Migration of plasticisers from PVC

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Preface

This thesis is part of the textile-engineering program at the Swedish School of Textiles, at the University of Borås. The study is an assignment made in cooperation with Volvo Cars Cooperation (VCC) and was performed at VCC in Gothenburg.

This study has been both interesting and meaningful. We have got the opportunity to relate our knowledge from our education with a problem that is relevant in practice. It has also been interesting to do this study in cooperation with VCC. Due to this we have had the opportunity to get an insight of how a company in this size is built-up and what kind of work we might come across in the future.

We would especially like to thank our supervisor at VCC Ann-Britt Tollhag, Karin Norqvist and Mats Olofsson. We also want thank our supervisor from the university in Borås, Martin Strååt.

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Abstract

A common problem with Polyvinyl chloride (PVC) is that plasticisers tend to migrate during use. When the plasticisers migrate the material gets stiffer, this can for example cause cracks in the PVC material. Some PVC tends to crack more easily than other; finding out what is causing this problem would bring answers to a number of questions.

We have done a study in cooperation with VCC. Former studies, by VCC, with variable results have been executed trying to solve the problem with cracks. We wanted to design a new test method to see if we were able to provoke cracks. If we were able to provoke these cracks, we could see when and why cracks appear in the current PVC item.

During our work, we evaluated two different PVC coated materials; PVC1 and PVC2. Both materials had two different structures - with foam backing and without foam backing. We performed mechanical, thermal and chemical treatments on the materials and with help from those experiments we were able to provoke cracks in one of our PVC coated materials.

According to our results, PVC1 shows a higher tendency to crack in comparison with PVC2, which only developed wrinkles. In PVC1 we could see cracks in an early stage during our mechanical testing. We evaluated our result by using a microscope and we observed a pattern in the tendency to develop cracks. PVC1 with foam backing had a higher tendency to crack in comparison with PVC1 without foam. Materials that have been abraded before flexing also tend to crack more easily.

In order to see if the plasticisers migrated into the foam during our experimental work we performed an extraction of PVC1, according to the results the plasticisers might have migrated to the foam.

The major conclusion from this study of PVC1 and PVC2 is that PVC1 tends to crack more easily than PVC2. The foam seems to have a negative effect on the PVC. The abrasion before ageing also have a negative effect on the PVC coated material. We could not see that the chemicals affected the materials.

One of the main purposes with this study was to find a new test method for PVC coated items. We think that our test method with the ageing of the material in combination with the mechanical tests as Martindale and Ballyflex is a suitable test method while testing PVC coated materials.

KEYWORDS: PVC, plasticisers, migration, cracks
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1 Introduction

1.1 Background and motives

This project embodies 15 hp and is a part of our education, in textile engineering, at the Swedish School of Textile at the University of Borås.

This study is a task presented and performed in cooperation with VCC. We were asked by VCC to investigate an item with PVC coated material. We also want to develop a proper test method for VCC to use in the future when testing these types of materials.

The first contact with the company included a deeper presentation of the actual problem. During the last years VCC has discovered a tendency for cracking, while testing, within some materials. These cracks occur in tricot plastics, consisting of PVC.

After examining these materials, where cracks already have occurred, we recognized a change in the material, from being soft to becoming a more stiff and rigid material. A common reason to this problem is the lack of plasticisers. The problem with PVC is that plasticisers tend to migrate sooner or later. When much of the plasticisers have migrated the material consequently gets stiffer and cracks will appear.

VCC have already done research, but no explanation to the problem has been found. VCC suspicions about what is causing the problem are similar to ours; we believe that the migration of plasticisers from PVC might be the problem. This is an assumption on the fact that PVC gets rigid and brittle when plasticisers migrate.

By combining ageing experiments with mechanical wear (Martindale-testing) and chemicals, we hope to discover the nature of the crack formation.

1.2 Problem statement

We want to find out what causes the cracks in PVC coated textiles. To be able to find the cause we intend to develop a method to provoke crack formation.

Large cracks (cm-sized) have been found in PVC-coated textiles subjected to mechanical wear, flexing and chemicals found in everyday use. The cracks have formed sooner than expected.

Figure 1 Crack formation in PVC1
1.3 Aim and question formulation

Our aim is to evaluate what can cause a crack in PVC-coated material. Our hypothesis is that the cracks appear as a result of migrating plasticisers. This evaluation will lead us into a direction whether the cracks depend on migrated plasticisers or not. In order to achieve that we formed the following questions:

- Will we be able to provoke cracks?
- Will mechanical testing affect the outcome?
- Will the treatments affect the outcome?
- Why, where and when do plasticisers migrate?

1.4 Delimitations

The study embodies 15 swedish credits, equivalent of 10 weeks of work.

Our report is restricted to focus on the migration of plasticisers in PVC. We also restrict our study to two specific types of coated materials, PVC1 and PVC2. These materials come from two different manufacturers.

We evaluate the effects from a combination of mechanical, thermal and chemical tests. The chemicals that we use in our study are a fat, a leather cleaner and hand sweat. This choice is based on which chemicals, from real life, that we believe might have an effect on the material.

The mechanical testing is restricted to abrasion and flexing of test pieces. When we do the flexing test we test our tricot material in two directions, length- and crosswise. This is a way to simulate what the material is exposed to during use. The material will be flexed in a temperature of -20°C.

Based on the limited amount of time we were forced to exclude some other interesting theories. Some of these theories were for example the effects of climate changes, design problems and UV-light. From our literature studies we learned that the combination of mechanical and chemical effects to be the most likely cause of the problem.

We decided to narrow down our study to only some of these mechanical and chemical possibilities. These tests will be performed on treated material, with different kinds of chemicals, ageing and abrasion with the help of a Martindale. We will also perform our tests on non-aged and non- treated material as references. The chemicals and ageing intend to simulate real life conditions.

We have chosen to compare PVC1 and PVC2, during our study, to see how or if the chemical, thermal and mechanical affect will separate them from each other. Both materials will be evaluated with several types of examination methods. Through this we can evaluate our test results to see if we are able to find the reason to why the material tends to crack.
1.5 Materials and methods

By using a hypothetic-deductive method we can examine our hypothesis accuracy.

Our study is based on a semi-quantitative approach, as we are looking for visible facts. The information was collected from literature, databases, the internet and articles and then summarized into a theory part.

1.5.1 Literature studies

To be able to comprehend and get a deeper understanding about PVC and plasticisers we have researched several relevant medias. Those medias has been both electronically and printed ones. All literature sources have been studied critically.

1.5.2 Data collection

While collecting information we have used secondary data. The data is information that we have received through meetings, with both employees at the company and our supervisor from the university. As we have spent most of our time at the company, exchange of information from surrounding employees have been naturally. The most frequently used data are different types of medias such as literature and articles.

Detailed information about the materials has been hard to find, due to the manufacturers business secrecy. Therefore some assumptions had to be made about the materials composition. Since the main purpose of our study is to evaluate the migration of plasticisers with the help of mechanical testing, these drawbacks will not have any significant affects on our results, but they will be considered.

Our laboratory part will collect data about the materials that we have used in our study.
1.5.3 Validity and reliability

Reliability and validity can only be achieved, to a satisfying degree, when a study is continuously critical examined and accurately performed.

To have a high reliability and use trustworthy information is a common goal for most studies. A high reliability is achieved when independent measurements of one phenomenon can be repeated with results that are the same or of small deviations.

The validity of a study is as important as the reliability. Even if the reliability is very high the study must have a high validity, as it considers whether the information covers the concept that the study is about or not.

1.5.3.1 Factors that may have affected our results

Due to the limited amount of time we were only able to perform our mechanical test on one test piece of each material and in each direction. Because of this we do not have any statistical security in our result and it only show a tendency of what happens with the material during mechanical tests.

Since we were two people who evaluated the result it also might be a difference between those evaluations. Most samples were evaluated by both of us, which means that these results are more reliable than when only one of us were evaluating.

We have constructed our research according to our aim and question formulation in order to achieve our intentions with this study. We believe that it is of a high validity as our test measures and data collections are joining together to answer some of our questions about our problem. We have successfully acquired the answers that we were looking for.

1.5.4 Working process

We started our work with creating a project plan with a timetable that shows our working process. The timetable is based on the number of weeks we have to our disposal during the study. There are five different parts in the timetable; literature studies, experimental, report writing, presentation preparation and poster making. Before we started our study we decided how many weeks we will spend on each part (Appendix A).

Our work started with a meeting with our supervisors at VCC to get a deeper understanding of the problem with cracks in PVC coated material. We discussed what we believed could be the reason for this. Based on these discussions we started to design a test method for our experiment that would simulate real life effects on the materials and hopefully provoke cracks.

During our literature study we collected information about PVC in general, plasticisers, migration of plasticisers in PVC and different kinds of plasticisers. The information we collected from our literature study was summarized into a theory part.
Based on this knowledge we started to analyse the problem with cracks in the material.

The experiments were a big part of our study and we performed a number of different tests. We started of by using the company’s own standards to design our mechanical tests. These methods where then evaluated and transformed to fit our study. All of our methods were designed in a way so that they are easily replicated. Our intention was to study how the mechanical, chemical and thermal treatments affect the migration of plasticisers in PVC. We also wanted to evaluate if the foam backing had any impact on the tendency to develop cracks.

All test pieces besides the references was exposed to ageing, for 3 or 6 weeks in an oven with 75°C. The mechanical tests that we performed were Martindale- and a Ballyflex test. In the Martindale a number of test pieces were exposed to abrasion, this test was performed before ageing.

After accelerated ageing the materials were exposed to flexing in a Ballyflex machine. This test was performed on all test pieces and references from the different materials.

We also performed a chemical test where we analysed if the plasticisers, in the materials with foam backing, had migrated during ageing and mechanical testing, to the foam or not.

When the experimental part was completed, we started to analyse the material with help from a magnifier, with 6x magnification. If no cracks were seen, we continued to analyse the material with help from a microscope, with an 80x magnification, to see if cracks could be seen at this stage. We also used a microscope to take photographs of the materials, we used these photos to perform a comparison of all test pieces.

When the materials had been analysed, with help from the microscope, we collected the result in Table VII and VIII to see if we could detect a pattern in the results, depending on pre-treatment, ageing and material with and without foam backing.

Some of our material was tested in a Soxhlet-extractor, this was to find out how much substances that were left in the PVC, respectively how much substances that had migrated into the foam.
2 Theory

2.1 PVC

Polyvinyl chloride (PVC) is one of the most commonly used polymers and can be used in a number of applications, such as pipes, packaging and coated textiles. PVC is well known for its low cost and versatility. Pure PVC has a softening temperature of 80°C and a low thermal stability. By adding a plasticiser, the softening temperature can be lowered far below room temperature, giving the PVC a flexible behaviour, thus making it suitable for coated textiles.

The PVC polymer consists of repeated vinyl chloride monomers. The vinyl chloride monomer contains carbon chains with hydrogen and chloride. These units are linked together through polymerization. By adding heat and pressure, to the vinyl chloride monomers, they join together in the form of a very large molecule, a process called polymerization. The number of repeating units in the polymer chain may range from 800 to 1600. The configuration of the chain could be either linear or three-dimensional networks, which also determines the plastic product properties.

There are two types of polymerization reactions, condensation and addition. In condensation reactions two or more monomers react, with each other in a stepwise process. At each step of the reaction one small molecule is lost. Addition polymerization is a chain reaction where the monomer units are added to the chain one at a time.

Normally PVC is a rigid material because of the strong interactions between the polymer chains. These strong networks contribute to its characteristic properties, such as the high tensile strength. When PVC is heated these strong bonds are weakened and as a result the PVC gets more soft and workable. By adding plasticisers this property can be achieved at lower temperatures. When it is cooled these bonds are reformed and it returns to its originally stiffness. PVC most often appears in the form

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1 MARCILLA, GARCIA and GARCIA-QUESADA, 2007
2 SKINNER and GOLDHAR. 1968, Environmental effects on polymeric materials, pp. 4-212
3 SKINNER and GOLDHAR. 1968, Environmental effects on polymeric materials, pp. 175-176
of a dispersed resin, which can easily be applied on the fabric through coating. The dispersion resin consists of fine particles that have a size about one micron.\(^5\)

Polymerization of vinyl chloride is accomplished through free radical process, 93-98\% of PVC consists of amorphous areas and therefore belongs to amorphous polymers. The crystallites work as physical cross linkers, which prevents deformation of the material, during pressure, above \(T_g\) (glass transition temperature).\(^6\) This is a very valuable property and is why softened PVC can be used on textiles and the reasons to why it stays on the surface without penetrating the textile.

\(T_g\) is the temperature where an amorphous polymer transforms from being stiff to be more flexible and softer. For polymers that are partially crystalline it is only the amorphous areas that are affected by \(T_g\), because it is only the amorphous areas that transforms. The polymer chains do not move, in relation to each other, while the temperature is below \(T_g\). The warming and cooling rate of PVC are critical for \(T_g\), a slow temperature change decreases \(T_g\), this contributes to change in properties.\(^7\) For PVC without plasticisers \(T_g\) is 75-80°C. If plasticisers is added the \(T_g\) can be decreased below room temperature.\(^8\) One way to calculate the glass transition temperature of a polymer-plasticiser compound is through the following equation:

\[
T_g = T_{g2} - kw_1 t
\]

(Eq.1)

Where:

- \(T_g\) glass transition temperature of polymer-plasticiser(s) mixture
- \(T_{g2}\) glass transition temperature of unplasticised polymer
- \(k\) plasticiser efficiency parameter
- \(w_1\) weight fraction of plasticiser\(^9\)

The largest consumer of PVC is the building and construction industry, where half of the PVC within this area are used to make pipes and conduits. Applications, made with PVC, for the automobile area are instrument and door panels, upholstery, armrests, side body moldings and floor mats.\(^10\)

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\(^5\) OCCIDENTAL CHEMICAL CORPORATION, 1996, pp. B10-B11
\(^6\) HJERTBERG, 2009
\(^7\) KLASON AND KUBÁT, 2004, Plaster materialval och materialdata, pp.50-53
\(^8\) HJERTBERG, 2009
\(^9\) GEORGE WYPYCH, 2004, Handbook of plasticizers, pp. 219
\(^10\) OCCIDENTAL CHEMICAL CORPORATION, 1996
A plastic material can age according to either physical or chemical effects. The physical effect depends on a molecular structure change in the material. This can for example mean shrinking in volume and the material can get stiffer. Both physical and chemical ageing appear faster at high temperatures.\textsuperscript{11}

\textsuperscript{11} KLASON AND KUBÁT, 2004, Plaster materialval och materialdata, pp. 46-55
2.2 Compounding of PVC

PVC is one of the most important thermoplastics on the market and the demand is increasing constantly. One reason for PVC's popularity is because of its high versatility in change of properties, which makes it possible to adjust to different sectors of application. The change in properties will be accomplished by adding additives, this because of PVC’s compatibility to a large number of other chemicals. Additives have different purposes and are added to fulfil a certain type of property. PVC in natural form is a colourless rigid material with low heat stability, because of this other ingredients needs to be compound with the polymer. Some common additives are stabilizers, fillers, pigments, plasticisers, lubricants and extenders.\(^{12}\)

By adding heat stabilizers the material can be processed, at elevated temperatures, without being discoloured and degraded. The heat stabilizers affect thermal reactions. While PVC degrades, HCl is formed.\(^{13}\) HCl is a caustic substance, it is therefore important to use stabilizers. Other types of stabilizers can also be added, for example when UV protection is needed.\(^{14}\)

A filler is also a non-reactive additive and it is added to lower the cost and for improvement of the compounds dimensional stability.\(^{15}\)

Extenders are relatively cheap and can be used to replace plasticisers to a certain degree and are often used in combination with plasticisers.\(^{16}\)

Lubricants are additives, used during hot molding, to increasing the external and internal antifriction properties, to make PVC more process able to produce.\(^{17}\)

\(^{12}\) BRYDSON, 1999, Plastics Materials, pp. 325
\(^{13}\) HJERTBERG, 2009
\(^{14}\) FORREST, 2002
\(^{15}\) OCCIDENTAL CHEMICAL CORPORATION, 1996
\(^{16}\) BRYDSON, 1999, Plastics Materials, pp. 336
\(^{17}\) DOMNINGHAUS, 1993, Plastics for Engineers, pp. 138
## 2.3 Plasticisers

The plasticisers play an important part of PVC and functions in three ways,
- Lower the processing temperature so that it can be processed below its decomposition temperature.
- Change the properties of the finished products.
- Adjust its processing properties.\(^\text{18}\)

With the help from plasticisers PVC can be more soft and flexible. The plasticisers reduce PVC’s viscosity and make it easier to shape at low temperatures.\(^\text{19}\)

There exist a number of plasticisers for PVC, the most commonly used are phthalates. Phthalates are fat-soluble and therefore they are able to migrate, from the polymer, while in contact with fat surfaces. The fact that they are fat-soluble also means they can penetrate human skin relatively easily. This is why they are dangerous to humans.

Plasticisers have different advantages and disadvantages and what type of plasticiser that is most suitable depends on which requirements it has to fulfil. A choice of plasticisers that are not well thought-out may affect properties of the product in the end.\(^\text{20}\)

In this kind of applications, PVC is a plastic that requires plasticized chemicals while other plastics might already be plasticized within themselves. Without plasticisers PVC would be too stiff to be processed, as for example plastic sheeting, films, tubing and flexible forms.\(^\text{21}\) After adding plasticisers PVC becomes a more workable melt, which can be used as coating.

![Figure 3 PVC structure, with and without plasticisers](image)

With help from the plasticisers the intermolecular forces, in the polymer, can be reduced. By separating the molecules the intermolecular bonds are weakened. By increasing the temperature the plasticiser is able to penetrate further in between the polymers.\(^\text{22}\) The plasticisers are able to interact with the PVC polymers chlorine atom, since PVC is a polar material. When PVC is heated to a melt and plasticisers are added a blend of polymers and plasticisers are created. The heat is necessary because of the plasticisers molecular size, which makes it more difficult for them

\(^\text{18}\) DI MATTIA, 1968, Environmental effects on polymeric materials, Vol. 2, Materials, p. 1504

\(^\text{19}\) DI MATTIA, 1968, Environmental effects on polymeric materials, Vol. 2, Materials, p. 1504-1507

\(^\text{20}\) WYPSCH, 2009, PVC Formulary, pp. 42

\(^\text{21}\) SKINNER and GOLDHAR, 1968, Environmental effects on polymeric materials, pp. 4-212

\(^\text{22}\) PRITCHARD, 1998, Plastics Additives, pp. 499-504
to diffuse into the polymer. For PVC to blend with the plasticiser a temperature of about 150°C is necessary. When this melt is cooled down, the plasticisers are able to create bonds directly to the polymer. When PVC is plasticized it goes through two main phases, gelation and fusion. Gelation is when PVC absorbs the plasticisers, which is controlled by temperature. This process does not give the mix its final properties; a fusion is required in order to develop the materials mechanical properties. When the fusion takes short time it is an indication that the plasticiser is compatible.

Darby and Sears describe six steps that are necessary for plasticizing PVC. In the first step, irreversibly, PVC absorbs, through penetration of the porous system, the plasticisers. After the first step the plasticisers solvate. Subsequently in the third step a diffusion process takes place and the PVC particles swell. In the fourth step of this process clusters are formed by the plasticisers between the polymer segments, where it solvates available polar groups and hydrogen bonding. In this step a homogenous blend between PVC and plasticisers are formed. Continued heating makes the melt fluid where clusters of plasticisers and polymer molecules disappear. In the final step the cooling takes place and the polymer crystallites and creates hydrogen bonds and weak Van der Waals forces, between the polymer segments and plasticiser molecules. These are the reason for why the polymer hardens in this step.

By using plasticisers the polymers are not able to reform their primary interactions, and thereby PVC's original properties are lost. This results in softer and more flexible PVC.

Many phthalates have negative effects on humans and the environment. Due to the low price and the fact that they are very high performing plasticisers there are difficulties in finding alternatives with similar properties. Some alternative plasticisers are polymeric plasticisers, phosphates trimellitates and aliphatic dibasic esters. However there are other methods to reduce the migration of low molecular plasticisers, for example by surface coating and multi-layered tubing. A disadvantage that may come from these methods is the sacrifice of properties such as thermal stability, flexibility and appearance.

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24 MARCILLA, GARCIA AND BELTRÁN, 2004, Handbook of plasticizers, pp. 179-191
25 GEORGE WYPYCH, 2009, Handbook of plasticizers, pp. 205
26 MARCILLA, GARCIA AND BELTRÁN, 2004, Handbook of plasticizers, pp. 179-191
28 HAKKARAINEN, 2008
2.3.1 Types of plasticisers

The properties required of the final product decide the selection of plasticisers in PVC. The reason for phthalates popularity is the combination of good properties and low price. The phthalates vary from being fairly volatile to being very high-boiling non-volatile.29

Phthalates general formula consists of one aromatic ring and two side chains, usually aliphatic ones. These plasticisers are often bioaccumulating and not easily biodegradable. Due to this they can be found in places where they are not ought to be, they have for example been discovered in polar bears on the North Pole.30

Plasticisers can be divided into two main categories, true plasticisers and extenders. True plasticisers can in return be divided into, primary and secondary. The primary has high compatibility with PVC and can be used alone, the secondary plasticisers most often are used in combination with primary plasticisers.31

The choice of primary plasticisers can affect tear strength, viscosity and sticking of the surface. Secondary plasticisers usually do not solvate easy, as they are dipole-deficient.32

Plasticisers can be either polymeric or monomeric. The polymeric ones are resistant to migration and solvents, since they are not crystallizing at low temperatures, they are low temperature resistant and non-volatile. The most common plasticiser is the monomeric plasticisers, as phthalic acid esters.33

To accomplish higher tensile strength and glass transition temperature, high molecular plasticisers can be used. Due to these advantages the material will be more difficult to process. One way to avoid this problem is to change the structure of the macromolecules to a branched chain instead of a linear.34

Linear polymers consist of difunctional polymers and their shape can be seen as a line. Branched polymers has branched polymer molecules, which can be either long or short, in comparison to the main chain. One difference for polymers with long side groups is that the molecular size is bigger.35

29 DI MATTIA, 1968, Environmental effects on polymeric materials, pp. 1507
30 TINGSVIK, 2010
31 DI MATTIA, 1968, Environmental effects on polymeric materials, pp. 1504-1507
32 DOMININGHAUS, 1993, Plastics for Engineers, pp. 136-138
33 DOMININGHAUS, 1993, Plastics for Engineers, pp. 136-138
34 HAKKARAINEN, 2008
35 HJERTBERG, 2009
When plasticisers are used they are normally added in combinations, this is because one single plasticiser most certainly does not have all of the required properties. The main purpose of adding plasticisers is to reach the form of an elastomer that also functions as a polymer at a wide range of temperature. By esterification of various alcohols and phthalic anhydride a plasticiser of the family phthalic acid esters can be created. These can be divided into a number of smaller groups. Many plasticisers consist of di-isoocyle phthalate (DEHP or DOP), di-isononyl phthalate (DINP) and di-isodecyl phthalate (DIDP). There are also phthalates manufactured with other properties, where specific requirements are expected.

Research according to reports done in 1983 about DEHP, showed tendency to cause tumours in rats and mice livers. After more intense research, done by an expert group in the area, DEHP was not classified as carcinogenic. This is because the effect on humans cannot be compared to the ones on rats and mice.

DIDP has relatively high heat resistance and volatility resistance. In flexible PVC the proportions of DIDP are normally between 25-50%.

2.3.2 Migration

Additives, for example plasticisers, stabilizers and other required ingredients for PVC, with low molecular weight, tend to migrate. This is a well-known phenomenon that has been thoroughly researched. Because of the risk of migrating from the large formulation, PVC with plasticisers should not be in packaging material for food. Studies have shown that both contact time and temperature affects the migration, of plasticisers, into food and packaging with high fat content. This has a potential risk for humans as the fat-soluble plasticisers easily migrate through the skin.

One of the main purposes of PVC additives is their performance in the PVC polymer; once they have been processed they should remain in the polymer. When it comes to plasticisers, especially flexible PVC, migration tends to be a problem. Migration of plasticisers can appear in many ways for example by evaporation from the PVC surface but also through contact with a liquid they can extract into the liquid, in direct contact with the surface of another material they can migrate in to the other material and under pressure the plasticisers can exudate. Depending on the formulation of the PVC the migration rate of plasticisers vary.

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36 DI MATTIA, 1968, Environmental effects on polymeric materials, pp.1504-1507
38 EDSHAMMAR, 2002, Plast – en materialguide för industriin, pp. 73-80
39 DI MATTIA, 1968, Environmental effects on polymeric materials, pp. 1504-1507
40 HAKKARAINEN, 2008
41 MARCILLA, GARCIA and GARCIA-QUESADA. 2007
PVC is a material with a high $T_g$ and to be able to reduce it, plasticisers are required. As some of these additives tends to migrate PVC’s performances in the long-term is affected negatively. This is because PVC requires a certain amount of plasticisers to be manageable and to be able to be used in more flexible products. There are different types of plasticisers; some tend to migrate more than the other. Polymeric plasticisers as for example polyesters tend to migrate less than the phthalate esters, for example dioctylphthalate (DOP). The reason for this is that the phthalates are monomeric plasticisers, which will make it easier for them to migrate because of their small size. To be able to determine the effects of migrated plasticisers it is imperative to find out what happens to the plasticiser while leaving the PVC. Three different way of migration are:

- If the plasticisers are totally blocked by an adhesive at the interface between adhesive and vinyl it will results in a loss of boundary between the two components.

- The adhesive is sometimes too accepting, which will lead to a decreased cohesive strength because of a weak polymer layer.

- The plasticisers migrate from the vinyl, which results in destroying or retarding bond formation.

Most often the problems do not occur from only one of these reasons, it is usually a combination of these three reasons.\(^{42}\)

\(^{42}\) GRAZIANO AND SJÖSTRAND, 1986
2.4 Health aspect

Monomer plasticisers can migrate into intravenous solutions and biological fluids. Research on heated plastic bags, containing intravenous solutions, has shown that low molecular particles, from PVC, migrate into the solution. The storage time showed to be contributing to the migration rate. Low molecular plasticisers can also migrate into food. Several studies show that plasticisers have a high tendency to migrate into food. The amount of migrated particles increased with increasing moisture and fat content, contact time and temperature. When it comes to children toys many plasticisers are strictly forbidden, such as DEHP and DBP. DIDP on the other hand are banned in toys that might be placed in the mouth. While studying children toys containing DEHP, it has been discovered that if the product is shaken the amount of migrated DEHP increase.43

Migration often appears while two materials are in contact with each other, as they are able to exchange components. This could happen when PVC is in contact with polyurethane-foam. In some cases adding a surface layer, which works as a barrier and prevents the migration of plasticisers, can reduce the migration.44

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43 HAKKARAINEN, 2008
44 MARCILLA, GARCIA AND BELTRÁN, 2004, pp. 248
2.5 Abrasion

When it comes to plasticisers migration from coated textiles not only the plasticisers size are of value but also the lacquers protecting barrier. This protecting barrier most certainly prevents the plasticisers from migrating. Most of the plasticisers will appear alongside the barrier and when it is weakened, for example by abrasion, the plasticisers can migrate easier from the material.

Abrasion is a combination of several factors such as rubbing, scuffing, sliding, wiping and scratching. As a result from abrasion parts of the surface material is removed. To simulate the conditions that the material should be exposed to, in real use, an abrasion resistance tests can be used. One way to determine the abrasion resistance is through use of a machine called Martindale, where abrasion and pilling resistance can be examined. This method rubs one material against another, at low pressure and with a constant change in direction.45

Some plasticisers and materials are more sensitive to abrasion than others. The big difference between high and low molecular weight plasticisers is that the low molecular weight has higher tendency to migrate. During abrasion the low molecular particles removes more easily. This is because they are not as integrated as high molecular plasticiser, which has a bigger surface that makes the adhesion greater.

Figure 5 Martindale abrasion tester

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45 CORPORATE STANDARD STD 1024,7122, 1994
3 Experimental

Migration of plasticisers from PVC is a common existing problem and it results in changes of the material, such as cracks. Plasticisers are fat-soluble and therefore easily migrate to fat surfaces such as the human body. Depending on the formulation of PVC and plasticisers the migration rate of plasticisers is more or less.

We will apply the same tests on PVC1 and PVC2. Both materials have two different compositions, one with foam backing and one without foam backing. This is also an aspect that we will consider, whether the plasticisers migrate to the foam or not.

When migration of these plasticisers appears the material tends to crack. The plasticisers that are used in our materials are DIDP and linear compounds with varying lengths, between six and twelve carbons in the chain.

3.1 Abbreviations and definitions

This report contains a number of abbreviations, which only have been briefly considered until this part. A short presentation of these materials is available here:

PVC1 - appears in two forms: one with a 6 mm foam lamination and the other one without foam lamination.

PVC2 - appears in two forms: one with a 6 mm foam lamination and the other one without foam lamination.

We have chosen to classify the names of VCC's suppliers and their material names as this information will not bring any necessary meaning to our report and also in respect of the suppliers. (For VCC's internal version of this report this information is displayed in Appendix B). In total we have four types of coated materials, from two different manufacturers, that were tested.
3.2 Materials

Both materials are composed in a similar way, with only a few differences. The main difference between the two is:

- The ether respectively ester based Polyurethane foam.
- The lacquer also differs between them as PVC1 has three layers of acrylate and Polyurethane while PVC2 has four layers of Polyurethane only.
- The weave within the textile differs between the two materials.
- PVC1 contains a higher content of flame-retardants.
- The materials have been manufactured and processed in two different machine set up.
- The top surface differs in the grade of embossing, PVC1 is more embossed than PVC2.
3.2.1 Chemicals used in treatment

- Leather cleaner - The leather cleaner contain surfactants that might accelerate the migration.
- Hand sweat - Hand sweat simulates how sweat might affect the plasticiser's migration.
- Centoplex - Centoplex is a fat used as a replica for different fats, to illustrate their effects.
- Diethylether - Dissolving agent, used for extraction, which has a boiling point of approximately 35°C.
3.3 Manufacturing process

The two different materials, PVC1 and PVC2 are manufactured in similar ways. There may be some small differences in their manufacturing.

Figure 8 shows principal process and the steps that the manufacturing process consists of.
3.4 Methods

In our study we want to evaluate when and why cracks appear. To be able to study this, we used different kinds of treatments, see Table I.

The treatments have been done on four different kinds of materials; PVC1 with foam backing, PVC1 without foam backing, PVC2 with foam backing and PVC2 without foam backing. We also compared our test pieces with reference material to see if our pre-treatment affects the migration of plasticisers.

Table I. Showing number of samples that were prepared before mechanical testing

<table>
<thead>
<tr>
<th></th>
<th>PVC1 with foam</th>
<th>PVC1 without foam</th>
<th>PVC2 with foam</th>
<th>PVC2 without foam</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference 3w</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Centoplex 3w</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Leather cleaner 3w</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Hand sweat 3w</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Reference 6w</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Centoplex 6w</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Leather cleaner 6w</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Hand sweat 6w</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Reference</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

MARTINDALE

<table>
<thead>
<tr>
<th></th>
<th>PVC1 with foam</th>
<th>PVC1 without foam</th>
<th>PVC2 with foam</th>
<th>PVC2 without foam</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference 3w</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Centoplex 3w</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Leather cleaner 3w</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Hand sweat 3w</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

TOTAL 52

The laboratory part started with preparing our materials with different kinds of chemicals, such as hand sweat, leather cleaner and fat. The materials might be exposed to these chemicals during use.

After the chemical preparation of the materials, we used accelerated ageing at an elevated temperature to simulate the ageing of a material, the temperature used was 75°C. The materials were aged for 3 respective 6 weeks.

Some of the materials were also exposed to abrasion before the chemical preparation and subsequent accelerated ageing. Samples were exposed to abrasion using a Martindale in order to study the impact of abrasion on the migration of plasticisers. During this test the material where exposed to abrasion from a canvas textile to simulate the friction of a pair of jeans, during a specific amount of cycles and pressure. Another reason to do this test was to see if the lacquer were affected, which might be a reason for the plasticisers to migrate easier. To see the impact on the
lacquer from the abrasion we compared these pieces with reference samples in a microscope.

In order to create cracks formation in the PVC coated materials we decided to use a flexing test and through this provoke cracks. All our tests were performed to evaluate the migration of plasticisers from PVC. This test was performed in a Ballyflex machine, with a temperature of -20°C during 10 000 respectively 30 000 cycles.

Some of the material where abraded and treated with chemicals before it was aged. After ageing for 3 respectively 6 weeks all of the materials were mechanically tested in a Ballyflex, see Table II.

Table II. Number of samples for mechanical testing

<table>
<thead>
<tr>
<th></th>
<th>Martindale</th>
<th>Ballyflex</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC1 with foam</td>
<td>8</td>
<td>52</td>
</tr>
<tr>
<td>PVC1 without foam</td>
<td>8</td>
<td>52</td>
</tr>
<tr>
<td>PVC2 with foam</td>
<td>8</td>
<td>52</td>
</tr>
<tr>
<td>PVC2 without foam</td>
<td>8</td>
<td>52</td>
</tr>
<tr>
<td>TOTAL</td>
<td>32</td>
<td>208</td>
</tr>
</tbody>
</table>
3.5 Mechanical, thermal and chemical treatment to simulate real life use

To be able to provoke cracks we used mechanical tests.

3.5.1 Martindale

Before using the Martindale the material needs to be punched out, in order to fit the abradant table on the machine. Eight pieces of each material was needed for our testing. The test pieces are then mounted on the six abradant tables over a piece of felted fabric. A weight helps to keep the materials in place before it is properly fixed on the abradant tables. After this the standard abradant is placed on a ring with a disc of foam, which has the same diameter as the standard abradant. The abradant material was chosen to be a canvas made from cotton, which would simulate the abradant effects from a pair of jeans. A standard piece holder is placed upon the test pieces, which is the opposite of how the machine is supposed to be used. This solution had to be used to finish in time. Usually the standard abradant is placed on the abradant tables. This gives a different result in comparison to if the machine were used as it is supposed to, the abrasion is less intense in this case. Finally weights are placed upon the standard pieces, to accomplish a pressure of 12 ± 0,3 kPa, which also is the standard pressure. These weights contribute to a more equal distribution of the abrasion. The numbers of cycles were chosen to be 20 000.

One aspect in our testing is that we used a canvas, which is a material with lots of structure. Usually a material with less structure made from polyester and wool is used. This results in a rougher but at the same time less intense abrasion with consideration to how the machine normally is used. The expected outcome of the abrasion was to reduce the thickness of the lacquer. This could potentially lead to a more rapid migration of plasticiser from the textile.

After the abrasion we looked at the materials in a microscope to see whether the abrasion has affected the materials or not.
Before and after the Martindale test we weigh the material to see if it lost lacquer, see table IV.

*Table IV. Showing weight loss of samples subjected to 20 000 cycles of abrasion. 8 samples were tested from each material.*

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight (g, before)</th>
<th>Weight (g, after)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC1 with foam</td>
<td>16,45</td>
<td>16,25</td>
</tr>
<tr>
<td>PVC1 without foam</td>
<td>13,11</td>
<td>12,62</td>
</tr>
<tr>
<td>PVC2 with foam</td>
<td>15,77</td>
<td>14,99</td>
</tr>
<tr>
<td>PVC2 without foam</td>
<td>12,86</td>
<td>12,48</td>
</tr>
</tbody>
</table>
3.5.2 Chemical treatment

We wanted to see if some common chemicals could affect the rate of the migration. Therefore we treated our materials with different kinds of chemicals that we believe the material can be exposed to during use. These chemicals are soluble in fats and as we suspect that they might accelerate the migration we have chosen to use them.

After deciding which chemicals to use we prepared the materials with each chemical. The chemicals were evenly distributed over the textile surface using a sponge. Leather cleaner 0,00033 ml/cm², Centoplex 0,00065 g/cm², Hand sweat 0,00065 ml/cm² were used.

3.5.3 Accelerated ageing

The PVC-coated materials were exposed to different times of accelerated ageing, see Table V.

*Table V. Showing the ageing time of samples.*

<table>
<thead>
<tr>
<th>Material</th>
<th>0 weeks</th>
<th>3 weeks</th>
<th>6 weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC1 with foam</td>
<td>1</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>PVC1 without foam</td>
<td>1</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>PVC2 with foam</td>
<td>1</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>PVC2 without foam</td>
<td>1</td>
<td>8</td>
<td>4</td>
</tr>
</tbody>
</table>
3.5.4 Ballyflex, DIN 53 351

In this test we expose all of our materials to flexing, to see if we were able to provoke the cracks. One side of the test piece is placed within a moving clamp while the other one is placed in a fixed clamp. When the upper clamp moves the test piece will be exposed to flexing. Standard DIN 53 351 can be viewed in Appendix C.

During our testing in the Ballyflex we evaluated two different directions within the material. These two directions, length and cross, have different properties as the cross direction is more elastic due to the construction of the textile.

Test pieces of a specific size were placed inside the machine, see Figure 11, and thereafter flexed 10 000 respective 30 000 cycles in a temperature of -20°C. The temperature, while testing, is based on our theory that this material gets stiffer while cold and therefore cracks easier. When the materials were flexed they were evaluated with help from a magnifying glass with 6x magnification. If cracks were not discovered at this stage the material were rigorously analysed in a microscope to see if they exist, with help from an 80x magnification. All results are graded according to the extent of the cracks.

Our results, from the Ballyflex testing, will be graded according to a scale, one to five, where one represents no cracks at all and five represents several cracks that can be seen with a six times magnifier.

1. No cracks
2. Few cracks seen with the help of a microscope, 80x magnification
3. Several cracks seen with the help of a microscope, 80x magnification
4. Few cracks that can be seen with a magnifier, 6x magnification
5. Several cracks that can be seen with a magnifier, 6x magnification
3.6 Microscopy

To evaluate our test pieces a microscope were used. We also used a magnifier, with 6x magnification. Cracks that were not visible in the 6x magnifier were subsequently evaluated in a microscope, with 80x magnifying instead of 6x. These observations where photographed to facilitate our following studies. We used the microscope LEICAMZ125, all photos will be within the same scale, see Figure 12.

Figure 12 Microscopy sample with scale
3.7 Soxhlet-extraction

With this equipment we were able to extract and separate certain components from PVC1. The tested materials were separated so that the PVC and the foam can be tested individually. This test was used to determine how much plasticisers that were in the PVC respectively foam.

A dissolving agent is added to extract substances within the material that has a high solubility. This agent will extract substances within the material, such as plasticisers. In this case we used diethylether, a very volatile dissolving agent which has a boiling point of approximately 35°C.

The weight of 5 different flasks is measured before and after the extraction to determine the possible increase in weight after the extraction. The increase in weight is the substrates that are left in the flask after they have been extracted and evaporated. The components that are left in the flask can then be examined through gas chromatography with mass spectrometry (GC-MS), to determine exactly what kind of substance it is.

![Figure 13 Soxhlet-extractor](http://www.homechemistry.org/images/SoxhletExtractor.gif)
4 Results

The results from the Ballyflex testing showed that samples with foam backing were more prone to crack, see Table VII. All test results can be viewed in Appendix D. The areas where all cracks occur has developed a white colour, which seems to be a result from the flexing.

4.1 Summary of results after 10 000 cycles in the Ballyflex

Table VII. Ballyflex testing during 10 000 cycles

<table>
<thead>
<tr>
<th></th>
<th>PVC1 with foam</th>
<th>PVC1 without foam</th>
<th>PVC2 with foam</th>
<th>PVC2 without foam</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Length</td>
<td>Cross</td>
<td>Length</td>
<td>Cross</td>
</tr>
<tr>
<td>Reference 0w</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Reference 3w</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Centoplex 3w</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Leather cleaner 3w</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Hand sweat 3w</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Reference 6w</td>
<td>2</td>
<td>2-3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Centoplex 6w</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Leather cleaner 6w</td>
<td>3</td>
<td>1-2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Hand sweat 6w</td>
<td>2-3</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>MARTINDALE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference 3w</td>
<td>2</td>
<td>3</td>
<td>2-3</td>
<td>2</td>
</tr>
<tr>
<td>Centoplex 3w</td>
<td>3</td>
<td>2-3</td>
<td>2-3</td>
<td>2-3</td>
</tr>
<tr>
<td>Leather cleaner 3w</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>2-3</td>
</tr>
<tr>
<td>Hand sweat 3w</td>
<td>3</td>
<td>3</td>
<td>2-3</td>
<td>2-3</td>
</tr>
</tbody>
</table>

Grading:

1. No cracks
2. Few cracks seen with the help of a microscope, 80x magnification
3. Several cracks seen with the help of a microscope, 80x magnification
4. Few cracks seen with help from a magnifier, 6x magnification
5. Several cracks seen with help from a magnifier, 6x magnification
4.1.1 PVC2, 10 000 cycles in Ballyflex

All Ballyflex tests with 10 000 cycles on PVC2 showed that the material had no tendency to crack. What could be seen was that wrinkles had developed in the material. The wrinkles were not bigger if the materials were exposed to abrasion in the Martindale or aged for 6 weeks in a comparison with materials from 3 weeks of ageing.

Figure 14 shows how the wrinkles appear in a microscope.

4.1.2 PVC1, 10 000 cycles in Ballyflex

4.1.2.1 Ageing

According to our results there was a pattern depending on the time of ageing. When the materials had been exposed to 6 weeks of ageing instead of 3 weeks it tends to have a higher amount of cracks after the Ballyflex test.

4.1.2.2 Cross and length direction

Test pieces from length direction had a higher amount of cracks than test pieces from cross direction. This occurs on the material with foam backing regardless of the ageing time.

This pattern was not seen when the material had been abraded with help from the Martindale. These test pieces showed no tendency to crack more in the length direction than in cross direction.

4.1.2.3 With and without foam backing

According to the test results PVC1 without foam showed a lower tendency to crack in comparison to PVC1 with foam backing. The crack formation in the materials with foam backing showed a tendency to increase when tested in length direction. Cracks in PVC1 without foam showed no pattern depending on the materials direction.

We also need to have in mind that the mechanical movement will be different on the material with foam in the flexing test, this because the materials with foam are thicker.
4.1.2.4 Abraded in Martindale before aged in 3 weeks

The materials that have been abraded in the Martindale showed a tendency to crack easier than the material that had been exposed to the same time of ageing and chemical treatment. Obvious changes in the materials surface structure were also observed, as the material got a glossier surface.

According to our results materials with foam backing have a higher tendency of cracking than materials without foam.

The differences in number of cracks, between the materials with and without foam backing, were not as obvious as with the non-abraded materials. There were no patterns of a higher amount of cracks in length or cross direction for the abraded materials.

4.1.2.5 Chemical treatment

In our limited test series, influence of chemicals on the abraded and aged material was not discovered.

4.1.2.6 References

According to our test results of PVC1, the reference that have been tested in the Ballyflex for 10 000 cycles did not show any tendency to crack.

Figure 15 shows how the references without foam looks like in a microscope with an 80x magnification.
4.2 Summary of results after 30 000 cycles in the Ballyflex

Table IX. Ballyflex testing during 30 000 cycles

<table>
<thead>
<tr>
<th></th>
<th>PVC1 with foam</th>
<th>PVC1 without foam</th>
<th>PVC2 with foam</th>
<th>PVC2 without foam</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Length</td>
<td>Cross</td>
<td>Length</td>
<td>Cross</td>
</tr>
<tr>
<td>Reference 0w</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Reference 3w</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Centoplex 3w</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Leather cleaner 3w</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Hand sweat 3w</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Reference 6w</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Centoplex 6w</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Leather cleaner 6w</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Hand sweat 6w</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>MARTINDALE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference 3w</td>
<td>2-3</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Centoplex 3w</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Leather cleaner 3w</td>
<td>5</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Hand sweat 3w</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

Grading:

1. No cracks
2. Few cracks seen with the help of a microscope, 80x magnification
3. Several cracks seen with the help of a microscope, 80x magnification
4. Few cracks seen with help from a magnifier, 6x magnification
5. Several cracks seen with help from a magnifier, 6x magnification
4.2.1 PVC2, 30 000 cycles in Ballyflex

Test results from the Ballyflex test on PVC2, that have been flexed for 30 000 cycles, showed that they had no tendency to crack. Wrinkles had developed, in some materials more than others. Other than these wrinkles we could not see any effects on PVC2 from chemical treatment, ageing, abrasion or flexing.

Figure 16 shows wrinkles on PVC2 with foam after 30 000 cycles in the Ballyflex.

4.2.2 PVC1, 30 000 cycles in Ballyflex

4.2.2.1 PVC1 – ageing

Depending on the time of ageing there is a difference in the number of cracks. As we expected the materials that have been aged for 6 weeks tend to develop more cracks than the materials that have been exposed to 3 weeks of ageing.

4.2.2.2 PVC1, cross – length direction

When the materials have been exposed for flexing in 30 000 cycles, a high amount of cracks could be seen in PVC1. According to the result from test pieces aged in 3 weeks, there was a higher amount of cracks in the length direction than in the cross direction. Test pieces exposed to abrasion before ageing in 3 weeks or test pieces that had been aged for 6 weeks did not tend to develop more cracks in length than cross direction.
4.2.2.3 PVC1 with and without foam backing

According to our results the materials that have been aged for 3 or 6 weeks before flexing with foam backing had a higher amount of cracks in comparison to the material without foam backing. This pattern could not be seen from the results of test pieces that had been abraded before ageing. Those test pieces had a high amount of cracks but it did not depend on the foam backing. Test pieces that have been abraded before ageing and flexing, without foam backing, had almost as much cracks as the ones with foam backing.

There was a difference between the materials that have been aged 3 or 6 weeks. Test pieces that have been exposed to ageing for 6 weeks had a higher amount of cracks and four of the test pieces had cracks that could be seen with the naked eye.

Figure 17 shows one of the cracks that appeared in PVC1 that have been chemical treated with centoplex before aged for 6 weeks and flexed in 30 000 cycles. This test piece had a high amount of cracks that could be seen in a microscope but also a crack that was seen with the naked eye.

4.2.2.4 Test pieces from PVC1, abraded in Martindale before aged in 3 weeks

Obvious changes in the materials surface structure were observed, as the material got a glossier surface. According to our results from microscope analysis there were many cracks in PVC1 that had been abraded before it was aged and flexed in 30 000 cycles. It was almost as many cracks as it were in the material that has been aged for 6 weeks with foam backing. We could not see a pattern of more cracks in length or cross direction, with or without foam backing.

Figure 18 shows an example of
how an abraded material will look like after 30 000 cycles in the Ballyfex. The cracks that can be seen in the figure are a common sight after this kind of chemical treatment and mechanical testing.

4.2.2.5 Chemical treatment on PVC1

The chemical treatment before ageing did not show any pattern of a higher amount of cracks depending on a specific chemical. A high amount of cracks was instead dependent on foam backing or not, time of ageing and if the material have been abraded before ageing.

4.2.2.6 References of PVC1

According to test results of reference material of PVC1 after 30 000 cycles in the Ballyflex a tendency to cracks in length direction could be seen. Some cracks could be seen in those test pieces during analyse in the microscope. There was a higher amount of cracks in PVC1 with foam backing in comparison to PVC1 without foam backing. In analyse of references in cross direction no cracks could be seen. When we compared the results with the material that have been exposed to ageing, chemical treatment and abrasion before ageing there were a big difference in the number of cracks, the pre-treated material had a much higher amount of cracks.

Figure 19 shows one of the cracks in the references of PVC1 with foam.
4.3 Extraction

The results from this analysis were an increase of each flask's weight. Which shows that some of the substances, possibly plasticisers, are still left in the PVC but also that some has migrated into the foam, see Table X.

Table X. Soxhlet-extraction results, from PVC1

<table>
<thead>
<tr>
<th>Material (PVC1)</th>
<th>Weeks of ageing</th>
<th>Weight, of the flask, before extraction (gram)</th>
<th>Weight, of the flask, after extraction (gram)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUR Foam</td>
<td>0</td>
<td>103,5380</td>
<td>103,7498</td>
</tr>
<tr>
<td>PUR Foam</td>
<td>3</td>
<td>122,5000</td>
<td>122,8244</td>
</tr>
<tr>
<td>PVC</td>
<td>0</td>
<td>108,7857</td>
<td>109,7157</td>
</tr>
<tr>
<td>PVC</td>
<td>3</td>
<td>102,0187</td>
<td>102,9443</td>
</tr>
<tr>
<td>PVC</td>
<td>6</td>
<td>106,5994</td>
<td>107,5176</td>
</tr>
</tbody>
</table>
5 Discussion

All of our results from the Ballyflex, Martindale and Soxhlet-extraction were evaluated and analysed. The fact that we were able to provoke cracks, in PVC1 and not in PVC2, results in an indication to why these cracks occur. Even though some of the cracks were small and only visible with a microscope the possibility that these cracks sooner or later will become visible to the naked eye is very likely. Especially as, at this stage, small cracks could facilitate the migration of plasticisers. The cracks were discovered within areas where the lacquer seems to have been affected, by the flexing, as these areas had turned into white spots. This discussion will focus mainly on the material, PVC1, that we were able to provoke cracks in. The reason for this is to find out why our experiments affected PVC1.

5.1 Different parameters impact

Some of the parameters that we believed would have an impact on the materials acted according to our assumption, such as ageing and abrasion, while the chemical treatment did not have any obvious impact on the materials. We were surprised by some of these results and the fact that some parameters, such as the foam backing, had such a significant impact.

5.1.1 Foam backing

As can be assumed from our results PVC1, with foam backing had high ratings from the Ballyflex evaluation. Due to the solubility of plasticisers the direct presence of foam seems to have a big impact. As the plasticisers possibly has started to migrate to a more attractive environment such as the foam.

During the flexing material with foam backing have a different radius compared to material without foam backing. This will lead to another mechanical impact from the flexing test on the material with foam backing. This could be the reason why the material tends to crack more easily than the material without foam backing. The effects on PVC1, with foam backing, were more significant during 30 000 cycles than in 10 000.

Another reason to why PVC1 tend to crack can be that PVC1 consist of ether based polyurethane foam instead of ester based polyurethane foam which PVC2 consist of.

5.1.2 Number of cycles

All together the results from 30 000 cycles in the Ballyflex showed a considerable effect on the outcome in comparison to 10 000 cycles. This was not a surprising result, as it seems more natural.
5.1.3 Chemicals

The impact of chemicals was surprisingly low. Due to our results the variation of impact from each chemical were random. The reason for the chemical treatment was to find out if the plasticisers migrated easier, when they were exposed to substances that they are soluble in. One reason to why the chemicals did not make any impact on the material could be that the chemicals require more time to affect the material.

5.1.4 Direction

The results from this test vary a lot and an obvious indication cannot be seen. The results from our tests in 10 000 cycles were more univocal, were the materials aged for 3 respectively 6 weeks showed a tendency to crack more within the length direction. This problem is a result from the materials elasticity in that direction, which will affect the PVC more. When the test pieces where exposed to 30 000 cycles the tendency of cracking more in length direction were no longer obvious. On the other hand the results between length and cross direction were either more in length or equal. This might be an indication and an intense study within this area might have given us a more obvious outcome.

5.1.5 Abrasion

During this test we wanted to accomplish a simulation of the kind of abrasion a material would be exposed to during use, in real life. We believed that if the materials were abraded the lacquer that acts as a barrier would be weakened. This would facilitate the migration of plasticisers, as they no longer have a layer that function as a wall for their transportation away from the material.

The results showed that the abrasion made the outcome more equal between the materials with and without foam. By comparing the abraded test pieces, aged for 3 weeks, with the non-abraded test pieces, aged for 3 weeks, we can get an idea about the impact of abrasion. The abraded materials were more prone to crack than the only aged material. This might be an indication that abrasion is a contributing cause to the cracks.

5.1.6 Ageing

The materials that were aged for 3 weeks did not crack as much as the ones that were aged for 6 weeks. This might be because that the 6 weeks aged material has had a longer simulated lifetime. This has possibly given the plasticisers more time to migrate, possibly into the foam, which results in a more rigid and thereby weakened material.
5.1.7 Structure

Another reason to why PVC1 seems to crack more easily than PVC2 could be that PVC1 have a more embossed surface than PVC2. This could result in a bigger impact from the thermal and mechanical treatments.

5.1.7 Extraction

These tests, to some extent, verify our test results from the mechanical tests. The results from these tests showed that plasticisers might have migrated into the foam. This is a possible reason to why PVC1 cracks, if the content of plasticisers within the PVC have decreased.
6 Conclusions

Our aim with this study was to see if we were able to provoke cracks in two different PVC coated fabrics. Through this, we could be able to see when and why cracks appear in PVC1 and PVC2.

After we had done a literature study on PVC and plasticizers, its advantages and disadvantages, we started to design an experimental part that we believed could provoke cracks in our materials. By performing some mechanical and chemical tests on those materials we could be able to see if we could provoke cracks and if PVC1 or PVC2 developed cracks easier than the other.

Our results showed that PVC1 develops cracks, which appeared in an early stage of the mechanical testing in the Ballyflex machine. There were some factors that affected the material negatively when it came to develop cracks, foam backing, ageing and abrasion seems to affect the material in a way that resulted in more cracks.

PVC2 did not develop any cracks during our testing and therefore appear to be more suitable to use in items that are exposed to those kind of mechanical and chemical environments. In a comparison with PVC1 we could see a big difference in the materials, PVC2 did not show any major impact from different kinds of treatment and mechanical testing. Based on these facts PVC2 is a better material than PVC1.

We believe that our test method with ageing and abrasion is a suitable method to provoke cracks in those kinds of items. During our study we could see that both abrasion and ageing have a huge impact on PVC1 but do not affect PVC2 more than that wrinkles are developed. The chemicals that we treated our materials with, before ageing, did not show any impact on the materials.

A test method combining mechanical treatment such as flexing, abrasion and thermal treatment seems to be a proper test method to evaluate PVC coated items.
7 Suggestions for further work

Cracking PVC is a very complex problem and a larger study would have been interesting to perform. Mostly referring to the fact that we were only able to test one piece of each material. During this study we have run into a number of possible causes that would be very rewarding to investigate more focused. Here are the ones most mentionable:

- A comparison between the two materials $T_g$, to see whether it affects the materials tendency to crack, is an interesting point of view. With the help from the chemical group at VCC we did get some test results, which showed that PVC1 have a higher $T_g$ than PVC2. This can be one of the reasons why PVC1 tend to crack easier.
- During our study we noticed that the carrying textile on PVC1 did not have a good adhesion to the PVC layer. While PVC2 has a much better adhesion between the carrying textile and PVC layer. This might be another reason to why PVC1 cracks.
- We believe that PVC1 might have a high content of secondary plasticisers. Secondary plasticisers are meant to be used in a smaller percental portion than primary. When they are used in higher proportion they tend to exudate, if this happens it becomes almost like an oil layer between the PVC and textile, which will decrease the adhesion.
- During our study we briefly consider how the presence of foam affects the migration of plasticisers. This area could beneficially be studied more closely, for example by the help from extraction and GC-MS methods. The fact that the PVC1’s foam contains ether, which has lots of dipoles, makes this theory possible
- Study the differences between different lacquers, to see why and if one lacquer is a better barrier than the other.
- A clear requirement specification for testing can be developed so that the cracks can be discovered on the same premises and at an early stage, for all PVC materials.
- From our results we can conclude that the abrasion from the Martindale had a substantially impact, mostly on PVC1 with foam aged for 3 weeks. Therefore it would be interesting to see the results from abraded materials that were aged for 6 weeks instead.
- In our study did we not test the material with foam backing without the foam in the Ballyflex machine. This could have an affect on our results. To see if the material with foam backing crack, as much as it did, without the foam backing, could be an important test for further work.
- Study the difference between ether and ester based polyurethane foam. Do the ether-based foam make plasticisers migrate more easily?
8 References

8.1 Literature


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8.2 Articles


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DR. GRAZIANO, LOUIS C and SJÖSTRAND, SVEN ERIK, 1986, development of acrylic latex pressure sensitive adhesive for plasticized PVC films, Journal of plastic film and sheeting, Volume 2

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8.3 Standards

CORPORATE STANDARD STD 1024,7122, 1994, Issue 2, VOLVO, Sweden
9 Appendix

9.1 Appendix A - Project time table

<table>
<thead>
<tr>
<th>Week</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<tr>
<td></td>
<td>Literature studies</td>
<td>Experiments</td>
<td>Report writing</td>
<td>Presentation preparation</td>
<td>Poster making</td>
<td></td>
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</table>

- Week 1: Literature studies
- Week 2: Experiments
- Week 3: Report writing
- Week 4: Presentation preparation
- Week 5: Poster making
9.2 Appendix B - Material declaration (only available for VCC)
9.3 Appendix C – Ballyflex standard

1. SYFTE & ANVÄNDNING

Testmetoden enligt denna norm tjänar till att bedöma veckningsegenskaperna vid upprepad veckning hos lärder och lårrets täckskikt och även hos konstläder och andra liknande material enligt DIN 16 922. Metoden passar bara för sådana produkter som utan tvång kan spännas in i testapparaten och och där provstycket kan veckas ihop och isår under försök.

Som mått för veckningsegenskaperna tjanstgör veckningsstalet(se p 2) eller provstykkenas utseende efter ett överenskommnet antal veckningar.

2. BEGREPP


Med synliga förändringar eller defekter menas

a) på lärder:
   - Bildning av stora narveck ("flytande narv")
   - Att en pressnarv försvinner
   - Brott i narvskiket
   - Förstöring av lärdefibrerna så att det bildas en krater, en spricka eller ett hål.

b) på lårrets täckskikt:
   - Ändring i färgnyansen (täckskiket blir grått eller någon annan defekt)
   - Brott i täckskiket
   - Täckskiket lossnar från lärret med eller utan färgändring på det
   - Separation mellan två täckskikt(utsläppning)
   - Täckskiket faller sönder.

c) på konstläder och liknande material:
   - Sprickor i täckskikt
   - Separation mellan olika skikt
   - Ändring av färgnyansen (täckskiket blir grått eller någon annan defekt).

3. KORT BESKRIVNING AV METODEN

Det veck, som bildas i provstykret vid inspänning, går isär och ihop igenom att den ena klämman vrids fram och tillbaka.

4. BETECKNING FÖR METODEN

Dauerfaltverhalten(veckningsegenskaper vid upprepad veckning) DIN 53 351 - A

5. APPARATER

Testanordningen består av en rörlig övre klämma enl bild 1 t o m 3 och en fast undre klämma enl bild 4.

Allmänna toleranser DIN 7168 - m
Bägge fastspänningsklämmorna måste vara i samma plan. Den rörliga klämman måste kunna svänga i 22,5° runt centrumpunktten A. Man måste även kunna svänga den för hand och svängningsarna måste vid motordrift under testing uppgå till 100-155 svängrörelser i minuten. När de två klämmorna står parallellt uppgår avståndet mellan den undre klämman överkant och kontaktytan L på den övre klämman (se bild 1 och bild 8) till 25 mm.

Bild 1. Övre klämman (hoptryckt)

Bild 2. Övre klämman (läge nr 2) med kontaktyta.

Bild 3. Övre klämman (läge nr 1)


Bild 5. Provstycke.

Bild 6. Provstycke, som är fastspänt i den övre klämman.

Bild 7. Inspänt provstycke med fri ända.
6 PROVER

6.1 Urskärning av provstycken och provbitar

6.1.1 Läder

Man skär ur provbitar enl DIN 53 302 del 1. Av dessa provbitar, som klimatiserats enl DIN 53 303 del 1, framställer man provstycken med ett mått av 70 mm x 45 mm. Anm: Man kan med avvikelse från denna norm använda provstycken enl bild 5 i vissa fall, som beskrivs i p 7, annm. 2.

6.2 Antal provstycken

För läder måste man testa minst 2 provstycken som tas ut ur provbitarna i lodrät riktning i förhållande till varandra, varvid den ena av riktningarna måste gå parallellt med rysglinjen, om denna är bekant. För konstläder måste man skära ut minst 3 provstycken längs efter och tvärs över tillverkningsriktningen för materialet i fråga.

6.3 Preparation av provstycken

Före testet anpassas provstyckena till normalt klimatet DIN 50 014 - 23/50 - 2, för läder enl DIN 53 303 del 1 och för konstläder enl DIN 16 906(f n utkast).

Om lädet skall testas i vått skick så gör man på följande sätt:

Provet görs i normalklimat enl DIN 50 014 - 23/50 - 2

Det enl p 6.3 preparerade provstycket viks på mitten så att den sida, som skall bedömas, ligger inåt och så att de längre kanterna är i jämnhög med varann.

Sen spänner man – vågrätt – in det vitka provstycket i den rörliga klämmen, som måste vara parallell med den fasta klämmen, på så sätt att det provstycket går mot spännstruten och ligger på på listen (se bild 6).

Provet görs i normalklimat enl DIN 50 014 - 23/50 - 2

Det enl p 6.3 preparerade provstycket viks på mitten så att den sida, som skall bedömas, ligger inåt och så att de längre kanterna är i jämnhög med varann.

Sen spänner man – vågrätt – in det vitka provstycket i den rörliga klämmen, som måste vara parallell med den fasta klämmen, på så sätt att det provstycket går mot spännstruten och ligger på på listen (se bild 6).

Provet görs i normalklimat enl DIN 50 014 - 23/50 - 2

Det enl p 6.3 preparerade provstycket viks på mitten så att den sida, som skall bedömas, ligger inåt och så att de längre kanterna är i jämnhög med varann.

Sen spänner man – vågrätt – in det vitka provstycket i den rörliga klämmen, som måste vara parallell med den fasta klämmen, på så sätt att det provstycket går mot spännstruten och ligger på på listen (se bild 6).

Man undersöker provstyckena antingen efter överenskommelse antal svängningar eller fortlöpande efter varje i tabellen bestämt antal veckningsbelastningar genom observation med en 6 ggr förstorande lupp med avseende på synliga förändringar eller defekter (se p 2).
Vid observation kan man i förekommande fall svänga den rörliga klämman långsamt eller också ta ut provstycket ur testapparaten. I det senare fallet måste man sätta in provstycket i apparaten igen i precis samma läge som förut (se ann. 2).

| Antal veckningsbelastningar för bedömning av provstycken (rekommer.) |
|--------------------------|----------------|----------------|----------------|----------------|
|                          | 200            | 315            | 500            | 800            |
| 1 250                    | 2 000          | 3 150          | 5 000          | 8 000          |
| 12 500                   | 20 000         | 31 500         | 50 000         | 80 000         |
| 125 000                  | 200 000        | 315 000        | 500 000        |                |

Anm. 1: Antalet veckningsbelastningar, som är utgångspunkt för bedömning, är uppdelade enl. den geometriska serien R 10 i enlighet med DIN 323 del 1.

Anm. 2: Många provstycken får märken av klämmornas tryckställen. Många provstycken töjs också ut under veckningen och får inte spännas vid förnyad fastsättning. För exakt förnyad inspänning rekommenderar vi provstycken enl. bild 5, där den övre och den undre klämman är försett med motsv. stift.

Om testapparaten stängs av för länge tid – t ex under en natt – med isatt provstyrke så måste klämmorna stå så att inte provstyrket är helt sträckt.

Vid testning av våta provstyrken får testapparaten endast stoppas så länge som är ovanligligen nödvändigt för att kunna kontrollera provstyrket.

8. TESTRAPPORT

I testrapporten skall man med hänsyn till denna norm ange följande:

a) Art & beteckning för provad produkt;

b) Antal testade provstyrken;

c) Uppgifter om provstyrkens placering i provbiten.

d) Testbetingelser, t ex våta prover;

e) Typ av synliga förändringar resp.

f) Defekter efter överenskommemt antal veckningsbelastningar, eller

g) veckningsstal, särskilt för varje prov;

h) Betingelser, som avviker från denna norm;

i) Testdatum.

CITERADE NORMER

DIN 323 del 1 (f n utkast) Normalta & normaltalsierer; huvudvärden, exakta värden, närmevärden.

DIN 7168 del 1 Allmänna toleranser; längd- & vinkelmått.

DIN 16 906 Testning av plastdukar; prov & provstyrke, urtagning, preparation, testklimat.

DIN 16 922 Böjliga & dukliknande material, som framställts av plast; teknologisk indelning.

DIN 50 014 Klimat och dessas tekniska användning; normalklimat.

DIN 53 302 del 1 Prövning av lätter; provtagning för fysikaliska prov.

DIN 53 303 del 1 Prövning av lätter; provpreparation; anpassning till normalklimat och snabbåldring för fysikaliska prov.

YTTERLIGARE NORMER

DIN 53 353 Prövning av konstläder & liknande platta material; bestämning av tjocklek med mekaniska avknäppningsinstrument.
FÖRKLÄRINGAR

Denna norm har utarbetats av FNK:s underutskott 403.4 "Kunstleder" i samarbete med NMP:s arbetsutskott 551 "Prüfung von Leder". Testmetoden kan ej användas i de fall det - p.g.a materialets egenskaper som t.ex tjocklek och styvhet - ej kan utbildas något löpande veck under veckningsrörelserna. Veckningstalen, vid vilka man skall bedöma provstycke, följer den geometriska serien R 10 enl DIN 323 del 1. Som bekant är det i princip ej meningsfullt att bedöma vecknings- eller böjningsegenskaper - efter upprepade rörelser - i förhållande till aritmetiska serier.

För att uppnå tillräcklig reproducerbarhet av mätresultaten är det nödvändigt att mätten på apparatens delar och hastigheten i svängrörelserna exakt motsvarar angivelserna i denna norm. Lika viktigt är det att följa föreskriftern för normalklimat och att spänna in provstycken på ett korrekt sätt.

International patentklassificering

G 01 N 3/20
G 01 N 33/44
9.4 Appendix D – Microscopy pictures
9.4 Appendix E – Microscopy pictures