Weathering of aromatic polyester coatings

Malanowski, P.

DOI: 10.6100/IR639672

Published: 01/01/2009

Citation for published version (APA):
Weathering of aromatic polyester coatings

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de Rector Magnificus, prof.dr.ir. C.J. van Duijn, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op maandag 26 januari 2009 om 16.00 uur

door

Przemysław Malanowski

geboren te Golub-Dobrzyń, Polen
Dit proefschrift is goedgekeurd door de promotoren:

prof.dr. R.A.T.M. van Benthem en prof.dr. G. de With

Copromotor:
dr. J. Laven
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General Introduction
1.1 Introduction

Man-made organic coatings are indispensable for enhancing the quality of human life. Such organic coatings are thin, often pigmented layers of a polymer network applied on a substrate. The main part of an organic coating is the polymeric binder which consists of a polymer having reactive groups (resin) and often a crosslinker. The most commonly used resins in coating technology are acrylics, polyesters, alkyds and epoxides\cite{1,2}. Coatings are mainly used for protection and decoration of goods made of wood, metal and plastic. They can be applied indoors (furniture, interior of buildings, electronic devices, etc.) and outdoors (cars, airplanes, bridges, exterior of buildings, etc.). One of the essential characteristics of a coating is its resistance to the influence of the environment in which it is used. This is especially important when coatings are used outdoors. In this case resistance to the environment can be defined as a “weathering durability”.

In outdoor conditions, many factors simultaneously influence the lifetime of polymeric coatings. The combined action of UV radiation, heat and moisture can cause changes in the chemical structure of the polymers\cite{3-6}. Degradation of polymers outdoors is usually referred to as “weathering”. UV radiation is known to be the dominant factor affecting durability of polymeric coatings. Degradation caused by UV radiation, is usually named “photodegradation”. The chemical reactions taking place such as chain scission, crosslinking and oxidation influence the physical properties of the coatings\cite{7-10} and ultimately may lead to cracking, gloss loss, blistering and delamination\cite{11,12}. Such a degraded coating can not maintain its protective and decorative functions anymore. Study of the photodegradation phenomena is essential to better understand and subsequently improve the weathering stability of polymeric coatings.

1.2 Mechanism of photodegradation

According to Rabek “Photodegradation (chain scission and/or crosslinking) occurs by the activation of the polymer macromolecule provided by absorption of a photon of light by the polymer”\cite{3}. A polymer macromolecule can be activated by light to its excited singlet ($S^*$) and/or triplet ($T^*$) states. If the energy of the absorbed UV light is sufficiently high (at least higher than the bond energy) the chemical bond may break down (photolysis) and two radicals are formed. In an inert atmosphere,
radicals can either recombine or abstract hydrogen from the polymer backbone. In the presence of oxygen, *photooxidation* takes place. The latter process consists of three main steps. (1) The *Initiation step* involves free radical formation. In the (2) *Propagation step*, the free polymer radicals react with oxygen. Polymer oxy- and peroxy-radicals as well as polymer secondary radicals are formed. Rearrangements and chain scissions can take place. The last step (3) *Termination* involves recombination of different radicals. These three steps will be discussed in detail below.

### 1.2.1 Initiation

Initiation takes place as a consequence of UV light absorption, resulting in the dissociation of a covalent chemical bond of the polymer P:

\[
P - P \xrightarrow{h\nu} P^\cdot + P^\cdot \quad (1.1)
\]

\[
PH \xrightarrow{h\nu} P^\cdot + H^\cdot \quad (1.2)
\]

The initiation step depends on the chemical structure of the polymer. In this respect polymers can be divided in two main groups: those which do contain chromophore groups in their repeating units (for example aromatic polyesters) and these ones which do not (for example polyolefins). In the first group, the initiation step can take place in each repeating unit. As far as the second group of polymers is concerned the initiation step can occur due to different mechanisms. For instance, the polymer can contain structural defects (carbonyls, double bonds, hydroperoxide), which find their origin in their synthesis or processing. These groups can act as chromophores and can be the source of the initiation process. Another reason for the initiation of the photodegradation can be impurities (denoted RH) like catalysts, initiators and solvent residues, present in the polymer. Such impurities can absorb UV light and as a consequence radicals are formed (1.3). These radicals can abstract a hydrogen atom from the polymer backbone (1.4) and in this way initiate photodegradation of the polymer. For the sake of shortness, in this work the hydrogen atom abstraction phenomenon will be denoted as hydrogen abstraction.

\[
RH \xrightarrow{h\nu} R^\cdot + H^\cdot \quad (1.3)
\]

\[
R^\cdot + PH \rightarrow P^\cdot + RH \quad (1.4)
\]
A common chromophore, which often participates in the initiation of photodegradation, is the carbonyl (C=O) group, either present as a ketone, aldehyde or ester group. This group can be present in the polymer structure both as a part of the repeating unit (polyester) or as a defect (polyolefins). It can also be part of an impurity. Absorption of UV light by molecules containing carbonyl group leads mainly to two reactions types, the Norrish reaction of type I and II.

- The Norrish type I reaction is a photocleavage of the bond in $\alpha$-position to the carbonyl generating two radicals: acyl and alkyl. The acyl radical can subsequently undergo decarbonylation:

\[
\text{hv} \quad \text{CH}_2 \text{CCH}_2 \text{C} \text{CH}_2 \text{O} + \text{CH}_3 \text{CH}_2 \text{O} \rightarrow \text{CH}_2 \text{C}^\cdot \text{CH}_2 \text{O} + \text{CH}_2 \text{CO}_2 \text{H}
\]  

- The Norrish type II reaction is a non-radical intramolecular process, in which the hydrogen is transferred from the $\gamma$-position to the oxygen of the carbonyl. This results in decomposition into a molecule with an unsaturated end group and a molecule that contains, after enol/keto tautomerization, a carbonyl end group:

\[
\text{CH}_2 \text{CH}_2 \text{O} + \text{CH}_3 \text{CH}_2 \text{O} \rightarrow \text{CH}_2 = \text{CH} + \text{CH}_2 = \text{CHO}
\]
1.2.2 Propagation

The most important process in the propagation step is the reaction of a polymer alkyl radical with oxygen which results in polymer peroxy radical formation:

\[ P' + O_2 \rightarrow \text{POO}^* \]  \hspace{1cm} (1.7)

In the next step a polymer peroxy radical abstracts hydrogen, giving rise to a polymer hydroperoxide and a new polymer alkyl radical:

\[ \text{POO}^* + \text{PH} \rightarrow \text{POOH} + P' \]  \hspace{1cm} (1.8)

Decomposition of hydroperoxide is presumed to take place as a result of energy transfer from an excited carbonyl or aromatic group (donor D*) to a hydroperoxide group (acceptor). This leads to polymer oxy and hydroxyl radicals:

\[ \text{D} \xrightarrow{hv} \text{D}^* \]  \hspace{1cm} (1.9)

\[ \text{D}^* + \text{POOH} \rightarrow \text{D} + \text{POOH}^* \]  \hspace{1cm} (1.10)

\[ \text{POOH}^* \rightarrow \text{PO}^* + \cdot \text{OH} \]  \hspace{1cm} (1.11)

Each of these radicals can initiate a chain of reactions (1.12, 1.13). A polymer oxy radical can undergo a number of different reactions. One of them is hydrogen abstraction (1.12).

\[ \text{PO}^* + \text{PH} \rightarrow \text{POH} + P' \]  \hspace{1cm} (1.12)

\[ \cdot \text{OH} + \text{PH} \rightarrow P' + \text{H}_2\text{O} \]  \hspace{1cm} (1.13)

If the oxy radical will be formed on the polymer chain, β-scission can occur, resulting in a carbonyl end group and a polymer alkyl radical:

\[ \begin{array}{c}
\text{O} \\
\text{O}
\end{array} \quad \begin{array}{c}
\text{CH}_2
\end{array} \quad \begin{array}{c}
\text{CH}\end{array} \quad \begin{array}{c}
\text{CH}_2
\end{array} \quad \xrightarrow{\text{O}} \quad \begin{array}{c}
\text{CH}_2
\end{array} \quad \begin{array}{c}
\text{CH}\end{array} \quad \begin{array}{c}
\cdot \text{CH}_2
\end{array} \quad \begin{array}{c}
\text{O}
\end{array} \quad \begin{array}{c}
\text{O}
\end{array}
\]  \hspace{1cm} (1.14)
An interesting phenomenon is the „cage effect”. Alkoxy and hydroxyl radicals created during decomposition of hydroperoxide can not easily escape from the cage formed by entangled macromolecules. Thus, a reaction with a neighboring point of the polymer chain is very probable. Usually it leads to the formation of the carbonyl group and water.

\[
\text{C} - \text{O} + \text{H}_2\text{O} \quad \text{(1.15)}
\]

1.2.3 Termination

The termination step can be one of a number of recombination steps of different radicals:

\[
P^\cdot + P^\cdot \rightarrow \text{P-P} \quad \text{(1.16)}
\]

\[
P^\cdot + \text{PO}^\cdot \rightarrow \text{POP} \quad \text{(1.17)}
\]

\[
P^\cdot + \text{POO}^\cdot \rightarrow \text{POOP} \quad \text{(1.18)}
\]

\[
\text{PO}^\cdot + \text{PO}^\cdot \rightarrow \text{POOP} \quad \text{(1.19)}
\]

\[
P^\cdot + \cdot\text{OH} \rightarrow \text{POH} \quad \text{(1.20)}
\]

Recombination of radicals may lead both to linear (1.21) and to crosslinked (1.22-1.23) structures. The crosslinking can have a chain coupling (1.22) or a grafting character (1.23). The crosslinking due to the chain coupling leads, in the initial stage, to larger but still soluble molecules (sol, 1.22A). Extensive crosslinking due to this mechanism leads to insoluble material (gel, 1.22B) formation. The crosslinking due to grafting (1.23) does not lead to insoluble material.
1.3 Photostabilization of polymers

The compounds which are used for the retardation and elimination of photochemical processes in polymers are usually referred to as “stabilizers”\cite{5,13,14}. They can be classified according to the mechanism of stabilization: UV screening, UV absorption, exited state deactivation (quenching) and free radical scavenging.

UV screeners protect a polymer by reflecting the harmful UV light. Carbon black, titanium dioxide TiO$_2$, iron oxides (Fe$_2$O$_3$, Fe$_3$O$_4$), chromic (III) oxide (Cr$_2$O$_3$) and zinc oxide (ZnO) are examples of UV screeners\cite{13}.

The mechanism of stabilization by UV absorbers involves absorption of UV light and a subsequent quick dissipation of absorbed energy in the form of harmless long wavelength radiation. In order to be effective, these stabilizers should have high absorption coefficients in the range of 290 – 400 nm. Since each UV absorber has its specific absorption spectrum, different combinations of them can be used for optimal efficiency. Derivatives of hydroxyphenylbenzotriazole, hydroxyphenylbenzophenone and hydroxyphenyl-s-triazines are used as UV absorbers.

Deactivation or quenching of excited states (singlet and/or triplet) of chromophoric groups can also avoid bond scission. Usually the energy of the excited
state is transferred to a quencher molecule which may dissipate the energy to a harmless form. Transition metal chelates can be used as quenchers[14].

Finally, radical scavengers can effectively stabilize polymers. The main function of these stabilisers is to inhibit the propagation step in the photooxidation process. The most often used type of radical scavengers is HALS (Hindered Amine Light Stabilizer). The mechanism of stabilization by HALS is described by the Denisov cycle (1.24 and 1.25). The active species in this process is a nitroxyl radical which is formed from the corresponding hindered free amine during degradation. A nitroxyl radical can recombine with an alkyl radical and form an alkylloxyamine (1.24). In the next step the alkylloxyamine may scavenge a peroxy radical (1.25). In this way the active species – the nitroxyl radical – is regenerated and can operate again[15].

\[
\begin{align*}
N\text{O}^* + P^* & \rightarrow N\text{O} - P \\
N\text{O} - P + POO^* & \rightarrow N\text{O}^* + POOP
\end{align*}
\]

Application of stabilizers can significantly extend the life time of a polymer material. The mechanisms of photostabilization are directly related to the mechanisms of photodegradation of the polymers[13]. Therefore, the effective stabilization of any particular polymer requires understanding of its photodegradation mechanism. The focus of these studies was to investigate the photodegradation mechanism of poly(neopentyl phthalate) polyesters on the molecular level. These polyesters are in fact semi-aromatic, however we will refer to them in short as aromatic. The effect of stabilizers on the durability was not studied in this work.

1.4 Photodegradation as a surface effect

Photodegradation is known to be a “surface effect” which implies that most of the photodegradation products are concentrated at the surface of UV irradiated material[16,17]. This phenomenon is mainly caused by two factors: (1) a high level of UV absorption of polymer and (2) a limited diffusion of oxygen into the polymer.

The combination of the UV absorption spectrum of the polymer and the spectral distribution of the irradiated light determines the penetration depth of the radiation and subsequently the distribution of degradation products throughout the
coating. This phenomenon can be explained using Beer-Lambert’s law\[^3\], which describes the absorbance \((A)\) by \(A = \log_{10}(I_0/I) = \alpha L\) where \(I_0\) is the intensity of the light before it enters the material and \(I\) is the intensity of light which passed through the material (Figure 1.1). The absorbance can thus be expressed as a product of the thickness of the material \(L\) and the absorption coefficient \(\alpha\), which is a material property that defines the extent to which a material absorbs light. In order to evaluate how much light is locally absorbed in a thin sheet within the coating, Beer-Lambert’s law can be interpreted in such a way that \(L\) now is the thickness of that sheet and \(I_0\) and \(I\) are the intensities of the light that enters and exits that sheet. A typical example is given in Figure 1.2. Real coatings have an absorption coefficient that is heavily dependent on the wavelength of the light. Thus, the light penetration also depends on the wavelength \(\lambda\) of the light: \(\log_{10}(I_0(\lambda)/I(\lambda)) = \alpha(\lambda)L\).

**Figure 1.1.** Schematic representation of Beer-Lambert’s law.

**Figure 1.2.** Schematic representation of the depth penetration of the light through an absorbing polymer.
The diffusion of oxygen is another factor which may influence the surface effect during ageing. Due to a limited diffusivity the local oxygen concentration deeper in the film may be appreciably lower than at the surface as schematically shown in Figure 1.3. Both diffusivity and solubility of oxygen depend on the chemical structure and morphology (amorphous, crystalline) of the polymer. A limited diffusion of oxygen into the polymer may restrict the photooxidation processes to a surface layer. It has to be noted that during photooxidation radicals, which are formed at the surface of the sample, react with oxygen. Accordingly, part of the oxygen is trapped at the surface which may even cause a more pronounced oxygen starvation in the bulk of the aged material than due to diffusion alone.

![Figure 1.3. Schematic representation of oxygen depletion throughout the polymer.](image)

### 1.5 Exposure conditions

#### 1.5.1 Outdoor weathering

Both for the service life time prediction of coatings and for investigating the mechanism of degradation, weathering tests are needed. Performing such tests is not a trivial task. The most suitable method is exposing polymers in conditions as close as possible to service environment\[^4\]. Unfortunately ageing in outdoor conditions usually takes many years. To some extent this problem can be overcome by using accelerated tests in the laboratory. However, the correlation between results obtained in outdoor and laboratory tests results in numerous problems\[^{18,19}\], as will be discussed in the next paragraph. Acceleration of the weathering processes can also be achieved outdoors. One way is to expose samples in extreme climates, where a high intensity of natural sun light is provided over the whole year (for example, Arizona is known as a hot dry and Florida as a hot humid climate). Results can be correlated, be it far from
perfect to the results obtained in any other natural service environment. Alternatively, acceleration of weathering outdoors can be achieved by increasing the intensity of light via focusing using mirrors. In addition to long exposure times, the major drawback of testing polymers outdoors is the lack of reproducibility and repeatability of the results. The climate at almost all locations shows variations every year. Thus, the results obtained at a particular location may significantly differ between years \(^{[20]}\). The conditions (spectral distribution and intensity of light, temperature, humidity, rainfall) of the outdoor exposure can not be controlled at all, but can be monitored and this is required for a proper interpretation of the results.

1.5.2 Laboratory weathering

As mentioned above, in order to accelerate weathering processes, laboratory tests are often conducted. In this case acceleration of weathering is achieved by using special chambers which are supposed to mimic outdoor conditions to a certain extent \(^{[3]}\). Laboratory testing in a short period of time can provide information on the stability of polymer. However, it is generally accepted that the higher the acceleration of weathering, the lower the correlation to outdoor exposure \(^{[4,6]}\). The main factor affecting weathering durability of polymers is UV radiation which induces photodegradation. Chambers used for laboratory testing (for example, Suntest XXL+, QUV, UVACUBE) are equipped with lamps (mercury, xenon, fluorescent) which provide UV light. The shorter the wavelength, the higher the energy of light. Therefore higher acceleration of photodegradation can be achieved by using lamps which provide short wavelength UV ($\lambda < 300$ nm). It has to be noted that the spectral distribution of natural sun light starts at about 300 nm. The presence of UV light with $\lambda < 300$ nm can strongly accelerate the kinetics of photodegradation but it may also initiate processes which will not take place in outdoor conditions \(^{[4]}\). In order to avoid these problems light provided by different lamps can be filtered using borosilicate type filters. For instance, the spectral distribution of xenon light filtered with borosilicate type filters resembles the spectral distribution of natural sun light. In this case acceleration of photodegradation can be achieved by using a higher intensity of light. Still, attention has to be paid when choosing the intensity. High intensity UV light for a short period of time can cause degradation extending into deep layers of the polymer, but such a short interval of time could be insufficient for oxygen diffusion.
(needed for photooxidation). In this case, reactions can take place in deeper layers of the material which probably will not occur in outdoor conditions or vice versa.

Acceleration of the weathering process can also be achieved by increased temperature. Usually laboratory weathering tests are performed at elevated temperatures. Unfortunately the increased temperature can influence the chemical pathway of the photodegradation processes\textsuperscript{[21]}. For example, the ratio between some reactions taking place can be changed which at the end will influence the final performance. The temperature of ageing relative to the glass transition temperature \( T_g \) of the polymer plays also an important role for the diffusion of oxygen. The diffusion of oxygen into the deeper layers of the polymer is especially limited at a temperature below \( T_g \) of the polymer. In this case the photooxidation will mainly take place at the surface. On the other hand, in accelerated tests at temperatures above \( T_g \) oxygen may more rapidly diffuse to the bulk and photooxidation will proceed also in the bulk.

Another important factor for laboratory weathering tests is humidity. It is known that in some cases the presence of water accelerates the photodegradation processes of polymers. Additionally, by a hydrolysis mechanism water can promote the decomposition of some polymers. In accelerated weathering chambers usually the humidity level can be controlled and additionally water spray imitating rainfall can be provided at regular intervals.

It is clear from the above mentioned examples that the selection of the proper parameters like the spectral distribution and intensity of light, the temperature and the humidity level are crucial for obtaining realistic results.

Laboratory weathering has some important advantages over outdoor exposure. For instance, in laboratory weathering tests the light exposure is continuous while outdoors the sun light is absent at night. As mentioned in the previous paragraph, the major drawback of outdoor weathering tests is the lack of reproducibility and repeatability. However, because of controlled conditions (light intensity, temperature, humidity) the results obtained in laboratory weathering show better reproducibility and repeatability as compared to results obtained outdoors. This is an important aspect for systematic studies of weathering processes.
1.6 Aim and outline of the thesis

The aim of this thesis is to investigate the molecular mechanism of photodegradation of aromatic polyester coatings, which is essential for a better understanding of the overall ageing process of such coatings and ultimately for improving their weathering stability. Another important aspect addressed in this work is to compare the established mechanisms under different degradation conditions. Finally, the influence of the chemical reactions taking place during ageing on some physical properties, in particular hardness will be discussed.

Aromatic polyesters are widely used in the field of coating technology. Thermally or UV cured aromatic polyesters form excellent coatings which are used for protective and decorative purposes. Advantages like good mechanical properties and low cost make these polymers very attractive in coating applications. On the other hand, most aromatic polyester coatings exhibit rather modest resistance to weathering. Absorption of UV light causes chain scission which leads to the decomposition of the polymer. The chemical reactions taking place influence the physical properties of coatings and ultimately may lead to cracking, gloss loss and blistering.

In recent years it was shown that polyesters based on isophthalic acid (IPA) show a higher resistance to weathering as compared to these based on terephthalic acid (TPA). In this thesis the main work was done on poly(neopentyl isophthalate) (PNI) and some experiments were also performed on poly(neopentyl terephthalate) (PNT). Investigation of the degradation of organic coatings is a complicated process. In most cases chemical changes taking place during UV exposure are studied using overall spectroscopic techniques such as FTIR and UV. Since organic coatings consist of polymer networks, the application of molecular analytical techniques such as chromatography and mass spectrometry was limited. More importantly spectroscopic techniques, like IR, do not provide detailed molecular information and some of the products of the photodegradation may not be detected, e.g. if they have low IR absorbance or other IR absorption bands are strongly overlapping. Thus, a more detailed characterization of the molecular mechanism of photodegradation is required. In order to study the mechanism of the degradation on the molecular level, in this thesis, non-crosslinked coatings were investigated. In this work MALDI-ToF MS was used as an important additional technique to study the mechanisms of photodegradation on the molecular level. This technique provides detailed structural
information on the degradation products, which allows establishing precise mechanisms of the degradation\cite{30-32}. The changes in the size of molecules were investigated with SEC. Formation of functional groups was studied with FTIR spectroscopy. The changes in the mechanical properties of UV exposed coatings were measured with nanoindentation.

As laboratory UV exposure tools two systems were used: the UVACUBE and the Suntest XXL+. The UVACUBE apparatus is equipped with a high pressure mercury lamp emitting radiation in the range of 254 to 600 nm. This device is equipped with a thermostatic box covered with quartz glass, which allows performing ageing experiments with different atmospheres (air/nitrogen) and temperature. The Suntest XXL+ is equipped with xenon lamps of which the light emitted is filtered with daylight filters ($\lambda > \sim 300$ nm). The spectral distribution of the light provided by the Suntest XXL+ nearly resembles the spectral distribution of natural light. Outdoor exposure was performed in Poland.

In Chapter 2 the photodegradation of poly(neopentyl isophthalate) (PNI) coatings exposed in the UVACUBE apparatus ($\lambda > \sim 254$ nm) is studied. This system highly accelerates the polymer photodegradation. The mechanism of the photodegradation is investigated with ATR-FTIR, SEC and MALDI-ToF MS. As a result of this investigation, a mechanism of the photolysis and photooxidation is proposed.

Chapter 3 describes the photodegradation of PNI coatings both exposed in the Suntest XXL+ ($\lambda > \sim 300$ nm) and aged in outdoor conditions. The mechanism of the photodegradation is studied with ATR-FTIR, SEC and MALDI-ToF MS. The mechanism of photolysis and photooxidation of PNI obtained in both Suntest XXL+ and outdoors is compared to the mechanisms obtained under highly accelerated conditions (UVACUBE: $\lambda > \sim 254$ nm). In particular, two aspects of degradation of polymers are discussed. First, the influence of the wavelength ($\lambda > \sim 254$ nm and $\lambda > \sim 300$ nm) on the mechanism of degradation is addressed. Secondly, the comparison between laboratory and outdoor exposure in respect to the mechanism is discussed.

The comparison of the mechanism of photodegradation and overall UV stability of poly(neopentyl isophthalate) (PNI) and poly(neopentyl terephthalate) (PNT) coatings as exposed in the Suntest XXL+ ($\lambda > \sim 300$ nm) light is presented in Chapter 4.
In **Chapter 5** the mechanism of crosslinking as a result of the UV exposure is investigated. In this respect the insoluble part of photodegradation (gel) is collected and first studied with ATR-FTIR. Secondly, the gel is decomposed by methanolysis and the products of this reaction is studied with LC-MS. As a result a mechanism of photocrosslinking is proposed.

In **Chapter 6** the influence the chemical reactions taking place during photodegradation have on the physical properties (hardness) of polyester coatings is discussed. UV exposure is carried out in different atmospheres (air and nitrogen), in order to distinguish oxygen dependent chemical reactions and their influence on the mechanical properties. As a result an explanation for the hardness increase as a result of ageing is proposed. In this chapter a typical weathering pathway – chemical reactions taking place during ageing leading to physical changes and finally to macroscopic failure, namely cracking – is presented.
Chapter 1

References

Molecular mechanism of photolysis and photooxidation of poly(neopentyl isophthalate)

Summary

The mechanism of photodegradation of poly(neopentyl isophthalate), an aromatic polyester as model for industrial polyester coatings, was studied on the molecular level. Changes in the chemical structure of molecules caused by UV irradiation (UVACUBE, λ > ~254 nm) were investigated using several analytical techniques. Photodegradation leads both to chain scission and to crosslinking, taking place simultaneously as measured by SEC. Generation of carbonyl C=O and hydroxyl OH/OOH groups in the polymer structure was monitored with ATR-FTIR. MALDI-ToF MS provided detailed structural information on the degradation products of the polyester. In the initial stage of degradation Norrish photocleavage (type I) takes place. Radicals generated in this reaction (photolysis) can directly abstract hydrogen or can react with oxygen creating primarily acid and hydroxyl end groups (photooxidation). Moreover hydrogen abstraction taking place along the polymer backbone followed by oxidation reactions leads to further fragmentation of the polymer chains. The highly informative data provided by MALDI-ToF MS allowed establishing the pathways of photolysis and photooxidation.

2.1 Introduction

Organic coatings are thin, often pigmented layers of a polymer network applied on a substrate. They are used for protection against corrosion and weathering as well as for decoration purposes. The main part of a organic coating is the polymeric binder which consists of a polymer having reactive groups (resin) and often a crosslinker. Most commonly resins used in coating technology are acrylcs, polyesters, alkyds and epoxies.

Many factors simultaneously influence the life time of a coating. The combined action of UV radiation, heat and moisture can cause changes in the chemical structure of polymer networks. Such chemical changes influence the physical properties of coatings and consequently lead to failure (cracking, gloss loss, blistering, etc.) and reduction of life-time. The most important factor affecting degradation is UV radiation[1,2].

Photodegradation of polyesters like poly(ethylene terephthalate) PET and poly(butylene terephthalate) PBT has been extensively investigated[3-10]. Day and Wiles studied photochemical degradation of PET[4-6]. Mainly based on the analysis of volatile products (CO and CO₂) and FTIR it was suggested that UV absorption by the aromatic ester group induced Norrish (type I and II) photocleavage. Later, Rivaton studied photodegradation of PBT using FTIR supported with chemical derivatization[7,8]. The data obtained confirmed the Norrish (type I and II) photocleavage and resulted in proposing more advanced mechanisms of the photodegradation of the aromatic polyester. However, IR does not provide detailed molecular information. Moreover, some of the products of the photodegradation may not be detected e.g. if they have low absorbance, or other absorbances are strongly overlapping. Thus, more detailed characterization of the molecular mechanism of photodegradation is still required.

Among industrially used polyester coatings, those based on neopentyl glycol and phthalic acid isomers, especially isophthalic acid, exhibit the best outdoor durability[11]. Although those polyester coatings are widely used in outdoor application, mainly because of their superior mechanical properties, improvement of their outdoor durability, at least up to the level of e.g. acrylic coatings, is still very desirable. This explains the industrial interest in investigations of the mechanisms of degradation in such polyesters, yet only a few papers have been published on this
Molecular mechanism of photolysis and photooxidation of PNI

topic up to now\textsuperscript{[11,12]}. Interestingly, in poly(neopentyl isophthalate) PNI only Norrish type I photocleavage is possible due to the absence of β-H in the neopentyl glycol moiety, making this polymer very suitable for a model study on a molecular level.

Investigation of the degradation of organic coatings is a complicated process. In most cases chemical changes taking place during UV exposure are studied using overall spectroscopic techniques such as FTIR and UV\textsuperscript{[11,12]}. Since organic coatings consist of polymer networks, the application of molecular analytical techniques such as chromatography and mass spectrometry has been limited. Here, we report on the photolysis and photooxidation of non-crosslinked poly(neopentyl isophthalate) PNI coatings aged in the UVACUBE (λ > ~254 nm). The mechanism of degradation is investigated using several analytical techniques: ATR-FTIR, SEC and MALDI-ToF MS. The most valuable information with respect to the mechanism of degradation is provided by MALDI-ToF MS. This technique allows studying individual polymer chains as a function of exposure time. In recent years the successful application of this technique to study the mechanisms of (thermal and photo) degradation of polymers has been demonstrated\textsuperscript{[13-15]}, including PBT\textsuperscript{[16]}. In the present work, MALDI-ToF MS is used to study photodegradation of poly(neopentyl isophthalate) PNI. In addition, the interpretation of complicated (isotope overlapping) MALDI-ToF MS data was made possible by in-house-developed software\textsuperscript{[17]} for the isotope distribution calculation, resulting in detailed structural information on the products of the photodegradation. Based on these highly informative MALDI-ToF MS data as well as on supportive FTIR and SEC data, the mechanisms of photolysis and photooxidation are being proposed.

The main purpose of this chapter is to investigate the molecular mechanisms leading to fragmentation of the polymer. The mechanism of photocrosslinking, which is the other process simultaneously taking place during the photodegradation, will be studied in Chapter 5.
2.2 Experimental

Materials

The model polyester poly(neopentyl isophthalate) PNI, used in this study was provided by DSM. This polyester was prepared from isophthalic acid and neopentyl glycol in a bulk polycondensation process (Reaction 2.1). Titanium(IV) n-butoxide (Ti(OBu)₄) was used as a catalyst. The synthesis was performed with an excess of neopentyl glycol resulting in a hydroxyl functional polymer ($OHV - 16 \text{ mg of KOH/g}$ and $AV - 1 \text{ g of KOH/g}$). $OHV$ is the hydroxyl value and is defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl groups in 1 g of the polymer. $AV$ is the acid value and is defined as the number of milligrams of potassium hydroxide required to neutralize 1 g of the polymer. $OHV$ and $AV$ were determined by titration. $M_n$ is the number average molecular weight. $M_n$ values based on titration data and on SEC equal 6600 g/mol and 9650 g/mol respectively. Its glass transition temperature $T_g$, as measured by DSC, was 58 °C.

\[
\begin{align*}
\text{isophthalic acid} & + 2x \text{ neopentyl glycol} & \rightarrow \text{poly(neopentyl isophthalate) PNI} - 2\text{H}_2\text{O} \\
\text{T, cat.}
\end{align*}
\]

Reaction 2.1. Polycondensation reaction of neopentyl glycol and isophthalic acid.

Coating preparation

PNI was dissolved in N-methyl-2-pyrrolidone (NMP) (30 w/w %). The solution was applied on an aluminium plate (cleaned with ethanol and acetone) using a doctor blade driven by a 509 MC Coatmaster applicator (Erichsen GmbH). Coatings were dried at 120 °C for one hour in an oven; all NMP was evaporated (checked with FTIR, C=O at 1675 cm⁻¹). The thickness of the resulting dry coating was approximately 12 μm as measured with a TWIN-CHECK Instrument (List-Magnetic GmbH).

UV exposure

The samples were aged using a UVACUBE apparatus, equipped with a high pressure Mercury lamp (Dr. Hönle AG) emitting radiation in the 254 – 600 nm range. The intensity of the light was 40 W/m² in range of 250 – 300 nm and 210 W/m² in range of 300 – 400 nm as measured with an AVS SD2000 Fiber Optic Spectrometer (Avantes). FC-UV050-2 fiber was used. Additionally, intensity of light was measured
using a UV Power Puck (EIT Inc.) in the ranges of UVA (400 W/m²) and UVB (150 W/m²). The UVACUBE was equipped with a thermostatic box (68 °C) covered by a quartz glass in which the PNI coatings were placed. All experiments were performed in dry air atmosphere. Exception to this rule is one experiment performed in dry nitrogen atmosphere. The distance from samples to the lamp was 20 cm. Samples (5 cm × 5 cm) were exposed to UV light for either 10 or 20 hours.

Analytical methods

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) was performed using a BioRad Excalibur FTS3000MX spectrometer equipped with a diamond crystal (Golden Gate). Spectra of the surface of the PNI coatings were recorded in the range of 4000 – 650 cm⁻¹ with a resolution of 4 cm⁻¹. For ATR-FTIR spectroscopy a small piece was cut from the coated panel and pressed on the ATR crystal. Spectra in the range of 2300 – 3700 cm⁻¹ were normalized to the peak at 2967 cm⁻¹ (CH₃ antisymmetric stretching) and in the range of 1500 – 1900 cm⁻¹ to the peak at 1716 cm⁻¹ (C=O stretching).

Size exclusion chromatography (SEC) was carried out using a WATERS 2695 separation module and a Model 2414 refractive index detector at 40 °C. The injection volume used was 50 µL. The column set consisted of a Polymer Laboratories PLgel guard column (5 µm particles, 50 × 7.5 mm), followed by two PLgel mixed-C columns (5 µm particles, 300 × 7.5 mm). The columns were calibrated at 40 °C using polystyrene standards (Polymer Laboratories, M = 580 up to M = 7.1*10⁶ g/mol). Tetrahydrofuran (Biosolve, stabilised with BHT) was used as eluent at a flow rate of 1.0 ml/min. Prior the SEC analysis, the polyester was removed from the substrate and dissolved in THF. In case of aged polyester the insoluble (crosslinked gel) part of the polymer was removed by filtration (0.2 µm PTFE filter) and the soluble part (concentration ~5 mg/ml in THF) was analyzed. Data acquisition and processing were performed using WATERS Empower 2 software. Chromatograms were scaled to the maximum peak height.

Matrix assisted laser desorption ionization time of flight mass spectra (MALDI-ToF MS) were recorded in reflector mode using a Voyager-DE STR instrument. Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malononitrile was used as a matrix. Samples were prepared by mixing matrix, potassium trifluoroacetate and polymer sample in a volume ratio 4:1:4, with THF as a solvent.
Prior to the MALDI-ToF MS test, polyester was removed from the substrate and dissolved in THF. In the case of the aged polyester the insoluble (crosslinked gel) part of the degradation was removed by filtration. The soluble part was analyzed. Copol analysis program by B. B. P. Staal was used to calculate isotopic distributions\textsuperscript{[17]}.

2.3 Results and discussion

2.3.1 ATR-FTIR analysis

ATR-FTIR spectroscopy was used to monitor the formation and disappearance of functional groups at the polymer surface during photodegradation. Spectra of the polyester irradiated in air atmosphere (Figures 2.1 and 2.2) exhibit significant surface changes in the carbonyl region (1850 – 1600 cm\textsuperscript{-1}) and in the hydroxyl/hydroperoxide region (3600 – 2500 cm\textsuperscript{-1}). The changes in the carbonyl region are probably caused by the following groups formed during degradation: anhydride (stronger band at 1780 – 1770 cm\textsuperscript{-1}; weaker band at 1725 – 1715 cm\textsuperscript{-1}); carboxylic acids: aliphatic (1725 – 1700 cm\textsuperscript{-1}) and aromatic (1700 – 1680 cm\textsuperscript{-1}); aldehydes: aliphatic (1730 – 1725 cm\textsuperscript{-1}) and aromatic (1710 – 1690 cm\textsuperscript{-1})\textsuperscript{[18]}. Whereas a sharp absorption in the hydroxyl region (3600 – 3300 cm\textsuperscript{-1}) is generally believed to be characteristic for non-hydrogen bonded hydroxyl groups, in our case (Figure 2.2) a broad absorption is observed, indicating hydroxyl groups that are hydrogen bonded with carboxyl groups. Hydrogen bonded, carboxylic hydroxyl groups are known to give a broad absorption band between 2500 – 3600 cm\textsuperscript{-1} (Figure 2.2).

PNI contains two ester carbonyl groups in each repeating unit. These groups may well serve as hydrogen bond acceptors for different types of hydroxyl formed during the degradation. Other carbonyl groups, originating from degradation, may have a similar role.
Figure 2.1. ATR-FTIR spectra (region of C=O band) of the PNI coating surface after UV-irradiation for 0, 10 and 20 hours. Normalized to the peak at 1716 cm⁻¹.

Figure 2.2. ATR-FTIR spectra (region of OH and OOH band) of the PNI coating surface after UV-irradiation for 0, 10 and 20 hours. Normalized to the peak at 2967 cm⁻¹.
2.3.2 SEC analysis

It was noted, when trying to dissolve the exposed polyester coatings in THF for SEC analysis, that some non-soluble material had been formed. We ascribe this to a photo-induced crosslinking reaction (gel formation) as has also been reported by others[^5]. The results of the analysis of this gel will be presented in Chapter 5. For the present study, the insoluble part of the sample is removed by filtration. Size Exclusion Chromatography was performed to determine changes in molecular weight. Figure 2.3 shows SEC chromatograms of the polyester aged for 0, 10 and 20 hours. As can be seen, molecules both with higher and lower molecular weight are formed during UV exposure. Photodegradation leads to break-down of the polymer chains. Simultaneously some of the radicals formed during this process may recombine and form crosslinked molecules. During this process a high molecular weight sol fraction (crosslinked molecules, still soluble) is formed first. Further crosslinking leads to gel (insoluble crosslinked molecules) formation.

![SEC chromatograms of PNI UV-irradiated for 0, 10 and 20 hours.](image)

**Figure 2.3.** SEC chromatograms of PNI UV-irradiated for 0, 10 and 20 hours.
2.3.3 MALDI-ToF MS analysis

In this experiment the soluble degradation products were identified using MALDI-ToF MS. All polymer molecules discussed consist of the same repeating unit (molecular mass of the isophthalic acid and neopentyl glycol residues, H₂O subtracted, 234 g/mol). Polymer chains are terminated with various end groups. Exceptions to this general description are cyclic oligomers (no end group) and anhydride or hemiacetal groups being present in the polymer chains. All identified oligomers are described and listed in Table 2.1 including the mass charge ratio (m/z) of the most abundant peak of that oligomer. Figure 2.4 shows enlarged parts of the MALDI-ToF MS spectra (one repeating unit) of the non-aged polyester (A), aged for 1 hour (B), 10 hours (C) and 20 hours (D), respectively. The main structure of the non-aged polymer (Figure 2.4A) is a sequence of repeating units terminated with neopentyl alcohol (Structure 1a, Table 2.1). Additionally, structures 1b, 6, 8a and 8b, were identified. These are thought to be species inherent to polycondensation reactions (cyclic oligomers: 8b) or species being formed during polycondensation as a result of thermal or thermo-oxidative degradation. Already 1 hour of UV exposure (Figure 2.4B) results in the formation of new structures. Ageing for 10 and 20 hours (Figures 2.4C and 2.4D) leads to an increase of existing structures and to the formation of many new products as photodegradation proceeds. Figure 2.5 shows enlarged parts of MALDI-ToF MS spectra (one repeating unit) of the PNI aged for 1 hour in air (2.5A) and 1 hour in nitrogen (2.5B).

The mass of a molecule shows up in a MALDI spectrum as a distribution of masses ("isotopic distribution") around a mean value, due to the occurrence of isotopes of C, O, N, etc. The shape of the isotopic distribution is an indication of the atomic composition of the structure. There are two main problems when analyzing isotopic distributions originating from two structures that have (almost) similar masses. First of all, molar masses of two molecules that differ by less than the resolution of the equipment (typically ~0.5 Dalton) will show up as a single peak and distinguishing them is impossible. This phenomenon is usually referred to as "isotope interference"[17]. Secondly, when two structures have mean values that differ by ~4 Daltons or less, these isotopic distributions overlap into a cluster of isotopic distributions ("isotope overlap"[17]). For example the isotopic distribution described by number 2 (Figures 2.4 and 2.6) is a result of isotopic distributions originating from two macromolecular species (2a, 2471 m/z and 2b, 2469 m/z, Table 2.1). This
phenomenon complicates the interpretation of the data. In order to overcome the problem of isotope overlap and to identify the products of degradation, in-house-developed software was used\cite{17}. This program calculates the isotopic distributions for given (expected) chemical structures and compares them to the experimental data. The usefulness of this software has been already proven in the investigation of the chemical composition and the topology of poly(lactide-co-glycolide)\cite{19}. In our experiment ultimately 15 isotopic distributions were found representing 28 molecules. The same isotopic distributions were found in different repeating units from 1000 \( m/z \) up to 7000 \( m/z \). Figure 2.6A shows an experimental and simulated enlarged part (one repeating unit) of the MALDI-ToF MS spectrum of PNI aged for 20 hours. In order to better visualize the experimental and simulated isotopic distributions, Figure 2.6A was split into A1 and A2. In all cases a good match between experimental and simulated data was found, which confirms the presence of the molecules listed in Table 2.1.

One of the disadvantages of MALDI-ToF MS is mass discrimination, i.e. smaller molecules have a higher possibility for being detected than molecules of higher molecular weight. For polymers with a higher polydispersity index, as in this case (photodegradation leads to chain scission and crosslinking) smaller molecules can be expected to dominate the spectra. This effect could explain why primarily products from photolysis and photooxidation (which mainly lead to chain scission) are observed, and no still soluble products of crosslinking and chain extended species are detected.
Figure 2.4. Enlarged parts of MALDI-ToF MS spectra (one repeating unit) of PNI non aged (A), aged for 1 hour (B), 10 hours (C) and 20 hours (D). The numbers of the isotopic distributions correspond to the structures listed in Table 2.1.

Figure 2.5. Enlarged parts of MALDI-ToF MS spectra (one repeating unit) of PNI aged for 1 hour in air (A) and aged for 1 hour in nitrogen (B). The numbers of the isotopic distributions correspond to the structures listed in Table 2.1.
Figure 2.6. Experimental and simulated enlargements of the MALDI-ToF MS spectrum of PNI aged for 20 hours. (A; one repeating unit: 2245 – 2495 m/z), (A1; enlargement of repeating unit: 2375 – 2480 m/z), (A2; enlargement of repeating unit: 2255 – 2375 m/z). The numbers of the isotopic distributions correspond to the structures listed in Table 2.1. The calculation was performed for 15 isotopic distributions. Between isotopic distributions 10/13 additional small isotopic distributions were found. Those small isotopic distributions presumably are superpositions of other larger ones and for these simulation was not performed.
Table 2.1. Structures of the molecules identified with MALDI-ToF MS.

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Chapter 2

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Table 2.1: Structures and their corresponding numbers.
2.4 Mechanism of photolysis and photooxidation

As reported in many papers\[^{3-9}\], Norrish type I photocleavage is the main initiation step of photodegradation of aromatic polyesters. The ester group can be cleaved at 3 different positions (Scheme 2.1, case: A, B, C), creating 6 different primary radicals (alkoxy A-1, acyl A-2, alkyl B-1, carboxyl B-2, formate C-1, phenyl C-2). Possible rearrangements, oxidation and termination reactions of these radicals are discussed and illustrated below according to the above mentioned cases (A - Scheme 2.2, B - Scheme 2.3, C - Scheme 2.4). Moreover the hydrogen abstraction in the polymer backbone followed by oxidation reactions is elucidated (Schemes 5 and 6). Structures described with numbers and small letters, e.g. 1a, refer to Table 2.1.

![Scheme 2.1. Norrish type I photocleavage of ester group, case: A, B, C.](image_url)
2.4.1 Norrish type I photocleavage, case A (Scheme 2.2)

Due to Norrish type I photocleavage of the ester group, in case A (Schemes 2.1 and 2.2) an alkoxo radical A-1 (\(\cdot\)O–CH\(_2\)–) and an acyl radical A-2 (\(-\cdot\)C\(\equiv\)O) are formed.

**Alkoxo radical A-1**

The alkoxo radical A-1 can be rearranged by formaldehyde elimination (Scheme 2.2) to the tertiary alkyl radical A-3 (\(-\cdot\)C<). Hydrogen abstraction by this alkyl radical leads to the formation of an isobutyl end group (Structures 3a, 4a, 4b, 5b, 5c and 9a). Alternatively the tertiary alkyl radical A-3 can disproportionate (Scheme 2.2) to an isobutene end group (Structures 3b, 5c and 9b). The presence of isobutyl and isobutene end groups was indicated by MALDI already after 1 hour of irradiation both in air and nitrogen conditions (clustered isotopic distribution 3, Figure 2.4 and 2.5), proving that the photocleavage according to case A takes place.

Furthermore the tertiary alkyl radical A-3 can also undergo oxidation processes (Scheme 2.2) resulting in the formation of a tertiary butanol (Structures 2a and 4a). To this end for example, the tertiary alkyl A-3 first reacts with oxygen to form a peroxy radical, which after hydrogen abstraction forms a hydroperoxide. Decomposition of the hydroperoxide followed by hydrogen abstraction leads to the formation of the tertiary butanol end group.

The alkoxo radical A-1 formed due to photocleavage, case A (Schemes 2.1 and 2.2) can also abstract hydrogen (Scheme 2.2) and form a neopentyl glycol end group (Structure 1a). Since this end group is also present in the virgin polymer, this does not lead to a new isotopic distribution in the MALDI spectrum. However, the broad band formed in the hydroxyl/hydroperoxide region of the ATR-FTIR spectra (Figure 2.2) suggests that hydroxyl groups are formed.

**Acyl radical A-2**

The Norrish type I photocleavage of the ester group, case A (Schemes 2.1 and 2.2) leads also to an acyl radical A-2 formation. After hydrogen abstraction of this radical a phthalaldehyde end group is formed (Structure 8a). This structure together with a cyclic oligomer (Structure 8b) is represented by the clustered isotopic distribution 8 (Figures 2.4 and 2.6) and was identified already before ageing. Although this isotopic distribution seems to rise in comparison to the isotopic distribution 1 (representing virgin polymer, Figure 2.4), it can not be concluded
beyond doubt that more of these molecules are being formed, because MALDI-ToF MS is not a quantitative technique.

In the presence of oxygen, the acyl radical A-2 can undergo an oxidation (Scheme 2.2) to a phthalic acid end group (Structures 7a, 7b, 9a, 9b, 11 and 12). During this process a peracid is formed first. Decomposition of the peracid leads to a carboxyl radical, which after hydrogen abstraction finally forms the phthalic acid end group. During MALDI ionization of those molecules, the proton of an acid end group –C(O)OH can be replaced with potassium –C(O)OK. This phenomenon results in an extra isotopic distribution in the MALDI spectrum (Structures 4c and 10b). Moreover the presence of acids was indicated by ATR-FTIR spectroscopy, in the hydroxyl and carbonyl region (Figures 2.1 and 2.2).

In addition the acyl radical A-2 can undergo decarbonylation and form a benzoic end group (Structure 10a).

Scheme 2.2. Photolysis and photooxidation pathways resulting from Norrish type I photocleavage A.
2.4.2 Norrish type I photocleavage, case B (Scheme 2.3)

As a result of Norrish type I photocleavage of the ester group, case B (Schemes 2.1 and 2.3) an alkyl radical B-1 (\(^{\cdot}\text{CH}_2\)) and a carboxyl radical B-2 (\(^{\cdot}\text{C(=O)O}^-\)) are formed.

**Alkyl radical B-1**

Hydrogen abstraction of an alkyl radical B-1 (Scheme 2.3) leads to a neopentyl end group (Structures 2b and 4b). The reaction of an alkyl radical B-1 with oxygen results in an alkoxy radical A-1 (also formed as a primary radical), the propagation of which was described above.

**Carboxyl radical B-2**

The carboxyl radical B-2 can abstract a hydrogen atom (Scheme 2.3) and form a phthalic acid end group (Structures 7a, 7b, 9a, 9b, 11 and 12). This end group was already identified after 1 hour of ageing both in air and nitrogen atmosphere (Figure 2.5). In the absence of oxygen, a phthalic acid end group can be formed only due to above mentioned mechanism. This proves the occurrence of photocleavage B.

In addition the carboxyl radical B-2 can undergo decarboxylation and form a benzoic end group (Structure 10a).

![Scheme 2.3. Photolysis and photooxidation pathways resulting from Norrish type I photocleavage B.](image)

2.4.3 Norrish type I photocleavage, case C (Scheme 2.4)

Chain scission due to Norrish type I photocleavage of the ester group, case C (Schemes 2.1 and 2.4) results in a formate radical C-1 (\(-\text{O}=\text{C}^{\cdot}\)) and corresponding phenyl radicals C-2 (\(\cdot\text{C}_6\text{H}_5\)).
Formate radical C-1

A formate radical C-1 can undergo decarbonylation or decarboxylation (Scheme 2.4). The first reaction leads to the formation of CO and an alkoxy radical A-1, the second to the formation of CO₂ and an alkyl radical B-1. The hydrogen abstraction of a formate radical C-1 would lead to the formation of a formate end group (Structure 14b). The m/z ratio of 2279 seems to correspond to this structure. However, it can also be attributed to, for example, oligomers terminated with a pivalic acid end group and also containing an anhydride (Structure 14a).

Phenyl radical C-2

As was illustrated in Scheme 2.1, case C and Scheme 2.4, the phenyl radical C-2 can be formed by photocleavage of the ester group. It can be also formed by decarbonylation of the acyl (Scheme 2.2) or by decarboxylation of the carboxyl radicals (Scheme 2.3). Phenyl radicals C-2 can abstract hydrogen (Schemes 2.2, 2.3 and 2.4) and form a benzoic end group (Structure 10a).

Although several of the possible photocleavage C products could be attributed to isotopic distributions observed in the MALDI-ToF MS spectra, these isotopic distributions could also be explained on the basis of photocleavage A and B and/or oxidation reactions from them. Hence there is no direct proof for the occurrence of photocleavage C.

Scheme 2.4. Photolysis and photooxidation pathways resulting from Norrish type I photocleavage C.
2.4.4 Hydrogen abstraction from the polymer backbone followed by oxidation reactions (Schemes 2.5 and 2.6)

The impact of hydrogen abstraction of all above mentioned processes is considerable. As was shown, polymer-free radicals and later formed oxy- and peroxy-radicals can abstract hydrogen. The by far most labile hydrogen atoms on the polyester backbone are located in the α-position of the ester group. Macromolecular alkyl radicals (Scheme 2.5), (–C•H–O–C(O)–) result from hydrogen abstraction on those positions. Such macroalkyl radicals can react with oxygen. First a peroxyradical is formed, which in turn, by hydrogen abstraction creates hydroperoxide. This hydroperoxide can undergo a homolysis reaction and the macroalkoxy radical (–C(O’)=O–C(O)–) is formed (Scheme 2.5). The above described reaction can take place in each repeating unit of the polymer. A macroalkoxy radical can undergo at least three different reactions.

First, macroalkoxy radical (–C(O’)=O–C(O)–) can convert into an anhydride (Scheme 2.5) (–C(O)–O–C(O)–) through a cage reaction (Structures 5a, 11, 13, 14a, 15b and 15c). Later such macromolecular anhydrides can undergo a Norrish I photocleavage reaction similar to those described above for the original polyester structure[8].

If the above described cage reaction would take place at the end group of a hydroxyl functional polymer chain (Scheme 2.6) (methylenegroup next to the alcohol group –CH2–OH), a pivalic acid end group would be formed (Structures 5a, 13 and 14a). Both reactions (anhydride and pivalic acid formation) result in the same change in mass (+14 Da) with respect to structure 1a. Taking the average molecular weight of the polyester (6600 g/mol, by titration) and the mass of a repeating cluster (234 g/mol) into account the average ratio of the repeating units to the end groups is approximately 14 to 1. In this respect the probability of formation of anhydride is much higher than that of a pivalic acid through a cage reaction mentioned before.

An independent proof of the presence of macromolecular anhydride groups (Scheme 2.5) is the formation of this moiety in the molecules both terminated with phthalic acid, where no confusion with pivalic acid is possible (Structure 11).

The macroalkoxy radical (–C(O’)=O–C(O)–) can also undergo a β-scission reaction (Scheme 2.5). As a consequence a carboxyl radical B-2 and an pivalic aldehyde are formed (Structures 1b, 7b and 15c). Since some traces of a pivalic aldehyde were already detected before UV irradiation it is difficult to evaluate if this
reaction really takes place. It is known that aldehyde in this conditions can easy undergo oxidation to acid (Scheme 2.5), (Structures 5a, 13 and 14a).

Finally, a macroalkoxy radical can abstract hydrogen and form a hemiacetal (Scheme 2.5), (Structure 15a).

\[
\begin{align*}
\text{Scheme 2.5.} & \quad \text{The hydrogen abstraction from the polymer backbone followed by oxidation reactions.} \\
\end{align*}
\]

\[
\begin{align*}
\text{Scheme 2.6.} & \quad \text{In many of the mechanisms proposed in this paper, a macromolecular hydroperoxide as intermediate species is proposed. Although we have successfully identified most of the products, we could not find direct evidence of hydroperoxides in the MALDI spectra. This is probably due to their low UV and thermal stability. As intermediate products, hydroperoxides, are known to accumulate only in very low concentration.}\[8]
\end{align*}
\]
2.4.5 Final remarks

In this investigation we have successfully identified products of the photolysis and photooxidation of poly(neopentyl isophthalate) using MALDI-ToF MS. The interpretation of complicated (isotope overlapping) MALDI-ToF MS data was supported with in-house-developed software for the isotope distribution calculation, resulting in detailed structural information on the products of the photodegradation. This technique allowed studying individual polymer chains as a function of exposure time.

Based on highly informative data obtained, it is confirmed that the Norrish type I photocleavage of the ester group takes place first. In the initial stage, radicals which are formed in this reaction (directly, or after rearrangement) abstract hydrogen from a neighboring segment and form new end groups. For instance, isobutyl and isobutene end groups (Structures 3a and 3b) were identified after 1 hour of irradiation. UV exposure of PNI for 1 hour under nitrogen resulted in formation of the same clustered isotopic distribution 3 attributed to isobutyl and isobutene end groups. This additionally confirms our interpretation of the data and proves that in the initial stage of degradation direct photocleavage followed by a hydrogen abstraction takes place. The products of oxidation are being observed in the later stages.

The primary radicals and later formed oxy- and peroxo- radicals can abstract hydrogen. The most labile hydrogen atoms on the polyester backbone are present in the α-position of the ester group. Oxidation processes taking place in the polymer backbone can directly (β-scission) or indirectly (anhydride) lead to further fragmentation of polymer chain.

As shown above there are two mechanisms leading to fragmentation of polymer chain. Direct Norrish type I photocleavage of aromatic ester and oxidation of the polymer backbone taking place respectively.

Norrish type I photocleavage can take place at three different positions of an aromatic ester group. Based on the bond dissociation energies of a model compound (ethyl benzoate), Day and Wiles suggested that the photocleavages A (88 kcal/mole) and B (84 kcal/mole) are more favorable then photocleavage C (102 kcal/mole)[6] (Scheme 2.1). The experimental data obtained in this chapter can confirm that photocleavages A and B are most predominant during degradation of PNI.
2.5 Conclusions

In this chapter, the molecular mechanism of the photolysis and photooxidation of an non-crosslinked poly(neopentyl isophthalate) (PNI), applied as a thin coating on an aluminium plate and aged in the UVACUBE (λ > ~254 nm) was studied.

Information on the changes in the size of the molecules was obtained by SEC. Both an increase and a decrease of molar weight were observed, indicating that crosslinking and chain scission take place simultaneously during photodegradation.

ATR-FTIR was used to detect groups such as C=O and OH/OOH generated in the polymer structure due to the break-down of polymer chain by photooxidation. Anhydrides and acids were clearly identified in the range of 1800 – 1600 cm⁻¹. Moreover, the formation of a very broad band in the range of 3600 – 2500 cm⁻¹ indicates the presence of different types of OH groups (alcohol, carboxyl and hydroperoxide).

MALDI-ToF MS revealed the molecular structure of the degradation products from the very first reactions taking place. It has been demonstrated that Norrish type I photocleavage reactions takes place, in accordance with the earlier published bond dissociations energies of the possible pathways. Radicals formed from those photocleavages can abstract hydrogens and form mainly isobutyl and phthalic acid end groups, which are observed in MALDI in early stages of degradation. Reactions of the above mentioned radicals with oxygen lead to acid and alcohol groups, and these photooxidation products are observed in MALDI in later stages of photodegradation.

Hydrogen abstraction from the polymer backbone plays an important role in photodegradation too. Radicals formed in the α-position to the ester due to hydrogen abstraction may react with oxygen. The alkoxy radical formed as a consequence of this process can rearrange to anhydride (via a cage reaction), which possibly later breaks down e.g. by hydrolysis. The alkoxy radical may also directly decompose via β-scission. These reactions taking place along the polymer backbone account for oxidation induced decomposition of polymer.

In general, the data obtained with MALDI-ToF MS and supported by SEC and ATR-FTIR allowed to establish mechanisms of the photolysis and photooxidation on a molecular level leading to a considerably improved understanding of the degradation processes of aromatic polyesters.
Chapter 2

References

Photodegradation of poly(neopentyl isophthalate) in laboratory and outdoor conditions

Summary
In this Chapter the mechanism of photodegradation of poly(neopentyl isophthalate) (PNI) in laboratory (Suntest XXL+, $\lambda > \sim 300$ nm) and outdoor conditions is studied. Changes in the chemical composition were studied with ATR-FTIR, SEC and MALDI-ToF MS. Results were compared with data presented in Chapter 2, on PNI coatings that were aged in the UVACUBE ($\lambda > \sim 254$ nm). Two aspects of photodegradation of polymers are addressed: the influence of different wavelengths and the comparison of laboratory and outdoor exposure regarding the mechanism of degradation. It was found that under short ($\lambda > \sim 254$ nm) and long ($\lambda > \sim 300$ nm) wavelength irradiation similar products of degradation are formed. However, the presence of short wavelength radiation dramatically accelerates the overall rate of photodegradation of PNI as shown by experiments and energy absorption calculations. The exposure of PNI in laboratory and outdoor conditions resulted in similar degradation products in the initial stage of ageing.
3.1 Introduction

Aromatic polyesters are widely used in the field of coating technology. Thermally or UV cured aromatic polyesters form excellent coatings which are used for protective and decorative purposes. Advantages like good mechanical properties and low cost make these polymers very attractive in coating applications. On the other hand, most aromatic polyester coatings exhibit rather modest resistance to weathering. Absorption of UV light causes chain scission which leads to the decomposition of the polymer. The chemical reactions taking place influence the physical properties of coatings and ultimately may lead to cracking, gloss loss and blistering\[^{1-3}\]. Such a degraded coating cannot maintain the protective and decorative functions anymore. Investigation of the degradation mechanisms of polyesters is essential for a better understanding of ageing processes and, subsequently, for improving their weathering stability.

A great deal of information on the photodegradation of polyesters like poly(ethylene terephthalate) PET and poly(butylene terephthalate) PBT is available\[^{4-9}\]. Norrish (type I and II) photocleavage has been considered as the main initiation step. The radicals formed in this chain scission reaction either abstract hydrogen or undergo oxidation processes. In addition, recombination of radicals may also lead to crosslinking reactions.

The previous studies, however, were mainly focused on polyesters based on the terephthalate (TPA) unit. In recent years it has been demonstrated that replacement of TPA by its isomer, isophthalate (IPA) in the polyester backbone considerably extends the lifetime of the polyester coating\[^{10}\]. The superior performance of IPA coatings under weathering is attributed to the lower absorption of UV light as compared to polyesters based on TPA\[^{11}\]. Yet the mechanism of photodegradation of polyesters based on IPA, like poly(neopentyl isophthalate) (PNI) has not been studied extensively. The understanding of these phenomena is essential for a further improvement of weathering stability of polyester coatings. Moreover, the mechanisms of degradation of polymers are usually studied with overall spectroscopic techniques such as FTIR and UV. In recent years the application of analytical techniques for molecular structure determination like MALDI-ToF MS gained increasing interest when studying the mechanisms of (thermal and photo) degradation\[^{12,13}\]. This technique provides detailed structural information on the...
Photodegradation products, which allows establishing precise mechanisms of the degradation.

In Chapter 2 the photodegradation of non-crosslinked poly(neopentyl isophthalate) (PNI) coatings exposed in the UVACUBE apparatus ($\lambda > \sim 254$ nm) was studied. It had been reported in literature that the presence of irradiation below approximately 300 nm can not only strongly accelerate the photodegradation but may also influence its mechanism\[^{1,2}\]. The chemical effects of photodegradation were studied with ATR-FTIR, SEC and MALDI-ToF MS. As a result of this investigation, a mechanism of the photolysis and photooxidation was proposed.

In this chapter we report on the photodegradation of non-crosslinked PNI coatings both aged in Suntest XXL+ ($\lambda > \sim 300$ nm) and aged in outdoor conditions. The spectral distribution of the light provided by the Suntest XXL+ nearly resembles the spectral distribution of natural light\[^{8,14}\]. The mechanism of the photodegradation is studied with ATR-FTIR, SEC and MALDI-ToF MS. MALDI-ToF mass spectrometry is used to establish the mechanism of photolysis and photooxidation on the molecular level, and to compare it with the previously reported mechanisms under highly accelerated conditions (UVACUBE: $\lambda > \sim 254$ nm). In particular, two aspects of degradation of polymers will be discussed. First, the influence of the wavelength ($\lambda > \sim 254$ nm and $\lambda > \sim 300$ nm) on the mechanism of degradation will be addressed. Secondly, a comparison of laboratory with outdoor exposure regarding the mechanism will be discussed. The mechanism of photocrosslinking reactions will be discussed in Chapter 5.

\[^{8}\] The Suntest XXL+ is equipped with Xenon lamps and daylight filters. The spectral power distribution (SPD) of the light provided starts at about 300 nm. However, it is possible that a small fraction of the light below 300 nm, down to about 285 nm, is present in the SPD. Due to the very low intensity of this light a precise quantitative measurement is difficult. However, since some polymers strongly absorb below 300 nm this small fraction may lead to a significant absorption. In view of the uncertainties involved, in this work, the light below approximately 300 nm is not taken into account.
3.2 Experimental Materials

A model polyester based on neopentyl glycol isophthalic acid (PNI) was used in this study. The polyester was prepared in a bulk polycondensation with Titanium (IV) n-butoxide (Ti(OBu)₄) as a catalyst. Synthesis was performed with an excess of neopentyl glycol resulting in a hydroxyl functional polymer. Hydroxyl value ($OHV$) is 16 mg of KOH/g and acid value ($AV$) is 1 mg of KOH/g. The number average molecular weight ($M_n$) based on titration data equals 6600 g/mol, and as measured using SEC equals 9650 g/mol. The glass transition temperature $T_g$, as measured by DSC, was 58 $^\circ$C.

Coating preparation

Polyester coatings were prepared according to the following procedure. First, PNI was dissolved in N-methyl-2-pyrrolidone (30 w/w %) and then applied on aluminium plates using a doctor blade driven by a 509 MC Coatmaster applicator (Erichsen GmbH). The thickness of the resulting dry coating was approximately 12 μm as measured with a TWIN-CHECK Instrument (List-Magnetic GmbH). Coatings were dried in an air circulation oven at 120 ºC for one hour; all NMP was evaporated (checked with FTIR, C=O at 1675 cm⁻¹).

Weathering conditions

PNI coatings were aged using a Suntest XXL+ (ATLAS), equipped with xenon lamps. The light emitted by xenon lamps was filtered with daylight filters ($\lambda > \sim 300$ nm). The intensity of light was 60 W/m² in the wavelength range of 300 – 400 nm. The chamber temperature was 45 ºC and the temperature of the black standard was 70 ºC. The relative humidity was 25%. Polyester coatings were aged for up to 10,000 hours, which corresponds to approximately 15 months.

Outdoor exposure was performed in Poland (2005 – 2007) for 17,000 hours which corresponds to about 2 years. Samples were suspended vertically, oriented to the south.

In this discussion we will use the word UVACUBE to refer to exposure to light of a high pressure Mercury lamp (Dr. Hönle AG) emitting radiation in 254 – 600 nm in the usual set up of a UVACUBE equipment. The intensity of the light was 40
Photodegradation of PNI in laboratory and outdoor conditions

W/m² in range of 250 – 300 nm and 210 W/m² in range of 300 – 400 nm. The intensity the light was measured with an AVS SD2000 Fiber Optic Spectrometer (Avantes). FC-UV050-2 fiber was used.

The spectral power distributions of light provided by the UVACUBE and the Suntest XXL+ were measured using an AVS SD2000 Fiber Optic Spectrometer (Avantes). For the Suntest XXL+ also an ultraviolet radiation spectroradiometer MSS 2040-UV was used. Essentially the spectral distributions collected by both instruments were identical. However, the quality of spectra collected by the spectroradiometer MSS 2040-UV was better, and accordingly we used these data in this chapter. In order to interpret the degradation due to outdoor exposure, we used the spectral power distribution of natural sun light, as measured at Geleen, The Netherlands, on August 28, 2001 at 13.15 h.

Analytical methods

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) was performed using the BioRad Excalibur FTS3000MX spectrometer equipped with a diamond crystal (Golden Gate). Spectra of the surface of the PNI coatings were recorded in the range of 4000 – 650 cm⁻¹ with a resolution of 4 cm⁻¹. For ATR-FTIR spectroscopy a small piece was cut from the coated panel and pressed on the ATR crystal. The BioRad Win-IR Pro software was used to process the data. Spectra in the range of 2300 – 3700 cm⁻¹ were normalized to the peak at 2967 cm⁻¹ (CH₂ antisymmetric stretching) and in the range of 1500 – 1900 cm⁻¹ to the peak at 1716 cm⁻¹ (C=O stretching).

Size exclusion chromatography (SEC) was carried out using a WATERS 2695 separations module and a Model 2414 refractive index detector at 40°C. The injection volume used was 50 µL. The column set consisted of a Polymer Laboratories PLgel guard column (5µm particles, 50 x 7.5 mm), followed by two PLgel mixed-C columns (5 µm particles, 300 x 7.5 mm). The columns were calibrated at 40°C using polystyrene standards (Polymer Laboratories, M = 580 up to M = 7.1*10⁶ g/mol) in series. Tetrahydrofuran (Biosolve, stabilised with BHT) was used as eluent at a flow rate of 1.0 ml/min. Prior to SEC analysis, the polyester was removed from the substrate and dissolved in THF. In case of aged polyester the insoluble (crosslinked gel) part of the polymer was removed by filtration (0.2 µm PTFE filter) and the soluble part (concentration ~ 5mg/ml in THF) was analyzed. Data acquisition and
processing were performed using WATERS Empower 2 software. Chromatograms were scaled to the maximum peak height. Molecular weights were calculated from chromatograms, (up to 17.5 min of the elution time).

Matrix assisted laser desorption ionization time of flight mass spectra (MALDI-ToF MS) were recorded in reflector mode using a Voyager-DE STR instrument. Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malononitrile was used as a matrix. Samples were prepared by mixing matrix, potassium trifluoroacetate and polymer sample in a volume ratio 4:1:4, with THF as a solvent. The polymer used for the MALDI-ToF MS had been first removed from the substrate and dissolved in THF. In the case of the aged polyester the insoluble (crosslinked gel) part of the degradation was removed by filtration. The soluble part was analyzed.

UV spectroscopy was performed using an UV/VIS/NIR spectrometer Lambda 900 (Perkin Elmer). Spectra were collected in the range of 500 – 200 nm. For such a measurement PNI was dissolved in chloroform and placed in quartz cuvettes. The concentration of PNI in chloroform was 0.177 g/dm³.

3.3 Results
3.3.1 ATR-FTIR analysis
The formation and disappearance of functional groups near the polymer surface during photodegradation was examined with ATR-FTIR. UV exposure of polyester coatings in the Suntest XXL+ leads to changes in the carbonyl (-C=O) (Figure 3.1) and in the hydroxyl/hydroperoxide (-OH/-OOH) (Figure 3.2) regions. The growth of the carbonyl band (1850 – 1600 cm⁻¹) is probably caused by the formation of anhydrides, carboxylic acids and aldehydes. The increase of the absorption in the 3600 – 2400 cm⁻¹ range can be attributed to hydroxyl groups originating from carboxylic acids (mentioned above), alcohols and hydroperoxides.

The changes in the carbonyl and hydroxyl regions of polyester aged in outdoor conditions are presented in Figures 3.3 and 3.4, respectively. Outdoor exposure for 17,000 hours leads only to very little changes in ATR-FTIR spectra. However, these spectra suggest that carbonyl and hydroxyl products formed outdoors are similar to those when the coating is exposed to light in the Suntest XXL+.
The extent of changes in the ATR-FTIR spectra of polyester aged outdoors for 17,000 hours (Figures 3.3 and 3.4) corresponds to what was found after 2,000 hours of ageing in the Suntest XXL+ (Figure 3.1 and 3.2).

**Figure 3.1.** ATR-FTIR spectra (region of C=O band) of the PNI coating surface, aged in the Suntest XXL+ for up to 10,000 hours. Normalized to the peak at 1716 cm\(^{-1}\).

**Figure 3.2.** ATR-FTIR spectra (region of OH and OOH band) of the PNI coating surface aged in the Suntest XXL+ for up to 10,000 hours. Normalized to the peak at 2967 cm\(^{-1}\).
Figure 3.3. ATR-FTIR spectra (region of C=O band) of the PNI coating surface, aged outdoors for up to 17,000 hours. Normalized to the peak at 1716 cm⁻¹.

Figure 3.4. ATR-FTIR spectra (region of OH and OOH band) of the PNI coating surface aged outdoors for up to 17,000 hours. Normalized to the peak at 2967 cm⁻¹.

3.3.2 SEC analysis

Size Exclusion Chromatography (SEC) was performed to determine changes in molecular weight. Figure 3.5 shows SEC chromatograms of the polyester aged in the Suntest XXL+ for up to 10,000 hours. The molecular weight distribution (MWD) plots are presented in Figure 3.6. As can be concluded from Figures 3.5 and 3.6, products with both higher and lower molecular weight are formed during UV exposure. Photodegradation leads to a break-down of the polymer chain, resulting in a decrease of the number average molecular weight $M_n$ as presented in Figure 3.7.
Simultaneously some of the radicals formed during photodegradation can recombine and form crosslinked molecules, leading to an increase of the weight average molecular weight $M_w$ again as can be seen in Figure 3.7. During this process crosslinked molecules, still soluble (sol), are formed first. In our experiment this phenomenon was observed for samples aged for up to 8,000 hours. Further crosslinking leads to gel (insoluble crosslinked molecules) formation, as noticed for coatings aged for 9,000 and 10,000 hours. In these cases, the insoluble part of the degraded polymer was separated in a filtration step and only the soluble part was analyzed by SEC. This may explain why for samples aged for 9,000 and 10,000 hours there is no consistent increase of $M_w$ (Figure 3.7).

Figure 3.8 shows chromatograms of polyester aged in outdoor conditions for up to 17,000 hours. Although only very little changes can be observed, it can be concluded that both chain scission and crosslinking take place.

The SEC results indicate that ageing of polyester outdoors for approximately 17,000 hours corresponds to ageing in the Suntest XXL+ for 1,000 hours.

![Figure 3.5. SEC chromatograms of PNI aged in the Suntest XXL+ for up to 10,000 hours.](image)
Figure 3.6. Molecular weight distribution (MWD) plots of PNI aged in the Suntest XXL+ for up to 10,000 hours.

Figure 3.7. Changes in $M_n$ and $M_w$ of PNI aged in the Suntest XXL+ for up to 10,000 hours. Error bars were determined experimentally.
3.3.3 MALDI-ToF MS analysis

Structural information of the products of photolysis and photooxidation of PNI were obtained with MALDI-ToF MS. All the structures found consist of a sequence of repeating units (molecular mass of the isophthalic acid and neopentyl glycol, H₂O subtracted, is 234 g/mol), terminated with various end groups. All identified oligomers are described and listed in Table 2.1, Chapter 2, where each one was given an identifier consisting of a number and optionally small letter e.g. 1a. Figure 3.9A – F shows parts of the MALDI-ToF-MS spectra (one repeating unit) of the non-aged polyester (A), aged in Suntest XXL+ for 2,000 hours (B), 4,000 hours (C), 6,000 hours (D), 8,000 hours (E) and 10,000 hours (F). The main structure of the non-aged polymer (Figure 3.9A) is a sequence of repeating units terminated with neopentyl glycol (Structure 1a). In addition, structures 1b, 6, 8a and 8b were identified. These are presumably species inherent in polycondensation reactions (e.g. cyclic oligomers: 8b) or species being formed during polycondensation as a result of thermal or thermo-oxidative degradation reactions. Ageing for 2,000 hour results in the formation of other structures indicated in Figure 3.9B with numbers 3 and 7. Further ageing leads to a further increase of structures 3 and 7 and also to the formation of many new products (see Figure 3.9C – F). Figure 3.9G shows one repeating unit of the MALDI-ToF MS spectra of polyester aged in outdoor conditions for 17,000 hours. It can be
concluded that ageing of polyester outdoors for 17,000 hours results in the formation of structures similar to those after exposure in the Suntest XXL+ for about 2,000 hours (Figure 3.9B).

Any molecular structure shows up in the MALDI-ToF MS spectrum as an “isotopic distribution”. One of the problems associated with the analysis of MALDI-ToF MS data is the “isotope overlap”. The presence of two or more molecules with a small difference in mass (2 – 4 Daltons) results in overlapping of isotope distributions (“clustered isotopic distribution”). This phenomenon complicates the identification of products. In the previous chapter, in-house-developed software\textsuperscript{[15]} to overcome this problem was successfully applied. That program calculates the isotopic distributions for given (expected) chemical structures and compares them with the experimental data. Figure 3.10 compares parts of MALDI-ToF MS spectra of polyester aged for 20 hours in the UVACUBE (A) (previously obtained) and of polyester aged for 8,000 hours in the Suntest XXL+ (B). In both cases the same 15 (clustered) isotopic distributions were found representing 28 molecules (Table 2.1). The same isotopic distributions were found when analyzing other repeating units from 1,000 \textit{m/z} up to 7,000 \textit{m/z}. In order to better visualize isotopic distributions, enlarged parts of the two MALDI spectra presented in Figure 3.10 were split into two parts. In all cases a good match in isotopic distribution between UVACUBE and Suntest XXL+ was found. This confirms that under both accelerated degradation conditions the same molecules are formed. Figure 3.9H shows one repeating unit of polyester aged in the UVACUBE for 1 hour (previously obtained). Ageing of polyester for 1 hour in the UVACUBE results in formation of products described with numbers 3 and 7. The same structures were identified after ageing for 2,000 hours in the Suntest XXL+ (3.9B) and 17,000 hours in outdoor conditions (3.9G).
Figure 3.9. Enlarged parts of MALDI-ToF MS spectra (one repeating unit) of PNI non-aged (A), aged in the Suntest XXL+ for 2,000 hours (B), 4,000 hours (C), 6,000 hours (D), 8,000 hours (E) and 10,000 hours (F), aged outdoors for 17,000 hours (G) and in the UVACUBE for 1 hour (H). The numbers of the isotopic distributions correspond to the structures listed in Table 2.1 of Chapter 2.
Figure 3.10. Enlarged parts of MALDI-ToF MS spectra (one repeating unit 2245 – 2495 m/z) of PNI, aged for 20 hours in the UVACUBE (A) and for 8,000 hours in the Suntest XXL+ (B). (A1, B1; enlargement of repeating unit: 2375 – 2480 m/z), (A2, B2; enlargement of repeating unit: 2255 – 2375 m/z). The numbers of the isotopic distributions correspond to the structures listed in Table 2.1 of Chapter 2.
3.4 Discussion

In Chapter 2 the photodegradation of PNI exposed to light in the UVACUBE ($\lambda > 254$ nm) was reported. Mechanisms of photolysis and photooxidation were proposed. This chapter reports on the photodegradation of PNI exposed to light in the Suntest XXL+ ($\lambda > \sim 300$ nm) and in outdoor conditions. Based on the data obtained two aspects of degradation of polymers are addressed.

The first aspect concerns the influence of the wavelength (UVACUBE: $\lambda > \sim 254$ nm and Suntest XXL+: $\lambda > \sim 300$ nm) on the mechanism of degradation. As it has been reported, the presence of the irradiation below approximately 300 nm, which is practically not present in realistic (outdoor) conditions, can strongly accelerate the kinetics of photodegradation. However, it can also influence the individual steps of the mechanism of degradation and may cause reactions which will not take place in outdoor conditions\cite{1, 2}. The mechanism of photodegradation was studied with three analytical techniques (ATR-FTIR, SEC and MALDI-ToF MS). Figure 3.11 shows changes in the ATR-FTIR spectrum (carbonyl region) of PNI exposed for 20 hours in the UVACUBE and 10,000 hours in the Suntest XXL+. It can be concluded that under both accelerated degradation conditions similar carbonyl groups are formed. Figure 3.12 shows SEC chromatograms of PNI aged for 20 hours in the UVACUBE and 10,000 hours in the Suntest XXL+. In both cases chain scission and crosslinking take place. It was mentioned that extensive crosslinking leads to gel (insoluble fraction) formation. In case of ageing in the UVACUBE some gel was formed already in the very early stages of exposure (5 hours) and continues to grow. Exposure for 20 hours resulted in a rise of the gel fraction to approximately 23%. In case of exposure in the Suntest XXL+ system, extensive fragmentation of the polyester takes place, before gel formation. The maximum of the peak in the chromatogram (Figure 3.12) shifts towards lower molecular weight. The first indication of a gel was noticed after 9,000 hours of exposure and after 10,000 hours the gel fraction was approximately 5%. The data on SEC and gel fraction indicate a higher crosslinking / chain scission ratio for PNI exposed in the UVACUBE as compared to the Suntest XXL+. As discussed below, in the UVACUBE most UV light is absorbed in the top layer of the coating whereas in the Suntest XXL+ it is presumed to be also transmitted to deeper layers of the coating. This will lead to a higher concentration of radicals in the top layer of the coating in the UVACUBE. If crosslinking is a recombination reaction between
radicals, the reaction is second order in radical concentration. (Note that in Chapter 5 it is indicated that crosslinking might partly follow a path that is first order in radical concentration). The two main reactions following Norrish photocleavage that do not directly lead to crosslinking (i.e. hydrogen abstraction and reactions with oxygen) are first order in radical concentration. Therefore in the UVACUBE the crosslinking/chain scission ratio will be larger and gel will be formed earlier as compared to the Suntest XXL+. In these studies as well as in the previous work the most relevant information with respect to the mechanism of photolysis and photooxidation was obtained with MALDI-ToF MS. It was found that ageing of PNI in the UVACUBE ($\lambda > \sim 254$ nm) and Suntest XXL+ ($\lambda > \sim 300$ nm) leads to the same products as investigated with MALDI-ToF MS (Figure 3.10). Based on these data we can conclude that similar mechanisms of photolysis and photooxidation take place in both accelerating degradation systems. Although the same products were observed under both accelerated degradation systems, besides differences in crosslinking / chain scission ratio, there is a considerable difference in the time scale of ageing. The intensity of the light in the range 300 – 400 nm provided by the Suntest XXL+ equals 60 W/m$^2$ while the intensity of light in the same range of the UVACUBE was about four times higher (210 W/m$^2$). Nevertheless the acceleration of degradation obtained by the UVACUBE in comparison to the Suntest XXL+ was observed to be in the range of hundreds. Due to differences in condition of ageing like temperature, a precise quantitative comparison is not possible. Nevertheless a dramatic influence of the short wavelength on the rate of reactions clearly can be observed.

The second aspect considered in this chapter deals with the difference between laboratory (Suntest XXL+) and outdoor exposure, in respect to the mechanism of degradation. In this comparison the spectral distribution of light in the Suntest XXL+ is similar to the spectral distribution of sun light. Nevertheless, differences in conditions of laboratory and outdoor ageing like intensity of light, the temperature and rain as well as a number of other factors like pollutants and mechanical or thermal stresses can influence the mechanism of degradation$^{[1-3,16]}$. The ageing of polyester under outdoor conditions for 17,000 hours leads only to limited chemical changes. Nevertheless, it was shown with ATR-FTIR, SEC and MALDI-ToF MS that the laboratory (Suntest XXL+) and outdoor exposure leads to the same products in the initial stage of ageing. In this case the acceleration of ageing was probably achieved by an increased light intensity and a higher temperature.
Finally, the ageing under all three degradation conditions (UVACUBE, Suntest XXL+ and outdoor) was compared using MALDI-ToF MS. The identification of the same products confirms similar mechanisms of degradation taking place in the initial stage of ageing for all three cases.

The differences in speed of degradation are mainly determined by a combination of spectral power distribution of the light source and the absorbance by the polymer. Figure 3.13 shows the UV absorption of poly(neopentyl isophthalate) while Figure 3.14 presents the spectral power distributions of light in the Suntest XXL+, UVACUBE and collected outdoors. PNI absorbs UV light in the UVACUBE, Suntest XXL+ and outdoors. However it is clear that in case of the UVACUBE the UV absorption is much higher if compared with the Suntest XXL+ and natural sun light. As a consequence, Norrish photocleavage and subsequent similar secondary reactions can occur in each of the three methods of ageing. The presence of high energy light in the range of 250 – 290 nm (which is strongly absorbed by PNI) in the spectral distribution of the UVACUBE can explain the much higher rate of photodegradation in the UVACUBE as compared to the Suntest XXL+ and outdoor conditions.

As explained in Chapter 1, photodegradation is known to be a “surface effect” which implies that usually products of photodegradation are concentrated in the top layers of the polymer. The relationship between UV absorption of the polymer and the spectral distribution of the light has a strong impact on the penetration depth of the light and subsequently on the distribution of degradation products throughout the coating. Based on the absorption coefficient of PNI it was calculated that the first 3 μm of the coating absorbs ~85% of the light in the range of 254 – 290 nm. This strongly suggests that in case of ageing in the UVACUBE most of the products of the photodegradation are probably located in the top 3 – 4 μm of the coating. On the contrary, only ~5% of the light at 300 nm is absorbed by the first 3 μm of the coating. This suggests that in the case of ageing in the Suntester XXL+ and outdoors products of the photodegradation are not especially located in the top but also in deeper layers of the PNI coating. The experimental data obtained with SEC of PNI aged in the UVACUBE and Suntest XXL+ confirms this. However, it has to be reminded that in this situation the oxygen diffusion can influence the distribution profile of photooxidation products too.
The mechanism proposed has been extensively discussed in Chapter 2 and involves Norrish photocleavage (type I) of the ester group. Overall six different radicals are formed (photolysis) (Scheme 2.1). These radicals can directly abstract hydrogen or can react with oxygen, generating primarily acid and hydroxyl end groups (photooxidation). Moreover, a hydrogen abstraction taking place along the polymer backbone, followed by oxidation reactions, leads to further fragmentation of the polymer chain.

Figure 3.11. ATR-FTIR spectra (region of C=O band) of the PNI coating surface, aged in the Suntest XXL+ for 10,000 hours and in the UVACUBE for 20 hours. Normalized to the peak at 1716 cm⁻¹.

Figure 3.12. SEC chromatograms of PNI aged in the Suntest XXL+ for 10,000 hours and in the UVACUBE for 20 hours.
Figure 3.13. UV absorption of PNI. The concentration of PNI in chloroform was 0.177 g/dm³.

Figure 3.14. Spectral power distributions of light in the UVACUBE, Suntest XXL+ and Outdoors.
3.5 Comparison of relative photodegradation rates of PNI as obtained experimentally and as predicted from calculated number of absorbed photons.

In order to more quantitatively explain the differences in the rate of ageing found between the different ageing methods we will now relate them to the amount of absorbed light quanta.

Figure 3.14 shows spectral power distributions \( p \) (Wm\(^{-2}\)nm\(^{-1}\)) of light in UVACUBE, Suntest XXL+ and natural sun. The measured absorbance \( A_s \) of PNI solution was converted into the absorption coefficient \( \alpha_p \) of the pure material, according to \( A_s = \alpha_p L c / \rho \) where \( L \) is the length of the cuvette used in the UV spectrometer, \( c \) is the polymer concentration (mass/volume) and \( \rho \) is the density of the polymer. Because the absorbance is defined as \( A = \alpha L = \log_{10}(I_0/I) \), where \( I_0 \) and \( I \) are the light intensities (Jm\(^{-2}\)) before and behind the slab of material, the absorbed amount per time per volume in an optically thin slab is given by 2.3\( \alpha L p \). Accordingly, the absorbed amount of energy per time per volume of polymer from light in a narrow range of wavelengths is given by 2.3\( \alpha_p d \lambda \). Consequently, the number of absorbed photons per unit of time is given by \( \xi d \lambda = 2.3 \lambda h^{-1} c^{-1} \alpha_p p d \lambda \) where \( c \) is the speed of light and \( h \) is Planck’s constant. The results are given in Table 3.1. When we suppose in a first-order approximation that all absorbed photons considered have the same probability to induce photodegradation (quantum efficiency of Norrish photocleavage) the calculated value for a number of photons absorbed per time per volume reflects the rate of photodegradation. By dividing such number by the corresponding value for PNI in the Suntest XXL+, we arrive at predicted photodegradation rates, relative to that of PNI in the Suntest XXL+. These numbers are given in columns 5, 6 and 7 of Table 3.2.

The next step is to compare the predicted rates with the experimental evidence. As shown with MALDI-ToF MS, the extent of photodegradation of PNI aged in the UVACUBE for 1 hour corresponds to what was found approximately after 2,000 hours of ageing in the Suntest XXL+ and 17,000 hours outdoors (column 2, Table 3.2). In order to obtain relative rates of photodegradation, the data were normalized using Suntest XXL+ level as 1 (column 3, Table 3.2). An additional correction was made for data obtained outdoors. Outdoors, sun light is present only for about half of the day and during this period its intensity is the highest only at
noon. In order to compare the data obtained outdoors with laboratory (UVACUBE, Suntest XXL+) data (obtained from continuously irradiated samples) the hours of outdoor exposure were multiplied by a factor of 4 (column 4, Table 3.2). Table 3.2 shows the comparison of relative photodegradation rates of PNI obtained experimentally and predicted from the number of absorbed photons in three different ageing methods (UVACUBE, Suntest XXL+ and outdoor). The comparison shown in the Table 3.2 is based on a number of approximations and assumptions both on the experimentally obtained results as well as on the predicted data. Nevertheless, overall the experimental and predicted rates of photodegradation for three different degradation methods seem to correlate well. This calculation shows that overall UV stability may be predicted knowing some of the characteristics of the polymer (UV absorption) and conditions of ageing (spectral power distribution of light used).

Table 3.1. Number of photons per second absorbed by PNI when exposed in the UVACUBE, Suntest XXL+ and Outdoors.

<table>
<thead>
<tr>
<th>Photodegradation Methods</th>
<th>(\lambda &lt; 325)</th>
<th>(\lambda &lt; 350)</th>
<th>(\lambda &lt; 400)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suntest XXL+</td>
<td>(4.53 \times 10^{21})</td>
<td>(9.57 \times 10^{21})</td>
<td>(1.33 \times 10^{22})</td>
</tr>
<tr>
<td>UVACUBE</td>
<td>(2.69 \times 10^{25})</td>
<td>(2.69 \times 10^{25})</td>
<td>(2.69 \times 10^{25})</td>
</tr>
<tr>
<td>Outdoors</td>
<td>(5.23 \times 10^{21})</td>
<td>(1.22 \times 10^{22})</td>
<td>(1.59 \times 10^{22})</td>
</tr>
</tbody>
</table>

Table 3.2. Comparison of relative photodegradation rates of PNI obtained experimentally and predicted from calculated number of absorbed photons in three different ageing methods (UVACUBE, Suntest XXL+ and outdoor). For the calculations, spectral distributions of light in Suntest XXL+ and outdoors were taken starting at 295 nm and in UVACUBE at 254 nm up to 400 nm. Additionally the calculation was performed for \(\lambda_{\text{max}}\) 325, 350, 400 nm.

<table>
<thead>
<tr>
<th>Photodegradation Methods</th>
<th>Experimental</th>
<th>Predicted relative rates of photodegrad.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hours of ageing for corresponding extent of photodegrad.</td>
<td>(\lambda &lt; 325) nm</td>
</tr>
<tr>
<td>Suntest XXL+</td>
<td>2,000</td>
<td>1</td>
</tr>
<tr>
<td>UVACUBE</td>
<td>1</td>
<td>2,000</td>
</tr>
<tr>
<td>Outdoors</td>
<td>17,000</td>
<td>0.12</td>
</tr>
</tbody>
</table>

|                   | Corrected relative rates of photodegrad. |                   |                   |
|                   | \(\lambda < 350\) nm | \(\lambda < 400\) nm |
|                   | 1 | 1 | 1 |
|                   | 2,000 | 2,000 | 2,800 |
|                   | 0.48 | 1.15 | 1.27 |
|                   | 400 nm | 2,000 | 1.20 |
3.6 Conclusions

In this chapter, the molecular mechanism of the photolysis and photooxidation of an non-crosslinked poly(neopentyl isophthalate) \((\text{PNI})\), applied as a thin coating and aged under different conditions (UVACUBE: \(\lambda > 254 \text{ nm}\), Suntest XXL+: \(\lambda > 300 \text{ nm}\) and outdoors) was studied. The main focus of this work was (1) on the influence of wavelength and (2) on the differences between laboratory and outdoor exposure with respect to the mechanism of degradation.

With respect to the influence of the wavelength on the mechanism, it was found that photooxidation promotes the break-down of the polymer chain and the generation of functional groups such as \(\text{C=O}\) and \(\text{OH/OOH}\) in the polymer structure, as detected by ATR-FTIR. Similar changes in the ATR-FTIR spectra were observed for ageing of PNI both in UVACUBE and in Suntest XXL+.

Size Exclusion Chromatography was performed to determine changes in the size of molecules. Both an increase and a decrease of molecular weight were observed, indicating that both photocrosslinking and chain scission are taking place during photodegradation in UVACUBE and Suntest XXL+ exposure. However, ageing in UVCUBE leads to higher crosslinking / chain scission ratio as compared to Suntest XXL+.

MALDI-ToF MS revealed molecular structures of degradation products. Despite the large differences in accelerated weathering conditions between UVACUBE and Suntest XXL+, identical photolysis and photooxidation products of PNI were identified. This strongly indicates that the molecular mechanism of photolysis and photooxidation is quite similar.

These three independent analytical techniques proved that a common mechanism is operative in the photodegradation of PNI in UVACUBE and Suntest XXL+. Nevertheless due to the high absorption of short wavelength irradiation by PNI, degradation takes place mainly at the surface. More importantly short wavelength irradiation causes a dramatic speed-up of the photodegradation process.

Secondly, the influence of laboratory (Suntest XXL+) and outdoor exposure on the mechanism of degradation was studied with ATR-FTIR, SEC and MALDI-ToF MS. Ageing of PNI in Suntest XXL+ and outdoors resulted in the formation of similar chemical structures in the initial stage of ageing as investigated with all three above mentioned analytical techniques. The spectral power distribution of light provided by
Suntest XXL+ resembles the spectral distribution of natural sun light. The differences in acceleration may be due to the higher temperature and intensity of light.

Comparison of relative photodegradation rates of PNI, obtained experimentally and predicted from the calculated number of absorbed photons, for the three different ageing methods (UVACUBE, Suntest XXL+ and outdoor) seem to correlate well.
References

Photodegradation of polyesters based on isophthalate and terephthalate units

Summary

In this chapter we describe the mechanism of photodegradation of polyesters based on isophthalic and terephthalic units. Poly(neopentyl isophthalate) (PNI) and poly(neopentyl terephthalate) (PNT) were aged in the Suntest XXL+ and the mechanisms of degradation were studied with ATR-FTIR, SEC and MALDI-ToF MS. All results confirm that PNI is much more UV stable than PNT. This can be explained by the fact that the absorption spectrum of PNT has much more overlap with the spectrum of the light source than PNI has. However, the nature of the photodegradation with respect to the mechanism is not different; in both cases the same type of products are formed.
4.1 Introduction

Aromatic polyesters are commonly used in the field of coating technology. Overall good mechanical properties and low cost make them very attractive for protection against corrosion and weathering as well as for decoration purposes. Aromatic polyesters are prepared in polycondensation reactions of acids and glycols. The chemical architectures of both the acid and the glycol unit determine the mechanical properties of the polyester and the final coating. More interestingly, the chemical architecture of monomers can also strongly influence the weathering stability of aromatic polyesters. For instance, polyesters based on terephthalic acid (TPA) before weathering show very good mechanical properties (flexibility) but poor weathering stability. On the contrary, polyesters based on isophthalic acid (IPA) exhibit poor mechanical properties before weathering but excellent weathering stability. The superior performance of IPA based coatings under weathering was attributed to the lower absorption of UV light as compared to polyesters based on TPA\[^{1,2}\]. Nevertheless, under the influence of UV light, these polymers undergo degradation in outdoor conditions. As described in the literature, a Norrish photocleavage of the aromatic ester group leads to chain break-down. Radicals, which are formed in this cleavage reaction, can abstract hydrogen or undergo oxidation processes\[^{3-8}\]. Chemical changes taking place influence the physical properties and finally lead to failure of the coating. Although coatings based on IPA exhibit very good stability in outdoor conditions as compared to coatings based on TPA, further improvement of the weathering stability of polyester coatings is still required. This can only be achieved by a more detailed understanding of the molecular degradation mechanisms.

Previous studies were mainly focused on the photodegradation of polyesters based on the terephthalate (TPA) unit\[^{4-8}\] and not much work was done, either on polyesters based on IPA or on the comparison of IPA to TPA. The establishment of degradation mechanisms as well as discovery of the cause of differences in durability of both polyesters based on TPA and IPA isomers is essential for a further improvement of the weathering stability of polyester coatings. The degradation mechanisms of polymers are usually studied with spectroscopic techniques such as FTIR and UV. Recently, there has been a growing interest in the application of molecular analytical techniques like MALDI-ToF MS to study the mechanisms of
Photodegradation of polyesters based on isophthalate and terephthalate units

(thermal and photo) degradation\cite{9,10}. This technique provides detailed structural information on the degradation products, which allows establishing precise mechanisms of the degradation.

In Chapters 2 and 3 we studied and established the mechanism of photolysis and photooxidation of non-crosslinked poly(neopentyl isophthalate) (PNI) coatings exposed in the UVACUBE (\(\lambda > \sim 254\) nm), in the Suntest XXL+ (\(\lambda > \sim 300\) nm) as well as outdoors, using ATR-FTIR, SEC and MALDI-ToF MS.

In this chapter, we compare the mechanism of photodegradation of non-crosslinked poly(neopentyl isophthalate) (PNI) and poly(neopentyl terephthalate) (PNT) coatings, as exposed in the Suntest XXL+ (\(\lambda > \sim 300\) nm) light using the same experimental techniques.

4.2 Experimental

Materials

Model polyesters poly(neopentyl isophthalate) (PNI) and poly(neopentyl terephthalate) provided by DSM were used in this study. The polyesters were prepared by a bulk polycondensation with Titanium (IV) n-butoxide (Ti(OBu)\(_4\)) as a catalyst. Synthesis was performed with an excess of neopentyl glycol resulting in hydroxyl functional polymers. The characteristics of PNI and PNT are presented in Table 4.1 where \(OHV\) – hydroxyl value, \(AV\) – acid value, \(M_n\) – number average molecular weight, \(T_g\) – glass transition temperature. These parameters were determined according to procedures described in Chapter 2.

<table>
<thead>
<tr>
<th></th>
<th>(OHV) (mg KOH/g)</th>
<th>(AV) (mg KOH/g)</th>
<th>(M_n) (g/mol) (based on titration)</th>
<th>(M_n) (g/mol) (based on SEC)</th>
<th>(T_g) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNI</td>
<td>16</td>
<td>1</td>
<td>6,600</td>
<td>9,650</td>
<td>58</td>
</tr>
<tr>
<td>PNT</td>
<td>13</td>
<td>7</td>
<td>5,600</td>
<td>3,850</td>
<td>53</td>
</tr>
</tbody>
</table>

Coating preparation

Polyester coatings were prepared according to the following procedure. First polymers were dissolved in N-methyl-2-pyrrolidone (30 w/w %) and applied on aluminium plates using a doctor blade driven by 509 MC Coatmaster applicator (Erichsen GmbH). Coatings were dried at 120 °C for one hour in an oven. The
thickness of the resulting dry coating was approximately 12 μm, as measured with a TWIN-CHECK Instrument (List-Magnetic GmbH).

**Weathering conditions**

Polyester coatings were aged using a Suntest XXL+ (ATLAS), equipped with xenon lamps. The light emitted by the xenon lamps was filtered with daylight filters (λ > ~300 nm). The intensity of light in the range of 300 – 400 nm was 60 W/m². The chamber temperature was 45 ºC while the temperature of the black standard was 70 ºC. The relative humidity was 25%.

**Analytical methods**

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) was performed using a BioRad Excalibur FTS3000MX spectrometer equipped with a diamond crystal (Golden Gate). Spectra of the surfaces of the PNI coatings were recorded in the range of 4000 – 650 cm⁻¹ with a resolution of 4 cm⁻¹. For ATR-FTIR spectroscopy a small piece was cut off the coated panel and pressed on the ATR crystal. The BioRad Win-IR Pro software was used to process the data. Spectra in the range of 2300 – 3700 cm⁻¹ were normalized to the peak at 2967 cm⁻¹ (CH₃ antisymmetric stretching) and in the range of 1500 – 1900 cm⁻¹ to the peak at 1716 cm⁻¹ (C=O stretching).

Size exclusion chromatography (SEC) was carried out using a WATERS 2695 separation module and a Model 2414 refractive index detector at 40 ºC. The injection volume used was 50 μL. The column set consisted of a Polymer Laboratories PLgel guard column (5 μm particles, 50 × 7.5 mm), followed by two PLgel mixed-C columns (5 μm particles, 300 × 7.5 mm). The columns were calibrated at 40 ºC using polystyrene standards (Polymer Laboratories, M = 580 up to M = 7.1*10⁶ g/mol) in series. Tetrahydrofuran (Biosolve, stabilised with BHT) was used as eluent at a flow rate of 1.0 ml/min. Prior to the SEC analysis, the polyester was removed from the substrate and dissolved in THF (~ 5 mg/ml). In the case of aged polyester the insoluble (crosslinked gel) part of the polymer was removed by filtration (0.2 μm PTFE filter) and the soluble part was analyzed. Data acquisition and processing were performed using WATERS Empower 2 software. Chromatograms were scaled to the maximum peak height. Molecular weights were calculated from chromatograms up to 17.5 min of the elution time in case of PNI and up to 18.1 min in case of PNT.
Matrix assisted laser desorption ionization time of flight mass spectra (MALDI-ToF MS) were recorded in reflector mode using a Voyager-DE STR instrument. Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malononitrile was used as a matrix. Samples were prepared by mixing matrix, potassium trifluoroacetate and polymer sample in a volume ratio 4:1:4, with THF as a solvent. Prior to the MALDI-ToF MS analysis, the polyester was removed from the substrate and dissolved in THF. In the case of the aged polyester the insoluble (crosslinked gel) part of the degradation was removed by filtration. The soluble part was analyzed.

UV spectroscopy was performed using an UV/VIS/NIR spectrometer Lambda 900 (Perkin Elmer). Spectra were collected in the range of 500 – 200 nm. For this measurement PNI and PNT were dissolved in chloroform (0.177 g/dm³) and placed in quartz cuvettes (1 cm).

The spectral power distribution of light in the Suntest XXL+ was measured using an ultraviolet radiation spectroradiometer MSS 2040-UV.

Film thicknesses were measured with a TWIN-CHECK Instrument (List-Magnetic GmbH).

4.3 Results

4.3.1 ATR-FTIR analysis

ATR-FTIR spectroscopy was used to observe the formation of functional groups at the polymer surface during UV exposure. Figures 4.1 and 4.2 show changes in the carbonyl and hydroxyl regions of PNI exposed for up to 10,000 hours. The changes in the carbonyl and hydroxyl regions of PNT aged for up to 6,000 hours are presented in Figures 4.3 and 4.4. Ageing both of PNI and of PNT leads to changes in the ATR-FTIR spectra. New carbonyl groups (1850 – 1600 cm⁻¹) formed during UV exposure can be attributed to anhydrides, carboxylic acids and aldehydes. The new hydroxyl groups (3600 – 2400 cm⁻¹) probably originate from carboxylic acid (mentioned above), alcohol and hydroperoxide¹¹.

Although ageing of PNI and PNT both lead to changes in the ATR-FTIR spectra, at similar wavenumbers, there is considerable difference in the kinetics of ageing. The changes in the ATR-FTIR spectra of PNI aged for 10,000 hours correspond to changes in PNT spectra recorded after about 1,000 hours of ageing. This confirms the empirically known much better UV stability of PNI over PNT.
Figure 4.1. ATR-FTIR spectra (region of C=O band) of PNI coating surface, aged for up to 10,000 hours. Normalized to the peak at 1716 cm\(^{-1}\).

Figure 4.2. ATR-FTIR spectra (region of OH and OOH band) of PNI coating surface aged for up to 10,000 hours. Normalized to the peak at 2967 cm\(^{-1}\).
Figure 4.3. ATR-FTIR spectra (region of C=O band) of PNT coating surface, aged for up to 6,000 hours. Normalized to the peak at 1716 cm\(^{-1}\).

Figure 4.4. ATR-FTIR spectra (region of OH and OOH band) of PNT coating surface aged for up to 6,000 hours. Normalized to the peak at 2967 cm\(^{-1}\)
4.3.2 SEC analysis

The changes in molecular weight of PNI and PNT as caused by UV exposure were determined using Size Exclusion Chromatography. Figures 4.5 and 4.6 show the SEC chromatograms and molecular weight distribution (MWD) plots of PNI aged for up to 10,000 hours. As can be seen from Figures 4.5 and 4.6, both products with higher and lower molecular weight are formed during ageing. UV exposure leads to a chain scission of PNI, resulting in a decrease of the number average molecular weight ($M_n$) and a reduction of $M_p$ (the position of the maximum of the MWD in Figure 4.6) with exposure time as can be seen in Table 4.2. At the same time an increase of the weight average molecular weight ($M_w$) is observed (Table 4.2). Some of the radicals formed during photodegradation can recombine and form crosslinked molecules. In the first stage of this process crosslinked molecules but still soluble (sol) are formed. Extensive crosslinking results in gel (insoluble material) formation. The gel formation was observed in samples aged for 9,000 hours and more. Part of the crosslinked molecules, which were fully detected by SEC before that moment, have become insoluble and thus were removed in the filtration step. This can explain the reduction of $M_w$ for samples aged 9,000 hours and longer. Both processes, chain scission and crosslinking, contribute to the increase of the polydispersity index (PDI) expressed as $M_w / M_n$ ratio, shown in Table 4.2.

Figure 4.7 shows chromatograms and Figure 4.8 MWD plots of PNT aged for up to 1,000 hours. The ageing of PNT also leads to simultaneous chain scission and crosslinking. This is supported by the data on molecular weight (Table 4.3) in analogy to what was discussed for PNI. However, in this case much shorter UV exposure is needed for significant changes in molecular weight. Whereas with PNI, both $M_n$ and $M_p$ steadily decreased with ageing time, with PNT these parameters initially (250 hours) slightly increased and later decreased with exposure time (Table 4.3). UV exposure of PNT for 500 hours resulted in further crosslinking and chain scission. Until that moment a gradual increase of $M_w$ (Table 4.3) was observed. Ageing of PNT leads to gel formation as well, which was found already after ageing for 750 hours and more. As with PNI, the insoluble fraction was removed in the filtration step and reduction of $M_w$ was observed. As chain scission proceeds $M_n$ and $M_p$ decrease and chromatograms are shifted towards lower molecular weight values.
Figure 4.5. SEC chromatograms of PNI aged for up to 10,000 hours.

Figure 4.6. Molecular weight distribution (MWD) plots of PNI aged for up to 10,000 hours.
Table 4.2. Changes in $M_n$, $M_w$, $M_p$ and PDI of PNI aged for up to 10,000 hours.

<table>
<thead>
<tr>
<th>Time of ageing (10^3 hours)</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>$M_p$ (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9,650</td>
<td>17,310</td>
<td>16,670</td>
<td>1.8</td>
</tr>
<tr>
<td>1</td>
<td>9,640</td>
<td>19,080</td>
<td>16,600</td>
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</tr>
<tr>
<td>2</td>
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<td>2.1</td>
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<td>2.2</td>
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</tr>
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</tr>
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<td>20,380</td>
<td>11,150</td>
<td>3.1</td>
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</table>

Figure 4.7. SEC chromatograms of PNT aged for up to 1,000 hours.
Figure 4.8. Molecular weight distribution (MWD) plots of PNT aged for up to 1,000 hours.

Table 4.3. Changes in $M_n$, $M_w$, $M_p$ and PDI of PNT aged for up to 1,000 hours.

<table>
<thead>
<tr>
<th>Time of ageing (hours)</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>$M_p$ (g/mol)</th>
<th>PDI</th>
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</thead>
<tbody>
<tr>
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<td>6,510</td>
<td>1.7</td>
</tr>
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<td>8,300</td>
<td>6,940</td>
<td>2.0</td>
</tr>
<tr>
<td>500</td>
<td>3,800</td>
<td>9,400</td>
<td>6,210</td>
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</table>

4.3.3 Thickness loss

Thicknesses of coatings were measured as a function of exposure time. Ageing of PNT coatings leads to a gradual loss of thickness. Every 1,000 hours of UV exposure, the thickness was reduced by about 1 µm. The initial thickness of coatings was 12 µm, so the thickness of a PNT coating after 6,000 hours of ageing has reduced to approximately 50%. This is a strong indication that extensive photodegradation is taking place, implying material loss via evaporation of small molecules (CO$_2$, CO, CH$_2$O etc.). Contrary to what was found with PNT, the ageing of PNI for 10,000 hours did not result in any significant reduction of thickness.
4.3.4 MALDI-ToF MS analysis

MALDI-ToF MS was used to obtain structural information on the products of photolysis and photooxidation of PNI and PNT. Each polymer molecule discussed in this paper consists of a sequence of repeating units terminated with various end groups. The repeating units of PNI and PNT are built up from the same neopentyl glycol (NPG) and different phthalic acid isomers: isophthalic (IPA) and terephthalic (TPA) acids. Due to this fact particular oligomers of PNI and PNT with the same end groups will have exactly the same mass. All identified oligomers are described and listed in Table 2.1 of Chapter 2. Structures are described with numbers and small letters, e.g. 1a, which refer to Table 2.1. Due to the above mentioned fact, Table 2.1 in Chapter 2 lists only structures based on IPA.

Any molecular species with a given atomic composition is represented by “isotopic distribution” in the MALDI-ToF MS spectrum. One of the problems associated with the analysis of MALDI-ToF MS data is the “isotope overlap”. The presence of two or more molecules with a small difference in mass (2 – 4 Daltons) results in overlapping of isotope distributions. As a consequence, one clustered isotopic distribution can represent two or more molecular structures. This phenomenon complicates the identification of products. In Chapter 2, we have successfully applied in-house-developed software \cite{12,13} to overcome this problem. That program calculates the isotopic distributions for given (expected) chemical structures and compares them with the experimental data.

Figure 4.9 shows one repeating unit of the MALDI-ToF-MS spectra of PNI, non-aged (A), aged for 2,000 hours (B), 4,000 hours (C), 6,000 hours (D), 8,000 hours (E) and 10,000 hours (F). The main structure of the non-aged PNI (Figure 4.9A) is a sequence of repeating units terminated with neopentyl glycol (Structure 1a). In addition, structures 1b, 6, 8a and 8b were identified. These are presumably species inherent in polycondensation reactions (cyclic oligomers: 8b) or species being formed during polycondensation as a result of thermal or thermo-oxidative degradation reactions. Ageing for 2,000 hours (Figure 4.9B) results in the formation of other structures. Further ageing leads to a further increase of those structures and also to the formation of many new products (Figures 4.9C – F). Overall, 15 (clustered) isotopic distributions were found representing 28 molecules (Table 2.1). The same isotopic distributions were found when analyzing other repeating units, from 1,000 m/z up to 7,000 m/z.
Figure 4.10 shows one repeating unit of the MALDI-ToF MS spectra of PNT, non-aged (A), aged for 250 hours (B), 500 hours (C) and 750 hours (D). The main structure of the non-aged PNT (Figure 4.10A) is a sequence of repeating units terminated with neopentyl glycol (Structure 1a). In addition oligomers terminated on one side with neopentyl glycol and on the other side with terephthalic acid (Structures 7a and 4c) were identified. Ageing of PNT for up to 750 hours (Figures 4.10B – D) resulted in the appearance of many other structures.

MALDI-ToF MS revealed the molecular structures of degradation products. It has to be noted that, as described above, the chemical compositions of non-aged PNI and PNT are slightly different. This results in differences in the MALDI-ToF MS spectra of virgin polyesters. Nevertheless, UV exposure of PNI and PNT resulted in formation of the same isotopic distributions as can be seen from comparison of Figure 4.9F and 4.10D. Although MALDI-ToF MS is not a quantitative technique, it can clearly be seen that similar changes in MALDI spectra were observed after ageing of PNI for 10,000 hours and after ageing of PNT for only 750 hours.
Figure 4.9. Enlarged parts of Maldi-ToF MS spectra (one repeating unit) of PNI non-aged (A), aged for 2,000 hours (B), 4,000 hours (C), 6,000 hours (D), 8,000 hours (E) and 10,000 hours (F). The numbers of the isotopic distributions correspond to the structures listed in Table 2.1 of Chapter 2.
Photodegradation of polyesters based on isophthalate and terephthalate units

Figure 4.10. Enlarged parts of Maldi-ToF MS spectra (one repeating unit) of PNT non-aged (A), aged for 250 hours (B), 500 hours (C), 750 hours (D). The numbers of the isotopic distributions correspond to the structures listed in Table 2.1 of Chapter 2.

4.4 Mechanism of the photolysis and photooxidation of PNI and PNT

As described in Chapter 2, under the influence of UV irradiation, the aromatic ester group can undergo Norrish type I photocleavage. The ester group can be cleaved at three different positions (Scheme 2.1, case: A, B, C). As a consequence six different primary radicals can be formed. These radicals can undergo several reactions like rearrangements, hydrogen abstraction, oxidation and termination.

Due to Norrish type I photocleavage of the ester group described as case A in Schemes 2.1 and 2.2, an alkoxyl radical A-1 and an acyl radical A-2 are formed. The alkoxyl radical A-1 can be rearranged by formaldehyde elimination to the tertiary alkyl radical A-3 (−C<). Hydrogen abstraction by this alkyl radical leads to the formation of an isobutyl end group (Structures 3a, 4a, 4b, 5b, 5c and 9a). Alternatively the tertiary alkyl radical A-3 can disproportionate to an isobutene end group (Structures 3b, 5c and 9b). The presence of isobutyl and isobutene end groups was indicated by MALDI spectra after UV irradiation of PNI for 2,000 hours (Figure 4.9B) and of PNT for 250 hours (Figure 4.10B). This strongly suggests that both for
PNI and PNT the photocleavage according to case A takes place. In chapter 2 it was proposed that the photodegradation mechanism of PNI followed not only case A, but also B and C (Scheme 2.1). Because the present study indicates that for PNI and PNT the same products are formed, it must be concluded that also in PNT photodegradation each of the cases A, B and C are operative.

Apart from the similarity in degradation mechanism for PNI and PNT, they clearly differ in degradation rate.

The photolytic and photooxidation mechanisms occur as a consequence of UV absorption by the aromatic ester group. Figure 4.11 shows a comparison of the absorption spectra of PNI and PNT together with the spectral power distribution of light provided by the Suntest XXL+. As can be seen both polyesters absorb some UV light in the Suntest XXL+. However, the absorption spectra of PNT more strongly overlap with the spectral power distribution of the light as compared to PNI. Additionally, PNT has a higher absorption at a particular wavelength comparing to PNI. The fact that both polyesters absorb UV can explain similar chemical reactions taking place during UV exposure. The higher UV stability of PNI over PNT, can in our view, be attributed to a lower UV absorption of this polymer. It has to be noted, that the difference in the UV stability of both polyesters might also be affected by differences in the quantum yield of the photolytic decomposition (Norrish type I) of PNI and PNT. In this work, however, this aspect was not studied. In Chapter 3 the influence of the wavelength (UVACUBE: $\lambda > \sim 254$ nm and Suntest XXL+: $\lambda > \sim 300$ nm) on the mechanism of photodegradation of PNI was studied. It was found that with these two accelerated degradation systems the same products were formed. However, radiation in the range of 254 – 290 nm (because it is strongly absorbed by PNI) has a dramatic, accelerating effect on the kinetics of photodegradation. Although in the present chapter two different polyesters are studied, still the same features apply: lower UV absorption leads to a lower rate but to similar products of photodegradation.

In Chapter 3 relative rates of photodegradation were predicted from the calculated number of absorbed photons and compared to experimental data. A similar calculation could be performed for a comparison of the UV stability of PNI and PNT. However, the calculation performed in Chapter 3 was based on a number of assumptions. In the present case an additional uncertainty is caused by possible
differences in the quantum yield of photolytic decomposition (Norrish type I) between PNI and PNT. In view of mentioned facts the calculation was not performed.

The combined effect of the absorption spectrum of the polymer and the spectral distribution of light determines the depth penetration of the light, and consequently the distribution of the degradation products through the cross-section of the coating (surface effect). The spectral power distribution of light provided by Suntest XXL+ begins at about 300 nm. Based on the absorption coefficient it was calculated that the first 3 μm of the PNT coating absorbs ~95% of the light at 300 nm. This suggests that most of the degradation products are probably concentrated in the surface of PNT coating. Note that PNT also absorbs at 310 nm. In this case only ~15% of light is absorbed in the first 3 μm of the coating. Although light at 310 nm has a lower energy that light at 300 nm, it probably can cause degradation in the deeper layers of coating as well. In case of PNI, about 5% of light is absorbed at 300 nm in the first 3 μm of the coating. This suggests that in case of PNI the products of degradation are not especially located in the surface but also in the deeper layers. Based on the experimental data obtained (SEC, ATR-FTIR) there is no clear evidence of differences in surface effect between PNI and PNT. This effect might be not clearly visible in this case due to small thickness of coating (12 μm). Additionally, due to differences in molecular weight of polyesters, a precise comparison is not possible. As already mentioned, in the previous chapter the influence of wavelength (UVACUBE: \( \lambda > \sim 254 \) nm and Suntest XXL+: \( \lambda > \sim 300 \) nm) on the photodegradation of PNI was studied. In that investigation, an indication of a different distribution of degradation products throughout the thickness of PNI coating aged in the UVACUBE and Suntest XXL+ was observed. However, in that case there was a significant difference in the spectral power distribution of light provided by UVACUBE (\( \lambda > \sim 254 \) nm) and Suntest XXL+ (\( \lambda > \sim 300 \)) in relation to the absorption spectrum of PNI. PNI shows strong UV absorption in the range of 254 – 290 nm and only limited above 300 nm. This resulted in a higher concentration of products in the top layers of coatings aged in the UVACUBE in comparison to the Suntest XXL+. In these studies, the differences in absorption spectra of PNI and PNT in relation to spectral power distribution of light provided by Suntest XXL+ are relatively small and in these particular experimental conditions ageing did not result in clear differences in the surface effect between these two polyesters.
Figure 4.11. UV absorption of PNI and PNT and spectral power distribution of light provided by the Suntest XXL+. The concentration of both PNI and PNT in chloroform was 0.177 g/dm³.

4.5 Conclusions

In this work the mechanism of photodegradation of non-crosslinked poly(neopentyl isophthalate) (PNI) and poly(neopentyl terephthalate) (PNT) was studied. Polyester coatings were exposed in Suntester XXL+ (λ > ~300 nm) and the chemical changes were investigated with ATR-FTIR, SEC and MALDI-ToF MS.

UV exposure both of PNI and of PNT lead to carbonyl and hydroxyl group formation as measured with ATR-FTIR. Although similar products of degradation of both polyesters could be indentified, a significant difference in the time scale of ageing was observed. The changes in the ATR-FTIR occurring after ageing of PNI for 10,000 hours are comparable with ageing of PNT for 1,000 hours.

SEC showed significant changes in the molecular weight of aged PNI and PNT. UV exposure of both polyesters leads to chain scission and crosslinking simultaneously taking place. Extensive exposure causes gel (insoluble fraction) formation. Also in this respect a large difference in rate of photodegradation was noticed between PNI and PNT. A gel fraction was found after UV exposure of PNI for 9,000 hours and PNT for 750 hour.

MALDI-ToF MS revealed molecular structures of photolysis and photooxidation products. Ageing of PNI and PNT leads to the same products. This strongly suggests that the molecular mechanism of photodegradation is similar.
Although MALDI is not a quantitative technique, also in this case spectra of PNI aged for 10,000 hours were comparable with spectra of PNT aged for 750 hours.

It was confirmed that PNI is much more UV stable than PNT is. More interestingly it was proved that the mechanism of photodegradation is similar for both polyesters. Both PNI and PNT absorb UV light in the Suntest XXL+. This can explain the similar mechanism of photodegradation. The higher UV stability of PNI over PNT can be attributed to a lower UV absorption of PNI as compared to PNT.
References

Mechanism of crosslinking of poly(neopentyl phthalate) during photodegradation

Summary

The mechanism of crosslinking of poly(neopentyl phthalate) as a result of photodegradation was investigated. UV exposure of these polyesters resulted in gel (insoluble material) formation. The gel material was collected and the morphology of the gel material was characterized with SEM. To obtain information on the crosslinking at a molecular level the gel was decomposed by methanolysis and the decomposition products were analyzed with LC-MS.
5.1 Introduction

UV exposure of aromatic polyesters leads to extensive chemical changes\cite{1-7}. The main chemical reactions taking place are photolysis, photooxidation and photocrosslinking. Under influence of UV irradiation an aromatic ester bond can dissociate in two radicals (photolysis). These radicals can abstract hydrogen or react with oxygen (photooxidation). Alternatively, radicals can recombine and form larger molecules (photocrosslinking). As a first step of this crosslinking process a high molecular weight sol fraction (crosslinked molecules, yet still soluble) is formed. Extensive crosslinking leads to gel formation (insoluble material). Photolysis and photooxidation are mechanisms which ultimately lead to the decomposition of the polyester and have attracted most of the attention of researchers. In contrast, the chemistry of crosslinking has not been extensively studied.

The chemistry of photocrosslinking of poly(ethylene terephthalate) was investigated by Marcotte et al. Based on ESR (Electron Spin Resonance), the formation of an intermediate phenyl radical was proposed\cite{1}.

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\end{array}
\]

The recombination of two such radicals would lead to the crosslinking of polymer chains.

\[
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\text{--} \\
\text{--}
\end{array}
\]

Later, other researchers referred to this reaction as a possible mechanism of photocrosslinking of aromatic polyesters. Rivaton\cite{5} studied the photochemistry of poly(butylene terephthalate) with IR and suggested the formation of a m-biphenyl structures as an alternative to the above mentioned mechanism of photocrosslinking.

\[
\begin{array}{c}
\text{--} \quad \text{--} \\
\text{--} \\
\text{--} \\
\text{--}
\end{array}
\]

The previous studies, however, have mainly relied on IR spectroscopy. The new groups formed by crosslinking, being carbon to carbon recombination products, do not have high IR absorption coefficient. In addition, new chemical structures involved in crosslinking may be present, each only present in very small
Mechanism of crosslinking of poly(neopentyl phthalate) during photodegradation

concentration. Therefore, detection and detailed characterization of crosslinking using spectroscopic techniques may be difficult. A more detailed analysis is required for the identification of chemically crosslinked species.

In the first part of this investigation the mechanism of the photocrosslinking of poly(neopentyl isophthalate) (PNI) was studied. UV exposure of PNI in a UVACUBE ($\lambda > \sim 254$ nm) resulted in gel formation. The gel contains the highest concentration of crosslinked structures, and therefore was regarded as the most interesting material to study the mechanism of crosslinking. Since a gel is an intrinsically non-soluble polymer material, there is a limited number of analytical techniques available which can provide structural information. To obtain information on the molecular level of the crosslinking, the gel was decomposed by methanolysis (break-down of ester group) and the decomposition products were analyzed with LC-MS. This approach allowed for a detailed characterization of crosslinked moieties, and finally to the proposition of an alternative mechanism of crosslinking than the already known phenyl-to-phenyl recombination.

Secondly, the photocrosslinking of poly(neopentyl isophthalate) (PNI) and poly(neopentyl terephthalate) (PNT) aged in a Suntest XXL+ ($\lambda > \sim 300$ nm) was examined.

5.2 Experimental

Materials

Model polyesters poly(neopentyl isophthalate) (PNI) and poly(neopentyl terephthalate), provided by DSM, were used in this study. The polyesters were prepared in a bulk polycondensation with Titanium (IV) n-butoxide (Ti(OBu)$_4$) as a catalyst. Synthesis was performed with an excess of neopentyl glycol resulting in hydroxyl functional polymers. The characteristics of PNI and PNT are presented in Table 5.1 where $OHV$ – hydroxyl value, $AV$ – acid value, $M_n$ – number average molecular weight. $T_g$ – glass transition temperature. These parameters were determined according to procedures described in Chapter 2.
Table 5.1. Characteristics of PNI and PNT.

<table>
<thead>
<tr>
<th></th>
<th>$OHV$ (mg KOH/g)</th>
<th>$AV$ (mg KOH/g)</th>
<th>$M_n$ (g/mol) (based on titration)</th>
<th>$M_n$ (g/mol) (based on SEC)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNI</td>
<td>16</td>
<td>1</td>
<td>6,600</td>
<td>9,650</td>
<td>58</td>
</tr>
<tr>
<td>PNT</td>
<td>13</td>
<td>7</td>
<td>5,600</td>
<td>3,850</td>
<td>53</td>
</tr>
</tbody>
</table>

Coating preparation

Polyesters were dissolved in N-methyl-2-pyrrolidone (NMP) (30 w/w %). The solution was applied on an aluminium plate (cleaned with ethanol and acetone) using a doctor blade driven by 509 MC Coatmaster applicator (Erichsen GmbH). Coatings were dried in an oven at 120 ºC for one hour; all NMP was evaporated (checked with FTIR, C=O at 1675 cm$^{-1}$). The thickness of the resulting dry coating was approximately 12 μm as measured with a TWIN-CHECK Instrument (List-Magnetic GmbH).

UV exposure

PNI coatings were exposed to radiation in the 254 – 600 nm range in a UVACUBE apparatus (Dr. Hönle AG, equipped with a high pressure Mercury lamp). The total intensity of the light was 40 W/m$^2$ between 250 and 300 nm and 210 W/m$^2$ between 300 – 400 nm. The intensity of the light was measured with an AVS SD2000 Fiber Optic Spectrometer (Avantes). A FC-UV050-2 fiber was used. In the UVACUBE a thermostatic box was placed containing coatings which were covered with quartz glass and set at 68 °C. The box was continuously purged with the gas selected. The distance from samples to the lamp was 20 cm. Samples (5 cm × 5 cm) were exposed to UV light for either 10 or 20 hours. Experiments were performed either in dry air or in a dry nitrogen atmosphere.

Additionally, PNI and PNT coatings were aged using a Suntest XXL+ (ATLAS), equipped with xenon lamps. The light emitted by the xenon lamps was filtered with daylight filters ($\lambda > ~300$ nm) so that the spectral distribution of the light provided by this system nearly resembles the solar spectral distribution. The intensity of light in the range of 300 – 400 nm was 60 W/m$^2$, the chamber temperature was 45 ºC and the temperature of the black standard was 70 ºC while the relative humidity was 25%.
Analytical methods

Gel fractions were determined gravimetrically. The adhesion of the polyester coating to the aluminium substrate was very high and peeling off the coating for gel fraction measurement was not possible. Instead the weight of the coating together with the substrate was measured first. Then, the polyester was washed off with THF and the weight of the bare substrate was measured. The soluble part of polyester was separated from the gel by filtration (0.2 µm PTFE filter). After evaporation of the THF (24 hours at 75 °C, vacuum oven) the weight of soluble fraction was measured. Knowing the weights of the coating with the substrate, the bare substrate and the soluble fraction, the weight of the gel fraction was calculated.

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) was performed using a BioRad Excalibur FTS3000MX spectrometer equipped with a diamond crystal (Golden Gate). Spectra of the gel were recorded in the range of 920 – 750 cm⁻¹ with a resolution of 4 cm⁻¹.

The methanolysis reaction of the virgin polyester (blank test) and the gel were performed according to the reaction presented in Scheme 5.1. The reaction was carried out in a 40 ml steel reactor (Parr Instrument) containing 10 ml of methanol and 20 mg of polymer. Titanium chloride TiCl₄ (0.3 % w/w in methanol) was used as a catalyst while the reaction conditions were 170 °C for 15 hours.

Scheme 5.1. Methanolysis of esters. During this reaction methanol can attack the carbonyl (-C=O) of the ester group, yielding a methyl ester (-C(O)OCH₃) and hydroxyl (-OH) groups. Methanol might also attack the methylene (-CH₂-) group, in which case carboxylic acid (-C(O)OH) and methoxy (-OCH₃) groups will be formed. Alternatively, OH-functional molecules can undergo Lewis-acid catalyzed etherification with methanol.

High performance liquid chromatography was performed using an Agilent 1100 series system consisting of a G1311A quaternary pump, a G1322A degasser and an G1313A autosampler. An Agilent 1100, G1315B, UV DAD (diode array detector) detector with detection wavelength 254 nm was used. Chromatographic separation
was obtained using Zorbax RX-C8 (150 mm × 2.1 mm; 5 µm) columns. The mobile phase was a methanol / water mixture with 0.1 % of acetic acid as modifier. The injection volume was 1 µl, the flow rate 0.25 ml/min and the column temperature 25 °C. The molecules were identified by mass spectrometry using an Agilent MSD type SL (G1946D) with Atmospheric Pressure Electrospray Interface. The mass spectrometer was operated in positive mode in the mass range 100 – 450 Da. The following parameters of ESI were used: drying gas temperature 350 °C at flow 13 L/min, nebuliser pressure 30 psi, capillary voltage 4,000 V.

Scanning electron microscopy (SEM) was performed using a Jeol JSM-840A Scanning Microscope at an accelerating voltage of 20 kV.

5.3 Results and Discussion

5.3.1 PNI aged in the UVACUBE (λ > ~254 nm)

5.3.1.1 Gel fraction

UV exposure of PNI leads to gel formation. Figure 5.1 shows the gel fraction of the polyester aged in air and nitrogen for 10 and 20 hours. As can be concluded, UV irradiation leads to a higher amount of gel in air then in nitrogen. The difference in the extent of crosslinking between air and nitrogen can be explained from the chemistry of the degradation processes. In nitrogen as well as in air, direct photolysis of the polyester takes place. Radicals generated can recombine forming C–C bonds resulting in crosslinked molecules. In air, photooxidation takes place additionally to direct photolysis. The mechanism of photooxidation is known to involve hydroperoxide formation. During photooxidation radicals (P’) formed due to direct photolysis of the ester group can react with oxygen and form peroxy radical (POO’). This radical can abstract hydrogen and form hydroperoxide (ROOH) and a new radical (P1’). Decomposition of the hydroperoxide will lead to polymer oxy (PO’) and hydroxyl (’OH) radicals. Each of these radicals can initiate a chain of reactions and in this way generate even more radicals. In nitrogen oxidation does not take place and radicals are formed only due to direct photolysis. Therefore in air there is a higher total number of radicals present as compared to nitrogen. A higher amount of radicals implies a higher probability of the radicals to recombine and thus a higher rate of crosslinking (gel formation). In addition to carbon-to-carbon recombination ether and perether bridges can be formed.
Mechanism of crosslinking of poly(neopentyl phthalate) during photodegradation

5.3.1.2 Gel morphology

When exposing polyester coatings to organic solvents (THF, chloroform) surprisingly it was noted that the insoluble top layer forms fibrous or needle like structures. After solvent evaporation, these structures were analyzed with Scanning Electron Microscope. Figures 5.2 and 5.3 show SEM graphs of the gel fraction collected from coatings aged for 20 hours in nitrogen and air conditions, respectively. As can be seen each individual fiber is in fact a rolled-up layer of a crosslinked polymer. This is a strong indication that crosslinked molecules form a skin layer on top of a UV exposed coating. This crosslinked layer (gel) has a non-uniform crosslinked density. The side of the layer that is directed to the surface of the coating will have the highest crosslink density. When exposed to a solvent this side has less tendency to swell than the other side of the crosslinked layer. As a consequence the side of the layer that is directed to the coating surface becomes the interior side of the roll that visually appears as needle. Possibly differential internal stresses due to gradient in crosslinking also contribute. The gel material in the coating is present in the form of a three dimensional network. After dissolving and drying for SEM analysis it obviously shrinks. Therefore from SEM graphs the evaluation of the actual thickness of the gel layer is difficult. However, an estimation of its thickness can be made in a different way. In these experiments coatings were exposed in the UVACUBE ($\lambda > \sim 254$). Approximately 85% of the light in the range of 254 – 290 nm

![Figure 5.1](image-url)
is absorbed by the first 3 µm of the PNI coating. Thus it can be assumed that upon ageing in a UVACUBE the gel is formed primarily in the top 3 to 4 µm of the coating.

Figure 5.2. SEM graphs of gel collected from PNI coatings UV exposed in the UVACUBE for 20 hours in nitrogen.

Figure 5.3. SEM graphs of gel collected from PNI coatings UV exposed in the UVACUBE for 20 hours in air.
5.3.1.3. Chemical characterization of the gel

**ATR-FTIR analysis**

ATR-FTIR spectroscopy was used to characterize the gel. The general inspection of gel with ATR-FTIR in the range of 3700 – 700 cm\(^{-1}\) did not generate information from which the chemistry of crosslinking could be deducted. However, interesting changes in the ATR-FTIR spectra were found in the range of 920 – 750 cm\(^{-1}\). Figure 5.4 shows comparison of ATR-FTIR spectra in the above mentioned range for the virgin polyester and the gel collected from coatings aged for 20 hours in nitrogen (A) and 20 hours in air (B) conditions, respectively. It can be concluded that the band at 825 cm\(^{-1}\) decreases and a broad band in the range of 850 – 920 cm\(^{-1}\) develops. The band at 825 cm\(^{-1}\) is probably due to C–H deformation of three adjacent hydrogens on an aromatic ring (1,3 substitution)\(^{[8,9]}\). A decrease of this band is an indication of phenyl substitution. The band developing in the range of 850 – 920 cm\(^{-1}\) can be associated with the C–H deformation of isolated hydrogens on an aromatic ring\(^{[8,9]}\) like, for example, 1,3,5 substitution. This may explain the decrease of band at 825 cm\(^{-1}\) and the increase in range of 850 – 920 cm\(^{-1}\). Although in this work we study a polyester based on isophthalic units, these results confirm the phenyl-to-phenyl recombination which was earlier proposed for polyesters based on the terephthalic unit.

![Figure 5.4. ATR-FTIR spectra of non aged PNI and of gel, after 20 hours of UV exposure in the UVACUBE, in nitrogen (A) and in air (B).](image-url)
Methanolysis and LC-MS analysis

In order to obtain detailed information on the chemistry of crosslinking, the gel material was decomposed by methanolysis and analyzed using liquid chromatography combined with mass spectrometry. In this approach insoluble material, which is generally difficult to characterize, is converted into soluble fragments and studied on the molecular level. A crosslinked structure can be formed either by “chain coupling” (A) and/or by “grafting” (B) reactions. Both resulting structures are shown in Scheme 5.2. As described in the experimental section, methanolysis breaks down ester bonds. Since crosslinking is expected to be carbon-to-carbon recombination, crosslinked sites (○, Scheme 5.2) should not be affected by methanolysis. It should be noted that, although unexpected, crosslinked sites not based on carbon-to-carbon recombination products, are likely to be lost in this process.

Scheme 5.2. Graphical illustration of methanolysis of the gel, formed by chain coupling (A) and by grafting (B).

As shown and explained in the experimental section (Scheme 5.1), methanolysis of polyester leads to the formation of small molecules with mainly methyl ester, hydroxyl, acid and methoxy end groups. Different combinations of these end groups will result in different polarities and masses of particular fragments. The gel material collected from coatings aged in nitrogen was chosen as study material in order to have the highest possible content of carbon-to-carbon crosslinked moieties. As a blank reference, a non-aged polyester was used. The separation of methanolysis fragments of the virgin polymer and the gel was performed with chromatography combined with an UV-DAD detector and with mass spectrometry. Figure 5.5 shows UV-DAD and ESI-MS total ion current (TIC) chromatograms of the methanolized non-aged polyester. The TIC chromatograms show more peaks as compared to the UV-DAD chromatograms. Probably structures represented by peaks in the TIC
chromatogram, while not observed in UV-DAD chromatogram, are present in small concentration and/or have low UV absorption. Figure 5.6 shows UV-DAD and TIC chromatograms of the methanolized gel. Both UV-DAD and TIC chromatograms of the methanolized gel (Figure 5.6) show a higher number of peaks as compared to the virgin polymer (Figure 5.5). This is an indication of a different chemical composition of the gel as compared to non-aged polyester. The mass spectrometry was performed in positive mode; most of molecules are protonated and/or sodiated species. All identified molecules, with masses and retention times, are presented in Table 5.2. The methanolysis of virgin polymer leads to original, monomer fragments (Structures 1, 2, 3, 4, 5 and 7, Table 5.2). For instance, Figures 5.7 and 5.8 show the mass spectra of molecules 1 and 4 which appeared in the TIC chromatogram (Figure 5.5) at 2.4 and 8 min of retention time. In the methanolized gel, in addition to the above mentioned molecules, the following structures were identified: 6, 8, 9, 10 and 11 (Table 5.2). The structures 9, 10 and 11 represent crosslinked monomers. These crosslinked moieties are believed to have been responsible for the gel formation. Figures 5.9 and 5.10 show mass spectra of crosslinked molecules (Structure 10 and 11, Table 5.2) represented in the TIC chromatogram (Figure 5.6) at 11.7 and 14.2 min of retention time.
Figure 5.5. UV-DAD and TIC (total ion current) chromatograms of methanolized non-aged PNI.

Figure 5.6. UV-DAD and TIC (total ion current) chromatograms of methanolized gel.
Figure 5.7. Mass spectrum of sodiated ($m/z$ 127) neopentyl glycol (Structure 1), corresponding to peak at 2.4 min retention time in TIC chromatograph of non-aged PNI.

Figure 5.8. Mass spectrum of protonated ($m/z$ 181) and sodiated ($m/z$ 203) mono-Methyl isophthalate (Structure 4), corresponding to peak at 8 min retention time in TIC chromatograph of non-aged PNI.
Figure 5.9. Mass spectrum of protonated ($m/z$ 195) and sodiated ($m/z$ 217) dimethyl isophthalate (Structure 5) and protonated ($m/z$ 249) and sodiated ($m/z$ 271) methylated NPG dimer (Structure 10), corresponding to peak at 11.7 min retention time in TIC chromatograph of methanolized gel.

Figure 5.10. Mass spectrum of protonated ($m/z$ 329) and sodiated ($m/z$ 351) phenyl to phenyl crosslinked molecule (Structure 11), corresponding to peak at 14.2 min retention time in TIC chromatograph of methanolized gel. The peak at 297 $m/z$ corresponds to fragment (M – MeO).
5.3.1.4 Mechanism of crosslinking

As described earlier, Norrish type I photocleavage is the main initiation step of photodegradation of poly(neopentyl isophthalate) (PNI). The ester group can be cleaved at three different positions creating six possible different primary radicals (Scheme 5.3). Under inert conditions, these radicals can directly, or after rearrangement, abstract hydrogen and form new end groups. The most labile hydrogen atoms on the PNI backbone are located in the \( \alpha \)-position of the ester group. As presented in Scheme 5.4, macromolecular alkyl radicals (\(-\text{CH}–\text{C(O)}\)) result from hydrogen abstraction from those positions. Recombination of these radicals will lead to crosslinking (Scheme 5.4). Structures 9 and 10 (Table 5.2) identified with LC-MS are clear evidence of “chain coupling” recombination taking place.

As was illustrated in Scheme 5.3, in case C the phenyl radical \( \text{C-2} \) can be formed by photocleavage of the ester group. It can also be formed by decarbonylation of the acyl or by decarboxylation of the carboxyl radicals. It was shown in Chapter 2 that phenyl radicals \( \text{C-2} \) can abstract hydrogen and form a benzoic end group. This structure was observed (MALDI-ToF MS). It appears that the phenyl radical can also react with an isophthalate unit of the polyester chain and in this way form “grafted” crosslinked molecules (Scheme 5.5).

As shown above, the mechanism of crosslinking can have a “chain coupling” (Structures 9 and 10) or a “grafting” (Structure 11) character. These findings are in line with the earlier suggested phenyl to phenyl crosslinking mechanism of PET.

\[
\text{Scheme 5.3. Norrish type I photocleavage of ester group, case: A, B, C.}
\]
Scheme 5.4. “Chain coupling”-like crosslinking.

Scheme 5.5. “Grafting”-like crosslinking.

Table 5.2. Molecules identified with LC-MS.

<table>
<thead>
<tr>
<th>Number</th>
<th>Structure</th>
<th>Mass (m/z) H⁺</th>
<th>Mass (m/z) Na⁺</th>
<th>Retention time (min)</th>
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</thead>
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<tr>
<td>1</td>
<td>HO-(\equiv)OH</td>
<td>105</td>
<td>127</td>
<td>2.4</td>
</tr>
<tr>
<td>2</td>
<td>HO-(\equiv)O</td>
<td>119</td>
<td>141</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>HO-(\equiv)C((\equiv))OH</td>
<td>167</td>
<td>189</td>
<td>5.4</td>
</tr>
<tr>
<td>4</td>
<td>HO-(\equiv)C((\equiv))O</td>
<td>181</td>
<td>203</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>O-(\equiv)C((\equiv))O</td>
<td>195</td>
<td>217</td>
<td>10.7</td>
</tr>
</tbody>
</table>
Mechanism of crosslinking of poly(neopentyl phthalate) during photodegradation

<table>
<thead>
<tr>
<th></th>
<th>Structure</th>
<th>λ (nm)</th>
<th>Δλ (nm)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td><img src="image6.png" alt="Structure 6" /></td>
<td>253</td>
<td>275</td>
<td>10.1</td>
</tr>
<tr>
<td>7</td>
<td><img src="image7.png" alt="Structure 7" /></td>
<td>267</td>
<td>289</td>
<td>12.3</td>
</tr>
<tr>
<td>8</td>
<td><img src="image8.png" alt="Structure 8" /></td>
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</tr>
<tr>
<td>10</td>
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</tr>
<tr>
<td>11</td>
<td><img src="image11.png" alt="Structure 11" /></td>
<td>329</td>
<td>351</td>
<td>14.2</td>
</tr>
</tbody>
</table>

5.3.2 PNI and PNT aged in the Suntest XXL+ (λ > ~300 nm)

The previous paragraph described the mechanism of photocrosslinking of PNI exposed in the UVACUBE (λ > ~254 nm). As it was shown in Chapter 2, the presence of irradiation below 300 nm strongly accelerates the photodegradation of the polyester. The other accelerated photodegradation system used in these studies is the Suntest XXL+ (λ > ~300 nm). UV exposure of poly(neopentyl isophthalate) (PNI) and poly(neopentyl terephthalate) (PNT) in the Suntest XXL+ also resulted in gel formation. Figure 5.11 shows the gel fractions collected from PNI aged for up to 10,000 hours and PNT aged for up to 6,000 hours. The higher UV stability of PNI over PNT was discussed in Chapter 4 and was related to the lower UV absorption of PNI as compared to PNT. In case of PNI the first indication of gel formation was found after 9,000 hours of ageing and after 10,000 the gel fraction reached about 5%. UV exposure of PNT leads to more extensive crosslinking then PNI (Figure 5.11).
After 2,000 hours of UV exposure the gel fraction reached about 50% and only slightly increased after an additional 1,000 hours of ageing. Further UV exposure apparently leads to decomposition of the gel which results in a reduction of the gel fraction to about 40%.

The morphology of the gel collected from PNT aged in the Suntest XXL+ was similar to the one collected from PNI aged in the UVACUBE (rolled up sheets). As shown in chapter 4, PNT strongly absorbs light in the Suntest XXL+. Approximately 95% of light at 300 nm and only 15% at 310 nm is absorbed by upper 3 µm of the PNT coating. This may lead to a gradient in the concentration of degradation products (including gel) through the thickness of coating. The morphology of gel collected from PNI in the Suntest XXL+ did not show needle-like structures. This might be due to a too low concentration of gel (only about 5% gel fraction). However, it has to be noted that, as shown in Chapter 3 and 4, PNI coatings in the Suntest XXL+ absorb only small amounts of light in the top layers. In this case it is likely that a gel structure is not especially formed in the top layer but also in deeper layers of coating.

![Figure 5.11. Gel fractions in PNI and PNT coatings, UV exposed in Suntest XXL+.](image)

5.4 Conclusions

In this chapter photocrosslinking of poly(neopentyl phthalate) was studied. In the first part of this investigation the mechanism of crosslinking of poly(neopentyl isophthalate) (PNI) as a result of photodegradation was studied. PNI coatings were exposed in the UVACUBE (\(\lambda > 254\) nm). UV irradiation resulted in gel formation (insoluble material). The gel was collected and chemically characterized. It was observed that when aged coatings are subjected to organic solvents (THF), the gel material forms needle-like structures. Using SEM it was shown that these needles are in fact rolled-up layers of crosslinked polymer. This indicated that gel material had formed a skin layer in the top of a UV irradiated coating. Chemical characterization of the gel was performed with ATR-FTIR and methanolysis combined with LC-MS. ATR-FTIR of the gel material indicated phenyl substitution (850 – 920 cm\(^{-1}\) area). During methanolysis the ester bonds of gel material were broken down, causing the insoluble material to become soluble again and suitable to be analyzed with LC-MS. In addition to the phenyl-phenyl coupling, it was found that radicals formed in the \(\alpha\)-position to the ester group can recombine and form crosslinked moieties.

Secondly, PNI and PNT coatings were aged in the Suntest XXL+ (\(\lambda > 300\) nm). UV exposure of PNI and PNT in these conditions also resulted in gel formation, much more in PNT than in PNI. The PNT gel did give needle-like structures in THF whereas PNI did not.
Chapter 5

References

Correlations between chemical and physical changes of polyester coatings under UV irradiation

Summary

The influence of chemical changes taking place during photodegradation of aromatic polyester coatings on the surface physical properties was studied. In order to distinguish between different chemical reactions, degradation experiments were performed in air and nitrogen atmosphere. Chemical changes were studied with ATR-FTIR spectroscopy and SEC chromatography. As investigated with ATR-FTIR, UV exposure in air leads to extensive carbonyl and hydroxyl group formation (photooxidation) in the polyester. On the other hand, upon ageing in nitrogen such groups are only formed to a minor extent. As proven with SEC, UV irradiation leads to simultaneous chain scission and crosslinking. The extent of both chain scission and crosslinking is higher when aging occurs in air than in nitrogen. Extensive crosslinking leads to insoluble material (gel) formation. Depth-sensing indentation was used to investigate the mechanical properties of aged coatings, showing an increase in hardness. It was established that photooxidation is the predominant cause of hardness increase as it leads to polar group formation.

Part of this chapter is submitted for publication: P. Malanowski, H. Kranenburg, F. Scaltro, R. A. T. M. van Benthem, L. G. J van der Ven, J. Laven, G de With, Correlations between chemical and physical changes of poly(neopentyl isophthalate) coatings under short wavelength UV irradiation.
6.1 Introduction

Polymeric coatings are used for protective and decorative reasons. Unfortunately in weathering conditions numerous factors like UV irradiation, water and temperature can cause changes in the chemical structure of polymeric coatings. This can influence the physical properties, ultimately leading to failure (cracking, gloss loss, blistering and delamination) and reduction of their lifetime [1]. The correlation of chemical reactions and resulting physical properties taking place during ageing is essential for a complete understanding of the weathering process.

UV light is known to be the dominant factor affecting durability of polymeric materials outdoors. One of the main chemical reactions taking place under the influence of UV radiation is chain scission (photolysis). Radicals formed from this reaction can abstract hydrogen or react with oxygen (photooxidation). Additionally, radicals can recombine and form networks (photocrosslinking) [1,2]. All these chemical reactions can change the chemical nature of the polymer (decrease or increase the molecular weight, increase the polarity) and thereby influence its physical properties [3-5]. In order to probe changes in mechanical properties, hardness is often measured as a function of exposure time. It has been reported that in some cases UV irradiation of polymers may lead to an increase [6-12], in other cases to a decrease [12,13] of hardness. However, in most of the cases an increase of hardness is reported. The impact of chemical degradation on the physical properties may depend on which reaction (chain scission, crosslinking) is dominant, the relative ratio of these reactions and possible synergetic effects.

Usually during ageing a number of mechanisms is involved simultaneously. Therefore establishing the contribution of each specific reaction to the change of physical properties is almost impossible.

In the first part of this investigation, poly(neopentyl isophthalate) (PNI) coatings, were aged in a UVACUBE (λ > ~254 nm). UV exposure was carried out in different atmospheres (air and nitrogen) in order to distinguish oxygen dependent chemical reactions and their influence on the mechanical properties. Since the temperature can influence the mechanism of photodegradation and consequently the physical properties, PNI coatings were aged at two different temperatures. The changes in chemical structure were studied with ATR-FTIR, SEC and by measuring
the gel fraction. Depth-sensing indentation was found to be a suitable tool to study the mechanical properties of aged coatings.

In the second part, poly(neopentyl isophthalate) (PNI) and poly(neopentyl terephthalate) (PNT) coatings were aged in a Suntest XXL+ (λ > ~300 nm). The difference in the extent of the chemical reactions taking place during ageing and their influence on the mechanical properties of both polyesters was investigated.

6.2 Experimental

Materials

Poly(neopentyl isophthalate) (PNI) and poly(neopentyl terephthalate) (PNT), provided by DSM were used in this study. The polyesters were prepared in a bulk polycondensation with Titanium (IV) n-butoxide (Ti(OBu)₄) as a catalyst. Synthesis was performed with an excess of neopentyl glycol resulting in hydroxyl functional polymers. The characteristics of PNI and PNT are presented in Table 6.1. OHV – hydroxyl value, AV - acid value, Mₙ – number average molecular weight. Tₕ – glass transition temperature. These parameters were determined according to procedures described in Chapter 2.

Table 6.1. Characteristics of PNI and PNT

<table>
<thead>
<tr>
<th></th>
<th>OHV (mg KOH/g)</th>
<th>AV (mg KOH/g)</th>
<th>Mₙ (g/mol) (based on titration)</th>
<th>Mₙ (g/mol) (based on SEC)</th>
<th>Tₕ (°C)</th>
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<td>6,600</td>
<td>9,650</td>
<td>58</td>
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<td>PNT</td>
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<td>7</td>
<td>5,600</td>
<td>3,850</td>
<td>53</td>
</tr>
</tbody>
</table>

Coating preparation

The polyester was dissolved in N-methyl-2-pyrrolidone (NMP) (30 % w/w) and applied on an aluminium plate (cleaned with ethanol and acetone) using a doctor blade driven by 509 MC Coatmaster applicator (Erichsen GmbH). Coatings were dried in an oven at 120 ºC for one hour; all NMP was evaporated (checked with FTIR, C=O at 1675 cm⁻¹). After drying the polyester remained amorphous (as checked with DSC). The coating thickness after drying was approximately 12 μm as measured with a TWIN-CHECK Instrument (List-Magnetic GmbH).
UV exposure

In the first part of this investigation PNI coatings were exposed to radiation in the 254 – 600 nm range in a UVACUBE apparatus (Dr. Hönle AG, equipped with a high pressure Mercury lamp). The intensity of the light was 40 W/m² in the range of 250 – 300 nm and 210 W/m² in the range of 300 – 400 nm, as measured with AVS SD2000 Fiber Optic Spectrometer (Avantes) using a FC-UV050-2 fiber. In the UVACUBE the PNI coatings were in a thermostatic box set at 68 °C or at 43 °C covered with quartz glass and continuously purged with the gas selected. The distance from samples to the lamp was 20 cm and samples (5 cm × 5 cm) were exposed to UV light for either 10 or 20 hours. Experiments were performed either in dry air or in dry nitrogen atmosphere.

In the second part of this investigation PNI and PNT coatings were aged using a Suntest XXL+ (ATLAS), equipped with xenon lamps. The light emitted by the xenon lamps was filtered with daylight filters (λ > ~300 nm). The spectral distribution of the light provided by this system nearly resembles the solar spectral distribution with an intensity of the light in the range of 300 – 400 nm of 60 W/m². The chamber temperature was 45 °C and the temperature of the black standard was 70 °C all experiments were at a relative humidity 25%.

Analytical methods

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) was performed using a BioRad Excalibur FTS3000MX spectrometer equipped with a diamond crystal (Golden Gate). Spectra of the surface of the PNI coatings were recorded in the range of 4000 – 650 cm⁻¹ with a resolution of 4 cm⁻¹. For ATR-FTIR spectroscopy a small piece was cut from the coated panel and pressed on the ATR crystal. Spectra in the range of 2300 – 3700 cm⁻¹ were normalized to the peak at 2967 cm⁻¹ (CH₃ antisymmetric stretching) and in the range of 1500 – 1900 cm⁻¹ to the peak at 1716 cm⁻¹ (C=O stretching). The ratio of the carbonyl peak area between 1900 and 1625 cm⁻¹ and the peak area at 723 cm⁻¹ attributed to the aromatic ring was calculated. The value of that ratio in excess over its starting value is defined as the “carbonyl index” and is used as a measure of the formation of carbonyl groups.

Size exclusion chromatography (SEC) was carried out using a WATERS 2695 separation module and a Model 2414 refractive index detector at 40 °C using an injection volume of 50 µL. The column set consisted of a Polymer Laboratories PLgel
Correlations between chemical and physical changes of polyester coatings under UV

guard column (5 µm particles, 50 × 7.5 mm), followed by two PLgel mixed-C columns (5 µm particles, 300 × 7.5 mm), calibrated at 40 °C using polystyrene standards (Polymer Laboratories, $M = 580$ up to $M = 7.1\times10^6$ g/mol). Tetrahydrofuran (Biosolve, stabilised with BHT) was used as eluent at a flow rate of 1.0 ml/min. Prior to the SEC analysis, the polyester was removed from the substrate and dissolved in THF. In the case of aged polyester the insoluble (crosslinked gel) part of the polymer was removed by filtration (0.2 µm PTFE filter) and the soluble part (concentration ~ 5mg/ml in THF) was analyzed. Data acquisition and processing were performed using WATERS Empower 2 software. Chromatograms were scaled to the maximum peak height.

Gel fractions were measured gravimetrically. The adhesion of the polyester coating to the aluminium substrate was very high and peeling off the coating for gel fraction measurement was not possible. Instead the weight of the coating together with the substrate was measured first. Later, the polyester was washed with THF off the substrate and the weight of the bare substrate was measured. The soluble part of polyester was separated from the gel part by filtration (0.2 µm PTFE filter). After evaporation of THF (vacuum oven, 24 hours at 75 °C) the weight of the soluble fraction was measured. From the weights of the coating with substrate, the bare substrate and the soluble fraction, the weight of the gel fraction was calculated.

Depth-sensing indentation was performed with a TriboIndenter (Hysitron), equipped with a 2D-transducer and a Berkovich tip, on polyester coatings at 25 °C and reduced humidity (13.2 ± 0.3 % RH). As the maximum indentation depth was at most 9% of the total coating thickness (12 µm), the obtained hardness was not influenced by the properties of the aluminum coating substrate. A loading scheme of 10 s loading to maximum load ($P_{\text{max}}$), 10 s hold at maximum load and 1 s unloading was applied. For each sample, at least one series of 10 experiments was performed in which the maximum load was varied in steps of 300 µN from 3,000 µN to 300 µN. For coatings that exhibited a relatively high surface roughness and low thickness (PNT after 4,000, 5,000 and 6,000 hours of ageing in a Suntest XXL+) additionally, a series of 8 measurements was performed at higher load levels, namely ranging from 4200 to 2100 µN. The first two measurements of each series were disregarded to exclude the effect of thermal drift. For samples where two or more series of ten indents were made, no significant differences were observed between the series.
The indentation load-displacement responses were analyzed using the procedure proposed by Oliver and Pharr\textsuperscript{[14]}. The mean contact pressure is taken as a measure of the hardness $H$ of the material:

\[ H = \frac{P_{\text{max}}}{A} \]  

(1)

where $P_{\text{max}}$ is the load at the beginning of the unloading and $A$ is the projected contact area, which depends on the contact depth $h_c$ and the tip shape. The tip area function calibration was performed on polystyrene, assuming a constant elastic modulus for polystyrene in the contact depth range from 126 to 954 nm (Appendix 6.1). The unloading responses were fitted from $0.95 \cdot P_{\text{max}}$ to $0.20 \cdot P_{\text{max}}$ with the conventional power law form to obtain the slope at the start of the unloading $S$, that is used in the calculation of the contact depth\textsuperscript{[14]}. The obtained fits match well with the unloading responses even outside of the range used for fitting: $R^2$ was observed to be larger than 0.999. The power law exponents ranged from 1.6 to 2.4. The cause for lower values than the value of 2, expected for the contact of a cone onto an elastic halfspace\textsuperscript{[15]}, are discussed by Bolsakov and Pharr\textsuperscript{[16]}. For some of the fits power values higher than 2 were obtained. This possibly is attributable to non-linear elastic and visco-elastic response of the polymer material. We noted that the hardness decreased with the contact depth. Therefore, in order to achieve a fair comparison, the hardness was evaluated at constant contact depth (400 nm, for the higher load series 550 nm) for the various ageing conditions (evaluation at another contact depth gives the same trends at somewhat shifted hardness values, Appendix 6.1), whereby a linear fit was applied to the hardness data as function of contact depth for the various ageing conditions.

It is acknowledged that the procedure to calculate the projected contact area has been developed for elastic-plastic materials and the actual projected contact area may be somewhat different for visco-elastic-plastic materials such as polymers\textsuperscript{[17,18]}. So, the hardness obtained by indentation depends on experimental settings such as the loading and unloading rate\textsuperscript{[19-21]}. We ascertained that the creep rate at the end of the hold period is small enough to safely ignore the effect of creep on the hardness. Though depth-scanning indentation does not provide absolute values for the hardness, the obtained hardness can be used as a reliable measure to compare different samples.

Scanning Electron Microscopy was performed using the Phenom™ Desktop SEM (FEI Company).
6.3 Results

6.3.1 PNI exposed in the UVACUBE (λ > 254 nm)

6.3.1.1 Chemical characterization

ATR-FTIR analysis

The formation of functional groups at the surface of the polyester coating during photodegradation was examined with ATR-FTIR. Figure 6.1 shows changes in the carbonyl region of the polyester exposed to UV in nitrogen and in air atmosphere at 68 °C. The corresponding changes in the hydroxyl region are presented in Figure 6.2. Ageing of polyester coatings in nitrogen leads only to little changes in the ATR-FTIR spectra as compared to ageing in air atmosphere. The development of carbonyl groups (1850 – 1600 cm\(^{-1}\)) is probably caused by the formation of anhydrides, carboxylic acids and aldehydes. The increased absorption in the OH region (3600 – 2500 cm\(^{-1}\)) can be attributed to hydroxyl groups originating from carboxylic acid (mentioned above), alcohol and hydroperoxide.

In addition, ageing of PNI in nitrogen and air was performed at 43 °C (Figures 6.3 and 6.4). Ageing at 43 °C leads to qualitatively similar changes in the FTIR spectra as at 68 °C. However, the rate of the changes at 43 °C is lower.

Overall, the rate of formation of polar groups (C=O, OH) at the polyester coating surface increases as a function of exposure time (10 and 20 hours) and temperature (43 and 68 °C). However, the most important factor determining the development of polar groups is the atmosphere (air vs. nitrogen). Figure 6.5 shows the development of the carbonyl index of the polyester coating when UV irradiated in nitrogen and air at 43 and 68 °C. Only exposure in air atmosphere leads to significant surface changes as observed with ATR-FTIR.

The differences in the formation of functional groups in air and nitrogen can obviously be explained by the accepted mechanism of photooxidation and photolysis. Under influence of UV irradiation, the polyester chains break-down (photolysis) and radicals are formed. Under nitrogen, these radicals can only abstract hydrogen or recombine. As a consequence of the hydrogen abstraction, only a small amount of additional hydroxyl and carbonyl groups can be formed. This explains the relatively small changes observed with ATR-FTIR of coatings aged in nitrogen. In an air atmosphere, the same radicals, apart from hydrogen abstraction and recombination, can react with oxygen (photooxidation) and form numerous new hydroxyl and
carbonyl end groups, which leads to the aforementioned larger changes observed with ATR-FTIR.

**Figure 6.1.** ATR-FTIR spectra (region of C=O band) of PNI coatings, UV exposed in the UVACUBE, in air and nitrogen conditions at 68 °C. Normalized to the peak at 1716 cm$^{-1}$.

**Figure 6.2.** ATR-FTIR spectra (region of OH/OOH band) of PNI coatings, UV exposed in the UVACUBE, in air and nitrogen conditions at 68 °C. Normalized to the peak at 2967 cm$^{-1}$.
Figure 6.3. ATR-FTIR spectra (region of C=O band) of PNI coatings, UV exposed in the UVACUBE, in air and nitrogen conditions at 43 °C. Normalized to the peak at 1716 cm⁻¹.

Figure 6.4. ATR-FTIR spectra (region of OH/OOH band) of PNI coatings, UV exposed in the UVACUBE, in air and nitrogen conditions at 43 °C. Normalized to the peak at 2967 cm⁻¹.
SEC analysis and gel formation.

Size Exclusion Chromatography was performed to determine changes in molecular weight. Figures 6.6 and 6.7 show SEC chromatograms of the polyester aged in nitrogen and in air at 68 °C and at 43 °C, respectively. As can be seen, both molecules with higher and with lower molecular weight are formed during UV exposure in nitrogen and air. This indicates that chain scission and crosslinking reactions take place simultaneously. The extent of both chain scission and crosslinking increases with time (10 and 20 hours) and temperature (43 and 68 °C) of UV exposure. The rates of both reactions differ between air and nitrogen conditions. However, the influence of air on the extent of the chain scission and crosslinking is not as much pronounced as on formation of polar groups at the surface observed with ATR-FTIR.

Extensive crosslinking leads to gel (insoluble crosslinked molecules) formation. Figure 6.8 shows the amount of gel collected from the polyester aged in nitrogen and air atmosphere at 43 and 68 °C. Also in this case, the extent of gel fraction increases with increasing time (10 and 20 hours), and temperature (43 and 68 °C). Moreover, the atmosphere (nitrogen and air) of ageing has a very important effect.

The difference between air and nitrogen for the extent of chain fragmentation and crosslinking can be explained by the chemistry of the degradation processes. In
nitrogen some of the radicals formed during photolysis can recombine and form carbon-to-carbon crosslinked molecules. In air, besides the radicals resulting from direct photolysis, photooxidative decomposition of the polymer chain leads to additional radical formation. The mechanism of photooxidation is known to involve hydroperoxide formation, which after decomposition result in a higher total number of radicals present in air as compared to nitrogen. A higher concentration of radicals implies a higher probability of recombination and higher rate of crosslinking (gel formation). Besides of carbon to carbon recombination, also ether and perether bridges can be formed.

Figure 6.6. SEC chromatograms of PNI coatings, UV exposed in the UVACUBE, in air and nitrogen conditions at 68 °C.
Figure 6.7. SEC chromatograms of PNI coatings, UV exposed in the UVACUBE, in air and nitrogen conditions at 43 °C.

Figure 6.8. Gel fractions in PNI coatings, UV exposed in the UVACUBE, in air and nitrogen conditions at 43 and 68 °C.

6.3.1.2 Surface hardness

In Figures 6.9 and 6.10 load-displacement responses are shown for PNI after ageing in nitrogen and air at 43 and 68 °C, respectively. The most compliant response is that of the starting material. Upon ageing, the material gets stiffer, especially when the ageing is performed in air. From these load-displacement responses, the hardness was evaluated using the method proposed by Oliver and Pharr\[14\]. These results are summarized in Figure 6.11. The hardness increases as a function of exposure time (10 and 20 hours) and temperature of ageing (43 and 68 °C). However, the
Correlations between chemical and physical changes of polyester coatings under UV atmosphere of ageing (air vs. nitrogen) was found to be the most important factor influencing the surface hardness of coatings. UV exposure of these polyester coatings for 20 hours at 68 °C under air leads to an increase of hardness for approximately 30% and under nitrogen only of approximately 7%. Ageing for 20 hours performed at 43 °C under air leads to an increase of hardness of about 18% and in nitrogen atmosphere of about 5%.

Figure 6.9. Load-displacement responses of PNI coatings, UV exposed in the UVACUBE, in air and nitrogen conditions at 43 °C. The fitted unloading curve is within the resolution of the unloading data points (this also apply to Figures 6.10 and 6.15).

Figure 6.10. Load-displacement responses of PNI coatings, UV exposed in the UVACUBE, in air and nitrogen conditions at 68 °C.
6.3.1.3 Discussion

As shown above, photodegradation strongly influences the chemical composition of polyester coatings and this finds reflection in their surface mechanical properties. There are three main mechanisms of photodegradation of polyester (photolysis, photooxidation and photocrosslinking) which can influence the mechanical properties. These mechanisms are interrelated. However, for sake of clarity their influence on physical properties will be discussed separately.

Photocrosslinking leads to gel formation. The presence of three dimensional networks is a possible explanation for the significant hardness increase of coatings. The highest gel fraction was found for coatings aged for 20 hours at 68 °C under air conditions. Indeed, these coatings show the highest hardness. However, the gel fraction and hardness data show no clear correlation. For instance, ageing of polyester coatings for 20 hours at 43 °C under air and for 20 hours at 68 °C in nitrogen result in similar gel fractions (~17%) but different hardnesses. The hardness of the coating aged in air increases by about 18% and the one aged in nitrogen by about 7% only. This shows that there must be at least one additional factor affecting the hardness of polyester coating.

Photolysis leads to chain scission. Related to the phenomenon of “physical ageing” of glassy polymers it has been suggested that due to faster relaxation of smaller molecules in the glassy state an increase of hardness can take place[8]. On the other hand it has also been proposed that fragmentation can lead to a decrease of the
Correlations between chemical and physical changes of polyester coatings under UV

hardness\textsuperscript{[12,13]}. In our case the chain scission was monitored with SEC. It was found that the extent of chain scission increases with exposure time and temperature, and is higher in air than in nitrogen. However, as can be seen by comparing Figures 6.6, 6.7 and 6.11, there is no clear correlation between fragmentation of the polymer and hardness.

Photooxidation leads to the formation of polar groups (mainly carbonyl and hydroxyl). These groups can interact with each other via hydrogen bonding and/or dipolar interaction. New carbonyl and hydroxyl groups may also interact with virgin polyester. PNI contains two ester carbonyl groups in each repeating unit, which may well serve as hydrogen bond acceptors. These interactions can strongly influence the physical properties of polyester coatings. The C=O formation shown by ATR-FTIR (Figure 6.5) clearly correlates with the hardness data (Figure 6.11). The ageing in air leads to a significant development of carbonyl and hydroxyl bands as well as to a large increase of hardness. Under inert conditions, photooxidation can not take place, so ageing under nitrogen leads only to very little changes in ATR-FTIR spectra and a small increase of hardness. This clearly shows the strong effect of photooxidation on the surface mechanical properties of polyester coatings.

6.3.2 PNI and PNT exposed in the Suntest XXL+ ($\lambda > \sim 300$ nm)

6.3.2.1 Chemical characterization

ATR-FTIR analysis

Photodegradation of PNI and PNT exposed in a Suntest XXL+ was extensively discussed in the Chapter 4. In the present chapter only the most relevant results for the current investigation are recalled. It was found that PNI is much more UV stable than PNT. Figures 6.12 and 6.13 show ATR-FTIR spectra (carbonyl region) of the PNI and PNT aged in the Suntest XXL+. As can be seen UV exposure of PNT for up to 6,000 hours leads to extensive changes in the ATR-FTIR. The formation of so many new carbonyl groups (probably: anhydride, carboxylic acids and aldehydes) is an indication of extensive photooxidation. In contrast, ageing of PNI only leads to minor changes in the ATR-FTIR spectra.
Figure 6.12. ATR-FTIR spectra (region of C=O band) of PNI coating surface, aged in the Suntest XXL+ for up to 10,000 hours. Normalized to the peak at 1716 cm\(^{-1}\).

Figure 6.13. ATR-FTIR spectra (region of C=O band) of PNT coating surface, aged in the Suntest XXL+ for up to 6,000 hours. Normalized to the peak at 1716 cm\(^{-1}\).

**Gel fraction**

Crosslinking leads to gel (insoluble crosslinked molecules) formation. Figure 6.14 shows the amount of gel collected from UV exposed PNI and PNT. Ageing of PNT leads to extensive gel formation. After 2,000 hours of UV exposure the gel fraction reached about 50% and only slightly increased after an additional 1,000 hours of ageing. Further UV exposure leads to the decomposition of the gel which results in reduction of the gel fraction to about 40% after 6,000 hours of ageing. In case of PNI
the first indication of gel was found only after 9,000 hours of ageing and after 10,000 it reached about 5%.

![Graph showing gel fractions in PNI and PNT coatings, UV exposed in Suntest XXL+](image)

**Figure 6.14.** Gel fractions in PNI and PNT coatings, UV exposed in Suntest XXL+.

### 6.3.2.2 Surface hardness

In Figures 6.15 load-displacement responses are shown for PNT coatings aged for up to 4,000 hours in the Suntest XXL+. Upon ageing, PNT coatings get stiffer. Figure 6.16 shows the hardness data of PNI and PNT as a function of exposure time. UV irradiation of PNT for up to 6,000 hours leads to a large increase of hardness. On the contrary, after 10,000 hours of UV irradiation no significant increase of the hardness of PNI was observed. As described in Chapter 4, the thickness of PNT coatings aged for up to 6,000 hours was reduced from 12 to 6 µm. When measuring the hardness of such thin coatings there is the possibility that measurements will be influenced by the substrate (aluminum). Additionally, extensive photodegradation leads to a high roughness, which also can influence the measurement. In order to examine the influence of low thickness and high roughness of degraded coatings on the obtained hardness, an additional series of indentation experiments was carried out with higher loads on PNT coatings aged for 4,000, 5,000 and 6,000 hours. The results (Figure 6.16) are almost identical to those obtained with lower loads, which confirmed accurate hardness determination.
Figure 6.15 Load-displacements responses of PNT coatings, UV exposed in the Suntest XXL+ (for up to 4,000 hours).

Figure 6.16. Development of hardness of PNI and PNT coatings UV exposed in the Suntest XXL+.

6.3.2.3 Discussion

In section 6.3.1 ageing of PNI coatings in the UVACUBE ($\lambda > \sim 254$ nm) under air and nitrogen conditions was discussed. It was found that, although crosslinking is a plausible reason for hardness increase, the presence of polar groups (C=O and OH) have a predominant effect on the mechanical properties of aged PNI coatings. In this section ageing of PNI and PNT coatings in the Suntest XXL+ was presented. The results obtained are in agreement with the data obtained in the previous section. UV exposure of PNT for up to 6,000 hours leads to extensive
Correlations between chemical and physical changes of polyester coatings under UV photodegradation. Polar groups and hardness of PNT increase also as a function of exposure time. The gel fraction rises for samples aged up to 3,000 hours. Even though further UV irradiation leads to a slight decrease of the gel fraction, the hardness still increases, as does the amount of polar groups. Ageing of PNI under these conditions resulted in relatively small changes in the carbonyl region of the ATR-FTIR spectra, and only in a small gel fraction. This resulted in a rather insignificant hardness increase.

A large increase in hardness is also an indication of rising stresses in the coating which may lead to cracking of material\textsuperscript{[22]}. This phenomenon was indeed observed for PNT coatings aged for 4,000 hours and longer. Figures 6.17, 6.18 and 6.19 show SEM graphs of PNT non-aged, aged for 4,000 hours and for 5,000 hours respectively. UV exposure of PNI coatings resulted in insignificant increase in hardness and no cracking was observed.

In section 6.3.1 PNI coatings aged in the UVACUBE ($\lambda > \sim 254$ nm) were investigated. Also in that case an increase of hardness (up to 30%) was observed but no cracking was noticed. This is probably due to the much lower extent of degradation of PNI coatings in the UVACUBE than of PNT in the Suntest XXL+. In case of PNT aged in a Suntest XXL+, the first cracking was noticed when the hardness was increased by about 100% (Figure 6.18, PNT aged for 4,000 hours).

![SEM graph of non-aged PNT coating.](image)

**Figure 6.17.** SEM graph of non-aged PNT coating.
Figure 6.18. SEM graph of PNT coating aged in the Suntest XXL+ for 4,000 hours.

Figure 6.19. SEM graph of PNT coating aged in the Suntest XXL+ for 5,000 hours.
6.4 Conclusions

In this chapter the influence of UV induced chemical changes on the surface physical properties of poly(neopentyl phthalate) coatings was investigated.

In the first part of the investigation, in order to distinguish between different reactions and their relative importance to changes in the physical properties, poly(neopentyl isophthalate) (PNI) coatings were aged under different conditions (air vs. nitrogen) in the UVACUBE (\( \lambda > \sim 254 \) nm). Ageing in air leads to an extensive development of carbonyl and hydroxyl groups, which is attributed to photooxidation. In contrast, UV exposure in nitrogen leads only to minor changes in the infrared spectra. In addition, the number of carbonyl and hydroxyl groups increases as a function of exposure time and temperature. UV exposure leads to both chain scission and crosslinking. Extensive crosslinking results in gel formation. The rate of both chain scission and crosslinking is higher when the polyester is UV exposed in air, as compared to nitrogen conditions, and increases with time and temperature of ageing. The surface hardness of PNI increases with time and temperature of exposure. It was found that photooxidation has the most dominant influence on the hardness. Carbonyl and hydroxyl groups formed during this process can interact with each other or with the virgin polymer via hydrogen bonding and dipolar interaction, and in this way strongly increase the surface hardness of coatings.

In the second part, photodegradation of PNI and PNT coatings aged in a Suntest XXL+ was studied. Chemical characterization (ATR-FTIR, gel fraction) of both polyesters showed that PNI is much more UV stable than PNT. This clearly is reflected in mechanical properties. The extensive chemical changes taking place in the structure of PNT leads to significant increase of hardness which resulted in cracking. In this case a typical weathering pathway was observed. UV exposure caused chemical changes (formation of polar groups, gel) in the structure of PNT, which resulted in physical changes (increase of hardness) and as a consequence of increased stress failure of the coating (cracking). PNI showed a much lower extent of degradation and as a consequence a minor increase of hardness and no cracking.
References

Appendix 6.1

Tip area function calibration

The tip area function was established on polystyrene ($M_n = 131$ kg/mol, PDI = 1.04) drop cast from a toluene solution and afterwards thoroughly dried under vacuum above its glass transition temperature, as the available load range did not allow to determine the tip shape up to the desired contact depth on fused quartz. Indentation experiments were performed employing various maximum load levels such that the contact depths ranged from 126 to 954 nm. The reduced modulus $E_r$ of the material determined for the three deepest indents using the ideal Berkovich area function was 5.22 GPa. The conversion from the reduced modulus $E_r$ to the modulus of elasticity involves a factor depending on the Poisson’s ratio $\nu$. Using $\nu = 0.35$, one finds a modulus of elasticity of 4.6 GPa, which is close to the value of ~4.5 GPa reported by Briscoe et al. for indentations in this indentation depth range (B. J. Briscoe, L. Fiori, E. Pelillo, J. Phys. D: Appl. Phys. 1998, 31, 2395-2405). Using $E_r = 5.22$ GPa, the indenter area function for lower depths was constructed using the shallower indentation responses, resulting in a relation the so-called area function, between the contact depth $h_c$ and the projected contact area $A$.

$$A = 24.5h_c^2 - 980.13h_c + 29506\sqrt{h_c}$$

This area function results in a projected contact area $A$ which is at 200 nm 23% higher than for a perfect Berkovich. For contact depths between 126 and 954 nm, the modulus of polystyrene was constant (by definition), while the hardness was 0.24 GPa for the deepest indents and increased ca. 13% with decreasing contact depth. The hardness is somewhat lower than the value of ~0.27 GPa observed by Briscoe et al. This can be probably attributed to the higher unloading rate used in the current work. The material hardness increase is also reflected by a decrease in the contact depth to maximum indentation depth ratio ($h_c/h_{\text{max}}$ decreased 3%, from 0.86 to 0.84) which may be due to the tip apex rounding (which results in a lower strain and therefore less plastic deformation). Moreover, due to the presence of inherent length-scales, such as the polymer chain length, self-similarity is not completely obeyed.
Evaluation of the hardness of aged PNI at a contact depth of 250 nm

The presented hardness values for PNI after various ageing conditions were evaluated at a contact depth of 400 nm. In that procedure, a linear fit was applied to the hardness data as function of contact depth; typically, the applied loading conditions and maximum load levels resulted in a contact depth range from 160 to 540 nm. Evaluation at other contact depths than 400 nm results in the same trends with ageing conditions as shown in Figure 6.20. However, the absolute hardness values are shifted somewhat. It is noted that, as discussed above, also for polystyrene a hardness increase is observed upon evaluating the hardness at smaller contact depths (at $h_c = 400$ nm, the hardness of the polystyrene was 0.265 GPa, while at 250 nm a hardness of 0.271 GPa was evaluated). Below, the hardness for the aged PNI as evaluated at 250 nm is shown.

![Figure 6.20](image-url)

**Figure 6.20.** Hardness of polyester coatings after various ageing conditions evaluated at a contact depth of 250 nm.
Epilogue
In outdoor weathering many factors simultaneously influence the ageing of polymeric coatings. The cooperative action of UV radiation, heat and moisture can cause changes in the chemical structure of macromolecules, thus influencing the physical properties of a coating, and ultimately leading to its failure (cracking, gloss loss, blistering, etc.) and a reduction of its life-time. The investigation of its photodegradation is essential to better understand and subsequently improve the weathering stability of polyester coatings.

The aim of this Thesis was to investigate the molecular mechanism of photodegradation of poly(neopentyl isophthalate) PNI and poly(neopentyl terephthalate) PNT, which belong to an important class of polymers used in coating technology. In order to be able to study the effects of degradation efficiently, we used non-crosslinked coatings.

In the first part of this work, photodegradation of PNI under highly accelerated degradation conditions (UVACUBE, $\lambda > \sim 254$ nm) was studied. It was shown that UV exposure of PNI leads to both chain scission and crosslinking occurring simultaneously. The main focus to this part of work was to establish mechanisms of photolysis and photooxidation (which mainly lead to decomposition of polyester). MALDI-ToF MS provided detailed structural information on the degradation products, which allowed establishing the mechanism of photolysis and photooxidation of PNI on the molecular level.

It is known that the mechanism of degradation can be affected by highly accelerated conditions (UVACUBE). In order to verify the established mechanism, PNI coatings were aged using more realistic method - Suntest XXL+ ($\lambda > \sim 300$ nm) - and exposed outdoors. It was found that the degradation of PNI in both UVACUBE and Suntest XXL+ experiments leads to similar products, which suggests that similar mechanism of photolysis and photooxidation of PNI occur under both accelerating degradation methods. However, the short wavelength UV radiation, present in the UVACUBE, strongly accelerates the overall rate of photodegradation due to the higher absorption. The experiments performed outdoors proved that in the initial stage of ageing under all three degradation conditions (UVACUBE, Suntest XXL+ and outdoor) similar mechanisms of degradation occur.

In order to prevent photodegradation, photostabilizers are often used. The mechanisms of photostabilization by such additives are directly related to the mechanisms of photodegradation. Studying the mechanisms and effects of
photostabilization of polymers requires knowledge on the mechanism of photodegradation. The mechanism proposed in this thesis can well serve for future studying the mechanism of photostabilization of PNI on the molecular level.

In the next step of our studies the mechanism of photodegradation of PNI and PNT exposed in the Suntest XXL+ was studied. PNI proved to have a much higher UV stability as compared to PNT. Nevertheless, it was shown that both polyesters degrade due to the same mechanism. The higher UV stability of PNI over PNT was attributed to a higher UV absorption of PNT as compared to PNI. In order to get more detailed information on these phenomena, it would be desirable to measure the quantum yield of the photochemical decomposition of both PNI and PNT in future. Such a measurement performed on model compounds using monochromatic light could bring more fundamental understanding of differences in UV stability of both polyesters.

Apart from fragmentation of polyester chains its photodegradation comprises crosslinking, which leads to insoluble material (gel). The chemistry of decomposition of polymers was extensively studied in the literature, but limited amount of work was done on the mechanism of crosslinking as result of photodegradation. In order to obtain information on the crosslinking at a molecular level the gel material was decomposed by methanolysis. In this way insoluble material became soluble and could be analyzed with LC-MS, which allowed the elucidation the mechanism of crosslinking. This approach appeared to be rather successful and can be used to study crosslinking of other polyesters.

Although there is a great deal of information available on photodegradation of polymers both for the chemical and physical aspects, the relationship between these two aspects is still not well understood. In this work we discuss how a number of chemical processes correlate with the increase of hardness as was observed upon ageing of polyester coatings. Polar groups like -OH and -C=O formed during photooxidation were found to be the predominant factor causing the hardness increase. The increase of hardness leads to an increase in internal stress of the coating which in turn, during prolonged ageing, leads to extensive cracking.

This work presents a fundamental approach towards photodegradation and is only a first step in the long term research program. The general knowledge obtained in this work should be translated and compared in future to more realistic – crosslinked – coatings.
Photodegradation is known to be a surface effect. Mainly due to absorption of UV light and the limited diffusion of oxygen into the polymer bulk, the degradation takes place mainly in the top layer of a coating. In this work the depth penetration of light was calculated from the absorption coefficient. In some cases the surface effect could also be deduced from SEC and gel fraction measurements. However, a more suitable approach to study the surface effect is cross-sectioning of degraded coatings and the analysis of such cross-sections. In our case due to the high brittleness and low thickness of PNI coatings, the proper preparation of cross-sections appeared to be impossible. Crosslinked coatings are more suitable for the preparation of cross-sections. In the future, the analysis of such cross-sections should focus both on chemical and on physical aspects and this should lead to valuable information on the distribution of products throughout the thickness of coatings. In this case, the depth profile of degradation predicted from light absorption and diffusion of oxygen can be directly compared to the experimental data.
Summary

The molecular mechanism of photodegradation during ageing under UV light was studied for model polyester coatings of poly(neopentyl isophthalate) PNI and of poly(neopentyl terephthalate) PNT. The ageing was performed using accelerated degradation methods in the laboratory (UVACUBE, $\lambda > \sim 254$ nm; Suntest XXL+, $\lambda > \sim 300$ nm) as well as outdoors. Changes in the chemical structure of the polymer caused by UV irradiation were investigated with several analytical techniques. Size Exclusion Chromatography was performed to determine changes in molecular weight. It was found that molecules both with higher and with lower molecular weight are formed, indicating that both chain scission and crosslinking take place simultaneously. ATR-FTIR spectroscopy was used to monitor the formation and disappearance of functional groups near the coating surface. Such a surface when irradiated in air atmosphere exhibits significant chemical changes (the appearance of carbonyl and hydroxyl/hydroperoxide bands) indicating extensive photooxidation. Detailed structural information on the products of decomposition was obtained using MALDI-ToF MS. Based on this highly informative data, the mechanism of photolysis and photooxidation is described. The mechanism of degradation involves Norrish (type I) photocleavage of the ester group. Radicals formed due to this reaction can abstract hydrogen or can react with oxygen and primarily form acid and alcohol end groups. Moreover, hydrogen abstraction taking place along the polymer backbone followed by oxidation reactions leads to further fragmentation of the polymer chain.

The photodegradation of PNI aged in the UVACUBE ($\lambda > \sim 254$ nm) and in the Suntest XXL+ ($\lambda > \sim 300$ nm) were compared. Under short ($\lambda > \sim 254$ nm) and long ($\lambda > \sim 300$ nm) wavelength irradiation similar products of degradation are formed as demonstrated with MALDI-ToF MS. This strongly suggests similar mechanisms of photolysis and photooxidation under these two different accelerated degradation conditions. The main effect of the short wavelength radiation is that it dramatically accelerates the overall rate of photodegradation of PNI as evident from both experiments and from energy absorption calculations. When comparing the exposure of PNI in laboratory and outdoors conditions in the initial stage of ageing again similar degradation products were formed.

A comparison of the degradation products of PNI and PNT, as obtained from a Suntest XXL+ experiment and analyzed by MALDI-ToF MS, shows that the same
type of products are obtained. However, the rate of photodegradation of PNT is much higher as compared to PNI which is in line with the much higher level of UV absorption.

Extensive crosslinking leads to the formation of insoluble material (gel). The chemistry of crosslinking of PNI was studied with methanolysis combined with LC-MS. It was found that the alkyl radicals formed in the α-position to the ester group can recombine and form crosslinking species. Additionally the phenyl to phenyl recombination was confirmed.

The physical properties of coatings will change along with the chemical changes. In order to investigate the physical properties of aged and non-aged coatings, nanoindentation tests were performed. The ageing of PNI and PNT coatings leads to an increase of surface hardness. It was shown that the formation of polar groups like -OH and -C=O (photooxidation) is the dominant factor causing the increase of hardness.
Acknowledgments

During the last four years I have met a number of great people how have contributed to the work presented in this thesis, and it is my pleasure to acknowledge them here.

First and foremost, I would like to express my sincere gratitude to my promoters and supervisors: Prof. dr. Rolf van Benthem, Prof. dr. Bert de With, dr. Jos Laven and Leo van der Ven. I would like to thank you for giving me the opportunity to work in SMG group. I am very grateful for your understanding, patience and constructive support. Your positive attitude and professional guidance have always been very helpful. I would like to express my appreciation for creating a great working atmosphere and for the help I have received regarding experimental work as well as writing this manuscript.

Secondly, I would like to thank the members of the doctoral committee: Prof. dr. hab. Halina Kaczmarek, Prof. dr. Fred Brouwer and Prof. dr. Cor Koning, for spending time to evaluate my thesis and sharing their valuable comments and remarks.

I am grateful to dr. Pieter Gijsman for fruitful discussions and his input to my work. I would like to thank Saskia Huijser for help with interpretation of complicated Maldi data. Hans Kranenburg, for nanoindentation measurements and interesting discussions on “correlations”. For SEM and molecular dynamic simulations, I have to thank dr. Srdjan Kisin. I am grateful to “Lab-monster” – dr. Tamara Dikic – for microtoming, XPS and NMR as well as for many interesting discussions. Thanks to Marjolein Diepens for providing spectral distributions of UV lamps. I would like extend my thanks to Marion van Straten for Maldi and LC-MS measurements and for her valuable suggestions, Wieb Kingma for SEC analysis and Otto van Asselen for FTIR analysis. For designing oxygen uptake instrument and for professional technical support I would like to thank Huub van der Palen. Many thanks to Marco Hendrix for SEM and XRD measurements.

I take this opportunity to acknowledge Francesca Scaltro for extensive discussions on the complicated degradation mechanisms, as well as for all her assistance with the experimental work.

I am very thankful to Imanda for being a super secretary. Dear Imanda, thank you for all your help and support I have received last four years.
Working in the SMG group was valuable experience. I would like to thank all former and present members of SMG, especially: Srdjan, Francesca, Tamara, Mark, Daniela, Olavio, Willem-Jan, Baris, Ming, Marshall, Catarina, Wilfred, Huub, Marco, Imanda, Svetlana, Beryl, Adolphe, Thanos, Sasha… Thank you for all scientific and non-scientific discussions as well as parties in the Fort and borrels – It was a great time!

The last couple of years I have met a number of great people with whom I spent unforgettable time. Łukasz, Gosia, Kasia, Roy, Francesca, Tamara, Petr, Srdjan, Mark, Baris, Olavio, Johan, Anka… Thanks for all crazy parties and nice moments we shared together.

Szczególnie chciałbym podziękować moim rodzicom i dziadkom za naukę, wiarę i wszystko, co dla minie zrobili. Dziękuję Wam bardzo, wasze wsparcie i modlitwa bardzo mi pomogły. Dziękuję również mojej siostrze i szwagrowi. Wiem, że zawsze mogę na was liczyć. Specjalne podziękowania dla mojego „złotka”. Dziękuję Ci Ninka za cierpliwość, wyrozumiałość i za to, że jesteś.
Curriculum Vitae

Przemysław Malanowski was born on 9 September 1979 in Golub-Dobrzyń (Poland). He studied Chemistry at Nicolaus Copernicus University, Toruń (Poland) and in June 2001 he received his Bachelor degree (B.Sc. Chemistry). Soon after, he started his Master studies in Chemistry at the same University and in June 2003 he obtained his M.Sc degree. Part of the Master graduation project entitled “Biodegradation and photodegradation of polymer blends” was performed at the Faculty of Chemistry and Industrial Chemistry, University of Genova (Italy). In August 2004 he started his Ph.D. research in the group of Material and Interface Chemistry at the Department of Chemical Engineering and Chemistry, Eindhoven University of Technology (The Netherlands). Within this group he worked under the supervision of prof. dr. R. A. T. M. van Benthem, prof. dr. G. de With, dr. J. Laven and L. G. J. van der Ven. The most important results from his Ph.D. work are described in this Thesis.