SAFE AND MORE RELIABLE USE OF PP-MATERIALS IN FLUE-GAS CLEANING

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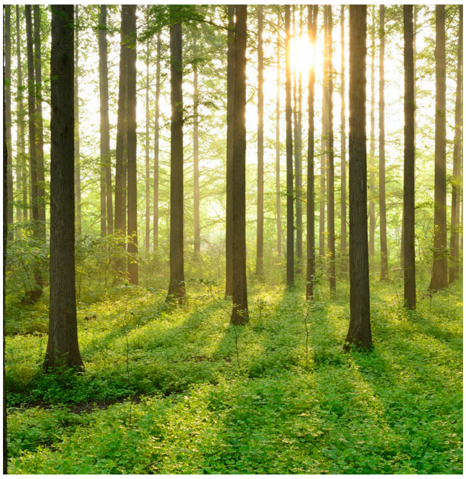

FUEL-BASED ELECTRICITY AND HEAT PRODUCTION

Energiforsk

Safe and more reliable use of PP-materials in flue-gas cleaning

Säkrare och pålitligare användning av PP-material i rökgasreningsanläggningar

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Förord

Denna rapport är slutrapportering av projekt M 38735 Säkrare och pålitligare användning av PP-material i rökgasreningsanläggningar (Energimyndighetens projektnummer P 38735) som faller under teknikområde material- och kemiteknik inom SEBRA, samverkansprogrammet för bränslebaserad el- och värmeproduktion.

Projektet har följts av en referensgrupp bestående av:

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SEBRA, samverkansprogrammet för bränslebaserad el- och värmeproduktion, är efterföljaren till Värmeforsks Basprogram och startade som ett samarbetsprogram mellan Värmeforsk och Energimyndigheten 2013. All forskningsverksamhet som bedrevs inom Värmeforsk ingår sedan den 1 januari 2015 i Energiforsk. Därför ges denna rapport ut som en Energiforskrapport.

Programmets övergripande mål är att bidra till långsiktig utveckling av effektiva miljövänliga energisystemlösningar. Syftet är att medverka till framtagning av flexibla bränslebaserade anläggningar som kan anpassas till framtida behov och krav. Programmet är indelat i fyra teknikområden: anläggnings- och förbränningsteknik, processtyrning, material- och kemiteknik samt systemteknik.

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Summary

The project had the overall objective of providing a better understanding of how the service life of PP materials is affected when used in facilities for flue gas cleaning and condensation. The main aims of the project have been: (1) to reduce the thermal expansion and contraction by adding fillers to the PP material, (2) to present a more sensitive technique to study stabilizer loss, and (3) to present in a database the results and other useful information regarding plastic materials in flue-gas cleaning facilities.

For the study on filled polypropylene three different types of PP materials were chosen, α-PP, β-PP and PP-R. The filler systems investigated were 5 wt% and 25 wt%. stearic acid coated calcium carbonate ($CaCO_3$) and 10 wt% of two different types of carbon black fillers. The high structured 600 JD and low structured XC72 were added to each of the three different plastics.

The mechanical, thermal and chemical resistance properties were then investigated for the samples. The chemical environments investigated were:

- 5 weight-% and 25 weight-% hydrochloric acid (HCl) for acidic environment at 60°C
- 5 weight-% and 30 weight-% sodium hydroxide (NaOH) for alkaline environment at 60°C
- 5 mg/l Chlorine dioxide (ClO_2) for an oxidative environment at 50°C
- High concentration NO/NO_2 gas mixture at room temperature.

The materials were exposed in these conditions for 48 days except the NO/NO_2 gas mixture in which the materials were exposed for approximately three weeks at room temperature.

The most important result of the study on filled polypropylenes was that the addition of 10 wt% of carbon black improved both the thermal and mechanical properties investigated. The material with 10 wt% 600JD showed both an increased tensile yield strength, modulus (not reported due to data collection problems), and impact resistance. The materials were also very little affected by the different chemical environments investigated. There was even some improvement in the stability to the oxidative/radical environment in the ClO_2 exposure and in the concentrated NO/NO_2 environment.

In addition it was concluded that there is an enormous variety of fillers and surface coatings available for polypropylene. There is also a very large variety of different polypropylenes. The very limited number of filler/material combinations evaluated in this work did show some effects on the thermal elongation, but this could most probably be greatly improved. It was also found that the processing largely determines the properties of the polypropylene. The beta nucleated material only showed very little beta crystallinity, and the α-PP and PP-R materials showed almost as much.

The addition of 5 wt% and 25 wt% stearic acid coated calcium carbonate did not result in any particular improvement in the material properties, except for some improvement in the impact resistance. The materials also showed an increased sensitivity to 25 wt% HCl and NO/NO_2 and ClO_2.

The purpose of the second part of the study was to develop a method for assessing the remaining service life of polypropylene by a qualitative and/or quantitative analysis of

stabilizers. FTIR is a powerful method, but the absorption peak from the hindered phenol is weak and difficult to detect with FTIR. However, through reaction with chlorine dioxide (ClO_2) a quinone structure is formed that binds water and this gives a much stronger signal in the spectrum. The aim was to investigate whether or not it is possible to relate the absorbed amount of water to the concentration of stabilizer in the polymer. In addition, other methods for the determination of the stabilizer type and concentration were also evaluated, such as extraction and subsequent analyses using FTIR, HPLC and ESI-MS and also DART-MS that does not require extraction.

It was found that the stabilizers in a material can be related to the water absorption after ClO_2 exposure within a material, but not between different materials. The water absorption peak increases with time until it stabilizes after 6 days (144 hours), that is when all hindered phenols have reacted with chlorine dioxide. The concentration of chlorine dioxide was of less importance for the water absorption as long as ClO_2 was in excess relative to the hindered phenols. For this study, 0.1 g/L was enough. It was also concluded that reaction with ClO_2 was more effective in 50°C than in room temperature. The chlorine dioxide method can also be considered repeatable within a specific material since similar values of the water absorption peak are obtained at separate experiments.

It is difficult to use HPLC for identification of the antioxidants that were analysed in this study. Because of the similar molecular structure of Irganox 1010 and Irganox 1076, it was impossible to achieve separation with an isocratic HPLC, since they were affected in the same way by the solid and mobile phase. It is also quite difficult to use FTIR to analyse which stabilizers are present in an unknown sample due to many overlapping peaks. However, with more experience this is probably a powerful method. The DART-MS method still needs more work in order to use it for the determination of stabilizers in an unknown polypropylene sample.

It was found that creating a database for collection of the data and experiences on materials in flue gas environments is quite complex and it is questionable that the polymeric material data is suitable for being presented that way. The amount of available data experiences on materials in flue gas environments on is so scattered and of varying origin and type that a database might be of little value. In addition there are a number of questions that will need to be investigated: What is the scope? Who should administer it? What type of data is of interest to share? How should it be financed? Are there any legal issues involved for sharing the results?

News value

The results of the investigation are important not only for the use of PP in flue gas plants, but for all environments where PP is used. In particular the positive effects seen on the mechanical and thermal properties and the chemical resistance of polypropylene by the addition of carbon black is very interesting.

Sammanfattning

Projektet har haft det övergripande målet att ge en bättre förståelse för hur livslängden hos PP material påverkas när de används i anläggningar för rökgasrening och kondensering. De viktigaste målen för projektet har varit: (1) att minska den termiska expansionen och kontraktionen genom att tillföra fyllmedel till PP-materialet, (2) att presentera en mera känslig teknik för att studera stabiliserarförlust, och (3) att i en databas presentera resultaten, och annan nyttig information, om plastmaterial i anläggningar för rökgasrening.

För undersökningen om fylld polypropen valdes tre olika typer av PP-material, α-PP, β-PP och PP-R. De fyllmedelsystem som undersöktes var 5-vikt% och 25-vikt% kalciumkarbonat ($CaCO_3$) belagt med stearinsyra och 10-vikt% av två olika typer av kimröksfyllmedel. Det högstrukturerade 600 JD och lågstrukturerade XC72. Alla olika fyllmedelstyper tillsattes till var och en av de tre olika plasterna.

De mekaniska, termiska och kemiska egenskaperna undersöktes sedan för proverna. De kemiska miljöer som undersöktes var:

- 5-vikt% och 25-vikt% saltsyra (HCl) för sur miljö vid 60°C
- 5-vikt% och-30 vikt% natriumhydroxid (NaOH) för alkalisk miljö vid 60°C
- 5 mg/l klordioxid (CIO_2) för en oxiderande miljö vid 50°C
- Högkoncentrerad NO/NO_2-gasblandning vid rumstemperatur.

Materialen exponerades i dessa miljöer under 48 dagar med undantag för NO/NO_2-gasblandningen i vilken materialen exponerades i cirka tre veckor vid rumstemperatur.

Det viktigaste resultatet i studien om fyllda polypropener var att tillsatsen av 10-vikt% kimröksfyllmedel till viss del förbättrat både de termiska och mekaniska egenskaper som undersökts. Materialet med 10- vikt% 600JD visade både ökad draghållfasthet, modul (dock inte rapporterat på grund av datainsamlingsproblem) och slagtålighet. Materialen var också mycket lite påverkade av de olika kemiska miljöer som undersökts. Det fanns även en viss förbättring i stabilitet gentemot den oxidativa/radikalmiljön vid ClO_2-exponeringen och i den koncentrerade NO/NO_2-miljön.

Dessutom konstaterades att det finns ett enormt utbud av olika fyllmedel och ytbeläggningar för polypropen. Det finns också en mycket stor variation av olika polypropener. Visserligen uppvisade det mycket begränsade antalet kombinationer av fyllmedel/material som utvärderas i denna studie bara låga effekter på den termiska förlängningen, men det är förmodligen något som kan förbättras avsevärt. Det konstaterades också att bearbetningen i hög grad bestämmer egenskaperna hos polypropen. Det betanukleerade materialet visade endast mycket lite betakristallinitet, och de material som bestod av α-PP och PP-R visade nästan lika mycket.

Tillsatsen av 5-vikt% och 25-vikt% kalciumkarbonat belagt med stearinsyra resulterade inte i någon särskild förbättring av materialegenskaperna, med undantag för en viss förbättring av slaghållfastheten. Materialen visade också en ökad känslighet för 25-vikt% HCl, NO/NO_2 och CIO_2.

Syftet med den andra delen av studien var att utveckla en metod för att bedöma den kvarvarande livslängden för polypropen genom en kvalitativ och/eller kvantitativ analys av stabilisatorer. FTIR är en kraftfull metod, men absorbanstoppen från den

steriskt hindrade fenolen är svag och svår att upptäcka med FTIR. Genom reaktion med klordioxid (ClO_2) bildas emellertid en kinonstruktur som binder vatten, och detta ger en mycket starkare signal i spektrumet. Syftet var att undersöka huruvida det är möjligt att relatera den absorberade vattenmängden till stabilisatorkoncentrationen i polymeren. Dessutom utvärderades också andra metoder för bestämning av stabilisatortyp och stabilisatorkoncentration, såsom extraktion och påföljande analyser med användning av FTIR, HPLC och ESI-MS och även DART-MS som inte kräver extraktion.

Det visade sig att stabilisatorerna i ett material kan vara relaterade till vattenabsorptionen efter ClO_2- exponering inom ett material men inte mellan olika material. Vattennabsorptionstoppen ökar med tiden tills den stabiliseras efter 6 dagar (144 timmar), dvs när alla hindrade fenoler har reagerat med klordioxid. Klordioxidkoncentrationen var av mindre betydelse för vattenabsorptionen så länge som ClO_2 var i överskott i förhållande till de hindrade fenolerna. För denna studie var 0,1 g/l tillräckligt. Det befanns också att reaktion med ClO_2 var effektivare i 50 °C än i rumstemperatur. Klordioxidmetoden kan också betraktas som repeterbar inom ett specifikt material, eftersom liknande värden för vattenabsorptionstoppen erhålles vid separata experiment.

Det är svårt att använda HPLC för identifiering av de antioxidanter som analyserades i denna studie. På grund av att Irganox 1010 och Irganox 1076 har liknande molekylstruktur, var det omöjligt att uppnå separation med en isokratisk HPLC, eftersom de påverkas på samma sätt av den fasta och mobila fasen. Det är också ganska svårt att använda FTIR för att analysera vilka stabilisatorer som är närvarande i ett okänt prov på grund av många överlappande toppar. Men med mer erfarenhet är detta dock förmodligen en kraftfull metod. DART-MS-metoden behöver fortfarande mer bearbetning för att kunna användas för bestämning av stabilisatorer i ett okänt polypropenprov.

Det visade sig att skapa en databas för insamling av data och erfarenheter om material i rökgasmiljöer är ganska komplext och det är tveksamt att de data som finns om polymera materialet är lämpligt för att presenteras på det sättet. Mängden tillgänglig data är så spridd och av varierande ursprung och typ att en databas kan vara av ringa värde. Dessutom finns det ett antal frågor som måste utredas. Vad är omfattningen? Vem ska administrera det hela? Vilken typ av data är av intresse att ta del av? Hur ska finansieringen gå till? Finns det några juridiska frågor som måste beaktas för att ta del av resultaten?

Nyhetsvärde

Resultaten av undersökningen är viktiga inte bara för användning av PP i rökgasanläggningar, utan för alla miljöer där PP används. Speciellt är de positiva effekterna för de mekaniska och termiska egenskaperna och den kemiska motståndskraften hos polypropylen genom tillsats av kimrök mycket intressanta.

Måluppfyllelse

Projektets övergripande mål är att utveckla metoder och metodik för att kunna kvalitetssäkra PP-material för en viss önskad livslängd, och för att kunna bedöma status och kvarvarande livslängd hos PP material i anläggningar för rening och kondensering av rökgaser. Detta kan delas upp i tre mer konkreta delar:

Minska problemen med skevning, deformation och spruckna svetsar till följd av termisk utvidgning/kontration med hjälp av addition av fyllmedel till PP-materialet

En viss effekt kan ses på värmeutvidgning efter tillsats av fyllmedel men den var tyvärr inte så stor som förhoppningen varit. Den minskning som ändå uppnåtts skulle antagligen minska problemen med skevning och spruckna svetsar något. Även den ökade styvheten kan bidra till att minska några av de problemen. Det är också viktigt att notera att antalet möjliga polypropen/fyllmedelskombinationer som har undersökts i detta projekt är mycket begränsade jämfört med vad som är möjligt att tillverka. Det kan finnas andra kombinationer med mycket bättre egenskaper. Detta projekt får ses som en startpunkt för vidare utveckling på området.

Minska risken för driftstörningar och kostsamma komponentbyten med hjälp av ökad precision på livslängdsbedömningar av PP-material i rökgasmiljöer.

Ett antal olika tekniker för att bestämma kvarvarande stabilisator har utvärderats. Klordioxidmetoden, som i det tidigare projektet visade stor potential, visade sig ha vissa nackdelar i att kunna ge jämförbara resultat mellan olika typer av steriskt hindrade fenolstabilisatorer. Arbetet har ändå lett till en ökad förståelse för möjligheterna och nackdelarna med de olika tekniker som finns.

Ge ett stöd vid nybyggnation eller utbyte av gamla komponenter genom att redovisa resultaten i en databas där även andra erfarenheter från användandet av plastmaterial i rökgasmiljöer kan samlas.

Det visade sig att skapa en databas för insamling av data och erfarenheter om material i rökgasmiljöer är ganska komplext och det är tveksamt att de data som finns om polymera materialet är lämpligt för att presenteras på det sättet. Mängden tillgänglig data är så spridd och av varierande ursprung och typ att en databas kan vara av ringa värde. Dessutom finns det några frågor om bland annat ägandeskap, underhåll och rättigheter som måste lösas först. Det är antagligen mer relevant att skapa en handbok och skadeatlas för polypropen riktad mot anläggningsägare likande den som Swerea KIMAB just avslutat i Energiforskprojektet M 37775 "Inspektion och OFP av processutrustning i glasfiberarmerad plast (GAP)".

Abbreviations

PP-H = polypropylene homopolymer

PP-R = random polypropylene copolymer

α-PP = alfa nucleated polypropylene

β-PP = beta nucleated polypropylene

OIT = Oxygen induction time (a measure of the oxidative stability of polypropylene)

DSC = Differential scanning calorimeter, a technique to measure thermal transitions polymers. Is used to measure OIT

TMA = Thermal mechanical analysis, can be used to determine thermal elongation

FTIR = Fourier Transformation Infrared Spectroscopy, a technique to measure chemical and physical properties of e.g. polymers and additives

HPLC = High-performance liquid chromatography, separates and analyses liquid system

XRD = Wide angle X-ray spectroscopy, a technique to measure crystal structure and amount

ESI-MS = Electrospray ionization - Mass Spectrometry

DART-MS = Direct Analysis in Real Time- Mass Spectrometry

ClO_2 = chlorine dioxide, an oxidant

HCl = hydrochloric acid, a strong acid

NaOH = sodium hydroxide, a strong base

NO/NO_2 = nitric monoxide/dioxide

Petrit P = Tunnel kiln lime, a bi-product from iron production. The main components are calcium oxide and carbon

$CaCO_3$ – Calcium carbonate

CTE - Coefficient of thermal expansion

Content

1 Introduction

he work presented in this report is a continuation of the Värmeforsk Project, M08-841 “Status, remaining service life and quality assurance of PP materials in facilities for flue gas cleaning and condensation” [1]. It was concluded in the previous report that the main limitations of polypropylene (PP) when used in flue gas cleaning facilities are:

- Thermal expansion/contraction
- Heat distortion (deflection) temperature (HDT)
- Leaching of stabilizers
- Oxidative or chemical attack
- Poor quality/wrong choice of material
- Risk of fire

The limitations are presented in the order after what has seemed to cause the most problems in the flue gas facilities. The problems caused by thermal expansion and contraction of the polypropylene materials were most severe, see Figure 1 for one example, followed by the heat distortion.

Figure 1. Typical example of distortion of PP components in a flue gas scrubber due to thermal expansion and contraction of the material.

Figur 1. Typexempel på PP-komponenter i en rökgasskrubber som blivit förvridna till följd av termisk expansion och kontraktion.

1.1.1 Polypropylene basics

Polypropylene is the third largest volume plastic (polyethylene is the largest, followed by PVC). The reasons for its popularity are its good properties in combination with a low weight and a low price. The material can be used in a variety of corrosive environments because of its excellent chemical stability. However, it is important to know that although it is true to say that polypropylene is a material with specific properties, it can also be described as a class of materials in which properties can vary considerably. Polypropylene is also probably the most versatile of all polymers. It can be processed with all methods used for thermoplastics, and by varying molecular weight, molecular weight distribution, crystallinity type and degree, copolymerization, and fillers a very large number of PP grades with different properties can be manufactured.

Polypropylene homopolymer (PP-H) contains only polypropylene monomer in the polymer chain. It has high stiffness and toughness, but, low impact strength at low temperatures. Polypropylene copolymers contain one or more different types of monomers in the polymer chain. Random copolymers (PP-R) are produced by adding e.g. ethylene in random sequences in the polypropylene chain. It has a lower crystallinity compared to PP-H, resulting in a lower melting point, which leads to lower softening and heat distortion temperatures. The glass transition temperature is slightly reduced, which somewhat improves the impact resistance at low temperatures. The material is also softer and more flexible than PP-H.

Chains of commercial grades of PP crystallise essentially into the α-form. It is, however, possible to obtain PP in other crystal forms by using special nucleating agents. The β-form, which has an improved impact strength compared to α-PP, predominates. It also has lower tensile yield strength and higher ductility than α-PP, and despite a slightly lower melting point, β-PP has a higher heat distortion temperature than α-PP. It is normally PP-H that is used for commercial β-PP but the β-form can also be formed in PP-copolymers.

1.1.2 Polypropylene in flue gas facilities

Polypropylene (PP) materials are attractive for use in metal corrosive environments because they are comparatively cheap and show good corrosion resistance. In recent years this has led to a substantial increase in the use of PP materials, for example in facilities for purification and condensation of flue gases. In installations for waste incineration, which is an area undergoing rapid expansion, comparatively much PP material is found in the flue gas cleaning systems and their auxiliary equipment. PP material is used mostly in the interior of scrubbers in parts and components such as demisters, fillers and other types of packing, water spray cooling systems, collecting drains, channels, elements for flow control, etc, Figure 2.

Figure 2. One example of the use of PP for droplet separators in flue gas scrubber in a waste incineration plant.

Figur 2. Ett exempel på användning av polypropen för droppavskiljare i en rökgasskrubber i en sopförbränningsanläggning.

PP material is also used as a cheaper alternative of fibre-glass reinforced plastics (FRP) in pipelines carrying lime slurry, and for smaller containers of the order of 20 m^3,

Figure 3. Moreover, PP is used for the lining of FRP mainly in slurry environments where the medium is abrasive. It is here assumed that the PP material has a service life as long as the facility components in general, i.e. at least 20 years. If this is not the case, the components must be replaced early, which can be a complicated and expensive project, not least for certain structures inside a scrubber where the narrow space and manhole size do not allow any major prefabricated elements to be inserted. If the PP status of the materials is not regularly monitored, unexpected accidents may occur with extra operational maintenance work and even costly breakdowns as a result.

Figure 3. A container made of polypropylene used in the water purification process in a flue gas facility.
Figur 3. En behållare av polypropen som används i vattenreningen i en rökgasanläggning

The work presented in this report is divided into three parts. The work in the first part aims at reducing the thermal expansion of polypropylene by addition of filler, without impairing the chemical resistance. The second part focuses on further developing improved methods for determination of service life of polypropylene and the third part has been devoted to the possibility of creating a database for experiences with materials in flue gas environments.

1.1.3 Thermal expansion and fillers

Fillers are added to reduce cost and/or to enhance mechanical properties. Fillers and reinforcements normally used in PP are:

- Calcium carbonate
- Mica
- Talc
- Barite
- Glass fiber
- Glass spheres
- Carbon fiber

The concentration of filler can be as high as 50% and in some special applications even higher. The brittleness of PPH at low temperatures is often increased by the addition of fillers, due to reduced mobility. As a result many reinforced polypropylenes are based on copolymers. The filler can have a negative effect on the stability and chemical resistance of a polymer. The reason for this can either be that adsorption of additives, such as antioxidants, on the surface of the filler makes it unreactive, or that the filler itself or the coupling agent (which sometimes is required to improve the bond between the filler and the polymer) shows a lack of chemical resistance.

Nurdina et al [2] analyzed the thermal expansion coefficient of the polypropylene (Titanpro 6431 and Titanpro 6431) with three different fillers. Three different fillers were; calcium carbonate ($CaCO_3$), silica and mica. Various filler contents of each filler were prepared (10-40 wt%). The thermal expansion coefficient was analyzed using a dilatometer with a heat flow rate of 5°C / min from room temperature to 125°C. It was found that the polypropylene with 40wt% mica had the lowest thermal expansion coefficient of 57.2 ppm/°C. Polypropylene with 40 wt% $CaCO_3$ had a thermal expansion coefficient of 99.5 ppm/°C. It was also investigated if surface treatment of the silica and mica, with silane and titanate, had any effect on the thermal expansion. It was found that the silane and titanate created nucleating sites which increased the crystallinity of the material and resulted in a lower heat expansion coefficient relative to non-modified PP materials. The lowest thermal expansion coefficient, 48.72 ppm/°C, was found in the polypropylene with 40 wt% silanized mica [3].

A study by Wang et al [4] showed that the mechanical properties of an isotactic polypropylene material (T30S) were improved by using talc as filler. A talc content ranging from 0 to 33 wt% was used in the study where both non-modified talc and talc surface-treated with silane were used. SEM images showed that both types of talcs were uniformly dispersed in the PP matrix, but at higher filler content, about 33 wt%, agglomerations could be seen. The conclusion of the study was that talc without silane surface treatment had similar mechanical properties as talc that had been surface treated with silane.

DeArmitt [5] concludes that fillers can improve the physical properties of the polypropylene as well as the processing properties. One of the most common fillers used in the polypropylene, calcium carbonate ($CaCO_3$) can improve the physical and mechanical properties and is also relatively inexpensive.

Calcium carbonate is often supplied as agglomerate and is dispersed in the polymer matrix by compounding it with the polypropylene material [6]. However, the particle-particle interactions that occur as a result of the particle size and the surface free energy can cause inhomogeneous distribution of e.g. calcium carbonate. This leads to processing difficulties and deteriorated mechanical properties [7]. One of the most common methods used for changing the particle-particle and particle-polymer interactions is to cover the surface of the filler with an organic low molecular weight substance. For calcium carbonate stearic acid is the most common modifier [5] [8], [9]. Stearic acid interacts with calcium carbonate by ion bonding and lowers the surface free energy of calcium carbonate significantly. Lowering the degree of particle-particle interactions leads to a much better dispersion of the filler in the polymer matrix. [10], [11].

In a study by Zuiderduin [6], the mechanical properties of PP filled with coated calcium carbonate were investigated. The $CaCO_3$ had different particle sizes ranging from 0.07 microns to 1.9 microns, and was added in levels between 0 and 60 wt%. The thermal properties of the material such as the melting point were affected very little by the filler, however, for the material with 60 wt% $CaCO_3$ the melting enthalpy could no longer be detected. This was assumed to be due to the polymer chains having a lower mobility in the matrix. Also, since the surface treatment with stearic acid has lowered the surface free energy of the filler, the filler does not create nucleating sites in the material (less polymer-particle interactions).

What is not so well studied is how different fillers are affected by chemical environments. In general fillers are often avoided in harsh chemical environments since they are often less stable than the polymer. E.g. in FRP the corrosion barrier contains less glass fiber since it generally has lower chemical resistance than the polymer matrix. For PVC and CPVC the chemical resistance is often determined by the additives, e.g. stabilizers, fillers, pigments and impact modifiers.

1.1.4 Petrit P (Tunnel kiln lime)

Petrit P which is a tunnel kiln lime is a bi-product from iron processing. An XRD-analysis shows that it contains mainly five minerals, Calcium oxide (CaO), Larnite ($2CaO{\cdot}SiO_2$), Portlandite ($Ca(OH_2)$), Gehelenite ($2CaO{\cdot}Al_2O_3{\cdot}SiO_2$) and carbon black. In addition there is also some metallic iron. Swerea has been involved in a project together with Höganäs for finding use of this bi-product where one of the ideas was using it as a filler for polypropylene.

1.1.5 Methods for determining the service life of polypropylene

The second part focuses on further developing improved methods for determination of service life of polypropylene. Today oxidation induction time (OIT) is often used as a measure of residual stabilizer content and also remaining life. A high value means a long and a low value a short remaining life. However, it has been found that zero OIT need not be the end of life, and therefore other more sophisticated techniques to study the stability and thermo-oxidative degradation of PP, such as FTIR and HPLC, should be evaluated. The connection between stabilizer concentration and the time when a PP component breaks down is also far from known. Figure 4 shows the droplet separators a the waste incineration plant which had an OIT of 0 minutes at the surface after only 6 months of service but have still lasted for many years without becoming brittle from oxidation.

Figure 4. Droplet separators in the scrubber in a waste incineration plant which had an OIT of 0 minutes at the surface after only 6 months of service but have still lasted for many years without becoming brittle from oxidation.

Figur 4. Droppavskiljare i skrubbern i sopförbränningsanläggning. De hade 0 minuters OIT på ytan efter bara 6 månader i drift men har ändå har klarat sig många år i drift utan att bli förspródade av oxidation.

In the previous report, it was concluded that in order to be able to better assess the status and service reliability of PP further development was needed on evaluation techniques such as Fourier transform infrared spectroscopy (FTIR) and FTIR line-scan. FTIR line-scan is a very good method to obtain an idea of the amount and distribution of stabilizers or filler over a cross-section. However, many of the commonly used stabilizers contain no easily detected group such as an ester, and since the phenolic peak is often difficult to detect, it has not been possible to study the stabilizer distribution with line-scan for these samples. To overcome this problem, a number of different reagents were tested to see if it is possible to find a compound that can react with the phenol group and form a compound that can be easily seen with IR. It turned out that such a compound was chlorine dioxide in combination with water. Chlorine dioxide is known for its rapid reaction with phenols. The reaction leads to quinine and other compounds which form strong hydrogen bonds with water. The PP sample with the sterically hindered phenol stabilizer will after reaction with a chlorine dioxide/water exhibit strong IR absorption in the hydrogen bond region around 3400 cm^{-1} and at 1640 cm^{-1}, Figure 5. The aim in the second part of the work presented in this report is to investigate whether or not it is possible to relate the absorbed amount of water to the concentration of stabiliser in the polymer.

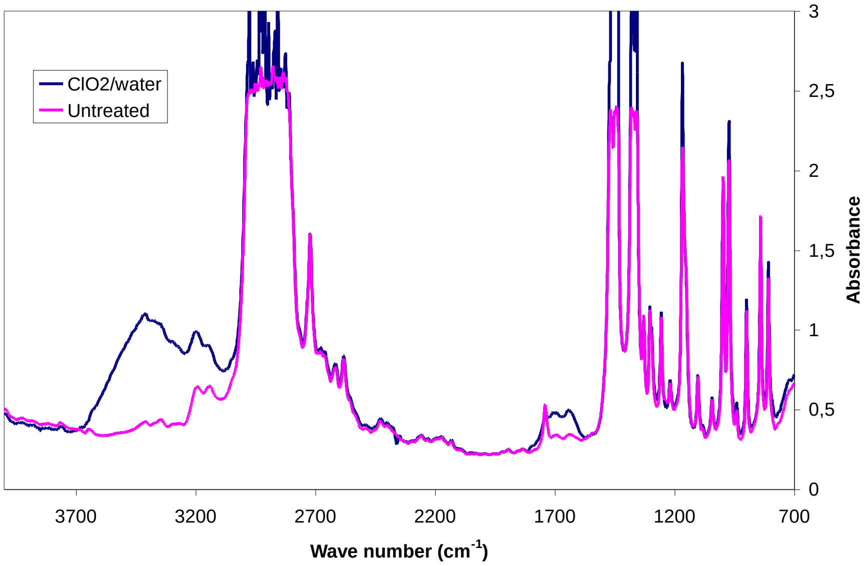

Figure 5. FTIR scan of an untreated PP sample containing a sterically hindered phenol stabilizer (in this case Irganox 1010) and a scan of the same sample after it has reacted with a chlorine dioxide solution.

Figur 5. FTIR scan av ett obehandlat PP-prov som innehåller en steriskt hindrad fenolstabilisator(I detta fall Irganox 1010) och ett scan av samma prov efter att det har reagerats med en kolrdioxidlösning.

1.1.6 Database

The last part of the project has looked into the possibility of collecting information about the service life of different materials (polymeric and/or metallic) in a database. This could then be of great help to those planning new construction or replacement of old components in flue gas facilities. Swerea KIMAB has over the years participated in a number of Värmeforsk projects and by this, accumulated a lot of experience and knowledge of plastic and metallic materials in flue gas environments. This knowledge, together with other experiences from the use of plastic materials in various types of flue gas environments, could serve as the basis for such a data. The difficulty lies in how it should be managed and maintained and what type of data that should be collected and if there is enough up-dated data available for it to be of relevance.

2 Experimental

2.1 MATERIALS

For the study on filled polypropylene, three different types of commercial PP materials, α-PP, β-PP and PP-R were chosen. Both the α-PP and β-PP are PP-H materials. All three were supplied by Borealis. The α-PP was a BE50, the β-PP a BE60 and the PP-R an RA130E. There are a vast number of different fillers used with polymers for a lot of different reasons. The fillers that were selected for this study needed to be able to potentially lower the thermal expansion of the materials without negatively affecting the chemical stability. The fillers also need to disperse well in the polymer matrix during processing. After discussions with the filler supplier Imerys, stearic acid coated calcium carbonate ($CaCO_3$) and carbon black were chosen as suitable fillers. In order to evaluate the impact that addition of fillers have to the materials, two different concentrations of $CaCO_3$ were processed. A lower amount with 5 wt% and a higher amount with 25 wt%. Two different carbon black fillers were selected, the high structured 600 JD and the low structured XC72. These were processed at 10 wt% for each of the three different plastics. Table 1 lists the concentrations of the different fillers. High structure carbon black has a high number of primary particles per aggregate, while low structure carbon black exhibits only a weak aggregation, see Figure 6.

Table 1. Filler type and concentration.

Tabell 1. Fyllmedelstyp och koncentration.

Filler [weight-%]	α-PP	β-PP	PP-R
$CaCO_3$	5	5	5
$CaCO_3$	25	25	25
Carbon black low structured (XC72)	10	10	10
Carbon black high structured (600 JD)	10	10	10

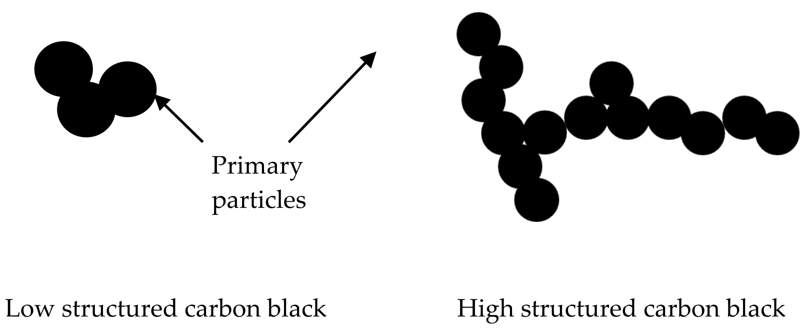

Figure 6. A schematic representation of low and high structured carbon black.

Figur 6. En schematisk beskrivning av låg- och högstrukturerad kimrök.

The compounding and injection moulding into 2 mm plaques (100 x 100 mm) was made at Swerea IVF. The compounding was made in a Coperion ZSK 26 K 10.6 which is a rotating double screw extruder with a special configuration for good dispersion of filler particles. The injection moulding was made using an Engel ES 200/110 HL Victory, with a 30 mm screw.

In addition to the materials described above also PPH with Petrit P, a waste product from iron casting described in the introduction, was investigated. In a previous project injection moulded tensile bars of PPH (BH345MO) had been prepared with 2, 10 and 25 wt% grinded Petrit P and the mechanical properties had been evaluated.

For evaluating the chlorine dioxide method, three different polypropylene materials were investigated, three polyethylene samples and three polypropylene samples. Two of the polypropylene samples were Borealis Beta (β)-PP BE60 grey homopolymer, where 0,1 wt% of Irganox 1010 was in addition to one of them. The third polypropylene sample was a Polystone P Homopolymer EuroGrey from Röchling Engineering Plastics.

Commercial antioxidants were purchased as reference in order to identify the antioxidants in the polymeric materials. Irganox 1010, Irganox 1076, Irganox 1330 and Irgafos 168 were purchased from Sigma-Aldrich and Cyasorb UV 2908 was purchased from Activate Scientific GmbH.

2.2 EXPOSURES

The following exposures were made:

- 5 weight-% and 25 weight-% hydrochloric acid (HCl) for acidic environment at 60 °C
- 5 weight-% and 30 weight-% sodium hydroxide (NaOH) for alkaline environment at 60 °C
- 5 mg/l Chlorine dioxide (ClO_2) for an oxidative environment at 50 °C
- High concentration NO/NO_2-gas mixture at room temperature.

The materials were exposed in these conditions for 48 days except the NO/NO_2-gas mixture in which the materials were exposed for aPP-Roximately three weeks at room temperature.

The samples with 25 wt% tunnel kiln lime were exposed to 30 weight-% sodium hydroxide (NaOH) at 60 °C for one year

2.2.1 The chlorine dioxide method

Slices of 100 µm thickness were prepared from each material for chlorine dioxide exposure using a RM2255 microtome from Leica. Five concentrations of ClO_2 in distilled water were prepared in order to investigate if there is an optimum concentration of ClO_2 for reacting with the sterically hindered phenol. The ClO_2 solutions were diluted from a stock solution into concentrations of 0.1, 0.5 0.75, 2.0 and 3.0 grams/litre, and placed into separated bottles. The bottles were then placed in an oven at 50°C.

The effect of ClO_2 was analyzed at five different times. Five slices of each material were placed in each of the five bottles. The first slice of each material was analyzed after 24 hours, the second after 48 hours, the third after 72 hours, the fourth after 144 hours and the fifth after 168 hours.

The commercial antioxidants were also exposed to ClO_2 in order to investigate if any of the sterically hindered phenols was more reactive towards ClO_2 or more prone to absorb water than the other after the reaction. The antioxidants were separately exposed to ClO_2 at a concentration of 0.1 g/l in 50°C for 6 days, before they were analysed with FTIR equipped with an ATR (Attenuated Total Reflectance) crystal.

2.2.2 Extraction and Identification of Antioxidants

The extraction of the stabilizers from the polymeric materials was carried out in 20 ml glass crimp neck vials sealed with aluminum caps containing natural rubber/Teflon septa. The polymeric material were cut into slices of 100 µm with an RM2255 microtome from Leica and about 0.5-1 g of each material were placed in a vial, respectively. The vials were then filled to aPP-Roximately two thirds with dichloromethane or until the polymeric material was completely covered with solvent. The vials where then placed in an oven at 40°C for 24 hours.

Both FTIR and HPLC were used for analysis of the extracted antioxidants and the commercial antioxidants. The commercial antioxidants was prepared by separately dissolving 25 mg of each antioxidant in 25 ml of a solution containing acetonitrile (ACN) and dichloromethane (DCM), (3:1). The extracted antioxidants was prepared by first pouring off the dichloromethane, from the samples that had been leached for 24 hours at 40°C, into new separated glass crimp vials for each polymer. The dichloromethane was then evaporated with nitrogen gas before 5 ml of the ACN:DCM-solution (3:1) was added to each vial.

The extracted antioxidants were examined with a FTIR, by placing a small amount of extraction liquid on a piece of zinc sulphide glass. The zinc sulphide glass was placed in a fume hood for the solvent to evaporate, leaving only antioxidants on the surface, before it was positioned in the FTIR.

2.3 ANALYTICAL TECHNIQUES

2.3.1 TMA (Thermomechanical analysis)

The TMA measurements were performed by Ruston Services Ltd in the United Kingdom. Fifteen samples were submitted for testing by TMA to determine the expansion coefficient according to ASTM 831-06. Pieces of material were cut from the tensile test “dumbbell” pieces supplied so that the test was carried out in the direction intended for the tensile test i.e. the long direction. The analysis was carried out using a PerkinElmer TMA 7e, serial number 519N7030702 controlled using PerkinElmer Pyris thermal analysis software version 9.0.

A heating rate of 5°C/min is normal for this type of analysis and the temperature program used in this work was as follows;

1. Isothermal at -30°C for 5 minutes to allow cooling and equilibrium of the sample
2. Heat at 5°C/min to 110°C

At the end of the temperature program, the analyser was returned to the “load” temperature which was set to be 20°C.

2.3.2 Gravimetric Analysis

The weight change, wt-%, was calculated by relating the initial mass, m_0, to the mass of the sample after exposure, m(t).

$$wt\% = \frac{m(t) - m_0}{m_0} \cdot 100\%$$

2.3.3 DMA (Dynamic Mechanical Analysis)

The initial tests to establish the coefficient of thermal expansion for the materials were carried out on a Perkin Elmer/Triton Technology 2000 DMA. The chosen experiment type was creep/TMA with the deformation mode set to tension. The analyses were performed from 25 to 100 °C at 1 °C/min. Single frequency / single strain was used.

2.3.4 DSC (Differential Scanning Calorimetry)

The melting endotherms, Tm1 and tm2, were analyzed using a Mettler Toledo DSC 821e/700. The samples were heated from 25 °C to 200 °C (10 °C/min) in nitrogen (80 ml/min). The samples were then cooled down to 25 °C again (-79.99 °C/min) and the cycle was repeated one more time.

2.3.5 XRD (Wide angle X-ray spectroscopy)

The degree and type of crystallinity (α, β and/or γ) was determined under ambient conditions using a Bruker D8 ADVANCE with Cu Kα1 radiation at 40 KV and 40 mA. Diffraction patterns were recorded by an energy dispersive detector (Sol-X) in the range 5-35° 2θ with a step size of 0.05° and the measuring time per step was 0.5s. A "parallel beam -set up" was used by a primary side Goeble mirror and a secondary side long Soller slit.

2.3.6 Mechanical Testing

The yield strength of the materials was gathered using an Instron 5566 with 10 kN loading cell in tensile mode. Contact extensometers from Instron were also used during testing. The samples were analyzed with a crosshead speed of 10 mm/min at 23 °C and 50% relative humidity. The extensometer gauge length was set to 10 mm and the sample gauge length was 15 mm.

2.3.7 Charpy impact test

The impact resistance of the samples was tested using Charpy impact test. The tests were done using a 150 kgcm hammer without notched samples under ambient conditions.

2.3.8 FTIR

A 2000 FT-IR from Perkin Elmer was used for analysis of the ClO_2 exposed polymer slices and measurements were performed both on wet and dry samples. All measurements were performed in an interval between 600 cm-1 and 4000 cm-1.

Thin slices of the cross-section were made using a microtome. An FTIR line scan within the interval 4000-700 cm^{-1} along the thickness direction of the slice was then made using a Spectrum Spotlight 400 FTIR Imaging System (PerkinElmer Inc., Shelton, CT, USA) or a Perkin Elmer System 2000 FT-IR fitted with an *i*-series microscope. Scans were performed every 50 µm over the cross section of the sample unless otherwise specified. The resolution were 2 or 4 cm^{-1}.

2.3.9 Oxidation induction time (OIT)

Oxidation induction time was measured at 200°C using a differential scanning calorimeter, DSC 821-e from Mettler Toledo. The samples were heated from 25°C to 260°C (10°C/min) in nitrogen (80ml/min)

2.3.10 HPLC

An isocratic 844 UV/VIS Compact IC with 819 IC Detector from Metrohm was used for the analysis with HPLC. A C18 column was used with silica particles as a solid phase, and the mobile phase consisted of a mixture of acetonitrile and MilliQ water (3:1). The separation was performed at a fixed temperature of 40°C.

2.3.11 DART-MS

DART stands for "Direct Analysis in Real Time" This is a new technology that allows analysis without prior extraction. DART can, together with high-resolution "Time of Flight" instruments, such as a mass-spectrometer (MS), give an almost direct composition of the components that are present in a sample and have a mass number below 1200. LSC laboratory in Uppsala made the analysis.

3 Results

3.1 UNEXPOSED MATERIAL

3.1.1 TMA

The coefficient of thermal expansion (CTE), seen in Figure 7 below, was measured using thermomechanical analysis. A lower CTE values corresponds to lower expansion and contraction of the material. It is seen that α-PP has the overall lowest CTE of the three materials. The addition of the high structured carbon black, 600JD, seems to have lowered the CTE across all three materials the most compared to the virgin materials.

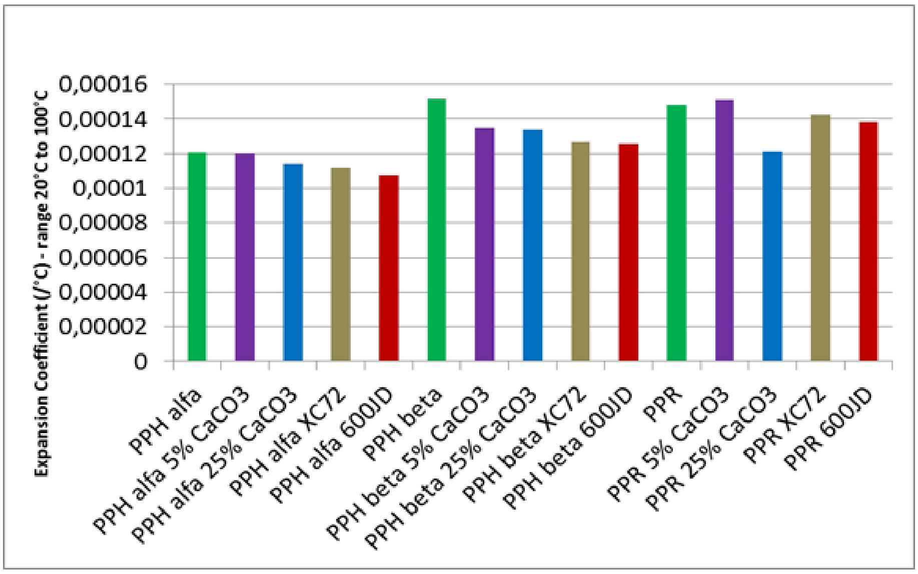

Figure 7. The coefficient of thermal expansion (CTE) for all the investigated materials.

Figur 7. Den termiska expansionskoefficienten för alla de undersökta materialen.

The results from using these numbers to calculate how much longer a 5 meter part (e.g. pipe) will be after heating it from 20 to 90 degrees is shown in Table 2.

Table 2. Elongation of a 5 meter long pipe when heated from 20 to 90°C (mm)
Tabell 2. Förlängningen av ett 5 meter långt rör när det värms från 20 till 90°C (mm)

Material	Elongation (mm)
α-PP	42
α-PP 5% $CaCO_3$	42
α-PP 25% $CaCO_3$	40
α-PP XC72	39
α-PP 600JD	38
β-PP	53
β-PP 5% $CaCO_3$	47
β-PP 25% $CaCO_3$	47
β-PP XC72	44
β-PP 600JD	44
PP-R	52
PP-R 5% $CaCO_3$	53
PP-R 25% $CaCO_3$	42
PP-R XC72	50
PP-R 600JD	48

3.1.2 DSC

Crystallinity content for α-PP and PP-R with compensation for weight of filler, can be seen in Figure 8 and Figure 9 below. The crystallinity for α-PP is the highest for the material without filler and is decreased with the addition of filler. The crystallinity content for PP-R is about 10% lower overall across the different materials compared to α-PP with the highest crystallinity found in PP-R with 25 wt% $CaCO_3$.

DSC cannot be used to calculate the crystallinity of beta nucleated polypropylene since this material shows two melting endotherms which overlaps with each other and have different ΔH-values.

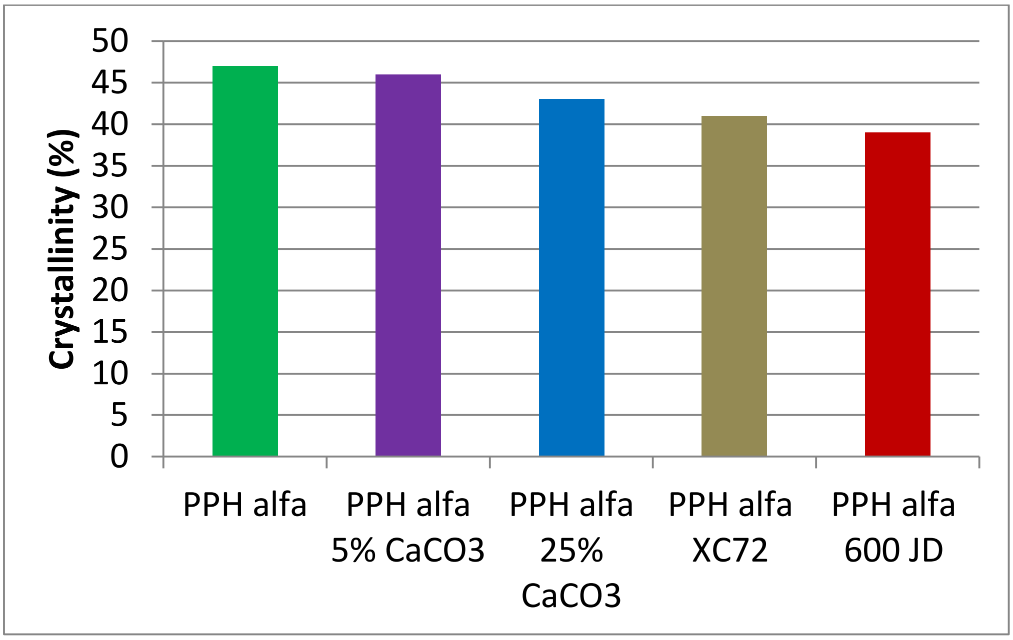

Figure 8. Degree of crystallinity of α-PP with compensation for weight of filler measured using DSC.
Figur 8. Kristallinitetsgrad i α-PP efter kompensation för vikten av fyllmedlet, mätt med DSC.

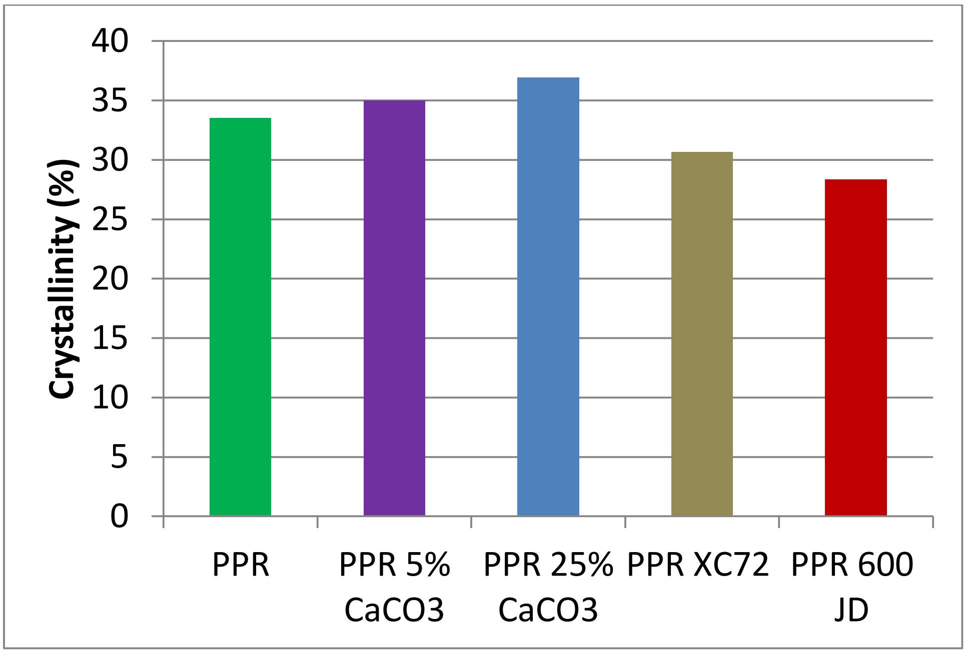

Figure 9. Degree of crystallinity of PP-R with compensation for weight of filler measured using DSC.
Figur 9. Kristallinitetsgrad i PP-R efter kompensation för vikten av fyllmedlet, mätt med DSC.

3.1.3 XRD

To calculate the total crystallinity content of β-PP and the amount of beta crystals, XRD was used. The total crystallinity and the amount of beta crystals of unexposed β-PP with and without fillers can be found in Table 3, Figure 10 and Figure 11 below. The peak at 2θ 30° comes from $CaCO_3$. To calculate the crystallinity, the spectra were integrated from 2θ 5° to 35°.

The K-value, which is a value of the relative amount of β-phase in the crystalline portion, was calculated from the X-ray diffractograms using the following equation:

$$K - value = \frac{H_{\beta}}{\left(H_{\alpha 1} + H_{\alpha 2} + H_{\alpha 3} + H_{\beta}\right)}$$

Where $H_{\alpha 1}$, $H_{\alpha 2}$ and $H_{\alpha 3}$ are the intensities of α-diffraction peaks corresponding to the angles 2θ = 14.2°; 17.0° and 18.8°, respectively and H_{β} is the intensity of the β peak at 2θ = 16.2°. A sample with only β-phase has a K-value of 1 [12].

Table 3. Degree of crystallinity and K-value of the filled and unfilled β-PP measured using XRD. Integrations of the peaks were made between 2θ: 5° and 35°.

Tabell 3. Kristallinitetsgrad och K-värde hos fylld och ofylld β-PP mätt med XRD. Integreringen av topparna gjordes mellan 2θ: 5° och 35°.

β-PP	No filler	5% $CaCO_3$	25% $CaCO_3$	10% XC72	10% 600JD
Total crystallinity [%]	46	62	64	58	64
K-value	30	28	18	30	21

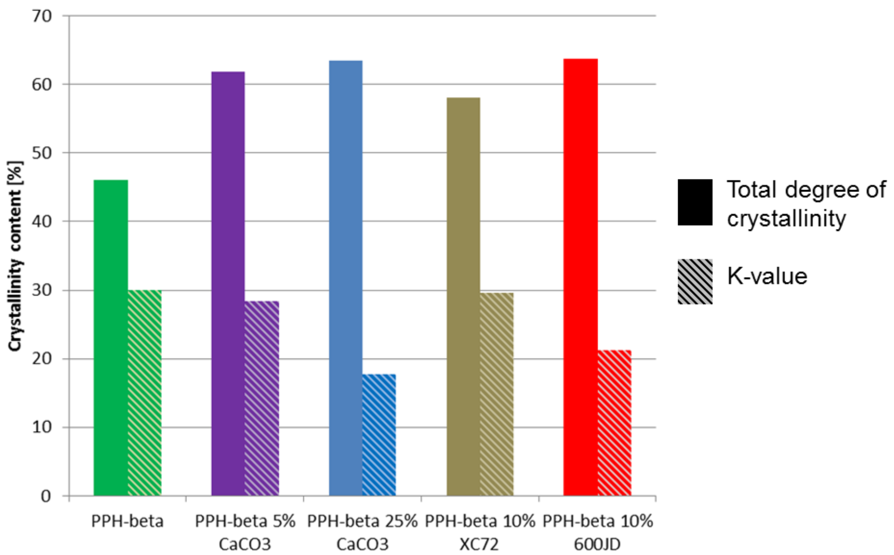

Figure 10. Graphical representation of the XRD results from Table 3 showing the crystallinity content and K-value of the filled and unfilled β-PP measured using XRD. Integrations of the peaks were made between 2θ: 5° and 35 °.

Figur 10. Grafisk presentation av XRD-resultaten från Tabell 3 som visar kristallinitetsgrad och K-värde hos fylld och ofylld β-PP mätt med XRD. Integreringen av topparna gjordes mellan 2θ: 5° och 35°.

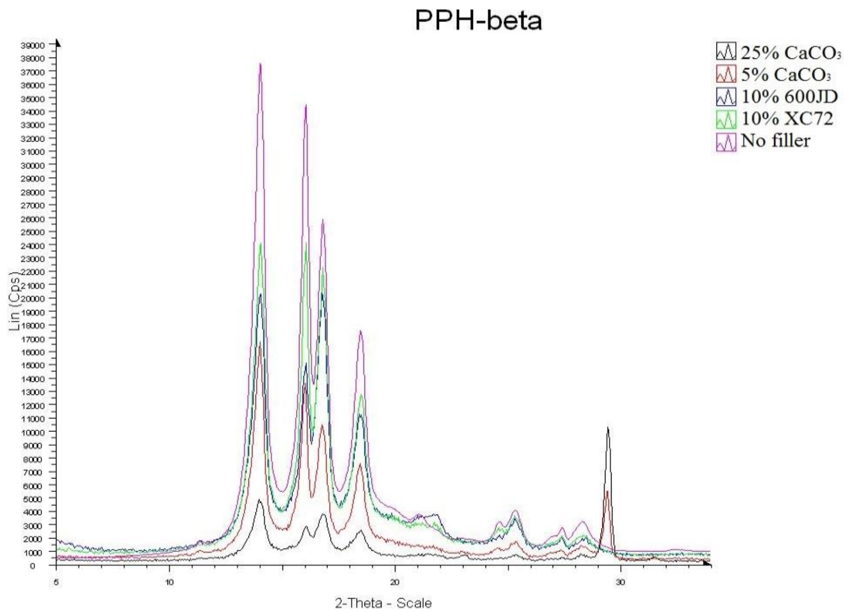

Figure 11. Spectra from XRD analysis illustrating the different β-PP materials.

Figur 11. Spektra från XRD-analysen som illustrerar skillnaden mellan β-PP materialen.

The crystallinity value calculated from DSC is not necessary the same as from XRD so they should not be compared with each other. Due to this XRD was also used to measure the crystallinity of the unfilled α-PP and PP-R samples, Figure 12 and Table 4. It was then found that also these materials had beta crystals as can be seen by the β peak at $2\theta = 16.2°$.

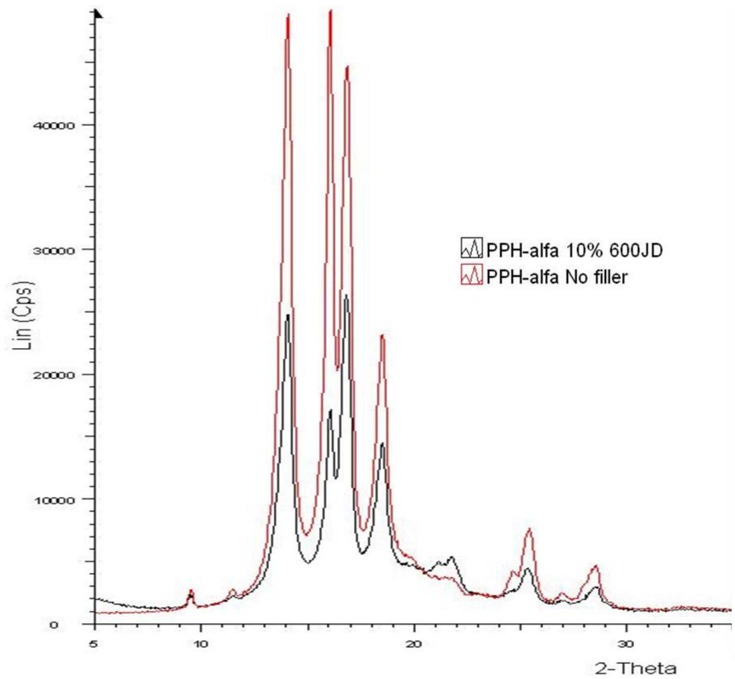

Figure 12. XRD spectra of the unfilled α-PP and the α-PP with 600 JD. As can be seen by the beta peak at 16.2º also these samples had beta crystals.

Figur 12. XRD-spektra av ofylld α-PP och α-PP med 600 JD. Betatoppen vid 16.2º visar att även dessa material har betakristaller.

Table 4. Crystallinity content and K-value of the unfilled α-PP and PP-R and the α-PP filled with 600JD measured using XRD. Integrations of the peaks were made between 2θ: 5° and 35°.

Tabell 4. Kristallinitetsgrad och K-värde hos ofylld α-PP och PP-R och α-PP fylld med 600JD uppmätt med XRD. Integreringen av topparna gjordes mellan 2θ: 5° och 35°.

	α-PP No filler	α-PP 10% 600JD	PP-R No filler
Total crystallinity [%]	59	56	50
K-value	30	19	21

3.1.4 Mechanical Testing

Figure 13 shows the tensile yield strength of the unexposed samples. The α-PP has higher tensile yield strength than the β-PP and PP-R materials. Addition of 25 wt% $CaCO_3$ decreased it and the addition of carbon black, particularly 600JD improved it.

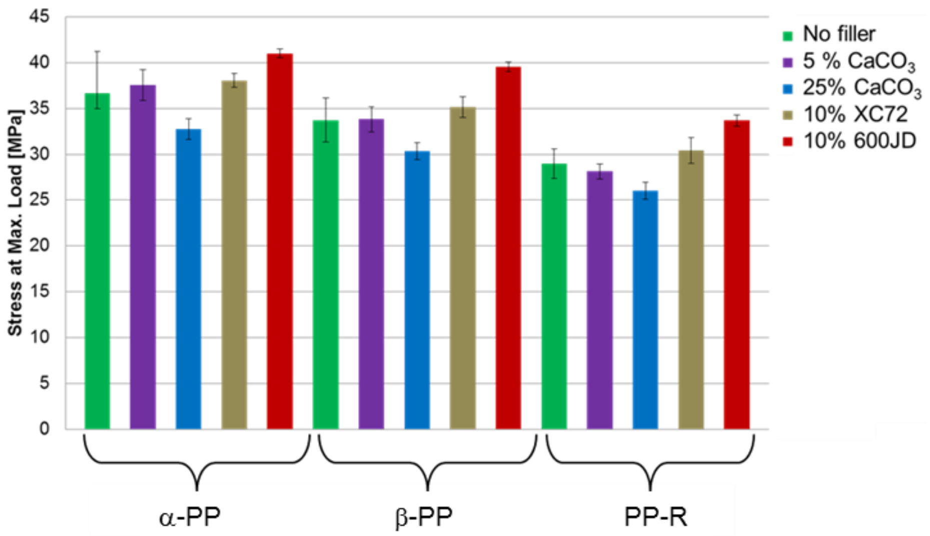

Figure 13. The tensile yield strength of the unexposed samples.

Figur 13. Dragbrottsspänning av de oexponerade materialen

3.1.5 Charpy Impact Testing

Some of the unexposed α-PP materials were subjected to charpy impact testing. The results can be seen in Figure 14 below. The impact strength is increased with addition of filler and the highest impact strength was seen in α-PP with filler 600JD. One out of the eight tested samples with 600JD broke, which is the reason for the large standard deviation of this material.

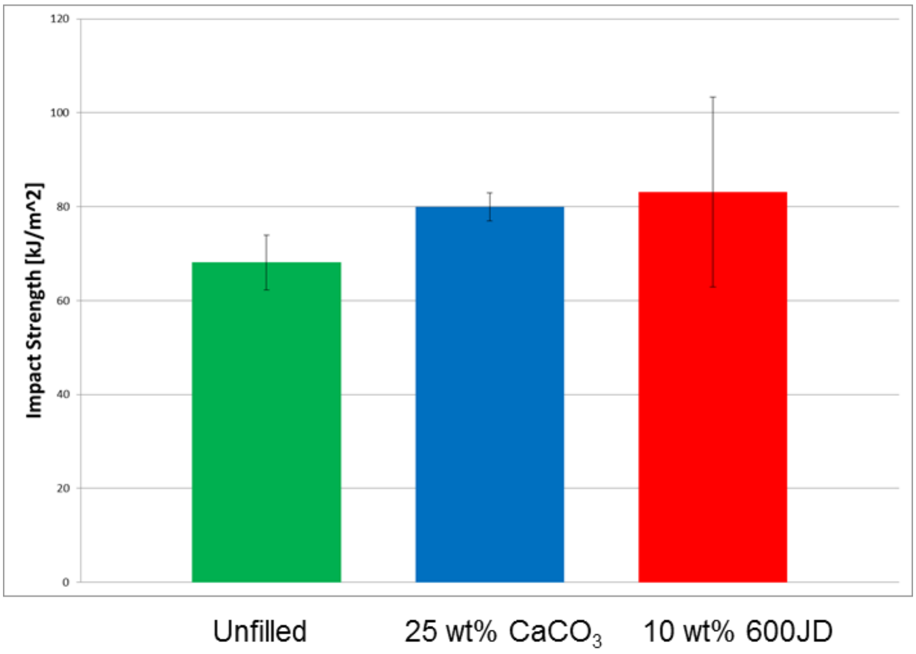

Figure 14. The results from the Charpy impact testing of the α-PP without filler, with 25 wt% $CaCO_3$ and with 10 wt% 600JD.

Figur 14. Resultaten från Charpy slagprovning av α-PP utan fyllmedel, med 25 vikt% $CaCO_3$ och med 10 vikt% 600JD.

3.1.6 OIT

OIT gives a value of the stabilizer concentration. The highest OIT value is found in the unfilled α-PP. There is a clear drop in concentration after compounding. Also addition of fillers has had an effect on the amount of stabilizer, se Figure 15.

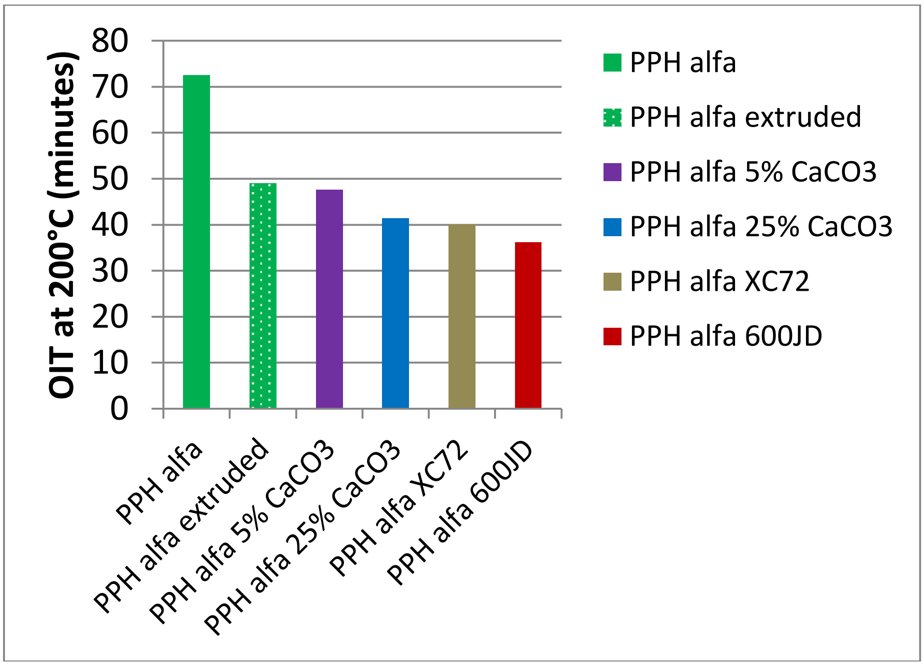

Figure 15. OIT of the α-PP samples.

Figur 15. OIT av α-PP proverna.

The OIT of the material with 25 wt% Petrit P (tunnel kiln lime) was also investigated, Table 5, but since this material was made using a different grade of PP, the results cannot be compared to the other materials. The material was investigated as a virgin unfilled granulate, after compounding the unfilled material and as an injection moulded sample with 25 wt% Petrit P.

Table 5. OIT values of the PP used for the Petrit P invetsigation. The material was investigated as a virgin granulate, after compounding the unfilled material and on the sample with 25 wt Petrit P.

Tabell 5. OIT värden av PP som användes för undersökningen av Petrit P. Materialet undersöktes som rent granulat, rent material efter en kompoundering och provet med 25 vikt% Petrit P.

Material	OIT [min]
PP (BH345MO) unfilled granulate	94 ±9
PP (BH345MO) compounded	49 ±14
With 25 wt-% Petrit T	31 ±5

3.2 EXPOSED MATERIAL

3.2.1 Gravimetric Analysis

The weight changes of the materials (α-PP, β-PP and PP-R) exposed in high and low concentration of HCl are found in Figure 16. The effect of the 25 wt% HCl is much larger than the 5 wt% HCl. It is also noteworthy that the samples with 5 wt% $CaCO_3$ gains weight while the material with 25 wt% loses weight.

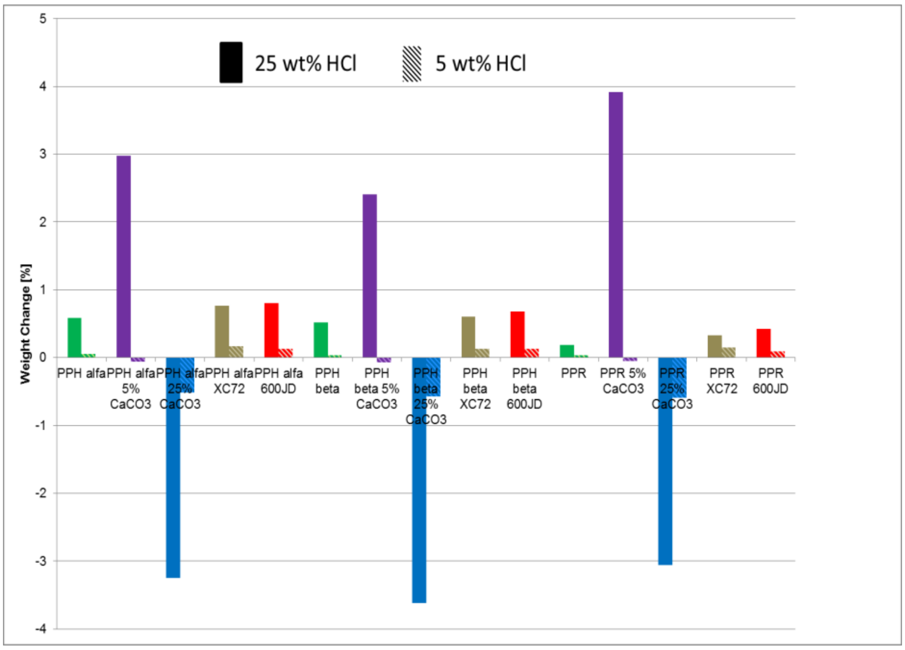

Figure 16. Weight change of α-PP, β-PP and PP-R after exposure to two different concentrations of HCl for 42 days at 60 °C.

Figur 16. Viktförändring av α-PP, β-PP och PP-R efter exponering till de två olika koncentrationerna av HCl i 42 dygn vid 60 °C

The weight change of α-PP, β-PP and PP-R after exposure to two different concentrations of NaOH for 42 days at 60 °C is shown in Figure 17. Note that the scale is different compared to the HCl exposure above, i.e. the effect on the weight up-take is much lower for NaOH. The most striking result is that the carbon black XC72 is gaining some weight in 5wt% NaOH.

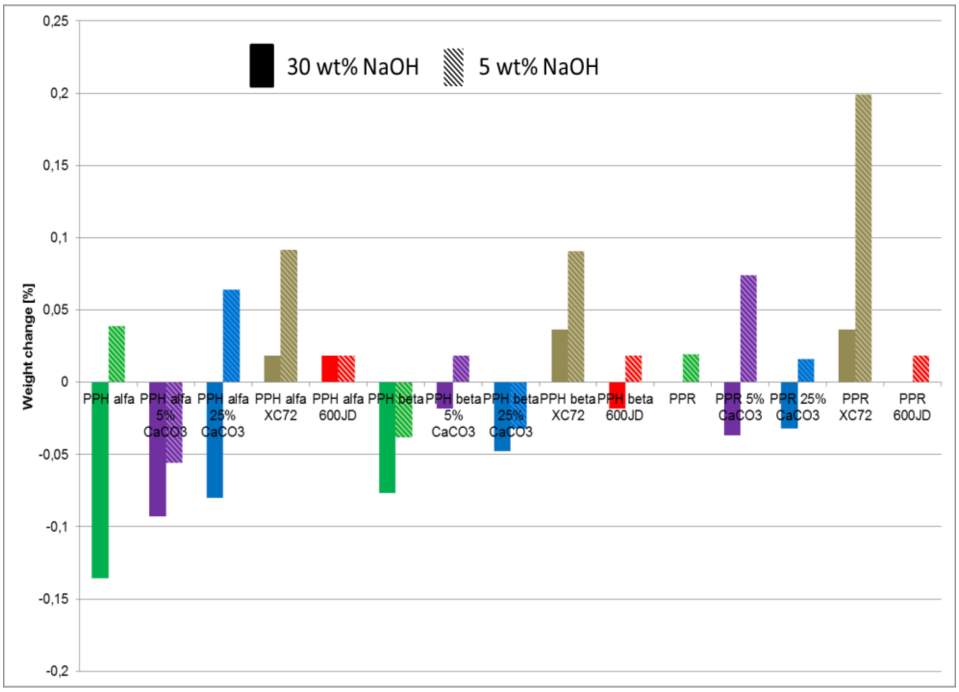

Figure 17. Weight change of α-PP, β-PP and PP-R after exposure to two different concentrations of NaOH for 42 days at 60 °C.

Figur 17. Viktförändring av α-PP, β-PP och PP-R efter exponering till de två olika koncentrationerna av NaOH i 42 dygn vid 60 °C

The tensile yield strength of the samples exposed to 5wt% HCl can be seen in Figure 18 and to 25wt% HCl in Figure 19.

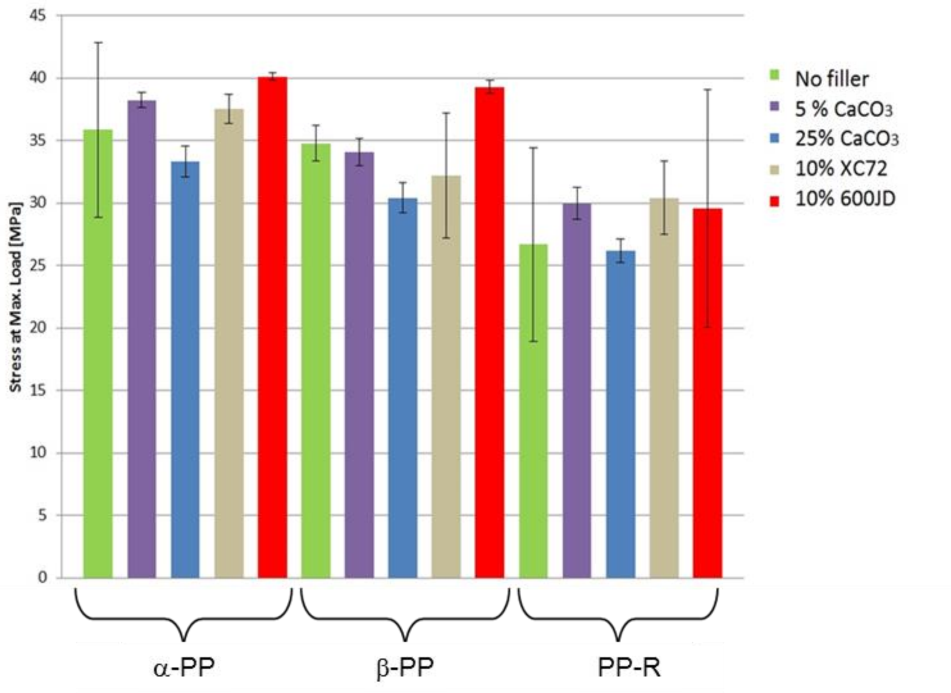

Figure 18. The tensile yield strength of the samples exposed to 5wt% HCl for 48 days at 60°C.
Figur 18. Dragbrottspänningen av materialen efter att de exponerats i 5 vikt% HCl i 48 dygn vid 60°C.

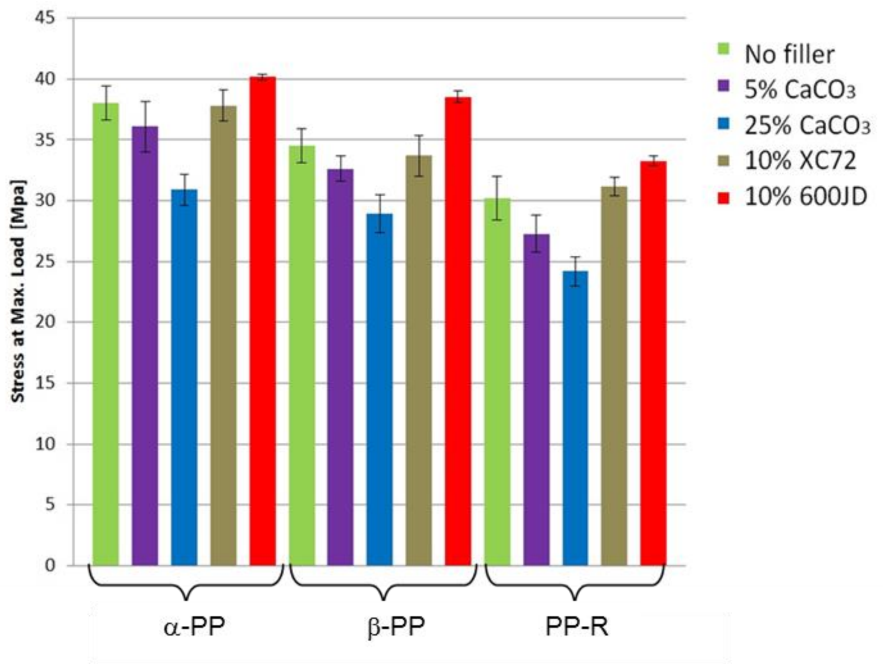

Figure 19. The tensile yield strength of the samples exposed to 25wt% HCl for 48 days at 60°C.
Figur 19. Dragbrottspänningen av materialen efter att de exponerats i 25 vikt% HCl i 48 dygn vid 60°C.

In Table 6 the values, with standard deviations, of the yield strength of the unexposed and the samples exposed to 5 and 25wt% HCl for 48 days at 60°C are shown to facilitate comparison. The tabulated data of the tensile yield strength of the unfilled materials are

36 MPa for the α-PP (BE50), 30 MPa for β-PP (BE60) and 25 MPA for the PP-R (RA130E).

Table 6. Comparison of the yield strength of the unexposed and the samples exposed to 5 and 25wt% HCl for 48 days at 60°C.

Tabell 6. Jämförelse av brottspänningen hos oexponerade och proverna som exponerats för 5 och 25 vikt% HCl i 48 dygn vid 60°C.

Specimen	Unexposed	Standard-Deviation	5 wt% HCl	Standard-Deviation	25 wt% HCl	Standard-Deviation
α-PP	36.7	4.6	35.8	7.0	38.0	1.4
α-PP 5% CaCO3	37.6	1.7	38.2	0.6	36.1	2.1
α-PP 25% CaCO3	32.7	1.1	33.3	1.2	30.9	1.3
α-PP 10% XC72	38.1	0.8	37.5	1.1	37.8	1.3
α-PP 10% 600JD	41.0	0.5	40.1	0.3	40.2	0.3
β-PP	33.7	2.4	34.8	1.4	34.5	1.4
β-PP 5% CaCO3	33.8	1.4	34.1	1.1	32.6	1.0
β -PP 25% CaCO3	30.4	0.9	30.4	1.2	28.9	1.5
β -PP 10% XC72	35.2	1.1	32.2	5.0	33.7	1.7
β -PP 10% 600JD	39.5	0.5	39.3	0.5	38.5	0.4
PP-R	29.0	1.6	26.7	7.8	30.2	1.8
PP-R 5% CaCO3	28.1	0.8	30.0	1.3	27.3	1.5
PP-R 25% CaCO3	26.0	0.9	26.1	0.9	24.2	1.2
PP-R 10% XC72	30.4	1.4	30.4	3.0	31.1	0.8
PP-R 10% 600JD	33.7	0.6	29.6	9.5	33.2	0.4

3.2.2 FTIR

ATR

FTIR ATR gives a measure of the type and amount of chemical changes at the surface of a sample. Only the results for the α-PP material is shown in this chapter, unless otherwise noted, since the chemical changes of the fillers by the different exposures are the same for α-PP, β-PP and PP-R.

Exposure to HCl at 60ºC for 48 days

The FTIT spectra of the α-PP material with high and low concentration of $CaCO_3$ before and after exposure to 5 wt% HCl for 48 days at 60ºC can be seen in Figure 20. In Figure 21 the same spectra have been zoomed in to show the fingerprint region between 1800 and 600 cm^{-1}. Note the much higher absorption at the $CaCO_3$ peaks at 1420, 875 and 712 cm^{-1} for the samples with 25 wt% $CaCO_3$ compared to 5wt%. These peaks are totally gone after the exposure.

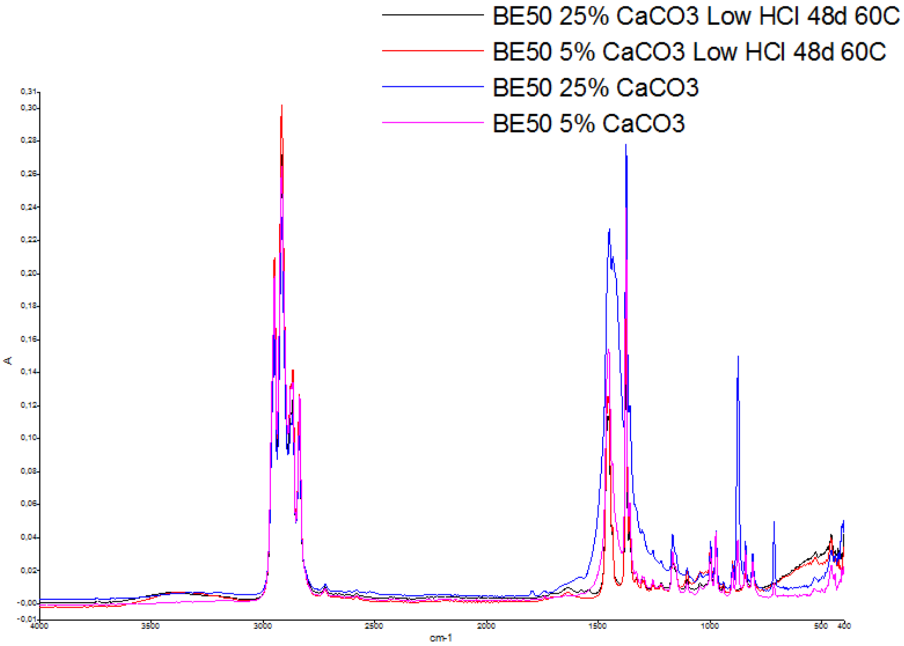

Figure 20. FTIR spectra of the α-PP material with high and low concentration of $CaCO_3$ before and after exposure to 5 wt% HCl for 48 days at 60°C.

Figur 20. FTIR spektra av α-PP materialet med hög och låg koncentration av $CaCO_3$ före och efter exponering i 5 vikt% HCl i 48 dygn vid 60°C.

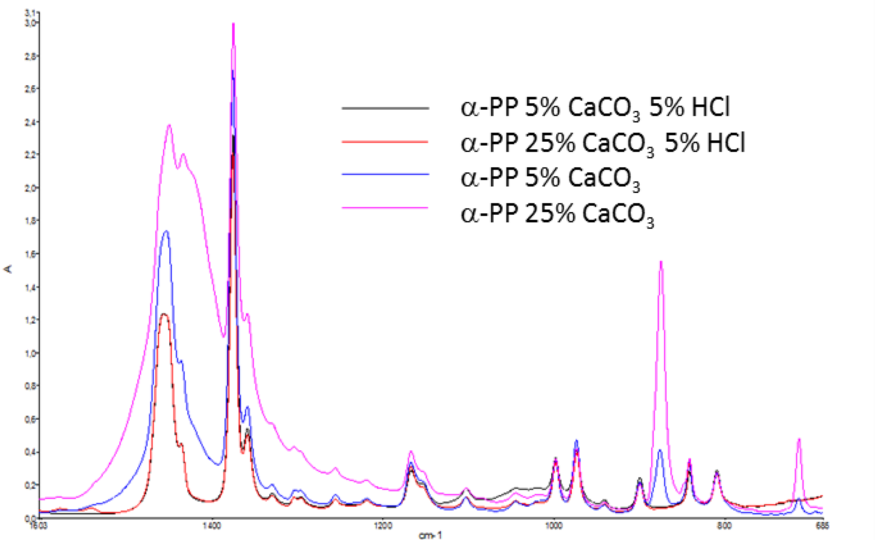

Figure 21. The same FTIR spectra as in Figure 20 but zoomed in to the fingerprint region between 1800 and 600 cm^{-1}. It shows the α-PP material with high and low concentration of $CaCO_3$ before and after exposure to 5 wt% HCl for 48 days at 60ºC

Figur 21 Samma FTIR spektra som i Figur 20 men inzoomad till fingeravtrycksområdet mellan 1800 och 600 cm^{-1}. Det visar α-PP materialet med hög och låg koncentration av $CaCO_3$ före och efter exponering i 5 vikt% HCl i 48 dygn vid 60°C.

Figure 22 shows the FTIR spectra of the α-PP material with high and low concentration of $CaCO_3$ before and after exposure to 25 wt% HCl for 48 days at 60ºC. The $CaCO_3$ peaks disappear after the exposure, just as for the lower concentration HCl but in addition there is also very high water absorption peaks in the 3400, 1640 and 600 cm^{-1} regions.

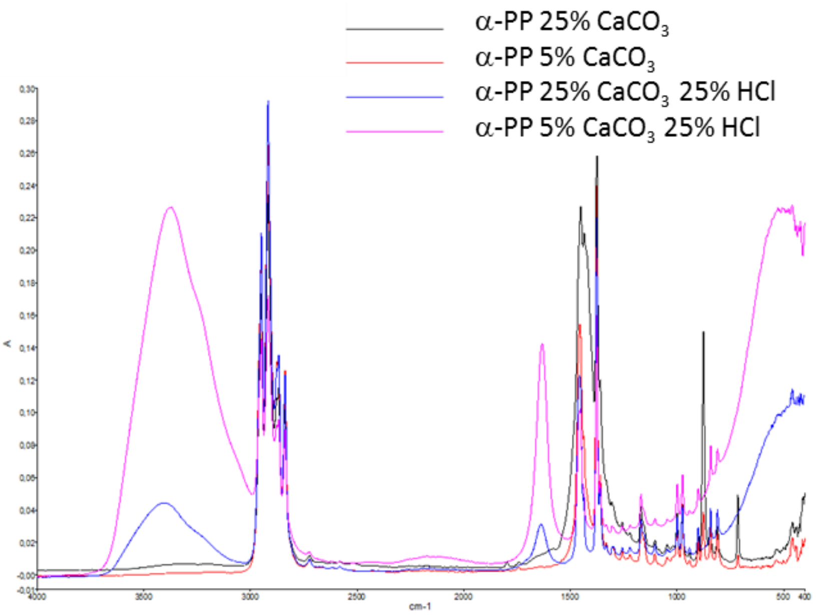

Figure 22. FTIR spectra of the α-PP material with high and low concentration of $CaCO_3$ before and after exposure to 25 wt% HCl for 48 days at 60ºC.

Figur 22. FTIR spektra av α-PP materialet med hög och låg koncentration av $CaCO_3$ före och efter exponering i 25 vikt% HCl i 48 dygn vid 60°C.

Figure 23 shows FTIR spectra of the α-PP material with high and low structured carbon black before and after exposure to 5 wt% HCl for 48 days at 60ºC. The main difference that can be seen after the exposure is from water on the sample with 10 wt% XC72 carbon black.

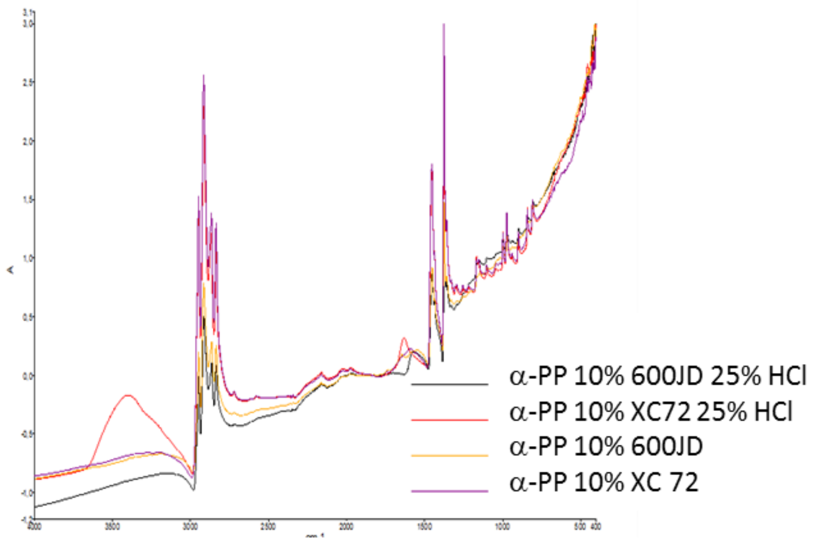

Figure 23. FTIR spectra of the α-PP material with high and low structured carbon black before and after exposure to 5 wt% HCl for 48 days at 60ºC.

Figur 23. FTIR spektra av α-PP materialet med hög- och lågstrukturerad kimrök före och efter exponering i 5 vikt% HCl i 48 dygn vid 60°C.

Exposure to NaOH at 60ºC for 48 days

FTIR spectra of the α-PP material with high and low concentration $CaCO_3$ before and after exposure to 5 wt% NaOH for 48 days at 60ºC can be seen in Figure 24.The spectra has been zoomed in to show the fingerprint region between 1800 and 600 cm^{-1}. Note the much higher absorption at the $CaCO_3$ peaks at 1420, 875 and 712 cm^{-1} for the samples with 25 wt% $CaCO_3$ compared to 5 wt%. Some reduction of these peaks can be seen after the exposure. In addition the double peaks at 1580 and 1540 cm^{-1} which are attributed to stearate are seen after the exposure for both materials.

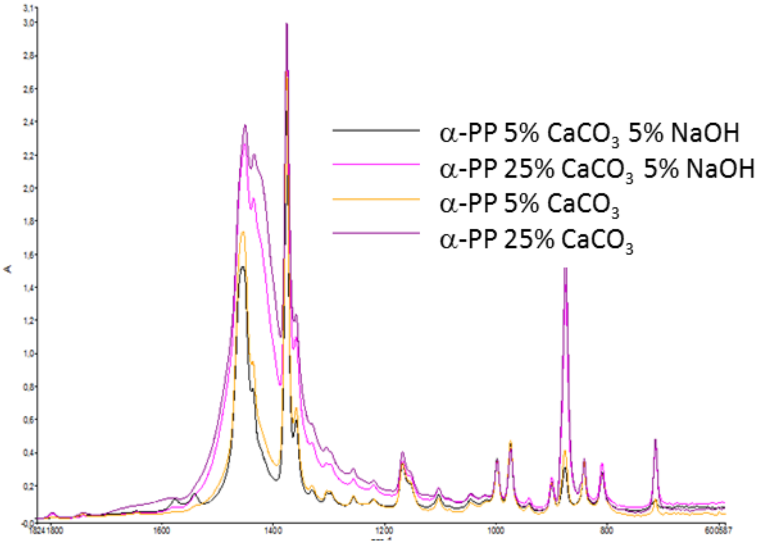

Figure 24. FTIR spectra of the α-PP material with high and low concentration $CaCO_3$ before and after exposure to 5 wt% NaOH for 48 days at 60ºC.

Figur 24. FTIR spektra av α-PP materialet med hög och låg koncentration av $CaCO_3$ före och efter exponering i 5 vikt% NaOH i 48 dygn vid 60°C.

Figure 25 shows a zoom in of the FTIR spectra in the fingerprint region between 1800 and 600 cm^{-1} of the α-PP material with high and low concentration $CaCO_3$ before and after exposure to 30 wt% NaOH for 48 days at 60ºC. Note the much higher absorption at the $CaCO_3$ peaks at 1420 and 875 cm^{-1} for the samples with 25 wt% $CaCO_3$ compared to 5wt%. Some reduction of these peaks can be seen after the exposure. In addition the double peaks at 1580 and 1540 cm^{-1} which are attributed to stearate are seen after the exposure for both materials.

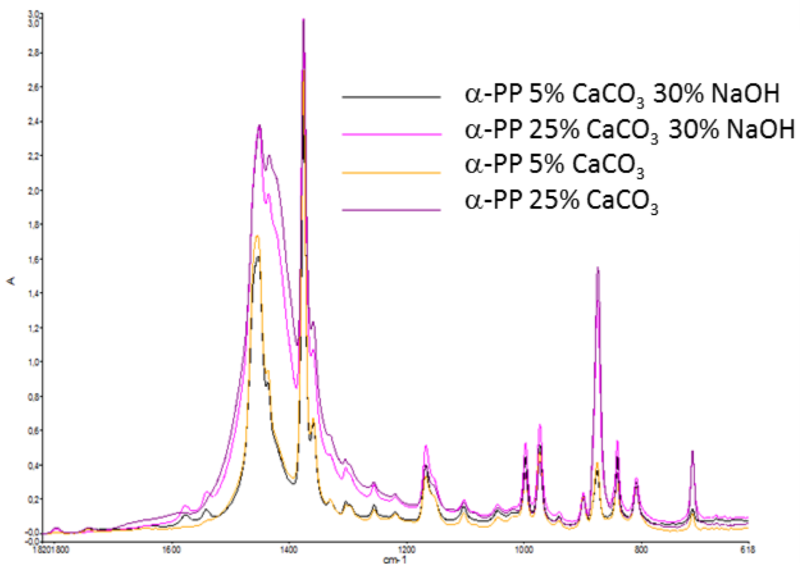

Figure 25. FTIR spectra of the α-PP material with high and low concentration $CaCO_3$ before and after exposure to 30 wt% NaOH for 48 days at 60ºC.

Figur 25. FTIR spektra av α-PP materialet med hög och låg koncentration av $CaCO_3$ före och efter exponering i 30 vikt% NaOH i 48 dygn vid 60°C.

Figure 26 shows FTIR spectra of the α-PP material with high and low structured carbon black before and after exposure to 5 wt% NaOH for 48 days at 60ºC. A loss of the absorption around 1640 cm_{-1} can be noted for both materials after exposure. In addition, the double peaks at 1580 and 1540 cm-1 which are attributed to stearate are seen after the exposure for both materials.

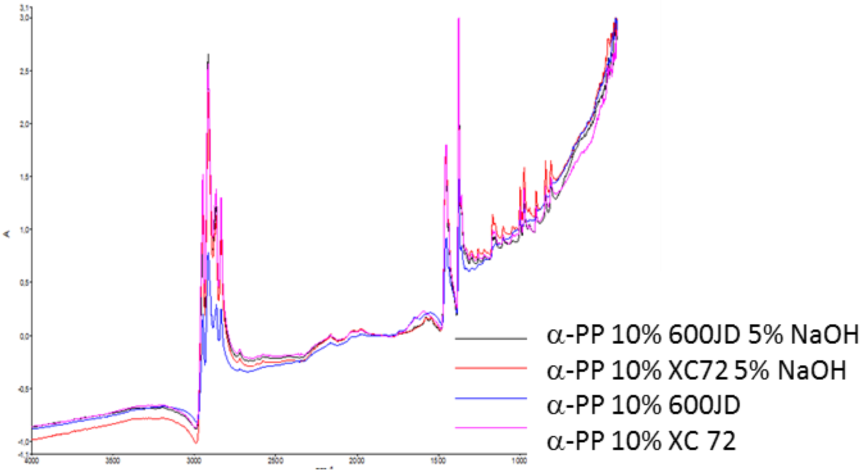

Figure 26. FTIR spectra of the α-PP material with high and low structured carbon black before and after exposure to 5 wt% NaOH for 48 days at 60ºC.

Figur 26. FTIR spektra av α-PP materialet med hög- och lågstrukturerad kimrök före och efter exponering i 5 vikt% NaOHi 48 dygn vid 60°C.

FTIR spectra of the α-PP material with high and low structured carbon black before and after exposure to 30 wt% NaOH for 48 days at 60ºC can be seen in Figure 27. Just as for the exposure in the low concentration NaOH, a loss of the absorption around 1640 cm^{-1} can be noted for both materials after exposure. In addition the double peaks at 1580 and 1540 cm^{-1} which are attributed to stearate are seen after the exposure for both materials.

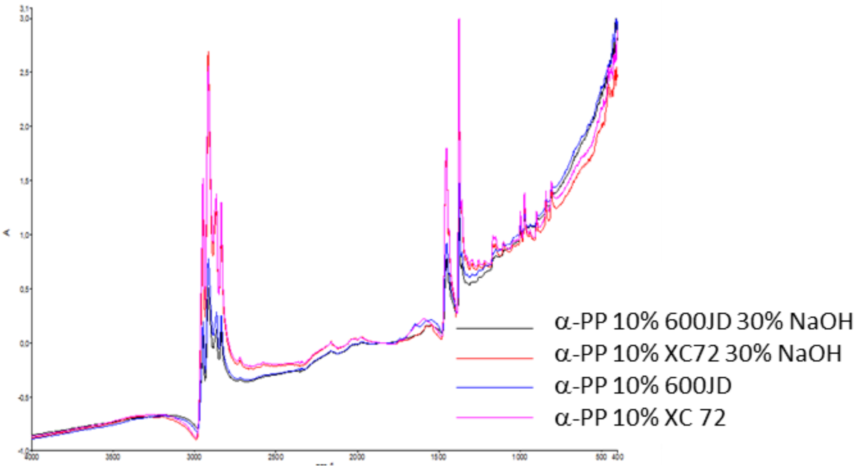

Figure 27. FTIR spectra of the α-PP material with high and low structured carbon black before and after exposure to 30 wt% NaOH for 48 days at 60ºC.

Figur 27. FTIR spektra av α-PP materialet med hög- och lågstrukturerad kimrök före och efter exponering i 30 vikt% NaOH i 48 dygn vid 60°C.

Exposure to concentrated NO/NO_2 at room temperature for three weeks

Figure 28 shows FTIR spectra of 5wt% $CaCO_3$ and 25wt% $CaCO_3$ filled α-PP before and after exposure to concentrated NO/NO_2 at room temperature for three weeks. A large increase in water absorption can be found in the samples after exposure. It is more pronounced in the samples with more $CaCO_3$.

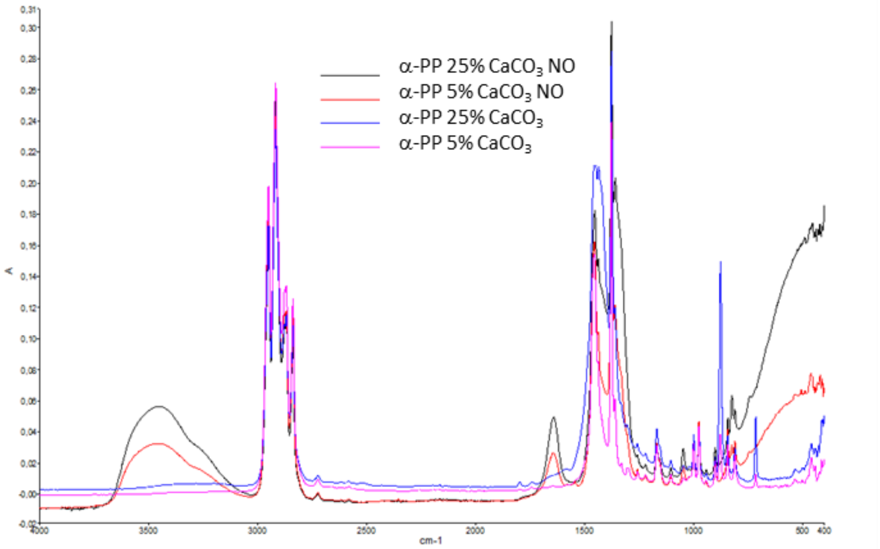

Figure 28. FTIR spectra of 5wt% $CaCO_3$ and 25wt% $CaCO_3$ filled α-PP before and after exposure to concentrated NO/NO_2 at room temperature for three weeks.

Figur 28. FTIR spektra av 5 vikt% $CaCO_3$ och 25 vikt% $CaCO_3$ fylld α-PP före och efter exponering i koncentrerad NO/NO_2 vid rumstemperatur i tre veckor.

Figure 29 shows a zoom in of the fingerprint region of the spectra in Figure 28 showing 5wt% $CaCO_3$ and 25wt% $CaCO_3$ filled α-PP before and after exposure to concentrated NO/NO_2 at room temperature for three weeks. The $CaCO_3$ peaks have disappeared after the exposure.

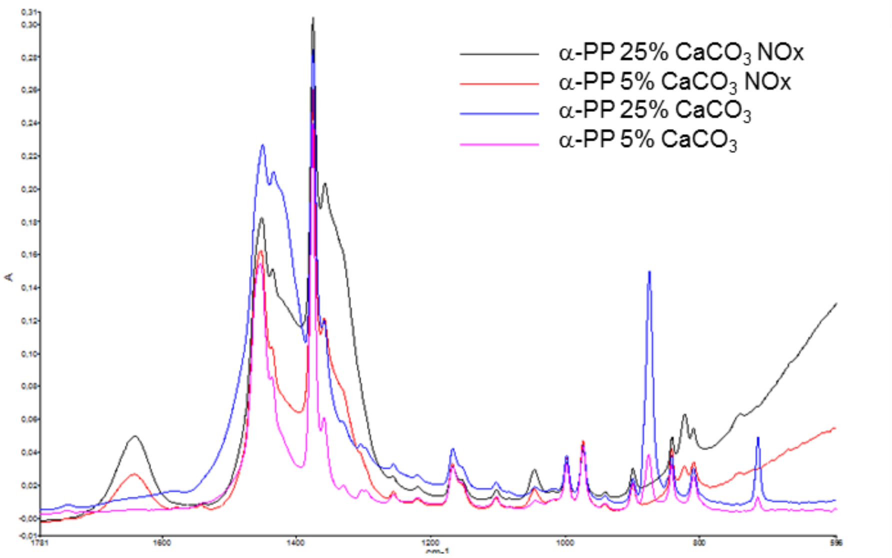

Figure 29. A zoom in of the spectra in Figure 28 showing 5wt% $CaCO_3$ and 25wt% $CaCO_3$ filled α-PP before and after exposure to concentrated NO/NO_2 at room temperature for three weeks.

Figur 29. En inzoomning av spektrat i Figur 28 som visar 5 vikt% $CaCO_3$ och 25 vikt% $CaCO_3$ fylld α-PP före och efter exponering i koncentrerad NO/NO_2 vid rumstemperatur i tre veckor.

Figure 30 shows FTIR spectra of unexposed, unfilled α-PP and unfilled, 5wt% $CaCO_3$ and 25wt% $CaCO_3$ filled α-PP after exposure to concentrated NO/NO_2 at room temperature for three weeks. Also the unfilled material shows an increase in water absorption but it is higher for the samples with $CaCO_3$.

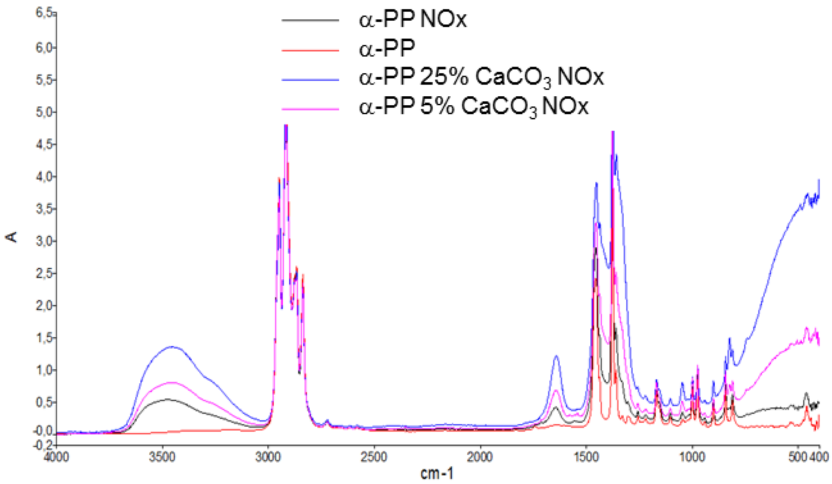

Figure 30. Unexposed, unfilled α-PP compared to unfilled, 5wt% $CaCO_3$ and 25wt% $CaCO_3$ filled α-PP after exposure to concentrated NO/NO_2 at room temperature for three weeks.

Figur 30. Oexponerad, ofylld α-PP jämförd med ofylld, 5 vikt% $CaCO_3$ och 25 vikt% $CaCO_3$ fylld α-PP efter exponering i koncentrerad NO/NO_2 vid rumstemperatur i tre veckor.

Figure 31 shows the FTIR spectra of the β-PP material with high and low structured carbon black before and after exposure to a high concentration of NO/NO_2 for 3 weeks at room temperature. No significant changes can be seen for the sample with 10 wt% XC72 carbon black. For the sample with 10 wt% 600JD there is a slight increase in the 3500 and 1570 cm^{-1} regions and some loss around 1640 cm^{-1}.

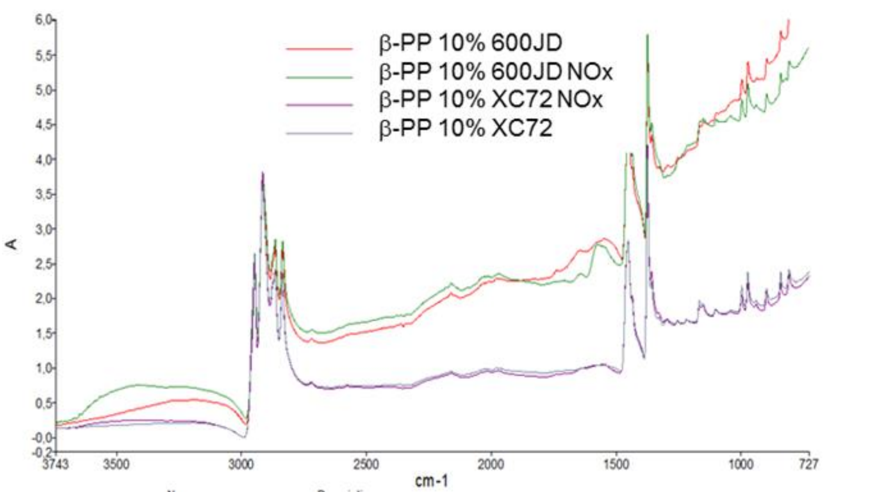

Figure 31. FTIR spectra of the β-PP material with high and low structured carbon black before and after exposure to concentrated NO/NO_2 for 3 weeks at room temperature.

Figur 31. FTIR spektra av β-PP materialet med hög- och lågstrukturerad kimrök före och efter exponering i koncentrerad NO/NO_2 vid rumstemperatur i tre veckor.

Exposure to 5 mg/l ClO_2 at 50ºC for 48 days

Figure 32 shows FTIR spectra of unfilled α-PP and α-PP with 5 and 25 wt% $CaCO_3$ after exposure to 5 mg/l ClO_2 at 50ºC for 48 days. It can be seen that there is a clear oxidation peak for all three materials in the carbonyl region around 1730 cm^{-1}. The unfilled material also shows water absorption in the 3400 and 1640 cm^{-1} regions. A zoom in of the spectra of α-PP with 5 and 25 wt% $CaCO_3$ before and after the exposure that can be seen in Figure 33 shows that there is also a loss of $CaCO_3$ during exposure.

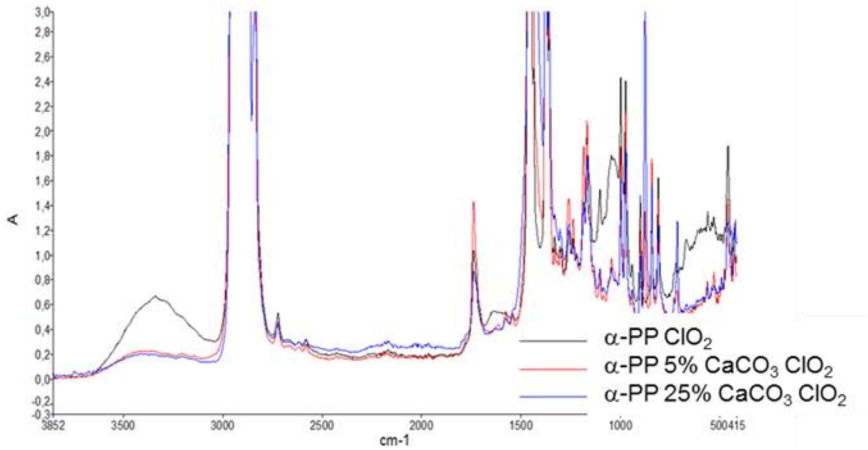

Figure 32. Unfilled α-PP and α-PP with 5 and 25 wt% $CaCO_3$ after exposure to 5 mg/l ClO_2 at 50ºC for 48 days.

Figur 32. Ofylld α-PP och α-PP med 5 och 25 vikt% $CaCO_3$ efter exponering i 5 mg/l ClO_2 vid 50ºC i 48 dygn.

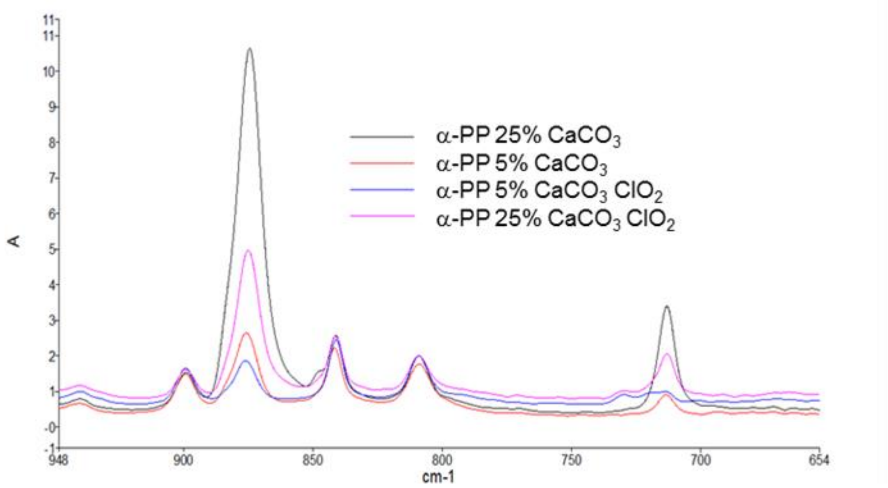

Figure 33. A zoom in of the spectra of α-PP with 5 and 25 wt% $CaCO_3$ before and after exposure to 5 mg/l ClO_2 at 50ºC for 48 days.

Figur 33. En in zoomning av spektra av α-PP med 5 och 25 vikt% $CaCO_3$ efter exponering i 5 mg/l ClO_2 vid 50ºC i 48 dygn.

Figure 34 shows the FTIR spectra of unfilled α-PP and α-PP with 10 wt% XC72 and 600JD carbon black after exposure to 5 mg/l ClO_2 at 50ºC for 48 days. As can be noted there is no oxidation seen in the samples with carbon black!

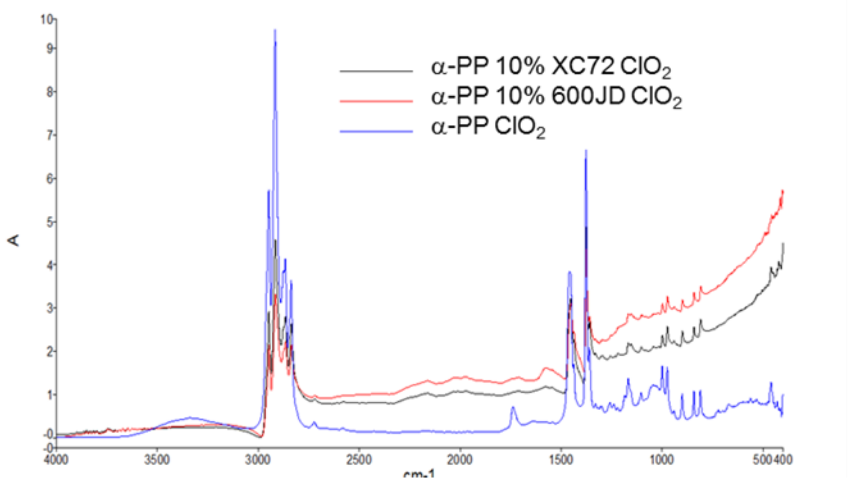

Figure 34. Unfilled α-PP and α-PP with 10 wt% XC72 and 600JD carbon black after exposure to 5 mg/l ClO_2 at 50ºC for 48 days.

Figur 34. Ofylld α-PP och α-PP med 10 vikt% XC72 och 600JD kimrök efter exponering i 5 mg/l ClO_2 vid 50ºC i 48 dygn.

A zoom in of the fingerprint region of the FTIR spectra of α-PP with 10 wt% XC72 and 600JD carbon black before and after exposure to 5 mg/l ClO_2 at 50ºC for 48 days can be seen Figure 35. No significant changes due to the exposure can be detected.

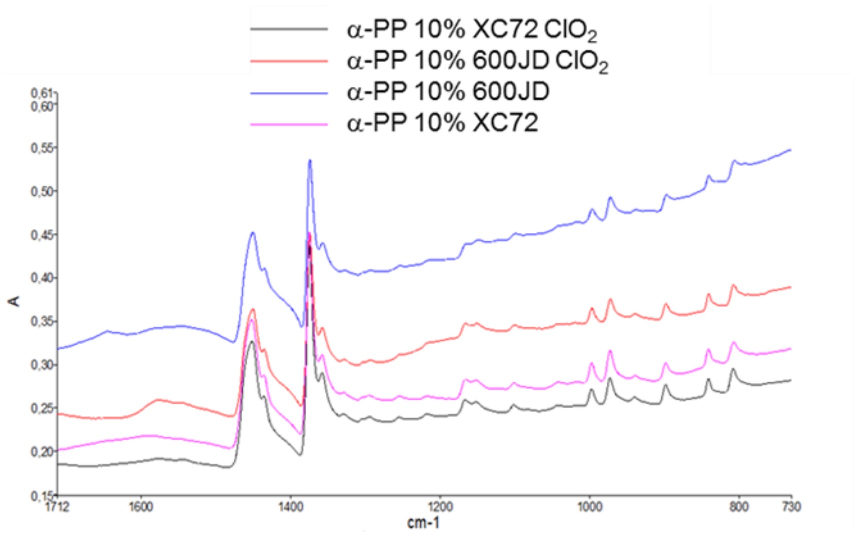

Figure 35. α-PP with 10 wt% XC72 and 600JD carbon black before and after exposure to 5 mg/l ClO_2 at 50ºC for 48 days.

Figur 35. α-PP med 10 vikt% XC72 och 600JD kimrök före och efter exponering i 5 mg/l ClO_2 vid 50ºC i 48 dygn.

Line scans

Line-scan analyses over the cross-section were carried out on selected materials. FTIR line-scan is a very powerful tool used to gather information about the amount, distribution and chemical changes of e.g. stabilizers or, in this case, fillers over a cross-section. Figure 36 shows line scans of the water absorption at 1640 cm^{-1} and the absorption of $CaCO_3$ at 876 cm^{-1} over the cross section of the α-PP material with 5 wt%

$CaCO_3$ after exposure to 25wt% HCl for 48 days at 60ºC. The peak at 1256 cm^{-1} was used as reference.

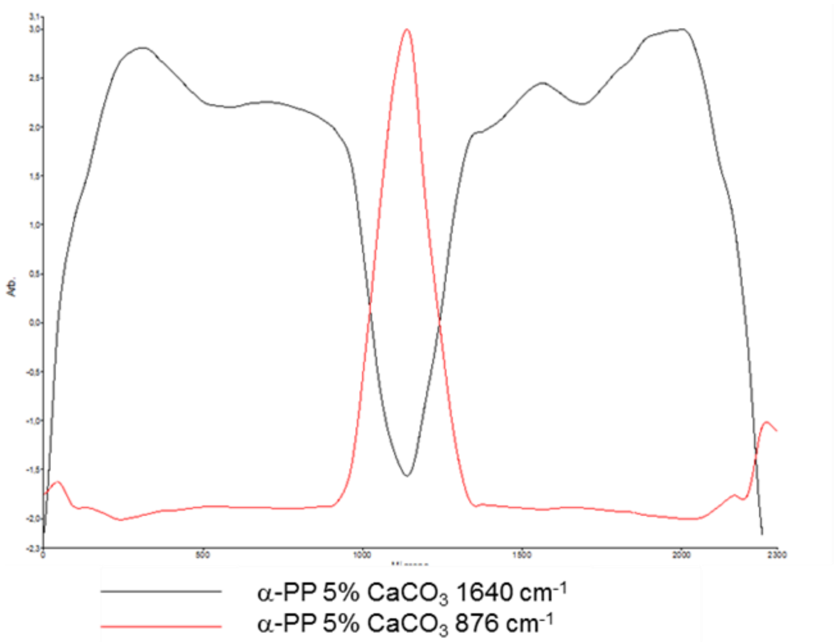

Figure 36. Line scans of the water absorption at 1640 cm^{-1} and the absorption of $CaCO_3$ at 876 cm^{-1} over the cross section of the α-PP material with 5 wt% $CaCO_3$ after exposure to 25wt% HCl for 48 days at 60ºC. The peak at 1256 cm^{-1} was used as reference.

Figur 36. Line scan av vatten bsorptionen vid 1640 cm^{-1} och absorptionen för $CaCO_3$ vid 876 cm^{-1} plottad over tvärsnittet av α-PP materialet med 5 vikt% $CaCO_3$ efter exponering i 25vikt% HCl i 48 dygn vid 60ºC. Toppen vid 1256 cm^{-1} användes som referens.

Line scans of the water absorption at 1640 cm^{-1} and the absorption of $CaCO_3$ at 876 cm^{-1} over the cross section of the α-PP material with 25 wt% $CaCO_3$ after exposure to 25wt% HCl for 48 days at 60ºC can be seen in Figure 37. The peak at 1256 cm^{-1} was used as reference.

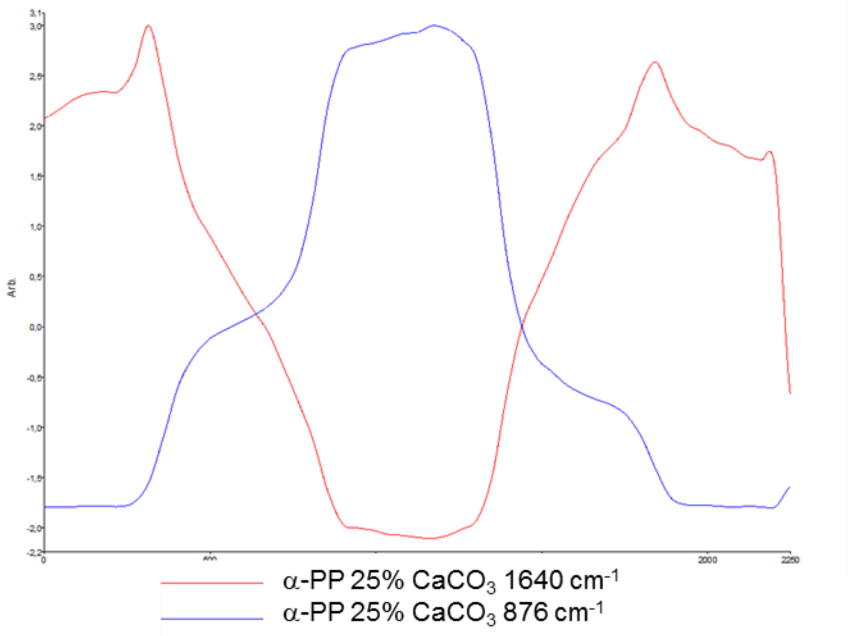

Figure 37. Line scans of the water absorption at 1640 cm^{-1} and the absorption of $CaCO_3$ at 876 cm^{-1} over the cross section of the α-PP material with 25 wt% $CaCO_3$ after exposure to 25wt% HCl for 48 days at 60ºC. The peak at 1256 cm^{-1} was used as reference.

Figur 37. Line scan av vatten bsorptionen vid 1640 cm^{-1} och absorptionen för $CaCO_3$ vid 876 cm^{-1} plottad over tvärsnittet av α-PP materialet med 25 vikt% $CaCO_3$ efter exponering i 25vikt% HCl i 48 dygn vid 60ºC. Toppen vid 1256 cm^{-1} användes som referens.

Line scans of α-PP with 5 and 25 wt% $CaCO_3$ exposed to the low concentration of HCl (5 wt%) did not show any change in the absorption at either 1640 or the 875 cm^{-1} peaks in the bulk. Figure 38 shows the line scans of the water absorption at 1640 cm^{-1} and the absorption of $CaCO_3$ at 876 cm^{-1} over the cross section of the β-PP material with 25 wt% $CaCO_3$ after exposure to concentrated NO/NO_2 for 3 weeks at room temperature. The peak at 1256 cm^{-1} was used as reference

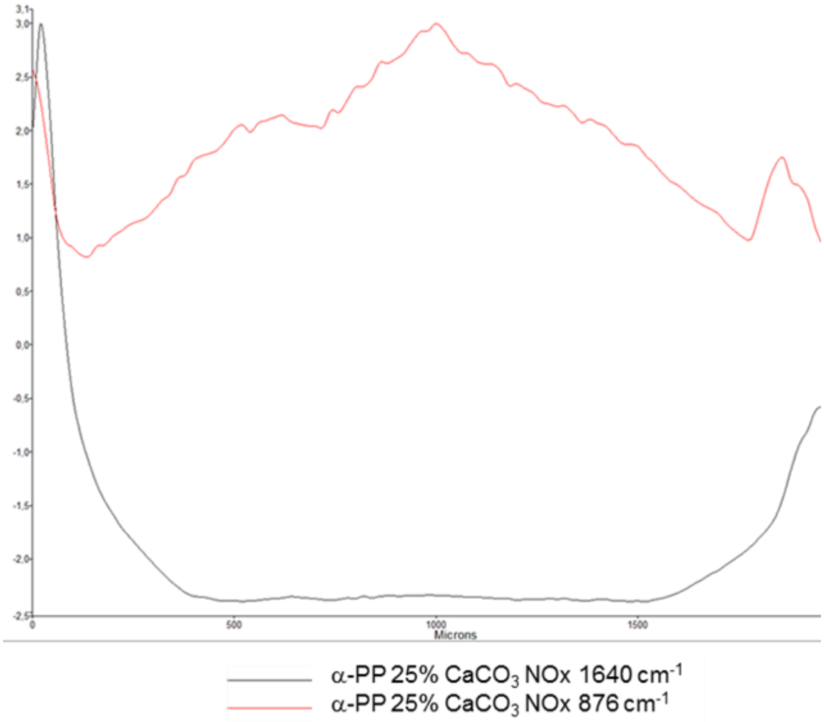

Figure 38. Line scans of the water absorption at 1640 cm^{-1} and the absorption of $CaCO_3$ at 876 cm^{-1} over the cross section of the β-PP material with 25 wt% $CaCO_3$ after exposure to concentrated NO/NO_2 for 3 weeks at room temperature. The peak at 1256 cm^{-1} was used as reference.

Figur 38. Line scan av vatten bsorptionen vid 1640 cm^{-1} och absorptionen för $CaCO_3$ vid 876 cm^{-1} plottad over tvärsnittet av β-PP materialet med 25 vikt% $CaCO_3$ efter exponering i koncentrerad NO/NO_2.i tre veckor i rumstemperatur. Toppen vid 1256 cm^{-1} användes som referens.

3.2.3 Colour change

The unfilled and the $CaCO_3$ filled materials showed some colour changes during exposure to the high concentrations of HCl, se Table 7 and Figure 39 and NaOH, see Table 8.

Table 7. Color changes of the unfilled and the $CaCO_3$ filled materials after exposure to 25 wt-% HCl at 60ºC for 48 days.

Tabell 7. Färgförändring av ofylld och $CaCO_3$ fyllda material efter exponering i 25 vikt% HCl vid 60ºC i 48 dygn.

Samples in 25 wt-% HCl	Discoloration/Stains/Spots
α-PP No filler	Spots
α-PP 5 wt-% $CaCO_3$	Slightly pink with spots
α-PP 25 wt-% $CaCO_3$	Pink with spots
β-PP No filler	None
β-PP 5 wt-% $CaCO_3$	Pink discoloration but very low
β-PP 25 wt-% $CaCO_3$	Slightly pink
PP-R No filler	Yellow with red spots
PP-R 5 wt-% $CaCO_3$	Strong red/orange
PP-R 25 wt-% $CaCO_3$	Strong red/orange

Figure 39. A photo of some of the samples after exposure to 25 wt-% HCl at 60ºC for 48 days.

Figur 39. Ett foto av några av proverna efter exponering i 25 vikt% HCl vid 60ºC i 48 dygn.

Table 8. Color changes of the unfilled and the $CaCO_3$ filled materials after exposure to 30 wt-% NaOH at 60ºC for 48 days.

Tabell 8. Färgförändring av ofylld och $CaCO_3$ fyllda material efter exponering i 30 vikt% NaOH vid 60ºC i 48 dygn.

Samples in 30 wt-% NaOH	Discoloration/Stains/Spots
PP-R No filler	Yellow stains
PP-R 5 wt-% $CaCO_3$	Yellow stains
PP-R 25 wt-% $CaCO_3$	Yellow stains

3.3 METHOD DEVELOPMENT

3.3.1 The chlorine dioxide method

Time dependence

The results from the chlorine dioxide exposure of PP Polystone® in at a concentration of 0.1 g/l at 50°C up to 7 days can be seen in Figure 40. A clear trend of the increasing water absorption peak is visible over time and the peak stabilizes after 144 hours (6 days).

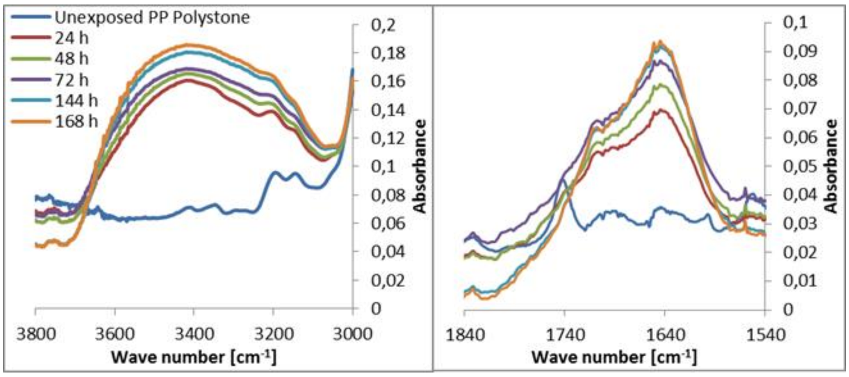

Figure 40. FTIR spectra of PP Polystone exposed to ClO_2 at concentration of 0.1 g/l in 50°C for up to 7 days. The FTIR spectra has been zoomed at 3400 cm^{-1} and 1640 cm^{-1} in order to highlight the water absorption peaks.

Figur 40. FTIR spektra av PP Polystone exponerad i ClO_2 med en koncentration av 0.1 g/l i 50°C i upp till 7 dygn. FTIR spectra har zoomats in runt3400 cm^{-1} och 1640 cm^{-1} för att förtydliga vattenabsorptionstopparna.

BE 60

The results from the chlorine dioxide exposure of BE 60 in 50°C are inconsistent with the results from the ClO_2 exposure of the Polystone. The water absorption peak increases with time and stabilizes after 144 hours (6 days) as seen in Figure 41.

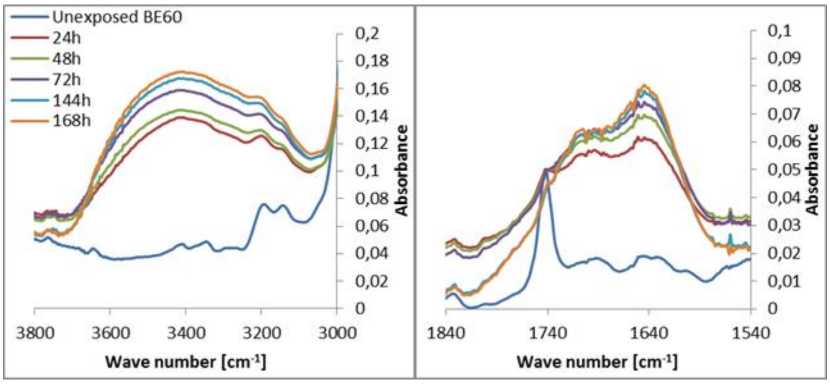

Figure 41. FTIR spectra of BE 60 exposed to ClO_2 at concentration of 0.1 g/l in 50°C for up to 7 days. The FTIR spectra has been zoomed at 3400 cm^{-1} and 1640 cm^{-1} in order to highlight the water absorption peaks.

Figur 41. FTIR spektra av BE 60 exponerad i ClO_2 med en koncentration av 0.1 g/l i 50°C i upp till 7 dygn. FTIR spectra har zoomats in runt3400 cm^{-1} och 1640 cm^{-1} för att förtydliga vattenabsorptionstopparna.

BE 60 with extra Irganox 1010

The results from the chlorine dioxide exposure in 50°C of BE 60, where additional Irganox 1010 had been added to the material, shows a similar pattern to all previous chlorine dioxide exposures. The water absorption peak increases with time and stabilizes after 144 hours (6 days). The strong water absorption peak is even larger after 24 hours than for the other two polypropylene samples.

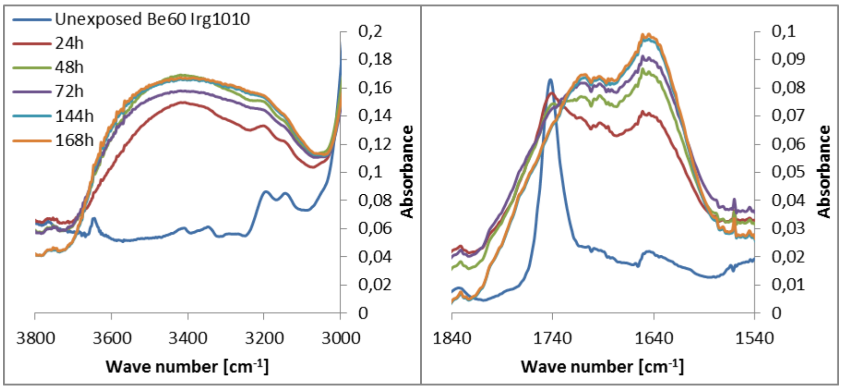

Figure 42. FTIR spectrum of BE 60, containing 0.1 wt% extra of Irganox 1010, exposed to ClO_2 at concentration of 0,1 g/l in 50°C for 7 days. The FTIR spectrum has been zoomed at 3400 cm^{-1} and 1640 cm^{-1} in order to highlight the water absorption peaks.

Figur 42. FTIR spektra av BE 60 med 0,1 vikt% extra Irganox 1010, exponerad i ClO_2 med en koncentration av 0.1 g/l i 50°C i upp till 7 dygn. FTIR spectra har zoomats in runt3400 cm^{-1} och 1640 cm^{-1} för att förtydliga vattenabsorptionstopparna.

To compare a sample with different amount of sterically sterically hindered phenol the BE60 with and without extra Irganox 1010 were compared after reaction with 0.1 g/l ClO_2 after 144 hours at 50ºC, se Figure 43. As can be seen the water absorption is higher at 1640 cm^{-1} for the sample with extra stabilizer.

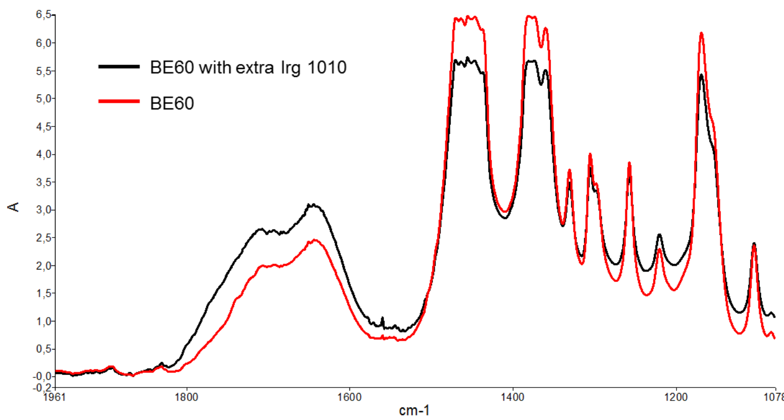

Figure 43. FTIR spectra of BE60 and BE60 with 1 ppm extra 1010 added after exposure to 0.1 g/l ClO2 for 144 hours at 50ºC.

Figur 43. FTIR spektra av BE60 och BE 60 med 0,1 vikt% extra Irganox 1010 tillsatt efter exponering i 0,1 g/l ClO2 i 144 timmar vid 50ºC.

Optimisation of the ClO_2 concentration

A part in the development of the chlorine dioxide method was to investigate the effect of different concentrations of ClO_2 on the water absorption peaks. As can be seen in Figure 44, Figure 45 and Figure 46 for the BE60 material the concentration of ClO_2 was of no importance within the investigated interval. This was also valid for the other PP materials investigated. The water absorption peaks has been divided with an internal standard in order to compensate for differences in thickness of the samples. The internal standard is a peak at 1330 cm^{-1}.

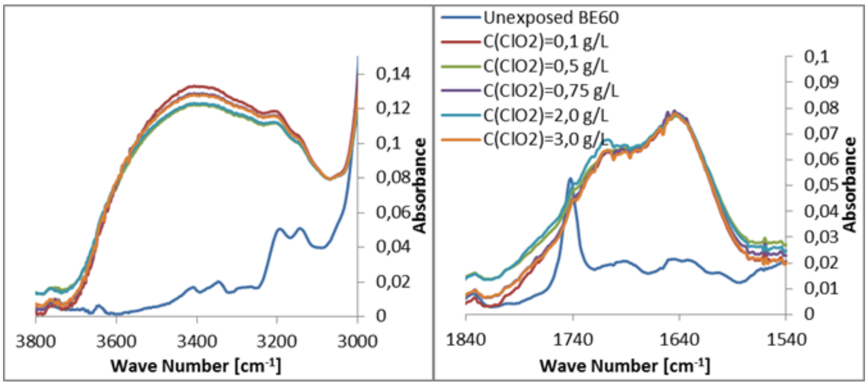

Figure 44. **FTIR spectra of a polypropylene BE60 that has been exposed for various concentrations of ClO_2 for 144 hours. The FTIR spectrum has been zoomed at 3400 cm^{-1} and 1640 cm^{-1} in order to highlight the water absorption peaks.**

Figur 44. FTIR spektra av BE 60 som exponerad i olika koncertrationer av ClO_2 i 144 timmar. FTIR spectra har zoomats in runt3400 cm^{-1} och 1640 cm^{-1} för att förtydliga vattenabsorptionstopparna.

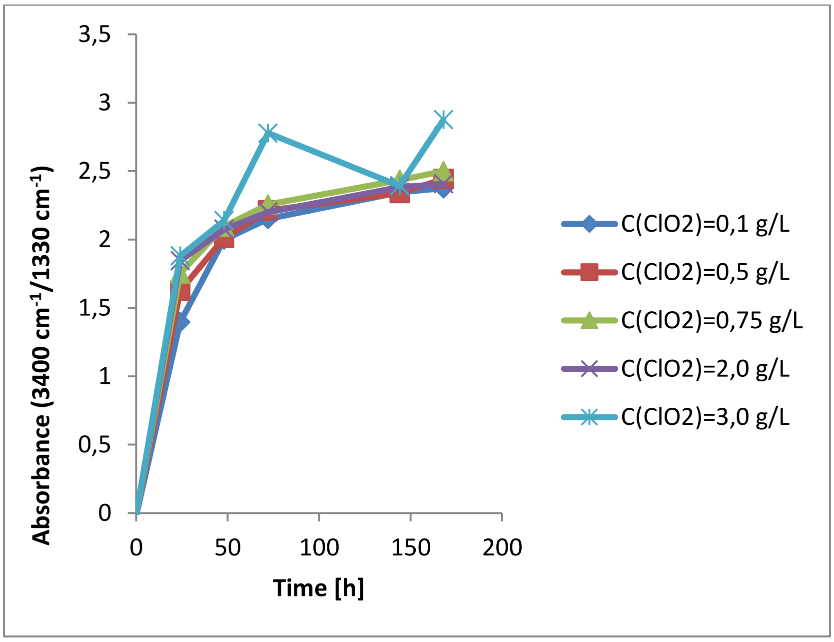

Figure 45. Change in the water absorption peak over time at 3400 cm^{-1} of BE60 for different concentrations of ClO_2.

Figur 45. Förändringen i vattenabsorptionstoppen vid 3400 cm^{-1} för BE 60 vid olika koncentrationer av ClO_2.

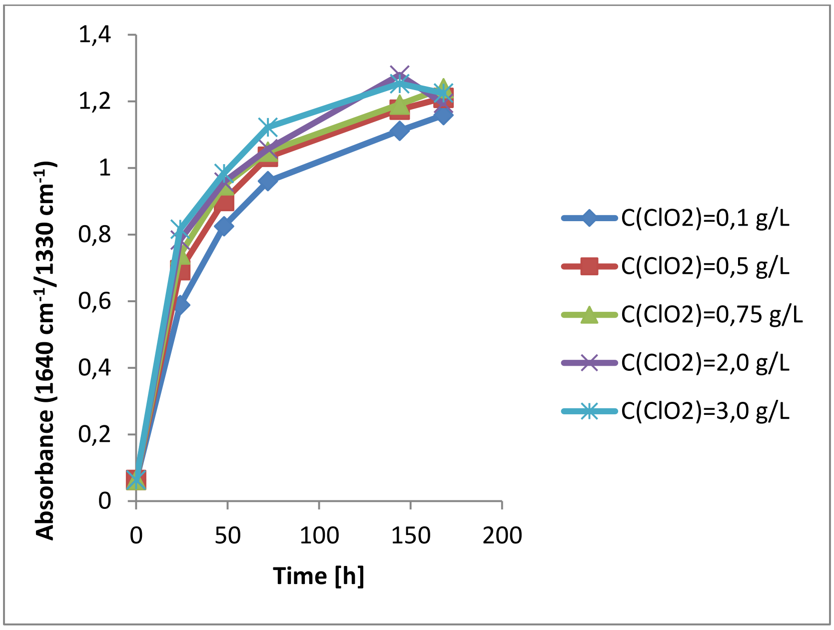

Figure 46. Change in the water absorption peak over time at 1640 cm^{-1} of BE60 for different concentrations of ClO_2.

Figur 46. Förändringen i vattenabsorptionstoppen vid 1640 cm^{-1} för BE 60 vid olika koncentrationer av ClO_2.

Repeatability of the Chlorine Dioxide Method

The repeatability of the chlorine dioxide method was investigated by making two different experiments during the first three days of ClO_2 exposure. Figure 47 shows the result from the water absorption peak at 3400 cm^{-1} and Figure 48 shows the result from the water absorption peak at 1640 cm^{-1}, for PP Polystone.

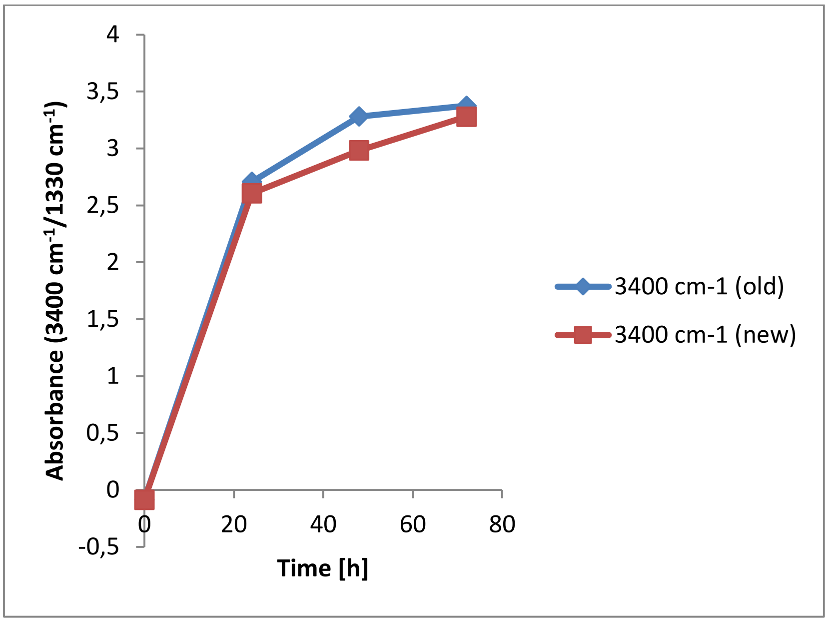

Figure 47. Change in the water absorption peak at 3400 cm^{-1} over the three first days of ClO_2 exposure for polypropylene Polystone during two different experiments, "old" and "new". Each graph represents the mean value from the different concentrations of ClO_2 for the corresponding time point.

Figur 47. Förändringen i vattenabsorptionstoppen vid 3400 cm^{-1} för de tre första dagarna av ClO_2 exponering av PP-Polystone vid två olika försökstillfällen (old and new). Varje graf representerar medelvärdet från de olika koncentrationerna av ClO_2 för respektive tidpunkt.

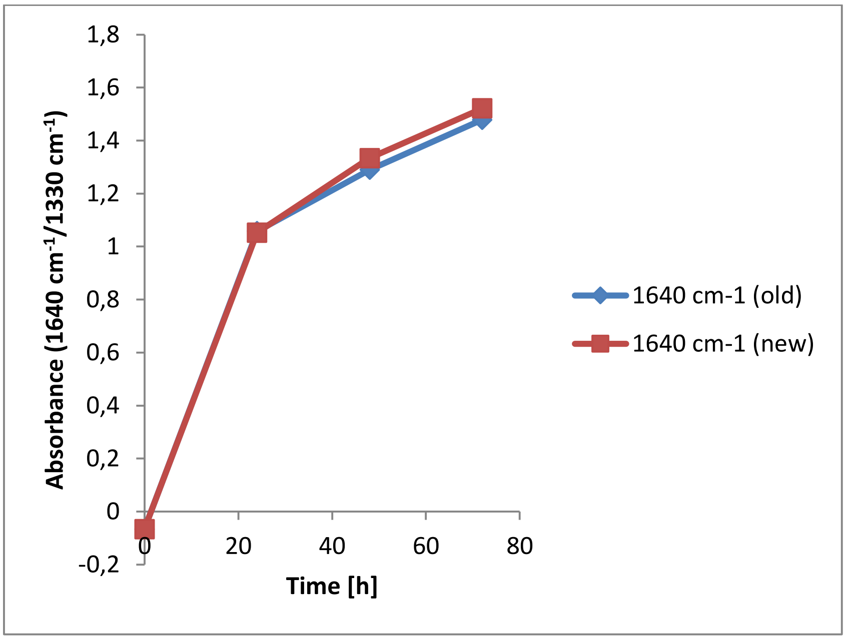

Figure 48. Change in the water absorption peak at 1640 cm^{-1} over the three first days of ClO_2 exposure for polypropylene Polystone during two different experiments, "old" and "new". Each graph represents the mean value from the different concentrations of ClO_2 for the corresponding time point.

Figur 48. Förändringen i vattenabsorptionstoppen vid 1640 cm^{-1} för de tre första dagarna av ClO_2 exponering av PP-Polystone vid två olika försökstillfällen (old and new). Varje graf representerar medelvärdet från de olika koncentrationerna av ClO_2 för respektive tidpunkt.

Oxidation Products

The dry samples of PP Polystone, analyzed with FTIR after ClO_2 exposure, indicated formation of oxidation products at 1715 cm^{-1}, se Figure 49. The ClO_2 exposed samples were leached in order to investigate if the oxidation products were related to the polymer or the antioxidants. The samples were also exposed to NO gas for 24 hours in room temperature in order to detect potential hydroperoxides before and after leaching. A peak at 1715 cm^{-1} is visible when dried after ClO_2 exposure, Figure 49. After leaching, the peak disappears which indicates that the oxidation products are related to the antioxidants rather than the polymer.

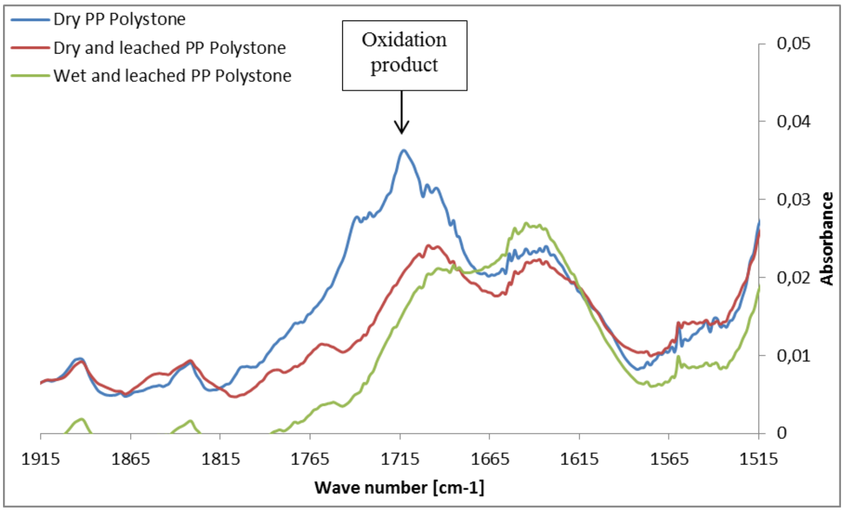

Figure 49. FTIR spectra of PP Polystone® after exposure in ClO_2 at a concentration of 3 g/l. The dry PP Polystone had been exposed for 72 hours and the dry/wet and leached PP Polystone® had been exposed for 48 hours. The exposures were made at 50°C. Oxidation products are detected at 1715 cm^{-1} and the FTIR spectra is zoomed to highlight that peak.

Figur 49. FTIR spektra av PP-Polystone® efter exponering i ClO_2 med en koncentration av 3 g/l. Den torkade PP Polystone hade varit exponerad i 72 timmar och den torra och våta urlakade PP Polystone® hade varit exponerad i 48 timmar. Exponeringarna gjordes vid 50°C. Oxidations produkter kunde ses vid 1715 cm^{-1} och spectra är in zoomat för att förtydliga den toppen.

FTIR Line-Scan Before and After ClO_2 Exposure

A sample of BE60 was placed in the oven at 130°C for 3 weeks in order to get migration of the antioxidants out of the material. Slices of 100 µm were prepared with the microtome from the oven aged BE 60, where one of them was exposed to ClO_2 for 6 days in 50°C and the other was left unexposed to ClO_2.

The cross sections of both ClO_2-exposed and unexposed BE 60 were analyzed after the oven ageing with FTIR line scan. The water absorption peak at 3400 cm^{-1} and at 1640 cm^{-1} was followed over the cross section for the ClO_2 exposed BE 60, while the strong ester peak at 1742 cm^{-1} was followed over the cross section for the unexposed BE 60. It can be seen in Figure 50 that the water absorption peak and the ester peak shows a similar pattern over the cross section.

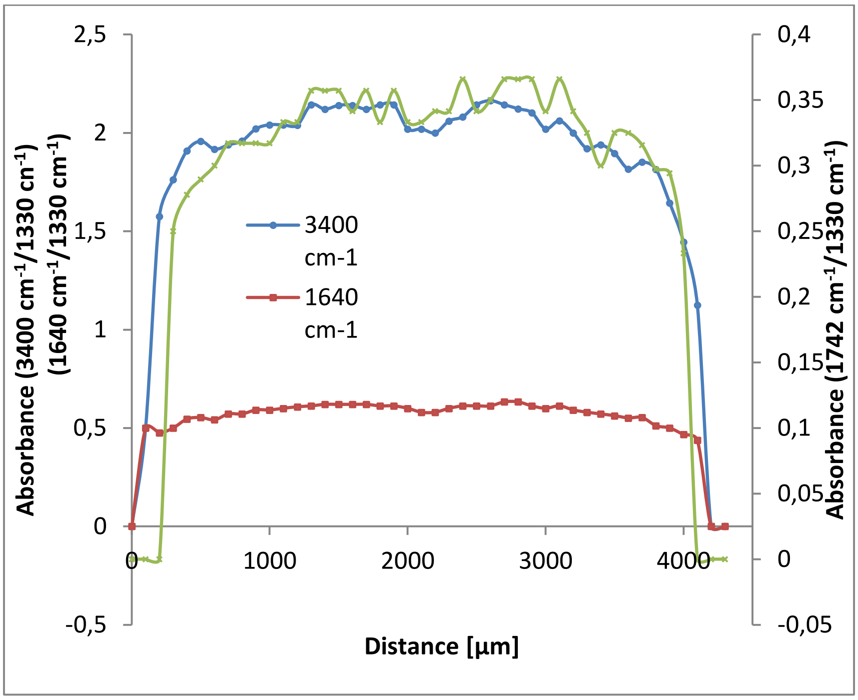

Figure 50. The stabilizer distribution measured over a cross section of BE 60 before and after ClO_2 exposure. The distribution of stabilizers has been measured from the ester peak at 1742 cm^{-1} of the unexposed BE 60, and related to the water absorption peak at 3400 cm^{-1} and 1640 cm^{-1} after ClO_2 exposure.

Figur 50. Stabilisatorkoncentrationen mätt over tvärsnittet av BE 60 före och efter ClO_2 exponeringen. Fördelningen av stabilisatorn mättes med estertopen vid 1742 cm^{-1} av den obehandlade BE 60, och relaterades mot vattenabsorptionstopparna vid 3400 cm^{-1} och 1640 cm^{-1} efter ClO_2 exponeringen.

Reactivity of the sterically hindered Phenols towards ClO_2

The reactivity of the sterically hindered phenols towards ClO_2 was studied in order to investigate if any of the sterically hindered phenols were more reactive towards chlorine dioxide or more prone to absorb water than the other after reaction with ClO_2. The water absorption peaks has been divided with an internal standard for the commercial antioxidants, in order to compensate for differences in amount of sample applied on the ATR crystal. The internal standard is a peak at 1434 cm^{-1}. As can be seen in Figure 51 and Table 9, there is a fairly large variation in reactivity between the different types. Irgafos 168 is not a sterically hindered phenol but most often added as a processing stabilizer. The other four investigated stabilisers are sterically hindered phenols.

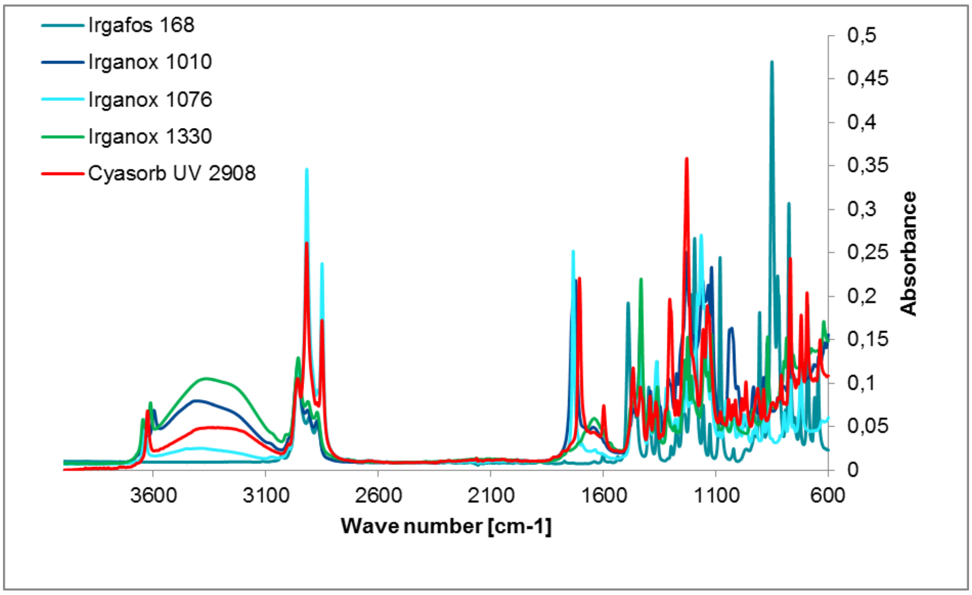

Figure 51. FTIR spectra of the commercial antioxidants after ClO_2 exposure in 50°C for 6 days.

Figur 51. FTIR spektra av kommersiella antioxidanter efter ClO_2 exponering vid 50°C i 6 dygn.

Table 9. The intensity of the water absorption peak, per reacted sterically hindered phenol, at 3400 cm^{-1} and 1640 cm^{-1} for commercial antioxidants after ClO_2 exposure. All the values are relative the internal standard to compensate for differences in amount of sample applied on the ATR crystal.

Tabell 9. Intensiteten av vattenabsorptionstoppen, per steriskt hindrad fenol vid 3400 cm^{-1} och 1640 cm^{-1} för kommersiella antioxidanter efter ClO_2 exponering. Alla värden är relativa en intern standard för att kompensera för olika mycket material på ATR-kristallen.

Antioxidant	Absorbance at 3400 cm^{-1}	Absorbance at 1640cm^{-1}
Irg 1010	0.098	0.040
Irg 1076	0.134	0.072
Irg 1330	0.145	0.057
Cyasorb UV 2908	0.536	0.536

3.3.2 Antioxidant extraction and FTIR analysis

To investigate if it is possible to extract the antioxidants and then to use FTIR to determine which type and amount, FTIR of commercial antioxidants were compared to extracts from the investigated polypropylene samples. The spectra of the commercial antioxidants dissolved in acetonitrile and dichloromethane (3:1), are presented in Figure 52 while the spectra from the extracted antioxidants in the polypropylene samples are presented in Figure 53.

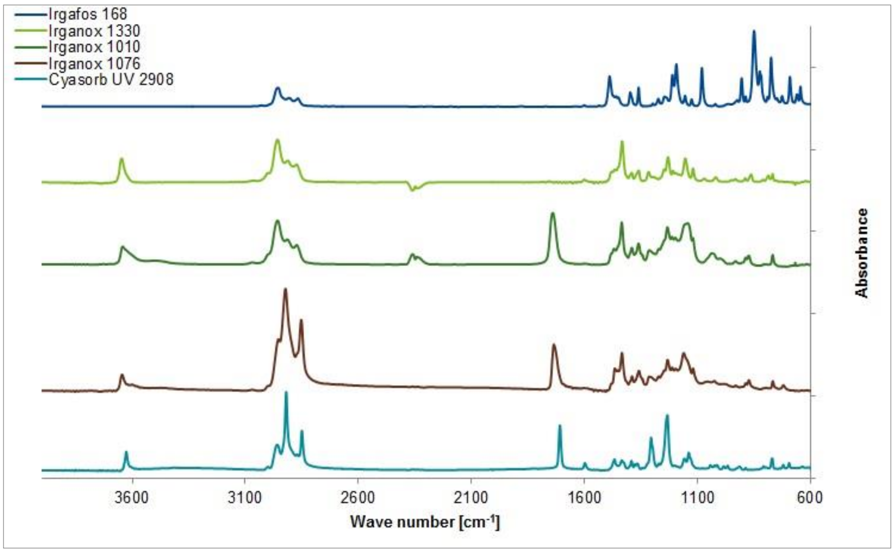

Figure 52. FTIR spectra of the commercial antioxidants, dissolved in acetonitrile and dichloromethane (3:1), and analysed on a zinc sulphide glass after evaporation of the solvent.

Figur 52. FTIR spektra av de kommersiella antioxidanterna, upplösta i acetonitril och diklorometane (3:1), och analyserad på ett zinksulfidglas efter att lösningsmedlet hade evaporerats.

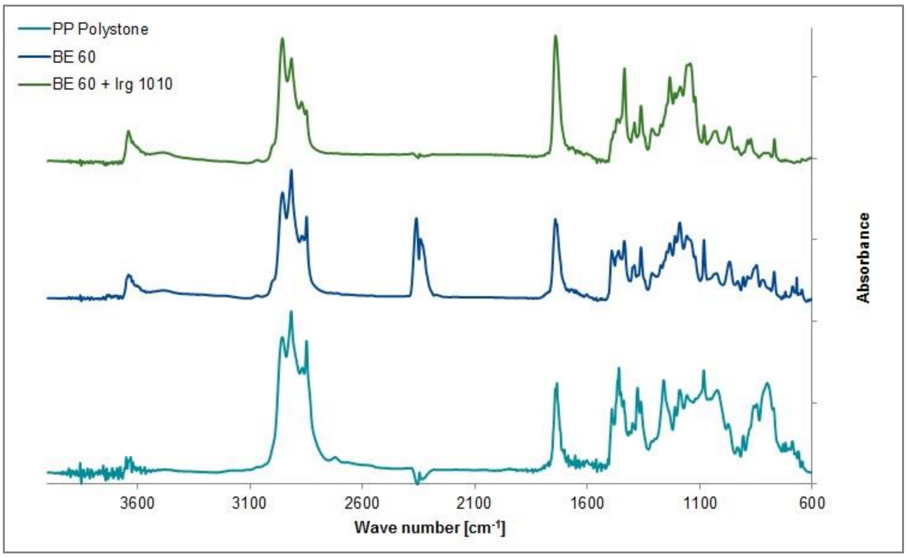

Figure 53. FTIR spectra of the extracted antioxidants in the polypropylene samples, dissolved in acetonitrile and dichloromethane (3:1), and analysed on a zinc sulphide glass after evaporation of the solvent.

Figur 53. FTIR spektra av de extraherade antioxidanterna, upplösta i acetonitril och diklorometane (3:1), och analyserad på ett zinksulfidglas efter att lösningsmedlet hade evaporerats.

Identification of Antioxidants with HPLC

Analysis with HPLC was also performed in order to identify the extracted antioxidants from the polymeric materials. The result was, however, that separation of Irganox 1010 and Irganox 1076 was impossible due to their similar molecular structure. Cyasorb UV 2908 and Irgafos 168 were not detectable in neither of the analyzed wavelengths. Irganox 1330 eluted after ~9 minutes and was the only hinderd phenol that could be identified in all of the six materials.

Irganox 1010 and/or Irganox 1076 together with Irganox 1330 could be found in all of the three investigated polypropylenes. There are several unknown peaks in the chromatograms and these could be related to other types of additives in the materials or to oxidized antioxidants.

Identification of Antioxidants with ESI-MS

Analysis with ESI-MS was performed on the extract from the BE 60 with Irganox 1010. A strong peak is visible at 1347 (m/z) is related to two oxidized Irgafos 168 sharing one sodium atom. A small peak is related to a Cyasorb UV 2908 molecule connected with a sodium atom. An even smaller peak at 1199 (m/z) is related to an Irganox 1010 molecule connected with a sodium atom. No other antioxidants could be identified with ESI-MS since they were in too low concentration relative the oxidized complex of Irgafos 168.

Identification of Antioxidants with DART-MS

Samples of the pure antioxidants and one piece of polypropylene with unknown stabilizer content were analyzed using DART-MS. The stabilizers that had been expected were Irgafos 168 and Irganox 802 and Irganox 1010 were expected to be present in the polypropylene. Table 10 shows the results from the analysis. The values have not been calibrated and no fragment analysis was made. The tabulated positive and negative modes from Haunschmidt are taken from reference [13] “Rapid identification of stabilizers in polypropylene using time-of-flight massspectrometry and DART as ion source” where in Haunschmidt et evaluates the possibility to use the DART-MS method for the direct analysis of plastic products.

Table 10. The results from the DART-MS analysis. The values have not been calibrated and no fragment analysis was made.

Tabell 10. Resultaten från DART-MS analysen. Värdena har inte blivit kalibrerade och ingen fragmentanalys har gjorts.

Prov # uncalibrated	Pos mode uncalibrated	Neg mode	Pos mode Haunschmidt [13]	Neg mode Haunschmidt [13]	Mw
Chimassorb 944	546.50	-			596 (frag)
Irgafos 168	647.48	482.29	647.46	645.44	646
Tinuvin 123	737.66	-			737
Irganox E201	431.40/165.00	-	431.38	429.37	431
Irganox PS802	683.64	-	683.60	681.58	683
Irganox 1010	310.25/181.09	296.88	1194.81 Note NH_4-adduct	1175.77 Note NH_4-adduct	1177
Irganox 1076	548.50/530.48	539.60	548.50	529.46	531
Irganox 1330	773.60/219.18	-	774.59	773.59	775
PP sample	279.17	-			

4 Discussion

4.1 INFLUENCE OF DIFFERENT FILLERS ON THE PROPERTIES OF PP

4.1.1 Measurements of the thermal elongation

It was found that measuring the thermal elongation of a polypropylene was not as straight forward as expected. There is a standard test method for Linear Thermal Expansion of Solid Materials with a Push-Rod Dilatometer (ASTM E228) but it was found that it was very difficult to apply this test on the dilatometer at Swerea KIMAB. It was also hard to find any other test facility that did this test. Instead it was investigated if it was possible to use the DMA instrument at Swerea KIMAB in the "TMA mode" as described e.g. by the instrument manufacturer Perkin Elmer in an application note [14]. It was, however, found that this did not give repeatable results. It was then decided to send the samples to Ruston Services in United Kingdom for TMA-analysis according to ASTM 831-06.

Adding calcium carbonate and carbon black as fillers to the polypropylene did not reduce the thermal elongation so much. The variation in thermal elongation between the two different types of PPH (alfa and beta) was larger than within each type of PP after adding a filler. However, some improvements were seen, particularly with the high structured carbon black (600JD). It should be noted that the number of fillers tested is very limited compared to the large variety available for polypropylene. Also within the types of calcium carbonate and carbon black there are large variations possible. The calcium carbonate chosen is coated with stearic acid to improve the dispersion in the polymer but it might be negative for the thermal properties and chemical resistance. The work presented here should thus be seen as a first attempt at optimizing the performance in thermal, mechanical and chemical properties of polypropylene. The results should thus not be taken as an indication that it is not possible to use fillers to achieve a significant reduction in thermal elongation.

4.1.2 Properties of the unexposed materials

Investigations of the properties of the unexposed materials showed that the α-PP and the PP-R material also had beta crystals while the beta nucleated PPH did not show as much beta phase as is normally expected, even in the unfilled material. The reason for the beta nucleation of the α-PP and PP-R materials is probably that after a beta nucleated material has been compounded in an extruder the nucleating agent sticks to the walls and the screws the machine and can be active also in the next batch that is processed. This is a known issue. However, since beta crystallinity often is beneficial to the properties of polypropylene it is normally not regarded to be a problem. The reason for the low crystallinity of the β-PP is unknown. Both examples show how large the impact of the processing can be for the properties of the product. It should also be noted that the crystallinity values shown for α-PP and PP-R as calculated from the DSC results are not really valid due to the presence of beta crystals in the samples.

The difference in thermal elongation between the α-PP and the beta is probably mainly related to the large difference in crystallinity between these two materials, 46 vs 59 %. As was mentioned in the introduction it is not clear from the literature if it is a nucleating effect of the filler that can cause a reduction in the thermal elongation or if it is a diluting effect, i.e. less polymer in the compound that elongates, or if the filler can hold the material together. Addition of filler did give some effect on the thermal elongation but there is no clear correlation between crystallinity and thermal elongation. For the β-PP, where the crystallinity was much higher for the unfilled material compared to the filled it is believed that some of the positive effect seen on the thermal elongation is related to the crystallinity. However, for the α-PP there is a reduction in thermal elongation of the when adding fillers at the same time as there is a decrease in crystallinity.

The tabulated data of the tensile yield strength of the unfilled materials are 36 MPa for the α-PP, 30 MPa for β-PP and 25 MPA for the PP-R. The measured values are of the same order even though both the β-PP and the PP-R show slightly higher values than expected. It can be seen that the addition of $CaCO_3$ is lowering the yield strength, especially when adding 25wt%. The addition of both the low, and in particular, the high structured carbon blacks increases the yield strength of all three polypropylenes. Since there is often a risk that the extra strength of the material will result in a more brittle material, the impact resistance was investigated for the α-PP material but only unfilled, 25wt% $CaCO_3$ and CB 600JD. It was found that only one of the investigated test specimens of the 8 tested for each material failed brittle. This could have been due to an imperfection in the sample. Both the filled materials absorbed more energy than the unfilled and the carbon black filled showed the highest impact strength.

The material with Petrit P was found to be slightly destabilised, probably by the free iron in the filler. Iron is known to accelerate oxidation in polypropylene. Due to this and the complex composition of the filler, the material was not considered to be suitable for the demanding environment in flue gas cleaning. In addition the filler needs to be grinded into a fine fraction to be useful as a filler in PP, which is costly.

4.1.3 Properties after chemical exposure

The chemical resistance was affected by the addition of the fillers. Not so much by the carbon blacks as for the calcium carbonate. The weight changes of the materials exposed to HCl are more than a tenfold greater than those exposed to NaOH. The effect is also, as expected, much higher for the 25wt% HCl than for the 5wt%. There is, however, still an effect, especially on the samples filled with 25wt% $CaCO_3$ even if the acid at 5 wt% is fully dissociated and thus does not diffuse into the material. The FTIR-ATR analyses, which only measure the surface, showed that there was a total reduction of the $CaCO_3$ peak after exposure both to 5 and 25 wt% HCl. However, the FTIR-line scan analysis showed that the $CaCO_3$ is not affected in the bulk for the 5 wt% HCl, only for the 25wt% HCl. Also the 5 wt% HCl did not result in the same water absorption seen for the 25 wt% HCl in either one of the $CaCO_3$ filled materials. The weight gain of the 5 wt% $CaCO_3$ material in 25 wt% HCl is probably due that the water absorption is higher than the loss of the $CaCO_3$. For the material with 25 wt% $CaCO_3$, on the other hand, the weight loss of the filler is higher than the gain from the absorbed water resulting in a total decrease in weight.

NaOH normally does not diffuse into polypropylene even at the higher concentration. The slight loss of $CaCO_3$ that can be seen from the samples is just a surface effect. What is most striking is that all three materials with the carbon black XC72 seems to gain some weight after exposure to both the high, but in particular the low concentration of NaOH. It is not understood what this is due to.

The concentrated NO/NO_2 affected the $CaCO_3$ filled materials. A large increase in water absorption can be found in the samples after exposure. Also the unfilled material shows an increase in water absorption but it is higher for the samples with $CaCO_3$ and increases with increasing filler contents. The $CaCO_3$ peaks disappear completely after the exposure. FTIR-line scan showed that the gas had diffused into the material causing water absorption and loss of the filler also in the bulk of the material. For the material 10 wt% XC72 carbon black no significant changes can be seen for the sample after the NO/NO_2 exposure. For the sample with 10 wt% 600JD there is a slight increase in the 3500 and 1570 cm^{-1} regions which could be due to absorption of the NO/NO_2. This type of absorption properties of carbon black is used in special types of structure packs and droplet separators used for dioxine removal [15].

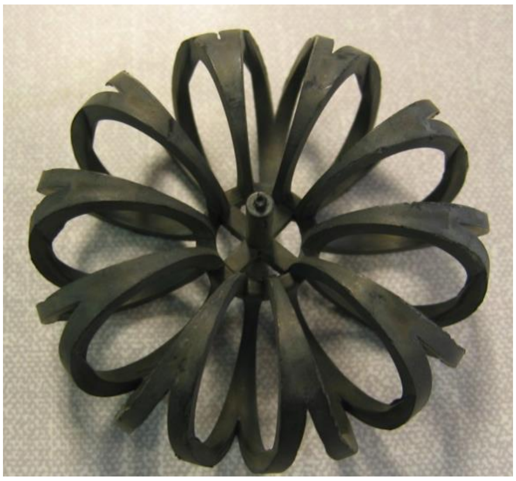

Figure 54. An ADIOX® structure pack filled with active carbon to adsorb dioxins.
Figur 54. En ADIOX® fyllkropp fylld med kimrök för att absorbera dioxiner.

Chlorine dioxide is an aggressive oxidant. As expected the unfilled sample showed oxidation of the surface after the exposure. The unfilled material also shows water absorption in the 3400 and 1640 cm^{-1} regions. This is the water absorption that is used in the chlorine dioxide method discussed below. Interestingly, the $CaCO_3$ filled materials do not show this water absorption. It is not clear what this is due to. The oxidation of the material with 5 wt% $CaCO_3$ seems to be more oxidized that the unfilled material. It was also found that there is also a loss of $CaCO_3$ during exposure even if this was not as complete as for HCl and NO/NO_2.

One of the most interesting results in this work is the fact that the carbon black filled materials do not show any oxidation after the exposure to the chlorine dioxide. It seems as if the filler acts as a stabilizer against the very aggressive radical attack that is normally found in chlorine dioxide environments.

4.2 EVALUATION OF THE CHLORINE DIOXIDE METHOD

From the observations made during the chlorine dioxide exposure, it can be concluded that the water absorption seem to be related to the distribution of stabilizers over a cross section within a material. The results from the analysis with FTIR line scan showed that the water absorption peak, followed over the cross section, had a similar pattern to the ester peak, which is related to the stabilizers. It has not, however, been possible to relate the water absorption to the amount of stabilizer in the material nor between different materials since the different materials absorbed unequal amount of water.

From the result in the part about concentration dependence, it can be concluded that the concentration of chlorine dioxide is of less importance regarding the water absorption peak, as long as ClO_2 is in excess relative to the sterically hindered phenols. In this case, 0.1 g/L ClO_2 was enough.

It can also be concluded that the size of the water absorption peak increases with time and stabilizes after 6 days (144 hours) of ClO_2 exposure for all of the three studied materials. At this point, all sterically hindered phenols have reacted with ClO_2. The optimum efficiency of ClO2 was found to be at 50 °C.

The results within the same polymer for two different experiment show similar values regarding the size of the water absorption peak which indicated good repeatability. This implies that a specific height of the water absorption peak could be related to the concentration of stabilizer in the material if a calibration curve with known concentrations of stabilizers was made. A calibration curve is, however, expensive to prepare since a controlled amounts of stabilizer has to be added in several samples of a specific polymer.

Higher amount of stabilizer in a material results in a larger water absorption peak. This is the reason to why the water absorption peak is larger for the polypropylene sample BE 60 where 0.1 wt% of Irganox 1010 had been added.

During analysis with FTIR on dry samples that had been exposed to chlorine dioxide, formation of oxidation products were observed at ~1712 cm^{-1}, If the oxidation products were to be related to the polymer, a part of the intensity of the water absorption peak would be affected by the degraded polymer. In that way it could be a problem to associate the water absorption to the amount of stabilizers in the material. If the oxidation products came from the polymer, it would also question the effect of the antioxidants regarding protection from polymer degradation. In order to determine if the oxidation product were related to the polymer or the antioxidant, the samples were leached in dichloromethane to see whether or not the peak at 1712 cm^{-1} was left when analyzed afterwards with FTIR. The peak disappeared after leaching which indicates that the oxidation products probably were related to the antioxidants.

Since it was not completely concluded which stabilizers that was incorporated in the studied materials, it cannot be established if the antioxidants influence the water absorption differently. Different sterically hindered phenols have different amounts of sterically hindered phenol groups per molecule. Irganox 1010 has 4 while Irganox 1330 has 3 and Irganox 1076 has 1 sterically hindered phenol group per stabilizer molecule. It is, however, not really clear if antioxidants with more sterically hindered phenols are capable of absorbing a higher amount of water. The UV stabilizer Cyasorb UV 2908 did, for example, absorb more water per formed quinone compared to the other stabilizers. This could be due to its slightly different character. Irgafos 168 did not react with ClO_2 at all due to the absence of sterically hindered phenol in the molecular structure.

4.3 IDENTIFICATION OF EXTRACTED ANTIOXIDANTS

An isocratic HPLC (which resolves a solute using a solvent system that does not change composition during the run) cannot be used for separation and identification of the antioxidants analysed in this study. The result shows that Irganox 1010 and Irganox 1076 elute at the exact same time (at ~7 minutes) which makes it impossible to determine if a polymeric material contain on of them or both. It is, however, possible to identify Irganox 1330 since it elutes after approximately 9 minutes and absorbs UV-light at another wavelength than the other antioxidants. Irgafos 168 and Cyasorb UV 2908 could not be detected with the UV detector at the studied wavelength. Separation was neither achieved with an HPLC with gradient eluent but, according to literature [16], it should be possible if enough time is spent on developing an optimal method. Although for this study, the time was not enough.

By analyzing the extracted antioxidants with FTIR it could be concluded that Irgafos 168 was present in all of the materials according to the characteristic peak at 1083 cm^{-1} [17]. None of the extracts could be specifically related to the spectrum of a commercial antioxidant due to overlapping peaks. A peak located at 1740-1743 cm^{-1}, characteristic for esters, was visible in the spectrum for all three materials. This implies that either Irganox 1010, Irganox 1076, Cyasorb UV 2908 or similar were present in the materials separately or mixed together.

According to the results, an isocratic HPLC cannot provide more information about Irganox 1010 and Irganox 1076 in a material than what the FTIR can. The advantage with HPLC is that Irganox 1330 is detectable from the extracted antioxidants, which cannot be achieved with FTIR. Irgafos 168 was the only antioxidant that could be identified with FTIR from the extracted antioxidants, since the other antioxidants do not have a characteristic peak that can be associated with a specific molecule. Normally this peak is also seen directly in the polymer and does not require extraction.

The analysis with ESI-MS did not reveal much more information about the composition of the extracted antioxidants. A strong peak is visible at 1347 (m/z). According to the literature, it is sometimes common that two equal molecules form complexes in ESI-MS. The strong peak corresponding to 1347 (m/z) is an example of this where two oxidized Irgafos 168 is sharing one sodium atom. Another peak is visible at 685 (m/z) which is a single oxidized Irgafos 168 together with a sodium [18] Because of the strong peak at 1347 (m/z) it was very difficult to detect other antioxidants since those peaks were in too low concentration relative the oxidized complex of Irgafos 168.

4.4 DART-MS

DART stands for "Direct Analysis in Real Time" This is a new technology that allows analysis without prior extraction. DART can, together with high-resolution "Time of Flight" instruments, such as a mass-spectrometer (MS), give an almost direct composition of the components that are present in a sample and have a mass number below 1200. Investigation of some the most common stabilizers showed good correlation between the pure stabilizers and their molecular weights except for Irganox 1010 which seemed to only show fragments. However, when testing a piece of polypropylene there was only one mass number found and this did not correspond to any of the investigated samples. Unfortunately, the computer evaluation is very difficult and there is a risk of drawing the wrong conclusions when studying unknown samples due to overlaps. In that sense it is similar to the problems experienced with

FTIR and HPLC of extracts. In order to find any real use of this technique for the determination of stabilisers in polypropylene much work must be put into analysing reference samples of both pure antioxidants and polypropylene samples with known contents.

4.5 DATABASE

A database could be a good way to share information and experiences with other using not just polypropylene or even polymers but material related questions in general. This could then be of great help to those planning new construction or replacement of old components in flue gas facilities. Swerea KIMAB has over the years participated in a number of Värmeforsk projects and by this, accumulated a lot of experience and knowledge of plastic and metallic materials in flue gas environments. This knowledge, together with other experiences from the use of plastic materials in various types of flue gas environments, could serve as the basis for such a data.

However, creating a database for collection of the data is quite complex and it is difficult to see what type of data that should be collected and if there is enough up-dated data available for it to be of relevance. It is questionable that the polymeric material data is suitable for being presented that way. The amount of available data is so scattered and of varying origin and type that a database might be of little value.

A difficulty also lies in how it should be managed and maintained. A database is very quickly out-dated if it is not maintained. It has to be decided who will be the administrator and owner of such a database. Swerea KIMAB has produced a number of databases. An example is the KorrField database with atmospheric corrosion data for metals which is shown in Appendix A. This database uses excel files to feed in new data, as described in Appendix B.

As mentioned above, it is not straight forward in what way the data should be structured in a database for materials in flue gas facilities. One example can, however, be as follows:

- Material

Carbon steel	Stainless steel	FRP	Polypropylene	Other metals	Other polymers	etc

- Position

scrubber	stack	incinerator	etc

- Temperature

Sub zero	0-20	20-50	50-70	70-90	90-150	150-250	Above 250

- Time

Start year	Start Month	Exposure Duration

- Location

Name of site	Country

- NDT inspection

Ultrasound	x-ray	Thermography	Microwave	etc

- Type of damage

Corrosion	Erosion	Weld failures	Thermal decomposition	etc

The lists can then go on and include new things as the database is being used.

It must also be decided who should finance the work of creating and maintaining the database. The cost for making it is rather high and it must be investigated if the number of potential users is large enough to cover the cost for making and maintaining it by just the funds that will come from the licensing.

5 Conclusions

5.1 GENERAL CONCLUSIONS

The most important results for the study of filled polypropylenes are:

- There is an enormous variety of fillers and surface coatings available for polypropylene
- There is also a very large variety of different polypropylenes
- The very limited number of filler/material combinations evaluated in this work did show some effects on the thermal elongation but this could most probably be greatly improved.
- It was found that the processing is very determining for the properties of the polypropylene.
- The beta nucleated material only showed very little beta crystallinity and the α-PP and PP-R materials showed almost as much.
- It is advisable to always use XRD rather than DSC to calculate the degree of crystallinity in polypropylene as it is possible that the material contains beta crystals even if a nucleating agent has not been added on purpose.
- The addition of fillers can affect the crystallinity.
- The addition of 5 wt% and 25 wt% stearic acid coated calcium carbonate did not result in any particular improvement of the material properties, except for some improvement of the impact resistance. The materials also showed an increased sensitivity to 25 wt% HCl and NO/NO_2 and ClO_2.
- The addition of 10 wt% of carbon black improvement both the thermal and mechanical properties investigated. The material with 10 wt% 600JD showed both an increased tensile yield strength, modulus (not reported due to data collection problems) and impact resistance. The materials were also very little affected by the different chemical environments investigated. There was even some improvement in the stability to the oxidative/radical environment in the ClO_2 exposure and in the concentrated NO/NO_2 environment.

The most important results for the study on the identification and quantification of stabilizers are:

- The stabilizers in a material can be related to the water absorption after ClO_2 exposure within a material, but not between different materials.
- The water absorption peak increases with time until it stabilizes after 6 days (144 hours), thus when all sterically hindered phenols have reacted with chlorine dioxide.
- The concentration of chlorine dioxide was of less importance for the water absorption as long as ClO_2 was in excess relative the sterically hindered phenols, for this study, 0.1 g/L was enough.
- It was also concluded that reaction with ClO_2 was more effective in 50°C than in room temperature.
- The chlorine dioxide method can also be considered repeatable within a specific material since similar values of the water absorption peak are obtained at separate experiments.
- It is difficult to use HPLC for identification of the antioxidants that was analyzed in this study. Because of the similar molecular structure of Irganox 1010 and Irganox 1076, it was impossible to achieve separation with an isocratic HPLC since they were affected in the same way by the solid and mobile phase.
- It is also quite difficult to use FTIR to analyze which stabilizers that are present in an unknown samples due to many overlapping peaks. However, with more experience this is probably a powerful method.
- The DART-MS method still needs more work in order to use it for the determination of stabilizers in an unknown polypropylene sample.

To create a database the following must be decided:

- Who should administer it?
- What type of data is of interest to share?
- Is the available data in the form that is suitable for a database?
- How should it be financed?
- Are there any legal issues involved for sharing the results?

5.2 FULFILMENT OF THE PROJECT OBJECTIVES

The overall project objective was to develop methods and methodologies to assure the quality PP materials for a specific desired service life, and to assess the status and remaining life of PP materials in facilities for purification and condensation of flue gases. The fulfilment of the three main objectives is described below:

Reduce the problems of warping, deformation and cracked welds due to thermal expansion/contraction by addition of filler to the PP.

The effect seen on the thermal expansion with the addition of fillers was not as large as was hoped for. Some reduction was, however, seen which would reduce some of the problems. Also the increased stiffness could help in reducing some of the problems. It is also important to note that the number of possible polypropylene/filler combinations that have been investigated in this project is very limited compared to what is possible to attain. There could be other combinations with much better properties.

Reduce the risk of downtime and expensive component replacement by increasing the precision of lifetime assessments of PP materials in flue gas environments.

A number of different techniques for determining the residual stabiliser contents have been evaluated. The chlorine dioxide method, which in the previous project showed great potential, was found to have some drawbacks in being able to give comparable results between different types of sterically hindered phenol stabilisers. The work has led to an increased understanding the drawbacks and potentials of the different techniques available.

Provide support for new construction or replacement of old components by presenting the results in a database where other experiences from the use of plastic materials in flue gas environments can also be gathered.

It was found that creating a database for collection of the data is quite complex and it is also questionable that the polymeric material data is suitable for being presented that way. The amount of available data is so scattered and of varying origin and type that a database might be of little value. In addition there are some questions about legal, finical and maintenance issues that will have to be resolved first.

6 Proposals for further research

The most interesting outcome of this work is the possibility of using carbon black as a filler in polypropylene. It has a positive impact on the mechanical and thermal properties and is also quite stable in all of the investigated chemical environments. For the radical/oxidative environment and the NO/NO_2 it seems to improve the chemical resistance.

The 600JD carbon black used seemed slightly better that the XC72. It is also considered the “Rolls Royce” of carbon blacks with a high price to follow. It would be of interest to see if the same good properties could be found with less expensive types of carbon blacks and also at lower concentrations.

It would also be of great interest to install test pieces in real service environment in flue gas plants to see how more realistic and longer exposure times will affect the material. It is of interest to test how much reduction in thermal elongation that is possible to achieve using talc as a filler. According to the literature this should give significant improvement. Also glass fiber can be used as filler in polypropylene and could be of interest, at least in some chemical environments.
For the chlorine dioxide method it must be concluded that it will only be possible to use as a relative measurement within the same type of polypropylene and to study cross sections of exposed materials. This is, however, also true for OIT which is widely used. Compared to OIT the chlorine dioxide method is more sensitive and will probably be of great use for stabilization and service life estimations in the future. This is probably also the case for extraction and subsequent FTIR analyses for the determination of stabilizer concentration and type.

To determine the scope and administration issues of creating and running a “materials in flue gas environments database” a dedicated investigating must be made. Swerea KIMAB has the experience of creating and administrating such databases. It is, however, probably more relevant to create a handbook and damage atlas for polypropylene similar to the one we have just produced for FRP (fiber reinforced plastics) in project M 37775 “Inspektion och OFP av processutrustning i glasfiberarmerad plast (GAP)”

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7 Appendix A

KorrField database with atmospheric corrosion data for metals. Version 2.1

KorrField database contains data for atmospheric corrosion of metals under unsheltered conditions. Climatic parameters and other information about the test site are included. References to literature source and exposure programme are given. Along with the database, a Windows based, dedicated computer program to search the database and to visualize the results has been developed.

Model predictions for first year corrosion is available for carbon steel, zinc, copper and aluminum. The models (dose-response functions) include average temperature, time of wetness and deposition of Cl and SO_2.

Front page

The front page is depicted in figure 1. A click on the logo will launch your internet browser and take you to the institute's homepage.

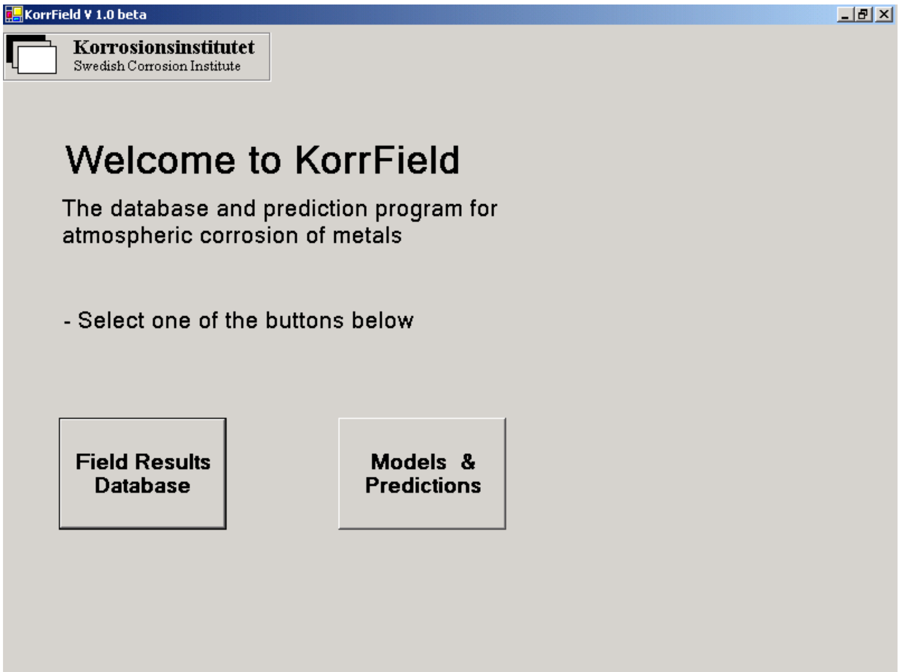

Figure 1.

The mode of operation; explore the database or use the prediction models, is selected by pressing the aPP-Ropriate button.

Field Result Database

Figure 2 shows the user interface for selection, extraction and presentation of data from the database.

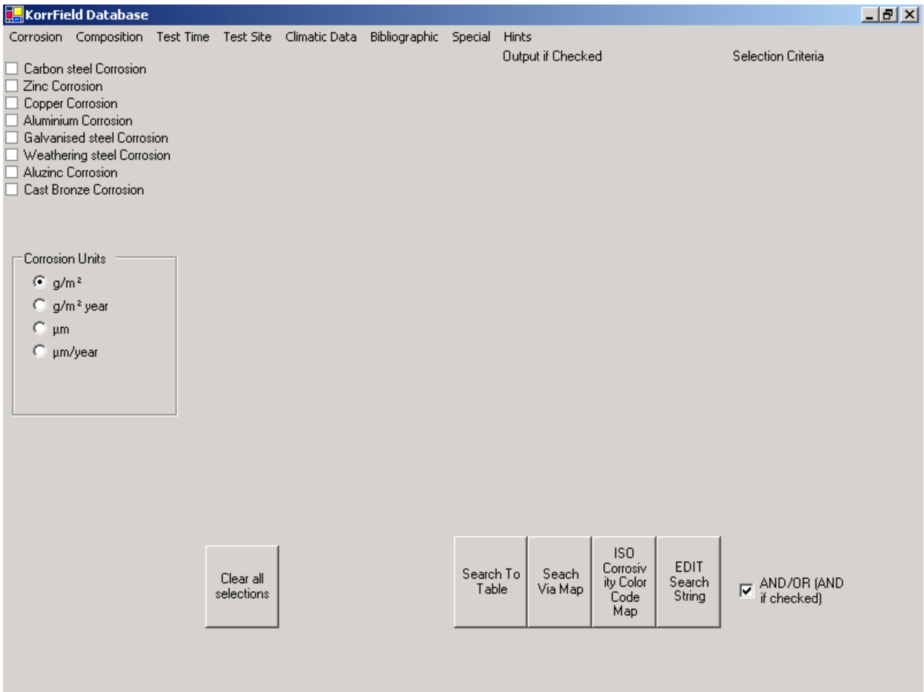

Figure 2.

KorrField database selection page allows any of the fields in the database to be output. The information fields are grouped into categories displayed as columns. The category names are displayed in the drop-down list.

The categories are Corrosion, metal/alloy Composition, Test time, Test site, Climatic data and Bibliographic.

Corrosion results in the database can be expressed as corrosion during the exposure (g/m^2 or µm) or as annual corrosion rate (g/m^2, year or µm/year). The preferred units are selected from the radio buttons in the middle left box.

The set of three buttons on the lower half offers three alternative modes for the search in the database. "Search to table" generates a table containing the selected fields. "Search via Map" displays a geographic world map with test sites that match the search criteria. "ISO Corrosivity Color Code Map" displays a geographic world map with test sites that match the search criteria. Here, each matching test site is marked by a color coded symbol. High corrosion rate - red symbol, low corrosion rate- green symbol.

The contents of the first column, 'Corrosion' is shown in figure 3.

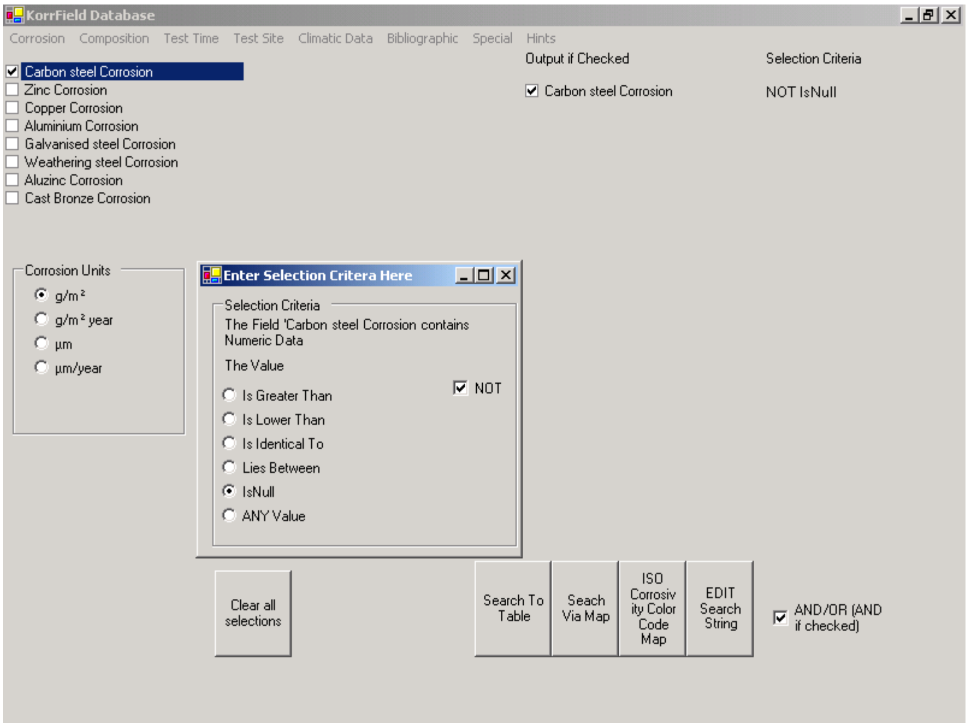

Figure 3.

To select a field for output, the box to the left of the field name is pressed. One click causes the selection criteria frame to appear and causes the selected field name to be copied to the Output list. A second click causes the field name in the output list to be checked. Selection criteria are entered by pressing the aPP-Ropriate button. The selection criteria frame displays that the selected field 'Carbon steel Corrosion' contains numerical data. If the "Is Greater than" button is pressed, a textbox to type the value in, is displayed.

Setting the selection criteria causes the criterion selected to be copied to the "Selection Criteria" column to the right in the KorrField database selection page.

The contents of the second column 'Composition' is shown in figure 4.

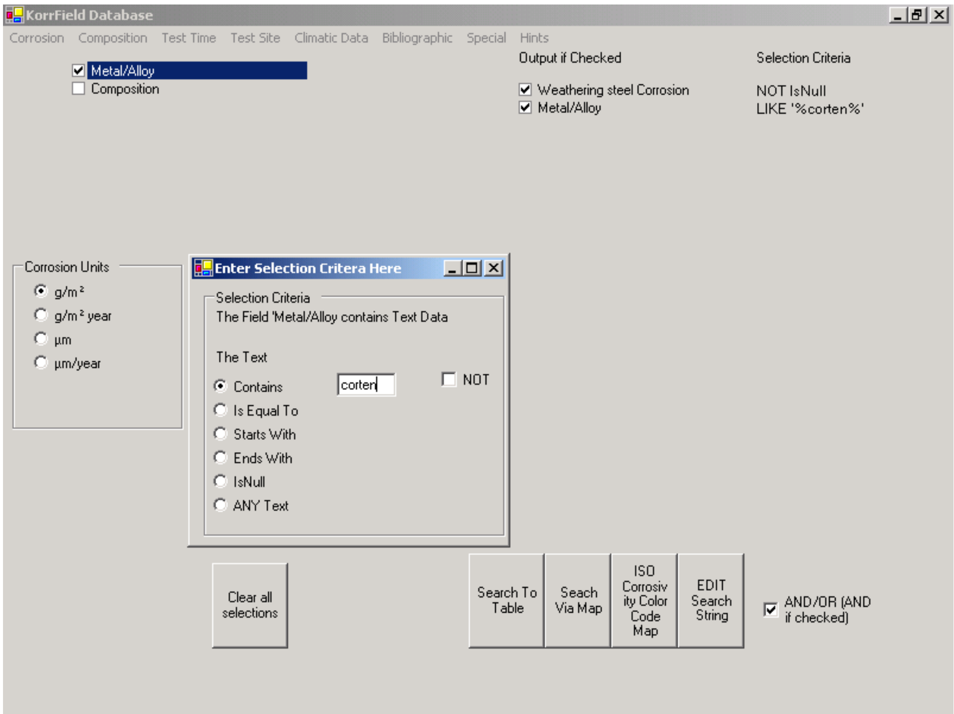

Figure 4.

The second column contains information about the metal or alloy. The field 'Metal/Alloy' may contain trade names and the field 'Composition' contains lists of the chemical composition of the material exposed. Both these fields contain data in text format. The selection criteria frame recognizes this and the radio buttons show alternatives suitable for text.

If the 'Contains' button is pressed, a textbox is displayed. Entering a text string e. g. 'corten' in that textbox causes the search to be limited to entries that contains the text 'corten' in the field 'Metal/Alloy'.

On the right hand side of the KorrField database selection page there is checkbox labelled 'AND/OR'. If this box is checked, the search will return all entries that contain corrosion data for weathering steel only if the field 'Metal/Alloy' contains the text 'corten'.

It is possible to select corrosion data for more than one metal of alloy at the time for output. However, the fields under the second column, will apply only to the first selected material.

The contents of the third column, 'Test time' is shown in figure 5.

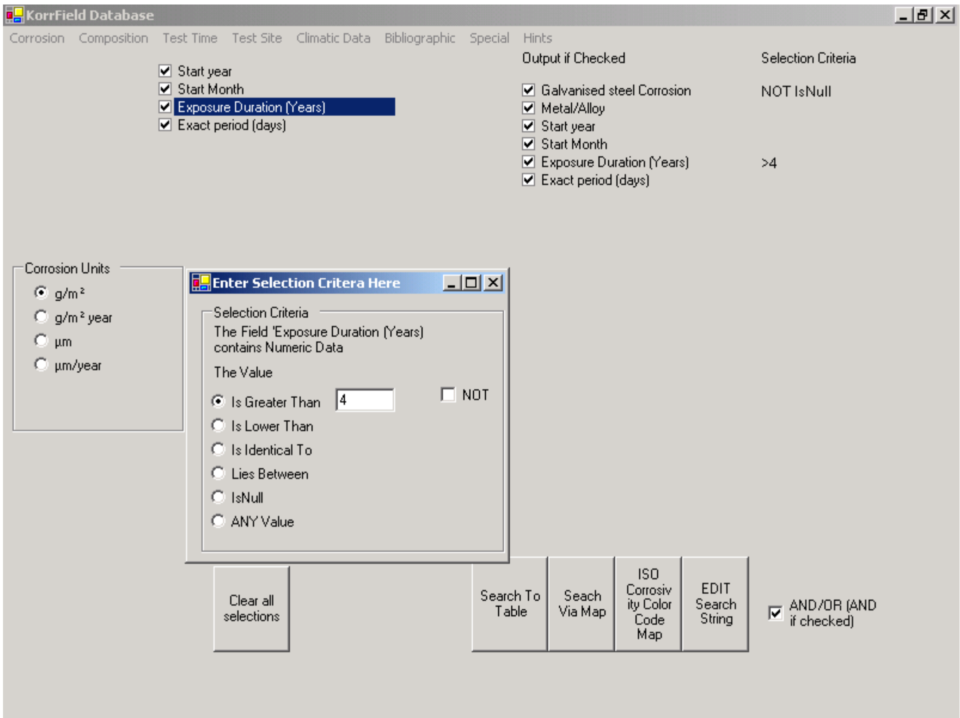

Figure 5.

The third column contains information about the test time. Data on Star year, start month, Exposure duration in years and Exact duration of the exposure in days are contained in numerical fields. The field ' Exposure duration (years) is automatically used when the corrosion units are set to 'g/m2, year' or 'µm/year'.

The contents of the fourth column, 'Test Site' is shown in figure 6.

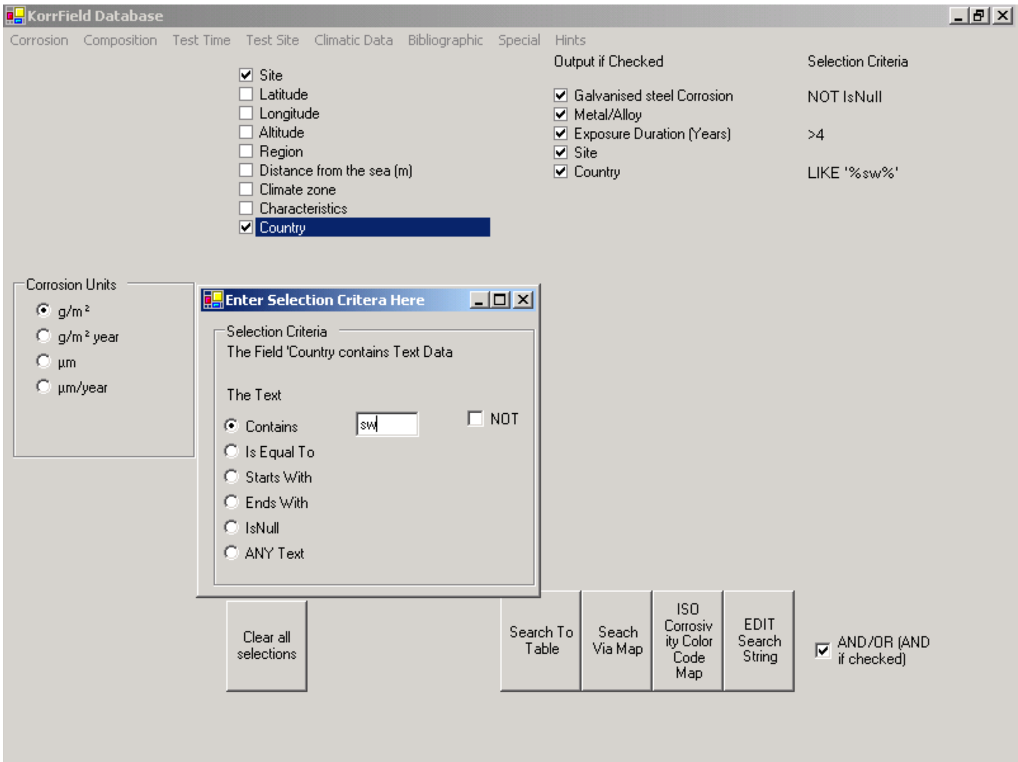

Figure 6.

The fourth column contains information about the test site. Site name, region, climate zone, characteristics and country are given as text fields. Site location as latitude, longitude, altitude and distance from the sea is given as numerical fields. Latitude and longitude are used to locate the test site on the maps, if any of these options are used.

The selection above will return only entries that contain data for galvanized steel corrosion and only data from Sweden or Switzerland.

The contents of the fifth column, 'Climatic is shown in figure 7.

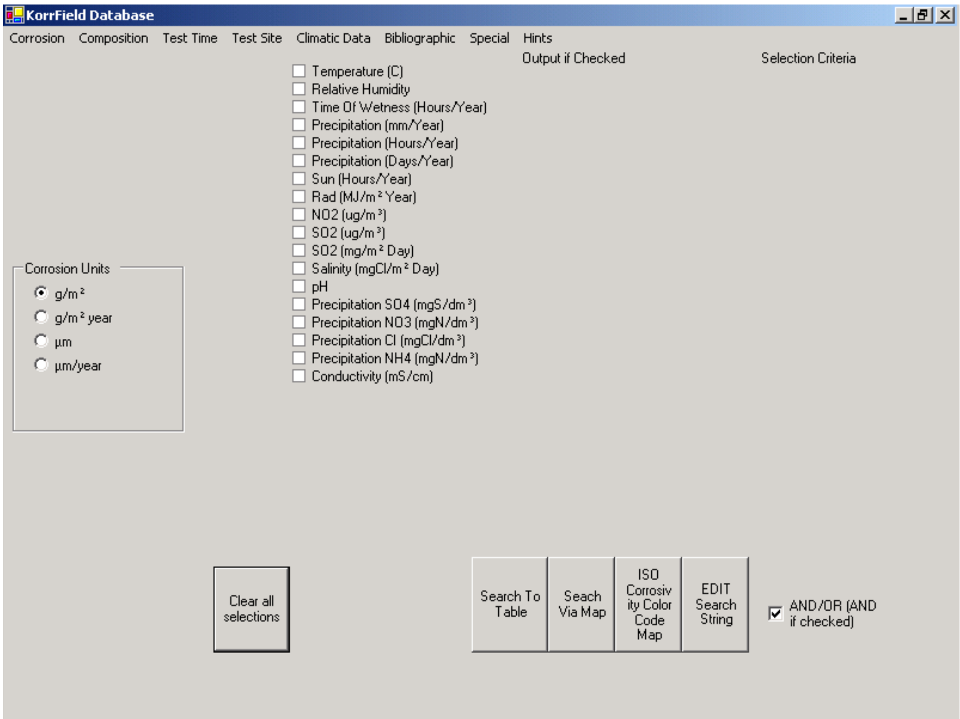

Figure 7.

The fifth column contains information about climate at the test site or about climatic parameters recorded during the exposure. A wide variety of measures are reported and the list of parameters is rather long. The first parameter is the annual average temperature at the site of the exposure. The following five parameters describe the humidity and precipitation frequency. The sun intensity is described by two parameters; the number of hours of sunshine per year and the total annual radiation energy per unit area. The presence of pollutants in the local atmosphere is recorded for NO_2 and for SO_2. The last seven parameters relate to the precipitation at the test site. The rate of precipitation of pollutants is described for SO_2 and Cl or salinity. The composition of the precipitates is characterized by the contents of SO_4, NO_3, Cl, NH_4 and the conductivity. Few if any exposure have been characterized by all these climatic parameters.

The contents of the sixth and last column, 'Bibliographic' is shown in figure 8.

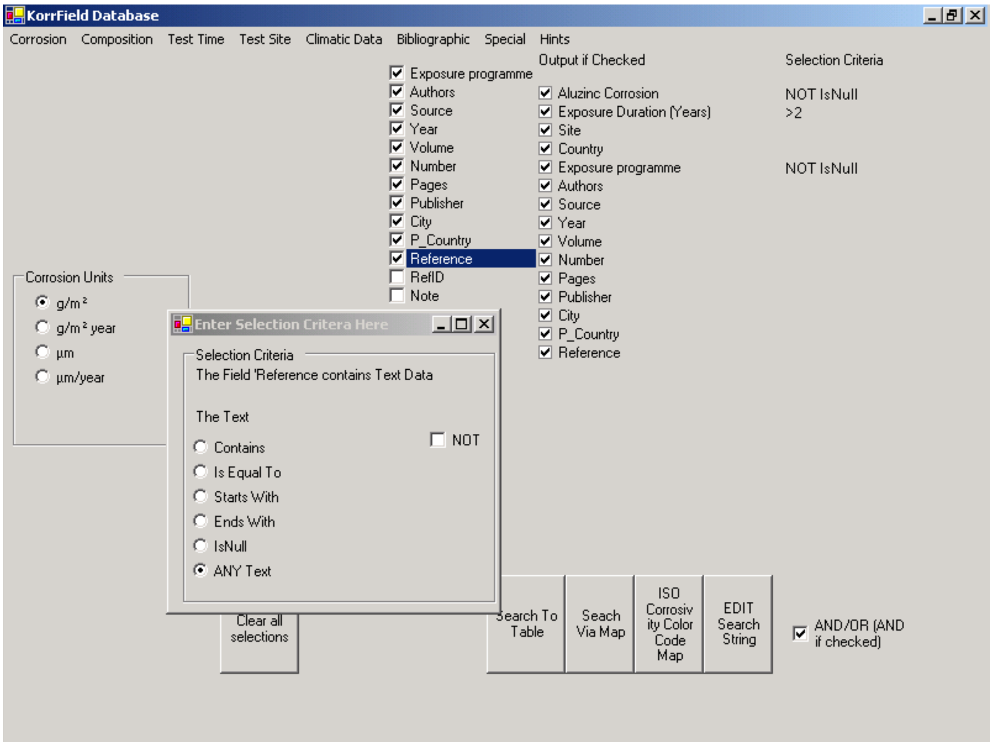

Figure 8.

The contents of the sixth column relate mainly to the literature source of the data. In cases where the observation belongs to a major exposure program, that information is contained in the first field. Notes on the observation are contained the last field. These notes are intended to contain information about the entry that does not fit into any of the other fields.

Energiforsk

Presentation of search results:

Search to Table

An example search with output to a table is given in figure 9. The table lists all entries in the database that contain corrosion data for zinc after an exposure duration between 4 and 10 years. The option to display results in mass loss per unit time and area is used.

The Result window displays the search results with columns ordered after the order in which they appear in the output list (Output if Checked). The row order is arbitrary. The result table can be ordered by pressing either one of the column headings. The number of matching entries is displayed below the table. One may have to expand the window by drawing the windows lower limit downwards to make the number of entries visible.

Pressing the column below the filled triangle causes the Result window to expand as shown in figure 10.

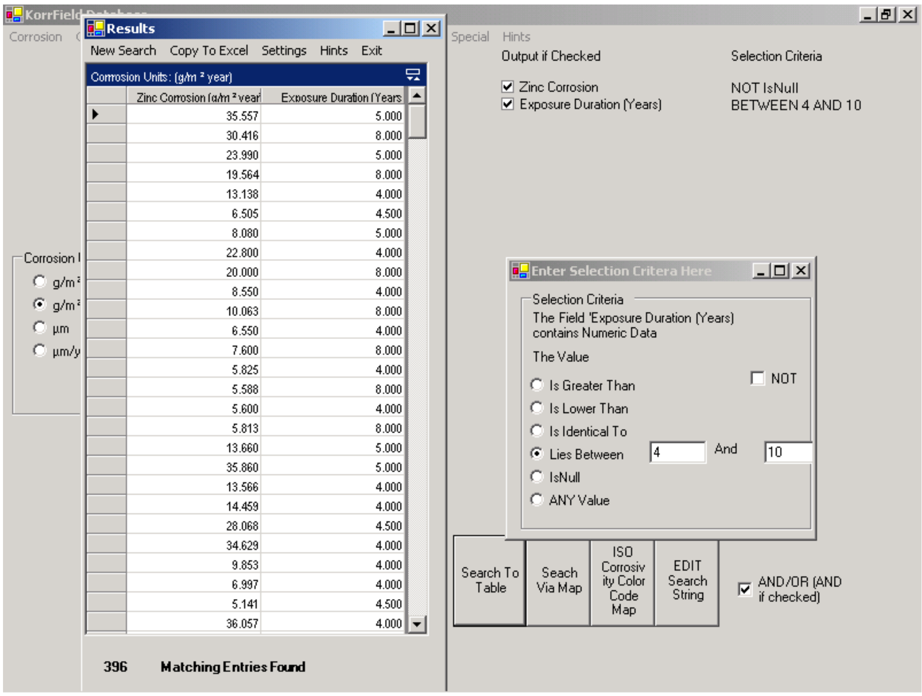

Figure 9. Search result table.

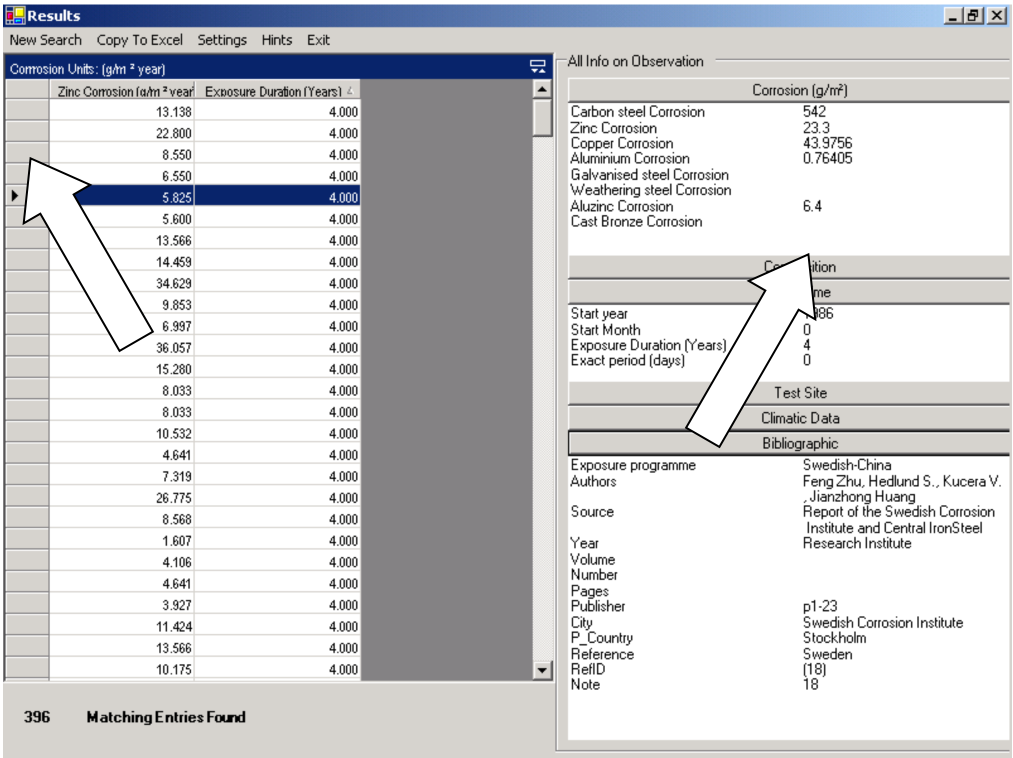

Figure 10. The result table expanded so that all information on the entry can be seen.

To the right a set of 'drawers' show up. When pressed, these 'drawers' open up to reveal all information for the particular entry selected. The information displayed in the 'drawers' is categorized in the same way as the dropdown menus in the selection page and the contents are in the raw format directly from the database e.g. corrosion is always expressed in g/m^2. A click on a data column in the result table causes the Result window to return to normal size again.

Search via map

In this example, multiple selection criteria are used and the results are displayed via a world map. The relation between the selection criteria is the logical 'AND' (AND/OR Checkbox checked). Pressing the Search via Map causes the Map Window to appear and the location of exposure sites are indicated by black squares. Only sites for which there are entries that fulfill the selection criteria are displayed.

By a click at a black square on the map, the requested information about the entry that fulfills the selection criteria is displayed in the Result Window. The Result window has the same functionality here as it does when the Search to Table method is used.

In the example here we click on Prague in the Check Republic. The program detects that there are several matching sites in that area and displays a table with alternate sites.

A final selection is made by a click on the site name or 'All sites in the table'. When there are no neighbouring sites displayed on the map, the result window is displayed directly.

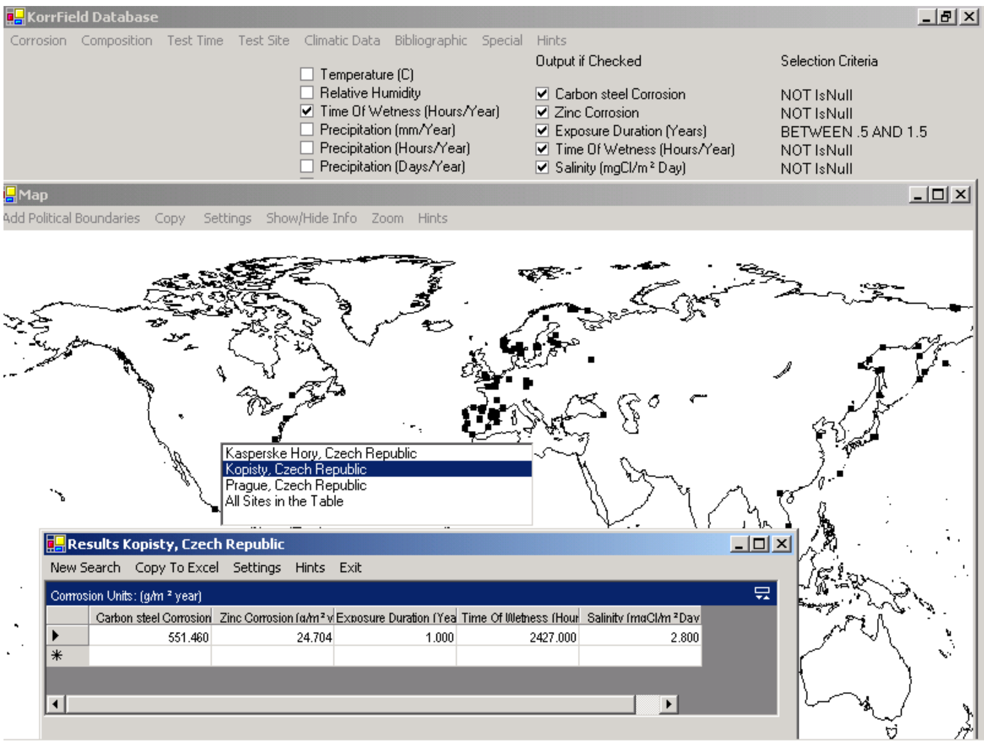

Figure 11. Search results presented via a world map.

ISO Corrosivity Map

Pressing the 'ISO Corrosivity Color Code Map' button again causes the world map to be displayed. Sites Only sites for which there are entries that fulfill the selection criteria are displayed. The locations of the sites are indicated by color coded squares. Most of the functionality is maintained from the 'Search via Map' option but corrosion is always expressed as a rate in µm/year. Color coding is available for Steel, Zinc, Copper and Aluminum.

Color coding can only be made for one material at the time. If more than one metal is selected for output or for selection criteria, the map will be color coded for the metal that appears first in the output list.

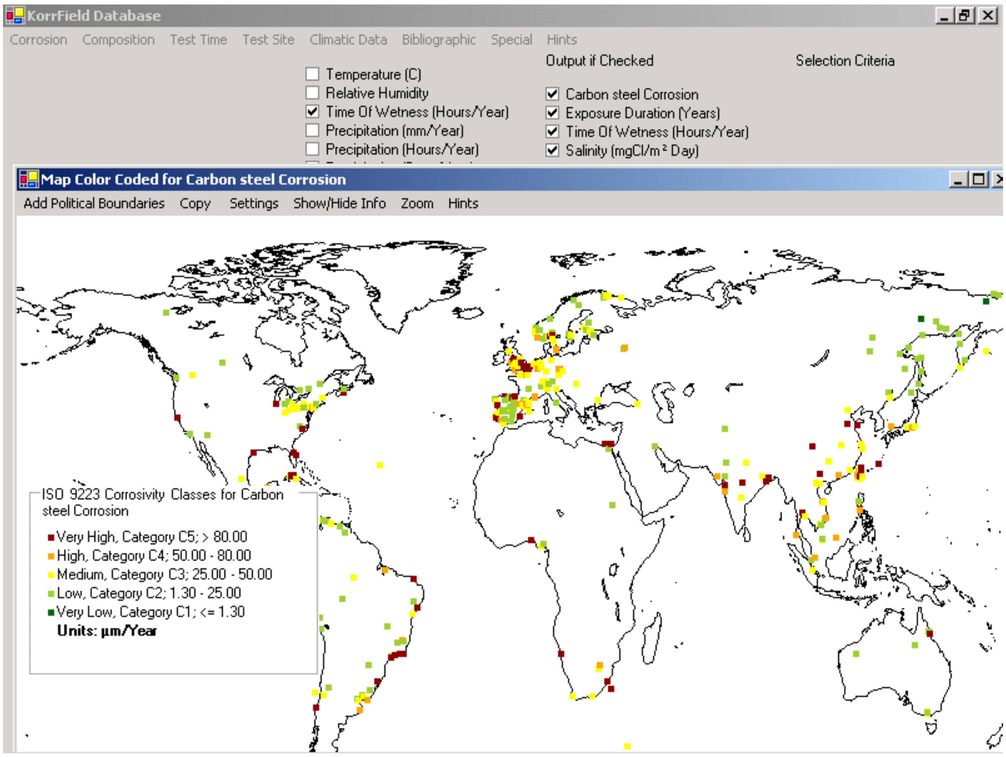

Figure 12. Search results displayed as a colour coded corrosivity map.

Advanced search options: Edit search string

Selection criteria can be very complicated. It would be next to impossible to make a simple user interface that allows all variants. At the same time it is recognized that some users may want to use complex selection criteria. As a compromise, it is possible to edit the search string in SQL-language. These strings are very lengthy but modifications are usually required only of the 'WHERE' clause.

In order to avoid extensive typing, a good practice is to let the program create a search string almost as you want it and then make a few minor changes manually.

If you make a selection via the drop down menus requiring that the entries must contain relevant data you can only use a logical AND or a logical OR relation between the criteria.

What you may want is that the entry must contain data on Aluminum corrosion OR Copper Corrosion. You require that the entry must contain Time of wetness OR Relative humidity. And the entry must contain data on SO2 pollution but you do not care how it was measured.

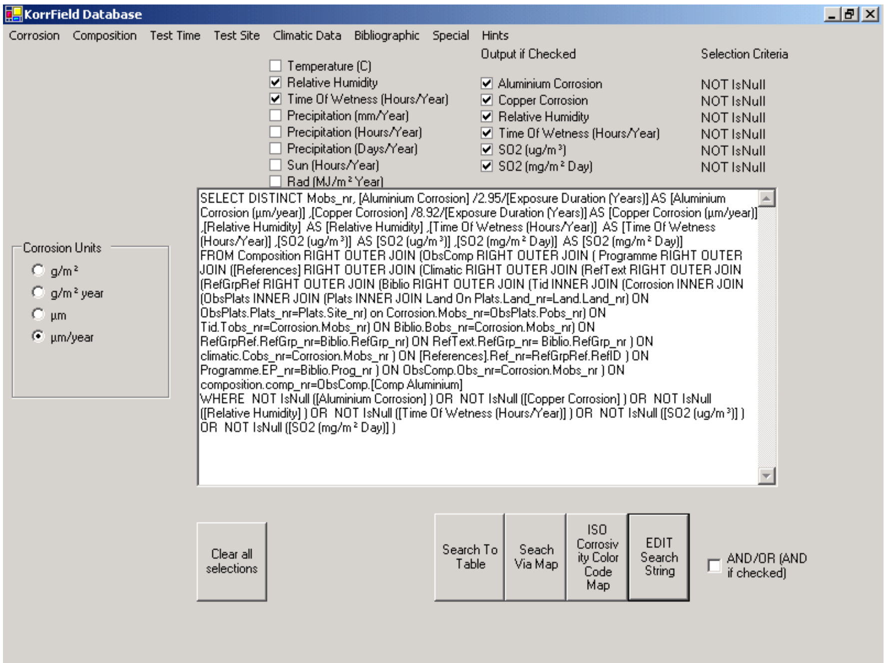

Figure 13 shows the search string in the textbox displayed for editing.
Figure 13. The search string in SQL language displayed for editing by advanced users.

The original 'WHERE' clause :

WHERE NOT IsNull ([Aluminum Corrosion]) AND NOT IsNull ([Copper Corrosion]) AND NOT IsNull ([Relative Humidity]) AND NOT IsNull ([Time Of Wetness (Hours/Year)]) AND NOT IsNull ([SO2 (ug/m ^{3})]) AND NOT IsNull ([SO2 (mg/m ^{2} Day)])

is modified to :

WHERE **(** NOT IsNull ([Aluminum Corrosion]) **OR** NOT IsNull ([Copper Corrosion])**)** AND **(**NOT IsNull ([Relative Humidity]) **OR** NOT IsNull ([Time Of Wetness (Hours/Year)])**)** AND **(**NOT IsNull ([SO2 (ug/m ^{3})]) **OR** NOT IsNull ([SO2 (mg/m ^{2} Day)])**)**

The modifications are here indicated by using bold face characters. The modified search string gives 960 entries as result. The original search string gives no matching entries.

It is possible to cut and paste to and from the displayed textbox. A favorite search string may be stored as a document in Word of Notepad and pasted into the textbox. However, at least one selection must be made first so that the program can generate a search string to display for editing.

The displayed search string is used only if the textbox is visible. The 'Edit Search String' button operates in a toggle mode. Whenever the textbox is not visible the search string is generated automatically.

The ISO Corrosivity Color Code Map always uses the search string generated automatically and disregards the textbox and any changes made there.

Models and Predictions

The predictions are based on empirical equations that describe the dependence of the first year corrosion on climatic parameters. The climatic parameters considered are temperature, time of wetness and deposition of SO_2 and chloride, respectively. Predictive models are implemented for carbon steel, zinc, copper and aluminum.

The equations used are:

$$C_{Steel} = 0.085 \cdot SO_2^{0.56} \cdot TOW^{0.53} \cdot e^{f(Steel)} \quad + \quad 0.24 \cdot Cl^{0.47} \cdot TOW^{0.25} \cdot e^{0.049T}$$
$$f(Steel) = 0.098 \cdot (T - 10) \quad when\,T \le 10°C, \quad otherwise \quad f(Steel) = -0.087 \cdot (T - 10)$$

$$C_{Zinc} = 0.0053 \cdot SO_2^{0.43} \cdot TOW^{0.53} \cdot e^{f(Zinc)} \quad + \quad 0.00071 \cdot Cl^{0.68} \cdot TOW^{0.30} \cdot e^{0.11T}$$
$$f(Zinc) = 0 \quad when\,T \le 10°C, \quad otherwise \quad f(Zinc) = -0.032 \cdot (T - 10)$$

$$C_{Copper} = 0.00013 \cdot SO_2^{0.55} \cdot TOW^{0.84} \cdot e^{f(Copper)} \quad + \quad 0.0024 \cdot Cl^{0.31} \cdot TOW^{0.57} \cdot e^{0.030T}$$
$$f(Copper) = 0.047 \cdot (T - 10) \quad when\,T \le 10°C, \quad otherwise \quad f(Copper) = -0.029 \cdot (T - 10)$$

$$C_{Aluminium} = 0.00068 \cdot SO_2^{0.87} \cdot TOW^{0.38} \cdot e^{f(Aluminium)} \quad + \quad 0.00098 \cdot Cl^{0.49} \cdot TOW^{0.38} \cdot e^{0.059T}$$
$$f(Aluminium) = 0 \quad when\,T \le 10°C, \quad otherwise \quad f(Aluminium) = -0.031 \cdot (T - 10)$$

C_{Me} = Corrosion attack after 1 year of exposure in µm of metal *Me*.

The equations are taken from
Tidblad, J,, Kucera, V., Mikhailov, A. A., and Knotkova, D.

"Improvement on the ISO classification system based on dose-response functions describing the corrosivity of outdoor atmospheres." Outdoor Atmospheric Corrosion ASTM STP 1421, H. E. Townsend Ed., American Society for Testing and Materials International, West Conshocken, PA, 2002

The Prediction screen that meets the user is shown in figure 14. There are four fields for numeric values for the different climatic parameters and buttons from which to select one of the four materials for which a prediction model is implemented. There are two units for corrosion rate to choose between. SO2 pollution can be entered as deposition in µg/m², day or concentration in mg/m³. Deposition is estimated as 0.8 times concentration. Calculations of corrosion rates are always based on deposition. Entering a value in the 'Concentration' textbox will cause an automatic change in the 'Deposition' textbox. Entering a 'Deposition' textbox will clear the 'Concentration' textbox.

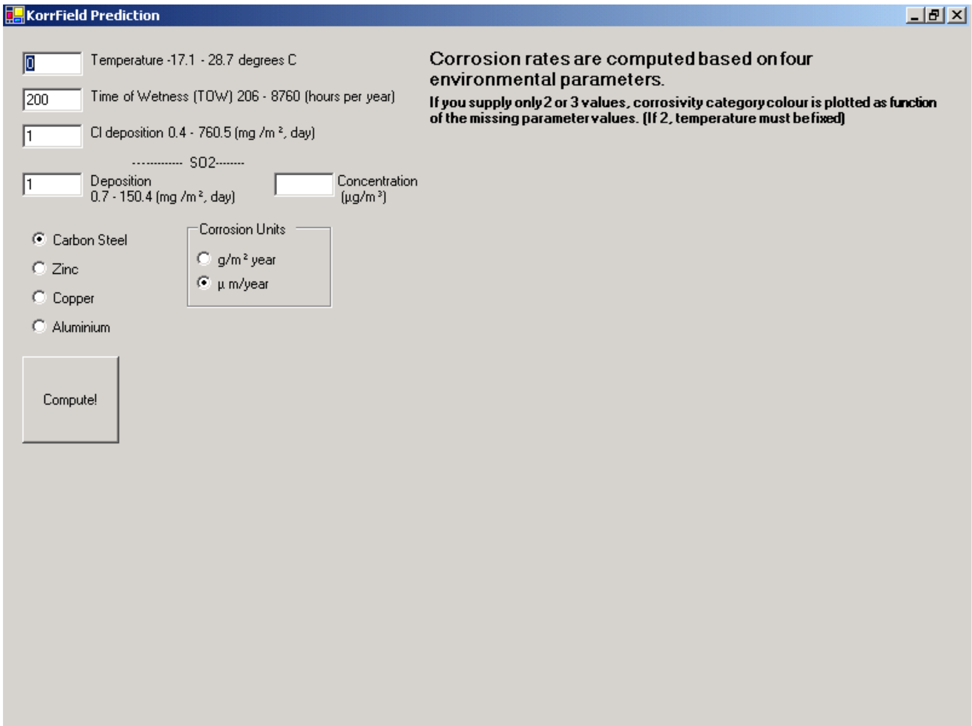

Figure 14. KorrField Prediction.

If you supply numeric values for all the four climatic parameters the result is presented as shown figure 15.

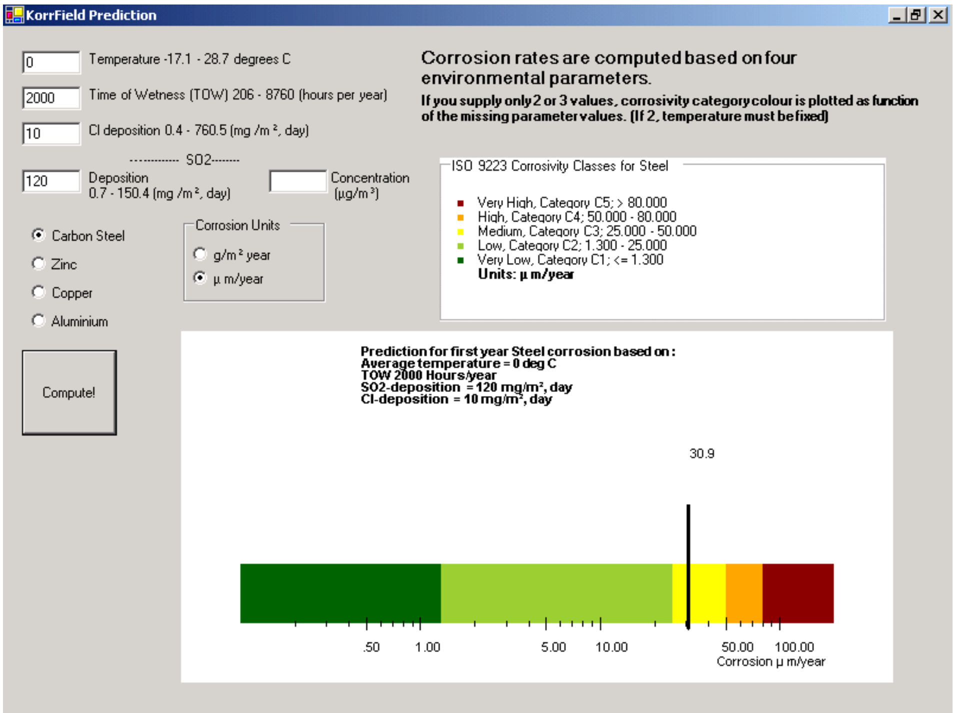

Figure 15. Example of the output results from a corrosion prediction.

The corrosivity classes are plotted along a corrosion rate axis. The computed result is shown as a bar on the corrosion rate axis and as a numeric value.

If you supply numeric values only for three climatic parameters and leave the fourth field blank, the result is presented as shown in figure 16.

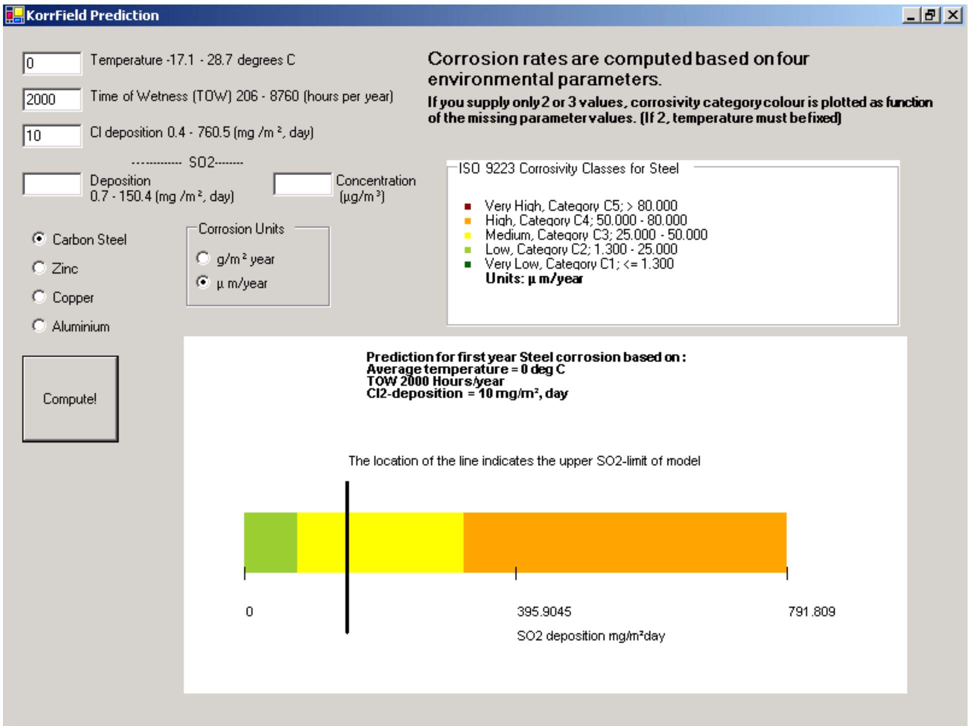

Figure 16.

No exact corrosion rate can be calculated without numeric values for all four climatic parameters. The figure shows the dependence of the corrosion rate on the value of the missing parameter. The diagrams shows that for carbon steel under these conditions, the corrosivity class will be low to medium as long as the SO_2-deposition is within the limits of the model.

If you supply numeric values only for two climatic parameters and leave the two other fields blank, the result is presented as shown in figure 17.

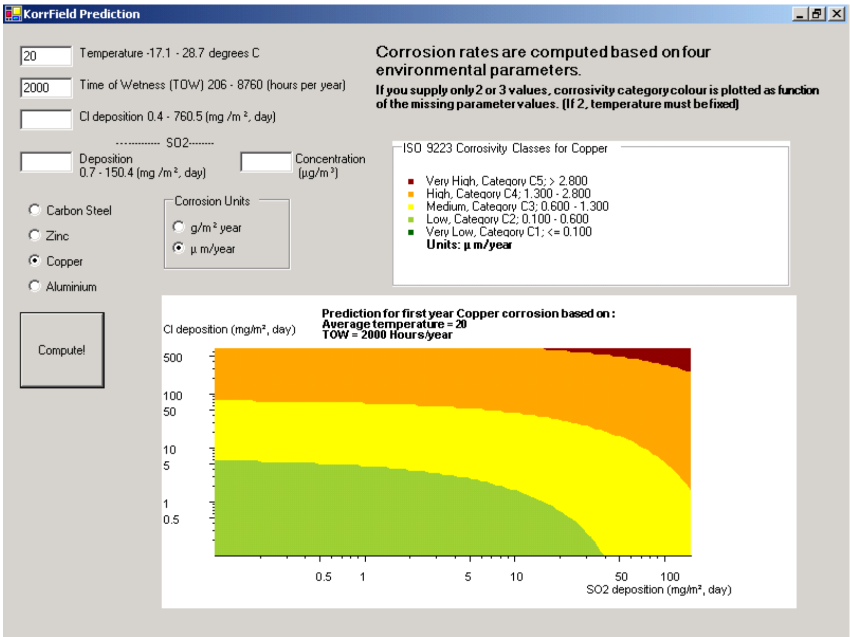

Figure 17.

The figure shows the dependence of the corrosion rate for copper on the value of the missing two parameters. The corrosivity classes are plotted as function of chloride deposition and SO_2-deposition.

NOTE These Screen shots were made using a screen resolution of 800 x 600 in order to maximize readability of the text in the screen shots. The program works well also with other resolutions e. g. 1024 x 768.

Appendix B

How to introduce new data into the database?

The database consists of tables in a excel workbook. The workbook is named "KorrField.xls". Each worksheet in this workbook contains a table that is used by the Korrfield database program; KorrField.exe.

It is possible to edit the Excel file so that company specific information is included in the database and displayed along with the default data. In order to introduce new data it is necessary to understand the structure of the database. Relations between tables are not apparent from the Excel file but are built into the program KorrField.exe.

The structure of the database

The file KorrField.xls contains thirteen named worksheets:

- Corrosion

Mobs_nr	Carbon steel Corrosion	Zinc Corrosion	Copper Corrosion	Aluminum Corrosion	Galvanised steel Corrosion	Weathering steel Corrosion	Aluzinc Corrosion	Cast Bronze Corrosion

- Composition

Comp_nr	Metal/Alloy	Composition	CRef_nr

- ObsComp

Obs _nr	Comp Carbon Steel	Comp Zinc	Comp Copper	Comp Aluminu m	Comp Galvanised Steel	Comp Weathering Steel	Comp Aluzinc	Comp Bronze

- Tid

Start year	Start Month	Exposure Duration (Years)	Exact period (days)	Tobs_nr

- Plats

Site	Site_nr	Latitude	Longitude	Altitude	Region	Distance from the sea (m)	Climate zone	Characteristics	Land_nr

- ObsPlats

Pobs_nr	Plats_nr

- Land

Country	Land_nr

- Climatic

Cobs_Nr	Temperature (C)	Relative Humidity	Time Of Wetness (Hours/Year)	Precipitation (mm/Year)	Precipitation (Hours/Year)	Precipitation (Days/Year)	Sun (Hours/Year)

(the list goes on, there are many columns in this table

- Biblio

Note	Bobs_nr	RefGrp_nr	Prog_nr

- RefText

Reference	RefGrp_nr

- RefGrpRef

RefID	RefGrp_nr

- Programme

Exposure programme	EP_nr

- References

Ref_nr	Authors	Source	Year	Volume	Number	Pages	Publisher	City	P_Country

Introduction of new data into the database

Corrosion data

Localize the worksheet named ‘Corrosion’. In column ‘A’ with the heading ‘Mobs_nr’ scroll down to the highest number. Add a new row with the next higher number in column ‘A’. Make a note of this number.

Enter the corrosion data for the metals according the headings. The units should be grams per square meter.

Enter material specifications

If you do not want to specify the metals beyond ‘Carbon Steel’, ‘Zinc’ etcetera the skip this section.

Browse the ‘Composition’ table. If you do not find any existing description or analysis that is the best in your case then scroll down to the end to the table. Enter a new number in column ‘A’, a name for the metal in column ‘B’ and an analysis in table ‘C’. Repeat this for all the metals included in the dataset. Use a new row number for each metal and make notes of these numbers (Comp_nr).

In the table ‘ObsComp’ the column ‘A’ should be identical to column ‘A’ in the table ‘Corrosion’. Since you have entered new rows to the table ‘Corrosion’ you should also enter the same new numbers in the table ‘ObsComp’. In column ‘B’, enter the ‘Comp_nr that you used in the ‘Composition’ table to describe Carbon Steel. In column ‘C’, enter ‘Comp_nr that you used in the ‘Composition’ table to describe Zinc.

This will link the metal descriptions to the corrosion data.

Time and duration of the exposure

In the table ‘Tid’, column ‘E’ should be identical to column ‘A’ in the table ‘Corrosion’. Since you have entered new rows to the table ‘Corrosion’ you should also enter the same new numbers in the table ‘Tid’, but in column ‘E’.

Column ‘A’ should contain the start year for the exposure, column ‘B’ start month and column ‘C’, Exposure Duration (in Years).

Site for the exposure

Browse the table ‘Plats’. If your site is not on the list then add a new site number to the column ‘B’ and the site name in Column ‘A’. Columns ‘C’ through ‘J’ contain parameters relevant to the site. Column ‘J’ should contain a number for the country. The proper number is found from the table ‘Land’. Make a note of your (new) site number(s).

Table ‘ObsPlats’ links the observation to the site. Column ‘A’ should contain the same number as column ‘A’ in the table ‘Corrosion’. Enter the new numbers and for each number enter the number for the site in column ‘B’

Longitude and latitude for the site must be supplied if the data are to show up in the map functions in the database program. Some help in finding longitude and latitude for a geographically well defined site is given by the map function in the database program.

With the map displayed, at any degree of magnification' right click with the mouse at any site on the map will the show the desired coordinates.

Climatic data

Column 'A' in table 'Climatic' should contain the same number as column 'A' in the table 'Corrosion' (and several other tables) Columns 'B' through 'S' contain headings for numeric climate data. N. B. Climatic data is directly linked to the observations of corrosion and only indirectly linked to the sites where the exposures were made.

Bibiographic data and references

Column 'B' in table 'Biblio' should contain the same number as column 'A' in the table 'Corrosion'. Column 'C' contains a pointer to a group of references and column 'D' contains a pointer to an Exposure Program.

The group of references that the pointer refers to is found in table 'RefGrpRef'. The value in column 'C' in 'Biblio' correspond to column 'B' in 'RefGrpRef'. The reference numbers in column 'A' in 'RefGrpRef' correspond to column 'A' in the table 'References'. But, since one observation may be related to several publications, the group of references also point to a text list of the reference numbers. This list is located in the table 'RefText'.

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Vidare har några metoder för att bedöma stabilisatorkoncentrationen, och därmed PP-materialets kvarvarande livslängd, utvärderats.

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