- Spread coat knifes
- Oven
- Thickness meter
- Analytical scale
- Surface gloss meter
- Surface tension meter

2.4 PROCEDURES

2.4.1 Sample preparation

Suspension PVC samples

- Weigh ingredients as determined by the experimental design
- Prepare mixture using mixer identifying each sample accordingly
- Prepare sheets at laboratory calender according to designed thickness, identifying each sample accordingly. Observe that sheets should present high gloss
- Handle samples with cloth gloves or tweezers
Emulsion PVC samples

- Weigh ingredients as determined by the experimental design
- Prepare sheets using high gloss paper and spread coat knives to match appropriate thickness and identify each sample accordingly
- Take over to conclude spread coat process
- Handle samples with cloth gloves or tweezers

Preparation of test specimens

- After samples have cooled, cut samples according to experimental design and attach to paper boards, prepared with horizontal lines for further separation in weekly “cells”.
- Split sheets in half with a vertical cut (see Fig. 2)
- Separate the two cuts and make horizontal cuts according to experimental design and attach a paper clip to each of the “cells”, for subsequent hanging.

![Fig. 2: Sample cutting procedure](image)

2.4.2 Exudation evaluation

Cleaning of the left sheet

- Every week, with a cloth damp in anhydrous ethanol, clean the left sheet of the sample, from the bottom up, leaving untouched the cell immediately below, so that:
  - On week 1, only the cell number 8 won’t be cleaned and all the other will be cleaned
  - On week 7, only cell number 1 will be cleaned
- Cleaning should be done with care to leave the surface completely clean and brilliant
- The sheet will be used at the end of the 8 weeks for a visual evaluation (see Fig. 3)
Fig. 3: Cleaning procedure

Week 1:

Sample A

Sample B

1
2
3
4
5
6
7
8

Clean area

Week 4:

Sample A

Sample B

1
2
3
4
5
6
7
8

Clean area

Week 7:

Sample A

Sample B

1
2
3
4
5
6
7
8

Clean area
Visual evaluation of left sheet

- A score from 0 to 5 should be attributed to each cell of the sample, where 0 indicates no exudation and 5 indicates maximum exudation.
  - Samples with materials with high exudation should be used as comparison parameter.
- Values shall be properly recorded on a spreadsheet
- A clean cotton swab may be used to help visualizing the exudation, that should be done against the light, taking advantage of the high superficial gloss of the surface

Surface analysis of separated cells (Braskem)

- Every week each cell shall be analyzed to obtain results on:
  - Gloss
  - Surface Tension
- Results shall be noted on a spreadsheet

Mass analysis of separated cells (Nexoleum and Elekeiroz)

- Weigh each cell with an analytical scale. Take note of the result ($W_{\text{initial}}$, g)
  - It is recommended to place a sheet of printer paper on the scale to avoid that exudates adhere to the surface of the scale’s plate
- With a cloth damp in anhydrous ethanol, clean the cell on both sides, until it is completely brilliant and free of residues.
- Wait for the ethanol to dry (1 to 2 minutes)
- Weigh the cell again with the analytical scale. Take note of the result ($W_{\text{final}}$, g)
- Measure height (H, cm) and width (L, cm) of the sample with a ruler
- Note the value of exudation (in g/m$^2$) of the sample using the following calculation:
  - $Exudation = \frac{W_{\text{initial}}-W_{\text{final}}}{H+L\cdot2} \cdot 10000$
- After weighing, note the average thickness of the cell, using the thickness meter.

2.4.3 Selected materials and experimental design

Plasticisers:

- General purpose (DINP)
- Low temperature (DOA)
- Second generation octyl epoxy ester (OES)
- Non-phthalate ciclohexanoate (DOCH)
- Third generation epoxy esters (MB50)

Sample size:

- Strip width: 10 cm (split in two parts with 5 cm)
- Strip length: 24 cm
- Cell size: 3 x 4 cm
Formulations:
- Resin: 100 phr (type according to design)
- Plasticiser (according to design)
- CaZn Stabilizer: 1.5 phr
- Black master batch (diluted in DINP): 7 phr

Design ($2^k$):
- For each plasticiser, 8 samples:
  - Thick and Thin sheets
    - Emulsion resin sample thickness: 0.25 and 0.50 mm
    - Suspension resin sample thickness: 0.50 and 1.00 mm
  - Low and High phr
    - Emulsion resin, plasticiser phr: 60 and 80
    - Suspension resin, plasticizer phr: 40 and 80
  - Emulsion and Suspension resins
    - Emulsion Resin: Norvin EP121 LM
    - Suspension Resin: Norvin P 1000

Experimental design formulations table:

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### 3 RESULTS AND DISCUSSION

The test samples were evaluated for 8 weeks, as planned. Two labs ran visual and weight loss tests (Nexoleum and Elekeiroz) and one lab ran the surface tests (Braskem). Elekeiroz’s and Braskem’s labs had temperature control, maintained at 23 °C. At the Nexoleum’s lab tests were conducted without temperature control, to evaluate simpler lab condition, and temperatures were consistently above 27 °C during days and at around 23° C at night throughout the experiment.

It is important to point out that the weight measurement does not take into account total weight loss of the sample, and it is not a measure of % exudates formation, but a measurement of the amount of material accumulated on the surface of the sample, in g/m².

The results are summarized in the charts below.

#### Fig. 4: Exudation comparison (measured by surface mass): emulsion and suspension resin

![Surface mass - Suspension Resin - 80 phr - Elekeiroz Lab](image1)

As seen on Fig. 4, the exudation weighed over the weeks was fairly similar for both suspension and emulsion resin samples. The evolution of the measured exudation over the weeks was not regular, with the trend of reducing over time for some products and increasing for others.

#### Fig. 5: Exudation (measured by gloss): emulsion and suspension resin

![Gloss - Emulsion Resin - 80 phr - Braskem Lab](image2)

As observed in Fig. 5, some products presented a reduction in gloss over time, which could be indicative of the presence of exudation on the surface. The gloss reduction was fairly slight, and
therefore raises concerns around accuracy of the measurement. There was consistency, though, as the higher rates of gloss reduction were observed in the two formulations that also presented higher exudation when measured by mass (comparing Fig. 4 and Fig. 5), OES and DOA. The other concern is that depending on the type of exudation, gloss effects may be masked and improperly accounted for. The measurement is also more susceptible to the initial gloss, which could be a surface effect that varies according to different formulations.

Fig. 6: Exudation (measured by surface mass): different labs

As seen on Fig. 6, there was a significant difference in surface mass exudation between labs. As tests performed at Nexoleum lab were not temperature controlled, surface exudation was far greater than the Elekeiroz lab. The interesting observation is that, if a factor of correction is used (multiplication of all Elekeiroz data by a factor of 4.0), the overall average evolution of all plasticizers was considerably similar. This observation suggests that the temperature and air movement control may not have significant influence in conclusions if intent is to compare products, and test is conducted with all test samples in the exact same area, under the same conditions. On the other hand, a controlled temperature and air movement environment will provide more reliable data over time, and also allow comparisons of exudations of different products at different conditions, if desired.

Fig. 7: Exudation (measured by surface mass): different thickness

The observation of Fig. 7 suggests that the thickness of the sample had very little influence in the test results. It is expected, as a theoretical assumption, that longer term tests would have greater
differences between thick and thin samples, as fast moving plasticisers and additives may be significantly depleted before the end of the experiment, resulting in an earlier depletion for thinner samples.

Surface tension measurements were not plotted in a chart, as all results had very little variation and absolutely no trend could be identified in the observed results.

Fig. 8 shows a picture of an example of the ongoing test, after 4 weeks. It is possible to see, once placed in angle against the light, the surface difference between are with 4 weeks exposure (bottom of sheet) and 1 week exposure (4th cell up from bottom).

Fig. 9 shows that visual observations were fairly consistent with the surface mass results, indicating that the visual impact of exudation can be associated with total mass of exudates on the surface of the flexible PVC compound. It is important to note, though, that higher levels of exudation may be more difficult to evaluate visually, resulting in a possible under evaluation in these cases.
4 CONCLUSIONS

The present paper presents an alternate test method to evaluate exudation, with the advantage of quantification and measurement over time. In this study, exudation is defined as the accumulation of exudates on the surface of the compounded flexible PVC, resulting from the movement of plasticisers and other additives to the surface at a faster rate than the evaporation of these materials under given conditions.

From the results, it was possible to observe that the method has an interesting potential to be considered as a standard for exudation evaluations.

Although these initial results take into account a small sample to obtain robust statistical analysis, it was possible to draw some preliminary conclusions about the procedures for a potential future standard.

Temperature and air movement greatly impact exudation, and therefore comparative tests are more reliable and they must be conducted with all test samples in the same environment.

Thickness of the sample has little effect on exudation, but the test specimens should be thick enough to avoid depletion of the plasticisers or other additives. The tests made with thickness as low as 0.32 mm did not apparently reach such low levels that would affect results.

Gloss presented some variation of results, indicating some usefulness as a measurement, but they were not fully consistent with surface mass and visual observations. This could be imparted by the fact that gloss may be affected differently with exudation, depending on the type of exudation (greasy, waxy, hazy). In general, it does not seem suitable as a measurement for the test.

Visual observations are subjective, but they can be considered supplemental to aid in the verification of total exudates and to determine type of exudation, as well as a tool to compare and predict the aspect of different materials in the final article.

The best and most consistent results were obtained with the surface mass measurements. The results were consistent when comparing different plasticisers in different conditions, demonstrating the reliability of the measurements. The measurements do not rely on the technician’s experience, as measurements are simple and the procedures are straightforward.

Verificamos que todos os plastificantes estudados apresentaram algum nível de exudação. É importante que o formulador identifique se esse nível de alteração poderá gerar algum problema de desempenho ou de aparência na sua aplicação, comparando com o padrão já empregado.

Although more data should be gathered to improve statistical significance it is possible to conclude that the proposed test presents a significant improvement over existing tests and should represent an interesting method to compare various formulations under known conditions. The consistency of these initial results especially with the surface mass measurements, the simplicity of procedures, the already indentified factors that impact results, suggest that the proposed method has an interesting potential to turn into a standard for exudation evaluation.
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REFERENCES


