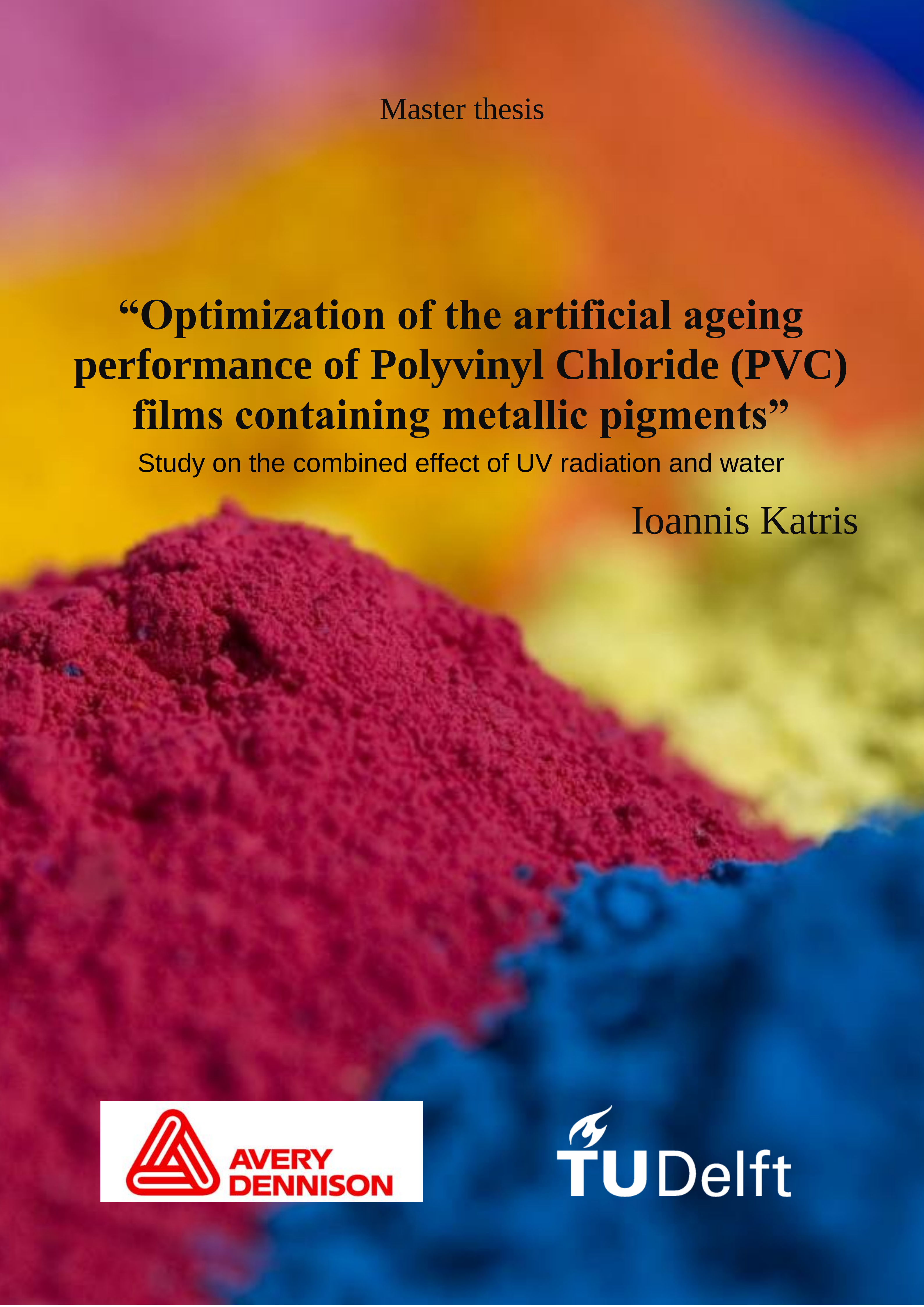

Master thesis

“Optimization of the artificial ageing performance of Polyvinyl Chloride (PVC) films containing metallic pigments”

Study on the combined effect of UV radiation and water

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“Optimization of the artificial ageing performance of Polyvinyl Chloride (PVC) films containing metallic pigments”

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By

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in partial fulfilment of the requirements for the degree of

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Preface

I moved to the Netherlands in August of 2017 and soon thereafter began with the Master program in Materials Science and Engineering with a focus in materials for engineering applications. As I drew closer to the end of my coursework, I began searching for projects to take part in for my thesis work. I have always taken an interest in the field of polymers, so when I was presented with an opportunity to work in Avery Dennison on a project that would be relevant for the investigation of poly(vinyl chloride) degradation when metallic pigments are implemented inside, I was thrilled. This experience was invaluable, as it helped me to gain a thorough understanding of the analytical techniques and materials used for this project. There are several people without whom this thesis would not have been possible. I would like to thank Daniela Saviello, Specialist Development Engineer, for the opportunity to work with her on this project and Mutlu Cavusoglu, Sr. R&D Manager in Avery Dennison. They were immensely helpful and ensured that I always had the resources I needed for my project. My supervisor, Associate professor Eduardo Mendes, was really supportive and our interesting discussions were significant for this project. His personal and academic support will forever be appreciated. Last but certainly not least, I would like to thank my family for ensuring I was able to realize the completion of my Master's degree.

Ioannis Katris
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Abstract

Metallic pigments are versatile, eye-catching and increasingly utilized materials to create unique effects in plastics. However, these pigments usually show a higher sensitivity to weathering factors like UV light and water in polymer formulations than other pigments. In the particular case of Polyvinyl Chloride (PVC), this is even more evident for pigments containing iron based compounds (the typical red and orange brilliant colors) because they can initiate a degradation processes or catalyze oxidation of the polymer or other components. Thus, an improvement of such formulations for a better long term stability of the final products is needed.

The present study was carried out in the Avery Dennison R&D laboratories. It was designed in order to carry out a preliminary test to address the issue of low durability of certain colored PVC based-films containing metallic pigments. Several sensitive pigments were selected as a case study for this project. In particular, the project aims to focus on understanding the effect of water on the surface of colored PVC cast films. Water retention on the surface of the films tends to cause accelerated and localized degradation of the PVC matrix enhanced by the effect of the metal oxides.

What was observed for the pigmented PVC films is that as the pigment loading increases, the weathering durability improves. The degradation spots were mostly observed on the sides of the tested films but in some cases degradation spots were observed on the surface as well. The localized degradation on the sides is attributed to the damaged flake/particles of pigments which causes the initiation and propagation of PVC degradation in combination with water retention. After the SEM analysis, the degradation on the surface can be attributed to pigment flakes/particles really close to the films surface or even protruding from it where they can easily come in contact with water.

Among all five selected additives (water scavenger, dispersants 1 and 2, fluorinated MICA and anticorrosive pigment), the ones with the best overall performance were the water scavenger and the anti-corrosive pigment. The water scavenger reacts with water avoiding its involvement in the PVC degradation process. Since water is not involved, less free radicals are formed and as a result, the propagation of PVC degradation is delayed. The anti-corrosive pigment increases the overall weathering durability of the system by protecting the sensitive metallic pigments with the Zn content of the anti-corrosive pigment surface treatment conferring sacrificial cathodic protection

Confidentiality

Due to the confidential character of the report, the commercial names of the classified compounds used in the research were changed or removed. The restrictions included the trade name of poly(vinyl chloride), which was mentioned as PVC in the report, the five different pigments which were referred as pigment 1, 2, 3, 4 and 5 and the four additives used to improve the water resistance were mentioned as water scavenger, dispersants 1 and 2, fluorinated MICA and anti-corrosive pigment.

Please do not share, copy or quote the information contained in this Master Thesis.

Abbreviations

AD	Avery Dennison
AFM	Atomic Force Microscope
BET	Brunauer, Emmett and Teller
CA	Contact angle
CIE	Commission Internationale de l'Elcairage
DSC	Differential Scanning Calorimetry
EDS	Energy Dispersive Spectroscopy
FTIR	Fourier-Transform Infrared
h	hours
HCl	Hydrochloric Acid
Inter	Intermediate loading
IR	Infrared
Min	Minimum loading
Max	Maximum loading
PET	Polyethylene terephthalate
PHR	Parts per hundred resin
PPM	Parts per million
PVC	Poly(vinyl chloride)
sec	seconds
SEM	Scanning Electron Microscopy
TDS	Technical data sheet
TGA	Thermogravimetric analysis
UV	Ultraviolet
VC	Vinyl Chloride
XRF	X-ray Fluorescence

1 Introduction

Since their early production, polymers have been increasingly and widely used materials in many industrial fields and applications. In particular, poly (vinyl chloride) (PVC), is one of the most versatile and important materials in the modern plastic industry [1-3]. The success of this material (PVC) is due to its valuable properties, such as chemical resistance, resistance to environmental degradation, outstanding tensile strength for a plastic and low production costs.

Despite all these favorable characteristics, plastic materials can show signs of degradation, sometimes immediately after their production and then when exposed to indoor and outdoor conditions. In fact, numerous physical processes and chemical changes occur when polymeric materials are exposed to environmental agents such as UV light, air and heat. In the case of PVC these reactions can involve dehydrochlorination (formation of conjugated double bonds), photo-oxidative and thermal degradation, with the consequence of deterioration of mechanical, physical and chemical properties. Degradation results in breaking of the polymer chains, reduces the molecular weight and produces radicals, leading to useless materials [1-5].

1.1 Aim of this study

In this research project, the available weathering data, of the previously prepared and artificially aged PVC films, from a diverse series of the Avery Dennison portfolio was carefully analyzed and a suitable database was created. Films with pigments with different chemistry, shape, size and coating, sensitive to weathering (lifetime ~ 1000 hours of artificial weathering → 1.3 years of real lifetime) were prepared.

The Avery Dennison films are composite materials consisting of metallic pigments dispersed in a PVC matrix with an adhesive applied on the backside of the film. Therefore, the degradation of the whole product may originate from mechanisms related to the PVC resin, the metallic pigments or the adhesive. Thus, the evaluation of the degradation of the films should be made in respect of the whole compound but also in respect of each component individually. The degradation process will be monitored under the combined effect of UV radiation and water in central Europe weather conditions with an emphasis in the effect of water since this effect is not extensively addressed in the literature.

After taking under consideration the previous paragraph, the main objectives of this study can be defined as:

- Evaluate the degradation mechanism of the films and determine the contribution of each component to the process.

- Relate the contribution of water to the degradation of the films (fig.1.1) and find a way (water scavenger) to minimize its contribution to the process.
- Relate the different characteristics of the chosen metallic pigments (chemistry, shape, size and coating) to the degradation of the films and propose mechanisms to approach these characteristics respectively (use of additives).
- Relate the contribution of the components of the films and the additives that will be used to changes on the films properties (roughness, porosity, mechanical properties, *etc.*) that affect their appearance (color, gloss) and durability.

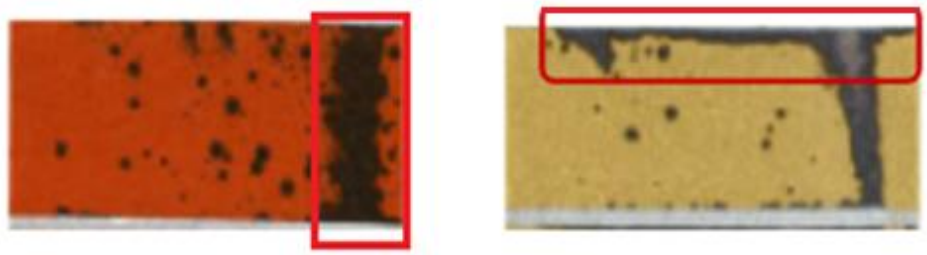


Fig.1.1. Water retention and localized degradation of PVC films after 1000 hours of artificial weathering.

In order to meet these objectives, a multi-analytical investigation was undertaken on the pigmented PVC films by using different ageing and analytical techniques such as: contact angle measurements, color and gloss measurements, tensile tests, Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Fourier-Transform Infrared Spectroscopy (FTIR) and Differential scanning calorimetry (DSC).

1.2 Avery Dennison

As the durability of the films in the Avery Dennison portfolio with custom-made colours is a quantitative and qualitative function of various factors, including PVC resin, plasticizer, stabilizers and pigments, a profound understanding of the different failure mechanisms faced by the materials is required. Additionally, a good prediction on the expected outdoor durability of the films, based on the chemistry of PVC, stabilization package and the fillers (e.g. pigments, additives), is desired. The main focus of this study is to analyze and improve the weathering performance of Avery Dennison’s PVC films under the effect of UV radiation and water in order to simulate better the environmental factors in the region of central Europe.

AVERY DENNISON

2 Literature review

2.1 Chemical structure of PVC

PVC [6] can be synthesized by three different methods: suspension, bulk or mass and emulsion polymerization [7]. Commercial production of PVC is 80 % based on the suspension process. The preparation method has an important influence on the physical properties of PVC. In general, the polymer synthesized during the suspension process is a very pure product and has a better transparency compared to PVC obtained during emulsion polymerization [8].

Suspension polymerization includes four main steps: polymerization (process of reacting monomer molecules together in a chemical reaction to form polymer chains), stripping residual vinyl chloride (reduction of vinyl chloride monomer concentration in poly vinyl chloride), centrifugation of water suspension, and drying. Each of these processes influences morphology of the final product. The PVC used in this research activity is obtained during the process of micro-suspension or emulsion polymerization. Emulsion polymerization (the reaction occurs in an aqueous medium where the monomer and water form an emulsion by means of stirring and the addition of an adequate emulsifier) is an alternative but far less common technology used to manufacture PVC. As a result of these processes (suspension and emulsion polymerization), produced resin grades are finer with much smaller particles compared with those obtained during suspension polymerization. This type of resin is often used for applications such as a paste for coating surfaces.

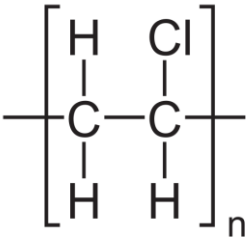


Fig.2.1. Repeat-unit of PVC polymer [6].

Vinyl chloride is the sole monomer used in the production of PVC. The polymerization occurs according to a free radical addition process (fig.2.2 and 2.3) [9]. The general reaction describing the VC polymerization is shown in figure 2.5.

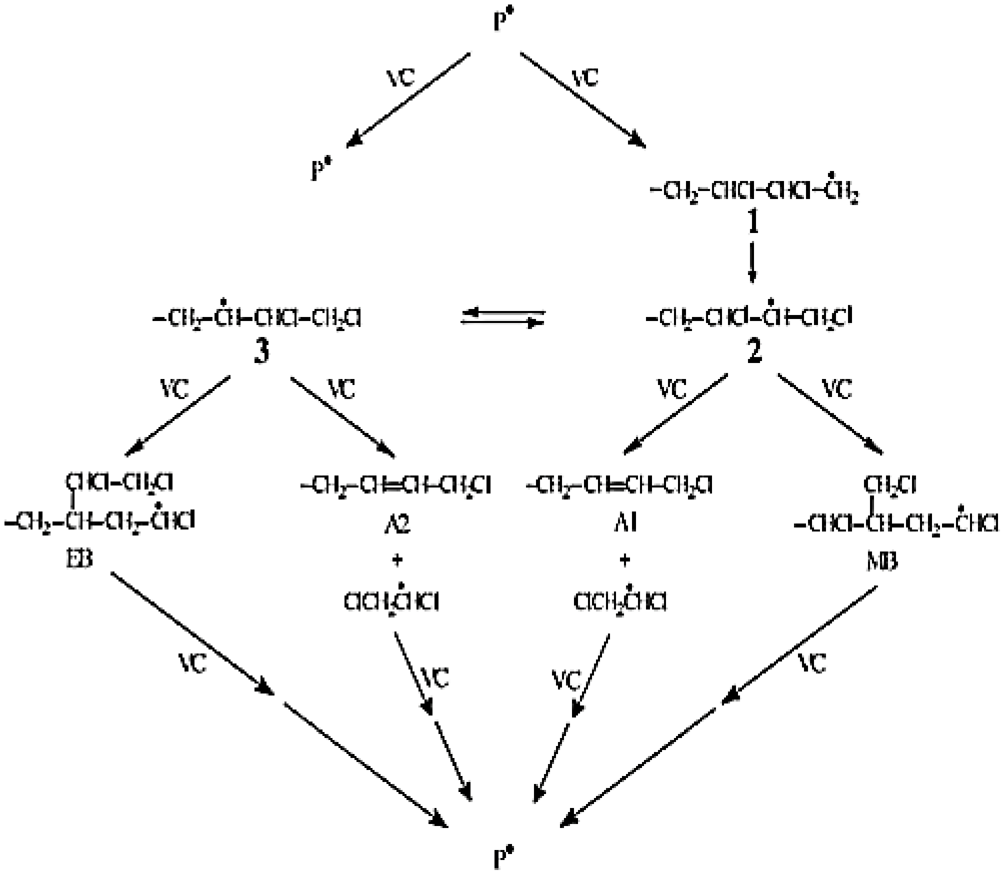


Fig.2.2. Chemistry resulting from the head-to-head emplacement of VC during its polymerization [9].

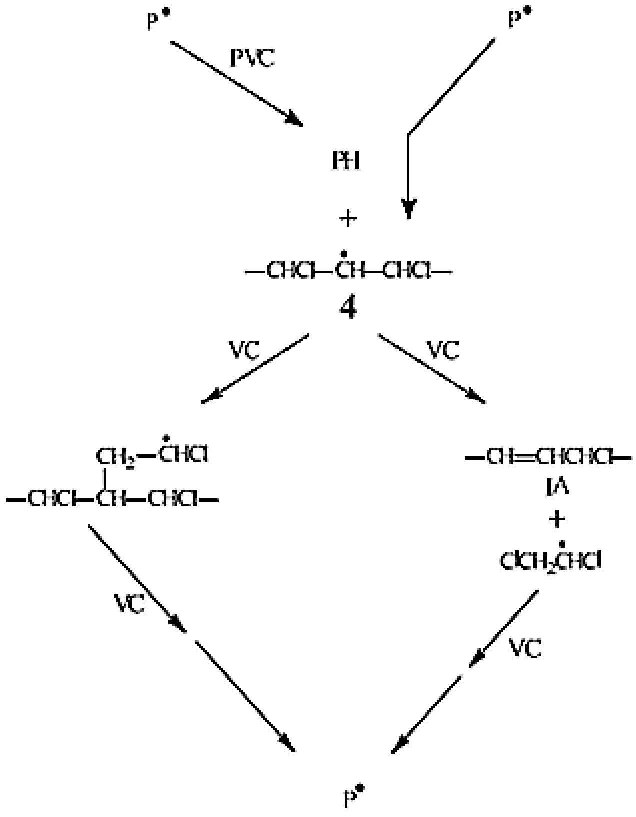


Fig.2.3. Auxiliary mechanism for chain transfer to the monomer during VC polymerization, where P$^{\bullet}$ is the head-to-tail macro-radical [9].

2.2 Degradation and stabilization

2.2.1 Photodegradation and Photostabilization

Even though, there is a great interest in the photodegradation of polymeric systems, and the topic has been extensively studied for years, the definitive mechanism of PVC degradation is still the subject of much speculation. A significant reason for the interest in the photodegradation of the macromolecular materials is their increasingly growing importance in commercial applications, where outdoor durability is a crucial consideration [10].

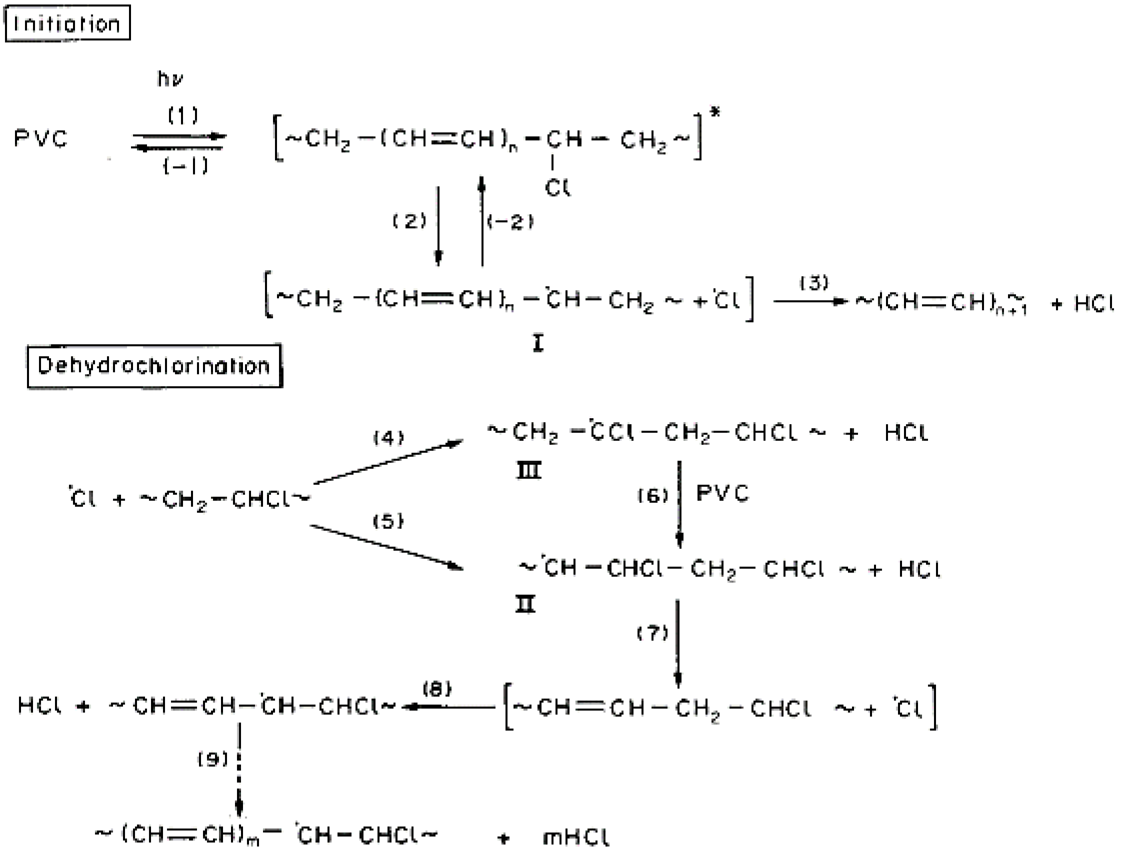


Fig.2.4. Photodegradation of PVC [11].

Photodegradation (fig.2.4) is a deterioration of a photodegradable molecule caused by the absorption of photons, particularly those wavelengths found in sunlight, including ultraviolet light, visible light and infrared light. Damage by absorption of near UV radiation is commonly the main reason for breaking down the chemical bonds in a polymer. Moreover, for colored PVC photodegradation causes discolouration of dyes and pigments, cracking of the material, chalking, and the loss of desirable physical properties [11].

PVC exposed to UV light, in the presence of oxygen and moisture, sustains a rapid dehydrochlorination and peroxidation process with the formation of polyenes and oxygen hydroperoxides, and due to the further reactions, the aliphatic ketones and aliphatic alcohols. The process is often called photo-oxidation [12, 13].

The effects of UV solar radiation are the most significant threat to the PVC durability in outdoor applications. More specifically, the combined effect of UV radiation and water causes the creation of a variety of free radicals that cause the initiation and propagation of the degradation process. Chemical and physical stabilization of the polymer against environmental degradation can be achieved by blocking any of the steps in the deterioration process. Various techniques have been developed to achieve the photostabilization of polymers such as addition of antioxidants, heat and light stabilizers [14].

2.2.2 Thermal degradation and stabilization

PVC has a significantly lower thermal stability than comparable low-molecular weight compounds. Commercially available PVC undergoes chemical changes and decomposes at temperatures higher than 120 ℃, if it is not stabilized before processing. Thermogravimetric analysis on low molecular weight substances of similar structures, corresponding to the regular structure of PVC such as 2,4,6-trichloroheptane, 2-chloropropane and 2,4-dichloropentane, shows that these model compounds are stable up to 200 °C more than PVC [15].

During the processing and utilization of PVC, the polymeric material is exposed to heat in the presence of oxygen, causing the appearance of strongly light-absorbing chromophores that probably take the predominant role of sensitization of the PVC chain, initiating thermo-oxidative deterioration.

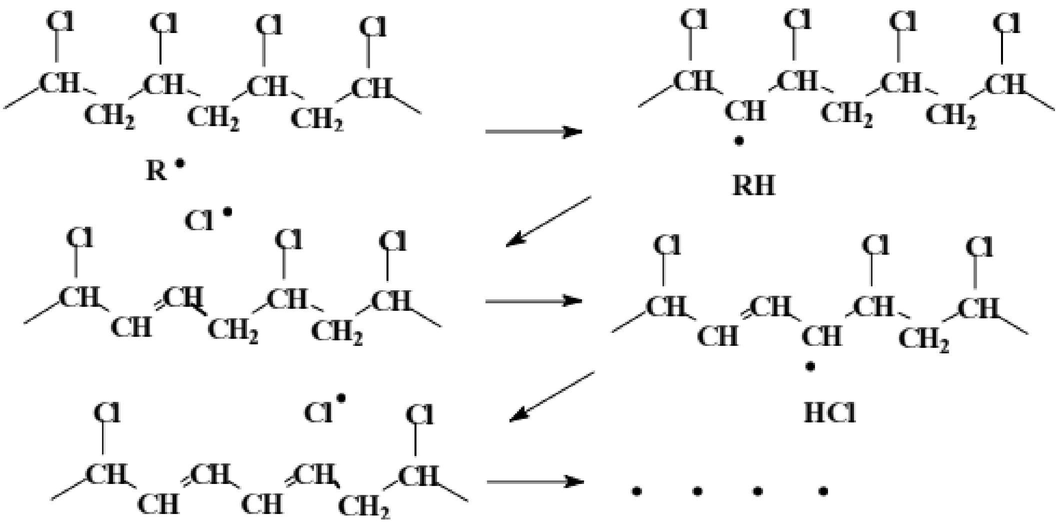


Fig.2.5. General PVC degradation mechanism [15].

Many mechanisms of PVC degradation have been proposed and the reactions occurring are still under investigation. However, it seems to be generally accepted that thermal degradation of PVC proceeds with evolution of hydrochloric acid (HCl) via zip-dehydrochlorination through the Cl radical and further degradation by oxidation through the polymer backbone radical (fig.2.5).

The primary process of thermal degradation includes three main steps: (1) initiation of dehydrochlorination, (2) elimination of HCl and simultaneous formation of conjugated double bonds, and (3) termination of dehydrochlorination. The process occurs by an autocatalytic dehydrochlorination reaction with the subsequent formation of conjugated double bonds. The excited polyenes are formed and stabilize by splitting off an allylic chlorine atom after the loss of the first HCl molecule.

PVC without stabilizers starts degrading at a lower temperature than the required to reach the processing conditions. Until the development of thermal stabilizers, PVC did not serve a great industrial purpose because the polymer could not be processed into useful objects without degradation at elevated temperatures. Pure PVC is a rigid fragile solid at room temperature. At chain lengths as low as 1000 (average) the PVC Glass Transition (T_g) reaches 80 °C, and on average, non-plasticized PVC exhibits $T_g = 87$ °C. The action of heat on a polymeric material causes a loss of physical, mechanical and/or electrical properties [16].

The main classes of thermal stabilizers in current use are metal soaps and organotin compounds. Until recently lead salts were the most significant in the thermal stabilization process of polymers, but due to the increasing safety and environmental awareness, use of those substances is limited or completely prohibited. The organotin stabilizers and metal soaps are safer than lead salts, but their stabilization properties are usually lower than those of lead salts. Organic salts are the main group of thermal stabilizers for chlorinated polymers, *e.g.* PVC.

2.3 PVC compounding

2.3.1 Plastisols and Organosols

A compound is defined as a substance formed when two or more elements are chemically bonded together. New compound formulations are developed to meet an application requirement or a processing limitation.

The convention in recording additive concentrations is based on parts per hundred of the PVC resin (phr). A compound is generated by intimately mixing together the ingredients, which is subsequently converted into the gelled article under the influence of heat (and shear). Depending on the type of PVC and additives, the compound prior to gelation can be a free- flowing powder (known as a dry blend) or a liquid in the form of a paste or solution. Chemists and formulation engineers create custom compounds by blending a variety of additives, pigments, modifiers and stabilizers with the PVC resin to achieve specific properties.

Plastisols are dispersions of the fine particle size type PVC resin in a plasticizer. A paste is formed the viscosity of which depends on the particular properties of the resin used and the type and level of the plasticizer. The paste is formed by mixing the PVC into the plasticizer with shearing to ensure dispersion of the PVC resin particles in the plasticizer. The ability to form a stable paste depends on the resin's particle size and the emulsifier coating on the resin. After the preparation of the paste, this liquid system may be spread onto a cloth, paper or metal substrate, or otherwise cast in a mold. After coating or molding, heat is then applied. The heat causes the PVC particles to dissolve in the plasticizer. Upon cooling, the solution of PVC in the plasticizer possesses all the properties of vinyl plastics. There are different changes that the plastisol system goes through from the initial liquid state to the final fused product.

The paste formed is generally quite stable and will, if kept at or near room temperature, remain unchanged indefinitely. Resins containing coarse agglomerates and poor wetting properties may show evidence of agglomerate settling, particularly in low viscosity compounds. Some resins show increased viscosity after a period of time. Part of this effect is thixotropic in nature and with agitation the compound will revert to a lower viscosity state. A portion of this viscosity is permanent. The reversible portion of viscosity increase is attributed to the resin particles flocculating into a loose network. If the plasticizer penetrates into the particle, then the effect is irreversible, leading to a permanent viscosity increase.

If the plasticizer levels are low, the viscosity increases since less plasticizer is available to separate the resin particles by diluting the continuous phase of the plasticizer. When the amount of the plasticizer used to form a paste is low, volatile dillutents are then added to the plasticizer phase so that enough liquid phase is available to form a fluid dispersion. Such systems are referred to as organosols.

Organosols are similar to plastisols, except that they contain high levels of solvents and usually low levels of plasticizers and they are usually applied to achieve thin coatings. Specific solvents are utilized in organosol formulations and a proper selection is needed, otherwise the PVC can solvate and eventually turn solid. The organosol is suspended rather than dissolved in an organic fluid. The dispersion technique permits the use of high-molecular-weight, relatively insoluble resins without the use of expensive solvents. In organosols, the fluid, or dispersant, consists of plasticizers together with a blend of inexpensive volatile diluents selected to give the desired fluidity, speed of fusion, and physical properties. The dispersant provides little or no solvating action on the resin particles until a critical temperature is reached at which point the resin is dissolved in the dispersant to form a single-phase solid solution. Since a portion of the liquid is made up of volatile diluents, the fusion process results in a proportional shrinkage. The heating is an essential stage in the organosol formulation process. Heating is accomplished in two stages. The volatiles are removed in the first stage at temperatures of from 93 to 121 °C, but fusion does not occur until a temperature of 149 to 191 °C is reached. The fusion stage accomplishes the union of the discrete vinyl particles into a single-phase solid. A balance must be achieved in the heating operation between the removal of the volatiles and the solvation of the resins because rapid heating results in solvent blistering, whereas the reverse causes a mud-cracking effect [17].

2.3.2 Heat and UV stability

As mentioned before, PVC is not particularly heat stable and decomposes when exposed to higher temperatures associated with fusion and degrades under UV radiation. The degradation product is HCl and as shown before the evolved HCl acts to further decompose the polymer as an autocatalytic degradation process. This process occurs by an autocatalytic dehydrochlorination reaction with the subsequent formation of conjugated double bonds. The excited polyenes are formed and stabilize by splitting off an allylic chlorine atom after the loss of the first HCl molecule. As a result, the formulation needs to be protected for the heat effect and of course UV radiation. This is accomplished with the use of thermal and UV absorbers.

The thermal stabilizers chemically absorb the evolving HCl and therefore reduce the catalytic influence of HCl to the extent that the paste can be processed at temperatures between 149 ^{o}C and 204 ^{o}C without any loss in properties due to thermal degradation. They are based on metallic compounds of barium, cadmium, zinc, lead and tin. The conventional stabilizer system based on barium, cadmium and zinc is designed to provide maximum heat stability with a minimum of yellowing during the fusion process. Barium is the most effective element in this process but when used alone the PVC develops a yellow color. For that reason, cadmium and zinc are used to minimize yellowing of the PVC organosol.

The UV absorbers can protect the PVC product from the harmful effects of light exposure and helps it maintain physical properties during demanding applications such as long-term weathering. These chemicals preferentially absorb ultraviolet light of wavelengths from 295 to 400 nm and their activity in PVC is based on their ability to absorb UV light and convert it to harmless forms of energy. Ultraviolet absorbers are most effective in PVC articles with thicker cross sections. They are only marginally effective in protecting PVC films and coatings because of limitations imposed by the Beer Lambert Law:

$$A = e \cdot c \cdot l\,. \tag{1}$$

According to this law, absorption (A) is directly proportional to concentration (c), extinction coefficient (e), the absorptivity of the absorbing species, and path length (l).

Typical UV-absorbers for PVC are oxanilides for polyamides and benzophenones [16].

2.3.3 Organosol Paste Fusion

In order to mix the paste properly, fusion heat is applied and the molecules of the plasticizer are driven between the polymer chains, distributing themselves along the polymer chains in such a way that upon cooling the plastic has useful physical strength. The optimum fusion process for a vinyl organosol is best done by the method of preparing films on glass or metal plates and fusing them in an oven under various temperature/time conditions (180-220 ^{o}C) [17]. The time required depends on the thickness of the product and temperature used.

2.4 Pigments

When pigments are incorporated in an organosol formulation, a complete dispersion of these pigments should occur. This is best achieved by pre-dispersing the pigments with plasticizer or pre-dispersing the pigments with solvent. Among the most commonly used pigments are titanium dioxide, carbon black, iron oxides and colored lead salt but also organic pigments may be used.

Plastics are the dominant materials of this century and with their expanding usage has come ever-stronger demands for dynamic and eye-catching colours and visual effects to attract customers and differentiate products. Those demands have been well met by the chemical industry through the creation of numerous different types of pigments.

Colour has always been an important factor in supporting the sales of plastic products and in the highly competitive markets of the 21st century it continues to play a critical role. Producers of plastic items can import colour to their products in a variety of ways. The main method is ‘through-colouration’ in which the whole polymer mass is coloured prior to being formed into its final form and shape.

Pigments, when used as colorants, possess some interesting advantages. They are seldom fully transparent so stronger colors than in the case of dyes are achievable. They perform well regarding their thermal stability and durability. In addition, they do not tend to migrate, which is really beneficial during the compounding of the formulation and they are cheaper than dyes and more compatible with the majority of polymer resins.

2.4.1 Decision factors in selecting pigments

There are numerous discussions in the literature regarding the parameters involved in the process of pigment selection [18-20]. Over the past decade this dialogue has intensified as economic pressures on the industry have forced the pigment colorants chain, from colorant manufacturers through masterbatches to plastics processors, (and even in some cases to the part designers and specifiers) to adopt a ‘right fitting’ approach. This term is used to refer to the establishment, for each application, of a clear understanding of the minimum performance required in each performance dimension, and selection of the lowest priced colorant(s) that will provide just sufficient performance for the specific application.

The basic requirements for pigments include: colour (hue*, chroma*, lightness, opacity and batch to batch consistency) (* alternatively redness/greenness, yellowness/blueness), polymer compatibility (more of an issue for engineering resins), heat stability (in particular the ability to withstand the polymer processing conditions), processing ease (colorant dispersibility in the polymer matrix), handling (tendency to create dust, ease of powder flow) and economic efficiency (colour strength, processing ease, batch to batch variability).

Depending on the application of the final product, additional requirements should be established such as: migration resistance, suitability for food contact applications, regulatory compliance, light resistance, weather resistance, warping tendency, heavy metal content, halogen content, organoleptic properties, electrical properties, absorption or reflection of specific wavelengths, solvent and chemical resistance, *etc.*

2.4.2 Organic and Inorganic pigments

Pigment chemistry is a large technical subject in its own right and beyond the scope of this study, however, an overview of the main classes is useful to appreciate the impact of some of the new developments [18].

All pigments used by the plastics industry are particulate and mostly crystalline materials and these days all are man-made. Within that group, however, some are described as organic (as they are created by processes of organic chemistry), some are described as inorganic (as they are based on ‘inorganic chemistry’ and typically have characteristics similar to minerals), some are called metallic (because they consist of minute metal flakes) and many of the special effect pigments (pearlescent, interference, iridescent, etc.) are principally inorganic, but are put into a category of their own because of their very different visual properties and manufacturing processes.

Much of the recent development in pigments for plastics has been in the organic area and has arisen through the dramatic growth of chemical technology over the last 100 years. This has created an extensive palette of strong, bright, stable colorants that has expanded the available colour space. This expansion of product ranges, combined with increased opposition to the use of ‘heavy metals’ has caused a slow expansion of organic pigments into many of the colouring applications previously supplied by inorganic pigments. In response the inorganic pigment producers have focussed on the major contributions of inorganic pigments (particularly opacity, and heat, light and weather stability) and have subsequently dominated outdoor applications demanding high durability. Thus the two types of pigment, organic and inorganic, play complementary roles.

2.4.3 Metallic pigments

The first special effect pigments were powdered metals. The most commonly used metallic pigments today are aluminium-based but copper, bronze, nickel, gold, silver, iron and graphite powders are also available. Aluminium powders in particular are available in a wide range of particle sizes, which enables effects from a fine metallic sheen to large bright sparkles [21-23]. Metallic pigments can be used on their own or in combination with transparent colorants. Use of opaque colorants substantially hides and diminishes the lustrous or sparkle appearance of the metallic pigment.

Typically, metallic pigments are produced as thin platelets. Their large aspect ratio (relatively long and wide but very thin) causes them to align very strongly with the direction of flow of the polymer matrix in which they are dispersed. This has the beneficial effect in most applications of ensuring that the pigment plates are parallel to the surface of the plastic part thereby maximising the specular (mirror-like) reflection. One of the unfortunate side effects is that where two flows meet in a mould or a film die, the merged stream does not undergo enough sheer to give a homogeneous alignment of the pigment particles and an unsightly boundary line is created [24].

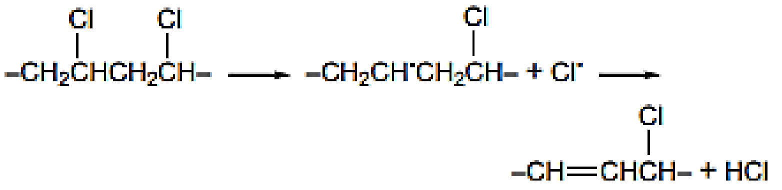
Metal pigments can also serve functional as well as decorative purposes as they can provide: reflection of electromagnetic radiation, a barrier to diffusion, heat conductivity, electrical conductivity and microwave absorption. The most common pigments used are based on glass, aluminum and mica and most of the times they are coated with a metal oxide [24].

Pigments consisting of metal oxide-coated glass flakes are industrially used for coloring since 1963. However, the available glass flake substrates have been rather thick, typically 10μm, making of the use of such pigments impractical in layers like automotive paints and printing inks. After improvements of the glass manufacturing technology, effective pigments based on thinner glass flakes were introduced to the market from 2014 [25, 26]. Compared to alumina and mica flakes, the glass flake substrates are more transparent and are in this aspect comparable to the silica flakes. However, they have a much broader thickness distribution than the latter. Therefore, color travel effects are not achieved by using single layer coatings on glass flakes.

Some metal flakes, especially aluminum platelets, can be coated with iron oxide in a CVD process [27]. These metal flakes are fluidized in nitrogen gas atmosphere at temperatures around 450 ^{o}C. Then the reagents $Fe(CO)_5$ and oxygen are injected into the fluidized bed. They must be highly diluted in the inert gas to achieve a proper coating. The thickness of the formed iron oxide layers on the aluminum is controlled by the reaction time. The pigments obtained show golden, orange and reddish metal-like effects. The pigments based on aluminum can be modified using an additional silicon dioxide layer, which is wet-chemically deposited. The iron oxide layer is formed with the CVD process after the formation of this SiO_2 layer. These pigments show strong color travel effects [28, 30]. Color travel is effect where the chroma-shift parts change colour because of a precise combination of pigments and dyes that display a geometric metamerism (compounds having the same molecular formula but different number of carbon atoms (alkyl groups) on either side of functional group (*i.e.,* -O-,-S-, -NH-, -C(=O)-)).

Mica-based effect pigments were first described in 1942. Their commercial success started in the 1970s due to improved reproducibility of production and accelerated in the mid-1980s due to the introduction of weather-resistant types for outdoor applications [31]. The latest significant development was the synthesis of optical multilayer-systems on mica at the end of the 1990s. Compared to the synthetic substrates, natural muscovite mica is rather inexpensive and available in large quantities in nature. Due to its crystal structure as a layered silicate, it can be cleaved to thinner flakes of a mean thickness of typically 200–500 nm. The diameters of the mica flakes are mostly in the range from 5–200 µm. Effect pigments based on mica are typically produced by the deposition of a metal oxide layer covering the mica in aqueous suspension followed by a calcination process [32]. Mica platelets are mostly covered by titanium oxide or Iron oxide. Titanium dioxide-mica pigments are manufactured starting from $TiO(SO)_4$ (homogeneous hydrolysis) or $TiOCl_2$ (titration). The interference color of these pigments is dependent on the thickness of the TiO_2 layers, which is typically in the range of 50–300 nm on both sides of the mica platelets. Therefore, the control of this thickness is one of the most important factors for the reproducible manufacture of the metal oxide-mica pigments. Iron oxide layers can be formed on the mica by a comparable process starting from iron sulfate or iron chloride.

As mentioned in the previous paragraphs, it is really common that pigment flakes are coated with a metal oxide in order to reach and keep the preferred color shade, unfortunately, the coexistence of PVC and metal oxides results in accelerated degradation. The liberated HCl reacts with the metal oxide on the pigments coating and the rate is faster at elevated temperature. Thus, the activation energy is lower than that for the degradation of pure PVC. Degradation follows a two-step mechanism (fig.2.6); in the first step chlorine free radical is formed as in the case of pure PVC, and in the second step, the chlorine free radical replaces oxygen from metal oxide to form metal chloride and an oxygen-free radical. Subsequently, the oxygen free radical reacts with hydrogen from the PVC to form water. The formation of the metal chloride is the rate-controlling step. The metal chlorides formed during the thermal degradation either volatilize or decompose simultaneously to lower grade metallic chlorides depending on the boiling point or the volatilization temperature [33].



$$-CH_2\overset{Cl}{\overset{|}{C}}HCH_2\overset{Cl}{\overset{|}{C}}H- \longrightarrow -CH_2CH^{\bullet}CH_2\overset{Cl}{\overset{|}{C}}H- + Cl^{\bullet} \longrightarrow -CH{=}CH\overset{Cl}{\overset{|}{C}}H- + HCl \qquad (i)$$

$$XCl^{\bullet} + M_xO_y \rightarrow MCl_x + YO^{\bullet} \qquad (ii)$$

Fig.2.6. Additional steps of PVCs degradation in the presence of metal oxides [33].

2.5 Chapter summary

PVC can be synthesized by three different methods: suspension, bulk or mass and emulsion polymerization. The preparation method has an important influence on the physical properties of PVC. The PVC used in this research activity is obtained during the process of emulsion polymerization since the produced resin grades are finer with much smaller particles compared with those obtained during suspension polymerization. This type of resin is often used for applications such as a paste for coating surfaces.

Despite all these favorable characteristics, PVC can show signs of degradation (photodegradation and thermal degradation), sometimes immediately after their production and then when exposed to indoor and outdoor conditions.

Photodegradation is a deterioration of a photodegradable molecule caused by the absorption of photons, particularly those wavelengths found in sunlight, including ultraviolet light, visible light and infrared light. The effects of UV solar radiation are the most significant threat to the PVC durability in outdoor applications. More specifically, the combined effect of UV radiation and water causes the creation of a variety of free radicals that cause the initiation and propagation of the degradation process.

The primary process of thermal degradation includes three main steps: initiation of dehydrochlorination, elimination of HCl and simultaneous formation of conjugated double bonds, and termination of dehydrochlorination. The process occurs by an autocatalytic dehydrochlorination reaction with the subsequent formation of conjugated double bonds.

Colour has always been an important factor in supporting the sales of plastic products and in the highly competitive markets of the 21st century it continues to play a critical role. Pigments, when used as colorants, possess some interesting properties especially metallic pigments. Unfortunately, the coexistence of PVC and metal oxides on the pigments surface results in accelerated degradation.

3 Materials and Methods

A multi-analytical investigation was performed on PVC films using different ageing and analytical techniques. The selected materials, techniques and procedures have been described in this chapter. All the tests took place at Avery Dennison facilities except for the Atomic Force Microscopy analysis that took place at the TU Delft.

3.1 Design of the experiment (DOE)

First step of the project was to gather the available data, such as chemical composition and degradation information about previously prepared and aged colored PVC films, in order to choose the most crucial and sensitive metallic pigments for the study. Five pigments were selected; two borosilicate glass-based (respectively pigment 1 and pigment 2), the first one is coated with titanium dioxide and small amounts of tin oxide and the second one with iron oxide, one with aluminum flakes coated with iron oxide (pigment 3) (fig.3.1) and two MICA-based (respectively pigment 4 and pigment 5), the first coated in a wafer-thin (10-30 nm) layer of iron oxide and the second in ferric oxide. The pigments were used as a stabilized dry powder as received from the manufacturer. Detailed specification of the dispersed pigments is included in table 3.2. The components of the formulation are: organosol, pigment, one of the five chosen additives, solvent, *etc.* The organosol is a mixture of the PVC resin with solvent, UV and thermal stabilizers, and plasticizer. The chosen additive is added when the formulation is prepared with the addition of the pigment, the plasticizer, the solvent and the UV stabilizer to the PVC organosol. Based on the formulation of these PVC films, and after a careful consideration of different additives, the experiment was designed as follows (table 3.1):

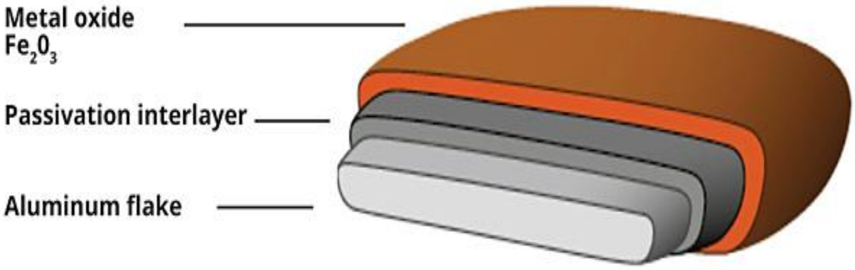


Fig.3.1. Schematic composition of pigment 3 particles.

Table 3.1. Design of the experiment.

Selected Pigment	Pigment loadings	Additives used for all five pigments	Additive loading according to TDS
Pigment 1		Water scavenger	
Pigment 2	15 phr	Dispersant 1	Minimum
Pigment 3	10 phr	Dispersant 2	Intermediate
Pigment 4	5 phr	Fluorinated MICA	Maximum
Pigment 5		Anticorrosive pigment	

Table 3.2. Chosen pigments information.

Pigments	Pigment 1	Pigment 2	Pigment 3	Pigment 4	Pigment 5
Description	Based on borosilicate glass		Aluminum flakes with iron oxide	Mica coated with iron oxide	Mica coated with ferric oxide
Particle size (µm)	10-20	25-35	5-10	5-10	5-10
Particle type	Flakes		Spherical particles		
Pigment color	Gold	Red	Red/orange	Orange	Bordeaux
First signs of degradation in standard PVC AD formulations (hours)	1000	500	500	1000	2500

3.2 Additives

The main objective of this study is to improve the water resistance of the PVC films with the implemented metallic pigments in order to delay PVC degradation. Five different additives were chosen for this study with different functionalities but the use of all of them aims to improve one thing; the resistance to degradation due to moisture. Each one of the additives and their specific properties are discussed in the following paragraphs.

3.2.1 Water Scavenger

The first additive used in this study is a compound used for the removal of moisture. It is a specially prepared finely dispersed calcium oxide with a stabilizing wetting agent and it is supplied as a paste.

The additive is capable of removing even large quantities of moisture in a very short time from the system to be processed. This is achieved by using wetting and dispersing carrier media. A special processing technology is used to activate and stabilize the inorganic moisture absorber, calcium oxide. This achieves an extremely favorable ratio of dosage/effect.

3.2.2 Dispersant 1

The second additive is an alkylammonium salt of a high molecular-weight copolymer. It is a dispersing additive for solvent-borne PVC organosols.

Dispersant 1 deflocculates (increase of repulsive forces between particles) pigments by means of steric stabilization. It is possible that this deflocculation may prevent water being trapped between flakes and eventually provoke degradation. The resulting repulsion effect and the steric stabilization prevents any co-flocculation which leads to non-floating coloring in pigment blends. As a result of the small particle size of the deflocculated pigments, high levels of gloss can be achieved and the color strength is improved.

3.2.3 Dispersant 2

This is a high molecular-weight copolymer with pigment affinic groups with a dispersing functionality for PVC organosols like dispersant 1 but it is also used for pultrusion (continuous process for manufacturing of composite materials with constant cross-section), and solvent-free UV printing inks. It also shares the same deflocculation effect as dispersant 1.

3.2.4 Fluorinated MICA

This additive is a fluorinated mica that combines the thermal stability of mica with the lubricant character of a fluoro-polymer. It has a small particle size (10 μm) and low moisture content (<1 %) and most importantly, the fluorine composition of the MICA is 15.02 % $^{w.}/_{w.}$ (weight percentage). The use of this additive can cause the flakes to exhibit an ability to shear and slide over one another without damaging each other. If the coating of the flake is not damaged then the amount of metal oxide provoking PVC degradation will be decreased.

3.2.5 Anti-corrosive pigment

The final additive used in this study is a zinc aluminium orthophosphate hydrate pigment. This pigment is a white pigment and mixed with one of the five pigments when used for the film formulations. This pigment consists of 38.5-40.5 % Zn, 4.0-5.5 % Al and 53-56 % PO_4^{-3} with an average particle size of 2-3.5 μm. The thought behind the use of this type of material is its intrinsic property to resist corrosion and as a result less corrosion products are produced and the overall degradation will be delayed.

3.3 Procedures

3.3.1 Formulation of PVC films

The pigmented plasticized PVC films were formulated and prepared according to the Avery Dennison standards. Firstly, the base blend called organosol was prepared, by the incorporation of PVC (resin), plasticizer (28 phr), solvent (17 phr), and a heat stabilizer (6 phr), into the mix. Five different pigments with 15,10 and 5 phr were used, and each additive was added in three different loadings (minimum, intermediate, maximum) to all five pigments formulations according to the supplier's suggestions in order to find the optimum amount needed in order to achieve the best performance (table 3.3).

Table 3.3. Additive loadings.

Additive	Minimum	Intermediate	Maximum
Water scavenger	0.75 % $^{w.}/_{w.}$ (of total)	1.62 % $^{w.}/_{w.}$ (of total)	2.5 % $^{w.}/_{w.}$ (of total)
Dispersant 1	0.38 % $^{w.}/_{w.}$ (of total)	0.57 % $^{w.}/_{w.}$ (of total)	0.76 % $^{w.}/_{w.}$ (of total)
Dispersant 2	0.38 % $^{w.}/_{w.}$ (of total)	0.57 % $^{w.}/_{w.}$ (of total)	0.76 % $^{w.}/_{w.}$ (of total)
Fluorinated MICA	5 % $^{w.}/_{w.}$ (of total)	6 % $^{w.}/_{w.}$ (of total)	7 % $^{w.}/_{w.}$ (of total)
Anti-corrosive pigment	1.9 % $^{w.}/_{w.}$ (of total)	3.3 % $^{w.}/_{w.}$ (of total)	5.7 % $^{w.}/_{w.}$ (of total)

The pastes were stirred using a mechanical stirrer at 40 rpm for 1 hour and degassed with a degassing oven (150 ^{o}C) in order to release all the possible air bubbles trapped inside the paste after stirring. The degassing process continued until there were no air bubbles trapped inside the paste. The removal of air bubbles is really important because if they remain, it is likely that they will cause defects during the casting process.

3.3.2 Air release

A great quantity of air bubbles is entrained in the compound during its preparation. The air release properties of an organosol refer to the ease with which these air bubbles are released by the compound. These bubbles may be subsequently removed in a vacuum deaerator and in some cases deaeration may be accomplished during the mixing procedure itself. This latter procedure involves the use of special mixers that will pull a vacuum while mixing.

Subsequently, during coating, molding or casting processing of the compound, additional quantities of air may be entrapped. For example, the casting knife of a casting table will gulp in air bubbles. These bubbles, if not sheared out as the paste is cast by the knife may show up as defects on the cast product. Coatings or films containing pigments tend to be less sensitive in this respect, but clear organosol coatings, on the other hand, cannot tolerate poor air release since the bubbles trapped inside the film are visible.

There is a general relationship linking air release with low shear viscosity. That is, as the viscosity of a paste is reduced by an increase in the plasticizer, an improvement in air release is expected. Notwithstanding this, the relationship between viscosity and air release does not hold when the same compound is prepared from different dispersion resins.

3.3.3 Casting of pigmented PVC films

The PVC films were made by using a casting table (fig.3.2) with a vacuum system installed and a casting speed of 1.2–1.5 mm/sec. The pigmented plasticized PVC liquid mixture was poured and evenly distributed over a Polyethylene Terephthalate (PET) substrate, by the means of a specially designed blade. Thickness of the films was established to be 60 μm +/- 2 μm. The PET substrate with the applied over PVC sample was dried in the oven. The oven conditions were controlled, and during the project set for the optimal drying of the PVC films. In addition to the films with the pigments and the five additives, a clear PVC film without additives, a clear film with additives and films with the pigments but without the additives were prepared in order to find out if the final properties and the durability of the films is dependent on the pigments and/or the scavenger and to check if the mechanical properties of the film are influenced by the addition of the scavenger.

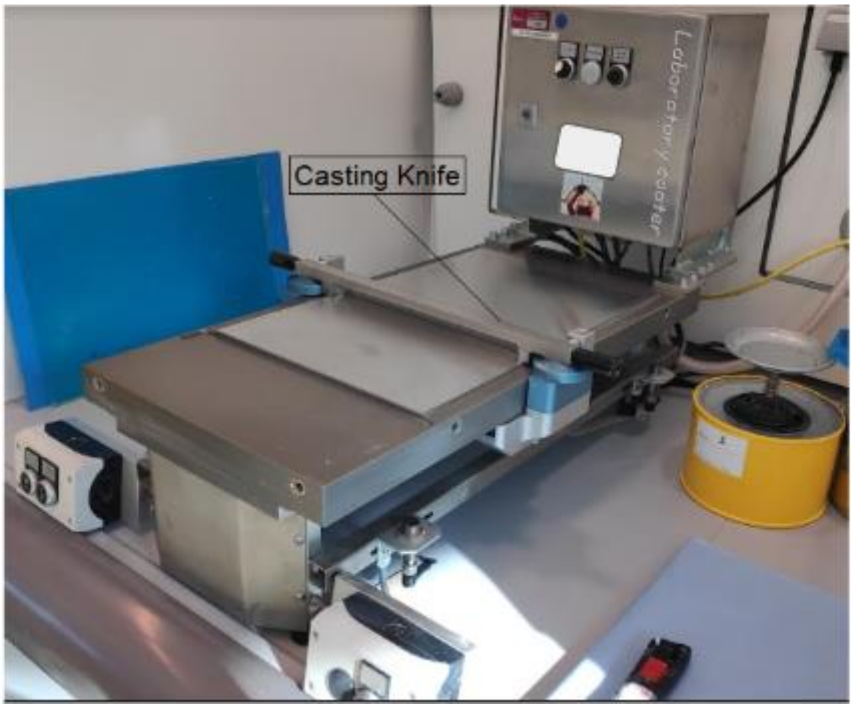


Fig.3.2. Casting table.

3.3.4 Sample preparation for weathering

After casting, the samples were prepared as A4 sized sheets after dried in an oven for 1.2 minutes at 182 °C without adhesive. The adhesive, a polyacrylate, was applied later in the laboratory by using a transferring tape. Afterwards, the samples were placed in a roll laminator (fig.3.3) in order to remove air bubbles. After lamination, samples were applied on an aluminum panel.

A Catena 35/65 Roll Laminator was used for the films lamination. It is a 4-roller laminator and the rolling speed used for the films of this project was 1.5 mm/s.

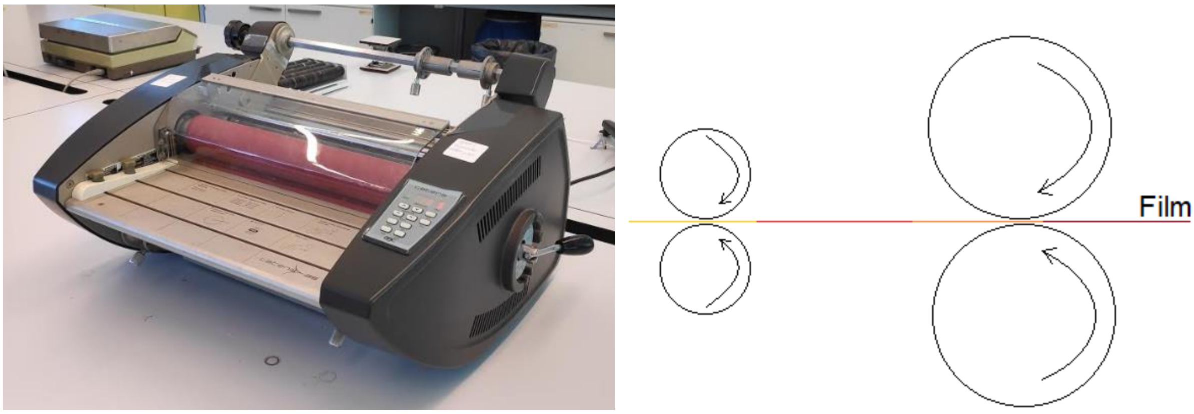


Fig.3.3. Film laminator (left), roller scheme (right).

3.4 Artificial ageing (weathering)

Atlas weathering machine (WOM, modified ISO 4892-2) was used on the pigmented PVC films in order to simulate the photo degradation of the materials in the outdoor conditions. The films are vertically aligned inside the weathering machine heated with xenon lamps and sprayed with water (fig.3.4). The conditions inside the weathering machine are shown in table 3.4. The real lifetime of the films is in comparison with the artificial weathering lifespan for central Europe conditions.

Fig 3.4. Interior of the weathering machine.

Table 3.4. Conditions inside the Weathering Machine.

Light exposure spectrum (nm)	295-800
Irradiance 300-400 nm (W/m^2)	60
Irradiance 340 nm (W/m^2)	0.51
Air Temperature (^{o}C)	50
Black Panel Temperature (^{o}C)	70
Humidity (%)	50
Light Cycle (hours/day)	Constant light
Water spray cycle	18 minutes every 2 hours

3.5 Analytical techniques

3.5.1 Contact angle (CA) measurements

The contact angle measurements were analyzed with the Owens, Wendt, Rabel and Kaelble method in order to see if the addition of the water scavenger affects the wettability of the films by using a KSV CAM 200 instrument. This is a standard method for calculating the surface free energy of a solid from the contact angle with several liquids. The surface energy is divided in two parts, a polar part and a disperse part. According to Young's equation (2), there is a relationship between the contact angle θ, the surface tension of the liquid σ_l, the interfacial tension σ_{sl} between liquid and solid and the surface free energy σ_s of the solid

$$\sigma_s = \sigma_{sl} + \sigma_l \cdot cos\theta. \quad (2)$$

The interfacial tension σ_{sl} is calculated based on the two surface tensions σ_s and σ_l and the similar interactions between the phases. These interactions are interpreted as the geometric mean of a disperse part σ_D and a polar part σ_P of the surface tension or surface free energy

$$\sigma_{sl} = \sigma_s + \sigma_l - 2(\sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^P \cdot \sigma_l^P}). \quad (3)$$

According to the two-component model, the interfacial tension depends on whether polar and disperse parts can form interactions with corresponding parts of the adjacent phase. The polar part of the solid is small, then the square root term $(\sigma_{Pl} \cdot \sigma_{Ps})^{1/2}$ assumes a low value. The polar interactions then only make a small contribution to reducing the interfacial tension; this corresponds to poor wetting and a high contact angle [34].

3.5.2 Microscopy

3.5.2.1 Portable Microscope

The films were investigated with the portable microscope (Dino Lite v.2, x1000 maximum magnification) (fig.3.5) in order to check if the pigment flakes are vertically oriented to the surface, if the flakes/particles are fully covered by the PVC resin and if they are protruding from the film because they can be starting points for degradation.

Fig.3.5. Portable Microscope.

3.5.2.2 Scanning Electron Microscope (SEM)

The films (3 films per formulation) were investigated with the scanning electron microscope Jeol JSM-IT100 in combination with an EDS detector. The IR imaging microscope combined is a Perkin Elmer Spotlight 400 with pixel size of 6.25 μm and a resolution of 4 cm^{-1}. The SEM is used to magnify a specific sample region using a high energy focused beam of electrons. The sample is under low vacuum (10's of Pa) to ensure the electron beam stays focused and does not interact with particles in the air. When the beam of electrons hits the sample, it causes secondary electrons to be released from the sample which are detected to provide an image based on the topography of the surface. The two detectors most commonly used include the Secondary Electron Detector (SED) and the Backscattered Electron (BSE) Detector. The electrons interact with the detector to create an image. SEM Analysis is more powerful than Optical Microscopy not only because of the much increased magnification power but also because of the increase in depth of field.

The sample region evaluated with SEM Analysis can also be analyzed to determine the specific elements that comprise the sample region by utilizing Energy Dispersion Spectroscopy (EDS). X-rays are also released from the surface of the sample that carry a unique energy signature that are specific to elements found in the sample. These X-rays are detected with the EDS detector to give elemental information about the sample. EDS provides data about the chemical composition of the sample and provides additional data about the features that are observed in the SEM micrographs. This combined technique is referred to as SEM-EDS or SEM-EDX analysis. The SEM-EDS technique is used in order to see if the flakes/particles point out of the film's surface and through the EDS analysis, the elemental composition of specific spots on the surface (flakes pointing out) can be analyzed [35].

3.5.2.3 Atomic Force Microscope (AFM)

Some of the films were investigated with the atomic force microscope in order to see the surface pattern on the films for possible directed orientation of the pigment flakes that may increase the surface energy of the films. AFM is a type of scanning probe microscopy (SPM), with demonstrated resolution on the order of fractions of a nanometer. The information is gathered by "touching" the surface with a cantilever. The cantilever runs over the ridges and valleys on the surface of the material. A laser shines on the cantilever at an oblique angle (fig.3.7), and allows for the direct measurement of the deflection in the cantilever by using a photodiode. In this way, an image may be created revealing the configuration of the special aspects on a surface [36].

In particular a NT-MDT Ntegra AFM (fig.3.6) was used in tapping mode using a probe having a spring constant. The images were obtained in 256 × 256 resolutions at 1 Hz scanning rate. The surface analysis and 3D representation was performed using Nova Px Software version 3.4 based on 10 by 10 μm images.

Fig.3.6. Atomic Force Microscope (AFM).

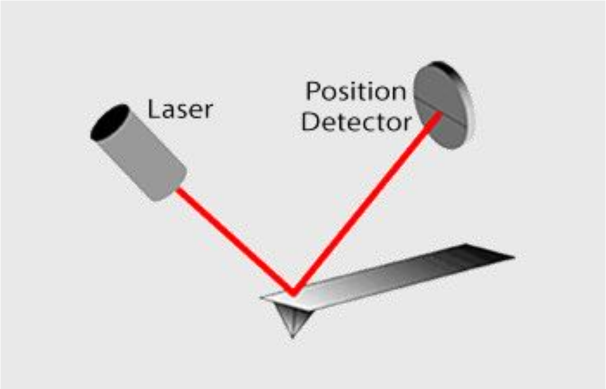


Fig.3.7. Laser beam deflection for atomic force microscope.

The AFM software was also used to provide the roughness of the films surface. The roughness was calculated on a surface (area) profile. Areal roughness parameters are defined in the ISO 25178 series. The resulting values are Sa, Sq, Sz. Sa is the extension of Ra (arithmetical mean height of a line) to a surface. It expresses, as an absolute value, the difference in height of each point compared to the arithmetical mean of the surface. This parameter is used generally to evaluate surface roughness

$$Sa = \frac{1}{A} \iint_A |Z(x, y)| \, dx \, dy \, . \qquad (4)$$

In order to calculate the Sa all the surface height changes are evaluated (fig.3.8).

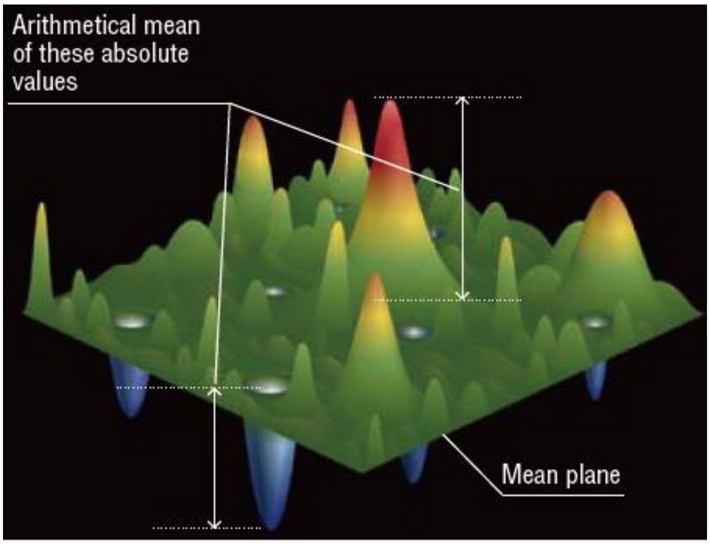


Fig.3.8. Example of height changes evaluation [36].

3.5.3 X-ray fluorescence (XRF)

X-ray fluorescence (XRF) is an analytical technique that can be used to determine the chemical composition of a wide variety of sample types including solids, liquids, slurries and loose powders. X-ray fluorescence is also used to determine the thickness and composition of layers and coatings. It can analyze elements from beryllium (Be) to uranium (U) in concentration ranges from 100 % $^{w.}/_{w.}$ to sub-ppm levels. XRF is an atomic emission method, similar in this respect to optical emission spectroscopy (OES), ICP and neutron activation analysis (gamma spectroscopy). Such methods measure the wavelength and intensity of ‘light’ (X-rays in this case) emitted by energized atoms in the sample. In XRF, irradiation by a primary X-ray beam from an X-ray tube, causes emission of fluorescent X-rays with discrete energies characteristic of the elements present in the sample (fig.3.9). The XRF analysis is used in this study to determine the elemental distribution on the surface of the PVC films. The instrument used is Rigaku NEX CG EDXRF analyser.

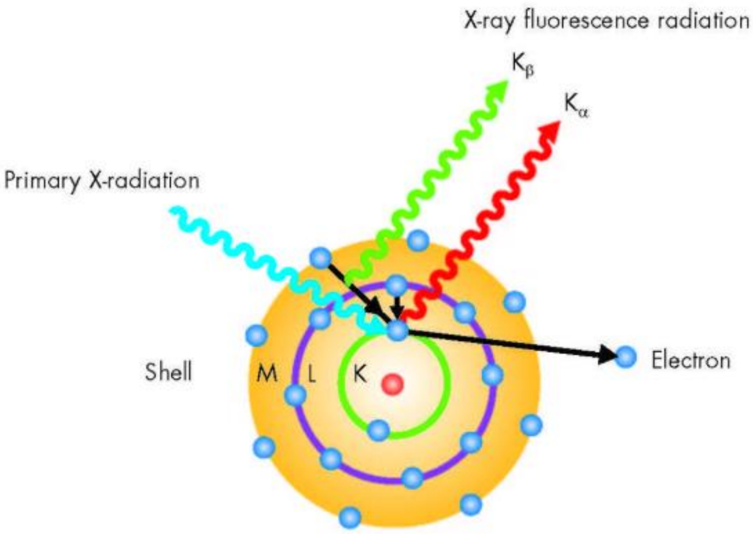


Fig.3.9. The principle of the X-Ray Fluorescence Spectroscopy (XRF).

3.5.4 Thermal Analysis (DSC)

DSC analysis measures the amount of energy absorbed or released by a sample when it is heated or cooled, providing quantitative and qualitative data on endothermic (heat absorption) and exothermic (heat evolution) processes. This analysis is used to measure melting temperature, heat of fusion, latent heat of melting, reaction energy and temperature, glass transition temperature, crystalline phase transition temperature and energy, precipitation energy and temperature, denaturization temperatures, oxidation induction times, and specific heat or heat capacity. For this study it was used to measure the glass transition temperature (T_g).

The sample is placed in a suitable pan and sits upon a constantan disc on a platform in the DSC analysis cell with a chromel wafer immediately underneath. A chromel-alumel thermocouple under the constantan disc measures the sample temperature. An empty reference pan sits on a symmetric platform with its own underlying chromel wafer and chromel-alumel thermocouple. Heat flow is measured by comparing the difference in temperature in between the sample and the reference chromel wafers. The DSC Q2000 from TA instruments (with Helium gas) was used for the specimens of this study at the modulated mode for all measurements which comprised a heating cycle (± 2 °C per 40 sec) with a linear ramp from -125 °C of 4 °C/min to 200 °C and a standard cooling cycle from 200 °C to -150 °C of 10 °C/min.

3.5.5 Fourier-Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy, also known as FTIR Analysis or FTIR Spectroscopy, is an analytical technique used to identify organic, polymeric, and, inorganic materials. The FTIR analysis method uses infrared light to scan test samples and observe chemical properties.

The FTIR instrument sends infrared radiation of about 10000 to 100 cm^{-1} (reciprocal wavenumber range) through a sample, with some radiation absorbed and some passed through. The absorbed radiation is converted into rotational and/or vibrational energy by the sample molecules. The resulting signal at the detector presents as a spectrum, typically from 4000 cm^{-1} to 400 cm^{-1}, representing a molecular fingerprint of the sample. Each molecule or chemical structure will produce a unique spectral fingerprint. Fourier Transform Infrared Spectroscopy is used in this study to monitor the PVC degradation after each stage of measurements.

A Perkin Elmer Spectrum One fourier transform infrared spectrophotometer (FT-IR) (p/n Q0315) (ISO-9001) (fig.3.10) with a range of 7800-350 cm^{-1} with a KBr beamsplitter, resolution of 0.5 cm^{-1} to 64 cm^{-1}, a wavelength accuracy of 0.1 cm^{-1} to 1600 cm^{-1} and the Perkin Elmer Spectrum software were used for the samples measurements and results analysis respectively.

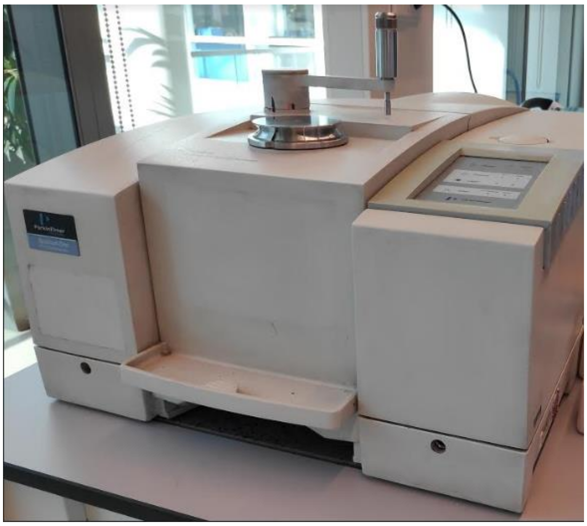


Fig.3.10. FT-IR spectrometer.

3.5.6 Gloss and Color measurements

After every stage of artificial weathering (every 500 hours) the gloss and the color of the PVC films were measured in order to see the difference before and after using the water scavenger and to compare it with the previous data collected. Gloss is determined by projecting a beam of light at a fixed intensity and angle onto a surface and measuring the amount of light reflected at an equal but opposite angle. The gloss is displayed in gloss unit (GU) in a scale from 0 to 120. The gloss of the samples was measured by BYK Mac Glossmeter with 3 angles (20 º, 60 º and 85 º) (ASTM D523) at the same time. The measurement at 60º was chosen primarily as it is universally used as the standard measurement angle with the complementary angles of 85 ° and 20 °, are often used for low and high gloss levels respectively [37].

The color measurement was performed by a spectrophotometer (BYK mac i), using specular component included (SCI) method instead of specular component excluded (SCE) method. Even though the SCE measurements are more close to the visual appearance of samples, the SCI measurements are less affected by the surface gloss, in other words, the surface roughness. The measured color value is interpreted by the CIE L*a*b* color space as shown in figure 3.11.

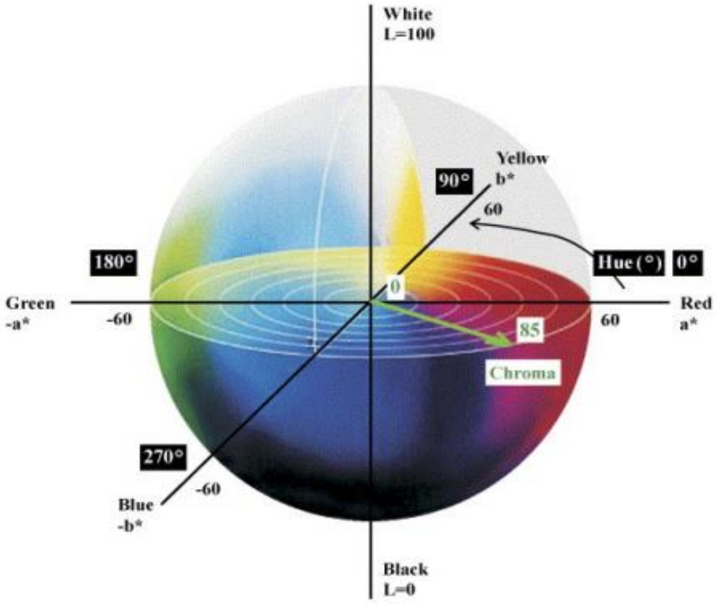


Fig.3.11. Color space. Color can be described by L∗ (lightness, black=0 and white=100), hue (positive a∗=more red, negative a∗=more green, positive b∗=more yellow and negative b∗=more blue) [37].

In this system, the L* represents lightness, a* and b* represent hue positions. The color value can be calculated as:

$$E^{*} = \sqrt[2]{L^{*2} + a^{*2} + b^{*2}} \tag{5}$$

and the color change can be evaluated as:

$$\Delta E^{*} = \sqrt[2]{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}. \tag{6}$$

The expression of the color change shows the distance between the altered color and the original color, and the bigger the ΔE^*, the more color change.

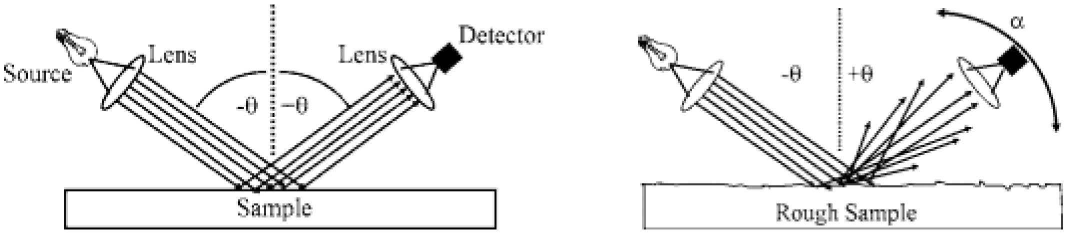


Fig.3.12. Design principle of a glossmeter (left), a rough surface distributes the specular light around the specular direction and decreases gloss (right) [38].

Both the color and gloss measurements are performed by collecting the light. The interaction between the light and the colored film happens at the surface and the inside layers. Therefore, the measured color and gloss values receive contributions from two components, the outer surface and the inner layers. Obviously, the outer layer makes the main contribution, however, the inner layers are also of significance.

3.5.7 Mechanical behavior

Tensile tests took place for all the films using ISO 527-1 and ISO 527-3 methods in machine direction, abbreviated MD, in order to monitor the mechanical behavior after the use of additives to improve the water resistance of the films and more specifically the tensile strength of the plasticized PVC films. Three films were tested per each formulation in rectangular shape with a legth of 130 mm and a width of 25 mm. The thickness of the samples was ~60 μm. A flat shoulder was used with pneumatic grips. In each pair one side is coated with rubber, the other side is round-shaped Aluminum .The length of the reduced section was 80 mm and the length of the grip section was 50 mm.

3.6 Chapter summary

A multi-analytical investigation was performed on PVC films using different ageing and analytical techniques. First step of the project was to gather the available data, such as chemical composition and degradation information about previously prepared and aged colored PVC films, in order to choose the most crucial and sensitive metallic pigments for the study. After consideration of all the above, five metallic pigments with different shapes, sizes and coatings were chosen.

The components of the formulation are: organosol, pigment, one of the five chosen additives, solvent, *etc*. Based on the formulation of these PVC films, and after a careful consideration of different additives, the experiment was designed.

The main objective of this study is to improve the water resistance of the PVC films with the implemented metallic pigments in order to delay PVC degradation. Five different additives were chosen for this study with different functionalities but the use of all of them aims to improve one thing; the resistance to degradation due to moisture. The five additives are: a water scavenger, dispersants 1 and 2, fluorinated MICA and an anticorrosive pigment.

The pastes for all the pigmented films were prepared according to the Avery Dennison procedures and then they were cast in order to get the film-products. The films were coated on the back side with an adhesive and then placed on an aluminum plate in order to be sent for weathering.

After each stage of weathering, the films were analyzed with various analyses such as FT-IR spectroscopy, Microscopy techniques (light microscope, SEM, AFM), contact angle measurements, X-ray fluorescence, thermal analysis, gloss and color measurements and mechanical tests. All those methods were used in order to see if the implementation of the additives has a positive or a negative effect on the films properties.

4 Results and Discussion

The main focus of this study is to monitor and improve the performance of PVC films pigmented with metallic pigments under the combined effect of UV radiation and water. All the procedures and the analytical methods mentioned in chapter 3 were used in order to prepare, test and analyze the results of the pigmented PVC films shown in this chapter.

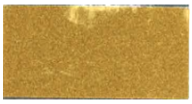
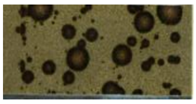
4.1 PVC pigmented films with the original formulation

PVC films with the five chosen pigments were prepared according to the Avery Dennison original formulation methodology.

4.1.1 Weathering results

The weathering results for the films with the five pigments and the original formulation are presented in the following tables.

Table 4.1. Weathering results for the three loadings of pigment 1.

Pigment 1 - Based on Borosilicate glass					
Pigment loading	500 h	1000 h	1500 h	2000 h	2500 h
15 phr					
10 phr					
5 phr					

The weathering results of the PVC/pigment 1 films from table 4.1 show that the degradation starts from the side of the films and this is in agreement with the preliminary estimation that water retention causes localized degradation on the pigmented PVC films. The film samples are cut and placed on a panel and as a result the pigment flakes near the surface are damaged. Damaged flakes/particles cause the exposure of the base material and the metal oxide surface coating to water and other PVC degradation products and as a result the film degradation propagates faster. The films with the lower loading of pigment show a faster degradation than the other two loadings. This can be attributed to the fact that metallic pigments can act as UV absorbers and increase the films durability [39].

Table 4.2. Weathering results for the three loadings of pigment 2.

<table>
<tr><th colspan="6">Pigment 2 - Based on Borosilicate glass</th></tr>
<tr><th>Pigment loading</th><th>500 h</th><th>1000 h</th><th>1500 h</th><th>2000 h</th><th>2500 h</th></tr>
<tr><td>15 phr</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>10 phr</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>5 phr</td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

The weathering results of the PVC/pigment 2 films from table 4.2 show that the degradation starts from random points on the films surface and continues with fast and homogeneous degradation. The difference between the 1000 h and 1500 h stages is large considering the small degradation spots at 1000 h and the fully degraded film at 1500 h. This pigment is also a glass-based one like the previous (pigment 1) but it has flakes of a bigger size (25-35 μm > 10-20 μm). Since this pigment has bigger flakes, if broken into smaller pieces, they can cover a large part of the films bulk.

The weathering results of the PVC/pigment 3 films from table 4.3 show that the degradation starts from random points on the films surface and the films end with severe degradation. Again like in the case of the previous pigment (pigment 2) the degradation started and proceeded really fast which is expected due to the sensitivity of the iron oxide in the coating of the pigment and the aluminum in the pigment base. The degradation of this film is so fast that the film with 5 phr loading becomes completely degraded and the panel is visible. For the 15 and 10 phr films, cracks are observed after 2000 h of artificial weathering. Pigment 3 has particles of a smaller size than the previous two (pigment 1, pigment 2), as a result the pigment occupies and protects a smaller part of the film as a UV stabilizer.

Table 4.3. Weathering results for the three loadings of pigment 3.

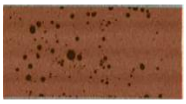
Pigment 3 - Aluminum flakes with iron oxide					
Pigment loading	500 h	1000 h	1500 h	2000 h	2500 h
15 phr					
10 phr					
5 phr					

Table 4.4. Weathering results for the three loadings of pigment 4.

Pigment 4 - Mica coated with iron oxide					
Pigment loading	500 h	1000 h	1500 h	2000 h	2500 h
15 phr					
10 phr					
5 phr					

The weathering results of the PVC/pigment 4 films from table 4.4 show that the degradation starts from the side of the films as shown for PVC/pigment 1 films (table 4.1) and this is in agreement with the preliminary estimation that water retention causes localized degradation on the pigmented PVC films. The degradation speed and severity is not of the magnitude of PVC/pigment 1 films due to the more durable pigment base (MICA) of pigment 4.

Table 4.5. Weathering results for the three loadings of pigment 5.

Pigment 5 - Mica coated with ferric oxide					
Pigment loading	500 h	1000 h	1500 h	2000 h	2500 h
15 phr					
10 phr					
5 phr					

The weathering results of the PVC/pigment 5 films from table 4.5 do not show any remarkable signs of degradation, at least at macroscopic observation. The ferric oxide on the pigment treatment and the weather resistant MICA base construct a really strong pigment.

Because of the resolution of the scanner, the pictures are not representative and as a result it is not really obvious when the degradation starts for the three loadings of the five pigments. For this reason, the weathering results are also included in the form of a graph as shown in figure 4.1.

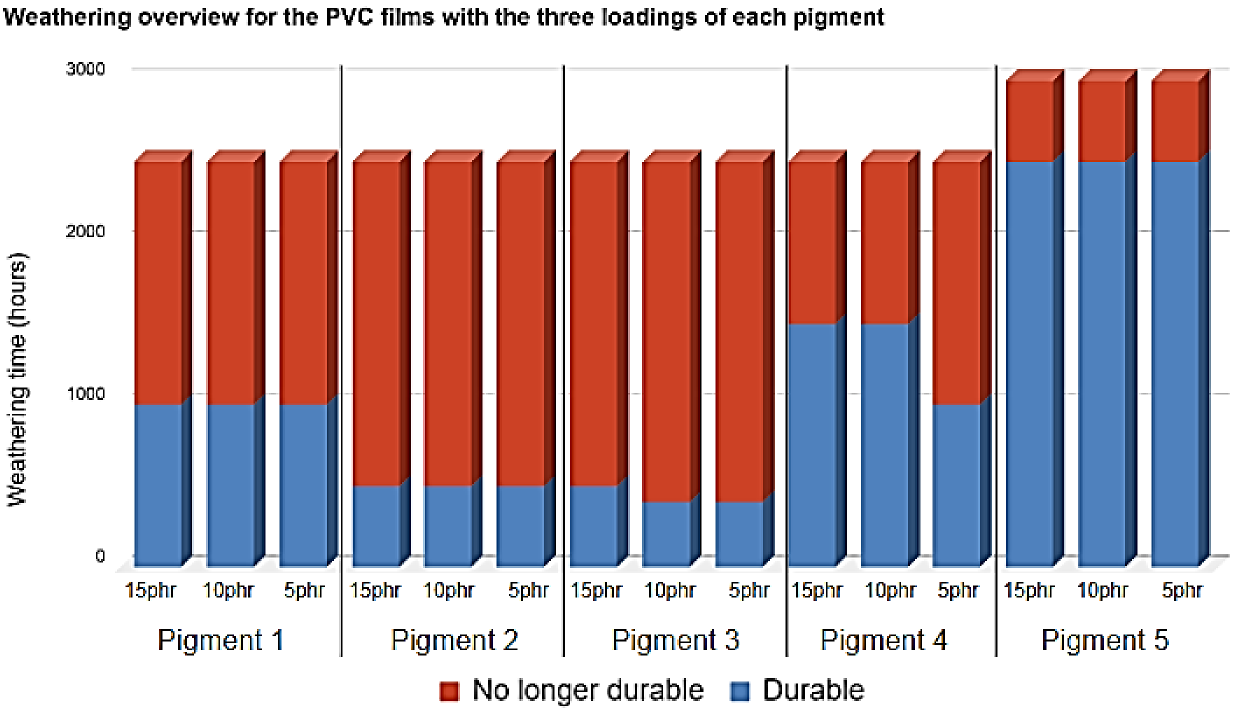


Fig.4.1. Weathering overview for the PVC films with the three loadings of all five pigments.

The weathering results from the tables 4.1 - 4.5 and from figure 4.1 confirm the poor weathering performance of PVC films pigmented with metallic pigments. Only pigment 5-based films, perform well until 2500 hours of weathering. This can be attributed to the fact that darker shades of colors absorb higher amounts of UV radiation so less is available to initiate PVC degradation [39]. Apart from pigment 5, the other four pigments can barely reach 500-1500 h of artificial weathering (fig.4.1) [40]. Taking under consideration that the pigments market continues to grow and change at a rapid pace ($1.20 billion by 2022, Grand View Research (GVR)) [41], finding a solution to improve the durability of polymeric films with sensitive pigments is a critical matter.

4.1.2 Portable microscope observation

All of the PVC films with the five pigments were tested with the portable light microscope at a magnification of around 750x in order to observe the orientation and distribution of flakes/particles of pigments. The microscope images of all the PVC films with the five pigments before and after degradation are presented below (fig. 4.2, 4.3, 4.4, 4.5 and 4.6).

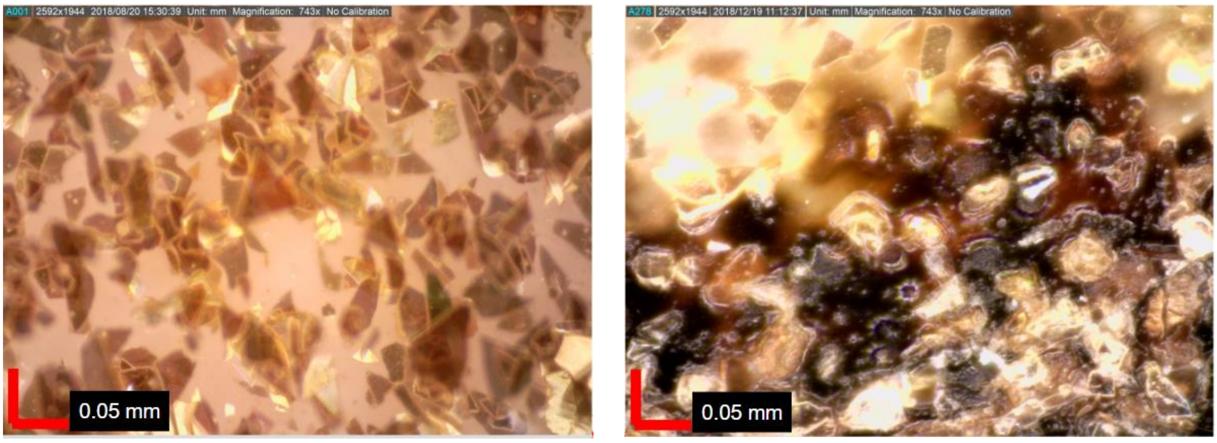


Fig.4.2. PVC/pigment 1 with 15 phr pigment loading before (left) and (right) after 2000 h of degradation after weathering (scale: 0.05 mm).

The pigment 1 flakes (fig.4.2, left) are randomly distributed inside the PVC matrix with a triangular shape and a size of 10-20 μm. There are areas where flakes are stacked together or one on top of the other. Most of them seem to be aligned almost horizontal to the film surface. The image of the degraded film (fig.4.2, right) shows that microscopically, the film matrix degraded but, since there is a blend of degradation products it is not immediately possible to state which component is degraded the most.

Figure 4.3 shows the pigment flakes distribution on the side of the film which is where the degradation started in this specific case. Smaller parts and damaged flakes are observed because of the sample being cut in order to be placed on the aluminum panel. Damaged flakes/particles cause the exposure of the base material and the metal oxide surface coating to water and other PVC degradation products and as a result the film degradation propagates faster than it would if there were not damaged particles.

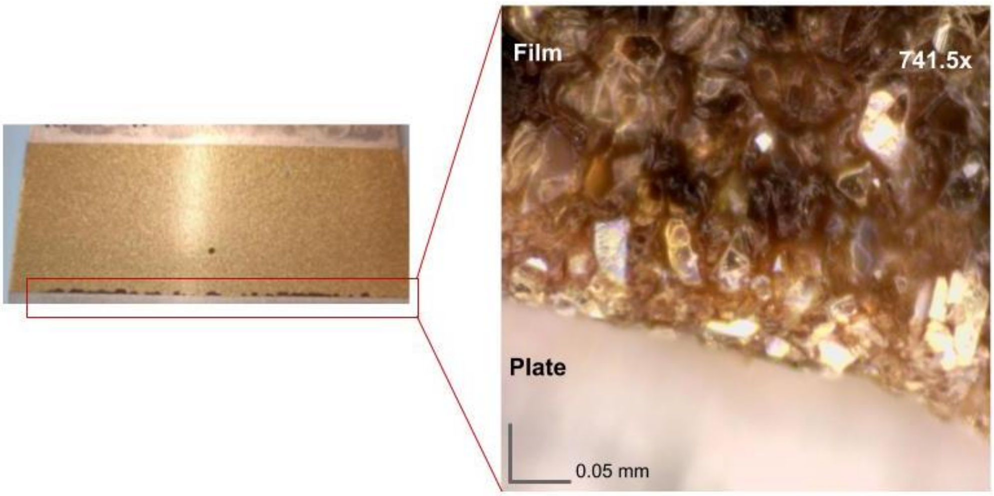


Fig.4.3. PVC/pigment 1 sample after 1500 h of weathering (left), magnified image of the film's side area (right) (741.5x).

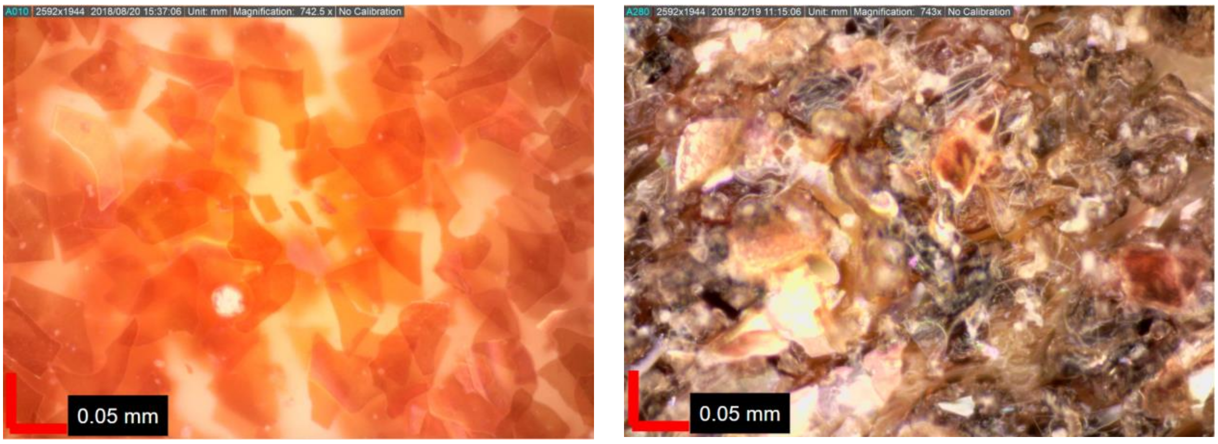


Fig.4.4. PVC/pigment 2 with 15 phr pigment loading before (left) and (right) after 2000 h of degradation after weathering (scale: 0.05 mm).

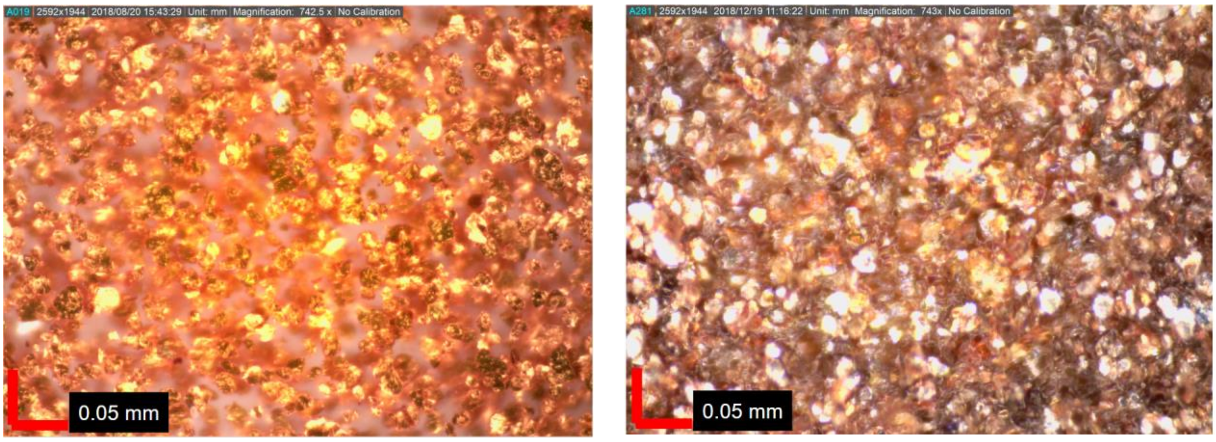


Fig.4.5. PVC/pigment 3 with 15 phr pigment loading before (left) and (right) after 2000 h of degradation after weathering (scale: 0.05 mm).

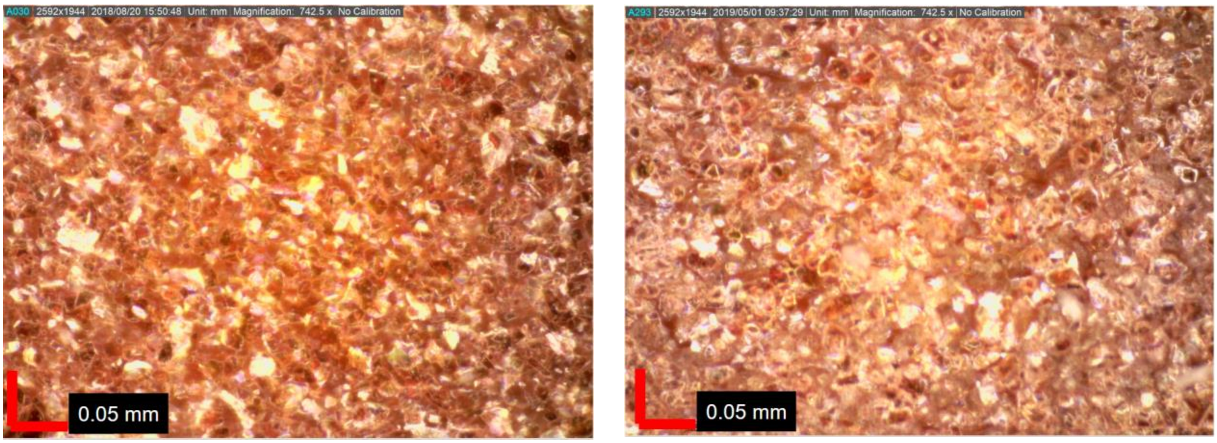


Fig.4.6. PVC/pigment 4 with 15 phr pigment loading before (left) and (right) after 2000 h of degradation after weathering (scale: 0.05 mm).

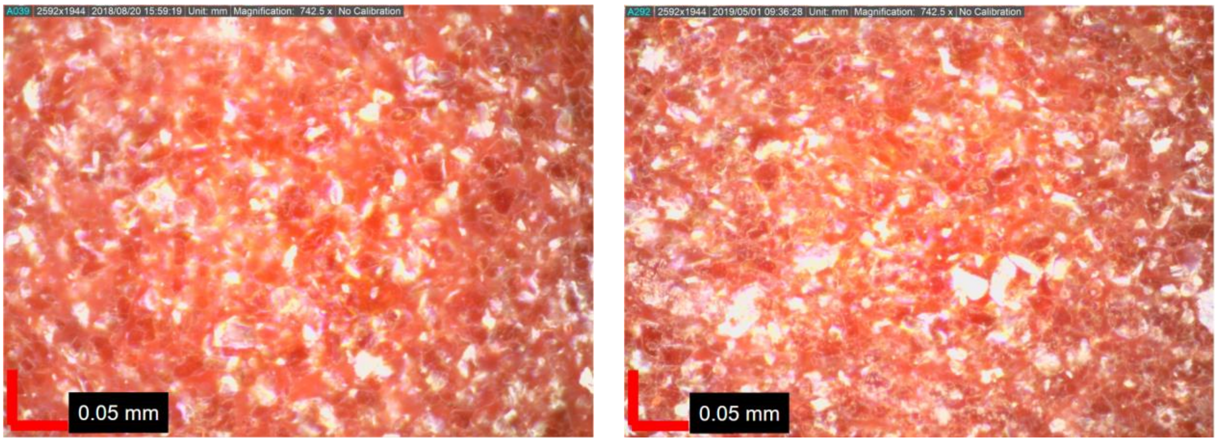


Fig.4.7. PVC/pigment 5 with 15phr pigment loading before (left) and (right) after 2000 h of degradation after weathering (scale: 0.05 mm).

The pigment 2 flakes (fig.4.4, left) are randomly distributed inside the PVC matrix with a flake shape due to their glass nature and a bigger size than pigment 1 flakes (25-35 μm). As in the case of pigment 1, there are areas where flakes are stacked together or one on top of the other. Most of them seem to be aligned almost horizontal to the films surface. The image of the degraded film (fig.4.4, right) shows that microscopically, the PVC matrix is degraded (darken because of the formation of double bonds in the backbone of PVC) and the flakes are also degraded due to corrosion of the metal oxide surfaces.

The pigments 3 and 4 (fig.4.5 and 4.6) are a little different than the previous two pigments since they consist of spherical particles with a size of 5-10 μm which are more well-distributed inside the PVC matrix than the flakes. The problem of the flake alignment is not an issue in this case due to the spherical shape of the particles. The image of the degraded film (pigment 3, fig.4.5) shows that microscopically, the PVC is degraded and the particles seem to either be degraded or the iron oxide from the pigment surface seems to be completely corroded leaving the aluminum substrate exposed to the PVC dehydrochlorination products. For pigment 4 (fig.4.6), the degraded film shows that the PVC matrix is degraded in some parts but its discoloration is not that intense compared to the previous pigments due to the intrinsic ability of MICA to be thermally stable even at high temperatures, without losing its surface treatment. As a result, PVC degradation is affected less from the metallic surface of the pigment [24].

Pigment 5 (fig.4.7) was expected to be the pigment that offers the highest weathering durability to the PVC films and this was confirmed by the films appearance after degradation. The PVC matrix does not look degraded after 2000 hours of artificial weathering and the spherical MICA particles (5-10 μm) with the ferric oxide treatment look unaffected.

The rest of the analytical investigation of these films will be presented in comparison with the results of the films after the use of the five additives in the following paragraphs.

Additional information

In order to check the contribution of the additive to the films degradation, pigmented films without adhesive on the back were tested. For the films for each one of the five pigments degradation spots were observed ~500 h earlier than in the case of the original films with the adhesive on the back. Thus, it is not only that the adhesive does not have a negative effect regarding durability but it actually supports the compound and offers higher stability compared to the films without the adhesive. This was also confirmed by FTIR analysis on the surface of the different films.

4.2 Additive 1: Water scavenger

The calcium oxide-based water scavenger was added to the original formulation and the prepared films were tested. This additive performance was monitored and analyzed in both clear and colored PVC formulations. As it was mentioned in section 3.1, three loadings (minimum, intermediate and maximum), were calculated according to the technical data sheets for all the chosen additives. These three additive loadings were implemented in the PVC films containing the five chosen pigments and they were tested accordingly.

4.2.1 Weathering results

In order to perform a preliminary check of the effect of the selected additives on the performance of standard PVC films, the additives have been added and tested with a clear film formulation. Results of weathering performances of the selected water scavenger are shown in figure 4.8, where the weathering durability achieved is considered to be the time until the first signs of degradation appear.

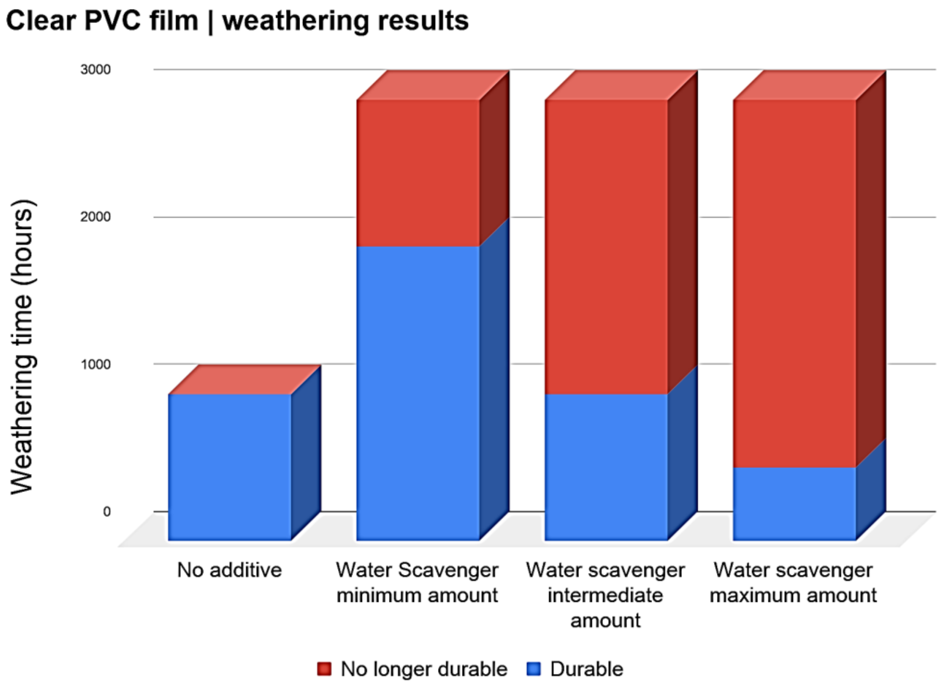


Fig.4.8. Clear PVC weathering results before and after the addition of the water scavenger.

As it can be seen from figure 4.8, the use of the calcium oxide-based additive increases the weathering durability of the clear PVC film with the minimum amount of water scavenger. The films with the intermediate and maximum amount show the same or worse durability than the film with the original formulation respectively. This water scavenger consists of calcium oxide (CaO) stabilized by a wetting agent. When the loading of additive is increased the amount of wetting agent inside increases as well. The PVC organosol used is solvent-based stabilized compound in a viscous liquid form. After the addition of the water scavenger, the wetting agent inside tends to disperse the organosol and gives the opposite effect than what was anticipated. This effect can be avoided after the addition of pigments as a filler material. This was concluded after the completion of the weathering tests that are presented below.

The first pigment tested (pigment 1) is a borosilicate glass base coated with titanium dioxide and small amounts of tin oxide. The borosilicate glass offers outstanding transparency and colour purity, owing to a very narrow particle size distribution and the two oxides offer the gold color. The weathering results for PVC/pigment 1 before and after the addition of the water scavenger are shown in figure 4.9.

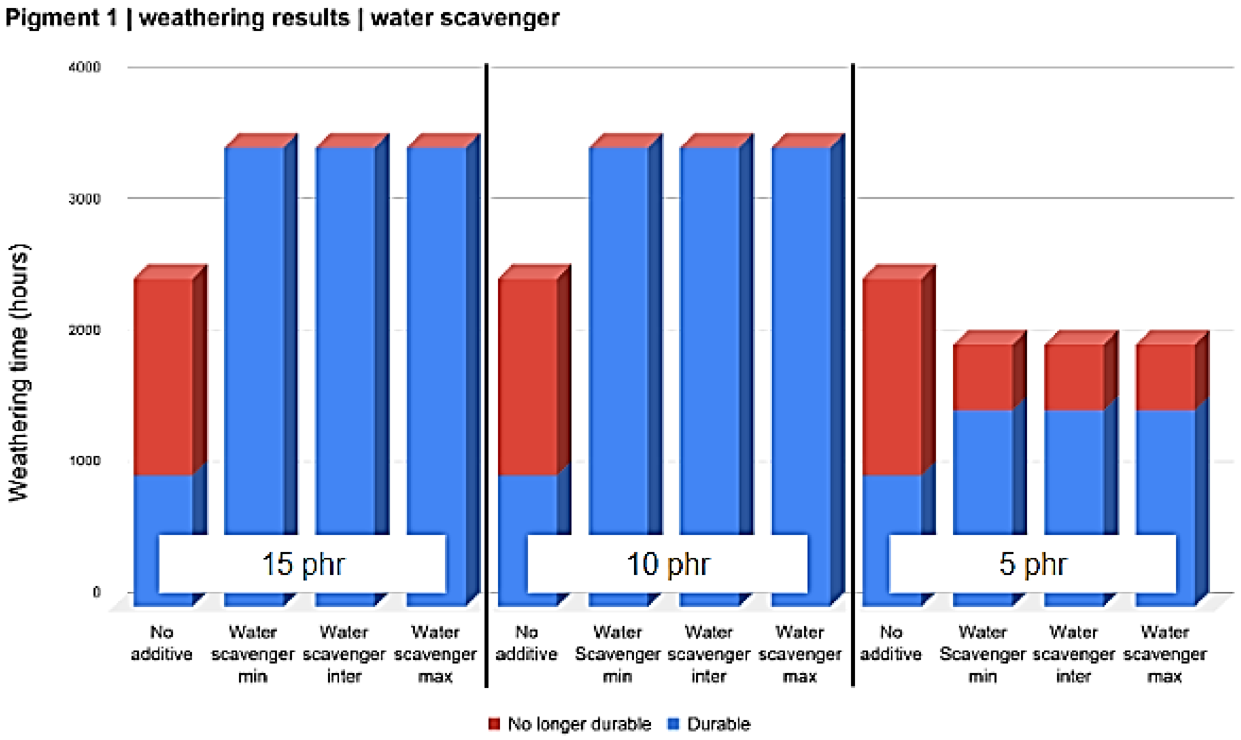


Fig.4.9. Weathering results of PVC/pigment 1 films before and after the addition of the water scavenger.

After the use of the CaO-based additive, it can be seen that there is a significant increase in the weathering durability of the PVC/pigment 1 for the pigment loadings of 15 and 10 phr from 1000 h to 3500 h of artificial ageing. The CaO reacts with water avoiding its involvement in the PVC degradation process. The effect is the same for all CaO-based additive loadings. For the 5 phr loading of the glass pigment there is only a small increase in durability from 1000 h to 1500 h due to the low pigment amount which makes the film more vulnerable to UV radiation considering that the metallic pigment itself acts as a UV absorber [39].

The second pigment tested (pigment 2) is a borosilicate glass-based pigment coated with iron oxide. The iron oxide offers the red color. The weathering results for PVC/pigment 2 with and without the addition of the water scavenger are demonstrated in figure 4.10.

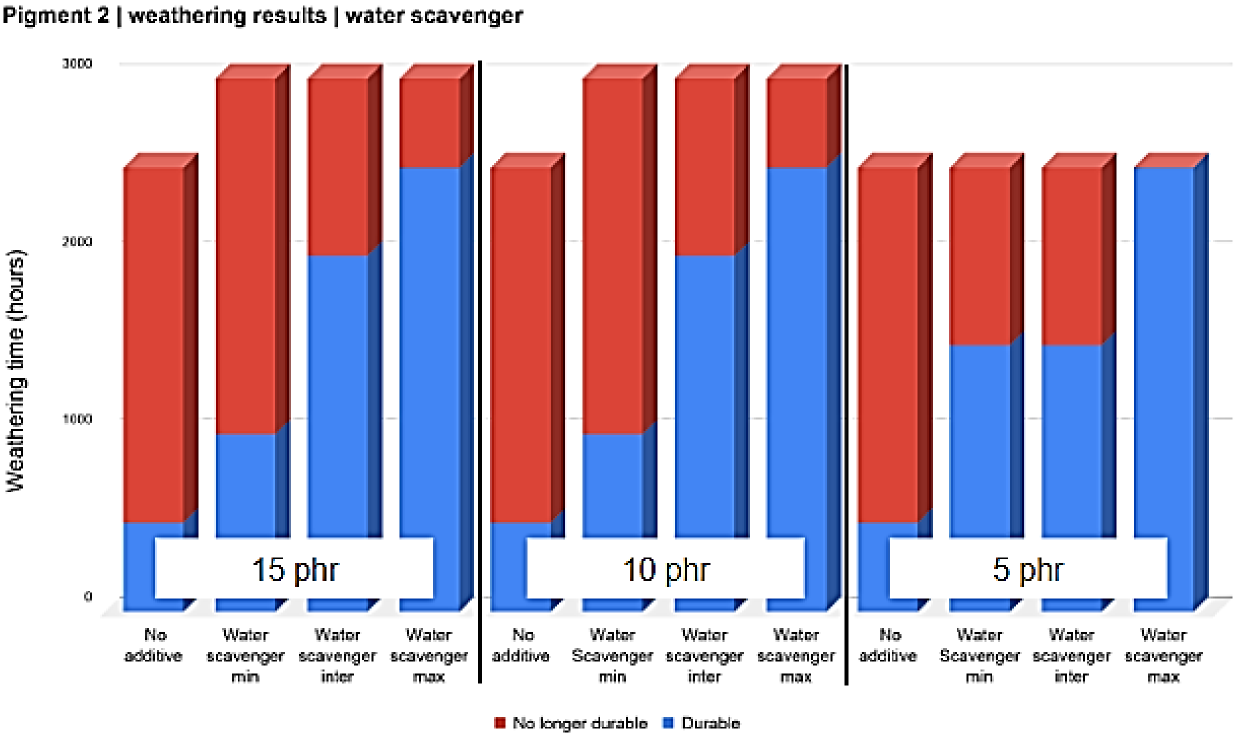
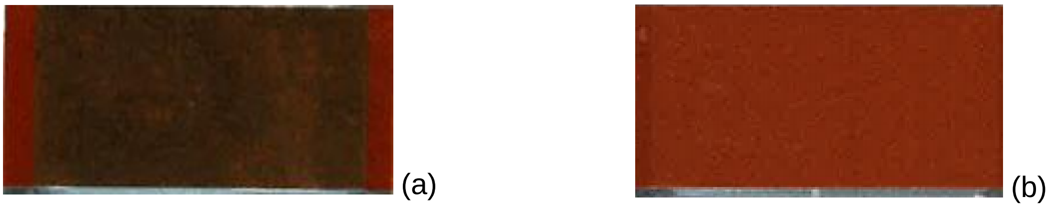


Fig.4.10. Weathering results of PVC/pigment 2 films before and after the addition of the water scavenger.

After the use of the water scavenger, it can be seen that there is a significant increase in the weathering durability of the PVC/pigment 2 for all three of the pigment loadings of 15, 10 and 5 phr from 500 h to 2500 h of artificial ageing when the maximum amount of CaO-based additive is used. The weathering performance is shown to improve as the loading of the water scavenger increases for all three loadings of pigment 2. The big difference between the films appearance before and after the use of the water scavenger when the maximum amount of the additive is used after 2000 h of artificial ageing is demonstrated in figure 4.11.


(a)

(b)

Fig 4.11. (a) Original formulation of 15 phr loading of pigment 2 after 2000 h of weathering, (b) result of 15 phr loading of pigment 2 after 2000 h of weathering after the use of the maximum amount of the water scavenger.

The original formulation is completely degraded and the color and gloss are completely gone. Conversely, the films after the use of the water scavenger are performing well until 2000 h and as can be seen from figure 4.9, its durability lasts until 2500 h which is five times better than the original. The CaO reacts with water avoiding its involvement in the PVC degradation process and results in the retardation of the film degradation.

The third pigment tested (pigment 3) consists of aluminum flakes coated with iron oxide. The aluminum offers good optical quality and together with the iron oxide coating, the flakes exhibit a distinct directed reflection, often described as crystal luster. The reason for this is the smooth surface combined with the relatively homogeneous thickness of the particles and the adjusted metal oxide layer thickness that offers the preferred color [31]. The weathering results for PVC/pigment 3 films with and without the addition of the water scavenger are demonstrated in figure 4.12.

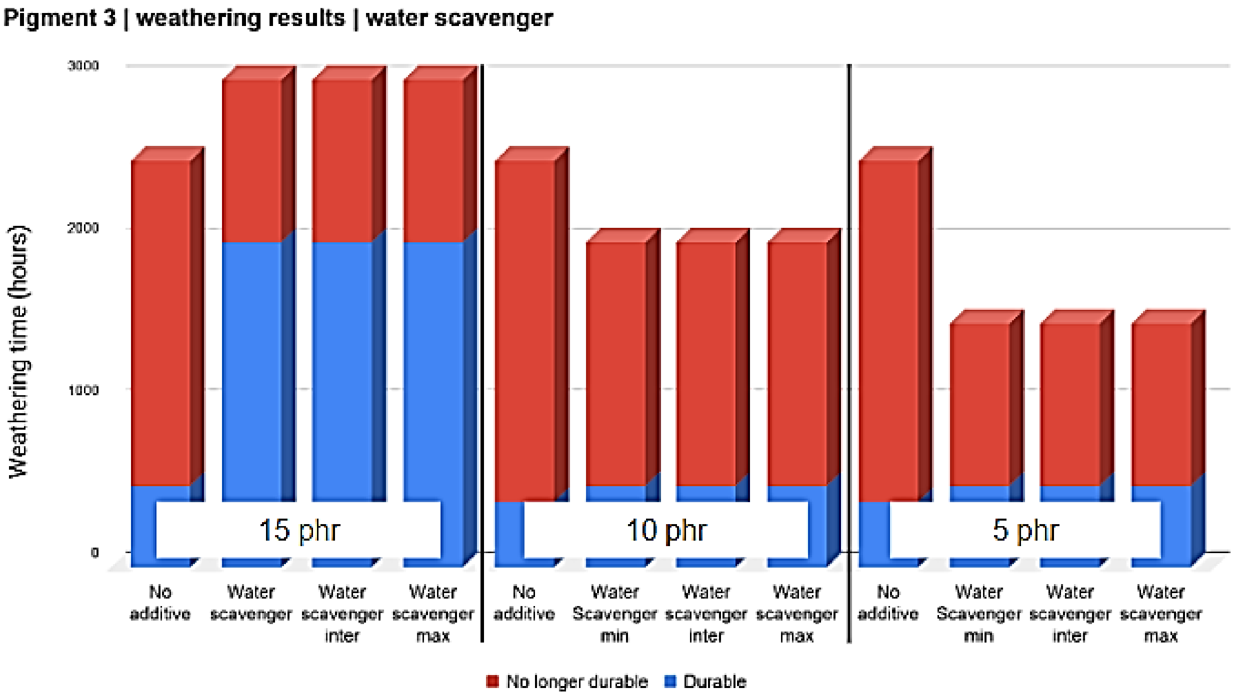


Fig.4.12. Weathering results of PVC/pigment 3 films before and after the addition of the water scavenger.

After the use of the water scavenger, it can be seen that there is a significant increase in the weathering durability of the PVC/pigment 3 only for the 15 phr loading from 500 h to 2000 h of artificial ageing for all three loadings of the CaO-based additive due to the water scavenger effectiveness. Conversely, there is no difference in the performance of 10 and 5 phr loadings of pigment 3 due to the low pigment amount which makes the film more vulnerable to UV radiation and due to the sensitivity of the iron oxide surface treatment of the pigment. Despite the fact that the degradation still starts at 500 h for the 10 and 5 phr loadings, the appearance is improved as can be seen in figure 4.13.

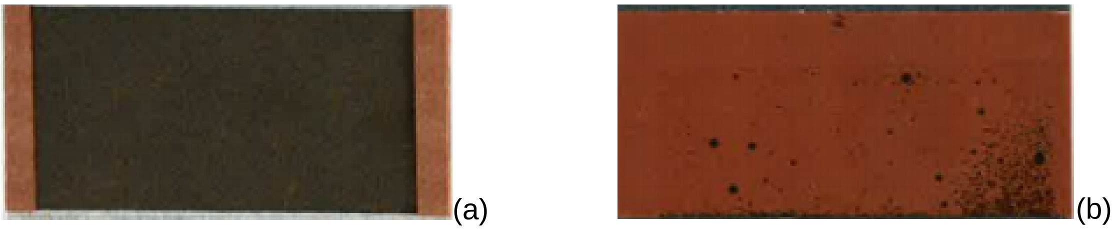


Fig 4.13. (a) Original formulation of 5 phr loading of pigment 3 after 1000 h of weathering, (b) result of 5 phr loading of pigment 3 after 1000 h of weathering after the use of the minimum amount of the water scavenger.

The original formulation film is completely degraded and the color and gloss are completely gone. The use of the water scavenger delays the degradation process by reacting with water, removing the reaction products and avoiding water retention on the surface of the films. However, this is not enough to improve the formulation for at least the 10 and 5 phr loading conditions.

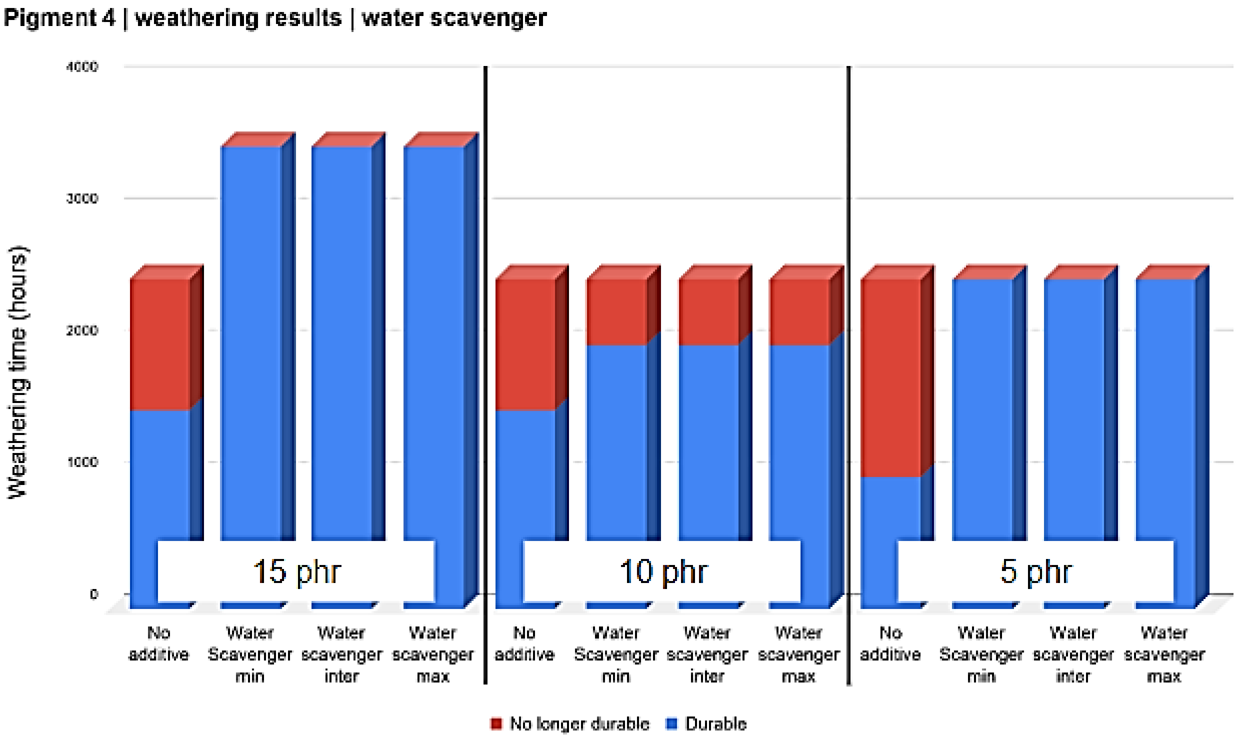


Fig.4.14. Weathering results of PVC/pigment 4 films with and without the addition of the water scavenger.

The fourth pigment tested is a MICA-based pigment coated with iron oxide. MICA-based pigments with single layers show an interference color that “turns on and off” because they consist of just one optical layer. Mica-based pigments with multilayers can show a pronounced angle dependent color effect, if the optical thickness of the layers are carefully chosen. The iron oxide coating offers the orange color to this specific pigment [31]. The weathering results for PVC/pigment 4 with and without the addition of the water scavenger are demonstrated in figure

4.14.

After the use of CaO-based additive, it can be seen that there is a significant increase in the weathering durability of the PVC/pigment 4 for all three of the pigment loadings (15, 10 and 5 phr). The 15 phr of pigment loading shows two times better durability than the original film, the 10 phr durability is 1000 h better than the original film and for the 5 phr the durability is two times better than the original film due to the intrinsic ability of MICA to be thermally stable even at high temperatures without losing its surface treatment. As a result, PVC degradation is affected less from the metallic surface of the pigment. The effect is the same for all three water scavenger loadings.

The last pigment is also a MICA-based pigment like pigment 4 but this one is coated with ferric oxide. The weathering results for PVC/pigment 5 before and after the addition of the water scavenger are demonstrated in figure 4.15.

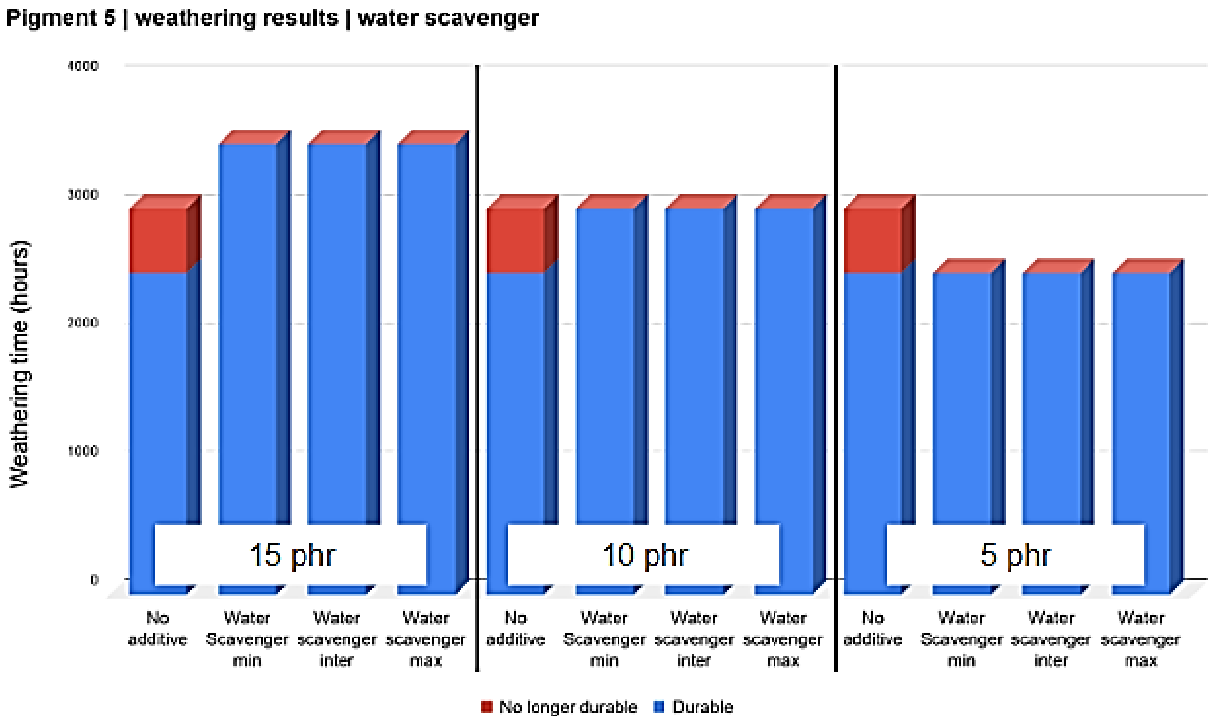


Fig.4.15. Weathering results of PVC/pigment 5 films with and without the addition of the water scavenger.

Pigment 5 is a little different than the other four since no signs of degradation of the original films were noticed until 2500 h of artificial weathering. The films with this pigment are quite durable to artificial ageing but it is also important to see that improved durability can also be achieved after the use of the water scavenger. The 15 phr films results show a 500 h increased weathering durability and it is still too early to comment on the behavior of this pigment after the use of the water scavenger.

4.2.2 Gloss and color measurements

The color and gloss of the pigmented PVC films were measured at 0 h and each 500 h for each stage of degradation in order to see if the implemented additive affects the appearance of the films after each weathering stage. The gloss results come from standard deviation of three spots on the film surface and the acceptable range is ±4 GU (gloss units).

Table 4.6. Gloss measurements at 60° for the 15 phr loading of pigment 1 for the three loadings of the water scavenger.

Additive amount	0 h	500 h	1000 h	1500 h	2000 h	2500 h	3000 h
No additive	110 GU	101 GU	101 GU	97.6 GU	97.4 GU	96.4 GU	Fully degraded
Water scavenger minimum	113 GU	87.7 GU	86.8 GU	82.2 GU	85.1 GU	86.7 GU	85 GU
Water scavenger intermediate	106 GU	72.6 GU	70.8 GU	66.3 GU	72.1 GU	69.8 GU	72.2 GU
Water scavenger maximum	97.5 GU	63.4 GU	61.9 GU	60.8 GU	63.2 GU	60.4 GU	62.1 GU

Table 4.7. Gloss measurements at 60° for the 10 phr loading of pigment 1 for the three loadings of the water scavenger.

Additive amount	0 h	500 h	1000 h	1500 h	2000 h	2500 h	3000 h
No additive	117 GU	111GU	111 GU	110 GU	110 GU	102 GU	Fully degraded
Water scavenger minimum	110 GU	87.9 GU	87 GU	92 GU	92.4 GU	90 GU	90 GU
Water scavenger intermediate	103 GU	71.2 GU	70.8 GU	73 GU	72.1 GU	69.5 GU	71.4 GU
Water scavenger maximum	94.3 GU	60.5 GU	59.5 GU	60 GU	63 GU	58.9 GU	63.9 GU

Table 4.8. Gloss measurements at 60º for the 5 phr loading of pigment 1 for the three loadings of the water scavenger.

Additive amount	0 h	500 h	1000 h	1500 h	2000 h
No additive	126 GU	121 GU	115 GU	121 GU	107 GU
Water scavenger minimum	114 GU	97.1 GU	96.1 GU	97 GU	98.7 GU
Water scavenger intermediate	101 GU	78.8 GU	74.4 GU	78.5 GU	78.6 GU
Water scavenger maximum	99.7 GU	61.9 GU	61.4 GU	61.7 GU	67.5 GU

From the gloss results of tables 4.6, 4.7 and 4.8, it can be observed that the addition of the water scavenger reduces the gloss of the 15, 10 and 5 phr PVC/pigment 1 films after degradation. In fact, as the amount of the water scavenger is increased, the gloss decreases. The minimum amount of the water scavenger causes the lower gloss reduction among the three additive loadings. The highest differences in gloss are observed at 500 and 1000 hours of weathering and the difference becomes smaller as degradation propagates. It seems that after the first stages of degradation the additive migrates to the surface, it increases the surface roughness and then it is washed away by the cyclic water spray. This hypothesis is confirmed by the atomic force microscope results that follow in the next parts of this section.

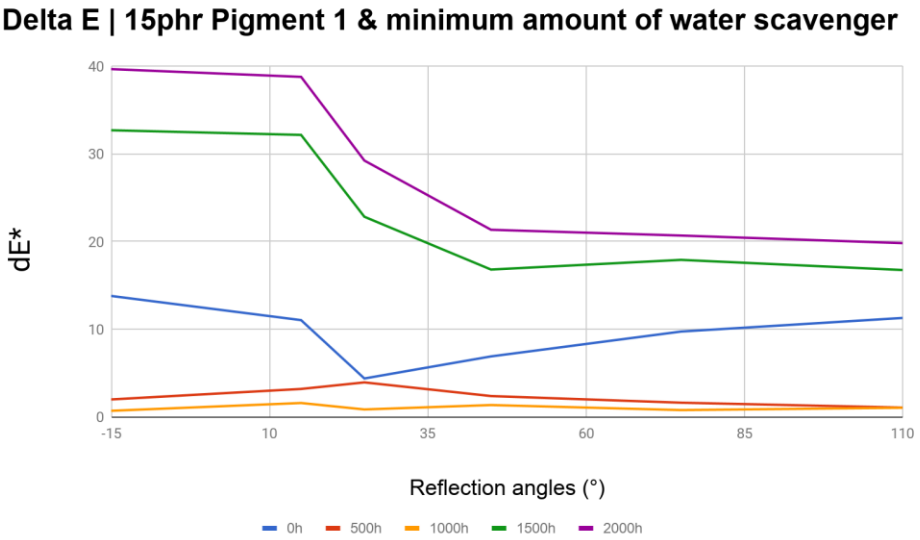


Fig.4.16. Color difference after the addition of water scavenger after each stage of degradation of 15 phr PVC/pigment 1 films.

In addition, film color measurements took place at different reflection angles because effect pigments change their appearance with viewing angle and lighting conditions. The results for the minimum amount of water scavenger are presented since this is the additive loading with the closest gloss values to the original films for the 15 phr of PVC/pigment 1 films which is the pigment loading with the strongest color (fig.4.16). The color difference (dE*) is defined as the color difference between the films with the additive and the respective ones of the original formulation at each stage of degradation.

According to figure 4.16, the results show an opposite trend to those of the gloss values since the 500 h and 1000 h stages show the smaller difference (dE*) in color compared to the rest of the weathering stages for the PVC/pigment 1 film after the addition of the minimum amount of the water scavenger. Pigments selectively absorb some wavelengths of incident light while reflecting or transmitting others. The film is an opaque material so most of the incident light is reflected. Color is seen in the diffuse reflection and gloss is seen in the specular reflection. The glossy appearance of the films becomes darker and less chromatic due to the dilution of the diffuse reflectance by the increase of the specular reflectance. The water scavenger migrates to the surface and changes the light diffuse and specular reflectance of the surface.

Table 4.9. Gloss measurements at 60º for the 15 phr loading of pigment 2 for the three loadings of the water scavenger.

Additive amount	0 h	500 h	1000 h	1500 h	2000 h	2500 h	3000 h
No additive	98.5 GU	93.7 GU	93.7 GU	Fully degraded	Fully degraded	Fully degraded	Fully degraded
Water scavenger minimum	99.5 GU	73.0 GU	73.0 GU	50.4 GU	85.1 GU	10.9 GU	10.9 GU
Water scavenger intermediate	95.0 GU	56.4 GU	56.4 GU	50.1 GU	27.0 GU	15.0 GU	14.1 GU
Water scavenger maximum	84.6 GU	40.9 GU	39.5 GU	36.3 GU	29.6 GU	19.6 GU	18.0 GU

Table 4.10. Gloss measurements at 60º for the 10 phr loading of pigment 2 for the three loadings of the water scavenger.

Additive amount	0 h	500 h	1000 h	1500 h	2000 h	2500 h	3000 h
No additive	101 GU	97.5 GU	97.5 GU	Fully degraded	Fully degraded	Fully degraded	Fully degraded
Water scavenger minimum	96.1 GU	74.8 GU	73.3 GU	80 GU	41.7 GU	10.0 GU	10.0 GU
Water scavenger intermediate	88.3 GU	57.8 GU	57.3 GU	51.8 GU	33.6 GU	25.2 GU	15.7 GU
Water scavenger maximum	65.3 GU	47.7 GU	47.3 GU	45.8 GU	34.5 GU	32.7 GU	22.2 GU

Table 4.11. Gloss measurements at 60º for the 5 phr loading of pigment 2 for the three loadings of the water scavenger.

Additive amount	0 h	500 h	1000 h	1500 h	2000 h
No additive	115 GU	112 GU	108 GU	Fully degraded	Fully degraded
Water scavenger minimum	104 GU	85.9 GU	83.9 GU	77.7 GU	74.3 GU
Water scavenger intermediate	95.6 GU	67.9 GU	67.7 GU	62.7 GU	60.1 GU
Water scavenger maximum	79.7 GU	55.4 GU	55.4 GU	53.7 GU	51.8 GU

From the gloss results of the tables 4.9-4.11, it can be seen that the addition of the water scavenger reduces the gloss of the 15 phr PVC/pigment 2 films after the first stages of degradation. In fact, as the amount of the water scavenger is increased, the gloss decreases. The minimum amount of the water scavenger causes the lower gloss reduction after degradation among the three additive loadings. The highest differences in gloss are observed at 500 and 1000 hours of weathering and the difference becomes smaller as degradation propagates. It can be concluded that the PVC/pigment 2 films follow the same pattern as the PVC/pigment 1 films.

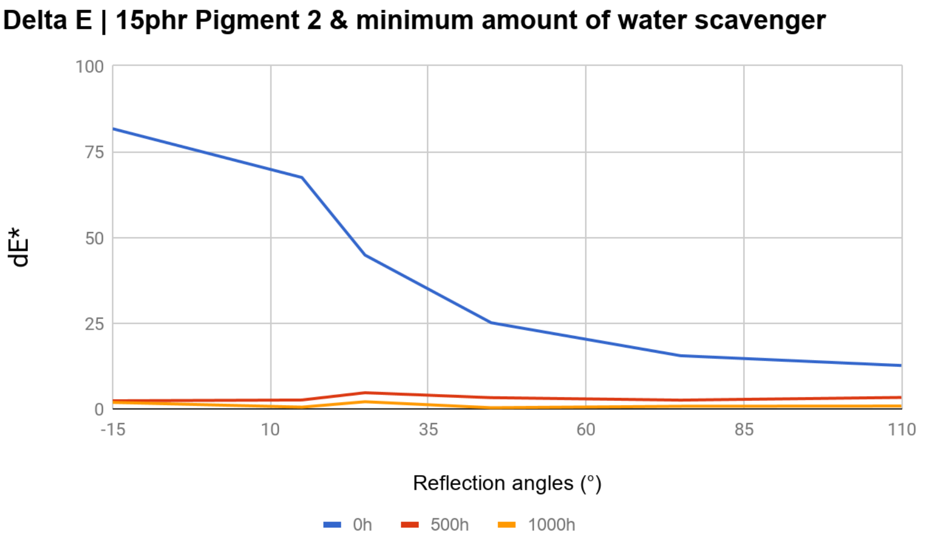


Fig.4.17. Color difference after the addition of water scavenger after each stage of degradation of 15 phr PVC/pigment 2 films.

According to figure 4.17, the results are similar to those of the PVC/pigment 1 films but this time there is a higher difference before degradation. After the first stages of degradation the color difference is similar to the original film. The additive tends to migrate to the surface and then be removed faster than in the case of PVC/pigment 1 films. Their difference is the surface treatment of the glass flakes so it can be assumed that the sensitivity of the metal oxide treatment plays a role in the effect of the additive.

Table 4.12. Gloss measurements at 60º for the 15 phr loading of pigment 3 for the three loadings of the water scavenger.

Additive amount	0 h	500 h	1000 h	1500 h	2000 h	2500 h	3000 h
No additive	97.0 GU	91.2 GU	Fully degraded	Fully degraded	Fully degraded	Fully degraded	Fully degraded
Water scavenger minimum	105 GU	78.9 GU	78.1 GU	75.6 GU	30.7 GU	Fully degraded	Fully degraded
Water scavenger intermediate	103 GU	66.7 GU	66.4 GU	66.4 GU	54.7 GU	Fully degraded	Fully degraded
Water scavenger maximum	103 GU	53.9 GU	53.3 GU	53.0 GU	46.1 GU	Fully degraded	Fully degraded

Table 4.13. Gloss measurements at 60º for the 10 phr loading of pigment 3 for the three loadings of the water scavenger.

Additive amount	0 h	500 h	1000 h	1500 h	2000 h	2500 h	3000 h
No additive	98.5 GU	95.7 GU	Fully degraded	Fully degraded	Fully degraded	Fully degraded	Fully degraded
Water scavenger minimum	91.2 GU	79.7 GU	Fully degraded	Fully degraded	Fully degraded	Fully degraded	Fully degraded
Water scavenger intermediate	92.1 GU	59.5 GU	Fully degraded	Fully degraded	Fully degraded	Fully degraded	Fully degraded
Water scavenger maximum	80.1 GU	37.7 GU	Fully degraded	Fully degraded	Fully degraded	Fully degraded	Fully degraded

Table 4.14. Gloss measurements at 60º for the 5 phr loading of pigment 3 for the three loadings of the water scavenger.

Additive amount	0 h	500 h	1000 h	1500 h	2000 h	2500 h	3000 h
No additive	112 GU	112 GU	Fully degraded	Fully degraded	Fully degraded	Fully degraded	Fully degraded
Water scavenger minimum	98.8 GU	75.6 GU	Fully degraded	Fully degraded	Fully degraded	Fully degraded	Fully degraded
Water scavenger intermediate	90.1 GU	46.6 GU	Fully degraded	Fully degraded	Fully degraded	Fully degraded	Fully degraded
Water scavenger maximum	73.2 GU	37.0 GU	Fully degraded	Fully degraded	Fully degraded	Fully degraded	Fully degraded

From the gloss results of the tables 4.12-4.14, it can be observed that the addition of the water scavenger has the same effect for the PVC/pigment 3 films as in the case of the PVC films pigmented with the previous two pigments (pigments 1 and 2) with the effect of the additive migration to the surface of the films.

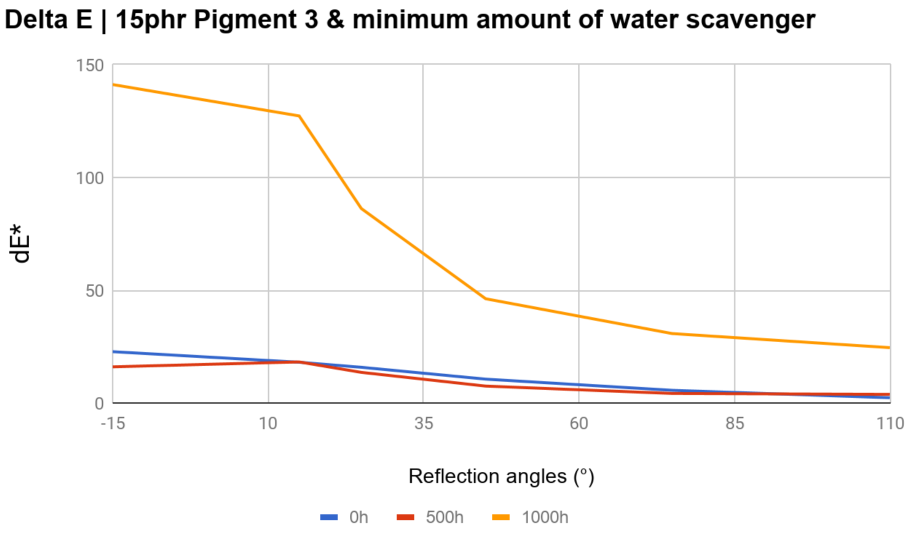


Fig.4.18. Color difference after the addition of water scavenger after each stage of degradation of 15phr PVC/pigment 3 films.

According to figure 4.18, the results for the PVC/pigment 3 films are different than the previous two since there is no major difference before and after the first stage of degradation but there is a huge color difference after 1000 h of degradation since the films with the water scavenger are still performing well but the original films are degraded.

Table 4.15. Gloss measurements at 60º for the 15 phr loading of pigment 4 for the three loadings of the water scavenger.

Additive amount	0 h	500 h	1000 h	1500 h	2000 h	2500 h	3000 h
No additive	101 GU	96.5 GU	93.4 GU	81.0 GU	67.1 GU	62.0 GU	Fully degraded
Water scavenger minimum	101 GU	72.7 GU	72.0 GU	71.4 GU	70.7 GU	69.0 GU	66.9 GU
Water scavenger intermediate	97.6 GU	58.7 GU	56.0 GU	56.0 GU	55.5 GU	52.8 GU	55.1 GU
Water scavenger maximum	82.8 GU	45.7 GU	43.7 GU	43.9 GU	43.4 GU	40.3 GU	44.3 GU

Table 4.16. Gloss measurements at 60º for the 10 phr loading of pigment 4 for the three loadings of the water scavenger.

Additive amount	0 h	500 h	1000 h	1500 h	2000 h
No additive	103 GU	101 GU	98.6 GU	101 GU	100 GU
Water scavenger minimum	105 GU	76.8 GU	87.4 GU	83.6 GU	83.6 GU
Water scavenger intermediate	97.0 GU	63.2 GU	62.0 GU	61.2 GU	61.2 GU
Water scavenger maximum	89.0 GU	50.8 GU	49.6 GU	51.1 GU	50.8 GU

Table 4.17. Gloss measurements at 60º for the 5 phr loading of pigment 4 for the three loadings of the water scavenger.

Additive amount	0 h	500 h	1000 h	1500 h	2000 h
No additive	108 GU	106 GU	108 GU	107 GU	107 GU
Water scavenger minimum	102 GU	79.6 GU	75.6 GU	72.8 GU	70 GU
Water scavenger intermediate	98.9 GU	55.8 GU	53.2 GU	52.0 GU	51.4 GU
Water scavenger maximum	83.3 GU	43.0 GU	39.3 GU	37.6 GU	36.6 GU

From the gloss results of the tables 4.15-4.17, it can be seen that the addition of the water scavenger has the same effect on the PVC/pigment 4 films as in the results of the films pigmented with the other three pigments (pigments 1, 2 and 3) following the same pattern with a reduction of gloss as the additive amount is increased.

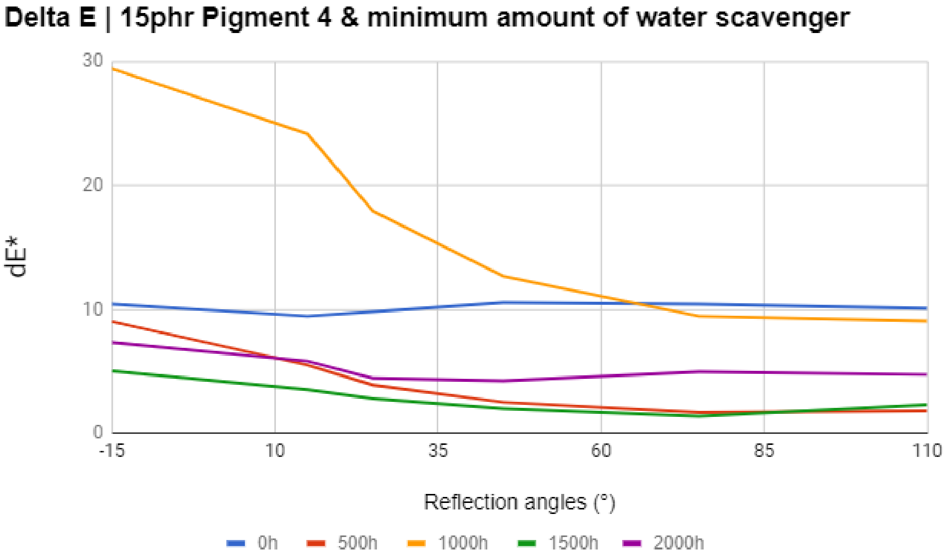


Fig.4.19. Color difference after the addition of water scavenger after each stage of degradation of 15phr PVC/pigment 4 films.

According to figure 4.19, the results for the PVC/pigment 4 films are different than the previous three since the biggest color difference is observed at the 1000 h stage of degradation and then the color difference becomes smaller once again. The additive migrates to the surface slower than in the case of the previous pigmented films (this will be confirmed later by the AFM analysis) and then after it is washed away by the cyclic water spray, the color difference is restored to a range of 4-7 (dE*).

Table 4.18. Gloss measurements at 60° for the 15 phr loading of pigment 5 for the three loadings of the water scavenger.

Additive amount	0 h	500 h	1000 h	1500 h	2000 h	2500 h	3000 h
No additive	92.6 GU	85.3 GU	83.9 GU	84.0 GU	83.5 GU	82.1 GU	82 GU
Water scavenger minimum	92.5 GU	66.6 GU	64.8 GU	65.9 GU	63.9 GU	63.5 GU	63.6 GU
Water scavenger intermediate	88.0 GU	47.7 GU	45.3 GU	45.6 GU	44.7 GU	43.9 GU	46.2 GU
Water scavenger maximum	85.3 GU	38.5 GU	38.5 GU	36.1 GU	35.7 GU	33.2 GU	38.6 GU

Table 4.19. Gloss measurements at 60^o for the 10 phr loading of pigment 5 for the three loadings of the water scavenger.

Additive amount	0 h	500 h	1000 h	1500 h	2000 h	2500 h
No additive	95.2 GU	90.4 GU	89.1 GU	89.2 GU	88.0 GU	87.7 GU
Water scavenger minimum	95.0 GU	66.2 GU	65.4 GU	66.9 GU	65.8 GU	65.1 GU
Water scavenger intermediate	94.0 GU	54.8 GU	53.6 GU	56.0 GU	52.8 GU	51.6 GU
Water scavenger maximum	92.0 GU	41.9 GU	41.1 GU	43.2 GU	41.9 GU	41.7 GU

Table 3.20. Gloss measurements at 60^o for the 5 phr loading of pigment 5 for the three loadings of the water scavenger.

Additive amount	0 h	500 h	1000 h	1500 h	2000 h
No additive	97.8 GU	95.1 GU	96.0 GU	95.6 GU	92.6
Water scavenger minimum	88.4 GU	66.6 GU	62.9 GU	62.9 GU	61 GU
Water scavenger intermediate	83.2 GU	47.7 GU	41.8 GU	41.4 GU	41 GU
Water scavenger maximum	72.8 GU	38.5 GU	33.9 GU	32.3 GU	31.1 GU

From the gloss results of the tables 4.18-4.20, it can be seen that the addition of the water scavenger has the same effect on the PVC/pigment 5 films as the four previous pigments.

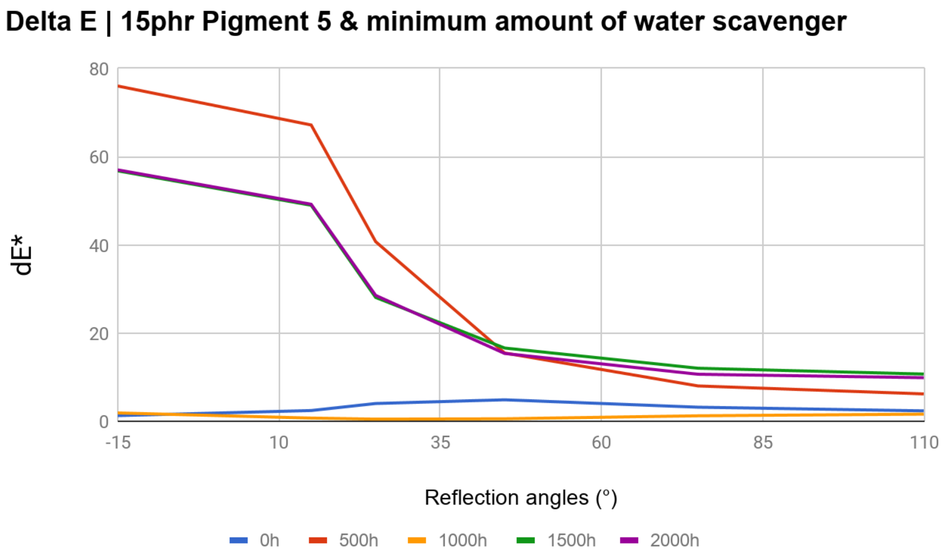


Fig.4.20. Color difference after the addition of water scavenger after each stage of degradation of 15phr PVC/pigment 5 films.

According to figure 4.20, the results for the PVC/pigment 5 films are different than the previous four since the biggest color difference is observed at the 500 h, 1500 h and 2000 h stages of degradation. The 1000 h color difference is lower compared to the stage of 0 h. This is most probably due to experimental error.

A general conclusion concerning the color difference is that each one of the five chosen pigments behaves differently after the addition of the water scavenger depending on the additive time needed to be washed away by the cyclic water spray.

4.2.3 Mechanical behavior

The tensile tests for the pigmented PVC films for the three loadings of the water scavenger were carried out in order to see if there is a significant change in the mechanical behavior of the films after the use of the CaO-based additive. For each film formulation three samples were tested in order to confirm the repetition of the same results. As it was mentioned before flat sheet type of samples was used. Apart from the pigmented films, clear PVC films with the three loadings of the water scavenger were tested to see if the implementation has a negative effect on the films mechanical properties and more specifically on the tensile strength .The results are shown in the following figures. The error bars of the graphs represent the standard deviation of the tensile strength results received from the three samples tested for each formulation.

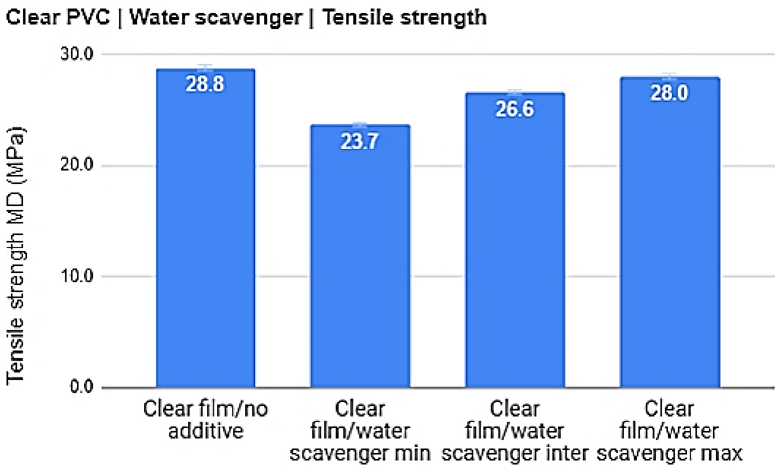


Fig.4.21. Tensile strength results for the clear film before and after the addition of the water scavenger.

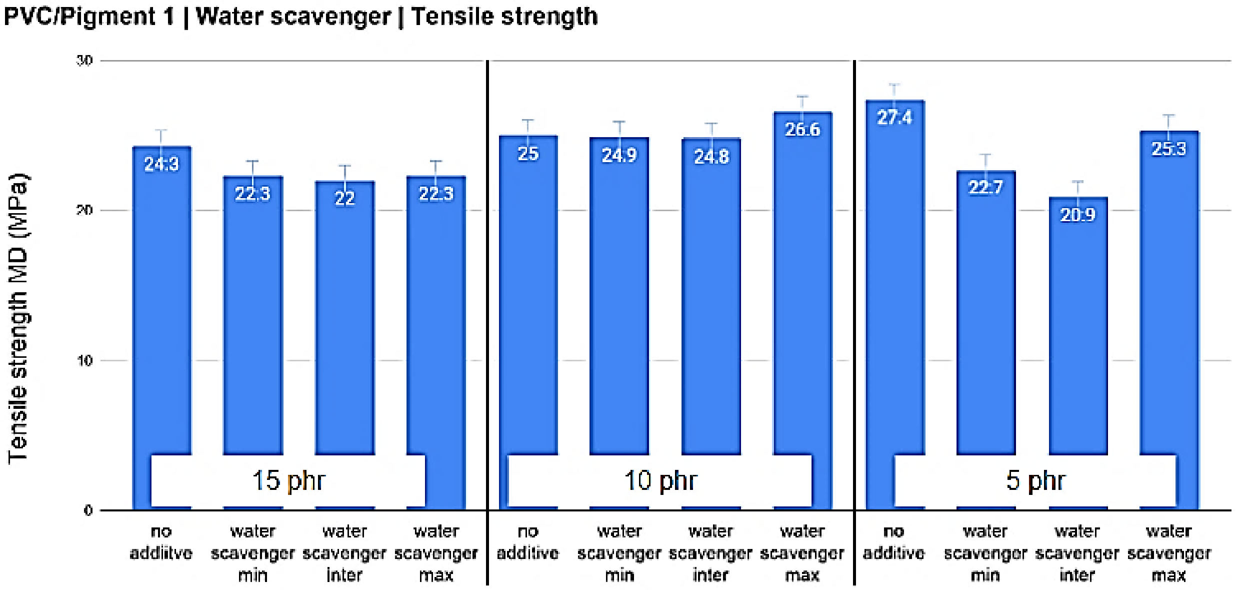


Fig.4.22. Tensile strength results for the three loadings of PVC/pigment 1 films before and after the addition of the three loadings of water scavenger.

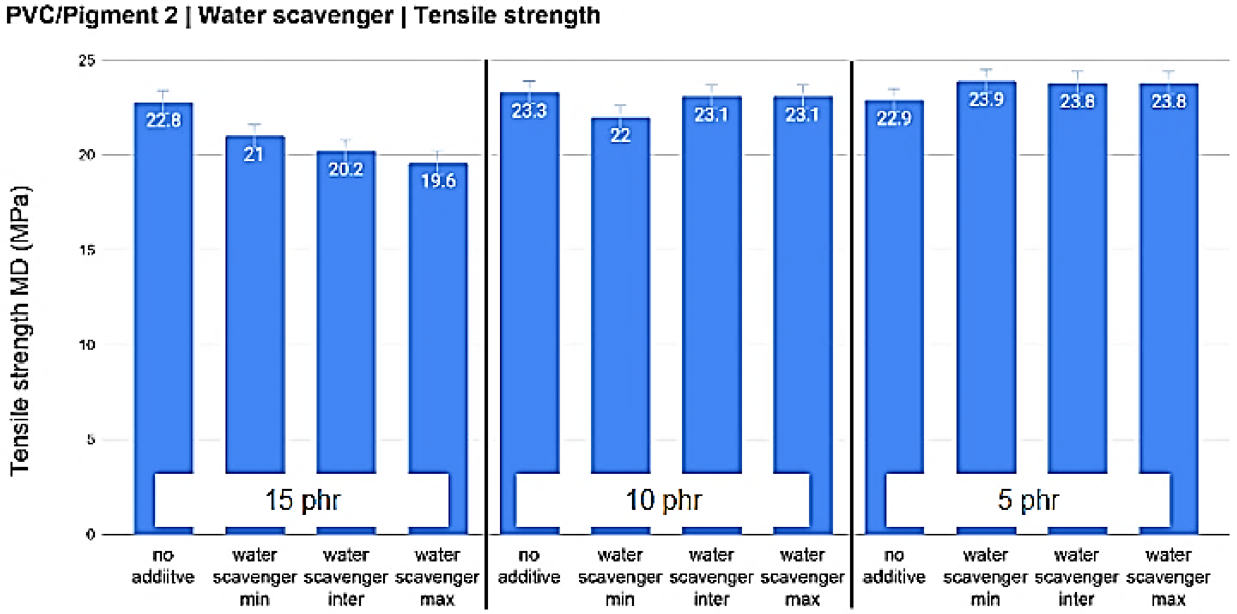


Fig.4.23. Tensile strength results for the three loadings of PVC/pigment 2 films before and after the addition of the three loadings of water scavenger.

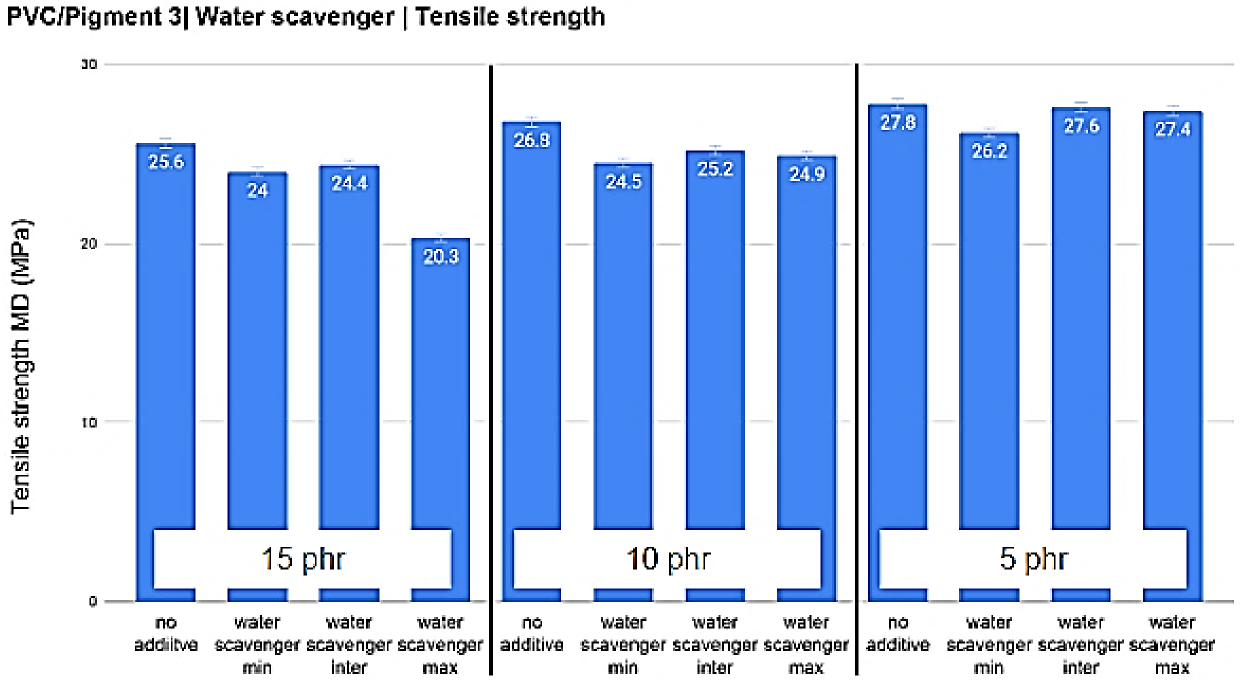


Fig.4.24. Tensile strength results for the three loadings of PVC/pigment 3 films before and after the addition of the three loadings of water scavenger.

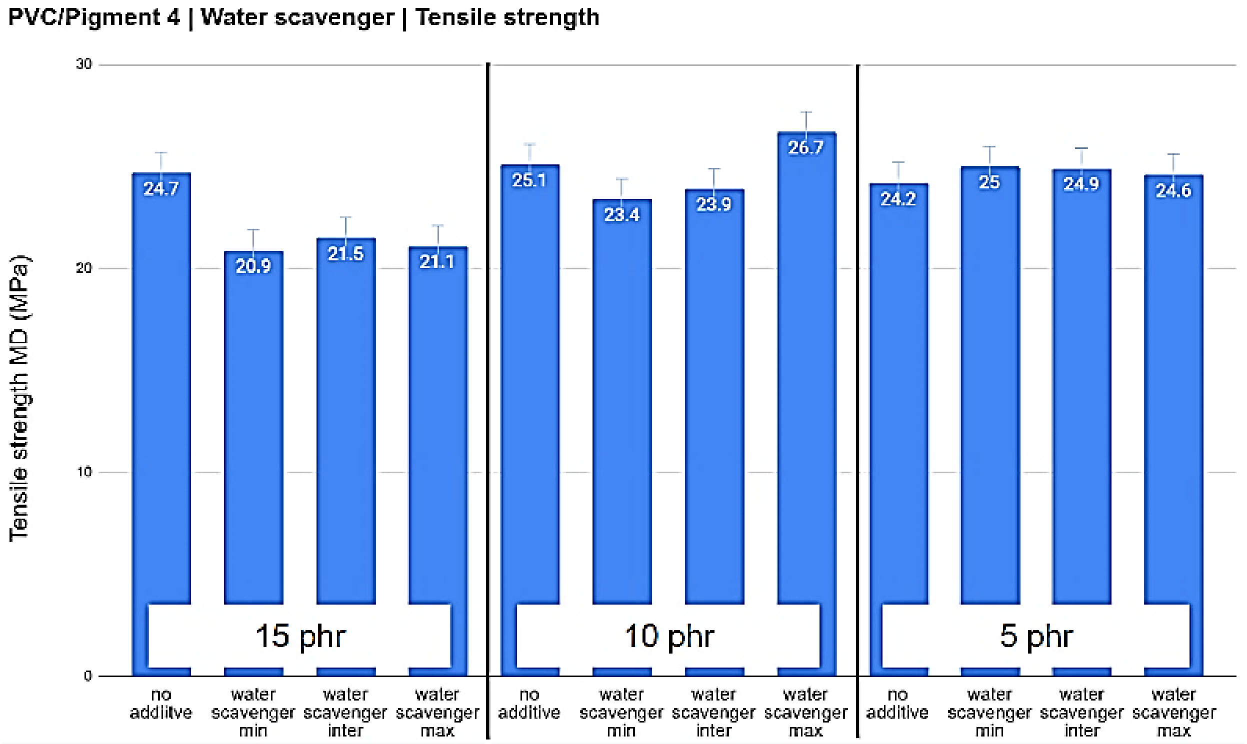


Fig.4.25. Tensile strength results for the three loadings of PVC/pigment 4 films before and after the addition of the three loadings of water scavenger

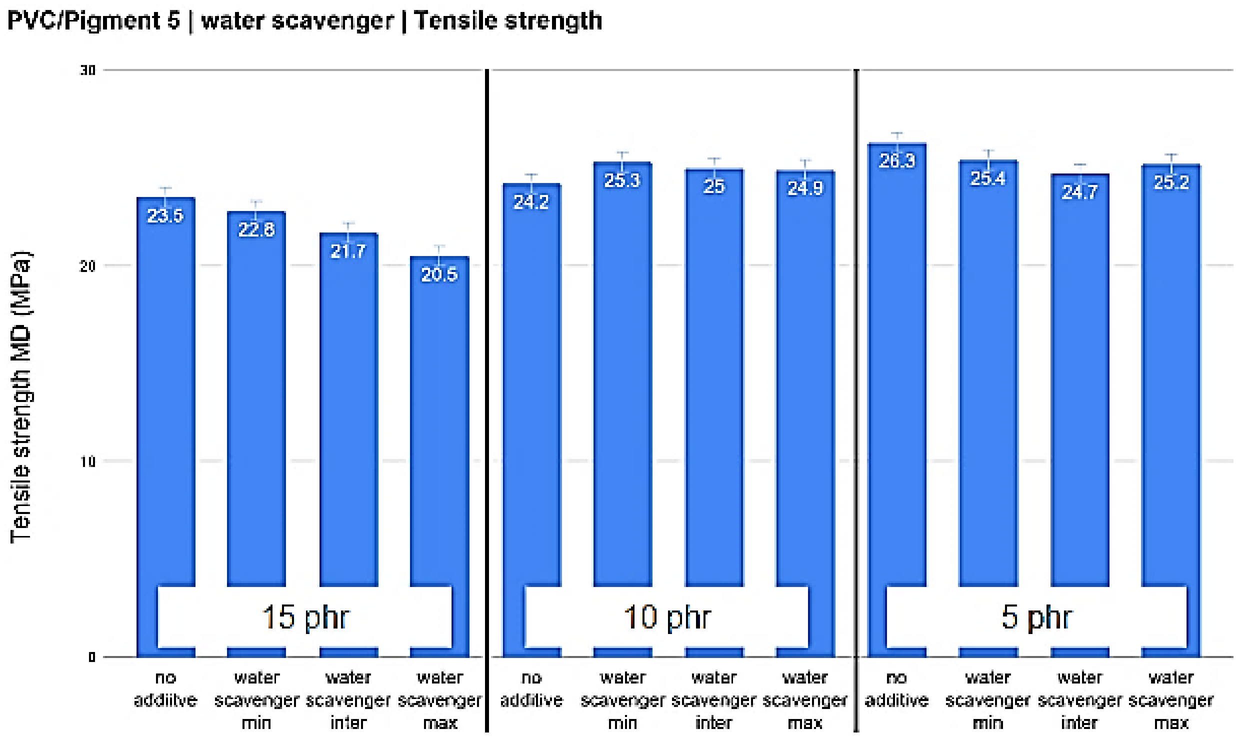


Fig.4.26. Tensile strength results for the three loadings of PVC/pigment 5 films before and after the addition of the three loadings of water scavenger.

A general conclusion is that for the 15 phr loading films, the tensile strength is reduced as the water scavenger loading is increased. The 15 phr loading of pigments is the highest loading examined which means that the number of the filler material particles (flakes/spherical particles) is high and CaO particles of the water scavenger are added as well. The addition of these two to the clear PVC films increases the possibility of the presence of defects inside the film. It should also be mentioned that for all pigments the addition of the water scavenger causes a small increase of the Young’s modulus which reflects the films smaller elastic strain and that is expected due to the presence of additional filler material.

4.2.4 Contact angle (CA) measurements

The contact angle results from the films with each one of the five pigments and the three different water scavenger loadings were analysed in order to check wettability of the films surface before and after the use of the water scavenger are shown in figures 4.27-4.31. The data referred to unaged films and films after 500 h of weathering for the original films and the 15 phr loading of pigment inside the films with minimum and intermediate amount of water scavenger since these are the films with the best weathering performance and optical appearance. For each film formulation two samples were tested and the error bars of the graphs represent the standard deviation of the CA results received from the two samples tested.

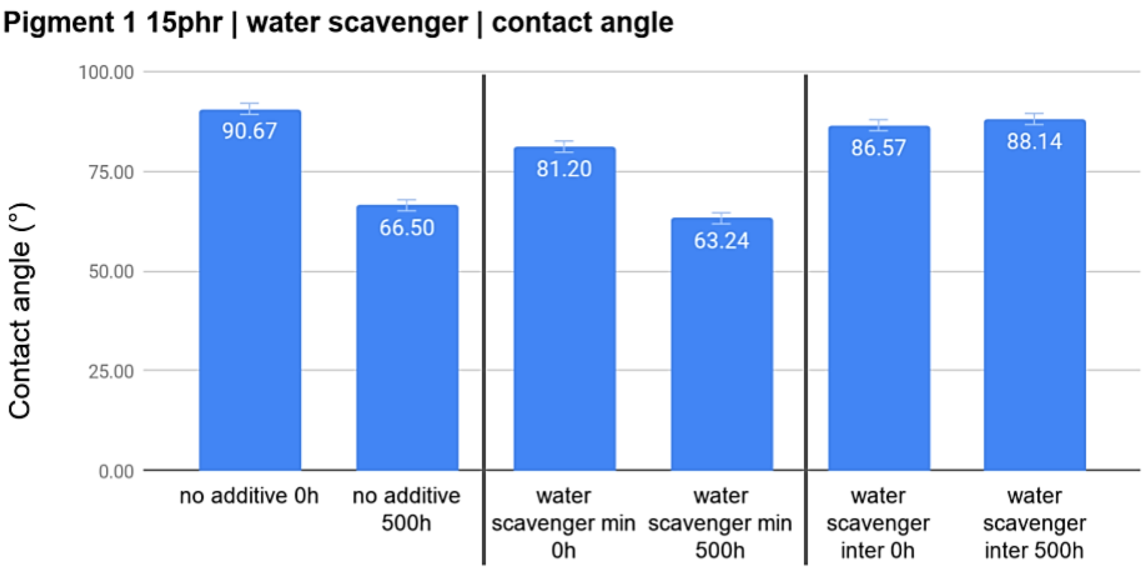


Fig.4.27. Contact angle measurements for the PVC/pigment 1 original formulation and after the use of the minimum and intermediate amount of water scavenger.

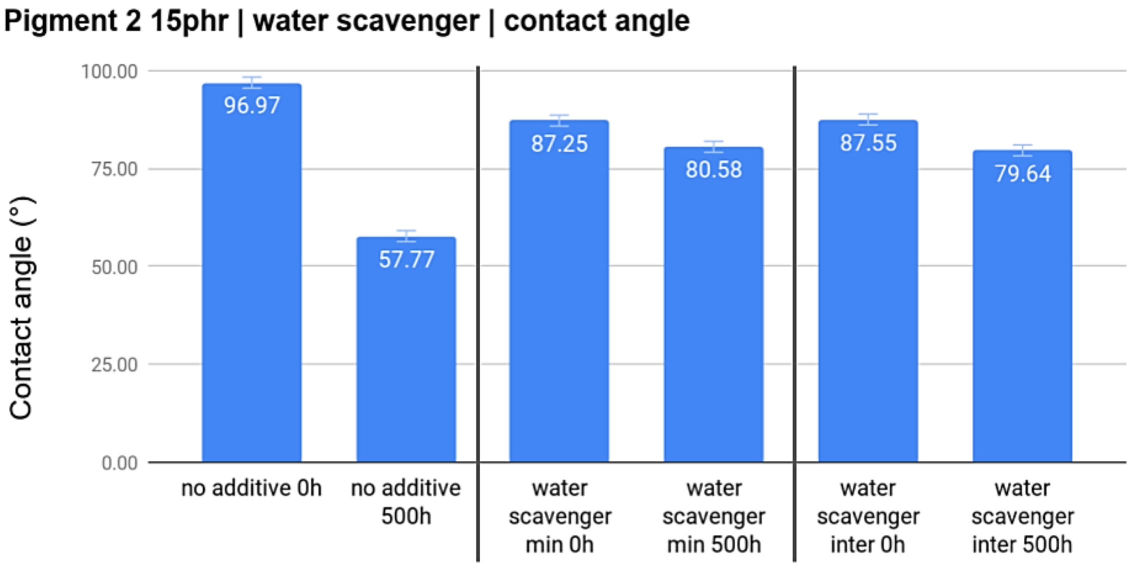


Fig.4.28. Contact angle measurements for the PVC/pigment 2 original formulation and after the use of the minimum and intermediate amount of water scavenger.

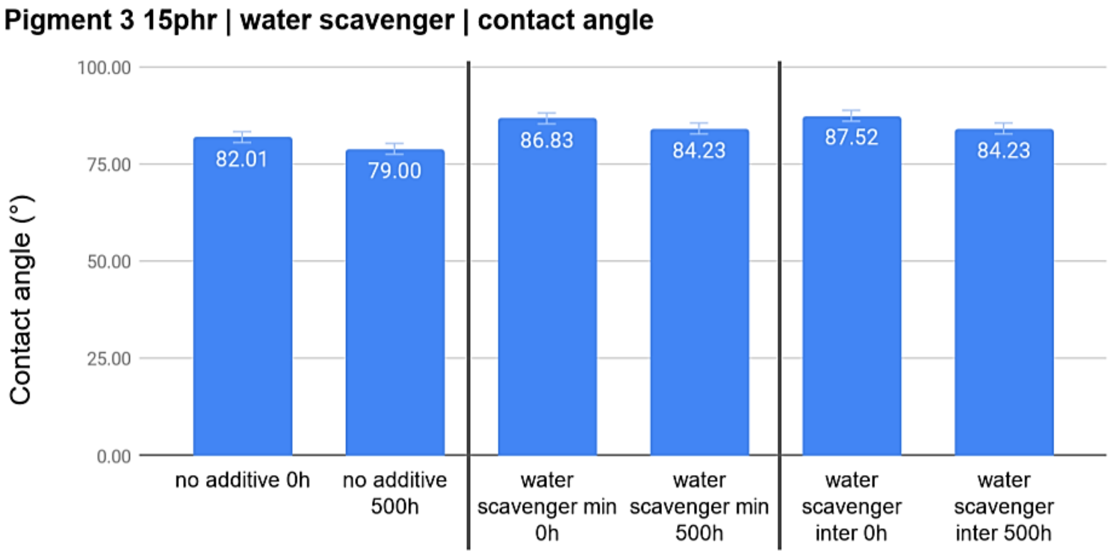


Fig.4.29. Contact angle measurements for the PVC/pigment 3 original formulation and after the use of the minimum and intermediate amount of water scavenger.

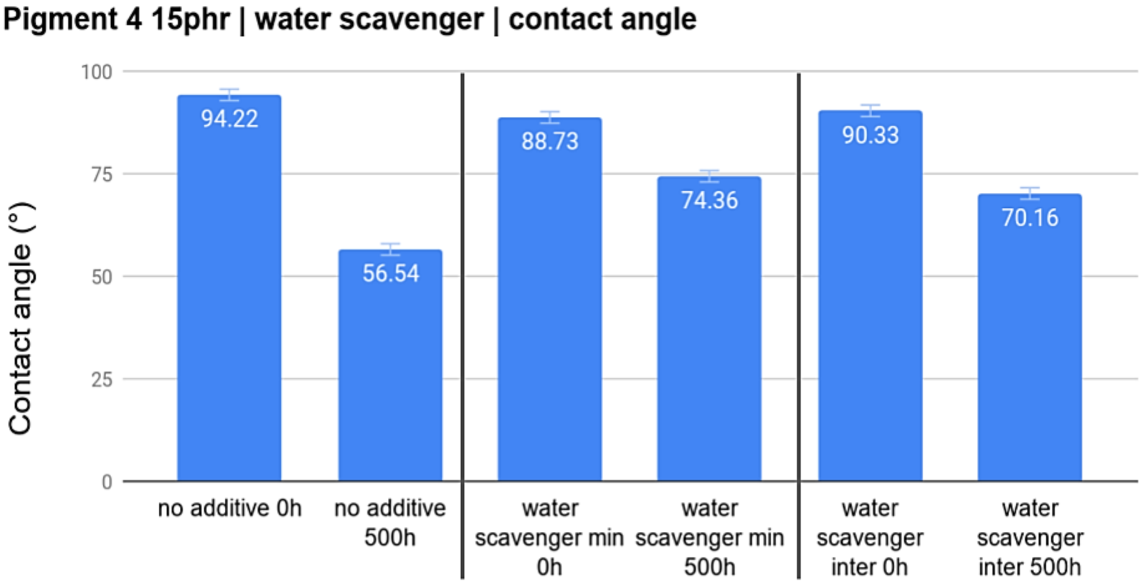


Fig.4.30. Contact angle measurements for the PVC/pigment 4 original formulation and after the use of the minimum and intermediate amount of water scavenger.

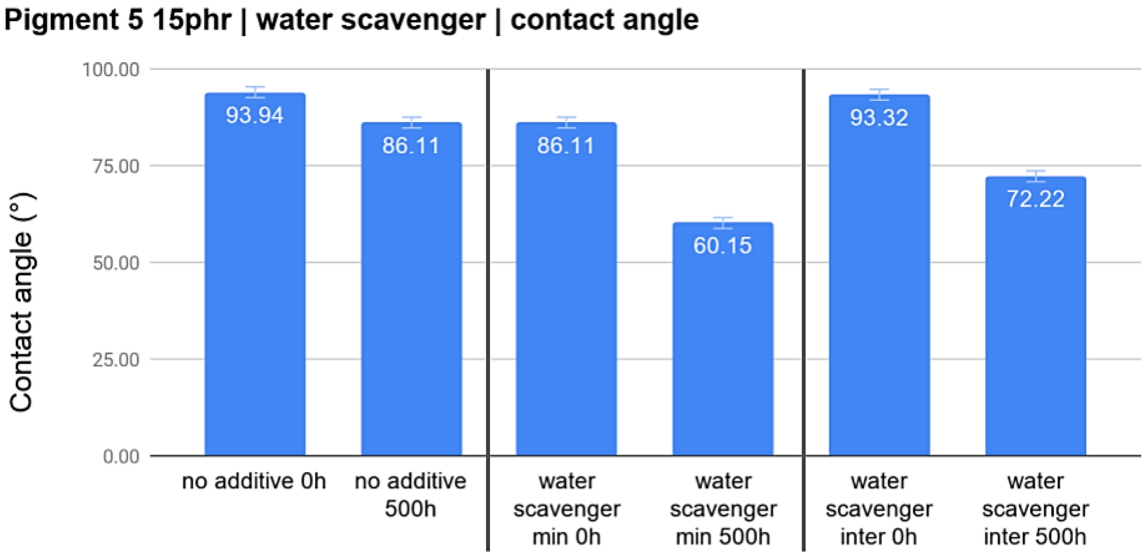


Fig.4.31. Contact angle measurements for the PVC/pigment 5 original formulation and after the use of the minimum and intermediate amount of water scavenger.

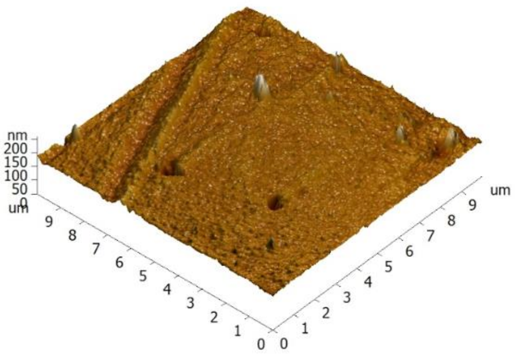
From the figures 4.27-4.31, it is clear that as there is a direct relation between the amount of water scavenger and the values of the contact angle. Such behavior was expected after the improved weathering results for the films with the three pigments (the contact angle increases as the water scavenger amount increases).

Apart from the films with pigment 3, the use of the water scavenger causes a small reduction of the contact angle at the initial stage before degradation (0 h) due to the increased surface roughness because of the wetting agent of the additive (this will be confirmed with the AFM analysis); and after 500 h, the films with the minimum and the intermediate amount of water scavenger have the same or higher contact angle than the original film after the same level of exposure with an exception for the films with pigment 5. This confirms the weathering results of the pigmented PVC films that show a better weathering performance after the use of the water scavenger since the increase of the contact angle means less wettability for the films with the additive. This is the most durable pigment among all five and it is the only one with this kind of behavior and it is not really clear where this comes from.

4.2.5 Atomic Force Microscopy (AFM) results

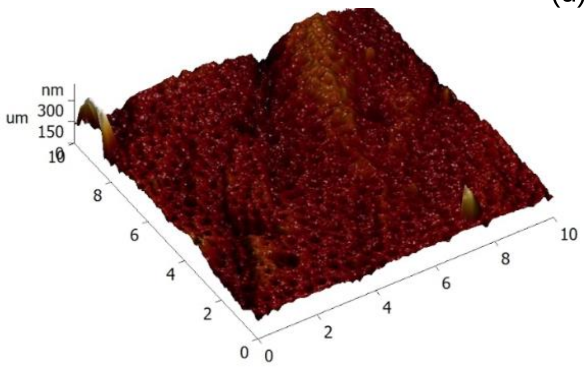
The AFM images for the films with the five pigments and the minimum water scavenger loading are shown in the following figures. The measurements were made in order to check the surface morphology of the films before and after the use of the water scavenger. The data refer to unaged films (0 h) and films after 500 and 1000 h of artificial weathering. The films examined are the PVC films with 15 phr pigment loading in the original formulation and the respective films with the minimum amount of water scavenger since these are the films with the best weathering performance and less gloss reduction.

(a)



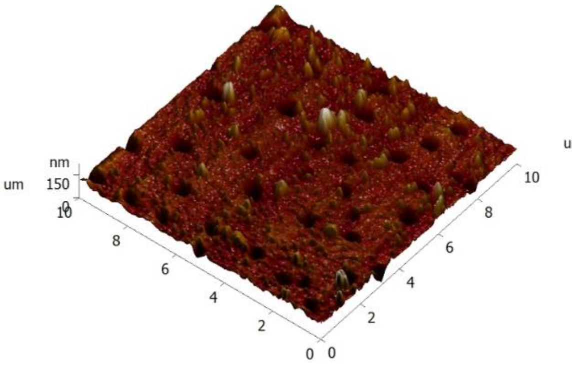
0 hours

(d)



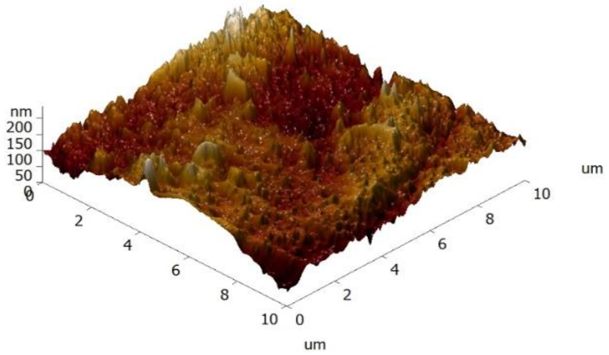
0 hours

(b)

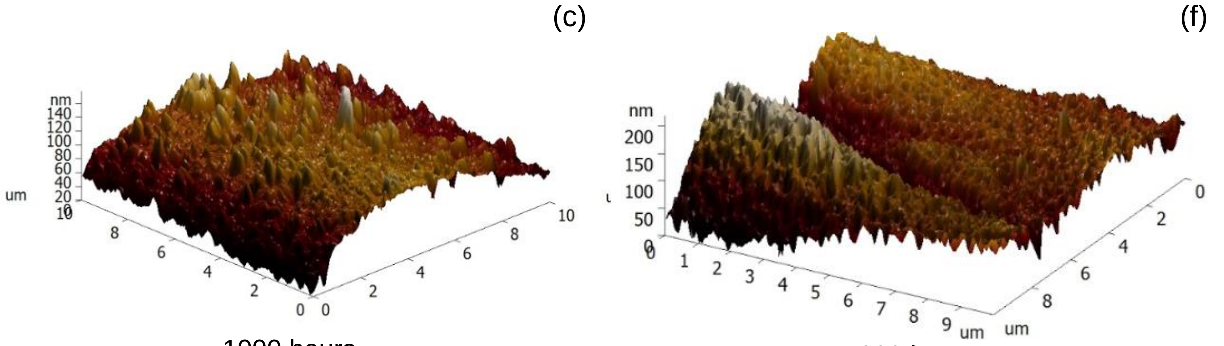


500 hours

(e)



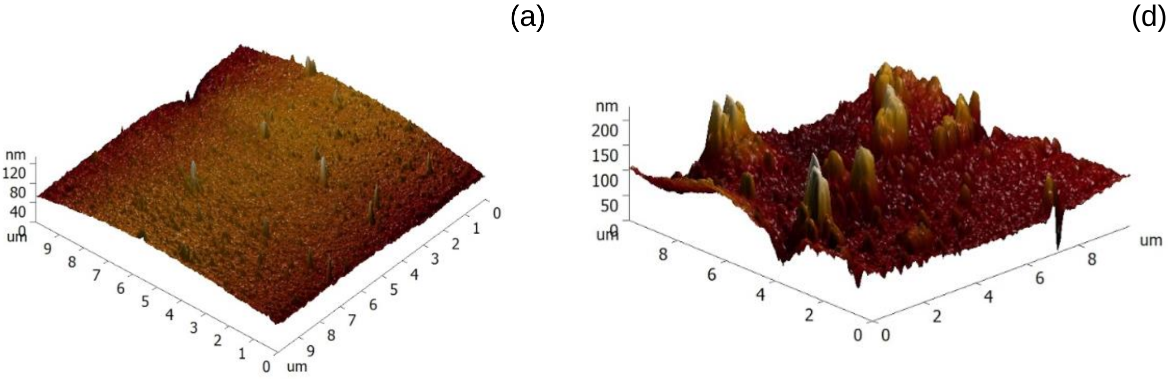
500 hours



1000 hours

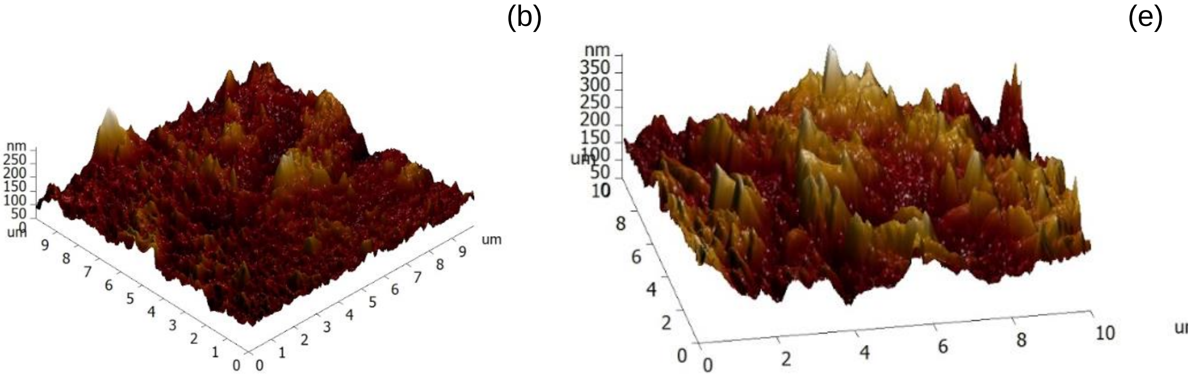
1000 hours

Fig.4.32. 3D AFM results for the PVC/pigment 1 films, (a), (b) and (c) are the results for the original formulation and (d), (e) and (f) for the films after the addition of the minimum amount of the water scavenger.



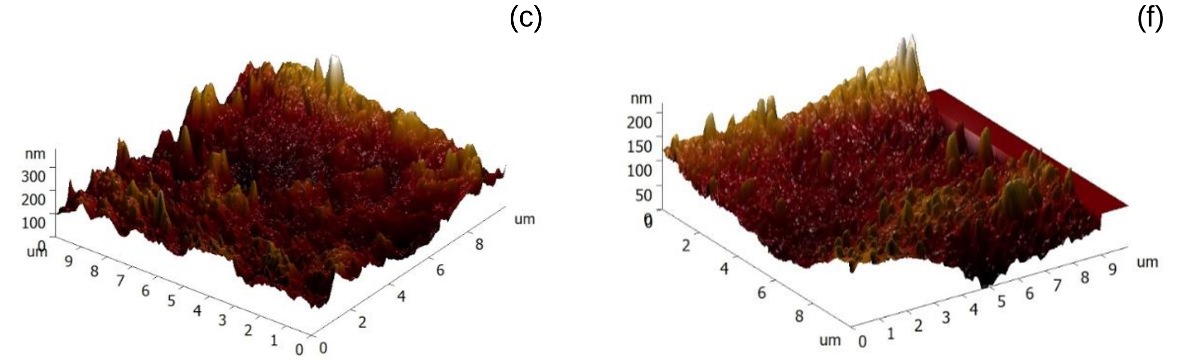
0 hours

0 hours



500 hours

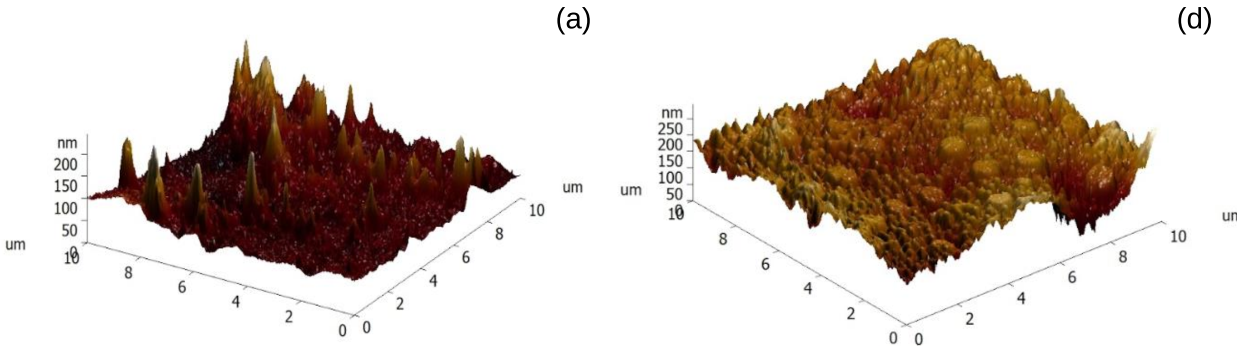
500 hours



1000 hours

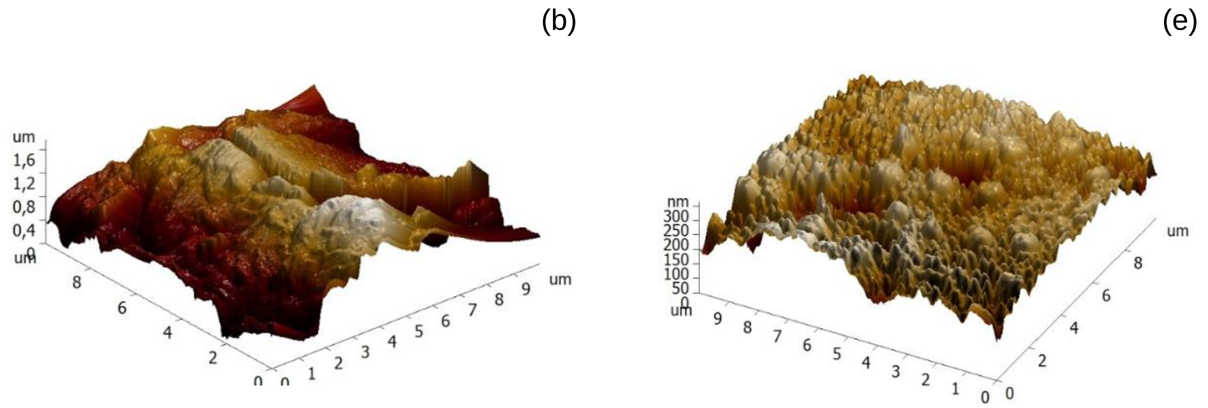
1000 hours

Fig.4.33. 3D AFM results for the PVC/pigment 2 films, (a), (b) and (c) are the results for the original formulation and (d), (e) and (f) for the films after the addition of the minimum amount of the water scavenger.



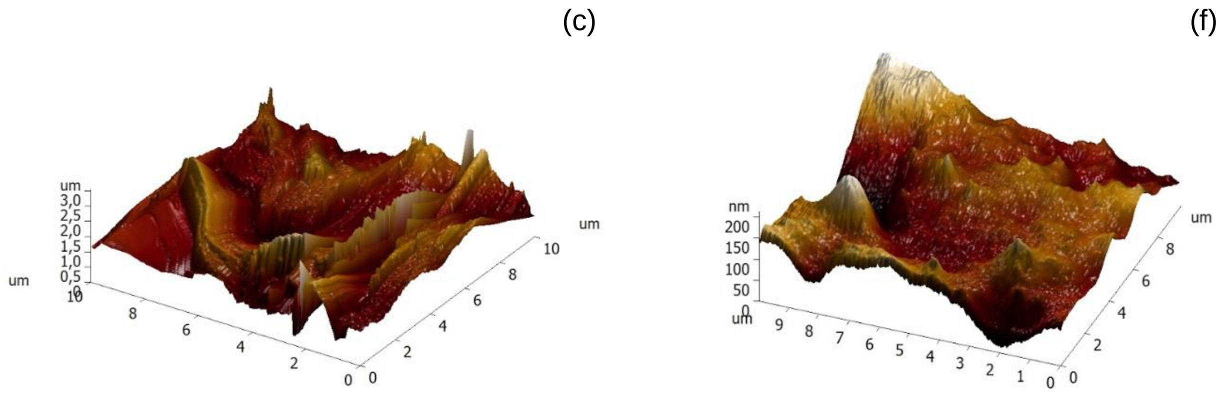
0 hours

0 hours



500 hours

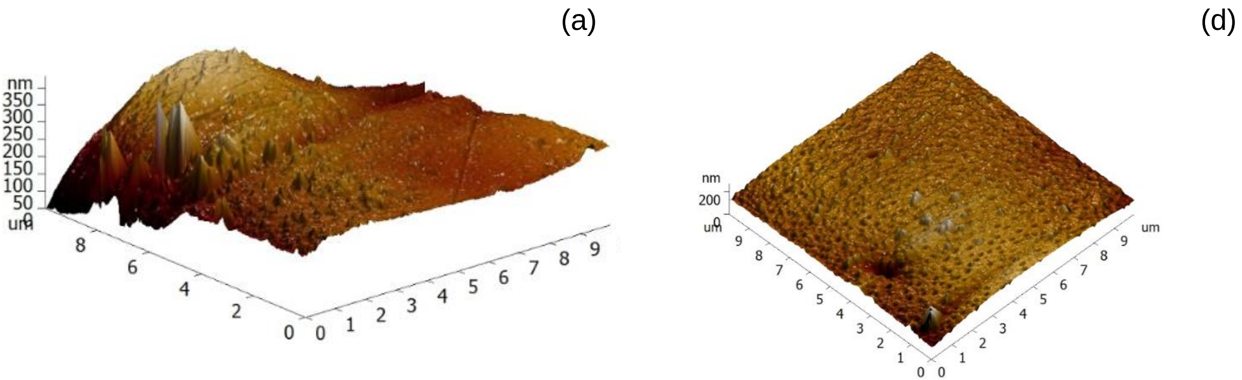
500 hours



1000 hours

1000 hours

Fig.4.34. 3D AFM results for the PVC/pigment 3 films, (a), (b) and (c) are the results for the original formulation and (d), (e) and (f) for the films after the addition of the minimum amount of the water scavenger.



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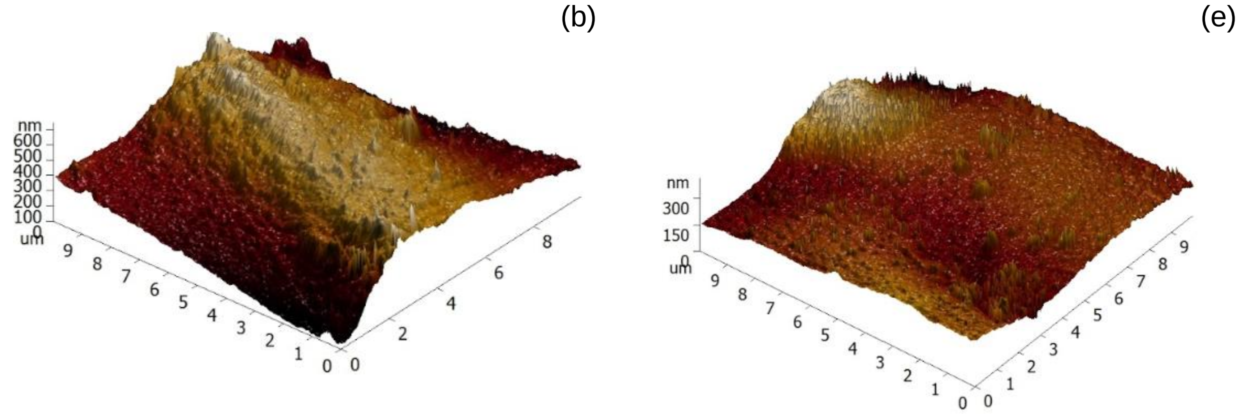
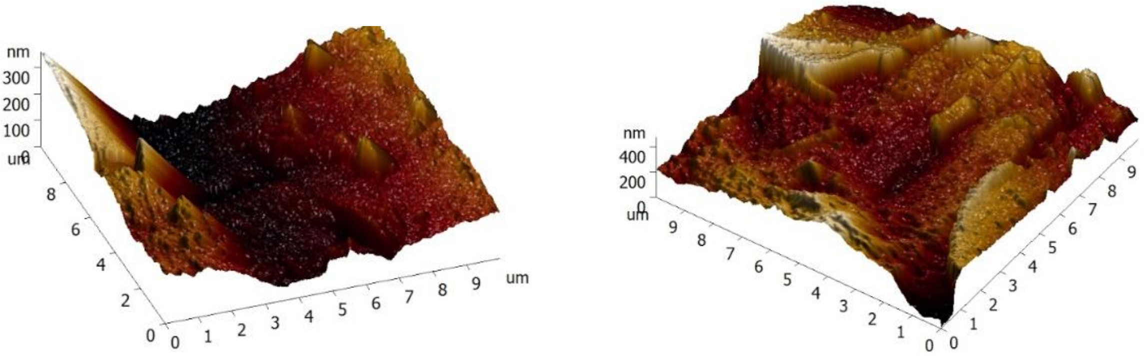


500 hours 500 hours

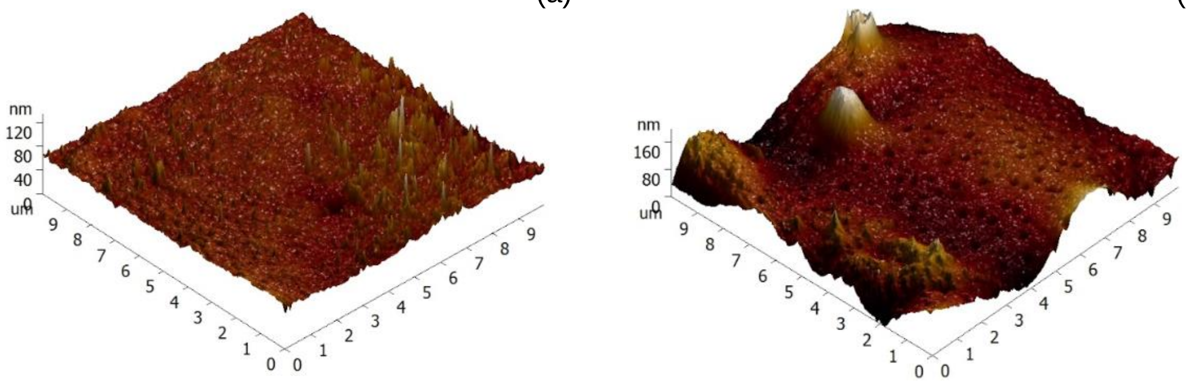
(c) (f)



1000 hours 1000 hours

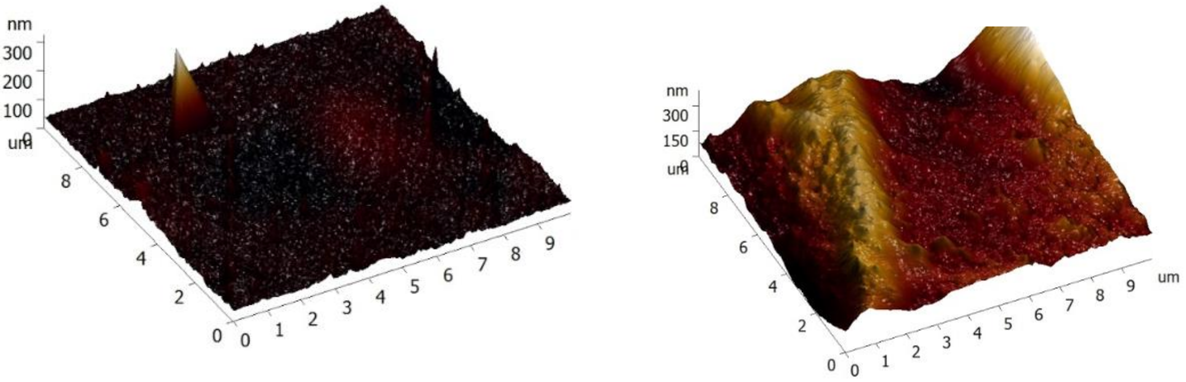
Fig.4.35. 3D AFM results for the PVC/pigment 4 films, (a), (b) and (c) are the results for the original formulation and (d), (e) and (f) for the films after the addition of the minimum amount of the water scavenger.

(a) (d)

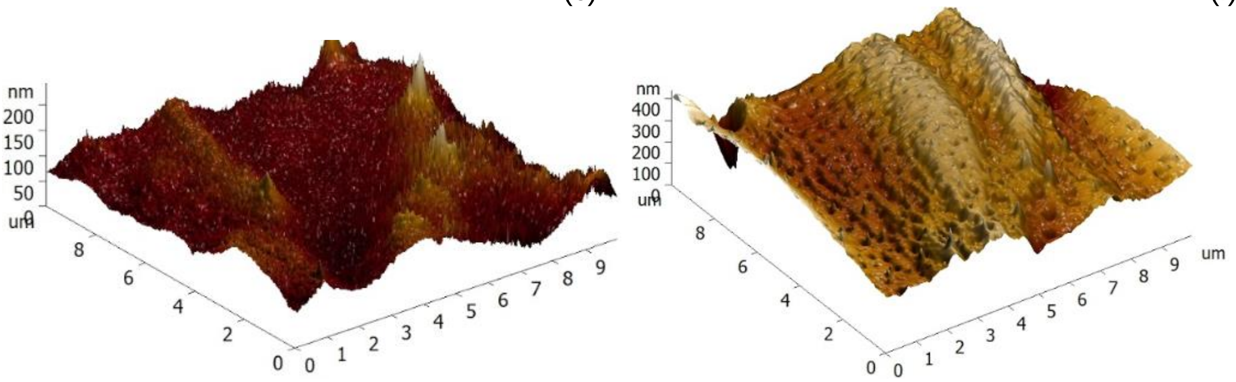


0 hours 0 hours

(b) (e)



500 hours 500 hours



(c) 1000 hours

(f) 1000 hours

Fig.4.36. 3D AFM results for the PVC/pigment 5 films, (a), (b) and (c) are the results for the original formulation and (d), (e) and (f) for the films after the addition of the minimum amount of the water scavenger.

Table 4.21. Roughness measurements for the pigmented PVC films before and after the addition of the minimum amount of the water scavenger.

Films	0 h	500 h	1000 h
PVC/pigment 1 films/ no additive	7.42 nm	15.4 nm	10.8 nm
PVC/pigment 1 films/ water scavenger min	18.8 nm	44.6 nm	18.7 nm
PVC/pigment 2 films/ no additive	3.53 nm	20.4 nm	10.11 nm
PVC/pigment 2 films/ water scavenger min	3.26 nm	31.75 nm	13.3 nm
PVC/pigment 3 films/ no additive	4.11 nm	13.5 nm	36 nm
PVC/pigment 3 films/ water scavenger min	18 nm	24.9 nm	23.5 nm
PVC/pigment 4 films/ no additive	2.7 nm	10.4 nm	57.49 nm
PVC/pigment 4 films/ water scavenger min	11.6 nm	30.9 nm	53.5 nm
PVC/pigment 5 films/ no additive	3.8 nm	4.67 nm	17.66 nm
PVC/pigment 5 films/ water scavenger min	17.5 nm	41.7 nm	36.4 nm

As can be seen from figures 4.32-4.36, the surface morphology of the pigmented PVC films after the addition of the minimum amount of water scavenger is changed and it seems like the additive migrates to the surface of the film. It can be seen that after the addition of the water scavenger there is an increase of the Z-axis values due to the rougher surface after the first stage of degradation but after the 1000 h stage these values decrease. This can be attributed to the mentioned hypothesis. In addition, the number of pores per 100 μm^2 is dramatically increased compared to the films of the original formulation. This increase can be the cause of the loss of gloss of the films with the water scavenger considering the roughness change presented in table 4.21.

The roughness was calculated on a surface (area) (Sa) profile. Sa expresses, as an absolute value, the difference in height of each point compared to the arithmetical mean of the surface. The roughness measurements of the films are in agreement with the appearance of the images in figures 4.32-4.36, according to which, the first stage of degradation (500 h) contains the critical information about the effect of the additive used. These results are in agreement with the early hypothesis from the gloss results that the additive migrates to the surface and then is washed off by the cyclic water spray.

It should be mentioned that for PVC/pigment 3 films (fig.4.34), the surface morphology was different than the films with other four pigments. In the AFM images of these films, circular shapes were observed on the surface which are usually signs of phase separation [42]. This can be an indication that the pigment was not actually a dry pigment but a dispersion and that was confirmed by the supplier. The pigment dispersant is phase separated with the wetting agent of the CaO and the result is the circular shapes on the films surface.

4.2.6 Scanning Electron Microscope (SEM) and X-ray fluorescence (XRF) results

The films (coated with gold sputtering) were analyzed with the Scanning Electron Microscope (SEM) before and after degradation. The SEM-EDS technique (BEC detector, x200 magnification) is used in order to check if the flakes/particles are protruding from the films surface and through the EDS analysis, the elemental composition of specific spots on the surface (flakes) was analyzed. The results are accompanied by the XRF analysis results.

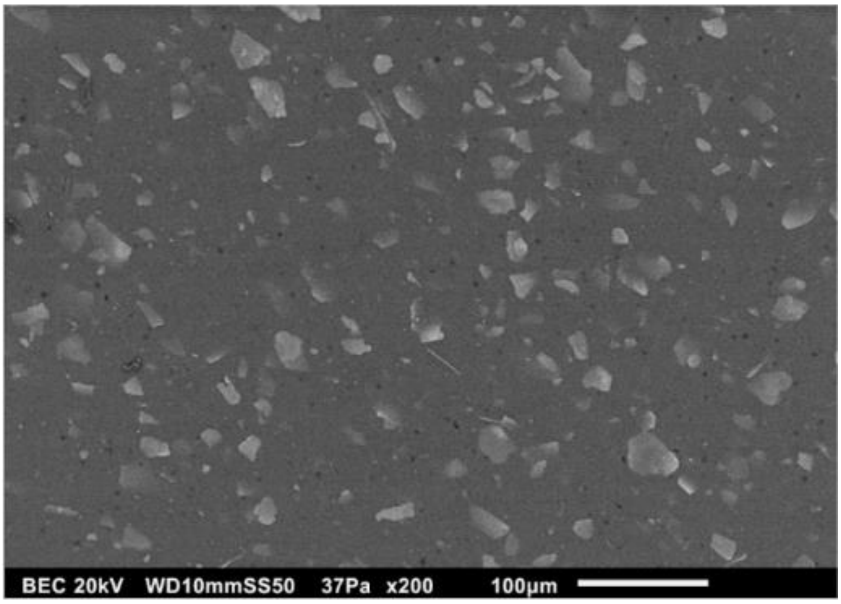


Fig.4.37. SEM analysis for the PVC/pigment 1 films (x200).

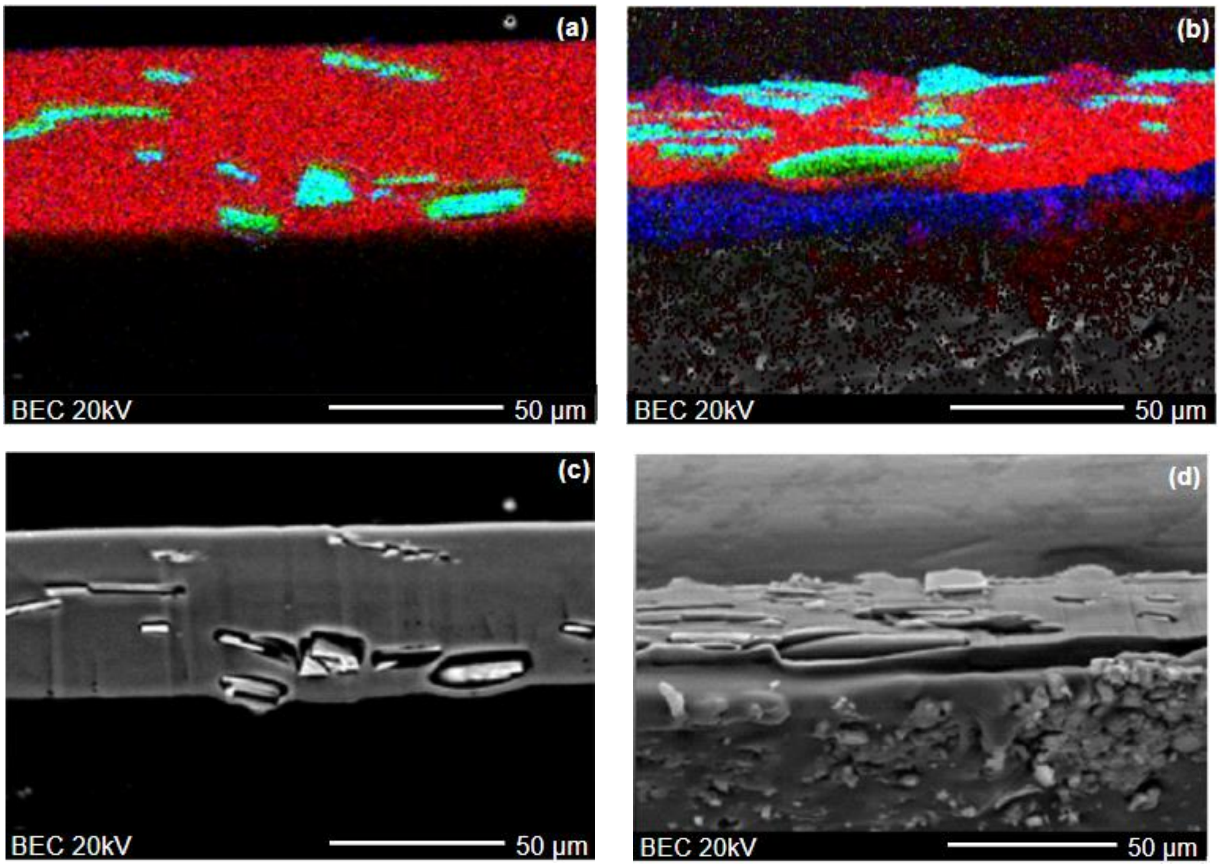


Fig.4.38. SEM-EDS analysis for the PVC/pigment 1 films cross-section, non-degraded film (a, elements map) (c, SEM image), degraded film at 2500 h (b, elements map) (d, SEM image), chloride (red), silicon (green) and oxygen (blue).

It can be seen from figure 4.38 that before degradation (fig.4.38 a and c), the flakes of the borosilicate glass-based pigment (green and turquoise parts in fig.4.38-a) are protruding from the edge of the film. After degradation (fig.4.38 b and d), they are protruding from the edge and the surface of the film. Also the film is thinner which is expected since as the degradation proceeds there is a loss of PVC and plasticizer [10].

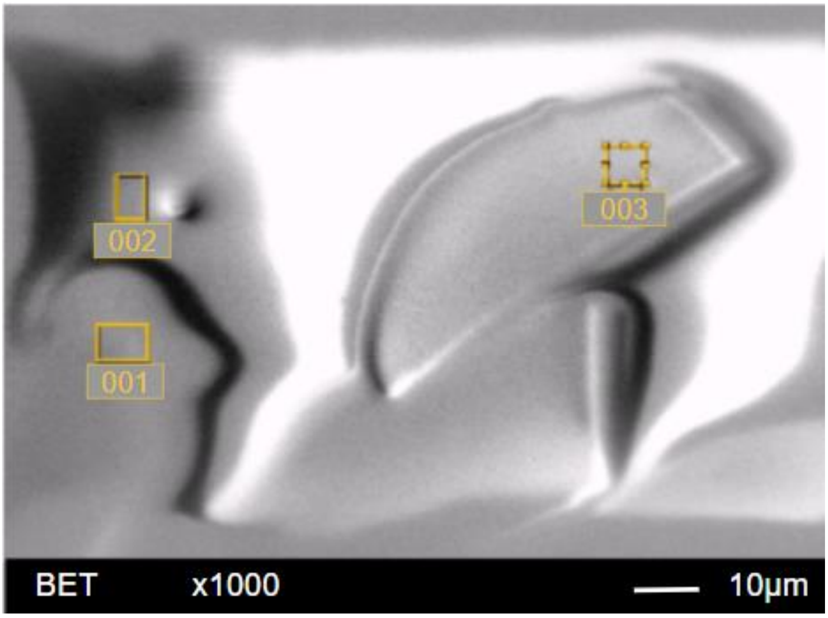


Fig.4.39. SEM-EDS (BET) for the PVC/pigment 2 films.

Table.4.22 EDS results for the PVC/pigment 2 films.

Spot	Fe	O	C	Mg	Al	Si	Cl	Ca	Ti
001	3.16	10.16	66.07	0.23	0.82	4.18	13.49	1.89	-
002	-	10.33	75.74	-	-	-	13.93	-	-
003	4.85	19.09	51.14	0.70	2.61	12.61	1.98	6.54	0.48

The BET (Brunauer, Emmett and Teller) topography image (fig.4.39) shows that the flake and PVC show a difference in morphology. EDS is performed to see if PVC is on top of the flake (point 003 in figure 4.39). In fact, this is the case, but less PVC is noticed covering the flake compared to a spot where a flake is deeper in the PVC film (point 001 in figure 4.39). The flakes that stand out on the surface if damaged, due to the thin PVC layer covering them, they can potentially be the trigger points for degradation. The PVC layer starts getting thinner as its degradation continues and eventually the flakes will be exposed to weathering conditions (UV radiation and water).

Table 4.23. EDS results for the PVC/pigment 1 films.

EDS	Al	Si	Cl	Ca	Ti	Fe
PVC/Pigment 1 no additive	8.16	3.14	15.94	-	-	12.85
PVC/Pigment 1 water scavenger min	3.66	2.54	18.75	1.28	3.1	-

Table 4.24. XRF results for the PVC/pigment 1 films.

XRF (ppm)	Al	Si	Cl	Ca	Ti	Fe
PVC/Pigment 1 no additive	16700	14400	325000	1040	3600	3450
PVC/Pigment 1 water scavenger min	17500	14600	329000	7150	4610	3220

It can be said that from tables 4.23 and 4.24 there is an agreement on the elements present inside the bulk (XRF analysis) of the films and in the areas close to the surface (SEM-EDS analysis). Ca is present close to the surface after the addition of the water scavenger and that is expected since the water scavenger is a CaO based additive. The Ca fingerprint in the bulk of the film is also affected by the addition of the water scavenger and in fact it went from 1040 ppm to 7150 ppm. Cl is present due to PVC, O due to the pigment surface treatment and the water scavenger and Ti due to the surface treatment of the flakes.

The same analysis was carried out with similar results for the rest of the pigmented films and the overall conclusion is that the flakes/particles close to the surface of the films are partly covered with PVC and other parts are protruding from the surface and damage to their surface treatment can expose them to the weathering elements.

4.2.7 Fourier-Transform Infrared Spectroscopy (FTIR) results

As mentioned in chapter 3 of this thesis, vibrational spectroscopic methods are widely used in the analysis of polymers. In the present work, FTIR was used to analyze the selected pigmented PVC films before and after each stage of degradation for the 15 phr pigment loading.

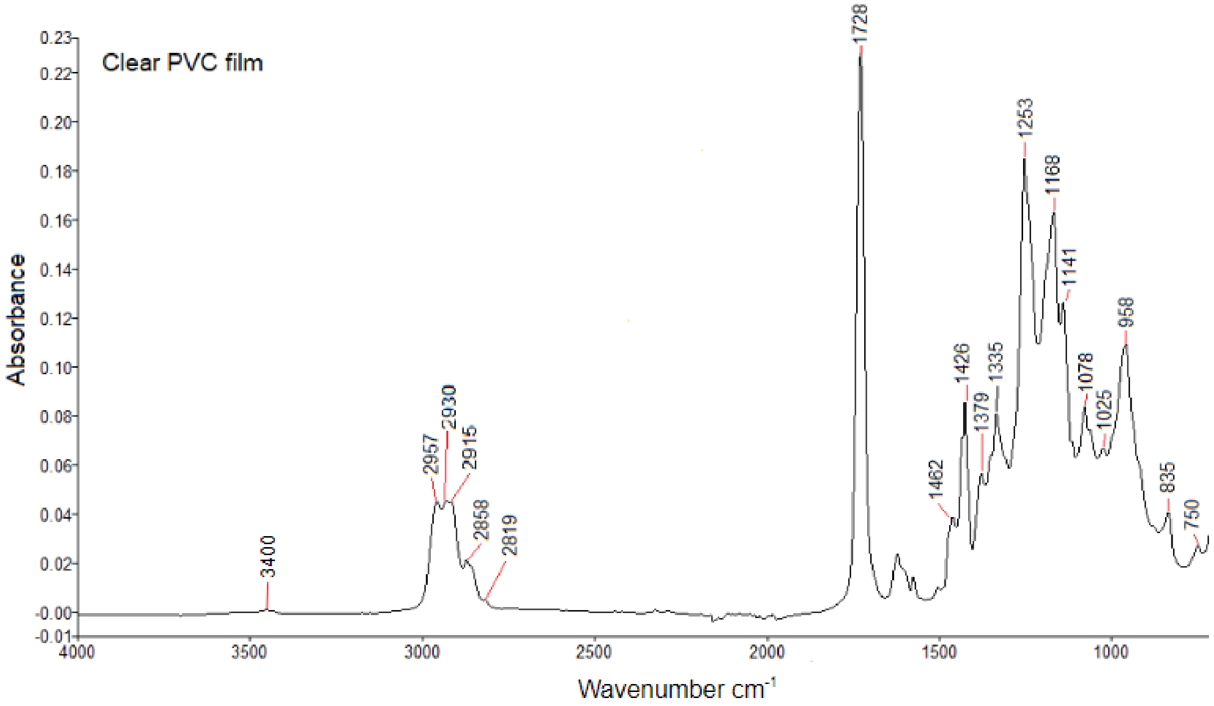


Fig.4.40. FTIR spectrum of unaged clear PVC film.

The peaks of the clear PVC film (fig.4.40) belong to the polymer, the plasticizer and the residual solvent. The assignment of the characteristic peaks are shown in table 4.25.

Table 4.25. Assignment of characteristic peaks in FTIR spectrum of the clear PVC film.

Peak/ cm^{-1}	**Assignment**		**Ref.**
3400	PVC	O-H stretching	[43]
2957	Plasticizer	γ CH_2	[43]
2930	Plasticizer	γ CH_3, CH_2 and CH, 2 or 3 bands	[44]
2915	PVC	γ CH_2	[43]
2858	PVC	γ CH_2	[43]
2819	PVC	γ CH	[43]
1728	Plasticizer	γ C=O carbonyl groups	[45]
1462	Plasticizer	Asymmetric aliphatic C-H deformation - methylene CH_2	[44]
1426	PVC	δ CH_2 crystalline	[43]
1379	Plasticizer & Solvent	CH_3 deformation, bending	[46]
1335	PVC	τ CH	[43]
1253	PVC	δ H-C-Cl	[43]
1168	Plasticizer	sulfonyl chloride stretching	[47]
1141	Plasticizer	stretching of sulfone	[47]
1078	Plasticizer	S=O sulfoxide stretching	[47]
1025	Plasticizer	S=O sulfoxide stretching	[47]
958	PVC	ρ CH	[43]
835	PVC	chain stretching	[43]
750	Plasticizer	=C-H bending	[46]

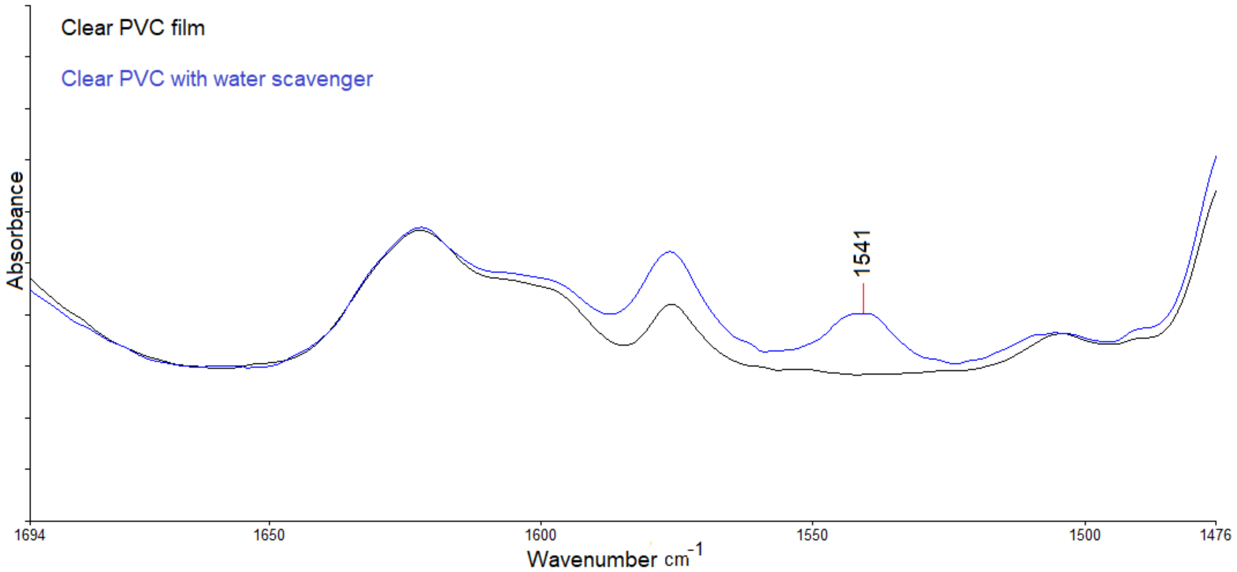


Fig.4.41. FTIR spectra between 1475 and 1694 cm^{-1} for the clear PVC film before (black) and after the addition of the minimum amount of water scavenger (blue).

After the addition of the water scavenger an additional peak (1541 cm^{-1}) was observed in the clear PVC film spectrum as can be seen in figure 4.41. The two spectra from figure 4.41 were normalized at the PVC reference peak at 1335 cm^{-1} [43].

The additional peak at 1541 cm^{-1} can be assigned to the CaO-based water scavenger and more specifically this peak is characteristic of antisymmetric stretching vibration of Ca-O which can be a product after the addition of the additive to the original formulation [48].

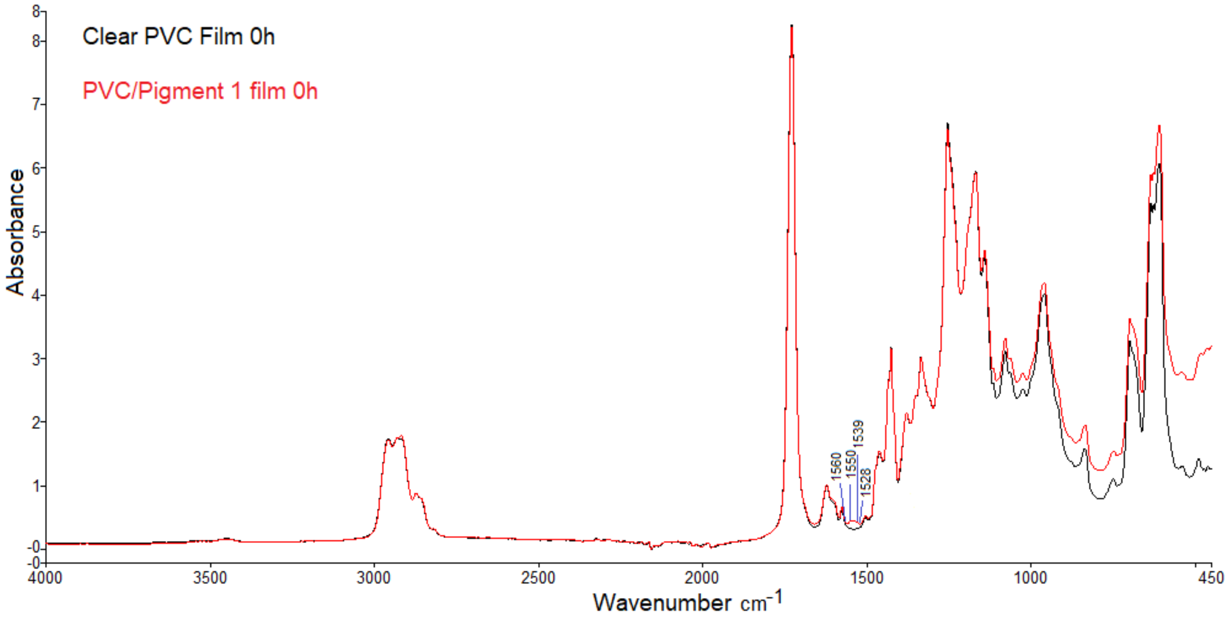


Fig.4.42. FTIR spectrum of unaged clear PVC film (black) and unaged PVC/pigment 1 film (red).

After the addition of pigment 1 (fig.4.42) inside the original formulation four additional peaks were observed (1528, 1539, 1550 and 1560 cm^{-1}). These vibrations can be assigned to the stretching of bonds of TiO_2 which is a component of the Pigment 1 surface treatment [48].

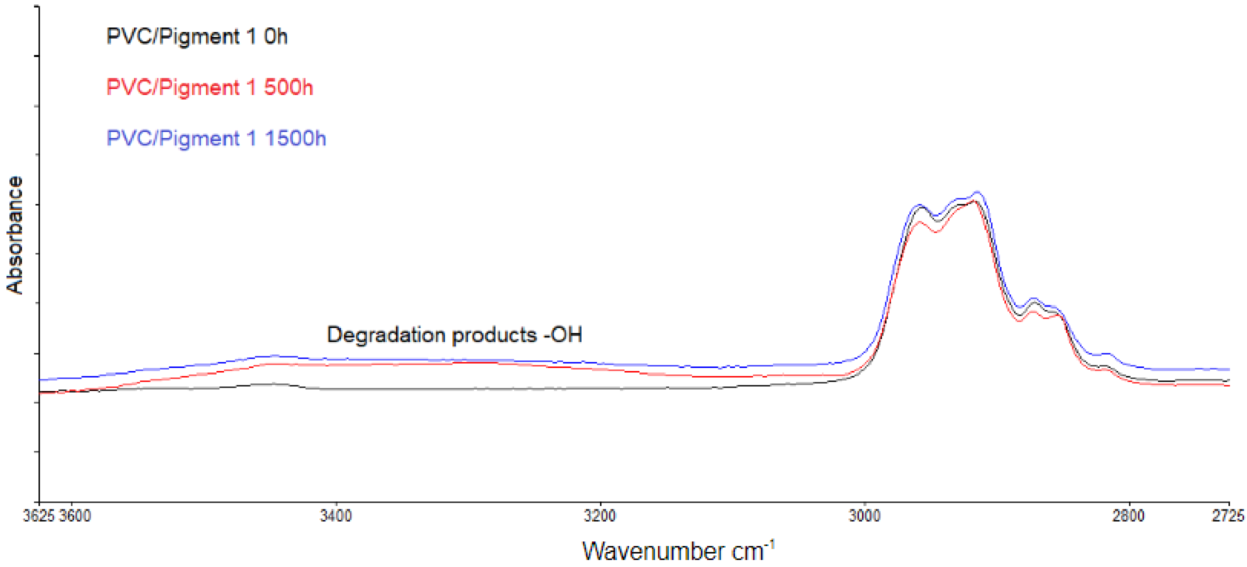


Fig.4.43. FTIR spectra between 2725 and 3625 cm^{-1} for the PVC/pigment 1 film before (black) and after 500 h (red) and 1500 h (blue) of degradation.

Figure 4.43 shows the behavior of the PVC/pigment 1 after 500 h and 1500 h of degradation. The most evident signs of degradation is the broad bands between 3200 - 3500 cm^{-1} characteristics of O-H stretching. Indeed, during the photo-oxidative degradation, the hydrogen abstraction from the polymer backbone can lead to the formation of alkyl radicals [49]; the reaction of these radicals with molecular oxygen, leads to peroxy radicals. Hydroperoxides are then formed and can be detected by the absorption range between 3200 - 3500 cm^{-1} [49].

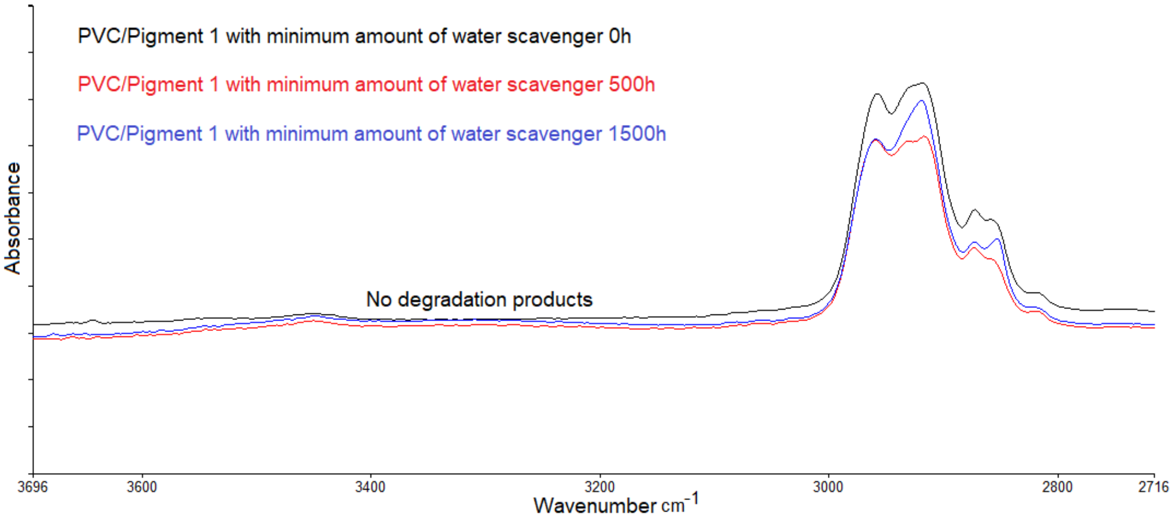


Fig.4.44. FTIR spectra between 2716 and 3696 cm^{-1} for the PVC/pigment 1 film with the minimum amount of the water scavenger before (black) and after the addition of the minimum amount of water scavenger at 500 h (red) and 1500 h (blue).

The PVC/pigment 1 films spectra are different after degradation because of the dechlorination processes leading to the formation of the conjugated polyene chains. However, the analysis has been carried out directly on the surface of the specimen, getting information just on the first few microns of the films. For the films with pigment 1 (fig.4.43) degradation products (hydroperoxides) are observed between 3000 and 3500 cm^{-1}. These degradation products are missing after the addition of the water scavenger as can be seen from figure 4.44. Apart from the missing degradation products from figure 4.44, the intensity of the plasticizer and PVC peaks between 2800 and 3000 cm^{-1} is smaller and this can be attributed to the fact that the information received is from the outer surface of the films (a few microns) on which the water scavenger migrates.

The degradation results for the PVC/pigment 2 films are expected taking under consideration the weathering results which were previously shown in paragraph 4.2.1. The degradation products (hydroperoxides) are present between 3000 and 3600 cm^{-1} accompanied with a decrease in the plasticizer amount since the peak assigned to the plasticizer (1728 cm^{-1}, carbonyl group) is broader and reduced. The same applies for the peaks between 2716 and 3696 cm^{-1}. This can be attributed to the fact that the plasticizer tends to migrate to the surface and get washed off eventually by the cyclic water spray as presented in figure 4.45.

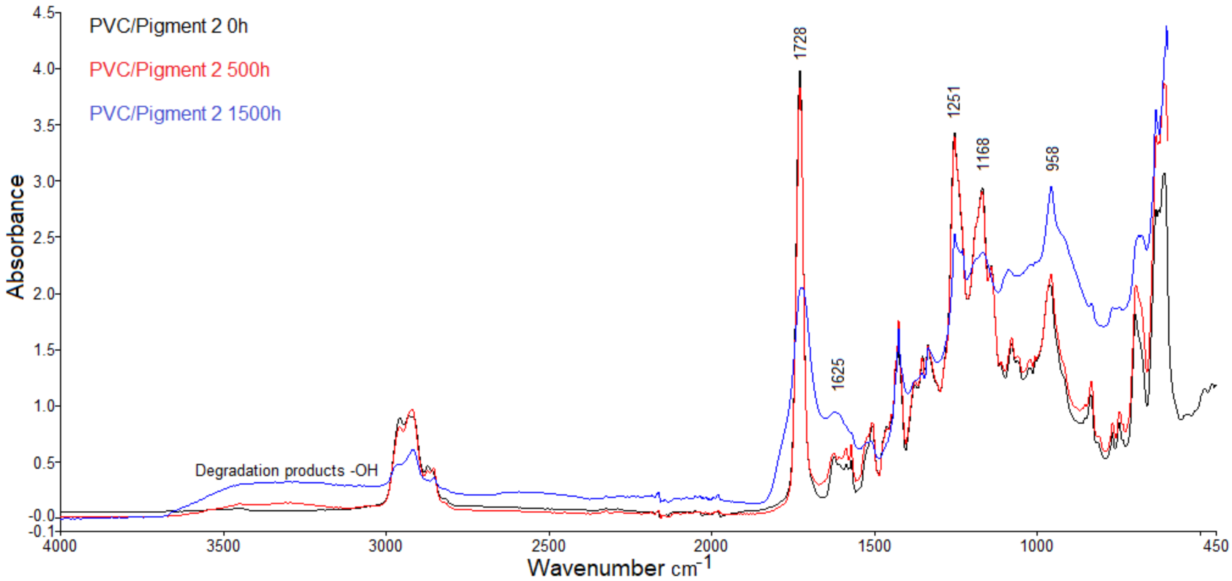


Fig.4.45. FTIR spectra between for the PVC/pigment 2 film before (black) and after 500 h (red) and 1500 h (blue) of degradation.

In figure 4.45, the breakdown of C-H bonds in the aged films resulted in a reduction of intensity of peak at 1251 cm^{-1}. The broad band centered at 1625 cm^{-1} is the result of the formation of polyene chains in the backbone of PVC. The intensity peak at 958 cm^{-1} is increased due to the formation of C-H bonds instead of C-Cl after the dehydrochlorination process during PVC degradation.

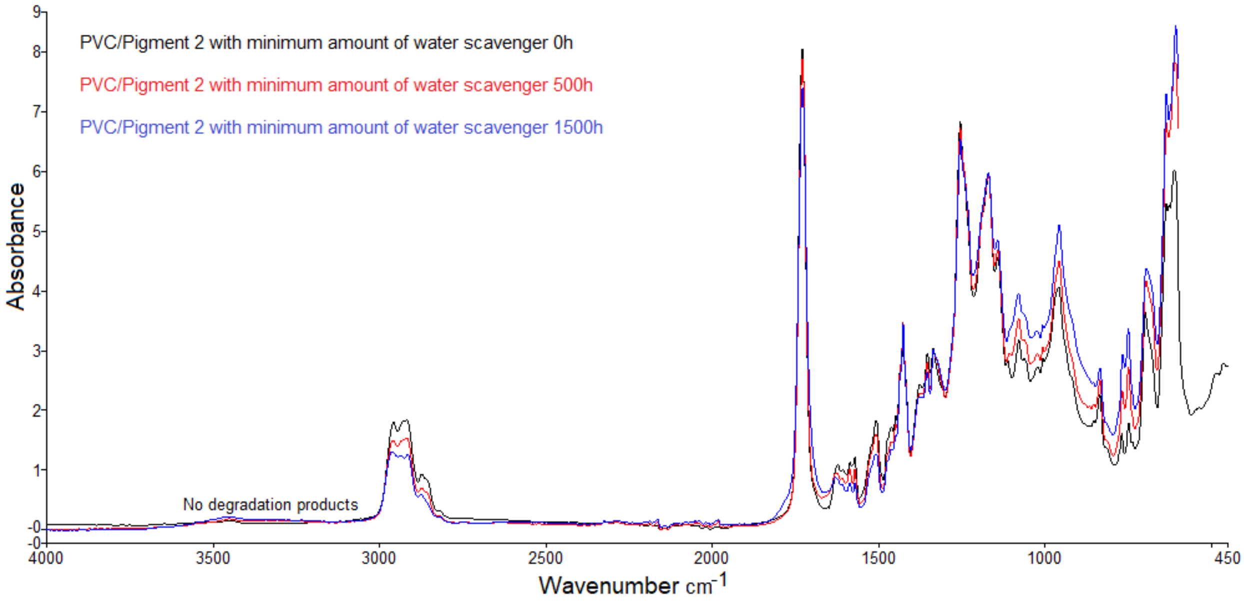


Fig.4.46. FTIR spectra for the PVC/pigment 2 film with the minimum amount of the water scavenger before (black) and after the addition of the minimum amount of water scavenger at 500 h (red) and 1500 h (blue).

Like in PVC/pigment 1 films case, for the PVC/pigment 2 no degradation products are visible between 3000 and 3500 cm^{-1} but loss of 12.4 % $^{w.}/_{w.}$ of plasticizer was observed at 1728 cm^{-1}

(fig.4.46) but it is less evident than in the case of the original films. Apart from the absence of degradation products from figure 4.46, the intensity of the plasticizer and PVC peaks between 2800 and 3000 cm^{-1} is smaller and this can be attributed to the fact that the water scavenger tends to migrate to the outer surface where the FTIR gets information from (0.17-0.66 μm).

The same pattern was observed for the rest of the pigmented films; even for the films with pigment 5 which are the most durable films among the five. As can be seen from figure 4.47. The peaks between 2790 and 3696 cm^{-1} become lower and wider as degradation proceeds and this can be attributed to the fact that the plasticizer tends to migrate to the surface and get washed off eventually by the cyclic water spray.

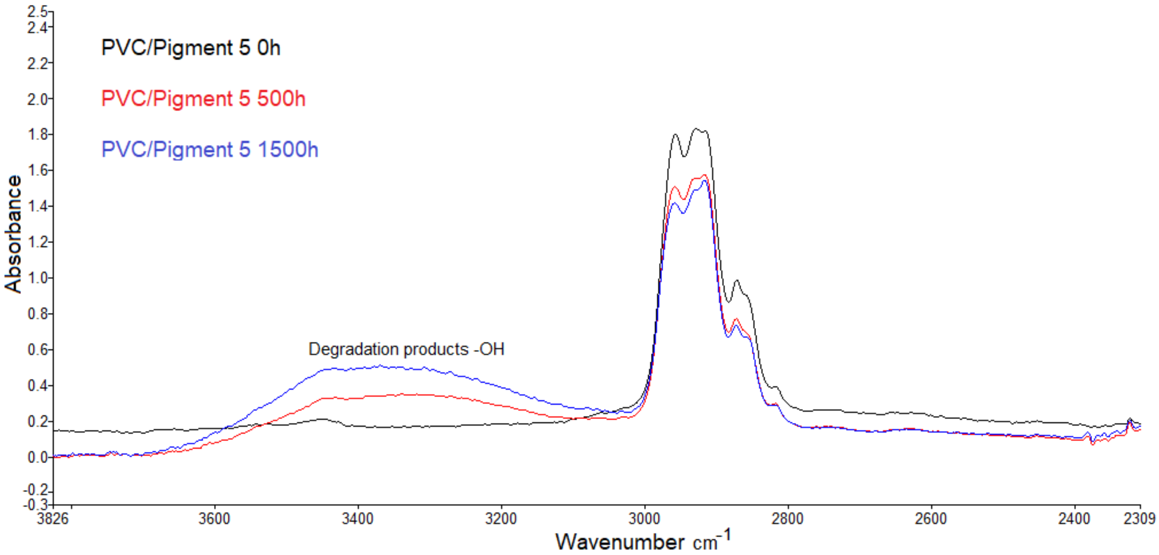


Fig.4.47. FTIR spectra between 2309 and 3826 cm^{-1} for the PVC/pigment 5 film before (black) and after 500 h (red) and 1500 h (blue) of degradation.

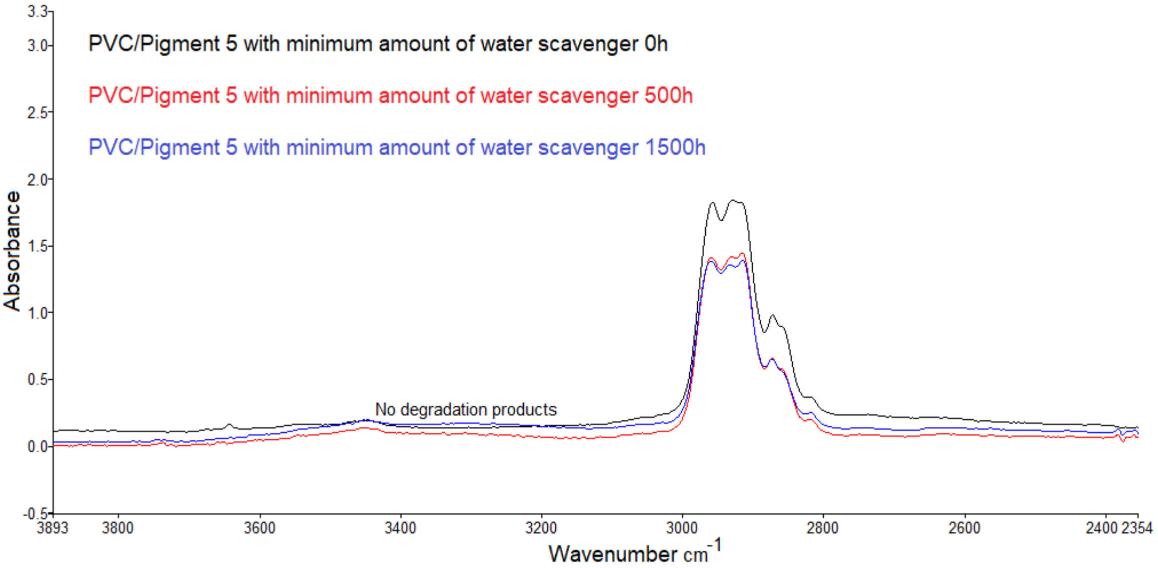


Fig.4.48. FTIR spectra between 2354 and 3893 cm^{-1} for the PVC/pigment 5 film with the minimum amount of the water scavenger before (black) and after the addition of the minimum amount of water scavenger at 500 h (red) and 1500 h (blue).

Once more, for PVC/pigment 5, there is an increase of degradation products (hydroperoxides) as degradation propagates and the fingerprint of plasticizer is reduced between 2800 and 3000 cm^{-1}. These degradation products are absent after the addition of the minimum amount of the water scavenger as can be seen in figure 4.48.

From all the results and all the pigments, it can be concluded that the water scavenger causes the reduction of the PVC degradation products (hydroperoxides). This decrease can be attributed to the effect of the water scavenger which reacts with the water and as a result the amount of the degradation products that cause the autocatalytic degradation process is minimized.

4.2.8 Thermal Analysis (DSC) results

Differential Scanning Calorimetry (DSC) is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and a reference material is measured as a function of temperature. It is used widely for examining polymeric materials to determine their thermal transitions and for this study, it was used to measure the glass transition temperature (T_g). The glass transition temperature is one the most important properties for polymers. It is the gradual and reversible transition in amorphous materials (or in amorphous regions within semicrystalline materials), from a hard and relatively brittle "glassy" state into a viscous or rubbery state as the temperature is increased.

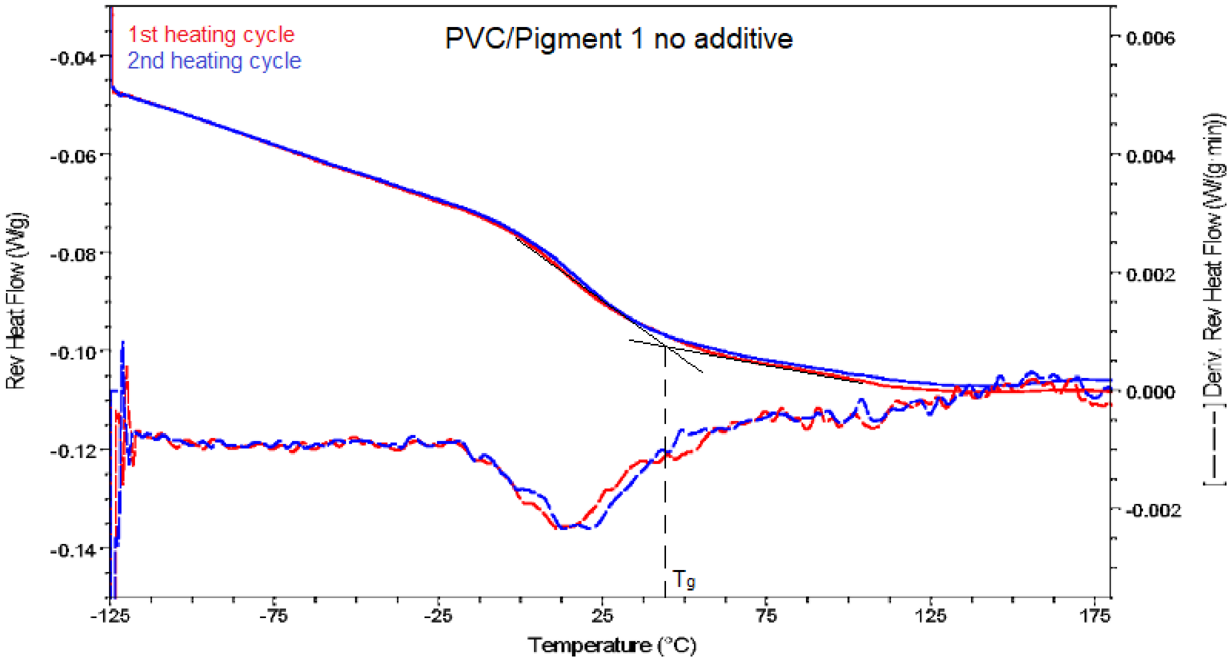


Fig.4.49. DSC spectrum for the PVC/pigment 1 film without any additive.

As shown in figure 4.49, for the PVC/pigment 1 films, the T_g was calculated and the same was done for the rest of the pigments before and after the addition of the minimum amount of water scavenger since these films show the best weathering performance with the least loss of gloss. The glass transition temperatures for all the pigments are shown in figure 4.50.

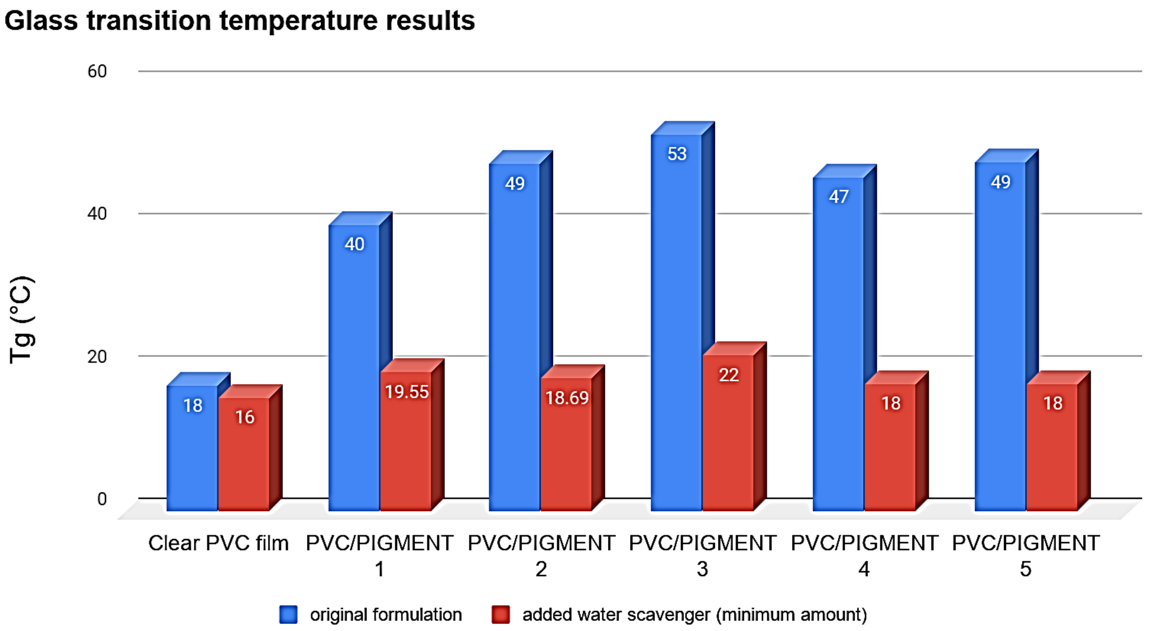


Fig.4.50. Glass transition temperature results for all five pigments (15 phr loading) and the clear PVC film before and after the addition of the water scavenger.

As can be seen in figure 4.50, there is a clear pattern of the T_g behavior, before and after the addition of water scavenger. However, there is also a difference before and after the introduction of the pigments to the PVC formulation. The clear PVC film T_g is 18 ^oC but after the introduction of the 5 pigments it goes higher than 40 ^oC. The pigments introduction causes a change in the PVC molecular structure which becomes more ordered (crystallization) [50]. The flakes/particles act as a filler material and make the PVC chain movement more difficult and this is reflected as an increase in the glass transition temperature.

Conversely, the use of the water scavenger does not affect the original formulation T_g but when used in the pigmented PVC films, it keeps the T_g close to the 18 ^oC of the original formulation. The source of this effect is connected to the wetting agent of the CaO-based water scavenger which helps the movement of the PVC chains and reduces the pigmented films T_g [50].

4.3 Additive 2: Dispersant 1

4.3.1 Weathering results

The weathering results of the pigmented PVC films after the addition of dispersant 1 are demonstrated in the following figures. These three additive loadings were implemented in the PVC films containing the five chosen pigments and they were tested accordingly.

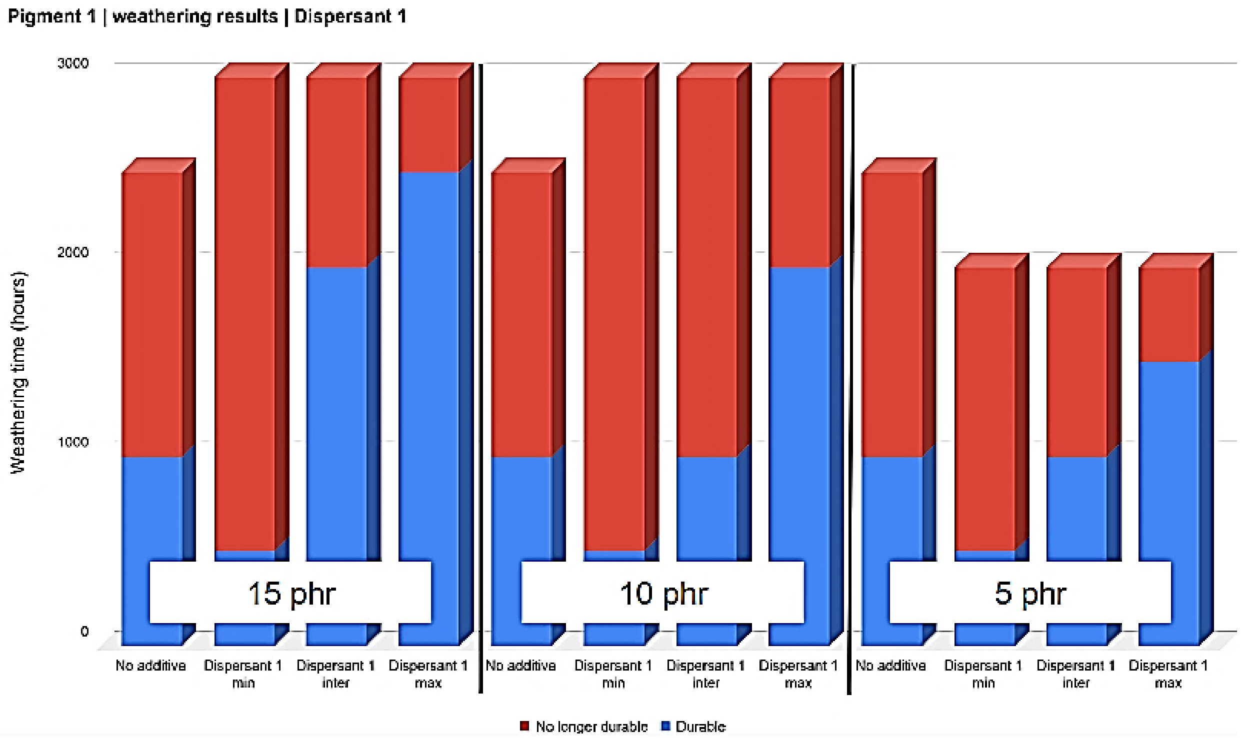


Fig.4.51. Weathering results of PVC/pigment 1 films with and without the addition of the dispersant 1.

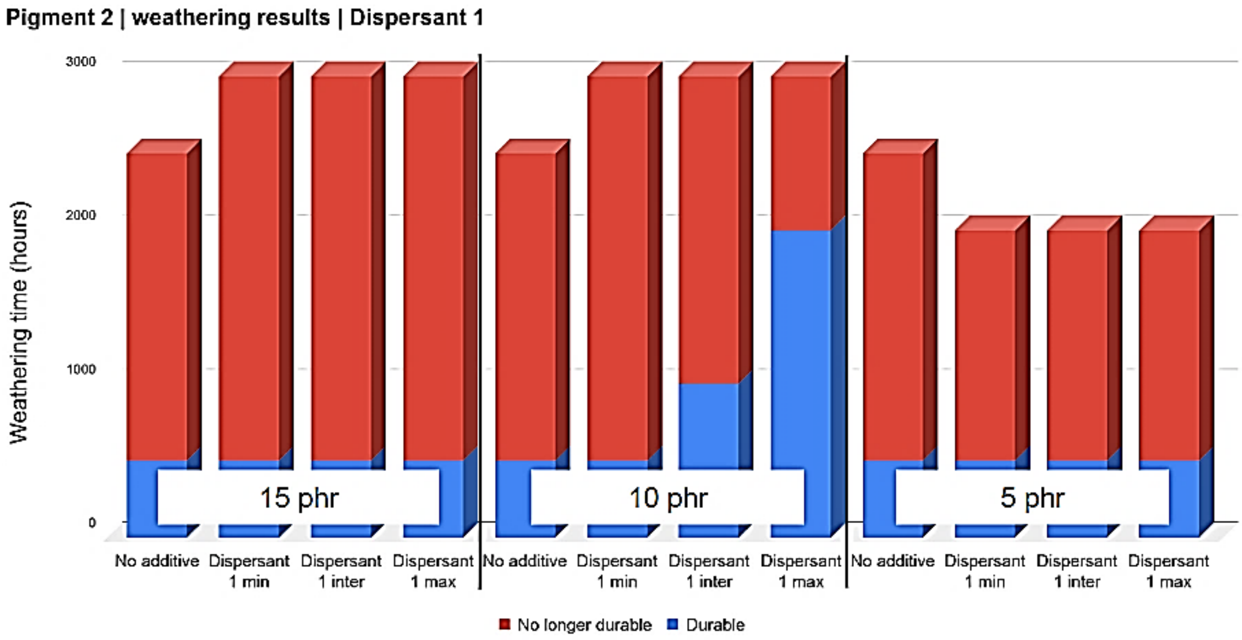


Fig.4.52. Weathering results of PVC/pigment 2 films with and without the addition of the dispersant 1.

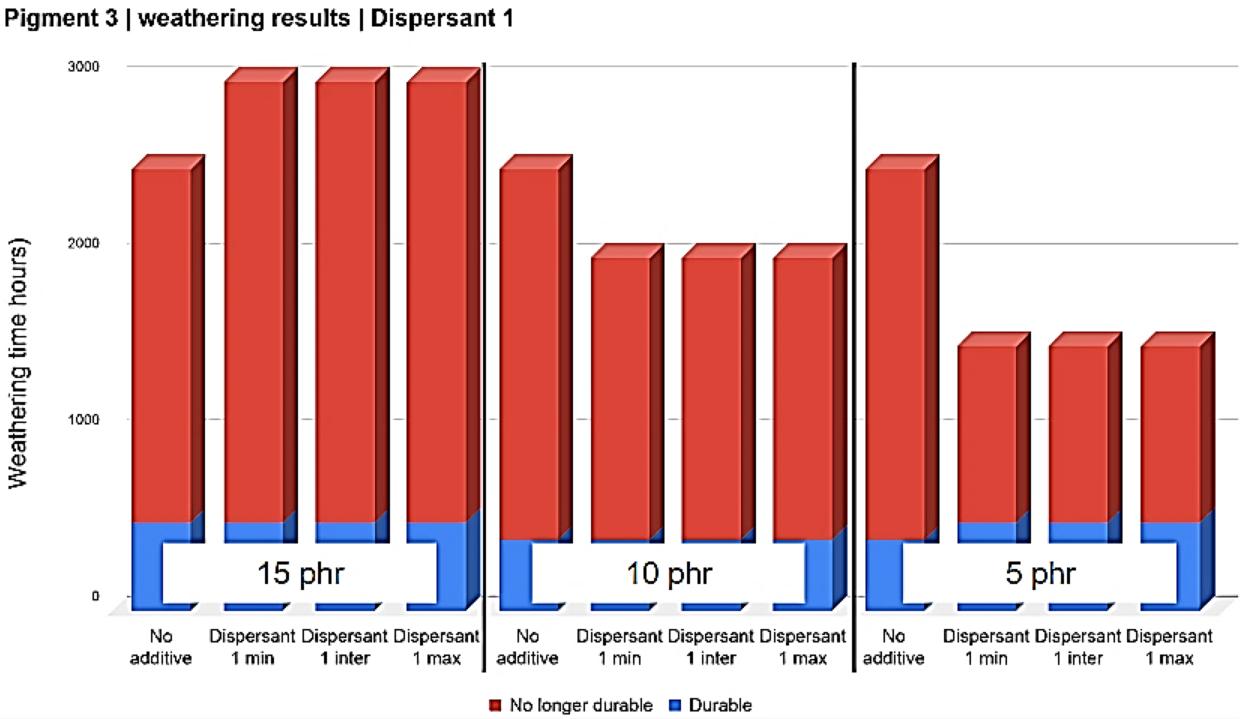


Fig.4.53. Weathering results of PVC/pigment 3 films with and without the addition of the dispersant 1.

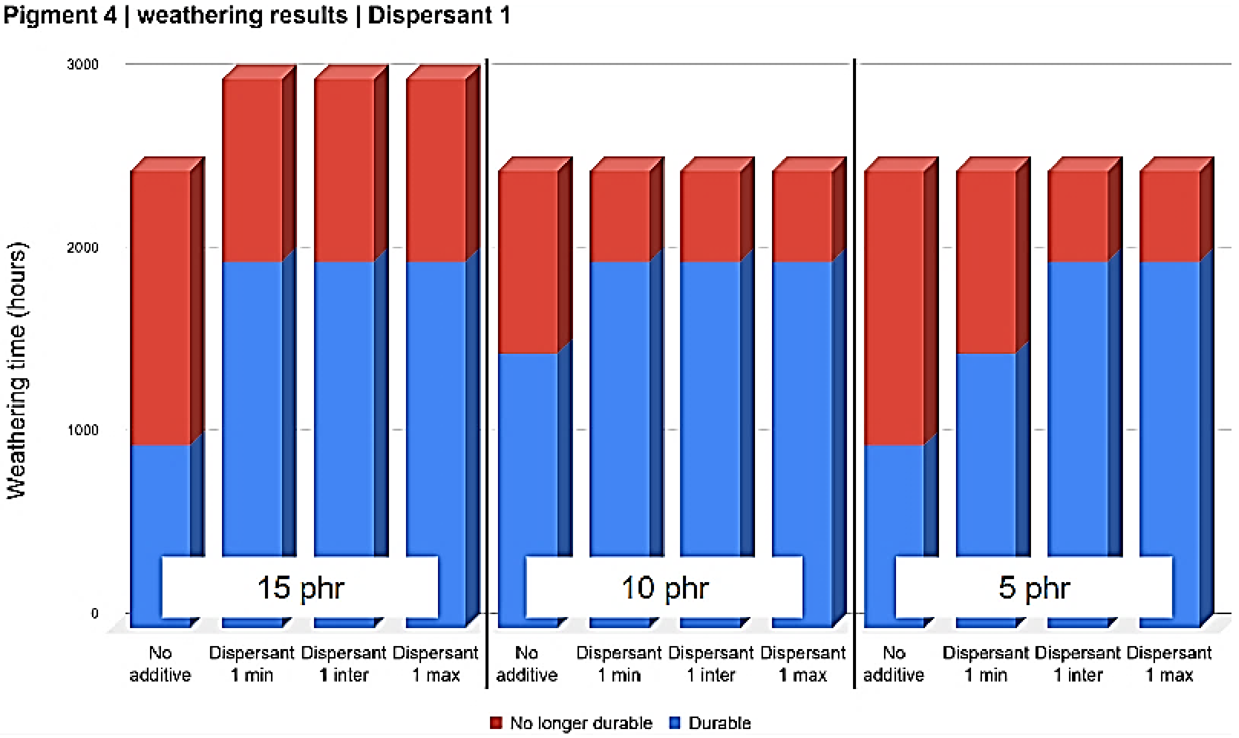


Fig.4.54. Weathering results of PVC/pigment 4 films with and without the addition of the dispersant 1.

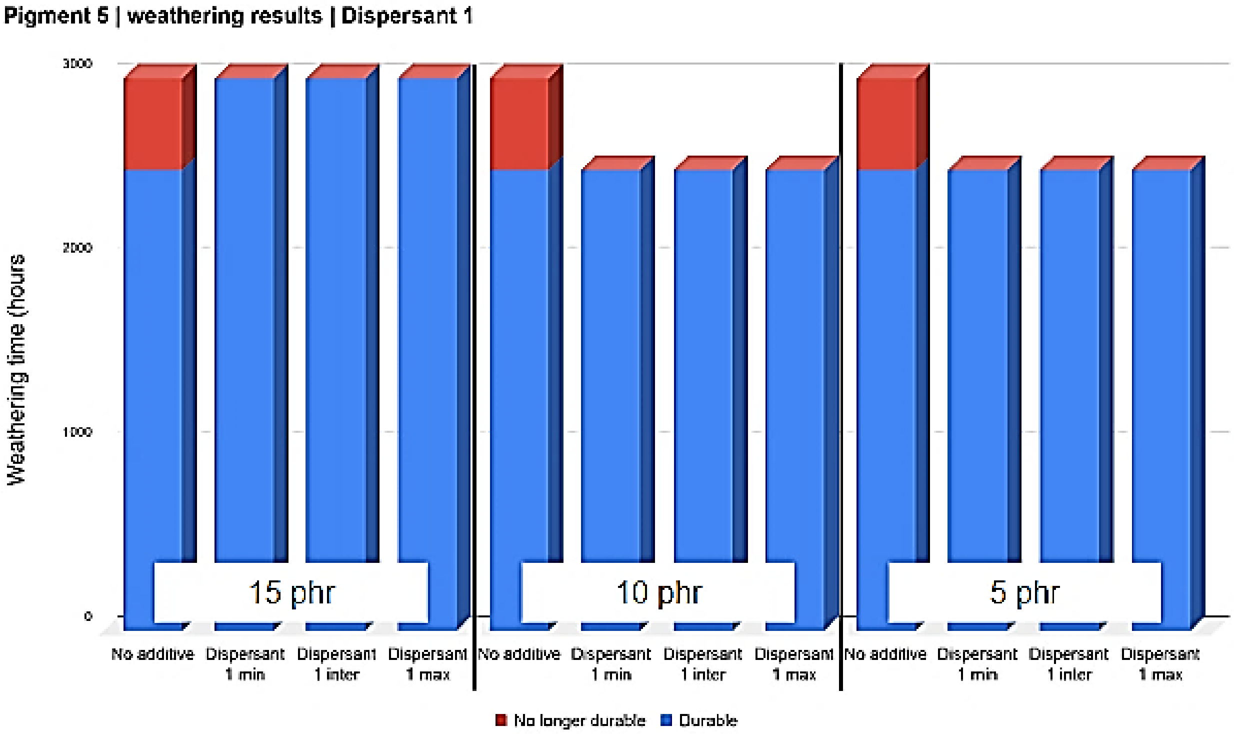


Fig.4.55. Weathering results of PVC/pigment 5 films with and without the addition of the dispersant 1.

After the use of dispersant 1, it can be seen (fig.4.51) that there is an increase in the weathering durability of the PVC/pigment 1 for the pigment loadings of 15, 10 and 5 phr as the additive amount is increased. The dispersant 1 increases the distance between the flakes of pigment 1 so less flakes are touching one another. As a result, it is less possible for them to damage each other and the films durability is increased. The highest durability achieved is 2500 h for the 15 phr pigment loading and the highest amount of additive. The lowest durability (500 h) was observed for the minimum amount of additive for all pigment loadings. It is not clear what is the cause of this behavior, although, a miscalculation during the preparation procedures can be the cause.

After the use of dispersant 1, it can be seen (fig.4.52) that there is an increase in the weathering performance only for the 10 phr of pigment 2 loading and it is not clear why this is happening. For the 15 and 5 phr, no significant change was observed. This can be attributed to the fact that pigment 2 has a bigger size of flakes (25-35 microns) and it is not as easy as in pigment 1 case to increase the distance between the flakes.

For the PVC/pigment 3 films, it can be seen (fig.4.53) that there is no improvement of weathering performance for all three pigment loadings. The main cause of that could be the shape of pigment 3 which is in the form of spherical particles in a smaller size (5-10 microns) than the previous two pigments since the smaller the particles the more difficult it is for them to be more dispersed.

For the PVC/pigment 4 films (fig.4.54) with the three amounts of dispersant 1 an improved durability up to 2000 h was observed. This pigment has a small size (5-10 microns) with a spherical shape as in the previous pigment (pigment 3) case and again it is more difficult to disperse these particles more but the pigment coating is more durable to weathering than the coating of pigment 3 and higher durability than before was achieved.

As it was mentioned before, pigment 5 (fig.4.55) is a little different than the other four since it is a more durability-effective pigment. In this case a 500 h-improved weathering durability was observed but the films with this pigment are still being tested so it is not possible to make safe comments until further weathering results are available.

4.3.2 Gloss and color measurements

The color and gloss of the pigmented PVC films were measured at 0 h and each 500 h for each stage of degradation in order to see if the implemented dispersant affects the appearance of the films after each weathering stage.

Table 4.26. Gloss measurements at 60° for the 15 phr loading of pigment 1 for the three loadings of the dispersant 1.

Additive amount	0 h	500 h	1000 h	1500 h	2000 h	2500 h	3000 h
No additive	110 GU	101 GU	101 GU	97.6 GU	97.4 GU	96.4 GU	Fully degraded
Dispersant 1 minimum	113 GU	106 GU	100 GU	100 GU	103 GU	97 GU	99.9 GU
Dispersant 1 intermediate	112 GU	103 GU	99.4 GU	98.8 GU	100 GU	95.3 GU	97.7 GU
Dispersant 1 maximum	108 GU	99 GU	97.9 GU	96.8 GU	95.2 GU	92.1 GU	93.4 GU

From the gloss results of table 4.26, it can be seen that the addition of the dispersant 1 shows a significant improvement of gloss compared to the results of the water scavenger. The dispersant 1 increases the distance between the pigment flakes and this makes it easier for more of them to reflect light at any single angle (specular angle) and the gloss is retained.

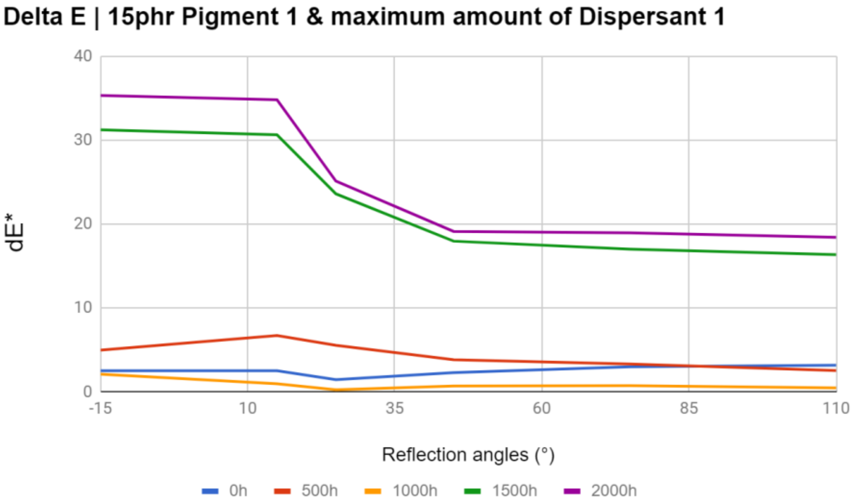


Fig.4.56. Color difference after the addition of dispersant 1 after each stage of degradation of 15 phr PVC/pigment 1 films.

After the addition of the dispersant 1, the same color difference was observed for the PVC/pigment 1 films with the dispersant 1 (fig.4.56) as seen for the water scavenger (fig.4.16). Some of the components of dispersant 1 may migrate to the surface as was the case for the water scavenger causing the color difference in the later stages of degradation.

Table 4.27. Gloss measurements at 60° for the 15 phr loading of pigment 2 for the three loadings of the dispersant 1.

Additive amount	0 h	500 h	1000 h	1500 h	2000 h	2500 h	3000 h
No additive	98.5 GU	93.7 GU	93.7 GU	Fully degraded	Fully degraded	Fully degraded	Fully degraded
Dispersant 1 minimum	100 GU	88.4 GU	87.4 GU	Fully degraded	Fully degraded	Fully degraded	Fully degraded
Dispersant 1 intermediate	98.9 GU	89.6 GU	85.4 GU	Fully degraded	Fully degraded	Fully degraded	Fully degraded
Dispersant 1 maximum	96 GU	89.0 GU	86.4 GU	Fully degraded	Fully degraded	Fully degraded	Fully degraded

From the gloss results of table 4.27, it can be seen that the addition of the dispersant 1 shows a significant improvement of gloss compared to the results of the water scavenger for the films with pigment 2 similar to the results of the PVC/pigment 1 films. The same applies for the rest of the pigmented films with the other three pigments.

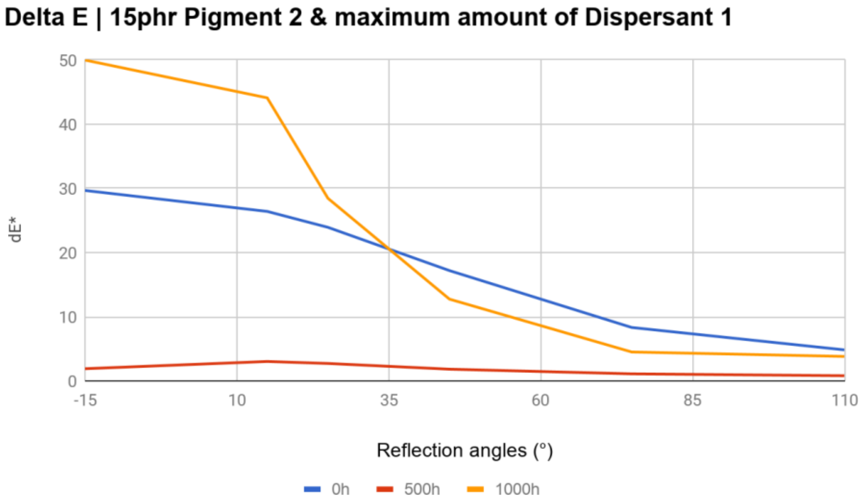


Fig.4.57. Color difference after the addition of dispersant 1 after each stage of degradation of 15phr PVC/pigment 2 films.

After the addition of the dispersant 1 (fig.4.57), a variation in color difference was observed at 1000 h compared to the results of the water scavenger (fig.4.17). As in the case of the water scavenger, the color difference behavior for the pigmented PVC films with the dispersant 1 is different for each pigment and depends on how each pigment adopts the nature of the added compound. They selectively absorb some wavelengths of incident light while reflecting or transmitting others. The film is an opaque material so most of the incident light is reflected.

4.3.3 Mechanical behavior

The tensile tests for the pigmented PVC films for the three loadings of the dispersant 1 took place in order to find out if there is a significant change in the mechanical behavior of the films after the use of the additive. For each film formulation three samples were tested in order to confirm the repetition of the same results. As it was mentioned before flat sheet type of samples was used. The error bars of the graphs represent the standard deviation of the tensile strength results received from the three samples tested for each formulation. The results are shown in the following figures.

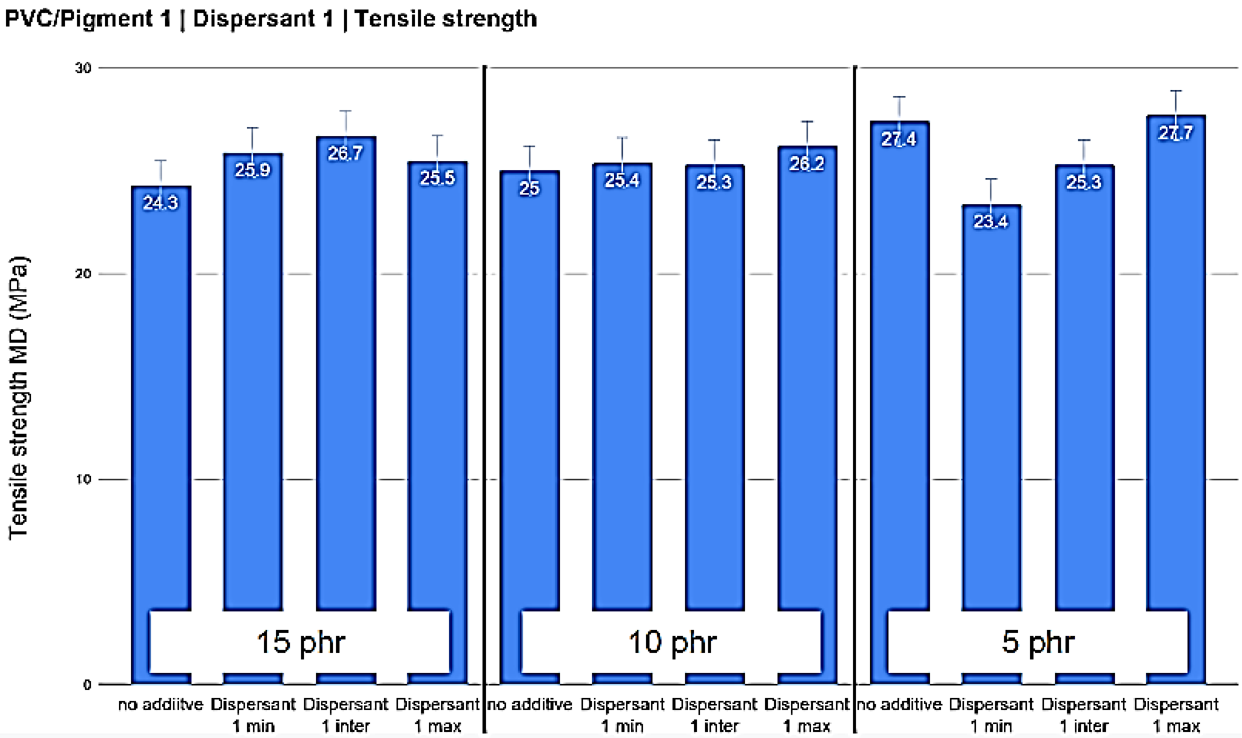


Fig.4.58. Tensile strength results for the three loadings of PVC/pigment 1 films before and after the addition of the three loadings of dispersant 1.

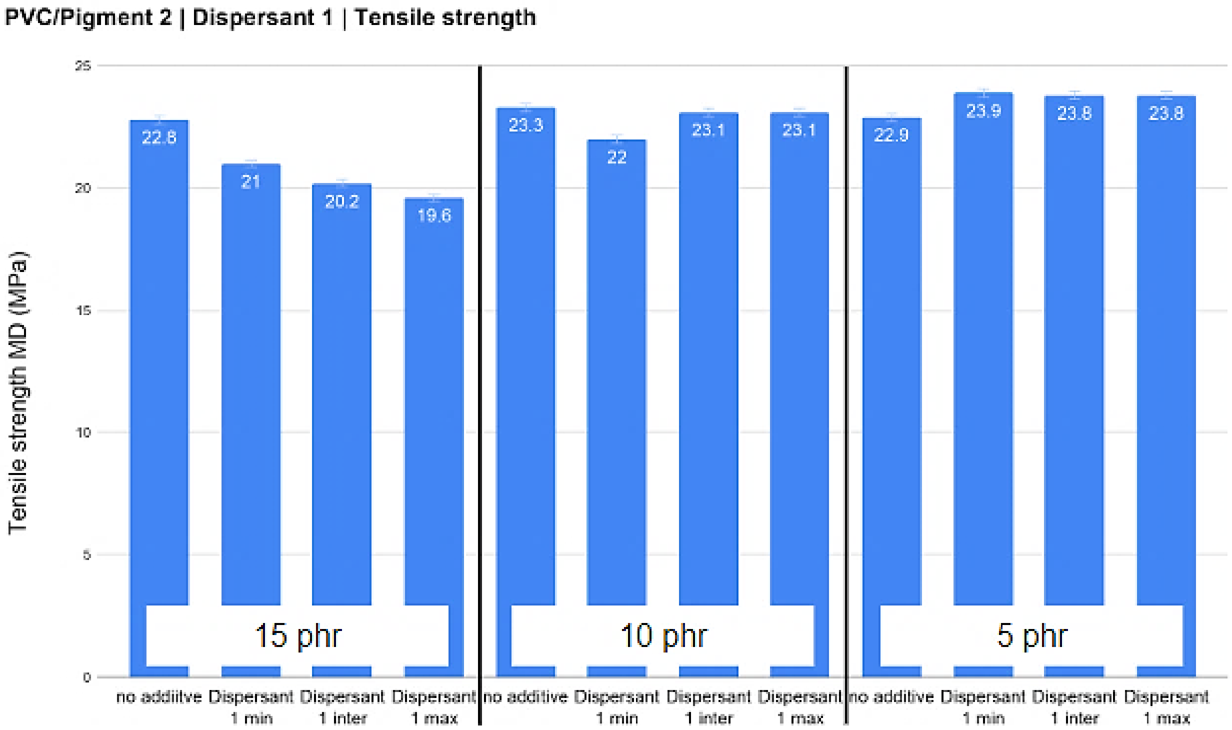


Fig.4.59. Tensile strength results for the three loadings of PVC/pigment 2 films before and after the addition of the three loadings of dispersant 1.

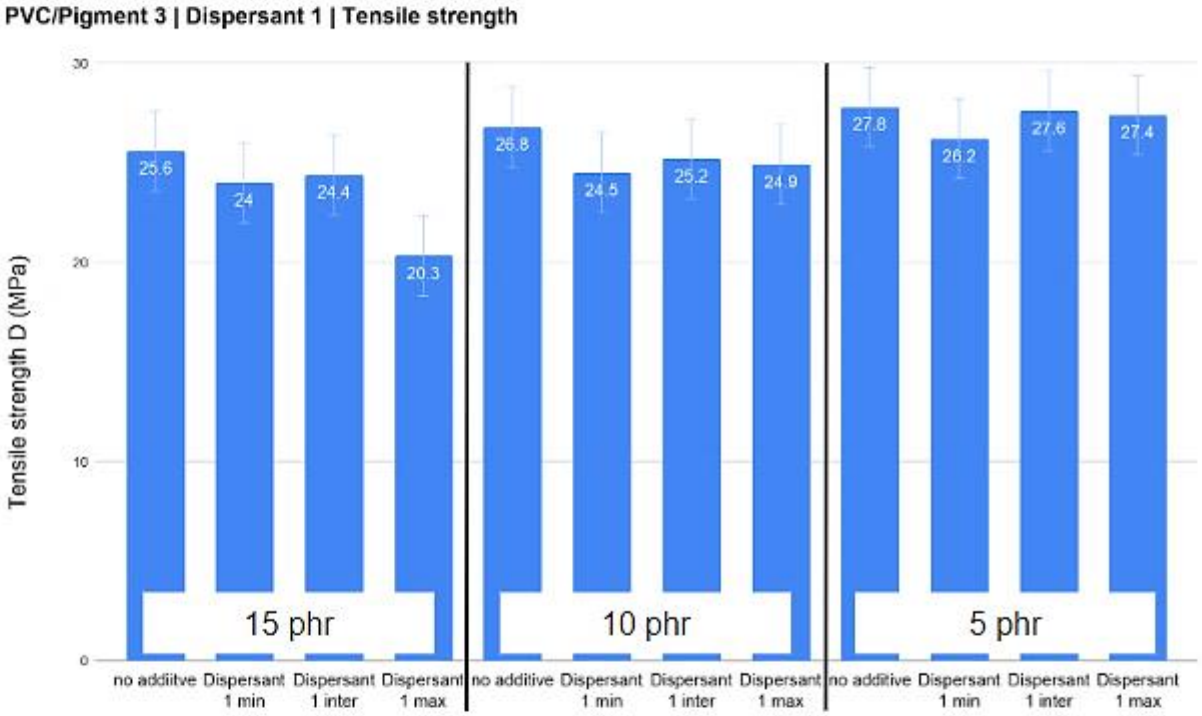


Fig.4.60. Tensile strength results for the three loadings of PVC/pigment 3 films before and after the addition of the three loadings of dispersant 1.

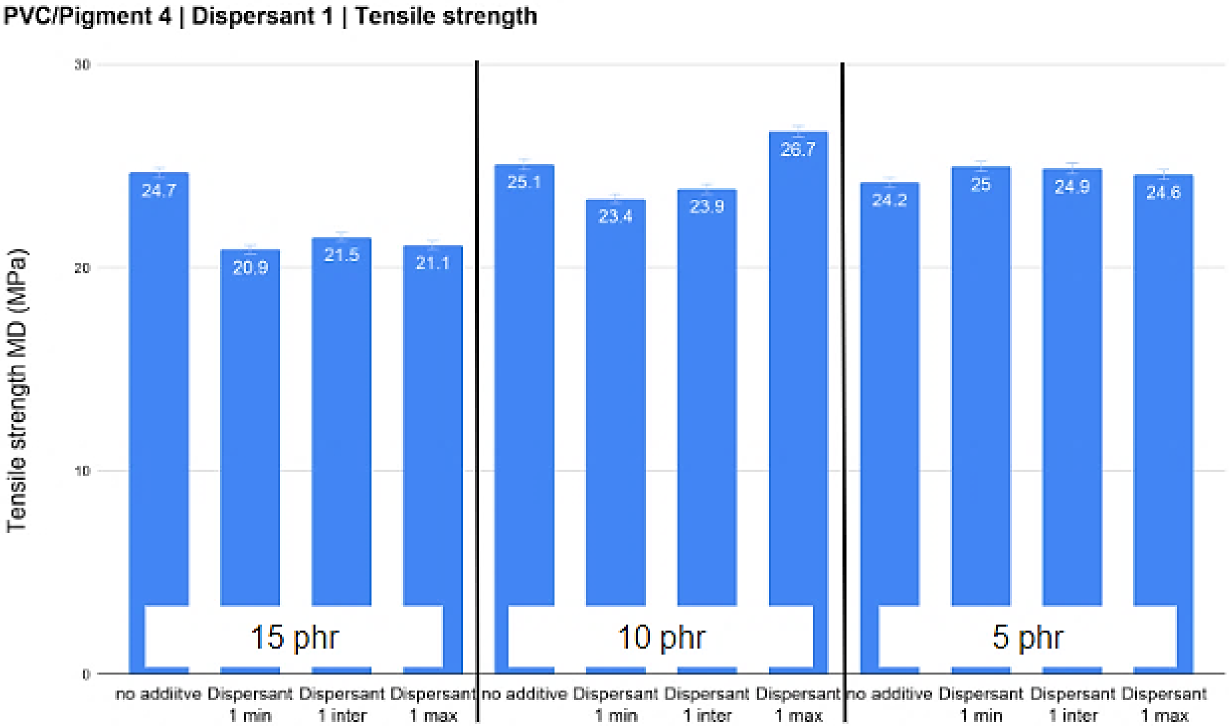


Fig.4.61. Tensile strength results for the three loadings of PVC/pigment 4 films before and after the addition of the three loadings of dispersant 1.

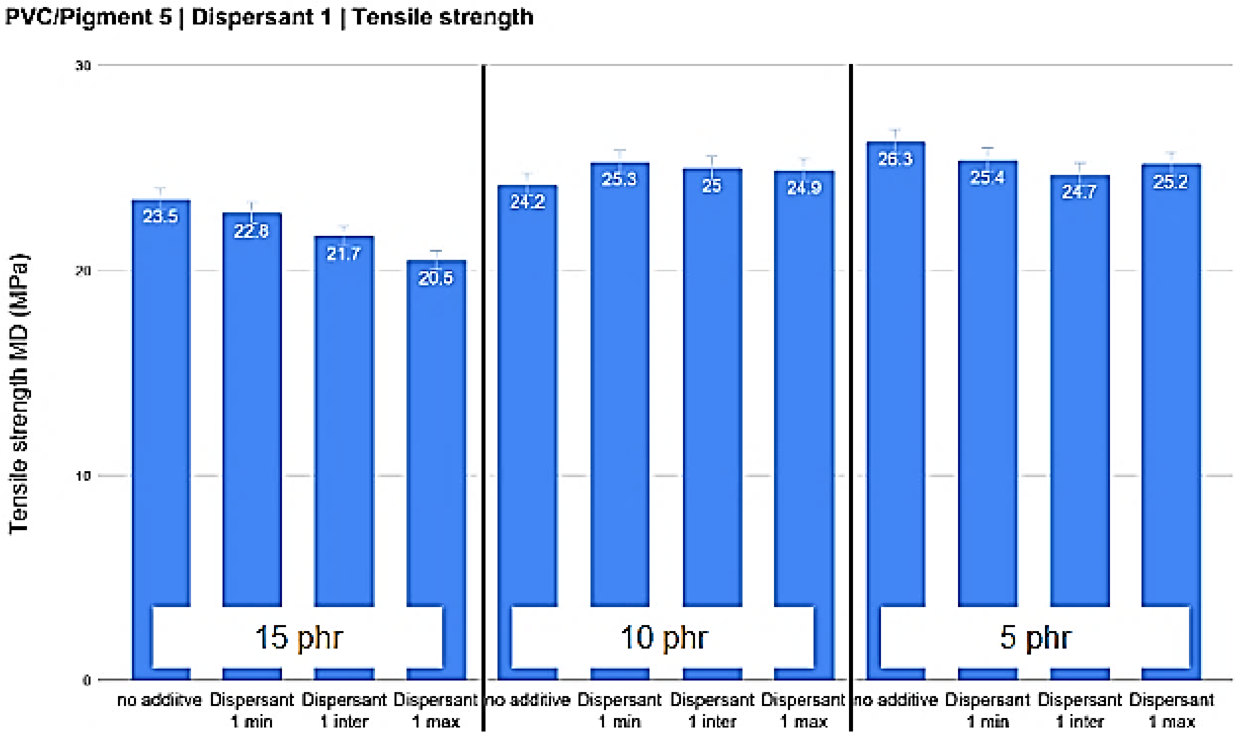


Fig.4.62. Tensile strength results for the three loadings of PVC/pigment 5 films before and after the addition of the three loadings of dispersant 1.

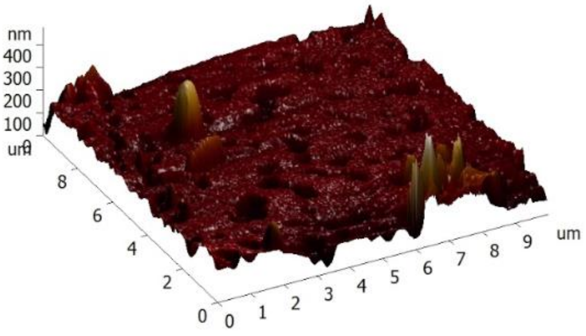
From all the previous figures (fig.4.58 - 4.62), it can be seen that there is a variation in the tensile strength results for the films with the five pigments but the differences in tensile strength and the rest of the mechanical properties is of the order of 3-6 MPa which is not a difference of a magnitude that can cause a problem in the use of the pigmented PVC films.

A general conclusion is that the tensile strength is reduced for most of the loadings of the pigments. The majority of the pigments (pigments 3, 4 and 5) are in the form of spherical particles and as a result it is more difficult for them to be dispersed and the PVC seems more affected. It looks like the dispersant 1 makes the movement of the polymer chains easier and decreases the Young's modulus which reflects the films higher elastic strain.

4.3.4 Atomic Force Microscopy (AFM) results

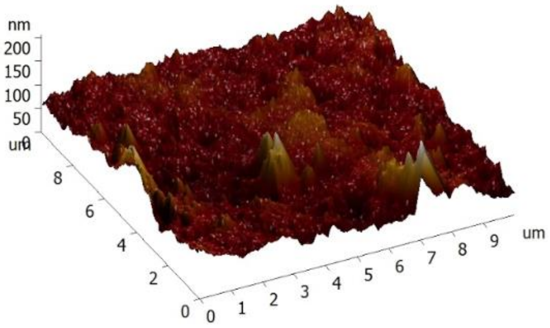
The AFM images taken for the films with the maximum loading of dispersant 1 in order to investigate the surface morphology of the films before and after the use of the additive are shown in the following figures. The data refer to unaged films and films after 500 h and 1000 h of weathering for the original films and the 15 phr of pigment 1 since these are the films with the best weathering performance and higher gloss retention.

(a)



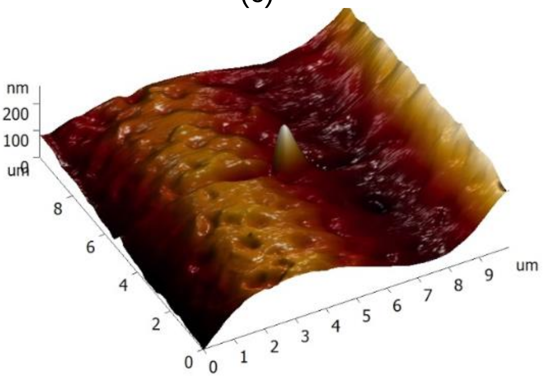
0 hours

(b)



500 hours

(c)



1000 hours

Fig.4.63. 3D AFM results for the PVC/pigment 1 films, (a), (b) and (c) are the 3D results for the films after the addition of the maximum amount of dispersant 1.

After taking under consideration the AFM results of figure 4.63, compared to the results from the water scavenger (fig.4.32), no considerable change in the surface roughness and no change in the number of pores was observed. The difference in the surface roughness is presented in table 4.28.

Table 4.28. Roughness measurements for the PVC/pigment 1 films before and after the addition of the maximum amount of dispersant 1.

PVC/pigment 1 films	0 h	500 h	1000 h
No additive	7.42 nm	15.4 nm	10.8 nm
Dispersant 1 max	9.39 nm	12.76 nm	13.6 nm

The table 4.28 demonstrates the surface roughness values for the films after the addition of the maximum amount of dispersant 1. The numbers show that the surface roughness of the films is really close to the ones of the films of the original formulation and way lower than the respective ones of the films with the water scavenger. These were the results for pigment 1 films before and after the addition of the maximum amount of dispersant 1 and the same behavior applies to the films with the rest of the pigments.

4.3.5 Fourier-Transform Infrared Spectroscopy (FTIR) results

As was done for the films with the water scavenger, the films with the dispersant 1 were also analyzed with the FTIR (see fig.4.64).

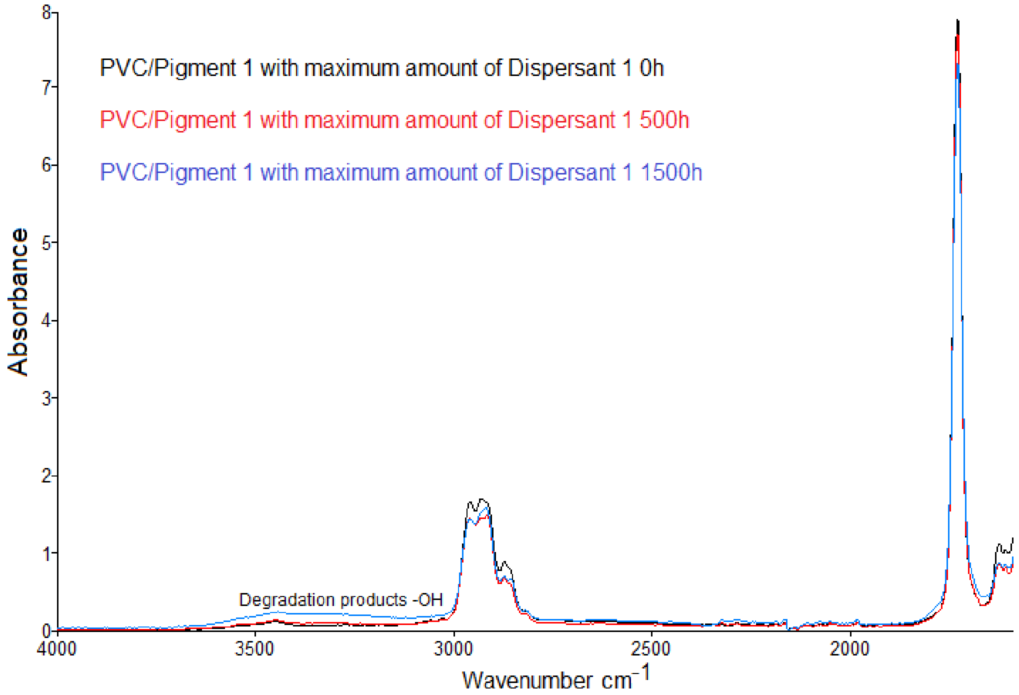


Fig.4.64. FTIR spectra between 1660 and 4000 cm^{-1} for the PVC/pigment 1 film with the maximum amount of dispersant 1 before (black) and after the addition of the additive at 500 h (red) and 1500 h (blue).

Considering the weathering results of the films with dispersant 1, the FTIR analysis of pigment 1 has an expected behavior. Up to 500 h, the films do not show degradation products (hydroperoxides). After 1500 h of weathering, degradation products (hydroperoxides) were formed between 3000-3500 cm^{-1} and decrease (7 % $^{w.}/_{w.}$) of the plasticizer peak (1728 cm^{-1}) was observed as well. The films with the water scavenger perform better than the films with dispersant 1 and this is also reflected in the FTIR spectra.

4.4 Additive 3: Dispersant 2

4.4.1 Weathering results

The weathering results of the pigmented PVC films after the addition of dispersant 2 are shown in the following figures.

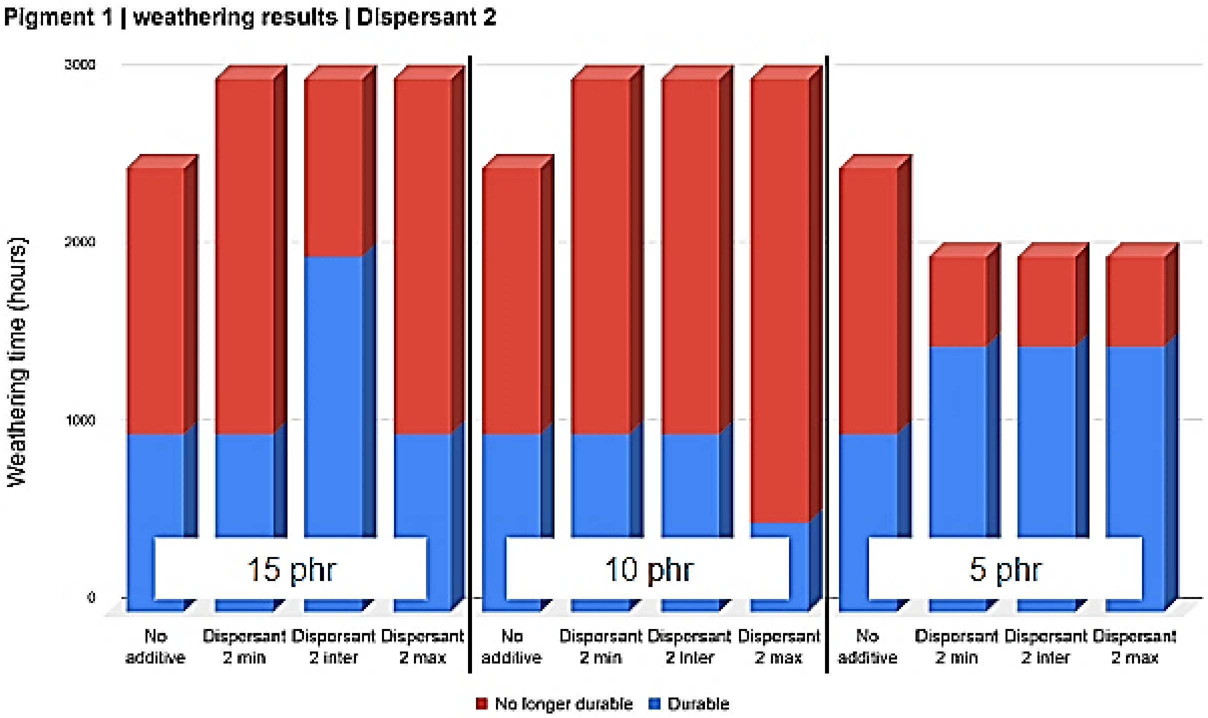


Fig.4.65. Weathering results of PVC/pigment 1 films with and without the addition of dispersant 2.

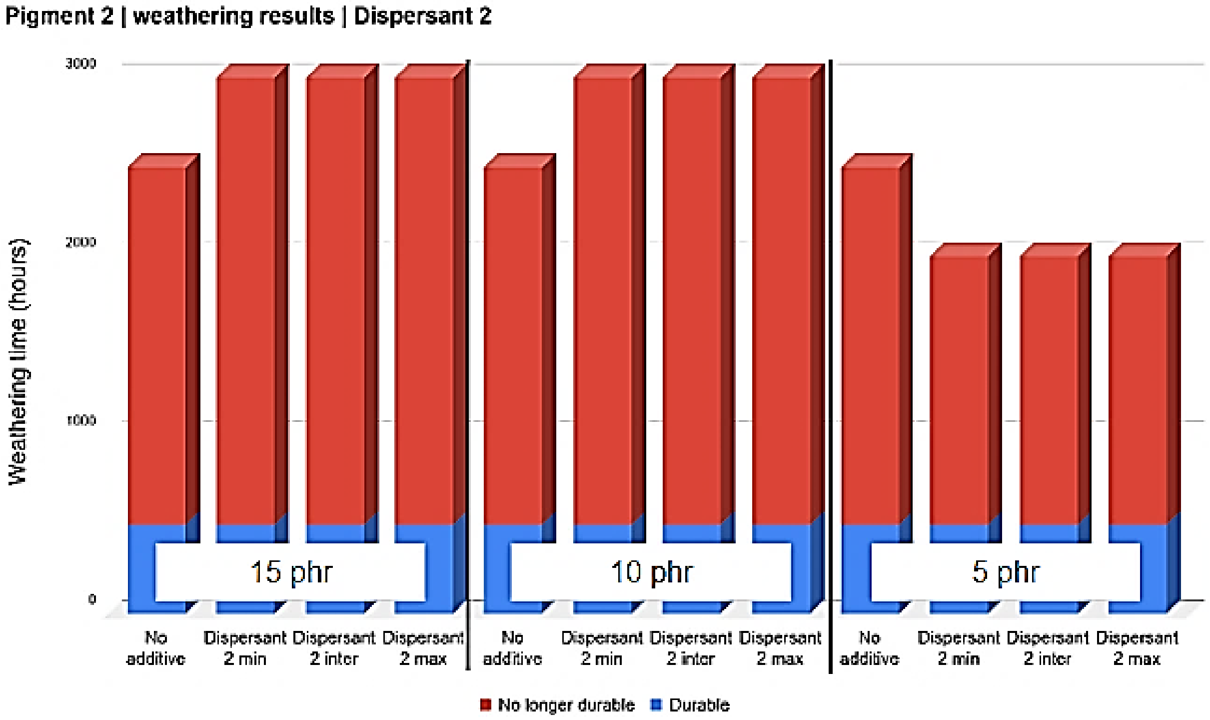


Fig.4.66. Weathering results of PVC/pigment 2 films with and without the addition of dispersant 2.

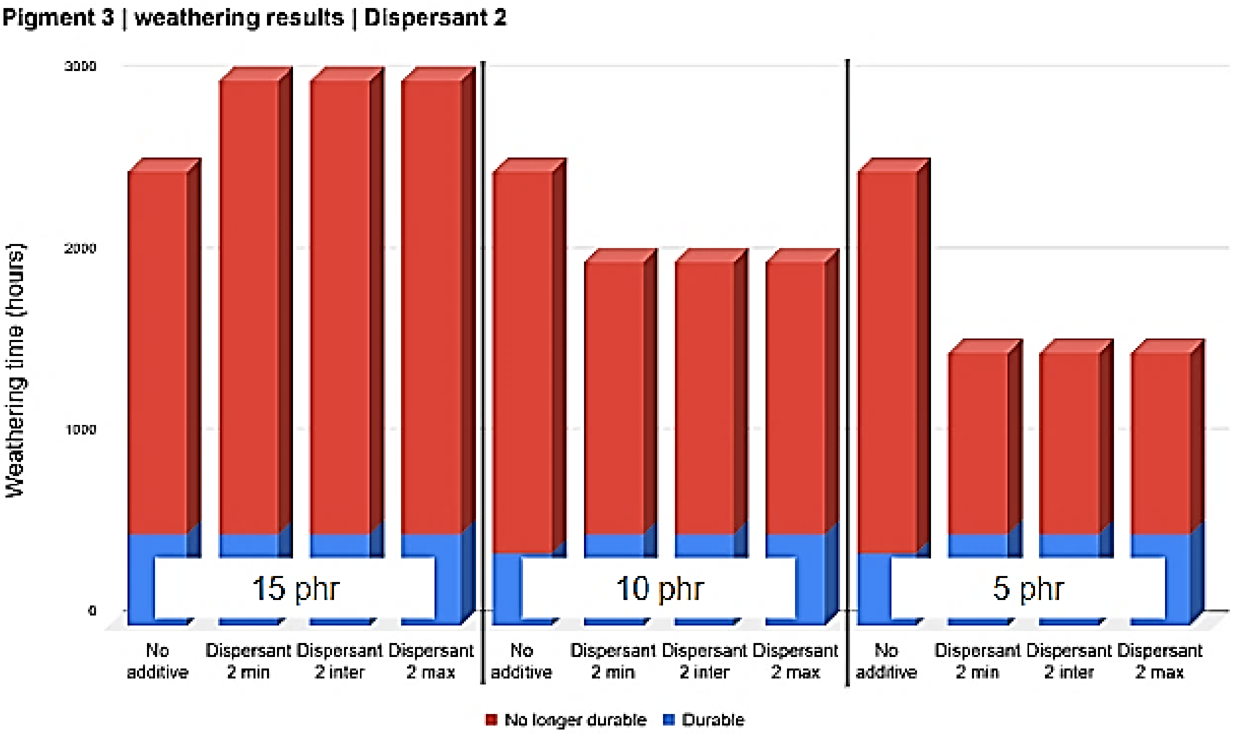


Fig.4.67. Weathering results of PVC/pigment 3 films with and without the addition of dispersant 2.

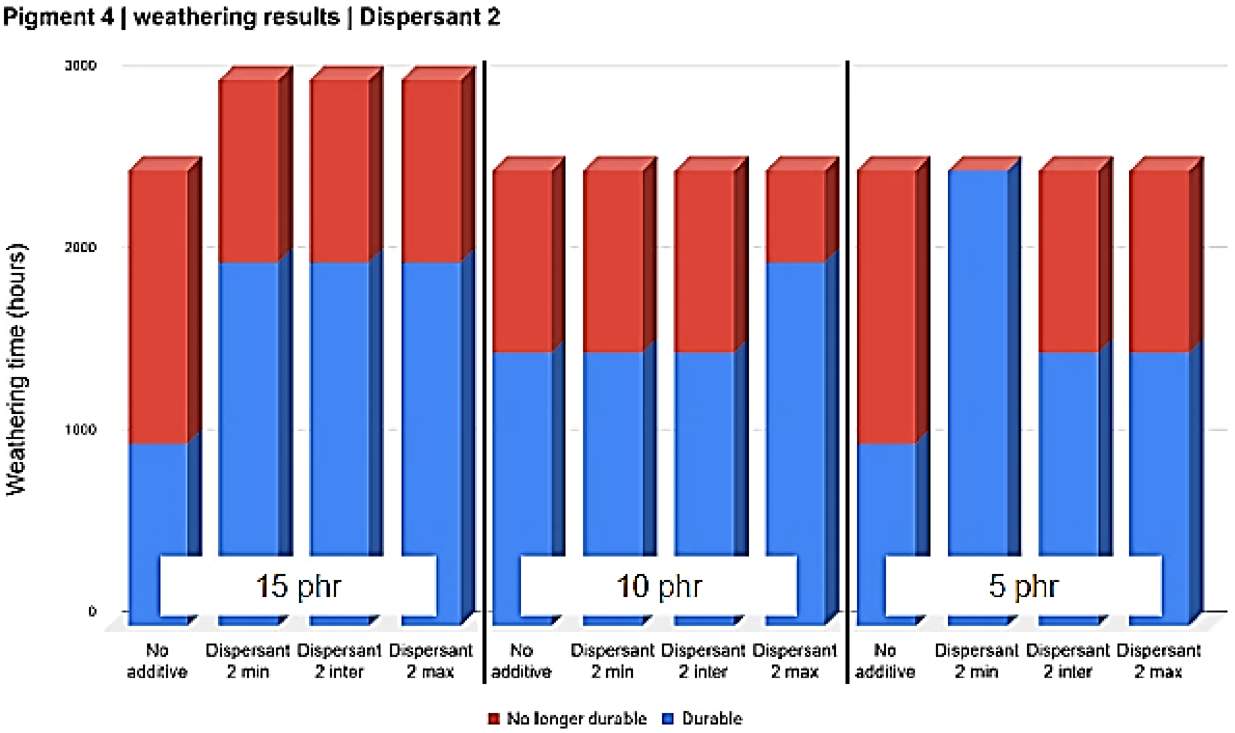


Fig.4.68. Weathering results of PVC/pigment 4 films with and without the addition of dispersant 2.

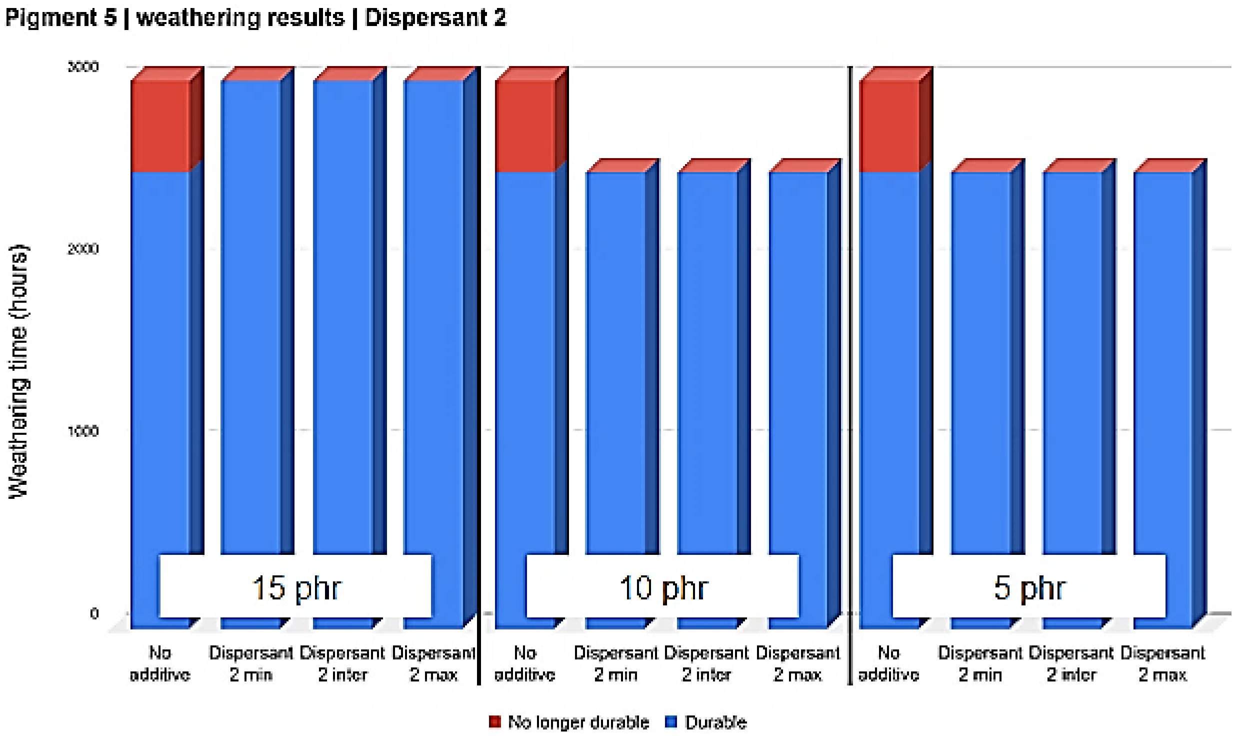


Fig.4.69. Weathering results of PVC/pigment 5 films with and without the addition of dispersant 2.

Figure 4.65 presents the weathering results for all three loadings of pigment 1 before and after the addition of the three loadings of dispersant 2. The dispersant 2 increases the distance between the flakes of pigment 1. As a result fewer flakes are touching one another and it is less likely that they damage each other, the films durability is therefore increased. Apart from the 15 phr PVC/pigment 1 films with the intermediate amount of Dispersant 2 that can reach 2000 h of weathering durability, the rest of the films can barely reach the same or 500 h-hours-improved weathering durability.

As can be seen from figure 4.66, no change in the films durability was observed for the films with pigment 2 before and after the addition of dispersant 2. This can be attributed to the fact that pigment 2 has a bigger size of flakes (25-35 microns) and it is not as easy as in the case of pigment 1 to increase the distance between the flakes.

For PVC/pigment 3 films (fig.4.67), no change in the films durability was observed after the addition of Dispersant 2. The main cause of that could be the shape of pigment 3 which is in the form of spherical particles with a smaller size (5-10 μm) than the previous two pigments since the smaller the particles the more difficult it is for them to be more dispersed.

A 1000 h-better durability was observed for the films with 15 phr of pigment 4 after the addition of dispersant 2 (fig.4.68). For the 10 and 5 phr only a 500 and 1000 h-increase in durability was observed for the maximum and minimum amount of dispersant 2 respectively. This pigment has a small size (5-10 μm) with a spherical shape as in the case of the previous pigment (pigment 3) and again it is more difficult to disperse these particles more.

In common with the previous additives used, no specific change was observed for pigment 5 films (fig.4.69) because as was previously mentioned, pigment 5 is a little different than the other four since it is a pigment that offers higher durability. In this case a 500 h-improved weathering durability was observed but the films with this pigment are still being tested so it is still not possible to make safe comments until further weathering testing is done.

4.4.2 Gloss and color measurements

The color and gloss of the pigmented PVC films were measured at 0 h and each 500 h for each stage of degradation in order to see the additive affects the appearance of the films after each weathering stage.

Table 4.29. Gloss measurements at 60º for the 15 phr loading of pigment 1 for the three loadings of dispersant 2.

Additive amount	0 h	500 h	1000 h	1500 h	2000 h	2500 h	3000 h
No additive	110 GU	101 GU	101 GU	104 GU	97.4 GU	96.4 GU	Fully degraded
Dispersant 2 minimum	114 GU	103 GU	102 GU	101 GU	100 GU	98.1 GU	96.6 GU
Dispersant 2 intermediate	112 GU	102 GU	101 GU	92.1 GU	97.8 GU	89.0 GU	93.6 GU
Dispersant 2 maximum	112 GU	96.2 GU	96.2 GU	95.4 GU	98.0 GU	95.2 GU	93.4 GU

From the gloss results of table 4.29, it can be seen that the addition of the dispersant 2 shows a significant improvement of gloss compared to the results of the water scavenger and comparable results with the films with dispersant 1. The dispersant 2 increases the distance between the pigment flakes and this makes it easier for more of them to reflect light in all directions and the gloss is retained.

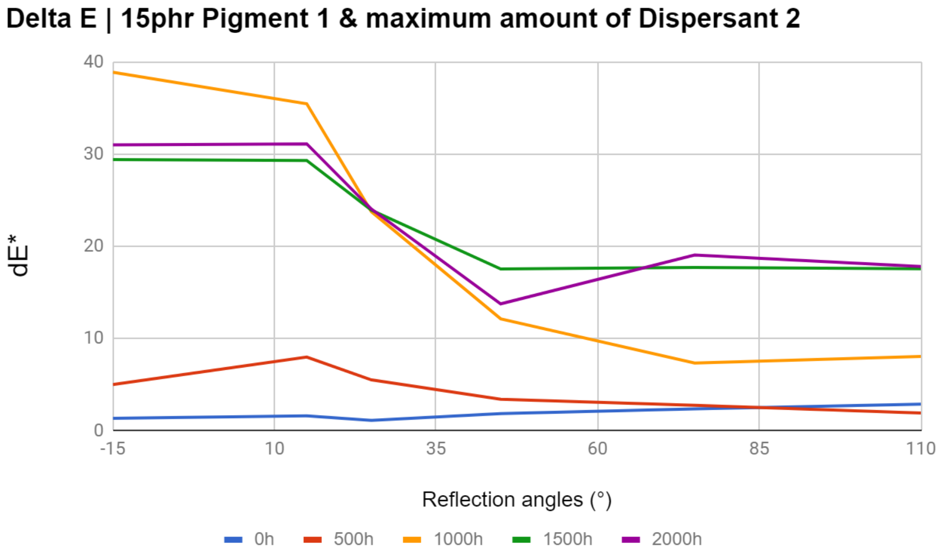


Fig.4.70. Color difference after the addition of dispersant 2 after each stage of degradation of 15phr PVC/pigment 1 films.

After the addition of the dispersant 2 in the PVC/pigment 1 15 phr films, a variation in color difference was observed at 1000 h and onwards. Some of the components of dispersant 2 may migrate to the surface like as was the case for the previous 2 additives (water scavenger, dispersant 1) and cause the color difference in the later degradation stages. As in the case of the water scavenger and dispersant 1, the color difference behavior for the pigmented PVC films with the dispersant 2 is different for each pigment and depends on how each pigment adopts the nature of the added compound.

4.4.3 Mechanical behavior

The tensile strength of the pigmented films after the addition of dispersant 2 are presented in the following figures.

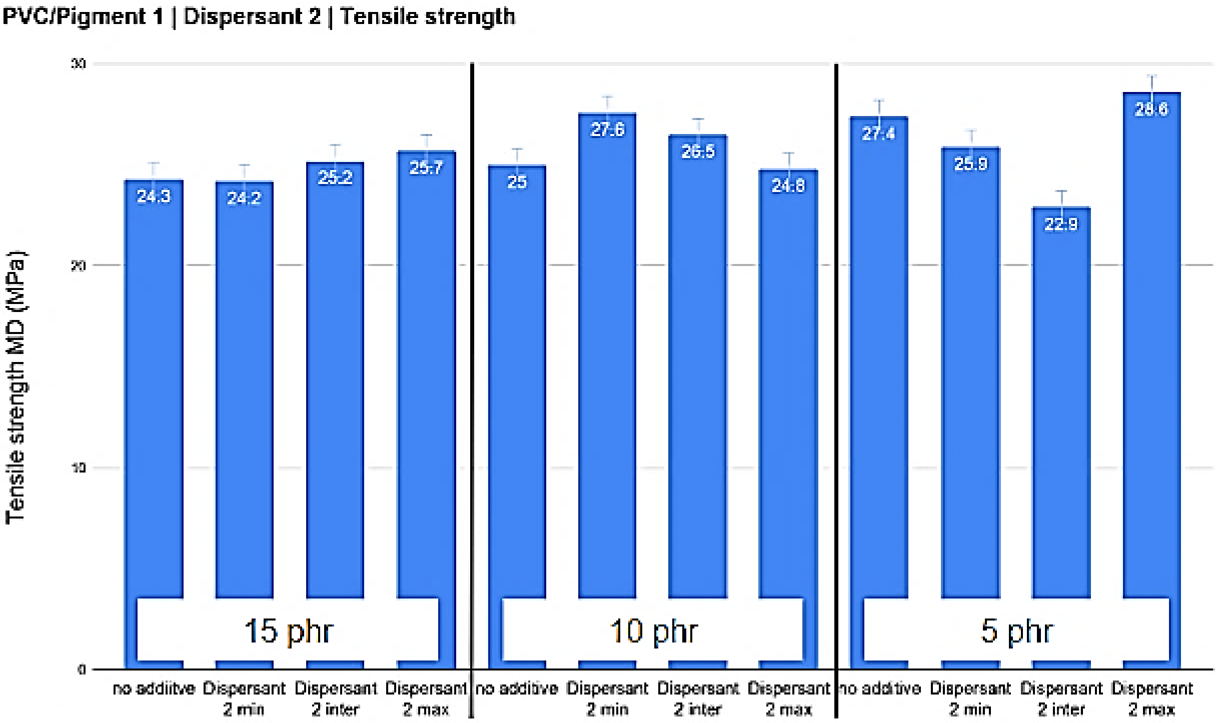


Fig.4.71. Tensile strength results for the three loadings of PVC/pigment 1 films before and after the addition of the three loadings of dispersant 2.

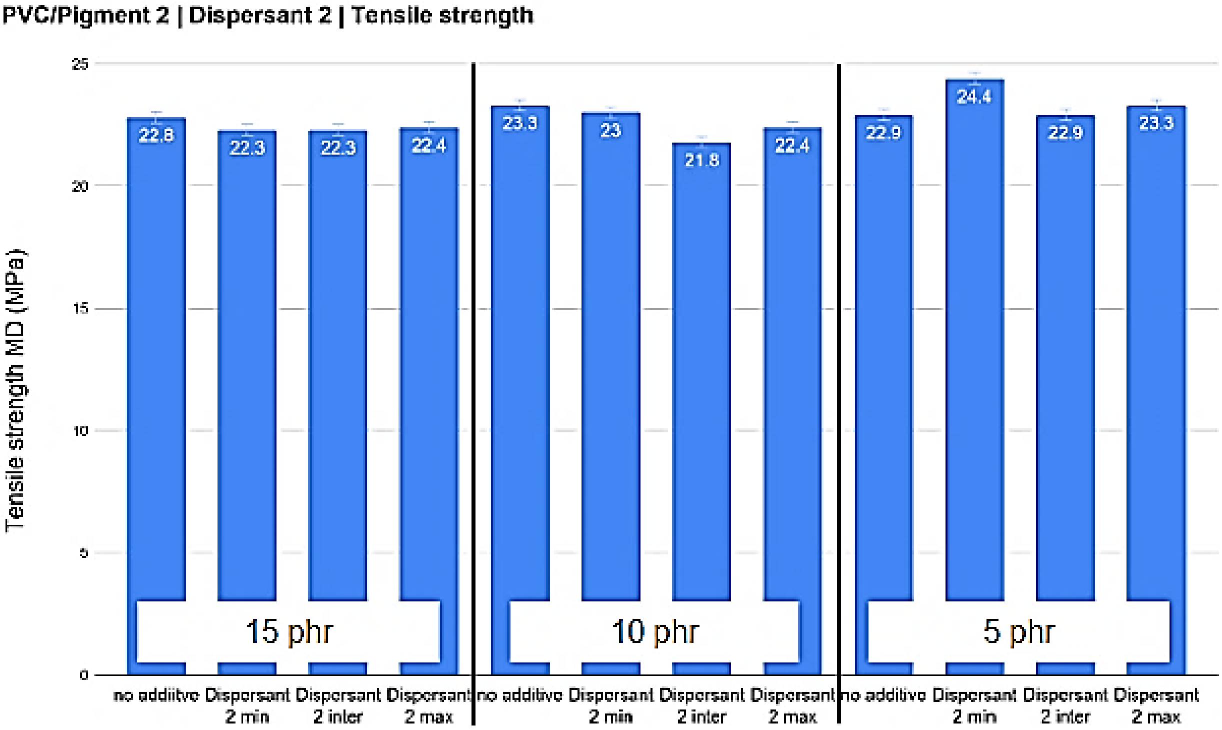


Fig.4.72. Tensile strength results for the three loadings of PVC/pigment 2 films before and after the addition of the three loadings of dispersant 2.

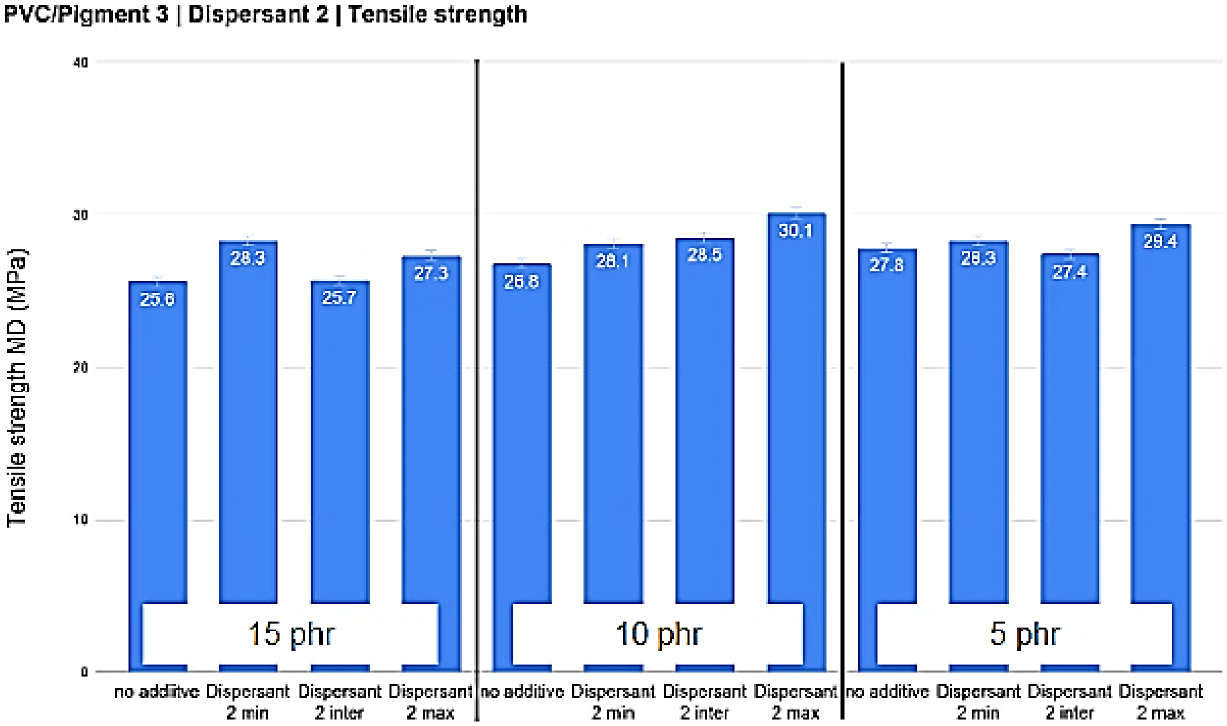


Fig.4.73. Tensile strength results for the three loadings of PVC/pigment 3 films before and after the addition of the three loadings of dispersant 2.

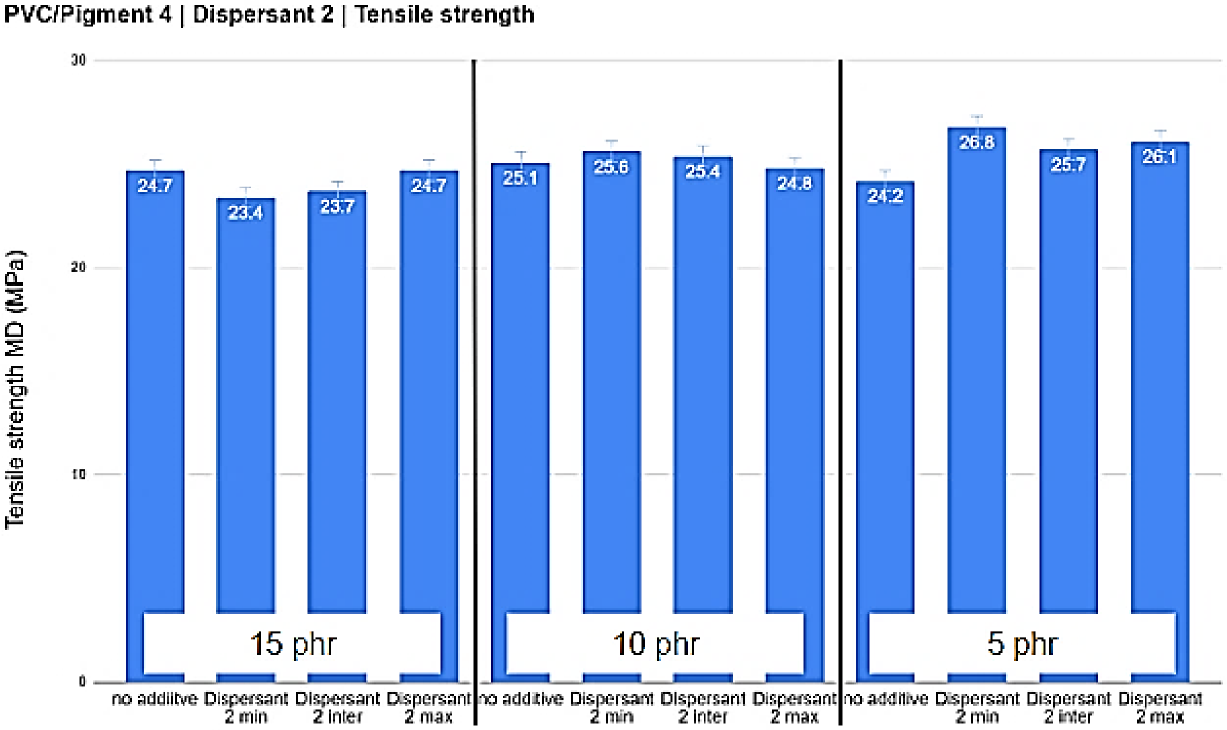


Fig.4.74. Tensile strength results for the three loadings of PVC/pigment 4 films before and after the addition of the three loadings of dispersant 2.

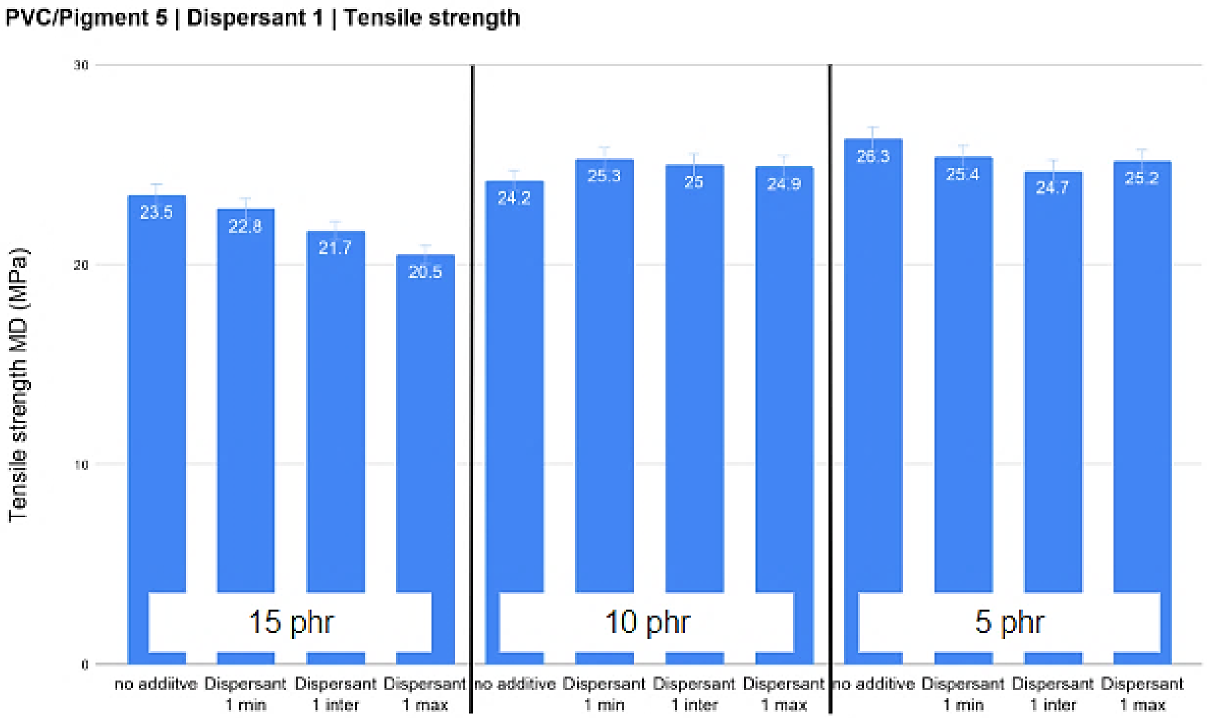


Fig.4.75. Tensile strength results for the three loadings of PVC/pigment 5 films before and after the addition of the three loadings of dispersant 2.

From all the previous figures (fig.4.71 - 4.75), it can be seen that there is a variation in the tensile strength results for the films with the five pigments but the differences in tensile strength and the rest of the mechanical properties is of the order of 0.2-7 MPa. The variation of results makes it difficult to come up with safe conclusions.

4.4.4 Fourier-Transform Infrared Spectroscopy (FTIR) results

The films with the dispersant 2 were also analyzed with the FTIR (fig.4.76).

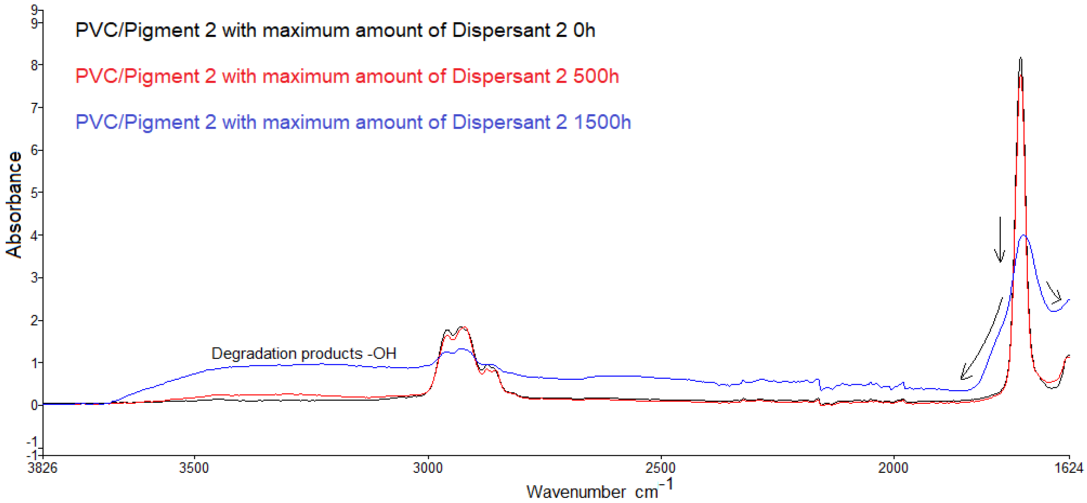


Fig.4.76. FTIR spectra between 1624 and 3926 cm^{-1} for the PVC/pigment 2 film with the maximum amount of dispersant 2 before (black) and after the addition of the additive at 500 h (red) and 1500 h (blue).

Considering the weathering results of the films with dispersant 2, the FTIR analysis of pigment 2 has an expected behavior. Up to 500 h the films show a small amount of degradation products (hydroperoxides). After 1500 h of weathering, degradation products were formed and 49 % $^{w.}/_{w.}$ decrease of plasticizer (1728 cm^{-1}) was observed as well. The same applies for the rest of the metallic pigments. The films with the water scavenger perform better than those with dispersant 1 and dispersant 2.

4.5 Additive 4: Fluorinated MICA

After the casting of the films for the three recommended amounts of fluorinated MICA, an additive agglomeration was observed for the intermediate and maximum amounts. As a result, only the minimum amount was chosen for the multi-analytical investigation.

4.5.1 Weathering results

The weathering results of PVC films with all five pigments after the addition of the minimum amount of fluorinated MICA are demonstrated in figure 4.77.

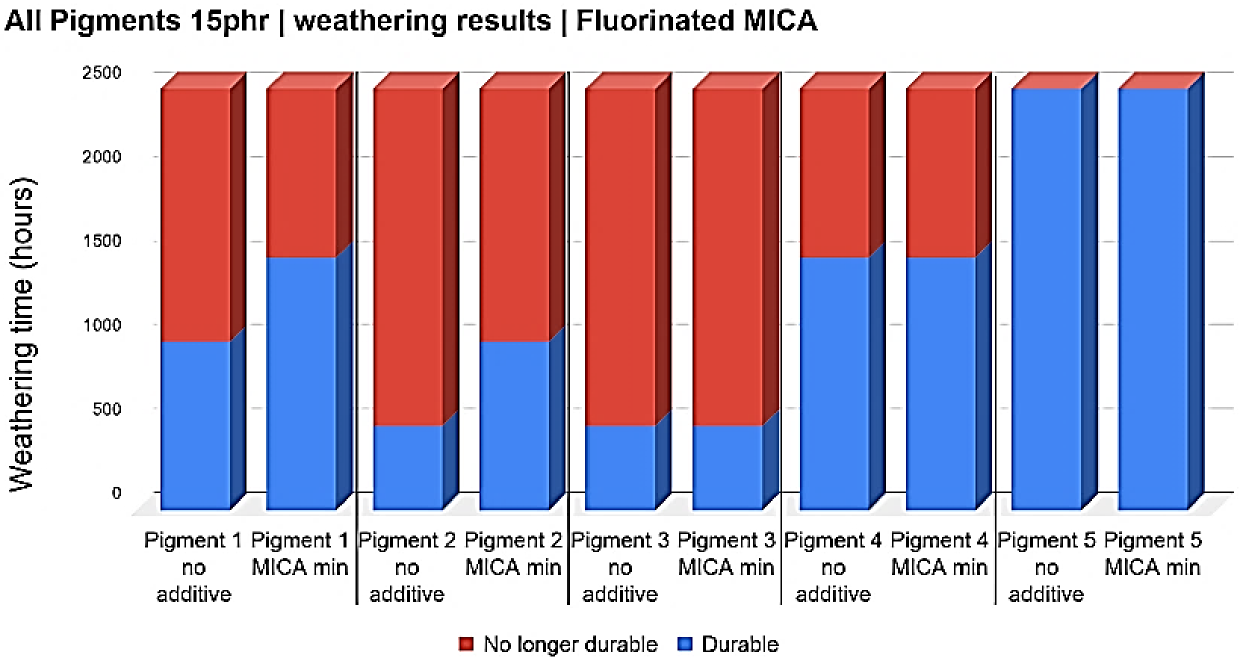


Fig.4.77. Weathering results of PVC/all pigments films with and without the addition of the fluorinated MICA.

After the use of the fluorinated MICA, it can be seen (fig.4.77) that there is a small increase in the weathering durability of the PVC/pigment 1 and PVC/pigment 2 films for the pigment loading of 15 phr. For the PVC/pigment 3 and PVC/pigment 4 films no improvement in durability was observed. No change was also observed for the PVC/pigment 5 films but that was expected since it is the most durable pigment. This additive was chosen for the flakes to exhibit an ability to shear and slide over one another without damaging each other but this is only achieved to a small extent. This factor has a lower effect for the pigments with spherical particles instead of flakes due to the shape of the particles. For spherical particles, it is already easier to slide one over the top of another than flakes.

4.5.2 Gloss and color measurements

The color and gloss of the pigmented PVC films were measured at 0 h and each 500 h for each stage of degradation.

Table 4.30. Gloss measurements at 60° for the 15 phr loading of all Pigments for the minimum loading of fluorinated MICA.

Films	0 h	500 h	1000 h	1500 h	2000 h	2500 h
Pigment 1 15 phr no additive	110 GU	101 GU	101 GU	97.6 GU	97.4 GU	96.4 GU
Pigment 1 15 phr fluorinated MICA	109 GU	92.2 GU	89.3 GU	86.9 GU	86.6 GU	84.5 GU
Pigment 2 15 phr no additive	98.5 GU	93.7 GU	93.7 GU	Fully degraded	Fully degraded	Fully degraded
Pigment 1 15 phr fluorinated MICA	95.2 GU	80.4 GU	79.9 GU	70.2 GU	Fully degraded	Fully degraded
Pigment 3 15 phr no additive	97.0 GU	91.2 GU	Fully degraded	Fully degraded	Fully degraded	Fully degraded
Pigment 3 15 phr fluorinated MICA	94.2 GU	79.3 GU	77.5 GU	Fully degraded	Fully degraded	Fully degraded
Pigment 4 15 phr no additive	101 GU	96.5 GU	93.4 GU	81.0 GU	67.1 GU	62.0 GU
Pigment 4 15 phr fluorinated MICA	96.2 GU	83.3 GU	82.8 GU	76.4 GU	76.4 GU	76 GU
Pigment 5 15 phr no additive	92.6 GU	85.3 GU	83.9 GU	84.0 GU	83.5 GU	82.1 GU
Pigment 5 15 phr fluorinated MICA	89.9 GU	76.4GU	73.5 GU	68.1 GU	68.9 GU	66.4 GU

From the gloss results of table 4.30, it can be seen that the addition of fluorinated MICA causes a decrease of gloss compared to the results of the films with the original formulation and the ones after the addition of the dispersant 1 and 2. The gloss values after the addition of MICA are comparable to the ones from the water scavenger. The dispersion of these white particles cause a more dull appearance of the pigmented films and reduces the gloss.

In addition, the color of the films was analyzed at different reflection angles. The results for the minimum amount of fluorinated MICA are presented in figure 4.78.

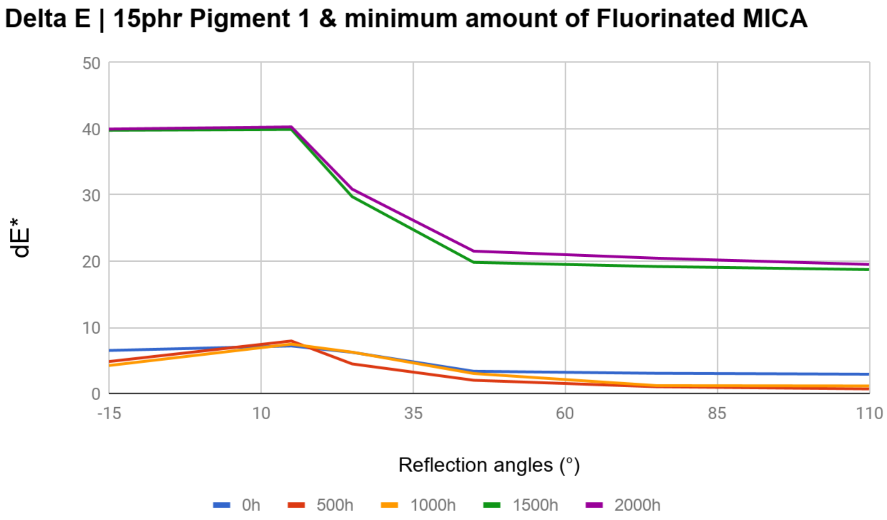


Fig.4.78. Color difference after the addition of fluorinated MICA after each stage of degradation of 15 phr PVC/pigment 1 films.

The color difference (fig.4.78) is stable until 1000 h but after 1500 h it increases similar to the performance after the use of the water scavenger and the same performance was observed for the rest of the metallic pigments.

The appearance of the pigmented films after the use of the fluorinated MICA is similar to the films with the water scavenger considering gloss and color. However, these films do not show the improved weathering performance that the films with the water scavenger have.

As in the case of the water scavenger, the color difference behavior for the pigmented PVC films with the fluorinated MICA is different for each pigment and depends on how each pigment adopts the nature of the added compound.

4.6 Additive 5: Anti-corrosive pigment

After the casting of the films for the three recommended amounts of the Anti-corrosive pigment, like in the case of fluorinated MICA, pigment agglomeration was observed but this time for all the amounts of the additive. As a result, several experiments were done in order to find the optimum amount of the anti-corrosive pigment to be added. The optimum amount was found to be 1 g which corresponds to 1.9 % $^{w.}/_{w.}$ of total formulation.

4.6.1 Weathering results

The weathering results of the PVC/pigment 1 films after the addition of anti-corrosive pigment are demonstrated in figure 4.79.

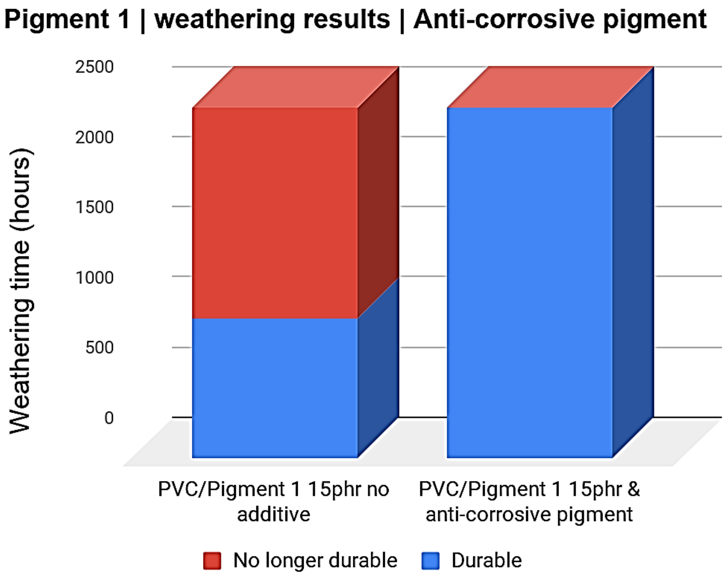


Fig.4.79. Weathering results of PVC/pigment 1 films with and without the addition of the anti-corrosive pigment.

After the use of the anti-corrosive pigment, it can be seen (fig.4.79) that there is a significant increase in the weathering durability of the PVC/pigment 1 films for the pigment loading of 15 phr. The weathering performance is 1500 h-better than the original films before the addition of the anti-corrosive pigment. The anti-corrosive character of this additive increases the overall weathering durability of the system by protecting the sensitive pigment 1 with the Zn (active metal) content of the anti-corrosive pigment conferring sacrificial cathodic protection [51]. The anti-corrosive pigment particles are in contact with the pigment 1 flakes and the Zn (anti-corrosive) protects the titanium and tin (pigment 1), which are already corrosion resistant. If the electrolyte (water) permeates the coating, the metallic pigment dissolves, releasing anions and cations that slow the anodic or cathodic partial reactions.

The electrolyte in the analyzed system is water. Water uptake is aided by a molecular level defect specific to organic coatings commonly known as “pore space”. Pore space generally refers to open space between polymer chains or molecules in the PVC film. This pore space is a natural consequence of PVC structure and is usually unavoidable allowing uptake and transport of water and ions that leads to coating degradation and corrosion.

4.6.2 Gloss and color measurements

The color and gloss of the pigmented PVC films were measured at 0 h and each 500 h for each stage of degradation.

Table 4.31. Gloss measurements at 60º for the 15 phr loading of pigment 1 after the addition of the anti-corrosive pigment.

Films	0 h	500 h	1000 h	1500 h	2000 h	2500 h
Pigment 1 15 phr no additive	110 GU	101 GU	101 GU	97.6 GU	97.4 GU	96.4 GU
Pigment 1 15 phr anti-corrosive pigment	104 GU	99.2 GU	95.8 GU	93.5 GU	81.9 GU	89.9 GU

From the gloss results of table 4.31, it can be seen that the addition of the anti-corrosive pigment shows comparable gloss values to the results of the films with the original formulation and the ones after the addition of the dispersants 1 and 2 and higher than the ones of the films with the water scavenger. The Zn of the anti-corrosive additive results in the gloss retention of the films [52].

In addition, color measurements took place at different reflection angles. The results for the 15 phr PVC/pigment 1 films with the anti-corrosive pigment are presented in figure 4.80.

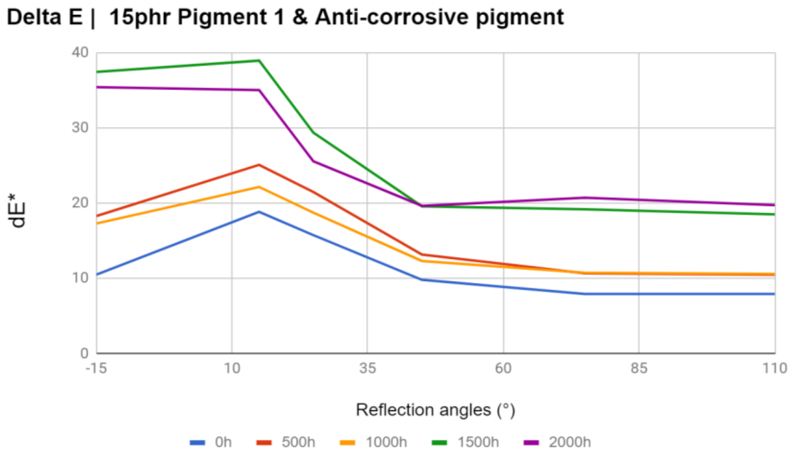


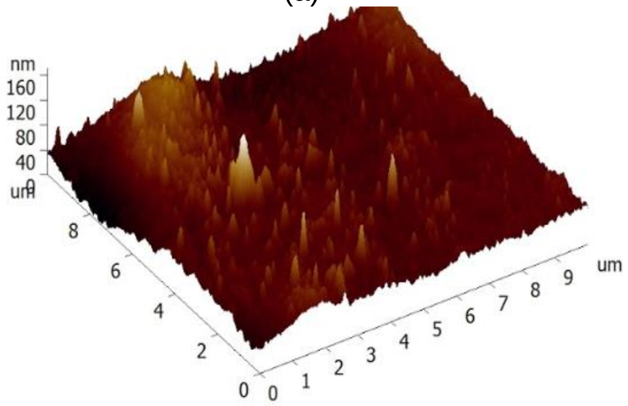
Fig.4.80. Color difference after the addition of the anti-corrosive pigment after each stage of degradation of 15 phr PVC/pigment 1 films.

As can be seen from the color difference results in figure 4.80, the color difference is stable until 1000 h like in the case of fluorinated MICA but after 1500 h, it increases similar to the performance after the use of the water scavenger. A general conclusion is that each one of the five chosen pigments behaves differently after the addition of an additive.

4.6.3 Atomic Force Microscope (AFM) results

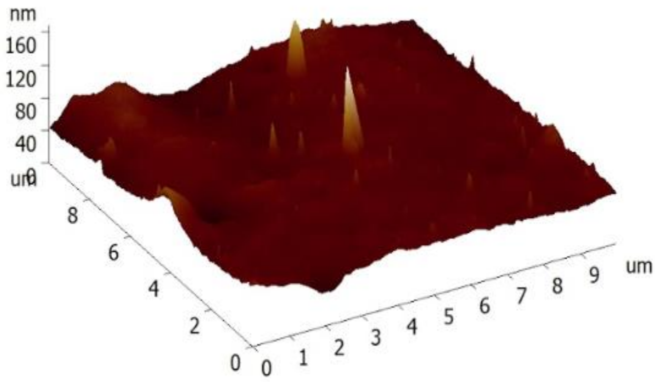
The AFM images taken for the films with the anti-corrosive pigment in order to check the surface morphology of the films before and after the use of the additive are shown in the following figure (fig.4.81). The data refer to unaged films and films after 500 h and 1000 h of weathering for the original films and the 15 phr loading of pigment 1.

(a)



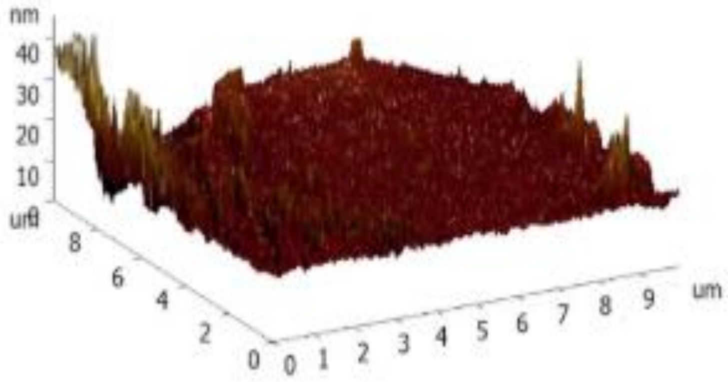
0 hours

(b)



500 hours

(c)



1000 hours

Fig.4.81. 3D AFM results for the PVC/pigment 1 films, (a), (b) and (c) are the 3D results for the films after the addition of the anti-corrosive pigment.

After taking under consideration the AFM results of figure 4.81 compared to the results from the previous additives (water scavenger, dispersant 1, dispersant 2 and fluorinated MICA) used, no considerable change in the surface roughness was observed since the anti-corrosive pigment does not migrate to the films surface. The porosity is not increased as was the case for the water scavenger due to the pore space reduction because of the anti-corrosive pigment. The difference in the surface roughness is presented in table 4.32

Table 4.32. Roughness measurements for the PVC/pigment 1 films before and after the addition of the minimum amount of the water scavenger.

PVC/pigment 1 films	0 h	500 h	1000 h
No additive	7.42 nm	15.4 nm	10.8 nm
Anti-corrosive pigment	10.1 nm	14.3 nm	14.1 nm

The table 4.32 demonstrates the surface roughness values for the films after the addition of the anti-corrosive pigment. The numbers show that the surface roughness of the films is really close to the one of the films of the original formulation and the films with the dispersants and way lower than the respective ones of the films with the water scavenger. The anti-corrosive pigment does not migrate to the surface and has no effect on its characteristics.

4.6.4 Fourier-Transform Infrared Spectroscopy (FTIR) results

As it was done for the previous additives, the FTIR analysis was performed for the films with the Anti-corrosive pigment as well.

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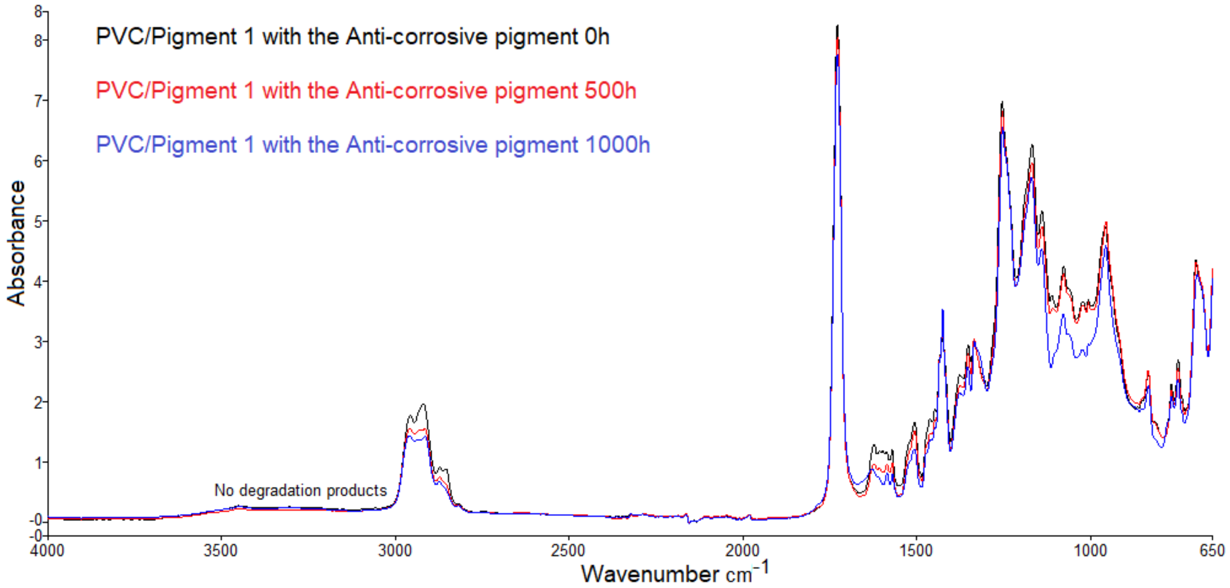


Fig.4.82. FTIR spectra between 650 and 4000 cm^{-1} for the PVC/pigment 1 film with the anti-corrosive pigment before (black) and after the addition of the additive at 500 h (red) and 1500 h (blue).

Considering the weathering results of the films with the anti-corrosive pigment (fig.4.82), the FTIR analysis of pigment 1 has an expected behavior. Up to 1500 h the films do not show degradation products (hydroperoxides). After 1500 h of weathering, a decrease of absorbance intensity (11.3 % $^{w.}/_{w.}$) was observed for some peaks mostly assigned to the plasticizer (1728 cm^{-1}, 2800-3000 cm^{-1}). The use of the anti-corrosive pigment is comparable with the water scavenger and this is also reflected by the FTIR spectra.

4.7 Additive combination (Additive 1 and Additive 2)

After the promising weathering durability results of the films with the water scavenger further investigation was undertaken in order to find a solution for the gloss reduction problem. One strategy was followed; it included a combination of the minimum amount of water scavenger and the maximum amount of dispersant 1. The films with the minimum amount of water scavenger showed the least loss of gloss among all three additive loadings and the films with the maximum amount of dispersant 1 showed comparable gloss values with the films of the original formulation.

4.7.1 Weathering results

The weathering results of the PVC/pigment 1 films after the addition of the combination of the minimum amount of water scavenger and the maximum amount of dispersant 1 are shown in figure 4.83.

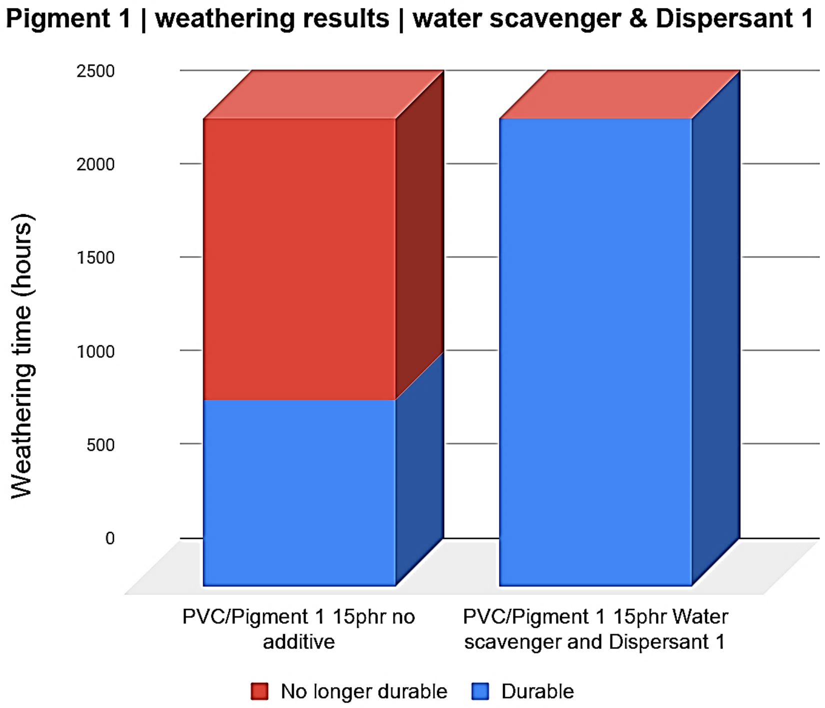


Fig.4.83. Weathering results of PVC/pigment 1 films with and without the addition of the minimum amount of the water scavenger and the maximum amount of dispersant 1.

After the use of the combination of the two additives, it can be seen (fig.4.83) that there is a significant increase in the weathering durability of the PVC/pigment 1 original film for the pigment loading of 15 phr. The weathering performance is 1500 h-better than the films before the addition of the combination of the two additives. The combination of additives keeps the preferable weathering durability of the water scavenger.

4.7.2 Gloss and color measurements

The color and gloss of the pigmented PVC films were measured at 0 h and each 500 h for each stage of degradation.

Table 4.33. Gloss measurements at 60º for the 15 phr loading of pigment 1 after the addition of the combination of the two additives.

Films	0 h	500 h	1000 h	1500 h	2000 h	2500 h
Pigment 1 15 phr no additive	110 GU	101 GU	101 GU	97.6 GU	97.4 GU	96.4 GU
Pigment 1 15 phr water scavenger & dispersant 1	103 GU	97.8 GU	96.6 GU	95.8 GU	71.1 GU	70.9 GU

From the gloss results of table 4.33, it can be seen that the films with the combination of the two additives show comparable gloss values to the results of the films with the original formulation and higher than the ones of the films with the water scavenger until 1500 h of artificial weathering. After 1500 h, the dispersant 1 that retains the gloss is washed off and as a result a considerable loss of gloss was observed.

In addition, color measurements took place at different reflection angles. The results for the 15 phr PVC/pigment 1 films with the combination of the two additives are presented in figure 4.84.

As can be seen from the color difference results in figure 4.84, the color difference is stable until 1000 h as in the case of fluorinated MICA, but after 1500 h it increases. Once more, the color difference is a factor that changes for each pigment and each additive or combination of additives used.

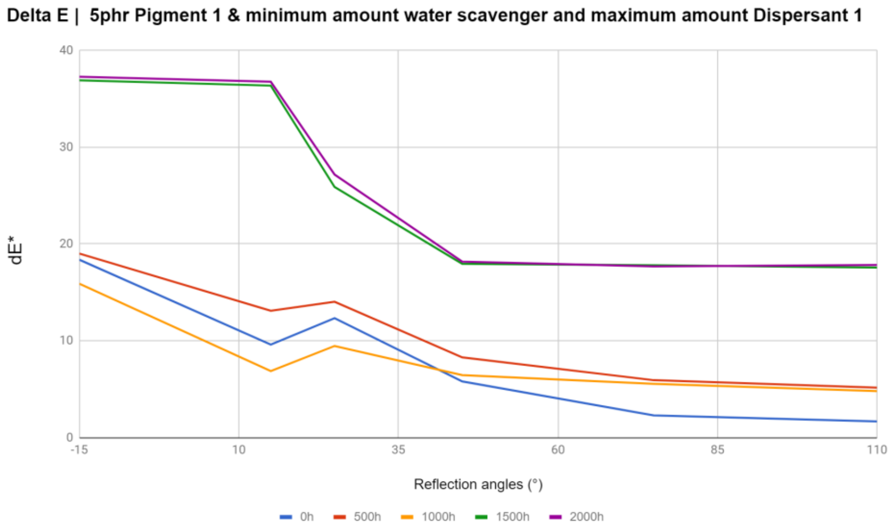
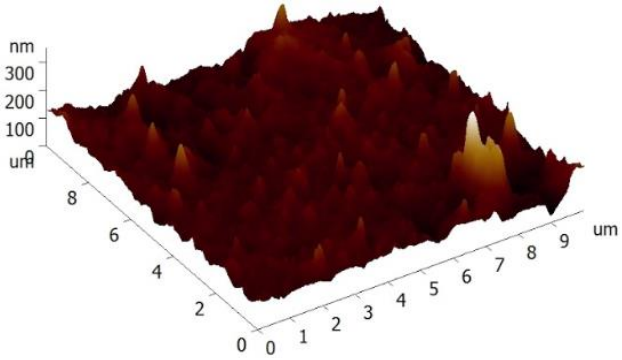


Fig.4.84. Color difference after the addition of the combination of the two additives after each stage of degradation of 15 phr PVC/pigment 1 films.

4.7.3 Atomic Force Microscope (AFM) results

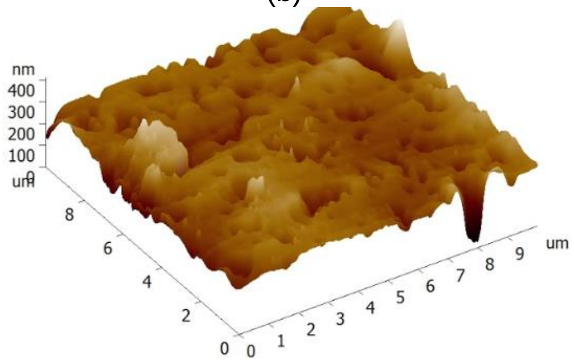
The AFM images taken for the films with the combination of the two additives in order to check the surface morphology of the films before and after the use of the additive are shown in the following figures. The data refer to unaged films and films after 500 h and 1000 h of weathering for the original films and the 15 phr of pigment 1.

(a)



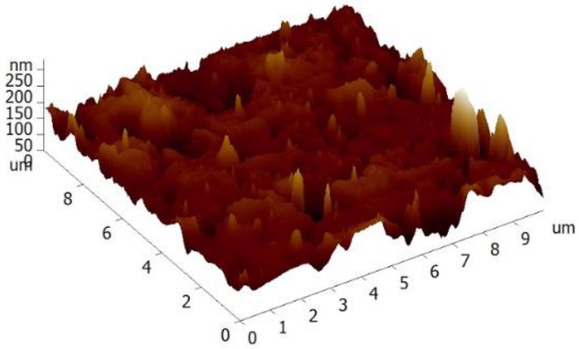
0 hours

(b)



500 hours

(c)



1000 hours

Fig.4.85. 3D AFM results for the PVC/pigment 1 films, (a), (b) and (c) are the 3D results for the films after the addition of the combination of the two additives.

After taking under consideration the AFM results of figure 4.85, compared to the results from the previous additives used, a considerable change in height was observed and after taking into consideration the results of the films with dispersant 1, it can be assumed that it migrates to the films surface due to its lower density and as a result a smoother surface was observed. The difference in the surface roughness is presented in table 4.34.

Table 4.34. Roughness measurements for the PVC/pigment 1 films before and after the addition of the combination of the two additives.

PVC/pigment 1 films	0 h	500 h	1000 h
No additive	7.42 nm	15.4 nm	10.8 nm
water scavenger & dispersant 1	8.4 nm	12.3 nm	17.7 nm

The data in table 4.34 shows the surface roughness values for the films after the addition of the combination of the two additives. The numbers show that the surface roughness of the films is really close to the one of the films of the original formulation and the films with the dispersants and way lower than the respective ones of the films with the water scavenger. A small increase of the order of 7.1 nm was observed after 1000 h. The migration of dispersant 1 to the surface results in the smoother surface of the films and as a result that enhanced the gloss retention as mentioned before.

4.7.4 Fourier-Transform Infrared Spectroscopy (FTIR) results

FTIR analysis was performed for the films with the combination of the two additives.

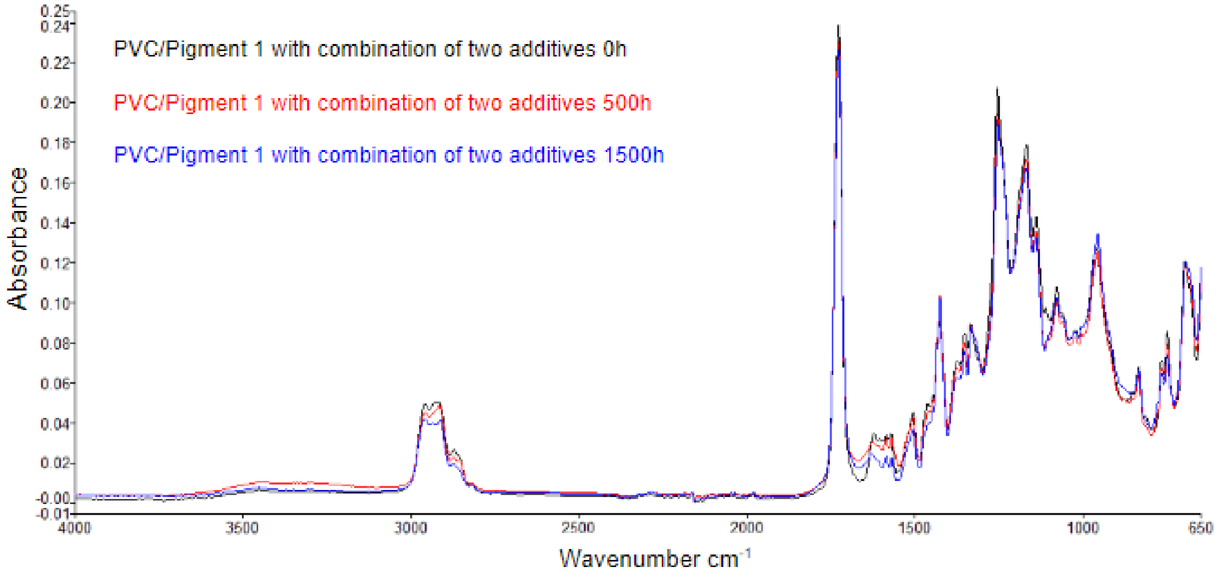


Fig.4.86. FTIR spectra between 1500 and 4000 cm^{-1} for the PVC/pigment 1 film with the combination of additives before (black) and after the addition of the additive at 500 h (red) and 1500 h (blue).

Considering the weathering results of the films with the combination of additives, the FTIR analysis of pigment 1 has an expected behavior (fig.4.86). Up to 1500 h the films do not show degradation products (hydroperoxides). After 1500 h of weathering, a decrease of absorbance intensity was observed for some peaks mostly assigned to the plasticizer. This behavior is better from the results of the films with dispersant 1 and this is also shown in the FTIR spectra. The dispersant 1 migrates to the surface as it was shown in the AFM images and though the FTIR analysis. Dispersant 1 migrates to the surface and no peak is now detectable at 1541 cm^{-1} (fig.4.86) that was assigned to the CaO-based water scavenger due to the depth-of-analysis limit of the FTIR method.

4.8 Chapter summary

The adhesive on the back of the film supports the film and offers stability instead of having a negative effect on durability. The flakes/particles close to the surface (protruding from the film) or the edges of the films when damaged, they can cause the initiation of the films degradation if combined with water retention on the films surface. The use of the five chosen additives to improve that showed a higher weathering durability for most of the films than the original formulations. Films with some of them performed better than others and a combination of additives was also tested and showed promising results.

Regarding durability, the films with the water scavenger performed better than the films of the original formulation. The main drawbacks of the films with the water scavenger were the gloss reduction after the first stage of degradation of the order of ~10 GU and the increased color difference compared to the original films. This was attributed to the fact that the water scavenger migrates to the surface and as a result, it increases the porosity and the roughness of the surface.

A variation of weathering results was observed after the use of the dispersants 1 and 2. Despite the variation of the results, the weathering durability was worse than that of the films with the water scavenger. This variation was also observed in the color difference compared to the original films. The problem with the gloss of the films with the water scavenger is not an issue for the films with the two dispersants. These additives also migrate to the surface but they do not increase the surface roughness, they decrease it.

The films with the fluorinated MICA showed the worse weathering performance among the films with the rest of the additives. The gloss reduction and the color difference is also an issue with results comparable to those of the films with the water scavenger.

The use of the anti-corrosive pigment inside the film formulations showed an improved weathering durability comparable to that of the films with the water scavenger. Regarding gloss, the films with the anti-corrosive pigment show lower (6-7 GU) gloss values than the original films but higher than the films with the water scavenger. The main drawbacks of the films with the anti-corrosive additive is the difference in color compared to the original films and the difficulties during the paste preparation.

The combination of the water scavenger with dispersant 1 showed a promising weathering performance like in the case of the water scavenger/films and gloss retention like in the case of dispersant 1/films. The best functionalities of the two additives were combined in the end. The dispersant 1 migrates to the surface and keeps the surface roughness low and the water scavenger prevents the formation of degradation products that cause the PVC autocatalytic degradation process.

5 Conclusions

5.1 General conclusion

This aim of the work reported in this thesis was to study the artificial ageing performance of PVC films containing metallic pigments and how to improve them. Among the three components (PVC organosol, metallic pigments and adhesive), the one that has a minor effect on the degradation process is the adhesive. Thus, the degradation of the films is mostly related with the PVC interaction with the implemented metallic pigments.

The pigments with the different surface treatments, sizes and shapes tested showed that these three factors play an important role in the PVC degradation process. Shape and size are equally significant for the degradation process since small particles can be better distributed inside the polymer matrix than bigger particles and it is less likely for them to stack together of damage one another. The shape also plays an important role considering that pigments with flakes can be damaged more easily than spherical particles and due to their edges it is more likely that they protrude from the surface of the films compared to the case of spherical particles. The most important of these factors is the surface treatment since some metals are more durable to weathering than others.

Regarding the surface treatment of the pigments, the use of an anti-corrosive pigment as an additive to offer cathodic protection to the sensitive metal oxides of the surface of the pigments had promising results (3 times better durability than the original films). Considering that, it becomes clear that the interaction of the treatment of the pigment with the other components of the formulation is a key to improve the overall durability and more research related to that needs to be done.

The methodology to minimize the amount of water on the surface and inside the film by the use of a water scavenger confirmed the importance of water in the degradation mechanism of PVC. The water retention on the edges of the films, because of flakes/particles protruding from it, causes the localized corrosion of the metallic treatment of the particles and that results in additional steps in the degradation of PVC. The weathering durability of the pigmented films after the limitation of the water effect becomes in some cases more than three times better than before.

It was proven that the water tunnelling between flakes/particles does not include an amount of water large enough to significantly affect the durability of the films. Even if the distance between the flakes is increased to minimize water tunnelling by the use of dispersants or fluorinated MICA, the durability of the films was the same or maximum 500 h better than before.

The surface characteristics of the films (roughness, porosity) have a very strong influence on the optical appearance of the pigmented PVC films considering that increased porosity and roughness cause variation of the color and low gloss values (<85 GU). It is true that PVC is a porous material but different additives that migrate to the surface have different effects on the surface of the films.

UV radiation is also an important factor in the degradation of PVC, however the effect of water was a topic that was not widely covered in the literature and this study offers a wide analysis to show that the influence of water on the degradation of PVC in conjunction with the effect of metallic pigments needs more attention and further investigation in the future.

5.2 Future work recommendations

In this research project, aging and multiple analytical techniques were introduced to establish the influence of photo-oxidative degradation on the pigmented plasticized PVC films. After the analysis of the studied samples, it is clear that an additional research or a different approach is needed to complete the missing information.

In future work, further investigation focused on the effects of the water scavenger and anticorrosive pigment can be undertaken or even a combination of these additives can be studied in order to achieve even better weathering durability. Firstly, the so-far artificial weathering results, were not sufficient for the extended and detailed analysis of the degradation pattern, of the investigated pigmented plasticized PVC films despite the fact that the results after the use of the water scavenger and the anti-corrosive pigment show a promising outcome. It was not possible to predict the performance of the analyzed samples after further weathering, and in which direction the degradation could have transpired. It is necessary, to continue the accelerated aging process to gain more data, which would make it possible to complete the evaluation of the degradation pattern.

Moreover, lower amounts of water scavenger can be used in order to decrease the loss of gloss problem but in combination with high weathering durability. For the anti-corrosive pigment, a better formulation preparation is needed in order to achieve higher loading of this additive that may further increase the weathering durability of the pigmented PVC films.

Furthermore, accelerated UV weathering is a method that could give important results in a short amount of time and accelerate the progress of the experiment. Another important weathering technique that could be used to check the real water resistance of the plasticized films is to use artificial weathering not under central Europe conditions but under conditions with higher moisture like northern America.

Additionally, the potential of FTIR spectroscopy which was used for the characterization of polymers can be significantly enhanced when combined with the other complementary spectroscopic techniques, such as Raman spectroscopy. The application of Raman, in the identification and monitoring of the metallic pigments, would be a valuable contribution to the analysis of the occurring degradation pattern in the researched PVC films.

Lastly, as the PVC/pigments films degradation process proceeds, the interfacial impedance falls to levels that can be effectively measured by electrochemical impedance spectroscopy (EIS). For this reason, EIS could be particularly effective for quantitatively evaluating the progress of the films degradation and metallic corrosion that occurs as a result.

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