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TAMPERE UNIVERSITY OF TECHNOLOGY

ANNE VEHMASVAARA
AGEING OF POLYMERIC FLOORINGS AND FLOOR ADHESIVES
IN ALKALINE AND HUMID ENVIRONMENT

Master of Science Thesis

Examiner: Asst. Prof. Essi Sarlin
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ABSTRACT

ANNE VEHMASVAARA: Ageing of Polymeric Floorings and Floor Adhesives in Alkaline and Humid Environment

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Plastic floorings, especially PVC (polyvinyl chloride) floorings, are popular and they are widely used both in private apartments and in public buildings. Yet, the use of PVC floorings has led to deterioration of indoor environment. Alkaline moisture of the concrete accelerates the aging of adhesive and flooring and volatile organic compounds (VOCs) are formed in the degradation process. Accomplice for the VOC emissions are the plasticizers used in PVC floorings. The development of the adhesives has led to new challenges, as the floorings detach due to their poor moisture resistance.

The aim of this thesis was to define where exactly and why the detachment occurs and to screen the suitability of different research methods for observing the changes in the materials that lead to the detachment. The experimental study of the thesis consisted of two parts – accelerated ageing tests and a case study. In the accelerated ageing tests, adhesive and flooring samples were immersed in solutions of different alkalinity and the aim was to study if immersion tests could be used for ranking of different materials in a simple, fast and effective way. The materials that were tested were acrylic dispersion and alkali-resistant adhesive, two homogeneous PVC floorings with different plasticizers and a heterogeneous flooring. The immersion solutions were NaOH solution (pH 13.0), concrete solution (pH 12.5) and ion-exchanged water (pH 6.0). Changes in the chemical structure and thermomechanical properties were studied.

The case study was performed in a Finnish school building, that is closed due to indoor environment related problems. The goal was to compare the attachment of the floorings in damaged sites to undamaged sites and to define the failure mode when the flooring was ripped off.

The result of the accelerated ageing was, that is not usable as such. The changes in T_g or onset temperature of degradation were very small and behaviour models in solutions of different alkalinities could not be created. Only the alkali-resistant adhesive showed a clear decrease in the onset temperature of degradation in NaOH solution, but it could not be confirmed, if it was it the higher pH or the composition of NaOH solution that caused the changes.

Pull-off tests showed that the pressure needed for detaching the flooring is much less on the damaged (high relative humidity, RH) sites than the undamaged sites. The surprising result of the failure mode inspection was that it was highly dominated by the cohesive failure in the screed, which hints that the detachment may not, after all, result neither from the adhesive nor the flooring. Thus, the role of the screeds should be studied more.

TIIVISTELMÄ

ANNE VEHMASVAARA: Muovisten lattiapäällysteiden ja lattialiimojen vanheneminen alkalisessa ja kosteassa ympäristössä

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Muovimattoja, erityisesti PVC-mattoja, käytetään yleisesti lattioiden päällystämiseen niin julkisissa tiloissa kuin yksityisissä asunnoissakin. Niiden käyttö on kuitenkin aiheuttanut sisäilmaongelmia, mikä johtuu alkalisesta kosteudesta betonista liimaan ja mattoon. Betonista nouseva alkalinen kosteus kiihdyttää liiman ja maton vanhenemistä ja hajoamisreaktioissa haihtuvia orgaanisia yhdisteitä (*VOCs, volatile organic compounds*) vapautuu sisäilmaan. Osa VOC-päästöistä johtuu PVC-lattioissa käytetyistä pehmittimistä. Ongelman parantamiseksi tehty liimojen materiaalikehitystyö on johtanut uusiin haasteisiin, kun matot irtoavat niiden heikon kosteudenkestävyyden takia.

Tämän diplomityön tavoite oli määrittää, mistä mattojen irtoaminen johtuu ja missä kohdassa rakennetta irtoaminen tapahtuu, sekä löytää sopivia menetelmiä maton irtoamiseen johtavien muutosten havaitsemiseen. Työn kokeellinen osuus koostui kahdesta osiosta – nopeutetusta vanhentamisesta ja tapaustutkimuksesta. Nopeutetussa vanhenemiskokeessa liima- ja mattonäytteet upotettiin alkalisuudeltaan erilaisiin liuoksiin ja tavoite oli tutkia, voidaanko upotuskoetta käyttää eri materiaalin järjestämiseen paremmuusjärjestykseen yksinkertaisella ja kustannustehokkaalla menetelmällä. Testattavat materiaalit olivat akryylidisperioliima, alkalinkestävä liima, kaksi homogeenista mattoa eri pehmittimillä ja heterogeeninen matto. Upotusnesteessä käytetyt liuokset olivat NaOH-liuos (pH 13,0), betoniliuos (pH 12,5) ja ionivaihdettu vesi (pH 6,0). Tutkimus keskittyi näytteiden kemiallisen rakenteen ja termomekaanisten ominaisuuksien muutosten havainnointiin.

Tapaustutkimus suoritettiin suomalaisessa koulurakennuksessa, joka on suljettu sisäilmaongelmien vuoksi. Tavoite oli verrata adheesio- ja vaurioituneessa kohdassa vaurioitumattomaan kohtaan ja määrittää murtumistyyppi lattiasta revityistä näytekappaleista.

Tuloksena nopeutetuista vanhenemistesteistä saatiin, ettei upotustesti sovellu sellaiseen materiaalien alkalinkestävyyden vertailuun. Muutokset T_g :ssä ja lämpötilassa, jossa hajoaminen alkaa, olivat pieniä eikä testimateriaalien käyttäytymistä eri alkalisissa liuoksissa ei voitu mallintaa. Ainoastaan alkalinkestävällä liimalla hajoamislämpötila NaOH-altistuksen jälkeen laski selkeästi. Testillä ei voitu kuitenkaan varmistaa johtuiko hajoamislämpötilan lasku liuoksen pH:sta vai sen koostumuksesta.

Pull-off testit osoittivat, että maton irtoamisherkkyys oli huomattavasti suurempi vauriokohdissa eli kohdissa, joissa lattian suhteellinen kosteus (RH) oli korkea. Yllättävä tulos murtumatyyppianalyyseissä oli, että kohesiivinen murtuma tasoitteessa hallitsi voimakkaasti, minkä perusteella mattojen irtoamisen syy ei ehkä olekaan liimassa eikä matossa. Tasoitteen roolia mattojen irtoamisessa olisi siten syytä tutkia lisää.

PREFACE

The topic of this Master of Science Thesis is received from the Laboratory of Materials Science and it is implemented in collaboration with the Laboratory of Civil Engineering.

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CONTENTS

1.	INTRODUCTION	1
2.	TYPICAL STRUCTURE OF POLYMER FLOORINGS.....	3
	2.1 Concrete	3
	2.2 Primer.....	3
	2.3 Screed.....	4
	2.4 Adhesive	4
	2.5 Plastic flooring	5
3.	AGING AND DEGRADATION OF POLYMERS	7
	3.1 Degradation due to moisture	7
	3.2 Thermal degradation	8
	3.3 Ultraviolet light degradation	10
	3.4 Oxidation.....	10
	3.5 Microbiological and enzymatic degradation.....	11
	3.6 Environmental stress cracking	12
	3.7 Artificial aging	13
4.	DEGRADATION OF FLOORING SYSTEMS	14
	4.1 Conditions in flooring systems	14
	4.1.1 Alkalinity and humidity of concrete	14
	4.1.2 Carbonation of concrete.....	16
	4.1.3 Water vapour transmission properties of plastic floorings	16
	4.2 Degradation of plastic floorings.....	17
	4.2.1 Plasticizers, their migration and susceptibility to hydrolysis	17
	4.2.2 Phthalates and their alkaline hydrolysis.....	18
	4.3 Degradation of adhesives	19
	4.3.1 Adhesives and water	19
	4.3.2 Acrylic adhesives.....	19
	4.3.3 Tackifiers and thickeners in adhesives	20
5.	ADHESION	21
	5.1 Fracture mechanisms of adhesive bonds.....	21
	5.2 Adhesive bond testing.....	22
	5.2.1 Peel test	22
	5.2.2 Pull-off test	23
6.	RESEARCH METHODS AND MATERIALS.....	24
	6.1 Accelerated aging in laboratory environment.....	24
	6.1.1 Samples and solutions.....	26
	6.1.2 Preparing alkaline solutions.....	26
	6.1.3 The exposure.....	27
	6.2 Case study	27
	6.2.1 Pull-off tests	28
	6.2.2 Fracture mechanisms	29

7.	RESULTS AND ANALYSIS.....	30
7.1	Accelerated aging in laboratory environment.....	30
7.1.1	Changes in chemical structure of the adhesives and floorings	30
7.1.2	Ageing of the adhesives as a function of exposure time.....	31
7.1.3	Ageing of the floorings as a function of exposure time.....	34
7.1.4	Rotational rheometry	38
7.2	Case study	42
7.2.1	Pull-off tests.....	42
7.2.2	Fracture mechanisms	44
8.	CONCLUSIONS	46
	REFERENCES	47

APPENDIX A: TGA results for alkali-resistant and acrylic dispersion adhesives

APPENDIX B: DMTA and TGA results for the floorings

LIST OF SYMBOLS AND ABBREVIATIONS

ω	Angular frequency
$ \eta^* $	Complex viscosity (absolute value)
2-EH	2-ethylene-1-hexanol
ATR	Attenuated total reflectance
Ca(OH) ₂	Calcium hydroxide
CaCO ₃	Calcium carbonate
CO ₂	Carbon dioxide
DEHA	Bis-2-ethylhexyl adipate
DEHP	Di-2-ethylhexylphthalate
DEHT	Di-2-ethylhexyl terephthalate
DGD	Dipropylene glycol dibenzoate
DIDP	Diisodecyl phthalate
DINCH	1,2-cyclohexane dicarboxylic acid diisononyl ester
DINP	Diisononyl phthalate
DMTA	Dynamical mechanical thermal analysis
DSC	Differential scanning calorimetry
ESC	Environmental stress cracking
FTIR	Fourier transform infrared spectroscopy
G'	Storage modulus
G''	Loss modulus
H ₂ CO ₃	Carbonic acid
H ₂ O	Water
HCl	Hydrogen chloride
HALS	Hindered amine light stabilizer
kPa	Kilopascal
MMA	Methyl methacrylate
N ₂	Nitrogen molecule
Na ⁺	Sodium ion
NaOH	Sodium hydroxide
OH ⁻	Hydroxide ion
PATTI	Pneumatic adhesion tensile testing instrument
PE	Polyethylene
PP	Polypropylene
PUR	Polyurethane
PVC	Polyvinyl chloride
RH	Relative humidity
tan δ	Damping factor
T _g	Glass transition temperature
TGA	Thermogravimetric analysis
UV	Ultraviolet light
UVA	Ultraviolet light absorber
VOC	Volatile organic compound

1. INTRODUCTION

Plastic floorings, especially PVC (polyvinyl chloride) floorings, are popular and they have been used for decades due to their durability and high resistance to environmental stresses. PVC floorings can be used both in private apartments and in public buildings, such as offices, schools and hospitals, where durability, as well as inexpensive and easy maintenance is of high importance. (Pacheco-Torgal *et al.* 2012, p. 29)

Despite the numerous advantages of plastic floorings, troubles with indoor environment have been encountered in places where plastic floorings are used. The problem lies either in the plastic flooring itself or the adhesive that is used for attaching it. In plastic floorings, plasticizers are used in order to provide flexibility and damping. Traditionally, phthalates have been used as plasticizer but due to their toxicity and tendency to leach or emit from the plastic into the surrounding environment, they are widely replaced with less hazardous plasticizers. Despite the change of phthalates to phthalate-free plasticizers, the harmful emissions are not completely eliminated. (Pacheco-Torgal *et al.* 2012, p. 30)

Solvents have been the main cause for volatile organic compound (VOC) emissions of the flooring adhesives and they can cause health effects and deteriorate indoor environment. Nevertheless, solvent-based adhesives are nowadays replaced with water-based and solid adhesives, which reduce the environmental impact. Still, VOCs can be released from the adhesive due to hydrolysis of the side groups. (Nelson & Hopps 2012, pp. 447–450; Anderberg & Wadsö 2007)

Water-based adhesives are less durable and more moisture sensitive than solvent-based adhesives. These durability and moisture issues have brought up new challenges in the form of unfastening of the plastic floorings even in newly built public buildings, such as schools and hospitals. This problem is met commonly in Finland and other Nordic Countries. Concrete contains always moisture and this alkaline moisture also induces degradation of adhesive or the flooring thus releasing or producing degradation products such as VOCs. (Nelson & Hopps 2012, pp. 447–450)

The cause of unfastening is the exposure of plastic flooring and adhesive to alkaline and humid conditions that are created by the concrete. The humidity of the concrete can be decreased by prolonging or accelerating the drying phase, whereas alkalinity can be decreased with screeds. Yet, neither the humidity nor the alkalinity can be completely removed if the building schedule is reasonable. (Merikallio *et al.* 2007, Nelson & Hopps 2012)

The focus of this thesis is on the flooring failures – where exactly the failure occurs and why. In theory section, the structure and some typical properties of a flooring system, the ageing mechanisms of polymers and adhesion testing are presented. The experimental part of the thesis is presented in chapter 6. During the project, the original test plans had to be changed, as the artificial ageing of the laboratory test specimens, which was done elsewhere, took longer than expected. Thus, the aims of the experimental part of the work were to study if immersion tests could be used to rank of different materials in a simple, fast and cost-effective way and to study the ageing mechanisms, adhesion strength and failure modes of polymeric components from samples ripped from public buildings.

The ageing of the floor adhesives and the floorings, as well as their resistivity to alkaline moisture have been generally studied via VOC emissions. In this thesis, different thermal analysis methods and mechanical testing are used and their usability in defining degradation of the adhesives and floorings are considered.

2. TYPICAL STRUCTURE OF POLYMER FLOORINGS

Flooring can be considered as a layer structure, in which the basis of the structure is concrete. Concrete is treated with primer and levelled with screed. Flooring is then installed by using adhesive. (Björk *et al.* 2003; Anderberg & Wadsö 2007) The structure of the floor is illustrated in figure 1.

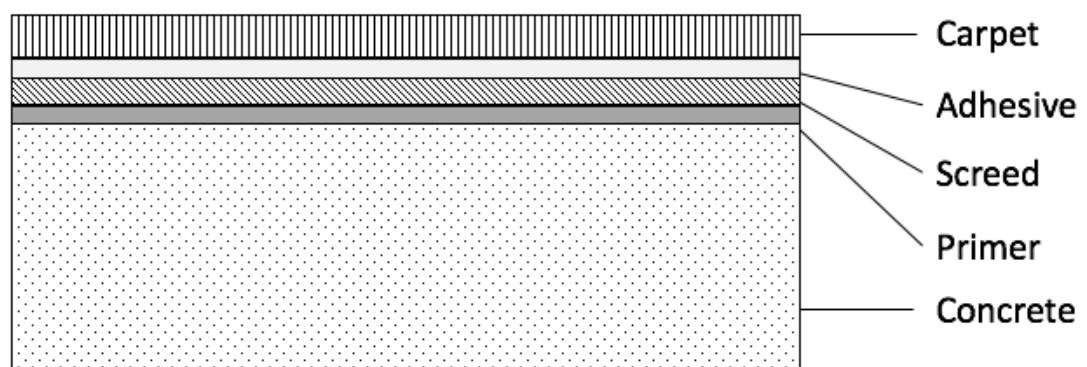


Figure 1. Floor structure.

2.1 Concrete

Concrete is an artificial mass that consists of cement, water and gravel. Additives can be used to modify the properties of the concrete. After curing, a concrete forms a rock-like structure with great compression strength and wear resistance. In addition, concrete is non-combustible material and due to these and many other of its properties it is one of the most used material in construction engineering. (Uusitalo *et al.* 1990, pp. 8–9)

In order to achieve a high quality concrete floor, the concrete mass should contain as little water as possible to minimize shrinkage and separation of materials. Small water-cement ratio also increases the strength of concrete but makes processing of it more challenging. Drying of the concrete can be accelerated by minimizing the water content, increasing porousness, using appropriate working methods during casting and by improving the de-hydration conditions. (Lindberg *et al.* 2002)

2.2 Primer

Primer is used on the concrete to improve the adhesion between the screed and the concrete. Generally, the primers are water-dilutable emulsions that form a transparent film

onto the concrete. In addition to increased adhesion, the primer treatment also prevents air bubble formation and hinders the absorption of the water of the screed into the concrete. (Lindberg *et al.* 2002)

On a more general perspective, primers are often used between the substrate and an adhesive or a sealant. The advantages of using primers can be, for example, controlling the free surface energy to improve wettability, dissolution of organic contaminants of the surface to prevent weak boundary layer formation, to intensify the chemical reactions between the substrates and to improve corrosion resistance during operating time. In addition, due to low viscosity of primers, they can penetrate porous materials thus improving mechanical interlocking. (Petrie 2006, pp. 195–196)

2.3 Screed

The purpose of the screed is the levelling of the roughness of the concrete surface and to decrease the alkalinity of the interface (Lindberg *et al.* 2002; Björk *et al.* 2003). Usually the screed is cement based material with additional polymers to improve the spreading. Most screeds withstand high humidity of concrete, but due to sensitivity of the floor coverings, the concrete is generally let to dry in certain level of relative humidity (RH) before applying the screed. (Lindberg *et al.* 2002) It is also notable, that applying the screed wets the surface dry concrete, so when estimating the drying time, both the screed and newly watered concrete must be taken into consideration (Suomen Betoniyhdistys 2015, s. 43).

Using low-alkaline screed reduces the risk of degradation of adhesive and flooring, which reduces the secondary emissions caused by alkaline humidity. (Eronen *et al.* 1998, Anderberg & Wadsö 2007) The term secondary emission is used for emissions that are produced by the chemical reactions between the product and the environment, whereas primary emissions are released directly from the product (Metiäinen 2009). Additionally, levelling works as a blotter that absorbs the solvent water of the adhesive thus letting the water-based adhesive to cure (Nelson & Hopps 2012, p. 545).

2.4 Adhesive

Adhesive refers to material that is applied to surfaces to form a permanent bonded joint. The adhesive is capable of forming bonds to the articles and the process is called an adhesive bonding process. (Ebnesajjad 2008)

The purpose of the adhesive in this study is to bond the flooring onto the screed. The selection of an appropriate adhesive is based on the application, as well as the base and flooring material. For example, water soluble dispersion adhesives, contact adhesives and two-component polyurethane adhesives can be used. The water vapour transmission of the adhesives vary but usually they are relatively impermeable. Adhesion between the base and flooring materials can deteriorate due to the alkaline humidity of the concrete.

(Lindberg *et al.* 2002) Adhesives and adhesion are discussed more in the chapters 4.3 and 5.

2.5 Plastic flooring

The most used polymers in plastic floorings are polyvinyl chloride (PVC), polyurethanes (PUR) and polyolefins. PVC and PUR have been criticized due to the effects they have for the environment, whereas polyolefins, such as polyethylene (PE), polypropylene (PP) and their mixtures are eco-friendlier if the additives that are used are acceptable. The biggest drawbacks of polyolefins as a flooring material are the more complicated maintenance and lower wear resistance compared to other plastic floorings. The preparation of sub-floor is also more demanding when polyolefins are used. Polyolefin floorings are not used in wet rooms due to their poor sealing ability. Even though the edges of the flooring are sealed with polyolefin weld rod, the seals will not be tight enough to be used in wet rooms. (Bokalders & Block 2009, p. 71)

The structure and thickness of the plastic floorings can differentiate. Traditionally, the floorings have been divided into homogeneous, layered or heterogeneous structures (figure 2). Homogeneous structures consist of only one component, whereas layered and heterogeneous structures contain layers. In layered structures, the lower layer consists of a homogeneous matter and it is covered by wearing course that is usually PVC or PUR. To improve the wear resistance of polyolefin floorings, wearing surface of PUR or acrylate can be added (Bokalders & Block 2009, p. 71). Usually the thickness of the wearing course is 0.2-0.8 millimetres and the thinnest wearing courses are used in sanitary cabins. Heterogeneous floorings can also have a wearing course of PVC or PUR reinforced PVC, but the base layers are heterogeneous. The base layer can, for example, contain an impact sound insulation. (Heikkilä *et al.* 2010, pp. 58–60)



Figure 2. Schematic picture of the cross-sections of different flooring types: a) homogeneous structure, b) layer structure, i.e. homogeneous layer with thin wearing course of PVC or PUR and c) heterogeneous structure.

Homogeneous and layered flooring structures can be supported with a structure made of glass fibre. Homogeneous floorings are used in applications where high wear resistance

is needed, such as public buildings. When average wear resistance is needed, layer structured flooring can be used. Heterogeneous floorings are typically used when only a low wear resistance is required, i.e. in house rooms. (Heikkilä *et al.* 2010, pp. 58–60) Antistatic agents, flame retardants, antioxidants, pigments and plasticizers can be added in plastic floors to modify the properties and appearance of the flooring (Bokalders & Block 2009, p. 71).

3. AGING AND DEGRADATION OF POLYMERS

The environment affects performance of polymers and plastics and the effects may be chemical, physical or a mixture of them. The understanding of the mechanisms and effects on the materials performance is highly advantageous. Chemical aging refers to aging mechanisms that are based on a chemical, such as oxidation or hydrolysis, whereas physical degradation can be thermal, mechanical, electrical or caused by radiation. (Kutz 2005, p. 153) There are also different definitions of the ageing – e.g. Ehrenstein and Pongratz define the irreversible ageing chemical and reversible ageing physical.

3.1 Degradation due to moisture

Water can cause aging of polymers in two ways; either by hydrolysis in which the water molecule causes a reaction of plastic or by hydrogen bonding, in which the water is absorbed by a plastic (Kutz 2005, p. 153). In hydrolysis, a polymer chain is broken down in shorter chains. Each water molecule is split in two and the parts join in different molecules. (Bishop 2001) As an example, a hydrolysis of polyester is presented in figure 3.

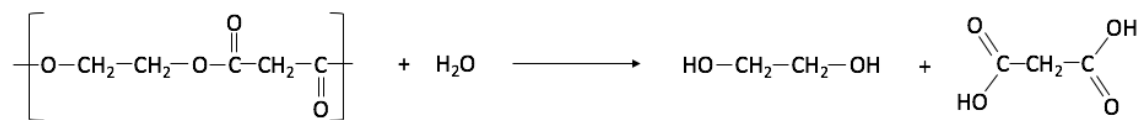


Figure 3. Hydrolysis of polyester forms diol and diacid.

The absorption of water causes swelling, leading to reduction in glass-transition temperature (T_g) and changes in crystallinity. Nevertheless, the change based on hydrogen bonding is reversible, i.e. after drying the polymer, the T_g returns to its original. That is why Ehrenstein and Pongratz define the hydrogen bonding as physical ageing. In case of hydrolysis, the reduction in T_g occurs due to bond cleavages thus being an irreversible reaction. (Kutz 2005, p. 153; Ehrenstein & Pongratz 2013, p. 55)

It is notable, that in addition to influence the polymer, water may influence the additives and fillers as well. Water is a unique media due to its ability to perform both as humidity and as precipitation. It also has the ability to wash off degradation products that would catalyze further degradation and extract water soluble additives. (Ehrenstein & Pongratz 2013 p. 54)

Many polymers, such as polyesters, polyamides, polyurethanes and polycarbonates, contain a hydrolysable linkage. Excluding some polyesters, all those polymers have a hydrolysable group in their main chain which leads to chain scission of the polymer via hydrolysis. Due to chain scission, the molecular weight of the polymer decreases rapidly and causes deterioration of mechanical properties. If the hydrolysable bond is pendant, chain scission is not based on hydrolysis and physical properties are not deteriorated if some of the pendant groups are modified. (Grassie & Scott 1988, pp. 213–214)

Enzymes, metal salts, acids and bases can act as a catalyst in hydrolysis reaction. Base catalyzed hydrolysis is also known as alkaline hydrolysis and in these processes bases are generally water solutions of alkali metal hydroxides. Alkali metal hydroxide can be, for example, sodium hydroxide (NaOH). (Kaye *et al.* 2004)

Water can also have a mechanical influence to polymer materials via hydrogen bonding reactions. Humidity changes in atmosphere can induce mechanical stresses in polymeric materials and lead to crack formation due to cyclical shrinking and swelling. Changes in the humidity of the atmosphere causes water absorption of the plastic, which leads to surface swelling while the dry core of the plastic tries to prevent swelling. This leads to formation of compression stresses on the surface and tensile stresses in the core. The magnitude of the stresses depends on the time of exposure due to the depth of the penetration increases as a function of time. The longer the time of exposure, the greater the humidity gradient between the surface and the core and the greater the stresses. (Ehrenstein & Pongratz 2013, p. 55)

3.2 Thermal degradation

Heating a polymer to a certain temperature increases molecular vibrations and it may cause random cleavage of chemical bonds. The bond cleavage can leave the polymer fragments unstable and reactive, which leads to further degradation or chemical reactions resulting a varying molecular weight. The smallest molecules may diffuse to the surface of an article. (Goldfarb *et al.* 1962)

Generally, vinyl polymers are extremely liable to thermal degradation even in relatively low temperatures. For example, dehydrohalogenation of PVC, that is discussed later, occurs approximately in 87 °C. The degradation of vinyl polymers can occur by chain scission or non-chain scission. In chain scission, the bonds in the polymer backbone break and free-radical segments are formed, whereas in non-chain scission, a double bond is formed by elimination of a molecule from substituent group. (Fried 2003, p. 264) These two mechanisms are presented in figure 4.

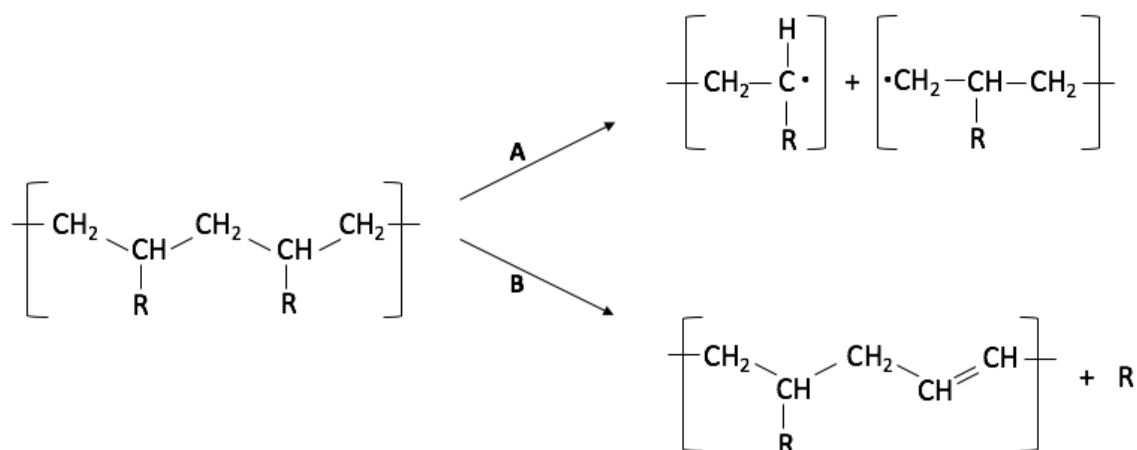


Figure 4. Thermal degradation of vinyl polymer can occur by (A) chain scission or by (B) non-chain scission mechanism. Modified from reference (Fried 2003, p. 264).

There are three different chain scission mechanisms that are random degradation, depolymerization and weak-link degradation. In random degradation, the site of chain scission is not foreseeable. In depolymerization, the ends of the polymer chains are active and they release polymer units, which gradually leads to decreased molecular weight. In weak-link degradation, the site of the breakage is based on the bonds with lowest energy. (Fried 2003, p. 265)

A common non-chain scission reaction is dehydrohalogenation, in which a bond between carbon and halogen breaks. As a consequence of the reaction, a hydrogen halide is formed. The most significant example of dehydrohalogenation is the degradation of PVC. Dehydrohalogenation of PVC occurs near to its T_g and it leads to formation of hydrogen chloride (HCl). If the dehydrohalogenation process proceeds, it eventually leads to formation of polyene, in which all the backbone bonds are replaced to double bonds. (Fried 2003, p. 267) Dehydrohalogenation process is presented in figure 5.

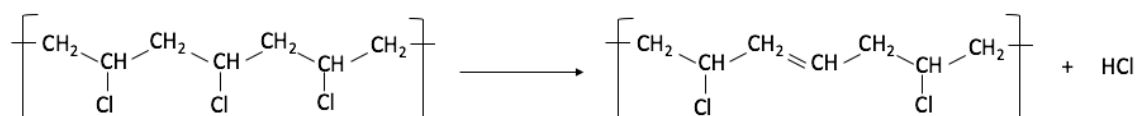


Figure 5. Dehydrohalogenation of PVC is a common non-chain scission reaction. Modified from reference (Fried 2003, p. 268).

The most thermally stable polymers are those that have highly aromatic structure, especially polymers with heterocyclic rings. Heterocyclic rings are aromatic rings that contain

some other element or elements in addition to carbon. Usually the other element is oxygen, nitrogen or sulphur. Due to high resonance stabilization energy of aromatic compounds, the strength of the main-chain bonds is high and thus they have high thermal stability. A drawback of improving thermal stability of polymers is that the same thermal stability improving factors also increases T_g and melt viscosity and reduces their solubility in common organic solvents. Thus the processing of the polymers by the most common methods can become challenging or even impossible. (Fried 2003, p. 268-269)

3.3 Ultraviolet light degradation

UV light absorbance causes polymer degradation in two mechanisms. Exposure to UV light increases thermal energy and induces thermal degradation or it causes excitation of the electrons in covalent bonds leading to higher energy level of electrons. The increase of energy level weakens the covalent bonds, which leads to easier degradation of polymer. (Strong 2006, p. 152)

Majority of UV light is originated from sunlight. The most significant difference between the energy from sunlight and the energy from thermal heating is the energy spectrum. Sunlight consists of higher energy spectrum of different intensities. Different intensities have different vibration frequencies of light energy, as for vibration frequencies are directly proportional to the energy. Because UV light frequencies locate almost in the highest part of the sunlight spectrum, the energy of UV light is high compared to other parts of the sunlight. In addition to that, the harmfulness of UV light to polymers is increased due to energy levels of UV light is similar to energy levels in most of the bonds in the polymers. (Strong 2006, p. 152)

UV light degradation can be prevented by adding materials (additives) that have high ability to absorb UV light to the polymer compound. The most used ultraviolet light absorber (UVA) is carbon black due to its low price and high UV light absorption efficiency. Carbon black is also used as a colorant or reinforcing filler but the drawback of it is, in some applications, the black color it gives to the product. Due to that, also other materials for prevention of the harm caused by UV light have been developed. Such materials can be divided in two groups by their behavior – UVAs and hindered amine light stabilizers (HALS). Unlike UVAs, HALSs do not absorb UV light but they prevent the effects of radiation by decomposing the harmful molecules caused by UV light, scavenger free radicals or quench the excited electrons. (Strong 2006, p. 152-153)

3.4 Oxidation

Most polymers, excluding fluoropolymers, are prone to oxidation that is closely related to UV degradation. Elevated temperature and exposure to ultraviolet light increase the susceptibility to oxidation and depending of the initiation, oxidation can be divided into

heat-initiated oxidation i.e. thermo-oxidation and light-initiated oxidation, i.e. photo-oxidation. (Fried 2003, p. 269; Strong 2006, p. 155; Szycher 2012, p. 23) Usually, ultraviolet radiation first breaks the bond between two carbon atoms, which leads to formation of free radicals. Because oxygen is often present, free radicals react with it. In the oxidation reaction, oxygen is incorporated into the polymer. Eventually, peroxides and hydroperoxides are formed. (Fried 2003, p. 269; Strong 2006, p. 155)

Oxidation can also initiate from heating. Heating causes vibration of the bonds that can lead to bond cleavage and these polymer ends can further react with oxygen. There are also other possible ways that can cause bond breakage, such as chemical exposure, which makes oxidation a common mechanism for polymer degradation. (Strong 2006, p. 155) Of the most used plastic flooring materials, PUR and polyolefins are susceptible for both the thermo-oxidation and photo-oxidation, whereas PVC is highly resistant to oxidation. (Szycher 2012, p. 23–24, Allen 1980)

Oxidation and other degradation mechanisms cause similar issues to polymer; deterioration of physical and mechanical properties, embrittlement and color fading. Usually oxidative degradation occurs slowly because the degradation requires oxygen atom to diffuse into the polymer and react with the bonds. Generally increasing the temperature accelerates the rate of oxidation. Certain properties of the polymers affect the susceptibility of plastic to oxidation and these are the energy of the bonds, electronegativity and the polymer structure. Low bond energy and greater attraction of the electrons for oxygen molecule lead to higher tendency for oxidation. Also, if the structure of the polymer molecule is open, it eases the diffusion of oxygen molecule into the plastic and increases oxidation tendency. (Strong 2006, p. 155)

To increase the materials resistance against oxidation, certain additives, i.e. antioxidants can be added into plastic. Antioxidants absorb oxygen or other molecules and thus protects the polymer chains from oxidation. Using antioxidants is highly advantageous during processing, due to high processing temperatures. If the oxidation is wanted to be minimized, the processing can be done in less reactive atmosphere, such as nitrogen gas. (Strong 2006, p. 155)

3.5 Microbiological and enzymatic degradation

Some plastics are prone to degradation by micro-organisms, such as bacteria, fungi and enzymes. The risk is more considerable to bio-based polymers and plastics that contain natural products. (Strong 2006, pp. 155-156) For example, biodegradation process of aliphatic polyesters is a combination of hydrolysis and attack of the ester groups by non-specific esterases. Degradation products are further metabolized by micro-organisms and biodegradation is complete when whole polymer is changed in gaseous end products or biomass. In addition, variety of microbes are able to degrade plasticizers, thus producing VOCs, such as 2-ethylhexanol. (Fried 2003, p. 277)

Alternatively, microbiological degradation can be considered a possibility for environmentally friendly plastic waste disposal. (Fried 2003, p. 277; Shah *et al.* 2008) Degrading plastics by bio-organisms would reduce the long-lasting changes to environment, that the accumulation of plastics has been caused. The efficiency of enzymes have been considered to be higher in fungi than in bacteria and Bhardwaj *et al.* have been studying the induced biodegradation rate in both environments. (Bhardwaj *et al.* 2012)

3.6 Environmental stress cracking

Environmental stress cracking (ESC) is a type of aging and it causes failure through surface interactions between plastic and chemical, which is generally surfactant or detergent. Simultaneous impose of stress and chemical have a synergist effect on failure, which leads to cracking of the material below its yield point. (Jansen 2015; Kutz 2005, p. 154)

ESC does not involve chemical reaction, molecular structure does not change and molecules do not degrade. The chemical only accelerates the stress cracking that would otherwise occur slowly in air. The chemical agent penetrates into the plastic and distracts the bonding forces between the polymer chains allowing them to disentangle. Thus, the energy needed for disentanglement decreases. Yet, the properties of the bulk materials such as stiffness and strength are not reduced because only the contact surface is affected. (Jansen 2015)

There are several factors that affect ESC, e.g. polymer composition, chemical agent and stress level. Molecular structure and functional groups affect the resistance of a polymeric material. The crystal structure of the polymer affect the amount of free volume in the material and due to that generally amorphous polymers, that have higher free volume, are more vulnerable to ESC than semi-crystalline polymers. (Jansen 2015)

The composition of the chemical agent is a crucial factor of defining the aggressivity of ESC. The affinity between the chemical and the polymer defines the interaction between them. If the intermolecular forces in the chemical agent are moderate, such as hydrogen bonds, the aggression of ESC tends to be high. Low molecular weight is also related to damaging ESC properties due to lower viscosity and greater mobility of the molecules. (Jansen 2015)

Higher stresses lead to shorter initiation time of environmental stress cracking. It is notable that the stress may be either external or internal. An example of internal stress are the residual stresses that may remain in the product after injection molding or other processing methods. (Jansen 2015)

3.7 Artificial aging

Formerly, it has been possible to determine the lifetime for the products in non-demanding applications based on the earlier experience of using (Maxwell *et al.* 2005). Because the aging of the product can take a long time, it has been essential to develop artificial, more time-saving and economic methods for accelerating the aging process (Ehrenstein & Pongratz 2013, p. 143). At present, polymer components are used extensively and their usage is still increasing. When the polymers are used in demanding applications that may cause serious accidents in case of failure, accelerated aging and understanding of the degradation mechanisms are on high demand. (Maxwell *et al.* 2005) Therefore, artificial aging is used for predicting life cycle of a product or for defining its shelf life before the actual lifespan has been determined under normal use. (Ehrenstein & Pongratz 2013, p. 143)

There are several different types of tests that can be used for evaluating of service life – aging in simulated conditions, accelerated testing, evaluation based on energy equivalence rule and parallel aging. In accelerated testing, the cause of aging (e.g. temperature, radiation intensity or humidity) is reinforced to fasten the aging process and shorten the testing time. (Ehrenstein & Pongratz 2013, pp. 144 – 145)

A number of standard test methods for accelerated ageing tests have been compiled and they include liquid absorption, thermal stability, ESC and weathering test methods, as well as evaluation of chemical resistivity (Maxwell *et al.* 2005). In this thesis, validity of immersion test (see subchapter 6.1) as an accelerating aging test method is experimented. Standards relevant to immersion tests do not exist, as the liquids absorption test standard concerns of swelling of the samples measured as the increase of weight. In general, it is of high importance that the ageing mechanisms in accelerated testing correspond to ageing mechanisms in real use.

4. DEGRADATION OF FLOORING SYSTEMS

The most significant challenges in flooring structures are the conditions in the system and features of different material layers. In this chapter, characteristics such as alkaline humidity and carbonation of concrete, use of plasticizers, especially phthalates, and water permeability properties of plastic floorings are underlined.

4.1 Conditions in flooring systems

4.1.1 Alkalinity and humidity of concrete

Concrete slabs are challenging substrates to apply adhesive and flooring due to their humidity. Concrete contains water as an integral ingredient. It is a necessary component for hydrating cement and improving workability, but the water that is not used for hydrating remains in the concrete. The drying of concrete after curing is slow but eventually, if evaporation is possible, it will dry to equilibrium with the environment. Respectively, it is also possible for concrete to absorb moisture from the surrounding environment. (Nelson & Hopps 2012)

Determining the drying time of concrete is challenging due to many variables that affect it. Even if the conditions were the most ideal, the drying to a point that has no effect on the floor adhesives can take several months. When flooring of low permeability is inserted, the concrete cannot dry further. Due to the prevented evaporation, moisture from the concrete stabilizes which leads to increase in the humidity right below the flooring. Hence the adhesive can be in direct contact with moisture. (Nelson & Hopps 2012) Typically, the relative humidity of 85% is considered as a limit value, that indicates an adequate drying. The depth of which the RH is measured depends of the thickness of the concrete. (Niemi 2010)

Alkaline humidity of concrete may cause degradation of adhesives and floorings, which can cause emission of VOCs into indoor air. Alkalinity is caused by hydroxide ion (OH^-) concentration. Humidity of the concrete dissolves OH^- ions, that can migrate within pore solution into the adhesive layer and induce chemical degradation. Usage of low alkaline screed on the concrete decreases the secondary emissions of the flooring and adhesive via decreased alkalinity. (Eronen *et al.* 1998) Generally, pH of newly placed concrete is 12–13 and low alkaline screed is 11. In case a cured concrete is in contact with carbon dioxide, it can carbonate, which may decrease the pH to 9. (Merikallio *et al.* 2007, Nelson & Hopps 2012)

Alkalinity itself does not cause degradation of the flooring material but the combination of alkalinity and humidity does. That is explained with the hydroxide ions that are only

present in water. The limit value of the humidity of the concrete depends on the products that are used on it. Some of the screeds, nearly every adhesive and some of the coating materials are sensitive to high humidity. When the humidity of the structure increases above relative humidity of 85 %, materials prone to humidity can lose their strength. High humidity can also initiate degradation processes of adhesives and floorings, which may lead to release of chemical compounds in the indoor air.

Relative humidity is the ratio of actual water vapour pressure in the air to the saturation vapour pressure at current temperature (equation 1).

$$\text{Relative humidity} = \frac{\text{Actual vapour pressure}}{\text{Saturation vapour pressure}} \times 100 \% \quad (1)$$

The relative humidity of concrete refers to relative humidity in the air of the pores inside the concrete. The profit of using low alkaline screed on the concrete is not significant if the concrete is dry enough. A sufficient drying of concrete can only be verified by measuring relative humidity from a hole drilled into it. (Merikallio *et al.* 2007, Nelson & Hopps 2012, Keinänen 2013, Suomen Betoniyhdistys 2014, s. 43–45)

Theoretical humidity behaviour of a concrete slab is presented in figure 6. The horizontal axis illustrates the humidity and vertical axis the thickness of the concrete in the floor structure. Line A describes the humidity right after casting. Line B illustrates the drying state and it shows that the drying is fastest on the surface whereas the lower part stays humid. When the concrete is coated (line C), the humidity profile stabilizes. (Lindberg *et al.* 2002)

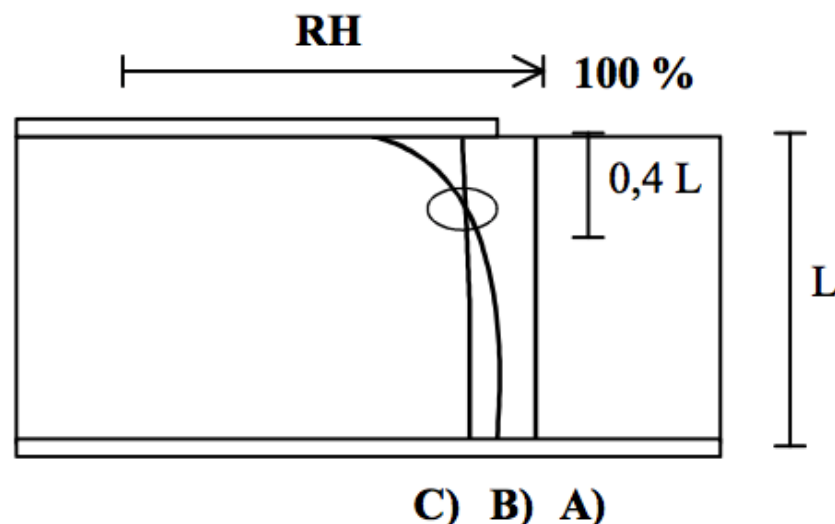


Figure 6. Theoretical humidity behaviour of a concrete slab when drying occurs in one direction. (Lindberg *et al.* 2002)

Concrete slab can store the degradation products of flooring and adhesive, which affect the later emissions of the floor structure. Even half of the degradation products can diffuse and accumulate into the concrete slab. Changes in surrounding conditions, such as humidity and temperature, can induce the emissions of harmful compounds into the indoor air and the releasing rate of the emissions is affected by the properties of plastic flooring. (Metiäinen 2009, Sjöberg 2001)

4.1.2 Carbonation of concrete

Carbonation is a reaction between wet concrete and carbon acid. Carbonic acid (H_2CO_3) is formed when carbon dioxide (CO_2) of air reacts with water (H_2O) (equation 2), and carbonic acid then reacts with calcium hydroxide ($\text{Ca}(\text{OH})_2$) of the concrete forming calcium carbonate (CaCO_3) and water (equation 3). Carbonation proceeds gradually from the outer parts of the concrete slab inwards and this diffusion process conveys CO_2 . Carbonation results in the decrease of alkalinity of the concrete, which is desirable from the view of adhesive and plastic flooring degradation. (Björk & Eriksson 2002)



The density of the concrete slows down the carbonation reaction i.e. the lower the water-cement ratio, the denser the concrete and the slower the carbonation (Suomen Betoniyhdistys 2002). Additionally, the humidity of the atmosphere affects the diffusion rate of the CO_2 . When the humidity of the air corresponds to the humidity of the concrete and their relative humidity is between 50% and 70%, the carbonation rate is at highest. If the RH of concrete is below 25%, the amount of water in the pores of the concrete would be too low for carbonic acid formation. Respectively, if the RH of the concrete is higher, the water in the pores would hinder the transportation of CO_2 due to lower transportation coefficient in water than in air. (Björk & Eriksson 2002)

4.1.3 Water vapour transmission properties of plastic floorings

The water vapour transmission properties of the flooring are of high interest because the humidity originated from the soil and lower floor structures should be able to leave the structures without damaging them. On the other hand, the flooring that is being used should withstand the humidity. (Lindberg *et al.* 2002, Pirinen 2006)

The higher the density of the flooring, the drier the concrete should be before applying the flooring to avoid the condensation of humidity under the flooring. For example, homogeneous flooring structure has significantly lower water vapour transmission proper-

ties than layered structure and thus the relative humidity must be lower when using homogeneous, less permeable flooring. These homogeneous floorings are often used in public buildings, such as schools and hospitals. (Lappi 2013)

Floorings used in houserrooms are softer and less dense, i.e. their ability to transfer water vapour is much higher. Usually, improving wear resistance of a plastic flooring decreases water vapour transmission factor. Floorings used in houserrooms generally have poorer wear resistance due to larger amount of fillers. (Lappi 2013)

4.2 Degradation of plastic floorings

4.2.1 Plasticizers, their migration and susceptibility to hydrolysis

Plasticizers are solvents that are used in plastics in such moderate concentrations that they cause swelling of the plastic rather than dissolving them. Swelling increases local chain movement resulting in more flexible and softer material. Plasticization means the change in material from a glassy state to a rubbery state, i.e. plasticization lowers the glass transition temperature of the material. (Strong 2006, p. 162)

The properties resulting from added plasticizers are critically dependent of the amount and method of adding them. Excess plasticizer can cause general chain movement instead of local movement, which leads to loss of strength. Respectively, unevenly distributed or too low concentration of plasticizer will not produce plastic material flexible enough. (Strong 2006, p. 162)

Polyvinyl chloride (PVC) is the most important commercial application of plasticized polymer. Unplasticized PVC is brittle and hard, whereas plasticized PVC is pliable and soft. Plasticized PVC can be processed in lower temperatures which helps to avoid thermal degradation during manufacture. One of the challenges in PVC plasticizers is volatility of the plasticizer. (Strong 2006, p. 163)

Another challenge is the migration of plasticizers. Generally, materials migrate from higher concentration to lower and the lowest concentration sites in most cases locate on the surface of the plasticized material. That is explained by the evaporation and wiping. (Strong 2006, p. 163-164, Metiäinen 2009) This plasticizer depletion causes embrittlement and discoloration. Newer, low volatile plasticizers ease this issue due to lower amount of plasticizer depletion and their ability for chemical saponification. (Ehrenstein & Pongratz 2013) As an example, phthalates strive to move into the surrounding atmosphere through the surfaces and their emission continues throughout the operating life of the plastic flooring. Small molecules are usually more efficient softeners but they also migrate faster than high molecular weight molecules. Due to that, compromises need to be done when selecting a plasticizer. (Strong 2006, p. 163-164, Metiäinen 2009)

In addition to the most used plasticizers, phthalates (discussed below), there are also other, phthalate-free, options. In PVC floorings, plasticizers such as vegetable oil based blends, acetylated monoglycerides of fully hydrogenated castor oil and isosorbide diesters are also used. These alternative plasticizers are also bio-based. Examples of syntetic, phthalate-free plasticizers are e.g., dipropylene glycol dibenzoate (DGD) and di-2-ethylhexyl terephthalate (DEHT). (Lott 2014)

According to available data, non-phthalate plasticizers cause less health hazards than phthalates yet being harmful for health. It is also a fact that PVC itself has inherent toxicities during its lifetime by the form of toxic by-products. The only option for manufacturing plasticizer-free but flexible flooring is to choose another material over PVC. (Lott 2014)

Plasticizers without any additives are not prone to hydrolysis nor saponification in neutral environment even at elevated temperatures. Hydrolysis of plasticizers requires acidic or basic composition to initiate thus emphasizing the relevance of pH conditions, not just eliminating water, in the surroundings when attempting to prevent hydrolysis of plasticizers. (Ehrenstein & Pongratz 2013)

4.2.2 Phthalates and their alkaline hydrolysis

Phthalates (phthalic acid esters) are the most used plasticizers especially when it comes to PVC even though they have been criticized due to their harmful health effects. Phthalates form a large group of organic compounds that all contain benzene ring and acid group, and due to its both polar and non-polar properties, it is an effective plasticizer. (Strong 2006, p. 164)

One of the traditionally used phthalates in PCV floorings is DEHP (di-2-ethylhexyl-phthalate). Alkaline humidity and ammonia cause the degradation of DEHP, which cause formation of 2-ethylene-1-hexanol (2-EH) as a degradation product. Chemical equation of the degradation process is presented in figure 7. The degradation principle is the same in many other plasticizers as well. (Merikallio *et al.* 2007)

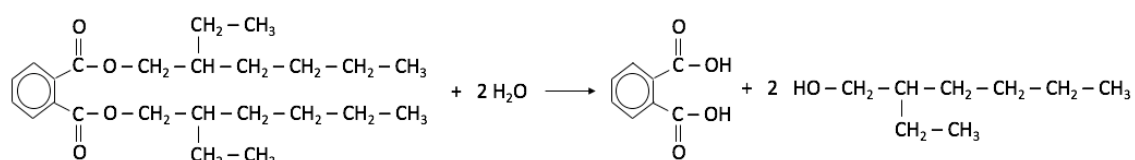


Figure 7. Degradation of DEHP leads to formation of 2-EH.

2-EH is traditionally considered as an indicator in humidity related harm. At present, DEHP have been widely replaced by other plasticizers, such as DINCH (1,2-cyclohexane dicarboxylic acid diisononyl ester), DINP (diidonyl phthalate), DIDP (diisodecyl phthalate) and DEHA (bis-2-ethylhexyl adipate). (Backlund & Talvitie 2014, Metiäinen 2009) Technical properties of DINCH are similar to DEHP whereas harmful health effects of DINCH are reduced compared to DEHP. Also the migration rate of DINCH is lower than the migration rate of DEHP (Nagorka *et al.* 2011). DINCH and DEHA are also a synthetic, phthalate-free plasticizer (Lott 2014).

4.3 Degradation of adhesives

4.3.1 Adhesives and water

All adhesives absorb water and water vapour and in the case of flooring systems, they are able to convey it to bond lines, i.e. the interface between adhesive and the flooring. If the flooring material is permeable, water diffuses through it. The diffusion rate of the water controls the deterioration of adhesive bond and the diffusion obeys Arrhenius equation denoting that the diffusion rate is strongly dependent on the temperature. As the temperature increases, also the diffusion rate increases leading to faster deterioration of the bond line. (Adams 2005, pp. 133–136)

Deterioration of adhesive joint due to water diffusion can occur in different ways. Reversible manners include changes in the properties of the adhesive, such as plastication whereas irreversible manners include crack formation and hydrolysis. Water may also attack the interface between the adhesive and adherent, as well as cause swelling stresses. (Adams 2005, pp. 136–137)

4.3.2 Acrylic adhesives

The most used structural acrylic adhesives are mixtures, in which polymers and methyl methacrylate (MMA) form a dispersion or a solution. These adhesives are two component adhesives that contain a peroxide compound and an amine or a metal salt. Components are mixed right prior application, and in the mixing process the salt and the peroxide component react, resulting free-radical polymerization of MMA monomer. (Ebnesajjad 2008, p. 85)

The most used acrylic monomers in adhesives are ethyl and methyl acrylate, methacrylic acid, acrylic acid, acrylamide and acrylonitrile. The addition of a catalyst leads to the polymerization of monomers and thus enhances bonding, for example, to plastics that have similar composition. (Ebnesajjad 2008, p. 85)

Today, the most used flooring adhesives, that do not, or only contain a small amount of VOCs, are water-based acrylic emulsions. Due to water as a solvent, exposure to water

may induce re-emulsification, and alkaline moisture of the concrete slab accelerates the degradation of the adhesive. The adhesives that were formerly used, contained solvents that were insoluble in water thus being less susceptible to degradation caused by moisture and pH. (Nelson & Hopps 2012)

Anderberg and Wadsö (2007) have investigated the degradation of commercial water-based floor adhesives as a function of pH by measuring the heat production of the degradation products by isothermal calorimetry. They used poly(butyl acrylate-co-2-ethylhexyl acrylate) based adhesive as a reference material. In the case of poly(butyl acrylate-co-2-ethylhexyl acrylate), butyl and 2-ethylhexyl groups are bonded to acrylate groups. In hydrolysis, that occurs in contact with concrete, the ester bonds are split off, which causes the release of butyl and 2-ethyl-hexyl as butanol and 2-ethylhexanol. Both butanol and 2-ethylhexanol are volatile compounds and the reaction is reversible.

Another floor adhesive tested in the same study was poly(ethylene-co-vinyl acetate). In the experimental part of this thesis two other flooring adhesives were tested: in Finland commonly used acrylic dispersion adhesive and less used alkali-resistant adhesive consisting of ethylene copolymer and vinyl acetate dispersion.

4.3.3 Tackifiers and thickeners in adhesives

In addition to binder and solvent of the glue, there are also other components of interest in the adhesive, such as tackifiers and thickeners. Tackifiers are used for increasing the tack of the formulation and they generally include aliphatic and aromatic hydrocarbons, rosin esters and terpenes. Addition of tackifiers also increase peel strength and decrease shear strength. (Petrie 2006, pp. 23 – 24) Thickeners are used for controlling viscosity, flow and the bond line thickness in an adhesive joint.

Björk *et al.* (2003) have researched the degradation of components in flooring systems in humid and alkaline environments and their study included polymer dispersion adhesives, different tackifiers and thickeners, PVC floorings and series of plasticizers and two different primers. The study points out that the components of the glue (polymer dispersions, tackifiers and thickeners) affect the formation of volatile emissions and some of them are dependent of the humidity and alkalinity of the environment.

5. ADHESION

The most important property of adhesives is a good adherence i.e. adhesion to the materials that are being bonded, which in this case are the flooring and the screed. Also, the internal strength i.e. cohesion of the adhesive is of high importance. (Saarela *et al.* 2007) If the adhesion between the adhesive and adherends, as well as the cohesion of the adhesive are on ideal level, the fracture must occur cohesively in the adherend (i.e. in the screed or flooring), which means that the maximum adhesive joint strength is achieved. Even though the loads that adhesive joints have to bear may be caused by many sources, the stresses that cause the failure of the bond, are either shear stresses or tensile stresses (Adams 2005, p. 92).

5.1 Fracture mechanisms of adhesive bonds

There are three possible failure modes when adhesive failure occurs. These failure modes are presented in figure 8, in which the adhesive bonds are tested in tensile mode i.e. the two articles are pulled apart so that the direction of the load is perpendicular to adhesive layer. (Ebnesajjad & Ebnesajjad 2014, p.86) In the shear mode the failure modes are alike.

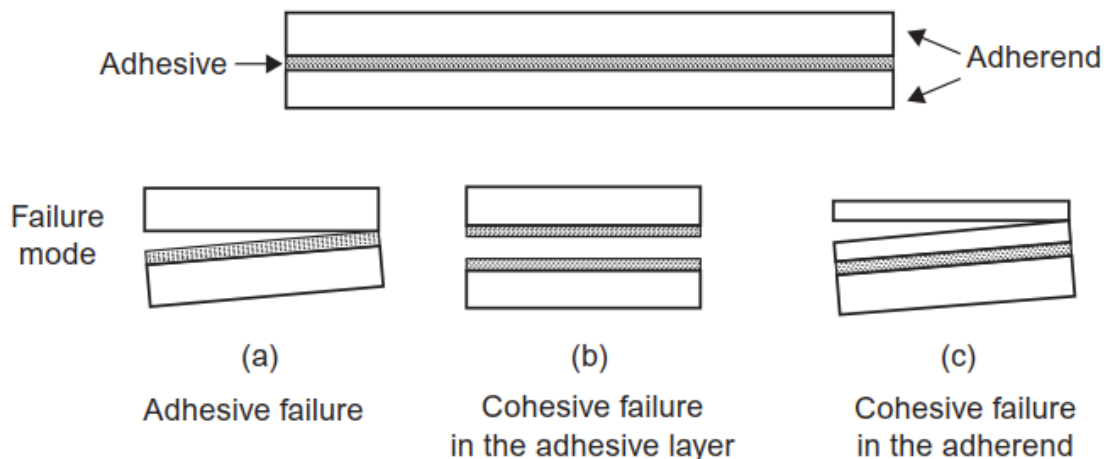


Figure 8. Failure modes of adhesive bond. (Ebnesajjad & Ebnesajjad 2014, p.86)

If the failure occurs on the interface between the adhesive layer and the adherent (figure 8.a), the failure mode is known as an adhesive failure. If the adhesive covers the both adherents after the failure, the mode is then called cohesive failure in the adhesion layer

(figure 8.b). Respectively, cohesive failure can also occur in adherend (figure 8.c), which tells that the weakest link in the structure is the adherend, not the adhesion or the cohesion of the adhesive. Usually more than one failure modes are present in a bond failure and the ratio of different mechanism can be described with percentage values. The most desired failure mode is the cohesive failure either in the adhesive or adherent – in cohesive failure, the maximum bond strength is accomplished. (Ebnesajjad & Ebnesajjad 2014, p.86–87)

5.2 Adhesive bond testing

There are many different ways to evaluate the strength of an adhesive bond, such as tensile tests, shear stress, cleavage and wedge tests, fracture resistance, peel tests and pull-off tests (Brockmann *et al.* 2009). Each test can contain a number of different testing modes. Choosing the best testing method is naturally highly dependent of the application in question and the loading state relevant to the application.

Peel test and pull-off tests are shortly presented in this thesis due to original plan of using both of them in the experimental part – peel tests for the samples prepared in the laboratory and pull-offs for the case study and the laboratory prepared samples. The purpose of the peel tests was to compare the peel strength of the adhesion in different material combinations. These two testing methods would have been compared by exploring, if the materials could be ranked in the same order by both methods.

5.2.1 Peel test

In peel test, two adherents that are bonded together with an adhesive are separated at defined rate. The purpose of the test is to define either the adhesive strength of the material or the adhesive bond strength between the materials. Peel tests can also be proceeded in different modes of which the most common are 90°-peel test, 180°-peel test and T-peel tests. (Brockmann *et al.* 2009) Principle of different modes are presented in figure 9.

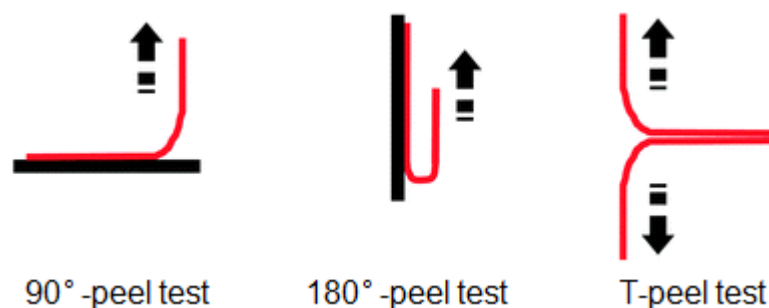


Figure 9. The most used variations of peel tests. (modified: Heinzmann *et al.* 2016)

In 90°- and 180-peel tests the other adherent is rigid and the other is flexible, whereas the T-peel test is carried out to two flexible adherents with equal thickness. All the tests can be ran in tensile testing machine. (Brockmann *et al.* 2009)

5.2.2 Pull-off test

Pull-off test defines the burst pressure needed for detaching an aluminium pull stub from the test surface. The burst pressure correlates with the adhesion on the test surface. The tests are ran by pneumatic adhesion tensile testing instrument (PATTI), which applies a tensile force align to the axis of the pull stub that has been bonded to the surface by using an adhesive. The principle of PATTI is presented in figure 10, in which the screw, glued on the substrate is in the middle, pulling force pointing upwards. The pressure that creates the pulling force, is directed into the system via pressure hose and causes the ascent of the reaction plate. Control module regulates the pressure and increases it until the screw is detached, the coating is disengaged from the substrate or the test is stopped. (Elcometer 2008, pp. 2–4)

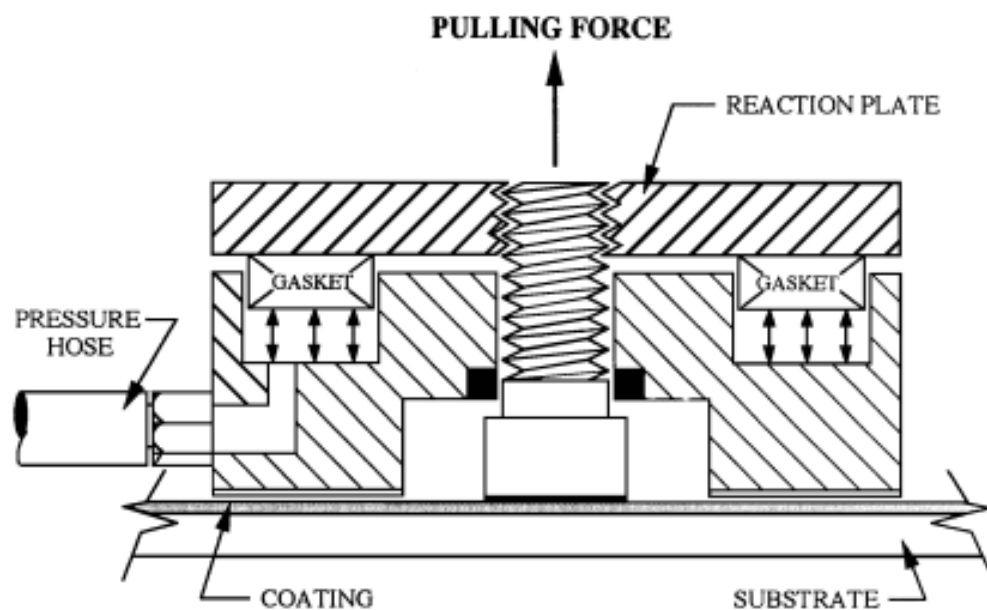


Figure 10. Cross-sectional schematic of self-aligning piston with pull-stub. (Elcometer 2008)

Pull-off tests are used, for example, for testing protective coatings, such as paints, and for developing the coating process. Low adhesion values in pull-off test suggest faster failure of the application and usually results from poor surface preparation of the substrate, such as improper cleaning of the surface. (Fletcher & Barnes, 2015)

6. RESEARCH METHODS AND MATERIALS

The experimental part of the thesis can be divided in two independent parts – laboratory tests of individual materials and a case study. The division and the testing methods are illustrated in figure 11.

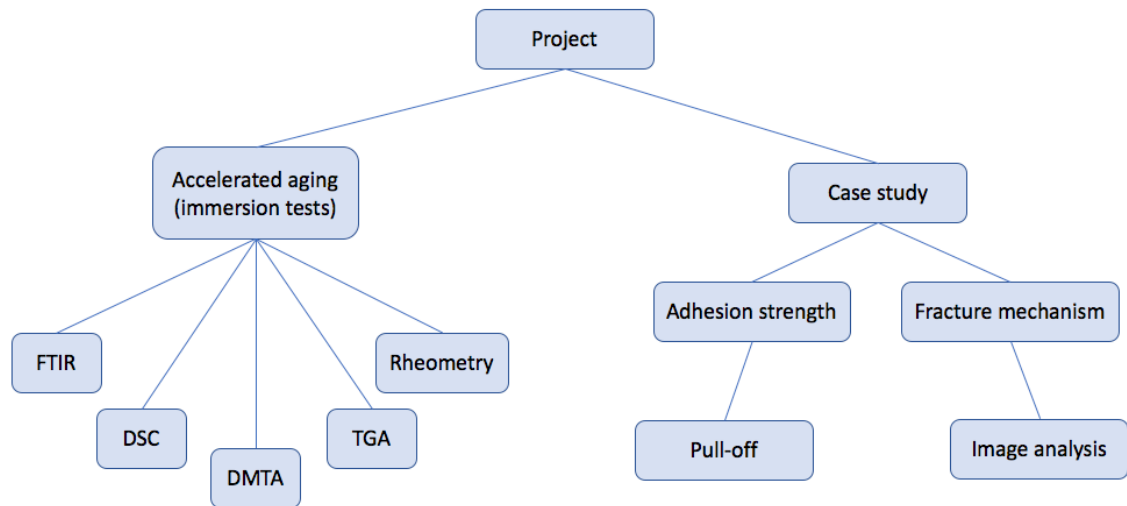


Figure 11. Schematic figure of the structure of the experimental part.

6.1 Accelerated aging in laboratory environment

Accelerated aging was implemented by immersing the samples in solutions of different alkalinity. Samples included three floorings and two adhesives. Two homogeneous floorings with different plasticizers (DINCH and DINP) and one heterogeneous flooring with DINCH as a plasticizer were tested. In the following chapters, the floorings are referred as “homogeneous DINCH”, “homogeneous DINP” and “heterogeneous DINCH” floorings. The adhesives tested were acrylic dispersion adhesive and so called alkali-resistant adhesive that consisted of ethylene copolymer and vinyl acetate dispersion. The screeds were not included in the experimental study.

The exposure solutions were NaOH solution (pH 13.0), concrete solution (pH 12.5) and ion-exchanged water (pH 6.0). Two different high alkaline solutions were chosen for the test to evaluate the effect of the composition of the solution. NaOH solution is a commercial product thus being an easier option for the exposure. Nevertheless, the composition of NaOH solution does not correspond the real environment of use of the adhesives or the floorings. Due to that, the other high alkaline solution, i.e. concrete solution, was selected

to simulate better the real environment. Ion-exchanged water was used for distinguishing alkaline hydrolysis from hydrolysis.

The samples were examined at minimum of four different time points (excluding the rheometer samples). Suitability of Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), dynamical mechanical thermal analysis (DMTA), thermogravimetric analysis (TGA) and rotational rheometry to detect ageing were examined. The testing equipment are presented in table 1.

Table 1. *The testing equipment.*

Equipment	Brand/model	Measured variable
FTIR	Bruker Tensor	Chemical bonds
DSC	Netzsch DSC 204 F1	Glass-transition temperature
DMTA	PerkinElmer Pyris Diamond DMA	Glass-transition temperature
TGA	Netzsch STA 409 CD	Mass reduction as a function of temperature
Rotational Rheometer	Anton Paar Physica MCR 301	Molecular weight (Cross-over point of G' and G'')

FTIR, i.e. Fourier transform infrared spectroscopy, is based on detecting the absorption or emission of infrared light of a material and it is used for defining the chemical composition of the organic sample. In practice, it compares the amount of infrared radiation penetrating the sample to the amount of radiation that comes to sample. This ratio is known as transmittance. The absorption of the radiation occurs at specific wave lengths for each functional group, which appear in the infrared spectrum as peaks.

By using attenuated total reflectance (ATR) accessory in FTIR (as it was done in this study), a surface properties of the material can be probed. When ATR accessory is used, the IR penetration depth of 1–2 μm is achieved thus outlining the exploration to surface instead of bulk properties. Both the background and the sample was scanned 128 times in room temperature.

DSC, i.e. differential scanning calorimetry, measures the amount of heat that is needed for increasing the sample temperature and compares it to reference. The amount of heat is measured as a function of temperature. DSC can be used, for example, for defining glass transition temperature (T_g), melting temperature or heat capacity of the sample or studying chemical reactions, such as oxidation. In this thesis, it was used for defining T_g . The tests were done in nitrogen (N_2) atmosphere using temperature range of $-90\text{ }^\circ\text{C} - 300\text{ }^\circ\text{C}$.

DMTA, i.e. dynamical mechanical thermal analysis is used for defining viscous and elastic properties of materials as a function of temperature, time, frequency, stress or strain.

For example, loss and storage modulus, T_g , melting, creep and stress relaxation can be defined. In this study, the sample was exposed to oscillating force (tension) at controlled temperature program and the T_g s were defined.

TGA, i.e. thermogravimetric analysis, measures the mass of the sample as a function of temperature and it can be used for defining, e.g. thermal degradation, phase transitions, oxidation and reduction. Several phenomena can cause a mass reduction in TGA curve. Such phenomena include evaporation of volatile compounds, desorption of gas, oxidative degradation etc. In this thesis, the thermal decomposition was the phenomenon under interest. The samples were heated to 600 °C at heating rate 20 °C/min in N₂ atmosphere. The flow rate of nitrogen gas was 50 ml/min.

Rotational rheometer is used for determining the flowability of material. For example storage modulus (G'), loss modulus (G''), viscosity, shear stress and shear strain can be determined. In this thesis, the aim was to study the changes in the molecular mass of the sample within the exposure.

6.1.1 Samples and solutions

Samples of plastic flooring were cut with carpet knife. DMTA samples were cut into right form and size (roughly 45 mm x 5 mm x 2 mm) before the exposure. The size of 10 mm x 10 mm samples were also exposed to be used in FTIR, TGA and DSC measurements.

Adhesive samples were prepared by applying adhesive onto microscope slides the size of 25 mm x 75 mm. The purpose was only to prepare a cured adhesive sample which can then be exposed and examined (FTIR), or of which samples (DSC, TGA) can be prepared. The adhesives were applied with a spatula and the thickness of the adhesive layer was approximately 1 mm. The samples were left in room temperature for several days to cure. According to manufacturers, the complete curing takes 3 days.

Another set of adhesive samples were prepared by applying glue between the single-used aluminium measuring plates of rotational rheometer. The plates were lightly pressed against each other to minimize the air bubbles in the adhesive. The samples were left to cure in room temperature for several days.

6.1.2 Preparing alkaline solutions

NaOH solution of pH 13.0 was generated by diluting 0.25 M NaOH solution with ion-exchanged water. Concrete solution was prepared by mixing drilled concrete dust to ion-exchanged water and filtering the mixture after that. The pH of the solution was 12.5. The mixing ratio was 7.5 g concrete dust to 50 ml ion-exchanged water and the mixing was done by magnetic stirrer. The pH of the distilled water was 6.0.

The pH values of NaOH and concrete solutions metered by Hanna Instruments HI2020 Multiparameter pH Meter. Calibration was performed as three-point calibration with calibration solutions of pH 7.01, 10.01 and 12.45. The pH of the distilled water was measured with Mettler Toledo SevenExcellence Multiparameter pH meter. Three-point calibration was performed with calibration solutions of pH 4.01, 7.00 and 9.21. pH was measured three times.

6.1.3 The exposure

All the samples were exposed in NaOH solution and water and the adhesives and homogeneous DINCH mat also in concrete solution, as it is demonstrated in the figure 12.

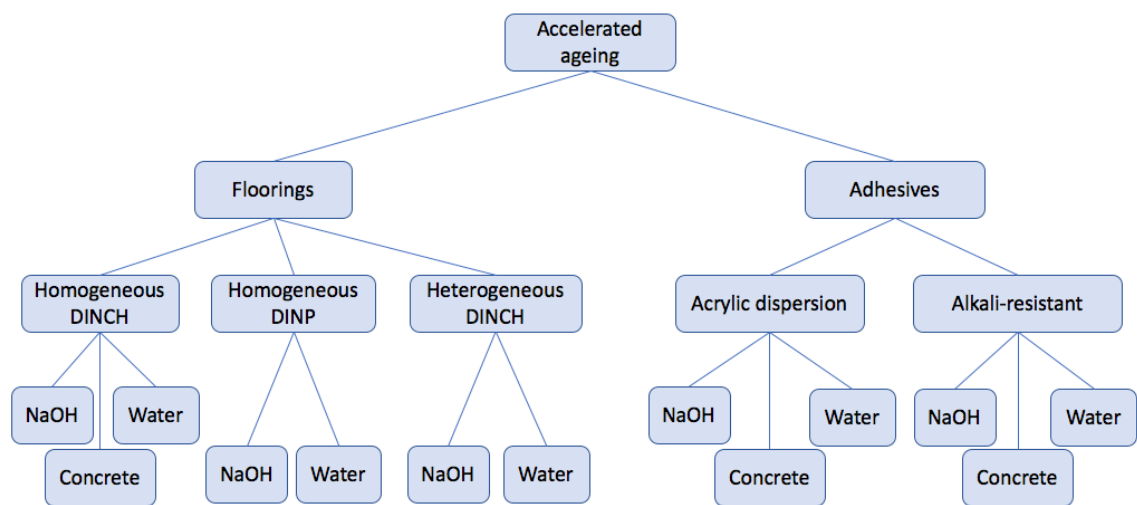


Figure 12. The exposure solutions used for each material in the immersion.

Slightly elevated temperature of 40 °C was used to speed up the ageing. The samples were examined at least in four time points between 1 and 35 days. The exact time points are presented in the appendices A and B.

Before the FTIR runs, right after taking the samples from the exposure solution, the samples were rinsed with ion-exchanged water and lightly dried with lens paper. The samples that were tested with another methods, were dried with lens paper and rotational rheometer samples by leaving it in room temperature for three days.

6.2 Case study

Adhesion of the floorings and fracture mechanisms were studied in a Finnish school, in which several indoor environment problems have appeared. Mechanical strength of the

adhesive bond was tested with pull-off tester, whereas the fracture mechanism of flooring removal was studied by image analysis with ImageJ[®]. The school is currently in prohibition of use.

6.2.1 Pull-off tests

The samples were taken from four different class rooms. In each room, the damaged site was right next to wall and undamaged site in the middle of the room. The reason for the damages was the lack of thermal insulation under the walls and the surface moisture was clearly increased at those points. The reference values were taken of the centre part of the rooms.

Pull-off tests were run with pneumatic adhesion tensile testing instrument (PATTI). At first, 16 mm diameter circles were cut through the mat by using a multifunctional tool Dremel 4000. A sharp-edged metal tube and a hammer were also tried and abandoned due to impossibility to detect the depth of the tube head, which should be on the interface between adhesive and screed layers. It is also possible that the repeated impacts damage the screed layer or deteriorate the adhesion.

Bolts of 12 mm diameters were then glued onto the mat and in the middle of circles by using instant glue. When the glue was dried, a pulling cylinder was placed around the bolt, reaction plate was fastened and the test was started. The setup is presented in the figure 13.

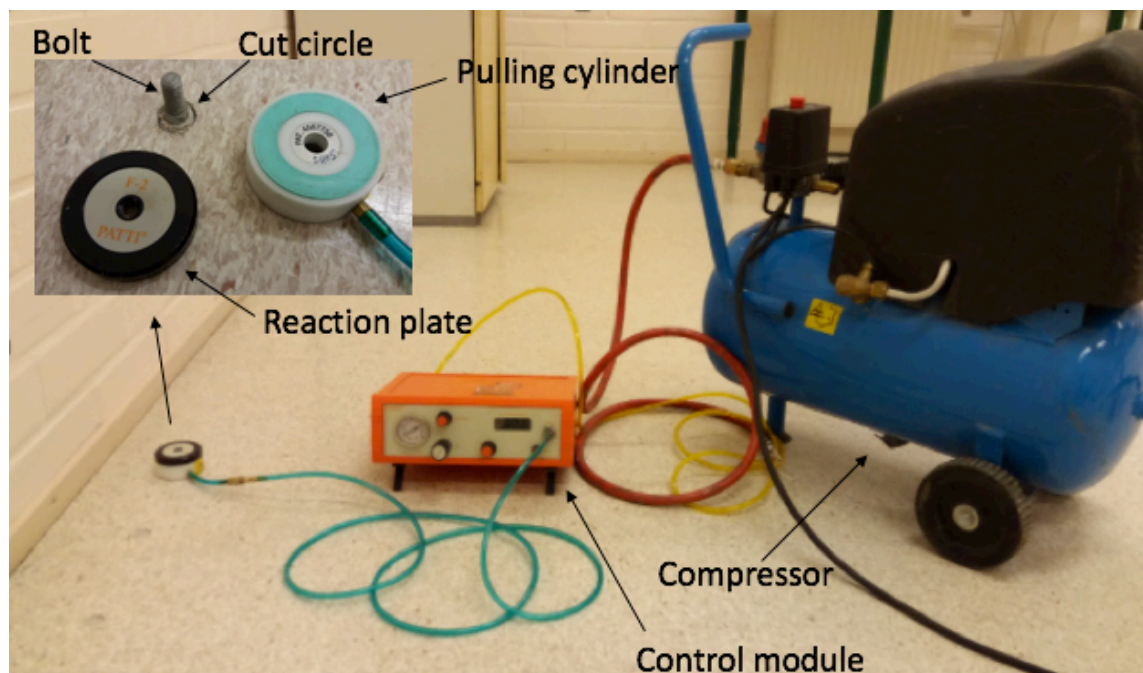


Figure 13. *The setup of the pull-off test.*

6.2.2 Fracture mechanisms

Pieces of flooring was ripped off from the school building and the area of adhesion was inspected. The samples were taken close the pull-off samples, i.e. damaged samples locating next to wall and undamaged samples in the middle of the room and the sample size was approximately 10 cm x 10 cm. The aim was to categorize the failure mode and to find out the site of breakdown.

The samples were examined by image analysis. The flooring pieces were photographed and the proportions of the screed and the adhesive were determined by using image processing program ImageJ[®] and its Threshold Color function. The number of pixels that contained the adhesive or the screed was counted in order to calculate the ratios.

An example of calculating the number of adhesive containing pixels is presented in figure 14. The adhesive can be seen as yellowish spots on the left picture, whereas the light grey is the flooring and dark grey is the screed.

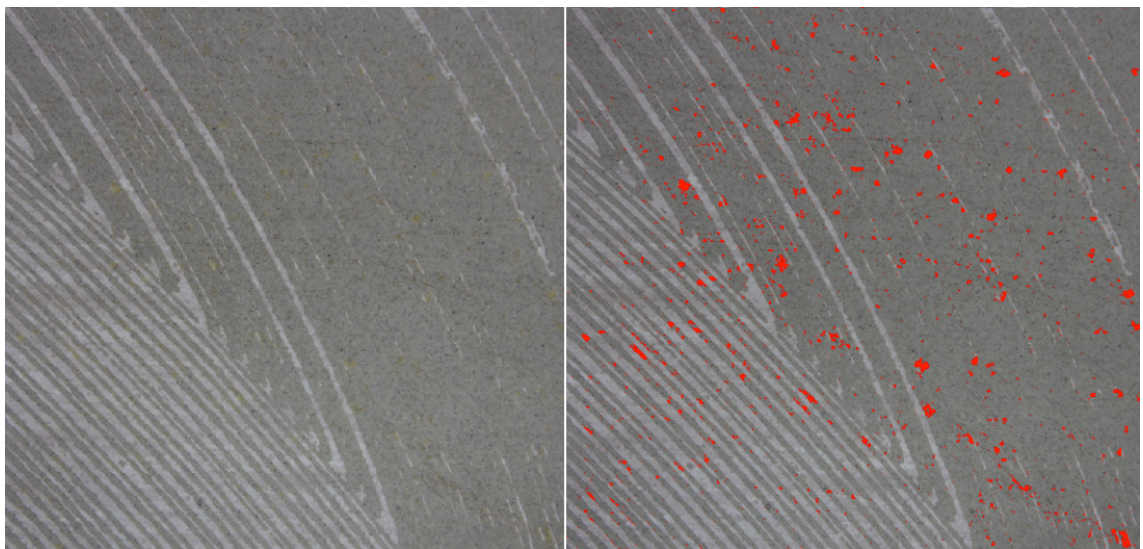


Figure 14. On the left is the original picture and on the right is the same picture, of which the amount of adhesive is being determined.

7. RESULTS AND ANALYSIS

7.1 Accelerated aging in laboratory environment

Ageing was studied via glass-transition temperature (DSC, DMTA), onset temperature of degradation (TGA), chemical structures (FTIR) and molecular mass (rheometer). The purpose of the immersion test was to expose the materials into different solutions instead of high relative humidity and thus accelerate the ageing compared to real situation. The maximum exposure time was defined by the schedule of the project.

According to a number of studies, the reason of the degradation of floorings and adhesives is the alkaline moisture. In this experiment, one of the aims was to define if the source of alkalinity effects the degradation by using both NaOH and concrete solution. NaOH solution is the easy and commercially available option for the immersion test, whereas the concrete solution mimics the real situation more accurately, but the concrete dust has to be drilled, collected, mixed with water and filtered to prepare the solution. The purpose of water immersion was to distinguish the alkaline hydrolysis from the hydrolysis.

7.1.1 Changes in chemical structure of the adhesives and floorings

Before the exposure the texture of the adhesive samples resembled of sanitary silicone, whereas after the exposure the samples were ropy and weak. Even though the texture of the adhesive changed clearly, the changes in chemical structure could not be detected by FTIR. If the samples were measured right after the NaOH exposure, the only changes were, that Na^+ and OH^- could be detected from the spectrum. This reveals that rinsing of the sample did not remove all the NaOH from the surface of the sample. The changes of the texture of the flooring samples could not be detected sensory and the FTIR curves did not show changes in chemical structure.

When the adhesive sample was left to dry in room temperature, NaOH disappeared from the spectrum and the FTIR curves of the reference and the exposed sample became identical. That can be explained by recrystallization of NaOH as the water evaporates and the ageing seems to be reversible. In the figure 15, the reference sample of acrylic dispersion adhesive (blue) is compared to a sample that is exposed to NaOH solution for 20 days (red). The exposed sample is let to dry before running the IR spectrum.

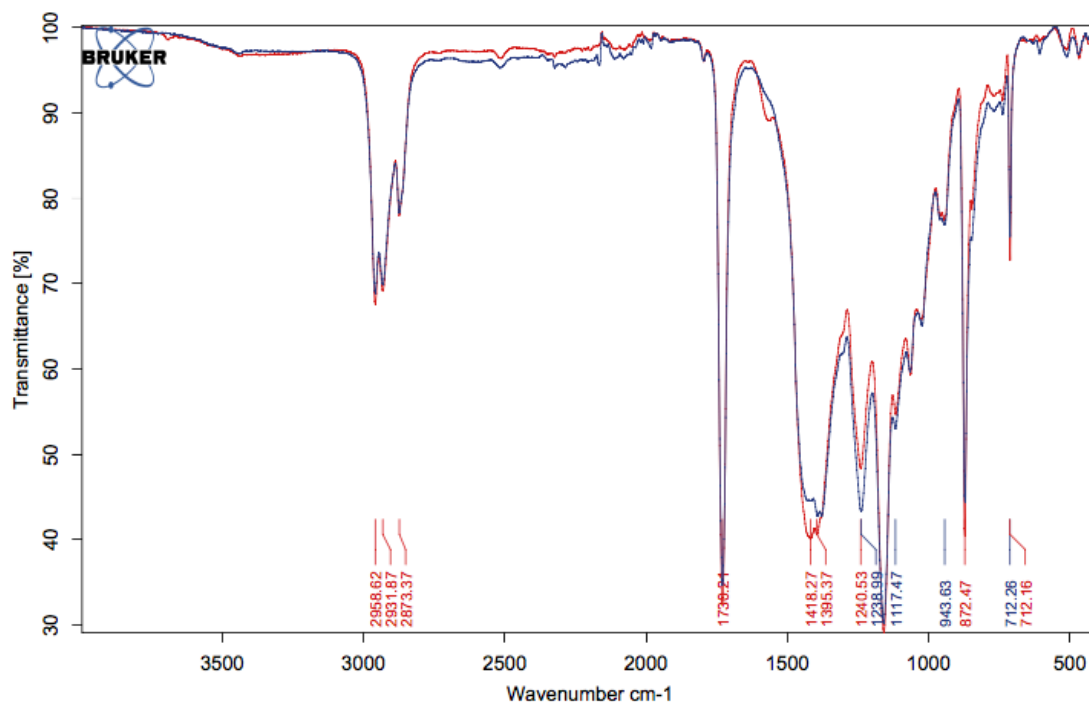


Figure 15. FTIR spectrum of reference sample (blue) and exposed sample (red). The exposed sample was immersed in NaOH solution for 20 days.

As a sensory analysis, when the sample is dried well, the texture of the adhesive returns to same as it was before the exposure. Supposedly, the changes in the texture are caused by absorption of water into the sample and the ageing method was reversible. Since the FTIR was discovered not to be valid method for detecting changes during the exposure, it was discarded. It would be possible to detect the changes if the exposure time was extended, but due to schedule of this project, it could not be trialed.

7.1.2 Ageing of the adhesives as a function of exposure time

Ageing was studied by inspecting the change of T_g and the onset temperature of the degradation with DSC, DMTA and TGA. DSC proved to be invalid method for defining T_g of the adhesives. T_g could not be observed from the curves as it is pointed out in figure 16. The DCS curves of the reference (pink) and exposed (blue) sample closely resemble each other. In an ideal case, the T_g is observed in the DSC curve as a step or a “shoulder” it is illustrated in the figure 17.

In the figure 16, acrylic dispersion adhesive no. 2 is tested. Acrylic dispersion adhesive no. 2 is very similar to the acrylic dispersion adhesive that is tested with other methods. The results are presumed to be alike. The reason for poor readability may also lie in the number of components in the adhesive composition, which leads to overlapping reactions and prevents the T_g from appearing.

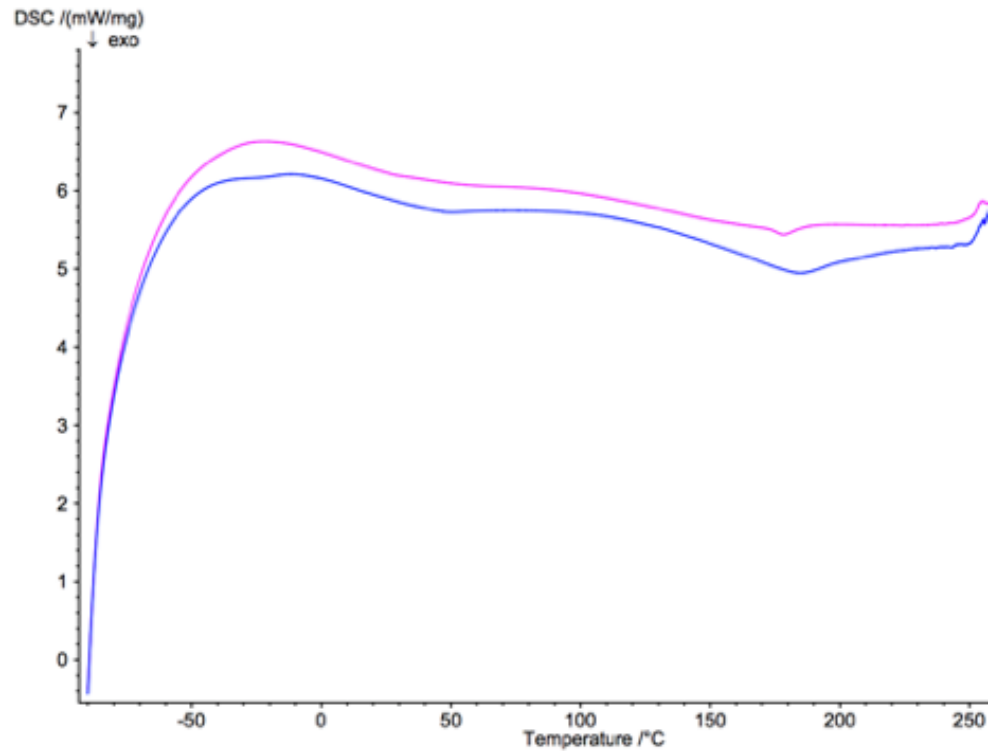


Figure 16. *DSC curves of the reference (pink) and the sample that was exposed for 23 days in NaOH of pH 13 at 40 °C (blue).*

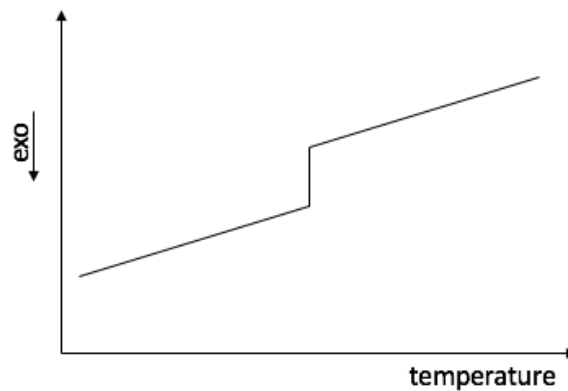


Figure 17. *In an ideal situation, T_g appears as a step in the DSC curve.*

Due to the significant change of the texture of the adhesive from solid to jelly-like and colloidal structure, DMTA samples could not be made thus leaving out the DMTA of the research methods. TGA was used for studying the initiation of the degradation of the adhesives as a function of the exposure time. The results are gathered in the appendix A and presented as graphs below (see figures 18-19).

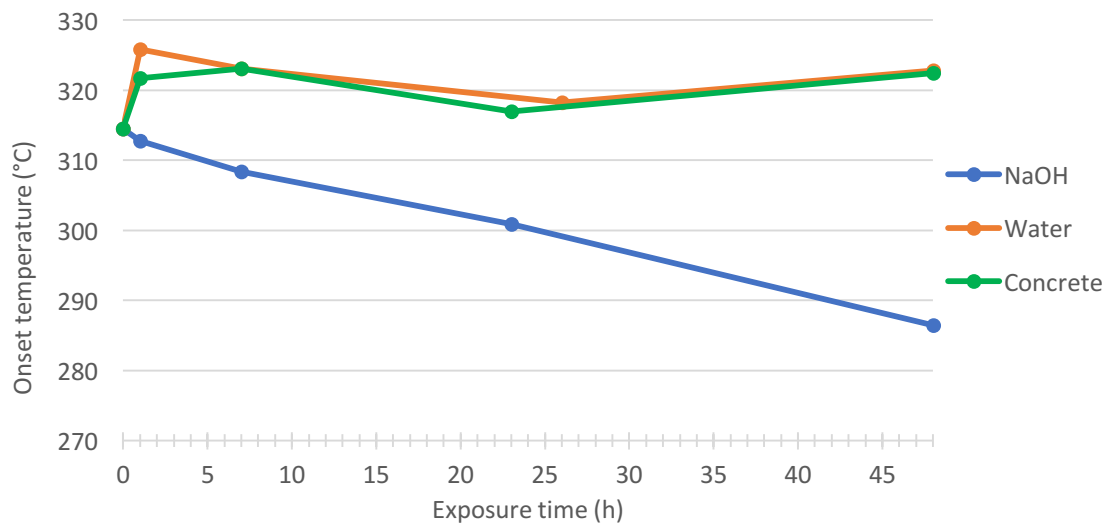


Figure 18. *The onset temperatures of degradation of alkali-resistant adhesive as a function of time in different exposure solutions.*

Figure 18 illustrates that already 48 hours exposure of the alkali-resistant adhesive to NaOH solution significantly decreases the degradation temperature, whereas exposure to ion-exchanged water or concrete solution does not. Difference of the behavior in sample in NaOH and concrete solutions can indicate basically two things – either the degradation in NaOH occurs due to slightly higher pH (13.0 vs 12.5), or due to different composition of the solution. If the reason is in the difference of the pH, the adhesive seems to have a critical value of pH between 12.5 and 13.0, above which the degradation of the adhesive initiates faster.

If the cause of different behavior is NaOH itself, the degradation of the adhesive is based on chemical reactions between the adhesive and NaOH. NaOH does not correlate to real environment of use of the adhesive and thus the conclusion would be that immersion to NaOH solution is not suitable for ranking the materials. Testing the adhesive in NaOH solution of pH 12.5 would give us more information of this issue.

The results of the immersion of acrylic dispersion adhesive (figure 19) reveal a decrease in the onset temperature of degradation when the sample is exposed to NaOH solution. Unlike the results of the alkali-resistant adhesive, exposure to ion-exchanged water and concrete solutions does not give as identical curves. Exposure to concrete solution does not decrease the degradation temperature, which may implicate that it is not only the alkalinity that affects the degradation. The deductions concerning the behavior of acrylic dispersion adhesive in the immersion tests reproduce those concerning alkali-resistant adhesive; the different behavior of the adhesive in NaOH and concrete solutions results either from the pH difference or the composition of the solutions.

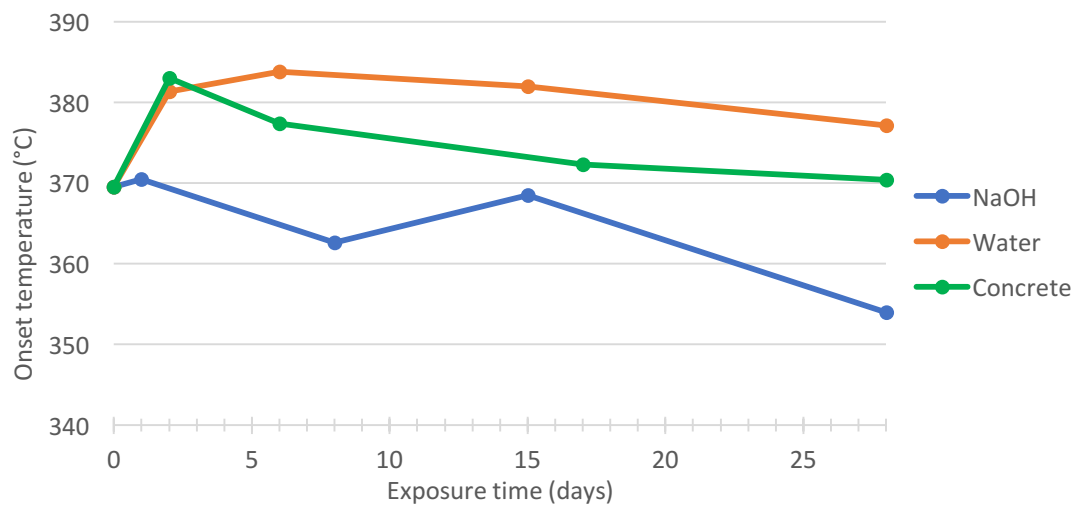


Figure 19. *The onset temperatures of degradation of acrylic dispersion adhesive in different exposure solutions.*

Visual inspection revealed that the alkali-resistant adhesive sample appeared to degrade into small pieces and to mix with NaOH solution during the 48 hour exposure. The pieces and NaOH formed a thin layer to the bottom of the decanter glass whereas the upper part of the solution stayed clear i.e. consisted only of NaOH solution. Same influence was not observed with acrylic adhesive even though the exposure time was much longer (up to 28 days). Nevertheless, also the texture of the acrylic adhesive changed and it was impossible to handle the sample without breaking it.

7.1.3 Ageing of the floorings as a function of exposure time

Glass-transition temperatures of the floorings could be defined with DMTA, which is a more sensitive apparatus than DSC. Both the DMTA and TGA results for the floorings are presented in the appendix B. Figures 20-24 present the same data more illustratively in graphs.

T_g was quantified as a peak in damping factor ($\tan\delta$) curve, that is the ratio between storage (G') and loss moduli (G''). Storage modulus G' describes the elastic behavior of the material and indicates the ability of the material to store energy, whereas loss modulus G'' describes the viscous behavior and the energy that dissipates as heat.

The effects of NaOH solution are presented in figures 20 and 21. As it can be observed from the figure 20, only the other layer of the heterogeneous flooring is affected by the NaOH solution. The decrease of T_g occurs most probably due to breakage of polymer

chains. The lower layer of the heterogeneous flooring was very soft and fabric-like material, probably used due to damping and to add convenience in private apartments, in which the heterogeneous floorings are used. Supposedly, the layer 2, is the lower layer and its mechanical properties are not as relevant as the mechanical properties of the layer 1. In addition, relative to this thesis, the performance of heterogeneous floorings in alkaline environment is not that interesting, due to focus on public buildings.

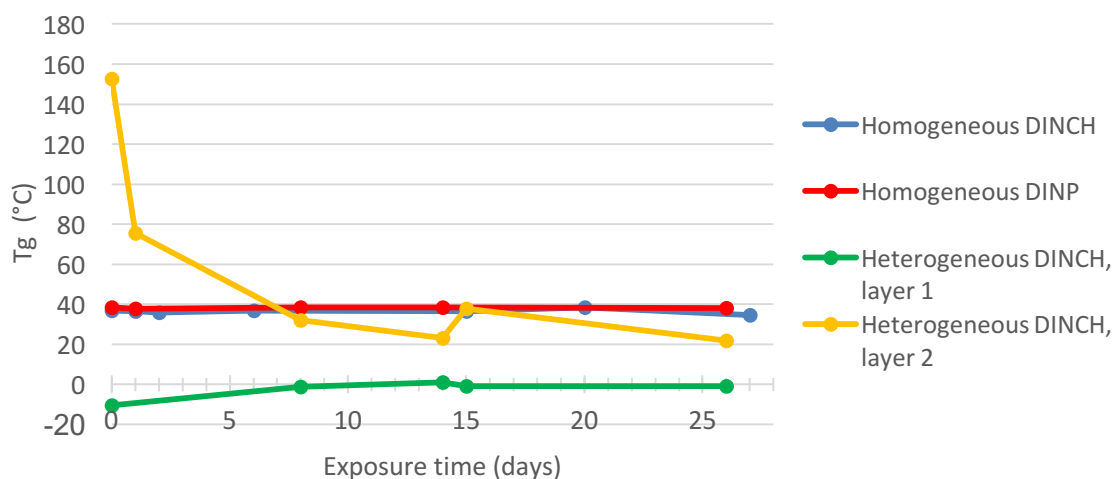


Figure 20. *Effect of the NaOH exposure to glass transition temperatures of the floorings.*

The results of TGA measurements after NaOH exposure are presented in figure 21. The onset temperature of degradation does not change remarkably and thus it can be deduced that the chemical compositions of the floorings do not change or the changes cannot be detected with TGA measurements.

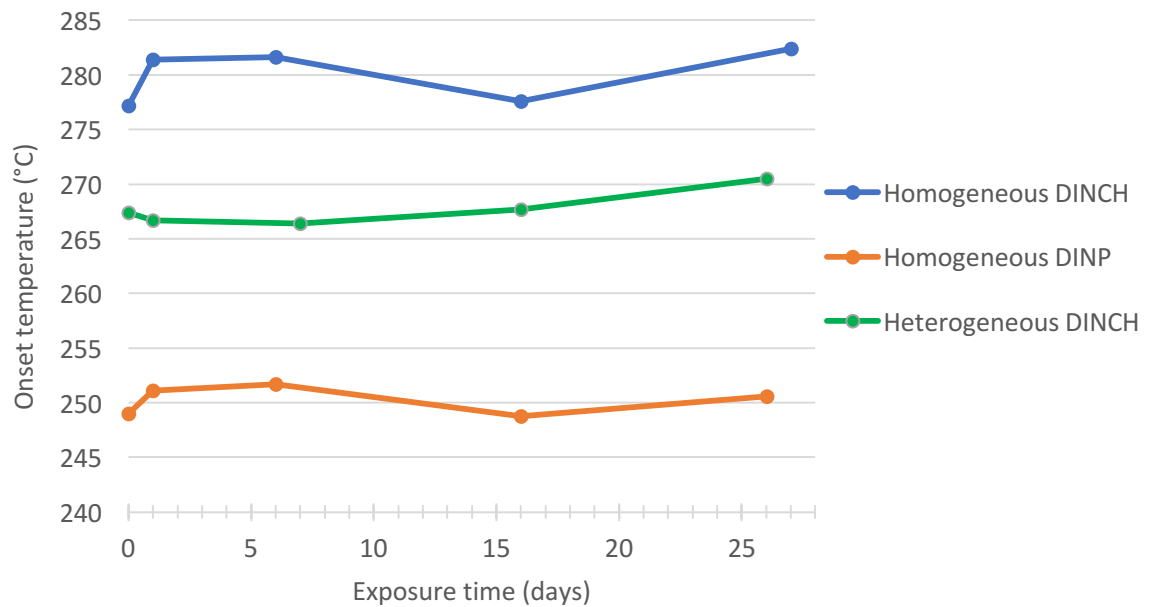


Figure 21. *The effect of the exposure time in NaOH solution on the degradation temperature of the floorings.*

In the figures 22-23, the effect of different solutions to homogeneous DINCH flooring is illustrated. There is no significant difference in the T_g , whether the flooring is immersed in alkaline solution or water. Taking the deviation of the measurement results in consideration, the decrease of less than 3 °C, cannot be regarded significant.

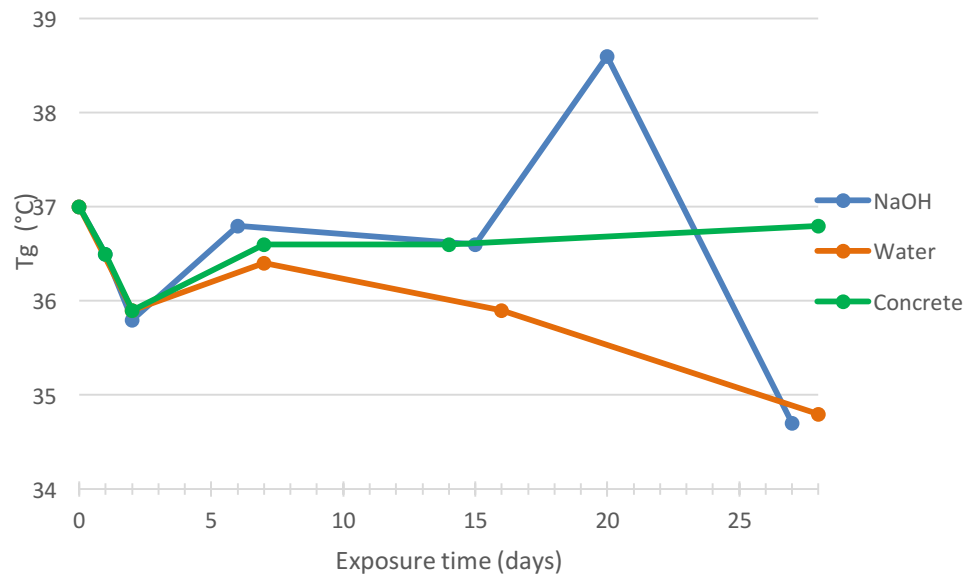


Figure 22. Changes in T_g of the homogeneous DINCH flooring after the exposure to different solutions.

The initiation temperature of the degradation of homogeneous DINCH flooring shows slight increase in the figure 23, but the fluctuation between the test points vary quite much. When the exposure of each flooring to both NaOH solution and water is taken into consideration (figure 24), the initiation temperature seems to remain fairly constant.

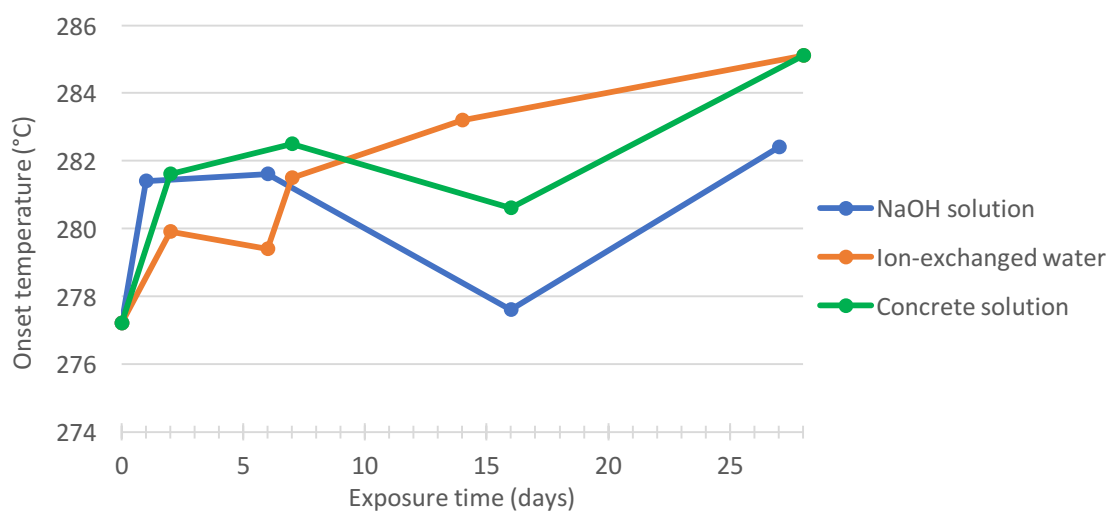


Figure 23. The effect of NaOH, water and concrete solution to T_g of the homogeneous DINCH flooring.

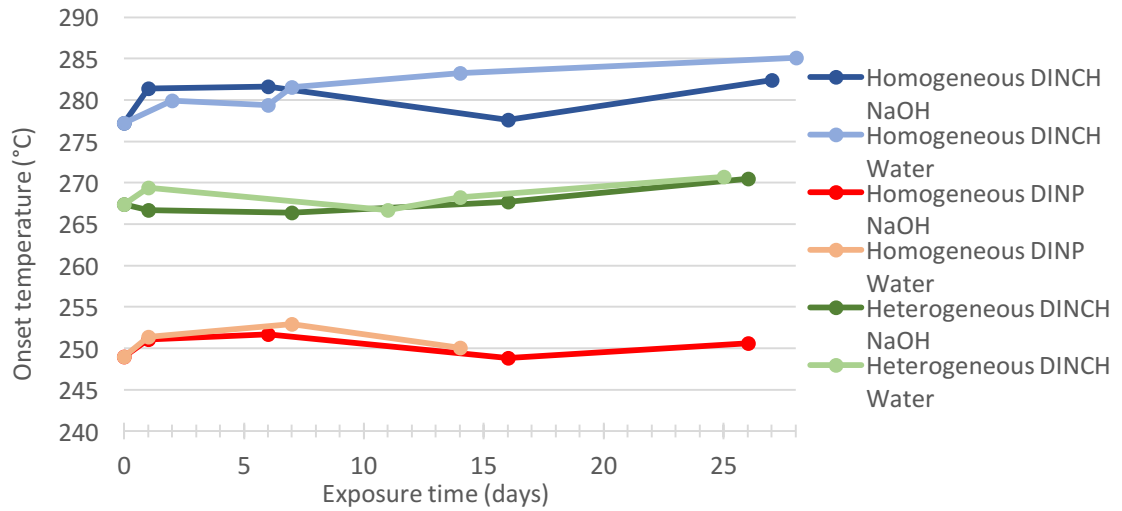


Figure 24. *The effect of the exposure to NaOH solution and ion-exchanged water to onset temperature of degradation of each flooring.*

As such, immersion tests do not seem to be useful method for evaluating the effects of the immersion to flooring. If the testing period would have been longer, the results of the TGA and DMTA measurements may have been more productive. Either way, the idea of the immersion test was to evaluate the resistance of the materials to high alkaline environment in an easy and, above all, quick way and based on that, the method does not appear promising.

7.1.4 Rotational rheometry

Both alkali-resistant and acrylic dispersion adhesives were tested with rotational rheometer after NaOH solution exposure. The results of alkali-resistant adhesive tests are presented in figures 25 and 27, and acrylic dispersion adhesive in figures 28 and 29.

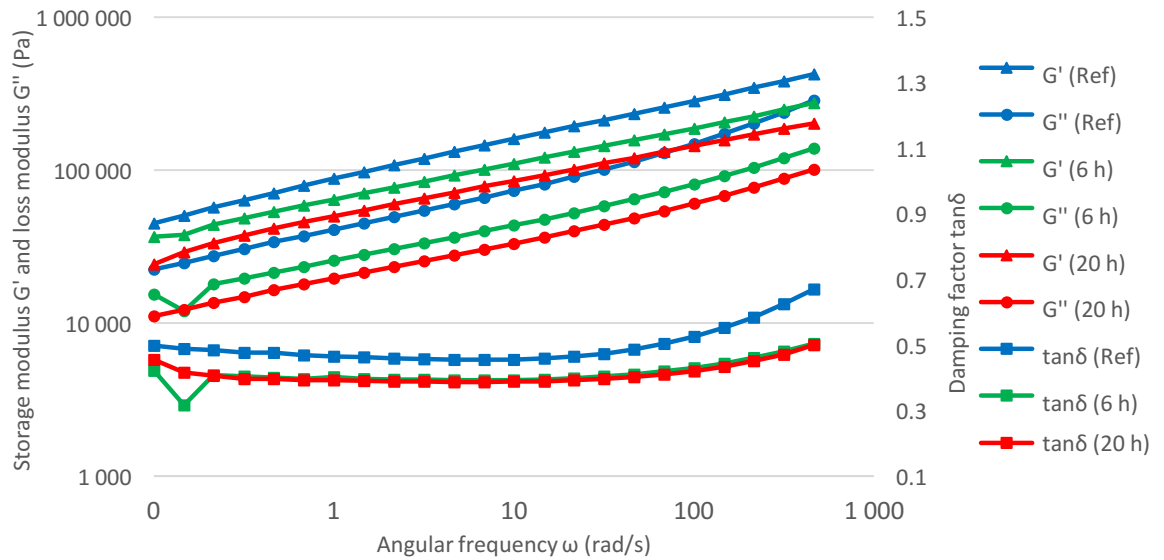


Figure 25. Storage modulus, loss modulus and damping factor of alkali-resistant adhesive as a function of time.

The cross-over point of G' and G'' can be used for studying the changes in molecular mass and molecular mass distribution of the tested material as it is illustrated in the figure 26. As the cross-over point of G' and G'' curves do not show in the figure 25, observations of the change of the molecular mass cannot be done with this method. The absence of the cross-over point may result from a measuring range too narrow. Another method for figuring out the cross-over point would be to perform the measurement as a function of temperature.

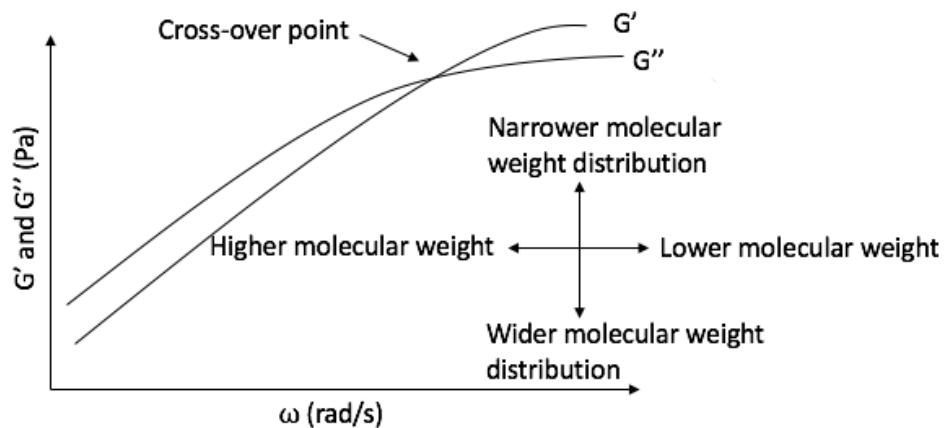


Figure 26. The effects of molecular weight and molecular weight distribution to cross-over point of the moduli. Modified from (Syranidou et al. 2017)

Yet, both the storage and loss modulus decrease due to exposure and the extent of the decrease evolves as the exposure time grows. Damping factor, $\tan\delta$, is calculated as the ratio of the loss and storage moduli and it is decreased due to exposure, which indicates

the decrease in mechanical properties of the adhesive. The decrease of mechanical properties result probably from the decrease in molecular mass.

In the figure 27, the complex viscosity of alkali-resistant adhesive is presented as a function of angular frequency. Complex viscosity takes both the elastic and the viscous properties of the material into account, as it is noticed from its definition in equation 4.

$$|\eta^*| = \sqrt{\left(\frac{G'}{\omega}\right)^2 + \left(\frac{G''}{\omega}\right)^2} \quad (4)$$

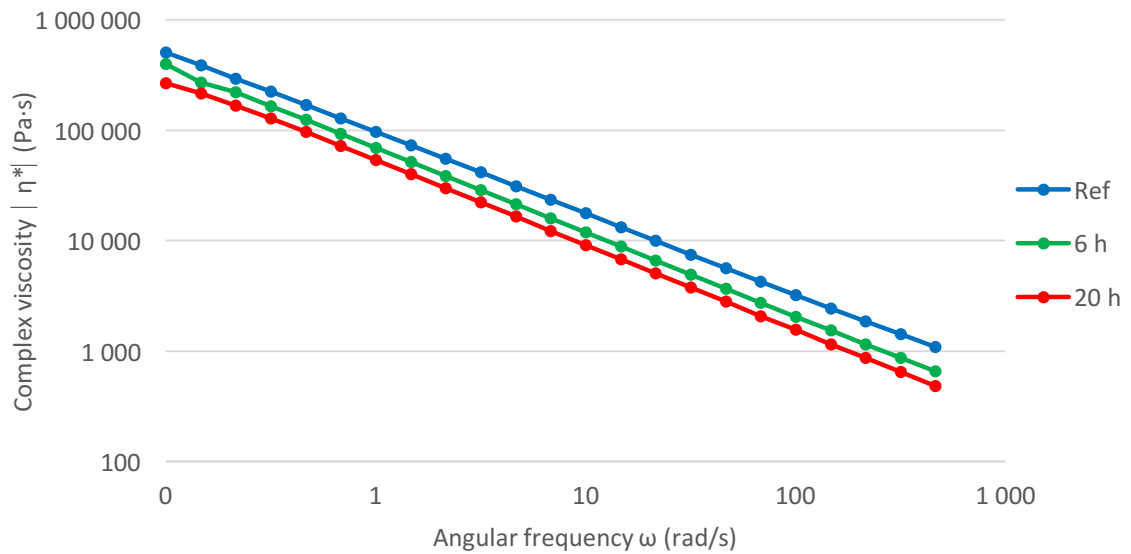


Figure 27. Complex viscosity of alkali-resistant adhesive as a function of angular frequency.

Complex viscosity of the sample decreases as the exposure time increases, which indicates the deterioration of mechanical properties of the sample and thus the decrease of molecular weight due to chain cleavage. Yet a number of variables, such as shear rate, temperature, (weight average) molecular weight and pressure affect the viscosity, of which only the temperature was constant (25 °C) in these measurements.

The results of acrylic dispersion adhesive are presented below (in the figures 28 and 29). Unlike in the case of alkali-resistant adhesive, the moduli values first increase as the sample is exposed 10 days and then decrease almost to original level as the exposure time is increased to 20 days. The increase of the moduli may result from the agglomeration inside the sample. $\tan\delta$ decrease as the exposure time increases thus describing the deterioration of mechanical properties during the exposure.

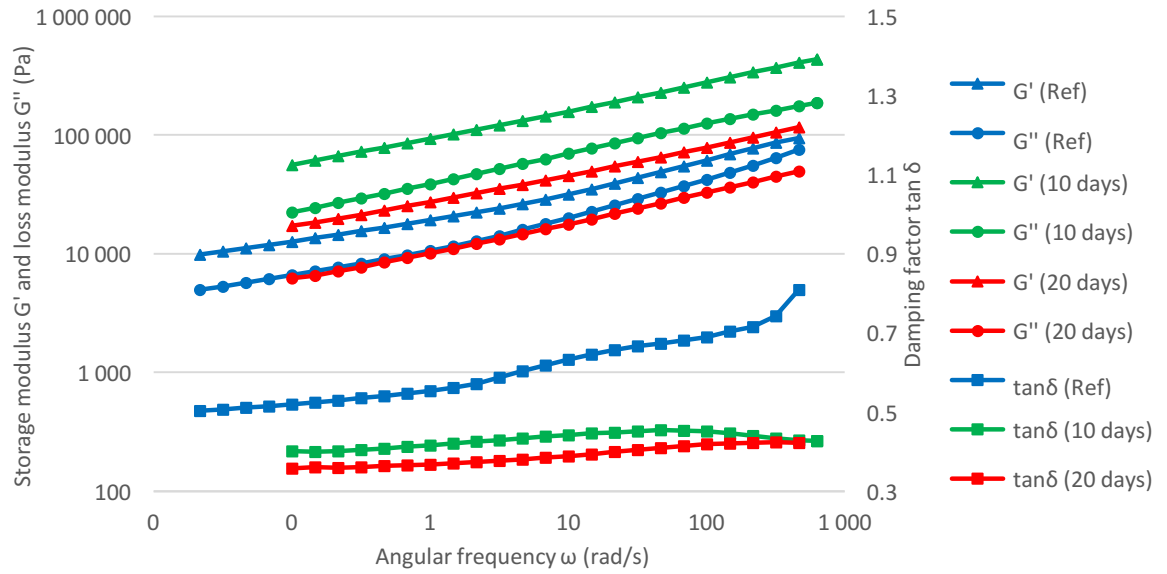


Figure 28. Storage modulus, loss modulus and damping factor of acrylic dispersion adhesive as a function of time.

Complex viscosity of the acrylic dispersion adhesive increases with the increasing exposure time, which supports the earlier deduction of the agglomeration inside the sample. The illogical behavior of first increasing and then decreasing viscosity can result from incomplete desiccation between exposing and measuring the sample. Due to fact that the sample was prepared and dried between the measuring plates, the drying was impossible to follow and may not have been complete.

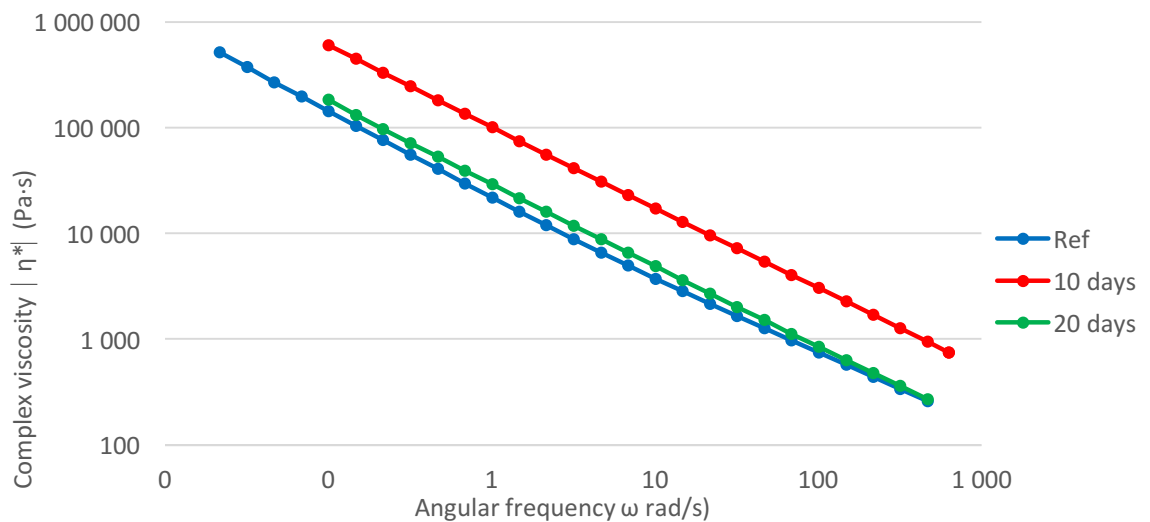


Figure 29. Complex viscosity of acrylic dispersion adhesive as a function of angular frequency.

As a summary of the rheological measurements, some estimations could be done of the changes in the molecular weight of the sample. Further analysis of the chemical reactions is somewhat impossible because the chemical composition of the samples was unknown.

Rotational rheometer was not included in the original plan of the experimental study of the thesis and thus only few samples were measured with it. Another reason for the limited sampling was the schedule of the thesis.

It would have been interesting to test more samples with rotational rheometry and use other exposure solutions as well. Longer exposure times and parallel samples could be tested in order to get more reliable results and to be able to draw a more exact conclusion. The knowledge of the chemical composition of the adhesive would bring depth to the analysis.

7.2 Case study

7.2.1 Pull-off tests

Three parallel tests were made in each four classrooms, both in damaged and undamaged sites. The result of each measurement, their average and standard deviation are presented in the table 2. Value 0.0 kPa describes fully detached flooring. Averages and deviations are presented more illustratively in figure 30.

Table 2. *The results of pull-off tests.*

(kPa)	Room 1	Room 2	Room 3	Room 4
Damaged	0.00	0.00	0.00	20.69
Damaged	6.89	6.89	0.00	20.68
Damaged	0.00	48.26	0.00	0.00
Average	2.30	18.38	0.00	13.79
Deviation	3.45	21.31	0.00	9.75
Undamaged	110.32	62.05	13.79	34.47
Undamaged	62.05	110.32	55.16	20.68
Undamaged	89.63	96.53	82.74	55.15
Average	87.33	89.63	50.56	36.77
Deviation	19.77	20.30	28.34	14.17

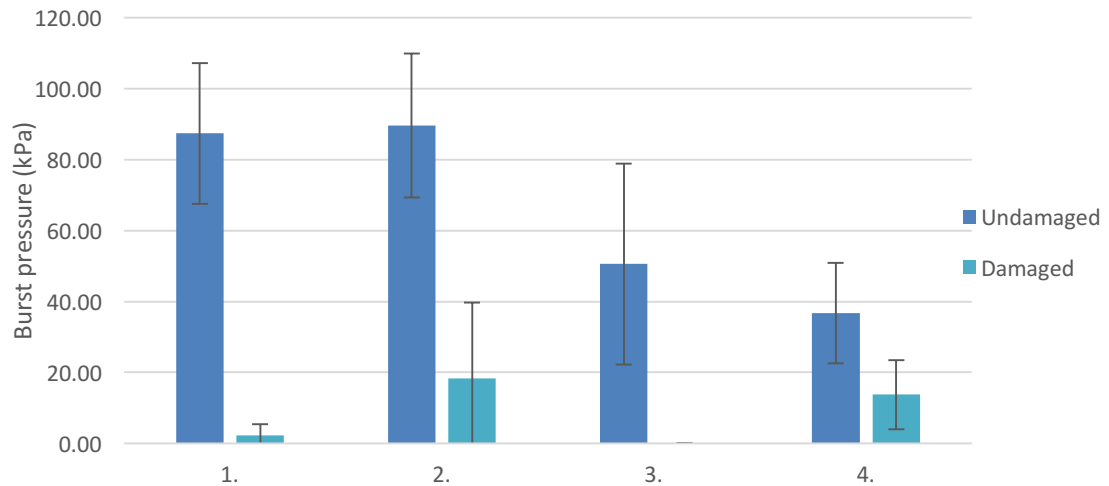


Figure 30. *Averages and standard deviations of the pull-off tests in damaged and undamaged sites. Standard deviation is presented with black line.*

As it is clearly detectable in the figure 30, the pressure needed for detaching the flooring in damaged sites (i.e. sites with high relative humidity) is significantly lower than in undamaged sites. The relative humidity of different measurement sites is presented in the figure 31. The relative humidity values were measured beneath the flooring by another quarter. As it can be observed, in most of the rooms the RH of the damaged site still rises above 85%, whereas in undamaged sites the RH is much lower. The data of the undamaged site in the room 2 was not available.

Figures 30 and 31 support the presumption, that alkaline humidity of the concrete reduces the adhesion of the flooring and causes the detachment. The question is, has the relative humidity of the concrete been too high when the concrete has been covered with screed, adhesive and the flooring during the construction phase, or, has the humidity appeared after the construction, during operational phase of the building.

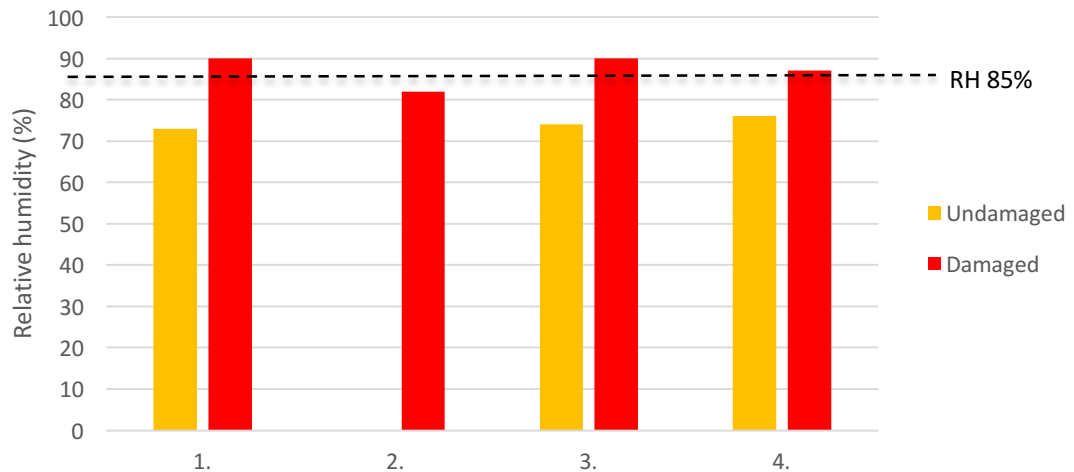


Figure 31. *Relative humidity under the flooring in different measurement sites.*

Building materials, including the floorings, adhesives and screed, used in this particular school building, are not documented and it is possible that the materials are not the same in each room. Thus, any kind of comparison to fresh materials was excluded. It is also impossible to evaluate the effect of working methods during the construction to the adhesion of the flooring and thus the results of the pull-off tests. Yet, the main reason for the poorer adhesion of the floorings on the damaged sites is the high RH caused by the lack of thermal insulation under the walls. A thing to consider is also the representativeness of the sample; how well does a sample of 16 mm of diameter represent the whole area of the interest?

Due to (typically) tight schedules of the construction work, it may be even impossible to ensure the proper and adequate drying of the concrete before applying other layers on it. It is also notable, that sufficient drying is not only related to drying time but also to humidity of the environment.

7.2.2 Fracture mechanisms

Visual examination reveals that the fracture occurs mainly as a cohesive fracture in the screed – layer of screen was adhered to both the floor and the flooring piece that was ripped of. The more specific inspection was done by image analysis, using ImageJ[®]. The aim of the image analysis was to define the percentage of different failure modes and locations. In this case, the failure occurred cohesively in the screed and adhesively between the screed and the adhesive. The proportions of failure modes are presented in the figure 32.

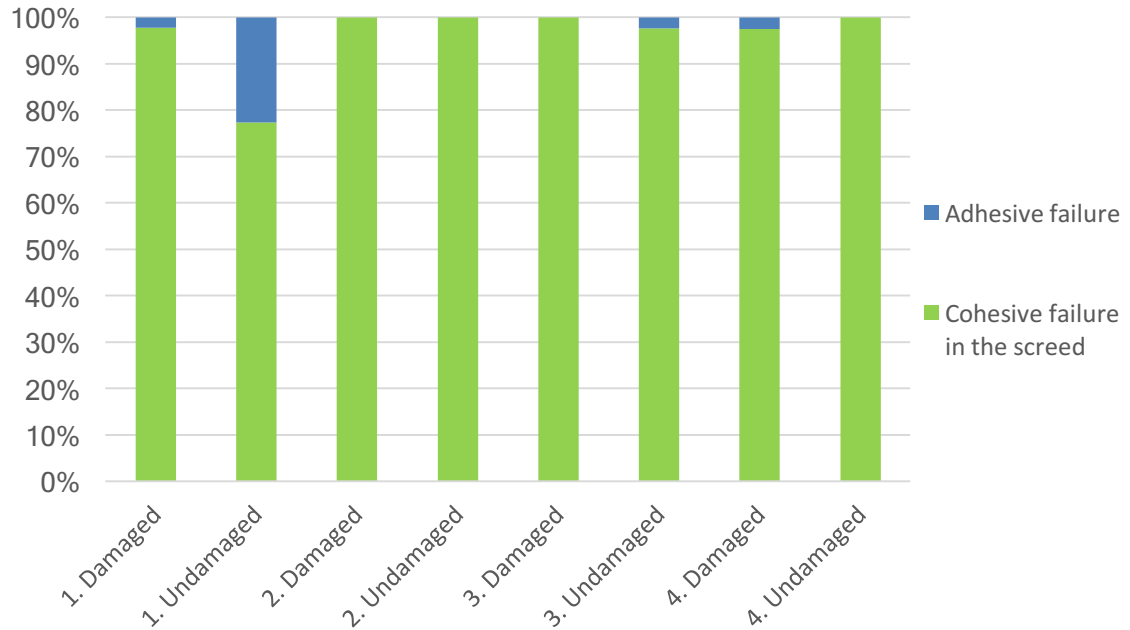


Figure 32. Percentages of adhesive failure between the screed and the adhesive and cohesive failure in the screed.

As noticed, the cohesive failure in the screed is highly dominating. Adhesive failure can be detected only from the half of the samples and their share is minimal compared to cohesive failure in the screed. Although the exploration of the screeds was excluded of this thesis, these results indicate the need for the study of their behavior in alkaline and moist environment.

The effect of the screeds to VOC emissions and the decrease of pH have been studied a lot and the study of the alkaline resistivity of floorings and adhesives have been focused on detecting the VOC emissions. The study of the adhesive bond strength would bring a new approach to this research topic. By comparing the strength of the adhesive bond of different material combinations, as it was planned in the first place, the optimal material combinations could be resolved. The right combinations would ease the detachment problem of the floorings and possibly the indoor environmental problems as well.

If the documentation of the construction phase would be improved, the results of the adhesion tests done in the laboratory could be compared to the results of the case studies. During this process, it also came up, that there would be a request for a definition of a limit value of adhesion within the industry. The limit value would facilitate and simplify the product development in industrial companies.

8. CONCLUSIONS

The aim of the experimental studies of this thesis was to explore, if immersion tests could be used for ranking different floor adhesives and plastic floorings in a simple and cost effective way. Also, in the case study the location of the failure was studied to find out where the floorings detach in use.

The novelty of this research exists in the research method, which is not used before in the study of floorings and adhesives and their resistance to alkaline humidity. No comparable studies or results were found during the process. Generally, the effects of alkaline humidity to floorings or adhesives has been research via VOC emissions, their quality and quantity.

As a result, it can be noted that immersion test cannot be used as such for ranking the materials. Yet it showed some potential in the study of the adhesives but it should be inspected if there is a difference in the behavior of the adhesive in concrete and in NaOH solution of same pH. If the behavior is the same, the samples can be tested in NaOH solution, which is commercially available and thus makes the testing easier. No relevant results were achieved when the floorings were tested. Estimations of the changes in the molecular mass of the adhesives could be done with rotational rheometer and it would be interesting to test more samples with it, as well as to use other exposure solutions.

Failure inspection was performed as a case study and the results showed that high RH in the floor causes weaker adhesion of the floorings. The dominating failure mode was cohesive failure in the screed which implicates the share of the screed to detachment of the floorings.

In the future, the behavior of the samples in concrete and NaOH solutions of same pH should be compared and the potential of immersion test could be reconsidered by continuing the exposure time, e.g., for two months. Longer exposure times and parallel samples should be tested in order to get more reliable results and to be able to draw a more exact conclusion. For carrying out a high-quality research of the chemical changes in the adhesives or floorings, the compositions of them should be given. Different analysis methods could be considered as well. In addition, the behavior of the screeds in alkaline and humid environment should be studied and their share to flooring detachment should be evaluated.

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APPENDIX A: TGA RESULTS FOR ALKALI-RESISTANT AND ACRYLIC DISPERSION ADHESIVES

	Exposure (hours)	Onset of degradation (°C)
Alkali-resistant adhesive NaOH solution (pH 13.0)	0	314.5
	1	312.8
	7,5	308.4
	23	300.9
	48	286.5
Alkali-resistant adhesive Ion-exchanged water (pH 6.0)	0	314.5
	1	325.8
	7,3	323.1
	26	318.3
	48	322.8
Alkali-resistant adhesive Concrete solution (pH 12.5)	0	314.5
	1	321.7
	7	323.1
	23	317.0
	48	322.5
	Exposure (days)	Onset of degradation (°C)
Acrylic dispersion NaOH solution (pH 13.0)	0	369.5
	1	370.5
	8	362.6
	15	368.5
	28	354.0
Acrylic dispersion Ion-exchanged water (pH 6.0)	0	369.5
	2	381.3
	6	383.8
	15	382.0
	28	377.1
Acrylic dispersion Concrete solution (pH 12.5)	0	369.5
	2	383.0
	6	377.4
	17	372.3
	28	370.4

APPENDIX B: DMTA AND TGA RESULTS FOR THE FLOORINGS

	Exposure (days)	T _g (°C)	Onset of degradation (°C)
Homogeneous DINCH NaOH solution (pH 13.0)	0	37.0	277.2
	1	36.5	281.4
	2	35.8	-
	6	36.8	281.6
	15	36.6	-
	16	-	277.6
	20	38.6	-
	27	34.7	282.4
Homogeneous DINCH Ion-exchanged water (pH 6.0)	0	37.0	277.2
	2	35.9	279.9
	6	-	279.4
	7	36.4	281.5
	14	-	283.2
	16	35.9	-
	28	34.8	285.1
Homogeneous DINCH Concrete solution (pH 12.5)	0	37.0	277.2
	1	36.5	-
	2	35.9	281.6
	7	36.6	282.5
	14	36.6	-
	16	-	280.6
	28	36.8	285.1
Homogeneous DINP NaOH solution (pH 13.0)	0	38.4	249.0
	1	37.8	251.1
	6	-	251.7
	8	38.4	-
	14	38.4	-
	16	-	248.8
	26	38.0	250.6
Homogeneous DINP Ion-exchanged water (pH 6.0)	0	38.4	249.0
	1	37.5	251.4
	7	-	252.9
	10	37.9	-
	14	37.9	250.1
	28	Failed	Failed
Heterogeneous DINCH NaOH solution (pH 13.0)	0	-10.5 and 152.8	267.4
	1	75.5	266.7
	6	-	266.4
	8	-1.1 and 32.1	-
	14	1.1 and 23.1	-
	15	-1.0 and 37.8	-
	16	-	267.7
	26	-0.8 and 21.7	270.5
Heterogeneous DINCH Ion-exchanged water (pH 6.0)	0	-10.5 and 152.8	267.4
	1	Failed	269.4
	7	-	-
	11	101.7 and 138.8	266.7
	14	Failed	268.2
	28	0.9, 105.3, 137.9	270.7