FATIGUE CRACK GROWTH RESISTANCE OF POLYPROPYLENE AND GLASS FIBER REINFORCED POLYAMIDE IN CHLORINATED WATER WITH VARYING CLORINE CONTENTS

Master Thesis
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This thesis is dedicated to my father’s soul who always wanted me to be proud and better than anybody else and who believed that this can be achieved by education. I express my warmest thanks to my mother, without whom I wouldn’t have achieved anything in this life, for providing me with unconditional support, believing in me, and motivating me to always work harder. I would also thank my brother and my sister for being such great role models, for all the support and advices they provided me, and for giving me the strength to keep going and never give up on my dreams. Additionally, thanks to all my friends who were like a family to me, pushed me to work harder and who gave a flavor to this experience and made it more intercultural.

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STATUTORY DECLARATION

I hereby declare that the thesis submitted is my own unaided work, that I have not used other than the sources indicated, and that all direct and indirect sources are acknowledged as references.

This printed thesis is identical to the electronic version submitted.

Linz, October 2017

Signature
ABSTRACT

In the last two decades a lot of efforts have been made to improve solar-thermal systems in terms of costs, weight, and overall performance by providing better alternatives than conventional materials. In order to replace conventional materials by polymeric materials, the envisaged materials must withstand the environmental and the mechanical loading conditions of this application and maintain a service life of 20 years. Solar-thermal systems are constantly exposed to different media (e.g., air and heat carrier fluid) and operate at elevated temperatures. Therefore, it is of utmost importance to investigate the different aging mechanisms of polymeric materials under service relevant conditions. Moreover, to provide drinking water that fulfills the safety standards, chlorine is used as a water disinfectant in many regions of the world. Hence, polymeric materials must have a sufficient chlorine resistance for the application in solar-thermal collectors.

The objective of this thesis is to investigate the effects of chlorinated water with varying chlorine contents at an elevated temperature on the properties of polymeric materials used for solar-thermal systems. For this particular purpose, three grades of polypropylene and three grades of glass fiber reinforced polyamide were characterized. Polypropylene included a commercial black-pigmented block copolymer pipe grade (PP_C) and two homopolymer-based PP grades. While the first homopolymer-based grade was stabilized with a UV-stabilizer (PP_U), the other grade was stabilized with an antioxidant and a UV-stabilizer (PP_AU). For the polyamide, a commercial aliphatic PA grade with glass fiber content of 30% (PAGF30_C) was used as benchmark and as base material for the other two material grades. Both material grades were stabilized with antioxidant packages. The first grade was stabilized with a phenolic-based stabilizer (PAGF30_P). Whereas the other grade was stabilized with an amino-based stabilizer (PAGF30_A).

In order to characterize the fatigue crack growth (FCG) resistance in chlorinated water with varying chlorine contents at 80 °C, both materials were characterized under superimposed mechanical-environmental loading using a specific test setup. For the PP grades cracked round bar (CRB) specimens and for the PAGF30 compact type (CT) specimens were used. While for the PP the tests were performed at 1, 2.5, 5 and 10 ppm, for PAGF30 they were performed at 1, 5, and 10 ppm. On the one hand, both materials showed that the crack initiation is affected by the environment. However, only the PAGF30 grades showed a clear correlation between the number of cycles to failure and the chlorine content. On the other hand, the FCG kinetics curves of the PP grades, unexpectedly, showed a superior FCG resistance at higher chlorine contents. In contrast, the PAGF30 grades revealed a different behavior, as the FCG resistance of PAGF30_C and the PAGF30_P was reduced at higher chlorine contents. While the FCG rate of PAGF30_C was enhanced by a factor of 4.8 at 10 ppm compared to 1 ppm, it was enhanced only by a factor of 1.8 for PAGF30_P. This can be attributed to the addition of the phenolic stabilizer package to the material. The FCG resistance of PAGF30_A remained stable at various chlorine contents and only a slight decrease in the slope was observed at higher chlorine contents.
# TABLE OF CONTENTS

ACKNOWLEDGMENT .................................................................................................................. I
STATUTORY DECLARATION .................................................................................................... II
ABSTRACT .................................................................................................................................... III
TABLE OF CONTENTS ............................................................................................................... IV

1 INTRODUCTION AND SCOPE .............................................................................................. 1

2 GENERAL BACKGROUND ....................................................................................................... 3
  2.1 Solar-Thermal Collectors ..................................................................................................... 3
      2.1.1 Collector types .............................................................................................................. 3
      2.1.2 Solar domestic hot water systems .................................................................................. 5
      2.1.3 Polymeric materials in solar water heating systems ....................................................... 8
  2.2 Environmental Effects on Polymeric Materials .................................................................... 11
      2.2.1 Effect of different media on polymeric materials .......................................................... 11
      2.2.2 Chlorinated water and its effect on polymeric materials ............................................. 16
  2.3 Fatigue Tests and Fracture Mechanics Concepts ................................................................. 19
      2.3.1 Fatigue of polymers .................................................................................................... 20
      2.3.2 Linear elastic fracture mechanics ................................................................................. 20

3 EXPERIMENTAL .................................................................................................................... 25
  3.1 Test Program ....................................................................................................................... 25
  3.2 Materials ............................................................................................................................ 26
  3.3 Specimen Preparation ......................................................................................................... 27
      3.3.1 Cracked round bar specimen for PP ............................................................................ 27
      3.3.2 Compact-type specimen for PAGF30 ........................................................................... 28
  3.4 Test Methodology ............................................................................................................... 29
      3.4.1 Chlorine depletion and water uptake ............................................................................. 29
      3.4.2 Infrared spectroscopy ................................................................................................ 30
      3.4.3 Differential scanning calorimetry ................................................................................. 30
      3.4.4 Fatigue tests at different chlorine contents ................................................................. 31
      3.4.5 Characterization of the fracture surfaces ................................................................. 35

4 RESULTS AND DISCUSSION ............................................................................................... 36
  4.1 Polypropylene .................................................................................................................... 36
      4.1.1 Oxidative induction time ............................................................................................ 36
      4.1.2 Fatigue crack growth resistance .................................................................................. 38
      4.1.3 Fracture surfaces ........................................................................................................ 43
  4.2 Glass Fiber Reinforced Polyamide ..................................................................................... 44
      4.2.1 Chlorine residual and water uptake ............................................................................ 44
      4.2.2 Infrared spectra .......................................................................................................... 47
      4.2.3 Fatigue crack growth resistance .................................................................................. 48
      4.2.4 Fracture surfaces ........................................................................................................ 52

5 SUMMARY AND CONCLUSIONS ........................................................................................... 54

6 REFERENCES .......................................................................................................................... 56
1 INTRODUCTION AND SCOPE

Polymeric materials have been used for infrastructural applications (e.g., PE pressurized pipes) since the 60’s of the last century (Vasile & Pascu, 2005). In the last two decades, polymeric materials have gained an increasing importance in renewable energy sector. One major area of the renewable energy sector is solar-thermal (ST) technologies, which are mainly used for domestic hot water (DHW) and solar assisted space heating (SH) (Lang et al., 2016). These ST systems can be categorized into pumped (active) and non-pumped (passive) systems. The active systems are widely deployed in more industrialized regions, such as Europe and USA. Whereas, the passive systems are mostly used in regions of the world, such as Asia, Latin America, Africa (Lang et al., 2016).

Some challenges are still limiting the deployment and the market penetration of these technologies. However, for the ST systems, it is believed that the substitution of conventional materials by polymeric materials can help to overcome these challenges by offering solar-thermal collectors with significant cost and weight reductions and more integrated designs (Koehl et al., 2012). In the last few years, several research projects have been conducted to achieve this goal, such as Task 39 of the IEA Solar Heating and Cooling Program (Koehl et al., 2012), likewise, the SolPol-4/5 project aims to develop pumped and non-pumped solar-thermal systems with all-polymeric or hybrid material designs (Lang et al., 2016; SolPol, 2017).

In solar-thermal applications a service life of 20 years is required (Koehl et al., 2012). Therefore, polymeric materials should have long-term durability, sufficient thermal resistance, and high aging resistance against UV and water (Smyth et al., 2006). Solar-thermal collectors operate at elevated temperatures and are constantly in contact with different media, including air, potable water, or heat carrier fluids. Hence, it is highly important to investigate the different aging mechanisms of polymeric materials under service relevant conditions to ensure long-term stability over prolonged service life (Kahlen et al., 2010; Povacz et al., 2016).

Different polymeric materials can be used for the solar-thermal absorbers. On the one hand, certain black-pigmented polypropylene grades have shown promising potential to be used for overheating controlled collectors (Lang et al., 2013; Povacz, et al., 2016). On the other hand, engineering thermoplastics, particularly short glass fiber reinforced polyamide, were proven to be a good alternative material for the non-pumped integrated collector storage systems (SCOOP, 2014). However, the solar-thermal absorbers are simultaneously exposed to to elevated temperatures, mechanical stresses, and various environmental media. While the absorber is surrounded by air from outside, its interior is exposed to the heat carrier fluid, which differs depending on the collector type and the climatic conditions (Koehl et al., 2012). For example, in the direct solar-thermal collectors, potable water is circulated within the system (Ogueke, 2009).
Since polymers are, in general, sensitive to the thermo-oxidative degradation, which occurs in oxygen-rich environments at elevated temperatures leading to undesirable changes in the material properties, different stabilizer packages are usually added to the material to minimize the oxidative degradation. Furthermore, in many regions of the world, chlorine is used as a disinfectant to ensure a safe drinking water (WHO, 2011). Therefore, additional requirements are imposed on the long-term performance of the polymeric materials, since pH and chlorine in the potable water create a more oxidative environment that can chemically attack the material and deteriorate its mechanical properties. Hence, several studies have been conducted to study the global aging of polymeric materials upon the exposure to different environments. The thermo-oxidative degradation of the material is usually analyzed by correlating the chemical changes upon the exposure to a certain environment to the mechanical properties of the material (Richaud et al., 2008; Beißmann et al., 2013; Schoeffl et al., 2014; Povacz, 2014; Geretschläger, 2015).

The main objective of the present thesis is to investigate the effects of the chlorine content in the chlorinated water at an elevated temperature on the fatigue crack growth resistance of polymeric materials used for solar-thermal applications. Materials used for both pumped and non-pumped systems were investigated, including polypropylene and short glass fiber reinforced polyamide grades. For ranking purposes, both material grades were initially characterized using cyclic fatigue tests with a specific test setup, in which superimposed mechanical and environmental loads are considered. Additionally, the stabilizer depletion, the chemical changes in the material, and the water uptake of the polyamide grades were investigated to provide a better understanding of the material behavior upon the exposure to these conditions.
2 GENERAL BACKGROUND

Polymeric materials have gained an increasing importance in renewable energy sectors, particularly in the solar energy sector. The environmental conditions and the effects of different media play a major role on the material properties. Therefore, many efforts have been made to understand the behavior of polymeric materials under various environmental conditions. This chapter provides an overview of the solar-thermal collectors including their types, mechanisms, and materials. Furthermore, a discussion on the effects of different media on polymeric materials, followed by a more specific discussion on the effects of chlorinated water on polyolefins and polyamide is provided. Finally, an overview of the basic principles of fatigue tests and fracture mechanics concepts is provided.

2.1 Solar-Thermal Collectors

Solar energy has become one of the major renewable energy sources that aim to bridge the gap between the energy demand and supply by offering more sustainable solutions (Buker et al., 2015). The global solar-thermal market has grown significantly over the last decade. This growth is more evident in more industrialized regions, such as Europe, the United States, and China with currently over 70 million households equipped with a solar hot water supply (Koehl et al., 2012).

A solar-thermal collector is a device that converts the solar irradiation into a useful heat energy and conveys it through a transport fluid, such as air or water. In order to reach the highest possible efficiency, the absorber must be able to absorb as much solar irradiation as possible. Furthermore, it should transfer the generated thermal energy to the fluid medium with very low losses to the surrounding (Koehl et al., 2012). Solar-thermal collectors can be used for different purposes and over a wide range of applications, such as water heating, space heating and cooling, solar-thermal power systems and industrial process heat (Kalogirou, 2004). However, in this thesis, I will focus on polymers that are used for solar collectors of domestic hot water systems (DHW).

2.1.1 Collector types

There are various types of solar collectors for different applications on the market. According to the statistics of the year 2015, three main types are most commonly used, as they account for over 99% of the total worldwide capacity in operation (Weiss et al., 2017):

**Unglazed collectors**

This type accounts for 6.2% of the global installed capacity in operation with 38.5 million square meters of collector area that generates 27 GWth (Weiss et al., 2017). These collectors are usually produced in a form of black mats or pipes. They simply collect the solar irradiation by an absorber and transfer the acquired energy to the fluid medium (Fig. 2.1a) (Koehl et al., 2012). Despite the high losses to the surrounding due to the lack of insulation, these systems work efficiently at low
operating temperatures (from ambient temperature up to 20 °C above the ambient). The main application areas of this technology are (Koehl et al., 2012):

- swimming pools
- domestic hot water (DHW), particularly in warm climates where the difference between the hot water and the ambient temperature is small
- solar assisted heat pump systems, where the collector collects both solar irradiation and heat from the surrounding
- central heating of buildings, only if air is used as the fluid medium

Various models of unglazed collectors are available on the markets, including polymeric and metallic unglazed collectors. To produce the polymeric unglazed collectors, EPDM, PP, and PE-HD are usually used (Koehl et al., 2012).

**Flat plate collectors**

Flat plate collectors (FPC) are mostly used in Europe and they make up more than one fifth of the worldwide installed solar collectors generating 95.7 GWth (Weiss et al., 2017). FPCs generally consist of a frame, which can be made of metal, wood or polymer, copper tubes mounted on a metallic absorber (aluminum, copper) and a transparent housing cover (glass or polymer). Usually, an insulation of foam or mineral wool is added to minimize the heat loss (Fig. 2.1b) (Koehl et al., 2012).

FPCs are typically used for applications that require low to medium temperatures (20-60 °C above the ambient temperature) (Koehl et al., 2012), such as:

- DHW preparation
- space heating
- solar cooling

In some commercial flat plate collectors, polymeric materials have been used as substitutes of metals, where PC twin-wall sheets are used as collector covers and the absorbers are made of silicon rubber, PA or PPS (Koehl et al., 2012).

**Evacuated tube collectors**

Evacuated tube collectors (ETC) have the largest share in the world with over 70% of the total installed capacity in operation covering an area of 445.8 million square meters and generating around 312 GWth. This type is particularly dominated by the Chinese market (Weiss et al., 2017). Unlike the other two types, which operate in sunny and warm climates, this type of collector was developed to overcome unfavorable weather conditions during cold cloudy days that may cause an early deterioration of the internal material, hence a reduced performance and system failure (Kalogirou, 2004). Although there are various types of evacuated tube collectors, they are all based on the same principle. They consist of a heat pipe inside a vacuum-sealed glass tube, in
order to reduce the thermal losses to the surrounding (Fig. 2.1c) (Kalogirou, 2004; Koehl et al., 2012).

Due to their efficiency and the characteristic to operate in colder climates, ETCs are mainly used for applications that require high temperatures (up to 80 °C above ambient temperature) (Koehl et al., 2012), such as:

- DHW preparation in a cold climate
- space heating in a cold climate
- solar cooling
- process heating

![Schematic illustration of different solar-thermal technologies: (a) unglazed collector, (b) flat plate collector, (c) evacuated tube collector (EPA, 2016).](image)

Fig. 2.1: Schematic illustration of different solar-thermal technologies: (a) unglazed collector, (b) flat plate collector, (c) evacuated tube collector (EPA, 2016).

### 2.1.2 Solar domestic hot water systems

Solar water heating or domestic hot water (DHW) is the main application of the solar-thermal collectors. In the EU, around 75% of the energy consumption in buildings is employed for water
and space heating (Koehl et al., 2012). Depending on the circulation of the heat transfer fluid, DHW systems are classified as passive or active systems (Norton, 2011). Another distinction between the systems is that they can either be direct systems, in which potable water is directly heated in the collector, or indirect systems where the heat is transferred to the water through a heat exchanger by another fluid that is heated in the collector (Kalogirou, 2004; Norton, 2011).

There are five main solar energy systems that can be used for water heating. Based on the previous classification, those systems can be categorized as non-pumped (passive) and pumped (active) systems (Kalogirou, 2004; Lang et al., 2016).

**Non-pumped (passive) domestic hot water systems**

Non-pumped solar-thermal domestic hot water systems include thermosiphon and integrated collector storage (ICS) systems. These two types are typically used in countries with relatively warm climates (i.e., frost-free climates), such as Southern European countries and China (Koehl et al., 2012). Thermosiphon systems can be equipped with evacuated tube collectors (ETC) or flat plate collectors (FPC) and they utilize the natural convection phenomenon to transport the heat from the collector to the water storage tank (Fig. 2.2) (Kalogirou, 2004; Norton, 2011). These systems can either be direct or indirect. In direct systems, solar-heated water rises from the collector to the top of the water tank due to the density difference between hot and cold water, while gravity-driven cooler water flows into the bottom of the collector to replace the heated water. Whereas in indirect systems, a heat exchanger has to be used and instead of potable water a heat carrier fluid flows through the collector (Morrison & Braun, 1985; Morrison G. L., 1986).

![Fig. 2.2: Principle of thermosiphon systems based on EZINC-AG series (Premium Solar LLC, 2017).](image-url)

On the other hand, an ICS is a compact system that combines both the solar collector and the hot water tank in one component, as the upper surface of the storage tank being used as an absorber. In ICS water supply and discharge operate similar as in the thermosiphon systems with a hot water...
outflow from the top of the tank, which is replaced by an inflow of cooler water into the bottom of the tank through separate pipes on the opposite side (Fig. 2.3) (Kalogirou, 2004).

**Fig. 2.3:** Principle of ICS systems based on the Solcrafte® system (Solar Direct, 2012).

The main disadvantage of ICS are the potential high thermal losses to the environment, especially at night. Since most of the surface area of the storage tank is deliberately used as an absorbing surface, it is difficult to thermally insulate it (Kalogirou, 2004). Therefore, an emphasis has to be taken to reduce the heat loss and to ensure an adequate thermal insulation without compromising the collection of solar irradiation (Smyth et al., 2006).

**Pumped (active) domestic hot water systems**

Pumped domestic hot water systems are most commonly used in Central and Northern Europe and the United States. Pumped or forced-circulation systems harness the power of a pump to circulate the heat carrier fluid within the system instead of just relying on natural convection. Nonetheless, this does not necessarily mean that they always have a higher operational efficiency than thermosiphon and ICS systems. In the active systems, storage tanks can be installed internally and only collectors have to be installed outside the building. Thus, a significant weight reduction on the roof is achievable. This gives them a major advantage over passive systems. However, pumped systems require sensors, a controller, and an electric pump, in order to maintain a good fluid circulation, which makes the system more complex (Norton, 2011; ESTIF, 2017). Based on the heat transfer within the system, it is distinguishable between two types of pumped systems direct and indirect systems. Both are typically equipped with flat plate collectors (FPC), evacuated tube collectors (ETC), or compound parabolic concentrator (CPC) (Kalogirou, 2004).

In the direct forced-circulation systems, shown in Fig. 2.4, potable water is directly circulated between the storage tank and the solar collector, so that cold water heats up and returns into the storage tank (Ogueke et al., 2009). This type is usually used in regions where frost does not occur frequently. In harsh weather conditions, freeze-protection can be achieved by recirculating warm
water through the system. Cold water can be supplied to the systems either by a cold water tank or by being directly connected to the city water mains. Direct circulation systems should be avoided if the city water is too hard or acidic, which may clog the pipes or corrode the collector (Kalogirou, 2004).

Fig. 2.4: Schematic illustration of a direct circulation solar water heating system (Kalogirou, 2004).

The indirect circulation systems (Fig. 2.5) are equipped with a heat exchanger, that can be mounted inside or outside the storage tank. Instead of potable water, a heat carrier fluid is circulated through a closed loop between the collector and a heat exchanger, where the acquired heat is transferred to the potable water. The most commonly used heat carrier fluids are antifreeze, air, distilled water, or organic heat-transfer fluids (Khalifa, 1998).

Fig. 2.5: Schematic illustration of an indirect circulation solar water heating system with the heat exchanger inside the tank (Kalogirou, 2004).

2.1.3 Polymeric materials in solar water heating systems

The use of solar-thermal (ST) systems has shown a remarkable growth in the last decade. Yet, available metal-based ST collectors are still heavy and comparatively high-priced. Therefore, the SolPol-4/5 project aims to develop new pumped and non-pumped ST technologies that substitute
metals with polymeric materials (Lang et al., 2016; SolPol, 2017). Apart from the better ecological impact, utilizing polymer technologies in ST applications can lead to a significant weight reduction (up to 67% lighter), substantial cost savings, and more integrated designs due to the diverse and flexible features and the highly automated manufacturing of plastics (Koehl et al., 2012; Chen et al., 2015). ST systems can be used over a wide range of temperatures (up to 1700 °C) depending on the application area. However, for solar collectors that are equipped with polymeric materials the area of interest is applications with relatively low service temperatures (below 130 °C), which are dominated by space heating and domestic hot water (Koehl et al., 2012).

**Absorber materials for non-pumped integrated storage collectors**

The hot water storage tank is the main component of an ICS system, whose primary function is to absorb the solar irradiation and to transfer the acquired heat to the adjacent stored water. The capacity of the solar absorption is affected by the size and shape of the tank along with its materials. The most commonly used materials in available systems are copper, aluminum and stainless steel. Recently, certain types of black pigmented polymers have been introduced as absorber materials (Smyth et al., 2006). Similarly to active ST systems, the high thermal conductivity of metals is counterbalanced by a poor corrosion resistance and the high weight. Hence, polymers have the potential to be better alternative materials (Lang et al., 2016). Certain polymers, such as polyethylene, polypropylene, polyvinylchloride, and polyamide are already used in DHW pipework (Lenel & Mudd, 1984). However, polymeric materials must be proven to have sufficient strength and long-term durability, adequate thermal resistance, and high aging resistance against UV and water (Smyth et al., 2006).

Glass fiber reinforced polyamides (PA-GF) have shown a reliable performance in the automotive industry. There they are constantly in contact with different fluids and exposed to elevated temperatures and humidity (Thomason J., 2007). Recently, reinforced PA grades were introduced into the production of solar-thermal collectors (SCOOP, 2012). In terms of DHW systems, reinforced polyamide is typically used as an endcap of ICS conventional steel pipe based absorbers or as components of all-polymeric absorber/storage-tanks (Fischer et al., 2016). Different glass fiber reinforced plastics were investigated to select suitable materials for the absorber/storage tank. Nevertheless, short glass fiber reinforced polyamide grades with 30% fiber content (PAGF30) were proven to have the most promising potential for this particular application (SCOOP, 2014).

**Absorber materials for pumped DHW systems**

As mentioned above, active solar water heating (SWH) systems are more complicated than passive systems, since they require a functional pump, a controller, sensors and a heat exchanger. Nonetheless, the solar-thermal collector is the major component of the SWH system and the central subject of research on this application (Kalogirou, 2004). Flat plate collectors are mainly
used for DHW applications, because of their suitable service temperature range, as well as their ease of manufacturing and the ability to efficiently absorb the solar irradiation from all directions, which give them an advantage over other collector types (Kessentini et al., 2014).

The development of all-polymeric solar-thermal collectors (Fig. 2.6) has been the main subject of extensive research projects for several years (Piekarczyk et al., 2016). In contrast to polymeric absorbers, conventional metal absorbers are prone to internal and external corrosion. Nevertheless, the thermal conductivity and the operating temperature range of metals (e.g., copper and aluminum) surpass those of polymers (Shukla et al., 2013). Therefore, determination of the expected range of the operating and stagnation temperatures is of utmost importance for a proper material selection for a particular solar-thermal absorber (Koehl et al., 2012). Additionally, overheat protection measures have to be implemented, such as back cooling, ventilation, and thermotropic switching for commodity plastics, as well as drain-back setups for engineering plastics (Ramschak et al., 2015).

Fig. 2.6: Eco-FLARE™ all-polymeric solar-thermal collector developed by Magen eco-Energy (SHC, 2011). An overheating controlled (OHC) glazed polymeric collector with a maximum operating pressure of 1.5 bar had already been developed in the collaborative research projects SolPol-1 and SolPol-2 (Lang et al., 2013). Furthermore, a black pigmented PP grade with a carbon black content of 0.8% and β-spherulitic structures was found as a potentially suitable absorber material for OHC systems. This material grade was particularly developed for hot water pipe fittings and was extensively characterized in SolPol-1/2 (Wallner et al., 2016).

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1 Stagnation temperature in performance testing of solar-thermal collectors is used as a reference to the maximum temperature the collector can reach with a stagnant fluid (Wikipedia, 2017)
2.2 Environmental Effects on Polymeric Materials

A service life of 20 years is required for solar-thermal collectors (Koehl et al., 2012). Polymeric solar-thermal absorbers are constantly exposed to elevated temperatures and to various surrounding media, such as air, potable water, or heat carrier fluids. Hence long-term stability under such conditions is essential (Kahlen et al., 2010; Povacz et al., 2016). Therefore, a comprehensive knowledge of the different aging mechanisms is of an utmost importance to maintain a long-term stability over a prolonged service life (Kahlen et al., 2010).

Various studies have been conducted to provide a better understanding of the long-term stability of polymeric materials under service conditions. The following section will present some of these studies and briefly discuss their results.

2.2.1 Effect of different media on polymeric materials

Polymers, in general, are susceptible to thermo-oxidative degradation, which is caused by complex reactions with oxygen at high temperatures leading to undesirable changes in the material properties (Celina, 2013; Beißmann et al., 2013). To minimize degradation, stabilizer packages against different forms of oxidative-degradation are usually added to the polymer before compounding (Dörner & Lang, 1998). Therefore, a proper identification of the suitable stabilizer system and the required concentrations is decisively important (Beißmann et al., 2013). A commonly used approach to analyze the thermo-oxidative degradation of polymers is by correlating chemical degradation to the mechanical properties of the material. Usually, polymeric materials are exposed to oxygen-rich environments to accelerate the aging process. Afterwards, mechanical and thermomechanical test methods are performed to quantify the changes in the material properties (Richaud et al., 2008; Beißmann et al., 2013; Schoeffl et al., 2014; Povacz, 2014; Geretschläger, 2015).

Polypropylene

Polypropylene (PP) is a commodity thermoplastic that belongs to the polyolefin class. In most commercial production processes, PP is polymerized at low pressure using Ziegler-Natta catalysts (Fig. 2.7) (Ebewele, 2000).

\[
\text{Propylene} \quad \xrightarrow{\text{Ziegler-Natta polymerization}} \quad \text{Polypropylene}
\]

Fig. 2.7: Polymerization reaction for the production of polypropylene (PP) (Carter, 2004).
Higher isotacticity usually indicates enhanced mechanical properties. Metallocene catalysis is another possibility to produce PP with an additional range of tacticities and structures (Sperling, 2005). Most of the commercial PP grades are isotactic with an intermediate to a high degree of crystallinity and a melting temperature of about 165 °C. In many aspects, polypropylene is similar to polyethylene, especially in their electrical properties and their solution behavior. The mechanical and thermal properties of PP are improved by the presence of the additional methyl group (CH₃), whereas the chemical resistance is decreased to a certain extent. The orientation of the chains increases the crystallinity of PP, which in turn improves the mechanical properties of the material. Concerning chemical properties, at room temperature polypropylene is resistant to all organic solvents except strong oxidants and has a good chemical resistance to a variety of chemicals at relatively high temperatures. Polypropylene is also a nonpolar polymer, hence it has a good moisture resistance. However, the solvent absorption of PP increases at elevated temperatures (Ebewele, 2000; Tripathi, 2002). Table 2.1 shows some of the essential properties of a polypropylene pressurized pipe grade.

Table 2.1: Typical property values of PP random copolymer for pressure pipe systems based on the datasheet of Polypropylene RA130E-6017, Borealis AG (Borealis, 2008).

<table>
<thead>
<tr>
<th>Material Properties</th>
<th>Typical Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>905</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Flexural modulus</td>
<td>800</td>
<td>MPa</td>
</tr>
<tr>
<td>Tensile modulus (1 mm/min)</td>
<td>900</td>
<td>MPa</td>
</tr>
<tr>
<td>Tensile stress at yield</td>
<td>25</td>
<td>MPa</td>
</tr>
<tr>
<td>Tensile strain at yield</td>
<td>13.5</td>
<td>%</td>
</tr>
<tr>
<td>Charpy notched impact strength (RT)</td>
<td>20</td>
<td>kJ/m²</td>
</tr>
<tr>
<td>Charpy notched impact strength (-20 °C)</td>
<td>2</td>
<td>kJ/m²</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.24</td>
<td>W/mk</td>
</tr>
</tbody>
</table>

The long-term behavior of polypropylene is governed by its resistance to the thermo-oxidative degradation (Richaud et al., 2008). Various studies have been conducted to characterize the long-term stability of PP using different accelerated aging methods and to ensure that such material can maintain the required durability under the imposed environmental conditions of solar-thermal applications (Beißmann et al., 2013; Grabmayer, 2014; Povacz, 2014). Polypropylene is insensitive to water exposure especially under low pressure and at low temperatures. However, several studies investigate the aging behavior of PP in hot water, because the thermo-oxidative degradation is usually observed under the exposure to high temperatures and oxygen, which is present in both, air and water. Fig. 2.8 illustrates the thermo-oxidative aging mechanism over time.
Kahlen et al., (2010) discussed the applicability of certain commodity plastics as solar-thermal absorbers. The focus of the study was to characterize the aging behavior of four different semi-crystalline polyolefins, including two polypropylene grades, in hot water at 80 °C for up to 16,000 h (maximum operating conditions) and in hot air at 140 °C for up to 500 h (stagnation conditions). Differential scanning calorimetry (DSC) and tensile tests were performed on two PP grades (random copolymers), which were stabilized using the same stabilizer package that comprises phenolic and phosphitic antioxidants. The results of this study showed that both PP types have the potential to be an excellent absorber material, particularly, for OHC systems in northern climates where stagnation temperatures are fairly low.

Another study was conducted by Povacz et al., (2016) to understand the degradation processes of black-pigmented polypropylene under service relevant conditions of solar-thermal applications. Since carbon black (CB) has a high UV-resistance, two carbon black based polypropylene block copolymer types were investigated. One type is widely used for unglazed solar collectors (2 vol.-% CB), while the other is a heterophasic copolymer that was, particularly, developed for hot-water pipe fittings (0.8 vol.-% CB). The researchers of this study based their analysis on different aging variables, such as the remaining primary stabilizer content, carbonyl index, oxidation temperature, and ultimate mechanical properties. Hence, DSC, DMA, and basic tensile tests were performed on the aged specimens, after they were conditioned in air and heat carrier fluid (60 vol.-% deionized water and 40 vol.-% propylene glycol) at 95 °C, 115 °C and 135 °C for up to 15,000 h. For both grades, a high efficiency of solar absorption was observed (96%). Furthermore, the oxidation temperature and the stabilizer content of the PP grade with lower carbon content decreased faster. Nevertheless, the long-term mechanical performance of this grade exhibited a superior stability, which makes it a better alternative as an absorber material. Two important conclusions of this study should be noted:
the aging behavior of PP is highly dependent on the stabilizer system and its interactions with carbon black.

- the exposure to hot air is more severe than the exposure to the heat carrier fluid. This is probably attributed to the lower content of dissolved oxygen and the triazole-based corrosion inhibitors in the heat carrying mixture.

**Polyamide**

Polyamide (PA) is an engineering thermoplastic. PA66, an often used PA grade, is produced by polycondensation of hexamethylene-diamine with adipic acid, see Fig. 2.9 (Ebewele, 2000).

![Polymerization reaction for the production of PA66](image)

**Fig. 2.9**: Polymerization reaction for the production of PA66 (Ebewele, 2000).

PA is one of the most versatile engineering polymers that can be used for numerous applications. Various PA grades are available on the markets with a diverse range of properties (e.g., PA6, PA66). For technical applications, a reinforcement with short glass fibers (GF) is usually added to PA to improve its mechanical behavior (Clavería et al., 2016). Short glass fiber reinforced PA is widely used due to its high strength-to-weight ratio and its high processability using injection molding to produce complex components (Arif et al., 2014). Table 2.2 shows the important properties of PA66-GF30.

Polyamides are hygroscopic materials that absorb moisture from its surrounding by up to 8%. In terms of mechanical performance and heat resistance, short fiber reinforced PA66 is an excellent composite material (Thomason & Ali, 2009). However, when polyamides are exposed to a hydrothermal environment, the polymer chains are displaced, because of the water uptake, resulting in swelling, reduction in mechanical performance, and irreversible hydrolytic decomposition. The imbalanced fiber-matrix volume expansion deteriorates the fiber-matrix interfaces (Arif et al., 2014). Moreover, the mechanical properties of the glass fibers are directly affected by leaching of alkali oxides that leads to surface micro-cracks. This is more evident in deionized water, due to its solute-free nature (Maxwell et al., 2005; Geretschläger, 2015).
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The water absorption occurs in polyamide thermoplastics due to hydrogen bonds. It primarily occurs in the amorphous region as the water molecules interact with the polar amide groups leading to weak hydrogen bonds, thus higher chain mobility (Monson et al., 2008). Experiments show that in aliphatic PA, α-amino-methylene are mainly affected by oxidation due to the weakened C–H bonds (Richaud et al., 2013). The thermo-oxidative degradation of polyamides is a complicated process that leads to the development of unstable hydroxyl compounds, hence the formation of aldehyde, carboxylic acid, carbonyl, or cyclic structures (Geretschläger & Wallner, 2016).

Thomason & Ali (2010) studied the effect of hydrothermal aging on aliphatic PA66 (reinforced and unreinforced). The specimens were conditioned in a water-glycol mixture at 70 °C for up to 400 h. Both dry and conditioned specimens were tested using dynamic mechanical analysis (DMA) and unnotched Charpy impact tests. This study reported pronounced changes in the weight, dimensions, and the thermomechanical behavior of the material due to the hydrothermal conditioning in a water-glycol solution. An increase in weight and dimensions were detected in all samples. Nonetheless, in reinforced samples, the empirical liquid uptake was much lower than what was expected from a polymer/composite content scaling. On the one hand, DMA results showed a marked decrease in the glass transition temperature of the saturated specimens.

### Table 2.2: The essential properties of PA66-GF30 based on the datasheet of Akulon® S223-G6 from DSM Engineering Plastics (CAMPUS, 2017).

<table>
<thead>
<tr>
<th>Material Properties</th>
<th>Typical values (dry/conditioned)</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile modulus</td>
<td>9500/7500</td>
<td>MPa</td>
</tr>
<tr>
<td>Stress at break</td>
<td>190/140</td>
<td>MPa</td>
</tr>
<tr>
<td>Strain at break</td>
<td>3/5</td>
<td>%</td>
</tr>
<tr>
<td>Charpy notched impact strength (RT)</td>
<td>12/20</td>
<td>kJ/m²</td>
</tr>
<tr>
<td>Charpy notched impact strength (-30 °C)</td>
<td>12/20</td>
<td>kJ/m²</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>260/-</td>
<td>°C</td>
</tr>
<tr>
<td>Water absorption</td>
<td>6/-</td>
<td>%</td>
</tr>
<tr>
<td>Humidity absorption</td>
<td>1.6/-</td>
<td>%</td>
</tr>
<tr>
<td>Density</td>
<td>1360/-</td>
<td>kg/m³</td>
</tr>
</tbody>
</table>
significant reduction in the storage modulus was also observed in the range 0-40 ºC due to water-glycol uptake. On the other hand, the fluid absorption markedly increased the storage modulus in sub-ambient range. At room temperature, all conditioned samples showed a similar behavior where the modulus continuously decreased by increasing conditioning time and absorption level.

Geretschläger & Wallner (2016) used a pressure cooker test (PCT) method to investigate the accelerated aging behavior of a heat-stabilized glass fiber reinforced polyamide 66 grade (PA66-GF30 H) in different media. The test was performed in air and deionized water. The results of this research showed that the material properties were drastically affected by the exposure to hot water. In the initial phase, because of the hygroscopic behavior of PA, swelling and mass gains were detected. A significant drop in E-modulus and tensile strength of approximately 40% and a reduction by over 75 ºC in the glass transition temperature were detected after exposing the material to deionized water for 24 h at 80 ºC. Further exposure to hot water led to a progressive degradation of the mechanical properties, degradation of the surface finish quality, and crack development due to material dissolution in water. In contrast, initial exposure to hot air reduced the material mass, because of the loss of moisture content in the material. Consequently, the stiffness and the strength of the dry material increased by 6% and 20%, respectively.

2.2.2 Chlorinated water and its effect on polymeric materials

In many regions of the world, a special water treatment is required to ensure that tap water fulfills the safety standards of drinking water. According to the world health organization (WHO), chlorine is, by far, the most widely used and the most affordable water disinfectant due to its ease of use and high efficiency against all different kinds of waterborne pathogens (WCC, 2008; WHO, 2011). The WHO set the limit to chlorine content in drinking water at 5 ppm (mg/L), so that the chlorinated water does not pose any risk to people’s health (WCC, 2008).

In many applications, such as pipes, purification membranes and pump parts, polymeric materials (e.g., PP, PE, and PA) are routinely in contact with chlorinated water and exposed to chlorine induced degradation (Dam & Ogilby, 2001). Therefore, additional requirements are imposed on the long-term mechanical performance of these polymers upon the exposure to hot potable water (Koehl et al., 2012). Freeman et al., (2005) reported that chlorine and pH in potable water play a secondary role, besides water and elevated temperatures, creating a more oxidative environment that can chemically attack the polymer chains causing a reduction in the mechanical properties. In thick components, the chemical degradation may occur only at the surface maintaining the mechanical properties longer (Gedde et al., 1994).

Effect of chlorine on polyolefins

Most of the available research on this topic focused on the oxidation of polymer pipes (e.g., PE) upon the exposure to potable water (Koehl et al., 2012). Freeman et al., (2005) classified relevant
polymeric materials for solar-thermal systems based on an experimental evaluation of the mechanical performance in hot chlorinated water. Polysulfone (PSU), polybutylene (PB), and polyamide 66 (PA66) were examined in this study. Each of these three polymers has a different molecular structure and exhibits a distinct aging behavior in hot potable water (Scott, 1999). PSU proved to have the best resistance against molecular degradation, because of the aromatic rings in its polymer chain and the strong carbon, sulfur, and oxygen bonds in its backbone chain. PB was stabilized with an antioxidant package. Hence, no significant changes in the mechanical properties were detected, at least, until the stabilizer was totally depleted. PA exhibited the worst performance with a significant reduction in the mechanical properties. However, this loss was mainly attributed to the water absorption, because approximately 85% of the mechanical strength was recovered after drying the specimens. Up to now, not a lot of the available research provides a comprehensive study that can extensively describe the physical and chemical degradation mechanisms of polymers under the operating condition of solar-thermal applications (Kahlen et al., 2010; Povacz M., 2014).

Hassinen et al., (2004) described the aging behavior of a PE-HD pipe grade upon the exposure to chlorinated water at elevated temperatures. The material was stabilized with a package of phenolic and phosphitic antioxidants. Based on a modeling study, Dear & Mason (2001) previously suggested that chlorine would chemically consume the stabilizers. Additionally, a reduction in the molecular mass, as well as small axial cracks, were observed in the specimens. These cracks could, of course, trigger a crack propagation through the whole thickness leading to ultimate failure (Dear & Mason, 2001). Hassinen et al., (2004) measured the oxidative induction time (OIT) using DSC method to determine the loss of stabilizer over exposure time. The results were consistent with those of Dear and Mason as they showed a rapid consumption of the antioxidants by the oxidative action of chlorinated water. Moreover, a pronounced polymer degradation was observed on the unprotected surface of the specimen (i.e., inner wall). This degradation was restricted to the amorphous regions of the semi-crystalline thermoplastic.

A different approach to investigate the effects of chlorinated water on a black-pigmented PP pipe grade was introduced by Fischer et al., (2016). The fatigue crack growth (FCG) resistance of cracked round bar (CRB) specimens was characterized under near service conditions of solar-thermal applications. Tests were carried out using a special test setup (superimposed mechanical-environmental test), which was primarily developed in a previous research (Schoeffl et al., 2014) and further adapted. Four different media, air, deionized water, ionized water, and chlorinated water, at two different temperatures (80 °C, 95 °C) were considered to adequately account for the operating conditions. On the one hand, increasing the temperature in general results in a reduction in the FCG resistance. On the other hand, the effect of different environmental media was more complex as the material exhibited worse performance in air at 95 °C compared to the other liquid
media. Whereas at 80 °C the air measurements show a better FCG resistance than that of chlorinated water.

**Effect of chlorine on polyamides**

Polyamide is known for being susceptible to free chlorine, which is present in chlorinated water (Dam & Ogilby, 2001). Therefore, polyamide chlorination has been the subject of numerous research studies, in order to provide a better understanding of the degradation mechanisms. According to literature, three main chemical changes may occur in PA upon chlorination (Buch et al., 2008):

- formation of N–Cl group due to the chlorination of the amide groups (N–H)
- Orton rearrangement, Fig. 2.10
- direct chlorination of the aromatic ring of the diamine unit

![Orton rearrangement](image)

**Fig. 2.10:** Orton rearrangement after initial chlorination of the amide group in aromatic PA (Konagayak & Watanabe, 2000).

According to literature, aromatic polyamide is very sensitive to the chlorine induced oxidation, because of its aromatic diamine compound (m-phenylenediamine), which can easily be replaced by free chlorine (Glater et al., 1983). Konagayak & Watanabe (2000) measured the chlorine uptake of three different polyamides with distinct chemical structures. The aim of this study was to describe the relation between the chemical structure and the chlorine resistance of PA. It was found that the chlorine uptake strongly depends on the chemical structure of the polyamide as chlorine resistance is related to the basicity of the aliphatic and aromatic diamines. Consequently, polyamides can be classified based on their chlorine resistance with aliphatic or cyclo-aliphatic polyamides as best performers and aromatic polyamides as worst performer.

Aliphatic polyamides do not undergo Orton rearrangement. Though, it is believed that the chlorination of the amide groups forming N–Cl, which readily occurs in all polyamides, essentially leads to the polymer degradation (Dam et al., 2001). Buch et al., (2008) investigated the effects of chlorine/chlorinated water on an aromatic-cyclo-aliphatic polyamide thin film composite, which
is used as a skin layer for reverse osmosis membranes\(^2\). The main objective of this study was to characterize the chlorine resistance of the membrane and to prove whether the chlorination of the amide group can alone lead to the polymer degradation. They reported a proportional decrease in the water permeability of the membrane after the exposure to different chlorine concentrations for 1 up to 10 days. This was attributed to the increase in the hydrophobic character of the material due to the N–chlorination triggered by the reactions with free chlorine in the water (Koo et al., 1986). Moreover, splits in the peaks of the amide I (C=O) and the amide II (C−N−H) bands were observed on the IR-spectra upon the exposure to chlorinated water (Fig. 2.11). The intensity of this splitting increased with increasing the chlorine concentration and the exposure time. Based on the observations of Buch et al., (2008), the N–chlorination adversely affects the performance of PA, even in the absence of the other degradation mechanisms.

![IR Spectra](image)

**Fig. 2.11:** A comparison of the IR-Spectra of polyamide thin film composite membranes between (a) virgin membrane and (b) conditioned in 5 ppm chlorine for 72 hours (Buch et al., 2008).

### 2.3 Fatigue Tests and Fracture Mechanics Concepts

Fatigue tests have been used for several years for lifetime assessments of plastic components (e.g., pressurized polyolefin pipes), as well as for material ranking (Frank, 2010). This section provides a brief overview of the fundamentals of linear elastic fracture mechanics (LEFM) and their applications in polymer testing.

\(^2\) Reverse osmosis (RO) is a water purification technology that uses a semipermeable membrane to remove ions, molecules, and larger particles from drinking water (Wikipedia, 2017).
2.3.1 Fatigue of polymers

In general, fracture of a material undergoes two stages until the ultimate failure, crack initiation and crack propagation. Depending on the deformation mechanism, under cyclic loads many reasons can lead to the formation of cracks in polymers. Sliding the molecular chains or the fracture of one molecular chain can act as crack points and locally weaken the material. Crazes are formed under cyclic loads and serve as micro-cracks after they sufficiently grow. If a crack propagates, stress concentration near the crack tip initiates more crazing generating fatigue striations due to the plastic deformation at the crack tip (Rösler et al., 2007).

The service loads are rather complex and time-dependent. For simplicity purposes, investigations are usually restricted to representative cases, such as sinusoidal cyclic loading (Fig. 2.12). Cyclic loads are usually characterized by the minimum stress $\sigma_{\text{min}}$, the maximum stress $\sigma_{\text{max}}$, and the mean stress (Eq. 2.1) (Rösler et al., 2007).

$$\sigma_a = \frac{\sigma_{\text{max}} + \sigma_{\text{min}}}{2} \quad (2.1)$$

Another parameter used to characterize the fatigue cyclic load is the so-called R-ratio, which is the ratio of the minimum stress to the maximum (Eq. 2.2). Although a high R ratio can reduce the influence of residual stresses, it tends to increase the apparent toughness of the material. An R ratio of 0.1 is recommended for cyclic fatigue tests by various standards (Anderson, 2005).

$$R = \frac{\sigma_{\text{min}}}{\sigma_{\text{max}}} \quad (2.2)$$

![Typical sinusoidal cyclic load](image)

**Fig. 2.12**: Typical sinusoidal cyclic load (Rösler et al., 2007).

2.3.2 Linear elastic fracture mechanics

Fracture mechanics (FM) is a tool used to characterize materials and components by defining the state of stress in the field near a crack tip considering the energy release during crack propagation. Linear elastic fracture mechanics (LEFM) account only for existing cracks and consider them to
be infinitely sharp with a zero notch radius. The stress intensity factor $K$ is a control parameter that indicates the critical condition of a crack (Perez, 2004; Rösler et al., 2007).

In fracture mechanics, according to the orientation of the load to the crack plane, it can be differentiated between three characteristic fracture modes (Fig. 2.13). Mode I is often referred to as the opening mode, because the principal tensile stress is induced by a perpendicular load to the crack-plane leading to a symmetric opening. In modes II and III the crack does not open because it is loaded in shear instead of tension. In these two modes, the crack surfaces slide with friction upon the application of the load. Mode II is known as the sliding mode as the load is perpendicular to the crack-front leading to a separation of the crack surfaces. In mode III, which is known as tearing mode, a shear load is applied parallel to the crack front in the plane of the crack.

In most cases, these fracture modes do not occur individually, but rather simultaneously. However, mode I is of an utmost importance for most technical applications, since it is assumed to govern the crack growth as it propagates under low loads (Lang, 1997; Rösler et al., 2007).

![Fig. 2.13: Illustration of the fracture modes in fracture mechanics (Rösler et al., 2007).](image)

The use of LEFM was initially restricted only to brittle materials. However, it was proven that it can also be used for ductile materials if the following criteria are fulfilled (Rösler et al., 2007; Lang, 1984):

- polymers with linear-elastic material behavior
- small deformation at the crack tip
- minimized residual stress effects

The propagation rate of a crack determines the fatigue life of a material by analyzing the growth of a macroscopic crack under cyclic loads (Rösler et al., 2007). According to LEFM, two methods can be used to investigate the fatigue crack growth. The first method is energy based and it considers the strain energy release ($G$) as the main parameter. The other approach investigates the stress field in the vicinity of the crack tip using the stress intensity factor ($K$) as the key parameter (Hertzberg, 1996).
The fatigue crack growth under cyclic loads occurs at low loads leading to a relatively small plastic zone near the crack tip. Consequently, the above-mentioned criteria of LEFM are fulfilled, thus the stress intensity factor can sufficiently describe the stress field (Rösler et al., 2007; Anderson, 2005). In this method, a crack is considered to be infinitely sharp with a zero notch radius leading to an infinite stress concentration at the crack tip. Therefore, the stress field attains singularity near the crack tip. According to the Griffith crack configuration, the material is assumed to be linear elastic and homogeneous, the stress field is described as plane stress, and the crack is loaded in mode I. Thus it is denoted as $K_I$ (Rösler et al., 2007). The stress intensity factor $K_I$ depends on the external stress and the crack size, and it can be calculated by equation (2.3), where $\sigma$ is the nominal stress, $a$ is the crack length and $Y$ is a dimensionless quantity for geometry correction (Hertzberg, 1996; Rösler et al., 2007).

$$K_I = \sigma \sqrt{\pi a Y} \quad (2.3)$$

The plastic zone is assumed to be a circular area with a radius $r_p$ next to the crack tip (Fig. 2.14). There are two methods to estimate the size of the plastic zone, the Irwin approach, and the strip yield model. While the strip yield model gives a better resemblance of the plastic zone shape in metals, the Irwin approach is considered to be more suitable for polymers. The Irwin approach estimates the elastic-plastic boundary using the elastic stress analysis (Anderson, 2005). While equation 2.4 gives a second-order estimate of the plastic zone size in plane stress conditions, in-plane strain yielding is suppressed by the triaxial stress state (Eq. 2.5), thus the plastic zone is smaller by a factor of 3 (Anderson, 2005), where $K_I$ is the stress intensity factor is and $\sigma_{YS}$ is the yielding stress.

$$r_p = \frac{1}{\pi} \left( \frac{K_I}{\sigma_{YS}} \right)^2 \quad (2.4)$$

$$r_p = \frac{1}{3\pi} \left( \frac{K_I}{\sigma_{YS}} \right)^2 \quad (2.5)$$

Furthermore, a certain threshold stress (critical stress) is required in order for the crack to open under cyclic loads. This value corresponds to a value $K_{op}$ of stress intensity factor below which the crack does not propagate. This value depends on the material itself, the $R$-ratio and the maximum stress, (Fig. 2.15). Usually, the cyclic loads are described by the cyclic stress intensity factor $\Delta K (K_{max} - K_{min})$ and the $R$ ratio and the crack propagation occurs when the threshold of the fatigue crack growth ($\Delta K_{th}$) is exceeded (i.e., when $K_{max} = K_{op}$) (Anderson, 2005; Rösler et al., 2007).
Fig. 2.14: Illustration of the stress distribution by the distance from the crack tip considering the first- and second-order estimates of the plastic zone size ($r_y$ and $r_p$, respectively) (Anderson, 2005).

Fig. 2.15: Illustration of the opening and the fatigue crack growth thresholds (Rösler et al., 2007).

The cyclic stress intensity factor $\Delta K$ is plotted against the fatigue crack growth (FCG) rate ($da/dN$) in a double logarithmic plot (Fig. 2.16). The FCG rate follows the widely known Paris law equation, which was introduced by Paris and Erdogan (Eq. 2.6), where $m$ and $A$ are material constants (Anderson, 2005; Rösler et al., 2007; Lang, 2016).

$$\frac{da}{dN} = A.\Delta K^m$$  \hfill (2.6)

On this plot, we can differentiate between three distinct regions. In region I, $\Delta K$ exceeds the FCG threshold triggering a stable crack propagation through region II where the FCG rate shows a linear relation with $\Delta K$. In region III, the maximum stress intensity factor $K_{max}$ approaches the
fracture toughness $K_{IC}$ leading to unstable crack propagation, large-scale plastic deformation, and eventually to ultimate failure (Rösler et al., 2007; Lang, 2016). Furthermore, a shift to higher $\Delta K$ values indicates a better material performance, because of the decrease in the FCG rates $da/dN$ at a given $\Delta K$, thus a higher FCG resistance (Bradler et al., 2017).

Fig. 2.16: The relation between the fatigue crack growth rate and the cyclic stress intensity factor representing a typical fatigue crack growth behavior (Lang, 2016).
3 EXPERIMENTAL

This chapter provides a general overview of the test program, followed by the information on materials investigated, specimen types and specimen preparation. Finally, a concise description of the test equipment and the applied test methods is provided.

3.1 Test Program

The test program consisted of several analytical and technological testing methods. For ranking purposes, both materials were mainly characterized using the superimposed mechanical-environmental fatigue tests. This test method was mainly performed to characterize the fracture mechanical performance of the materials upon the exposure to chlorinated water with various chlorine concentrations at elevated temperatures. Furthermore, analytical test methods were performed to provide a better understanding of the material behavior in these conditions. These test methods included chlorine depletion and water uptake, differential scanning calorimetry (DSC), Infrared (IR) spectroscopy. Finally, the fracture surfaces of the specimens were characterized using optical microscopy. The test program is shown in Fig. 3.1.

<table>
<thead>
<tr>
<th>Specimen conditioning</th>
<th>Infrared-Spectroscopy</th>
<th>Differential scanning calorimetry</th>
<th>Stereomicroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyamide (PA)</td>
<td>Polyamide (PA)</td>
<td>Polypropylene (PP)</td>
<td>Polyamide &amp; Polypropylene</td>
</tr>
<tr>
<td>Chlorine (Cl) depletion</td>
<td>Chemical changes upon Cl-exposure</td>
<td>Oxidative induction time (OIT)</td>
<td>Fracture surfaces</td>
</tr>
<tr>
<td>Water uptake</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Analytical Characterization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen conditioning</td>
</tr>
<tr>
<td>Polyamide (PA)</td>
</tr>
<tr>
<td>Chlorine (Cl) depletion</td>
</tr>
<tr>
<td>Water uptake</td>
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<tr>
<td>Infrared-Spectroscopy</td>
</tr>
<tr>
<td>Polyamide (PA)</td>
</tr>
<tr>
<td>Chemical changes upon Cl-exposure</td>
</tr>
<tr>
<td>Differential scanning calorimetry</td>
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<tr>
<td>Polypropylene (PP)</td>
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<tr>
<td>Oxidative induction time (OIT)</td>
</tr>
<tr>
<td>Stereomicroscopy</td>
</tr>
<tr>
<td>Polyamide &amp; Polypropylene</td>
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<tr>
<td>Fracture surfaces</td>
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</table>

<table>
<thead>
<tr>
<th>Performance Characterization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Superimposed mechanical-environmental test</td>
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<tr>
<td>Chlorine content (ppm)</td>
</tr>
<tr>
<td>Polypropylene</td>
</tr>
<tr>
<td>Polyamide</td>
</tr>
<tr>
<td>Temp. 80 °C</td>
</tr>
<tr>
<td>Specimen type</td>
</tr>
<tr>
<td>Cracked round specimen (CRB)</td>
</tr>
<tr>
<td>Compact-type specimen (CT)</td>
</tr>
</tbody>
</table>

Fig. 3.1: Illustration of the test program.
3.2 Materials

The tests were performed on two material types, polypropylene (PP) and short glass fiber-reinforced polyamide 66 (GF-PA66). Three different grades of each material were investigated in this thesis including one commercial type of each material as a benchmark and two other grades with different stabilizer packages.

Polypropylene

The PP materials included the commercial black-pigmented block copolymer grade and two homopolymer-based PP grades that were stabilized with two different stabilizer packages. The commercial black-pigmented PP BA160E is a heterophasic copolymer grade provided by Borealis (Austria). For the other two material grades, a homopolymer PP grade (Ineos Compound AG, Switzerland) was used as a base material. These two grades were stabilized with two different stabilizer packages. The first type was stabilized with an ultraviolet (UV) stabilizer (Brenntag Austria GmbH, Austria). Whereas, the other type was stabilized with the UV-stabilizer and an antioxidant (BASF Group, Germany). An overview of the material designation and stabilizer types is provided in Table 3.1.

Table 3.1: Material designation of the PP grades.

<table>
<thead>
<tr>
<th>Material designation</th>
<th>Base material</th>
<th>Stabilizer type</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP_C</td>
<td>Black-pigmented block copolymer</td>
<td>Commercial</td>
</tr>
<tr>
<td>PP_U</td>
<td>Homopolymer</td>
<td>Ultra violet (UV) stabilizer</td>
</tr>
<tr>
<td>PP_AU</td>
<td>Homopolymer</td>
<td>Antioxidant &amp; UV-stabilizer</td>
</tr>
</tbody>
</table>

Glass fiber reinforced polyamide 66

The commercial aliphatic PA grade Zytel 450 HSL (DuPont de Nemours International S.A, Switzerland) with a glass fiber content of 30% was used as a benchmark and base material for the other two grades. Two different stabilizer packages were added to the base material due to a pre-manufactured masterbatch in the injection molding process with varying stabilizer type. The stabilizer packages were provided by Gabriel Chemie, Austria. The first masterbatch included a supporting material and a phenolic-based stabilizer (Brüggolen H164). Whereas, the second masterbatch consisted of a supporting material and amino-based stabilizers (Irganox 1098 and Stabilisator 9000). An overview of material designation and composition is shown in Table 3.2.

Table 3.2: The material designation of PA grades including and composition.

<table>
<thead>
<tr>
<th>Material designation</th>
<th>Zytel 450 HSL</th>
<th>Supporting material</th>
<th>Brüggolen H164</th>
<th>Irganox 1098</th>
<th>Stabilisator 9000</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAGF30_C</td>
<td>100 m%</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PAGF30_P</td>
<td>90 m%</td>
<td>9 m%</td>
<td>1 m%</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PAGF30_A</td>
<td>89.5 m%</td>
<td>9 m%</td>
<td>—</td>
<td>0.5 m%</td>
<td>1 m%</td>
</tr>
</tbody>
</table>
3.3 Specimen Preparation

Initially, specimens were produced for the cyclic fatigue tests with the specified geometries for each material type. Cracked round bar (CRB) specimen for polypropylene and compact-type (CT) specimen for glass fiber reinforced polyamide. Subsequently, after the specimens were aged in chlorinated water at 80 °C, different specimen types for other characterization methods were produced out of them.

3.3.1 Cracked round bar specimen for PP

The CRB specimen production consisted of the two stages plate production and specimen production (machining).

Plate production

The three polypropylene grades were provided as granules. Consequently, plates with the dimensions (100mm × 100mm × 15mm) were produced by the compression molding with the machine P200T (Vogt Maschinenbau GmbH, Germany) with a maximum load of 200 kN.

The polymer granules were filled into the mold and were pre-compressed at 20 bar in order to degas the mold. Meanwhile, the mold was heated up from room temperature to 210 °C, whereby the melting process started. Then the applied pressure was increased to 28 bar and held for 10 min. After 10 min, the pressure was increased again to 80 bar and kept for 5 min. Subsequently, the pressure increased to 100 bar and the mold was cooled down to room temperature with a cooling rate of about 30 K/min.

Additionally, the real pressure on the mold surface was calculated by equation 3.1, where $A_1$ is the surface area of the machine cylinder (D=80 mm) and $A_2$ is the surface area of the mold. An overview of the compression molding parameters is provided in Table 3.3.

$$P_2 = P_1 \cdot \frac{A_1}{A_2} \quad (3.1)$$

Table 3.3: Overview of the compression molding process parameters for the production of PP plates.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Pressure (bar)</th>
<th>Real pressure (bar)</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degassing</td>
<td>20</td>
<td>10</td>
<td>23 up to 210</td>
<td>-</td>
</tr>
<tr>
<td>Holding 1</td>
<td>28</td>
<td>14</td>
<td>210</td>
<td>10</td>
</tr>
<tr>
<td>Holding 2</td>
<td>80</td>
<td>40</td>
<td>210</td>
<td>5</td>
</tr>
<tr>
<td>Cooling</td>
<td>100</td>
<td>50</td>
<td>23</td>
<td>17</td>
</tr>
</tbody>
</table>

Specimen production

The CRB specimens for the cyclic fatigue test were produced from the plates. A disc saw type Precisio CS 70 EB-set (Festool GmbH, Germany) was used to cut the plates into smaller
rectangular bars, which were thereafter turned on the lathe EMCOMAT-14D (EMCO Maier GesmbH, Hallein, Austria) to produce the round pre-finished specimens. After the round bars were produced a notch was introduced to the specimens by a tailor-made cutting tool using the same turning machine. The dimensions of the final CRB-specimen are given in Fig. 3.2.

![Fig. 3.2: Selected dimensions of the CRB specimen (Pinter et al., 2007).](image)

3.3.2 Compact-type specimen for PAGF30

Similar to the polypropylene, polyamide was provided as granules. Plates were produced at the Institute of Polymer Injection Molding and Process Automation (JKU-Linz, Austria) using the injection molding machine (ENGEL Victory 60). Consequently, the compact-type (CT) specimens were produced by machining at the Institute of Polymeric Materials and Testing (JKU-Linz, Austria) by the milling machine EMCO Mill E600 (EMCO Maier GesmbH, Austria) with the dimensions shown in Fig. 3.3. In order to accelerate the crack initiation, an additional notch with a depth of approximately 1 mm was introduced into the specimen using a razor blade. Afterwards, all CT specimens were pre-conditioned in chlorinated water at 80 °C before the cyclic fatigue test, as explained in section 3.4.1 in order to test saturated specimens.

![Fig. 3.3: Selected dimensions of the CT specimen.](image)
3.4 Test Methodology

The following sections provide a comprehensive overview of all the testing methods and testing equipment, as well as data evaluation routines that were used in this thesis.

3.4.1 Chlorine depletion and water uptake

These two tests were mainly performed to determine the parameters and the time span for specimen pre-conditioning of the polyamide (PA) specimens. As mentioned in the previous section, PA is a hygroscopic material that absorbs moisture from its surrounding by up to 8%. Therefore, the water uptake of the three different PA grades had to be measured at the test temperature in order to define the required time until the saturation is reached. However, a significant reduction in chlorine content in chlorinated water is usually observed. According to literature, a loss of around 40% of the chlorine content in chlorinated water can be observed at room temperature (23 °C) after 24 h (Haas et al., 2002). Moreover, increasing the water temperature accelerates the chlorine decay rates (Kirsch et al., 1994). Therefore, in order to pre-condition the specimens properly under test-like conditions, the chlorine depletion rate and the chlorine residual had to be measured to determine the time intervals for changing the water and perform the specimen conditioning accordingly. The chlorine residual in both tests was measured using a photometer of the model Prominent Dulcotest DT1B (Prominent Group, Germany) with special reagents for this model.

**Chlorine depletion**

This measurement consisted of two parts. In the first part, one liter of chlorinated water with 5 ppm chlorine content and a pH of 6.9 (± 0.1) was stored for 24 hours in a laboratory oven (Binder, Germany) at 80 °C. The chlorine residual was measured every hour for the first 12 h to determine the chlorine depletion rate and the time interval for changing the water. Then another measurement was taken at the end of the 24 hours to determine the total loss of the chlorine content after 24 h at 80 °C. Afterwards, in the second part, the same measurement was repeated at the same temperature. However, in this part, PA specimens were soaked in the chlorinated water with two different chlorine contents (5 ppm, 10 ppm) to check the influence of the material on the chlorine depletion.

**Water uptake**

It was mentioned in a previous study (Schläger, 2015) that the water absorption rate of PA increases with the temperature. Thus, PA specimens were soaked in deionized water and chlorinated water with chlorine contents corresponding to the cyclic fatigue test conditions. Then they were stored in a laboratory oven at 80 °C for seven days. According to the chlorine depletion measurement, a time interval of 12 h was set to change the chlorinated water and measure the weight gain in the specimens. The specimens’ weights were measured using a laboratory precise
scale of the type KERN PLS 720-3A (KERN & SOHN GmbH, Germany). The water uptake was calculated as the difference between the initial mass and the measured mass.

3.4.2 Infrared spectroscopy

IR spectroscopy was used to assess the chemical aging in the material due to the exposure to chlorine at elevated temperatures. Both materials were tested using IR-spectroscopy, but only the polyamide grades showed some changes due to the exposure to chlorinated water. The test was performed at 23 °C according to the standard ISO 10640 (2011) on a Perkin Elmer spectrum100 IR equipment with an ATR unit for solid samples (Perkin Elmer, USA), (see Fig. 3.5a). Samples of all three material grades were tested including samples of virgin material and pre-conditioned samples in deionized water and chlorinated water (7 days at 80 °C ) with two different chlorine contents (5 ppm, 10 ppm).

3.4.3 Differential scanning calorimetry

Based on the differential scanning calorimetry (DSC) measurements the oxidative induction times (OIT) of the polypropylene specimens were measured after the exposure to various chlorine contents at 80 °C. The samples were taken from the aged CRB specimens after conducting the cyclic fatigue tests. The measurements were performed on a DSC equipment of the model PerkinElmer DSC 4000 (Perkin Elmer, USA) with a heating rate of 10 K/min (Fig. 3.5b).

The test procedure followed the ISO standard ISO 11357-6 (2008). Around 8 mg were taken from each specimen, placed into an aluminum pan and then covered by an aluminum lid. Nitrogen was used during the preheating stage, which was performed up to 200 °C for the materials PP_U and PP_AU and 210 °C for the commercial type PP_C. Afterwards, the DSC data was plotted with the heat flow as the Y-axis and time as the X-axis, then OIT was determined as shown in Fig. 3.4.

![Fig. 3.4: Determination of oxidative induction time (OIT).](image-url)
3.4.4 Fatigue tests at different chlorine contents

The fatigue tests for both materials were carried out on a linear-torsion electro-dynamic testing machine ElectroPlus E10000 (Instron, USA). Both, the CRB and the CT specimens were loaded under a linear sinusoidal loading with a fixed loading frequency of 10 Hz. The data acquisition was done by the software WaveMatrix (Version 1.5.6, Illinois Tool Works Inc.), which was provided by the machine manufacturer. The R-ratio was set to R=0.1, for all cyclic fatigue tests.

In order to test the materials simultaneously under mechanical and environmental loads, the superimposed mechanical-environmental test setup was used, which was primarily developed in previous related research (Schoeffl et al., 2014; Fischer et al., 2016). The main objective of implementing this test setup is to test the material under service-near conditions in different environments including air and liquid media. However, the focus of this study was only the medium chlorinated water at an elevated temperature. A schematic illustration of the test setup is shown in Fig. 3.6. This test setup consisted of a tailor-made containment (Fig. 3.6b), in which the specimens were mounted on the machine by a specific clamping system for each specimen type. Within the containment, the specimens were being constantly exposed to chlorinated water, with the specified chlorine contents, at 80 °C. The test setup was equipped with a chlorine control unit (Fig. 3.7) through which a constant flow of chlorinated water was directly provided to the containment. Moreover, in order to keep the temperature constant at 80 °C throughout the whole measurement, the containment was well insulated by a foam case and connected to a compatible heating and cooling system produced by (Peter Huber Kältemaschinenbau AG, Germany) and a thermometer. Furthermore, the test setup was equipped with a camera Baumer LXG-120M (Baumer Holding AG, Switzerland) for image acquisition. The image analysis and the crack length measurement was done with the software Vision Builder (VDM2013 National Instruments, USA).
Fig. 3.6: Schematic illustration of the superimposed mechanical-environmental test: (a) CRB specimen, (b) CT specimen, (c) liquid media containment with different clamping systems, (d) the linear torsion electro-dynamic test machine equipped with an optical crack length measuring camera (Fischer et al., 2016).

Fig. 3.7: Chlorinated water test arrangement including a chlorine control unit.
Fatigue tests with CRB specimens

The clamping system of the CRB specimen allows the specimen to rotate $360^\circ$ in two directions with a minimum torque in order to measure the crack growth from different angles. While the specimen is rotating, the camera takes a set of 18 images at the maximum force after a fixed time interval, showing the crack opening from different angles (Freudenthaler, 2017). A light source (LED) was positioned opposite to the camera to allow a proper image evaluation and crack length measurement. This light source was only flashing during image acquisition to avoid overexposure due to constant illumination (Bradler, 2014). Subsequently, the crack length was measured on both sides by comparing the pixels of the crack with a known reference length. The specimen circumference was used as the reference point. Because of the accumulation of the released bubbles due to the water chlorination and the high temperature (Fig. 3.8), this had to be done manually.

![Image](image-url)

**Fig. 3.8:** Crack length measurement of CRB specimens.

Afterwards, the average crack lengths were calculated and used to plot the crack length versus the number of cycles curves, which were later on used for the calculation of the crack growth kinetics. However, all CRB specimens showed a slight crack growth at the beginning of measurement due to blunting followed by a constant crack size (Fig. 3.9). Hence, this region was neglected and the apparent initial crack length was used for the calculations of the FCG kinetics instead of the theoretical initial crack length in order to increase the accuracy of the measurement.

The cyclic stress intensity factor $\Delta K_I$ (Mpa.m$^{0.5}$) was calculated using the equation that was introduced by Benthem and Koiter in 1973 (3.2), where $a$ is the crack length in mm, $R$ is the outer radius of the specimen in mm, $\Delta F$ is the difference between the maximum and the minimum force.
in N, \( b \) is the radius of the remaining cross section, and \( f \left( \frac{b}{R} \right) \) is a non-dimensional correction function that can be determined according to equation 3.3 (Fig. 3.2) (Pinter et al., 2007).

\[
\Delta K_I = \frac{\Delta F}{\pi b^2} \cdot \sqrt{\frac{\pi a b}{R}} \cdot f \left( \frac{b}{R} \right) 
\]

(3.2)

\[
f \left( \frac{b}{R} \right) = \frac{1}{2} \cdot \left[ 1 + \frac{1}{2} \left( \frac{b}{R} \right) + \frac{3}{8} \left( \frac{b}{R} \right)^2 - 0.363 \left( \frac{b}{R} \right)^3 + 0.731 \left( \frac{b}{R} \right)^4 \right]
\]

(3.3)

**Fig. 3.9:** Crack length vs. the number of cycles of CRB specimens and the apparent initial crack length.

**Fatigue tests with CT specimens**

A different clamping system was used for the CT specimens (Fig. 3.10), which does not allow the rotation and keeps the specimen fixed at 0°. Hence, the camera only took an image of the front of the specimen at the maximum force after a fixed time interval. The specimen was illuminated from the same side as the camera using a constant light source that illuminates the front of the specimen. Afterwards, the acquired images were evaluated to determine the crack growth. The crack length was determined by measuring the distance between the crack tip and a known reference point, which was, in this case, the center of fastening bolt of the clamping system. The crack length values were directly used for the calculation of the crack growth kinetics.

The cyclic stress intensity factor \( \Delta K_I \) (Mpa.m\(^{0.5}\)) for a CT specimen was calculated according to the equation 3.4, where \( a \) is the crack length in mm, B is the thickness of the specimen in mm, \( \Delta F \) is the difference between the maximum and the minimum force in N and \( W \) is the width of the specimen in mm. \( f \left( \frac{a}{W} \right) \) is a non-dimensional correction function that can be determined according to equation 3.5 (Fig. 3.3).

\[
\Delta K_I = \frac{\Delta F}{B \sqrt{W}} \cdot f \left( \frac{a}{W} \right)
\]

(3.4)
\[ f \left( \frac{a}{W} \right) = \frac{(2 + \frac{a}{W})^{1.5}}{(1 - \frac{a}{W})^{2}} \cdot [0.886 + 4.64 \left( \frac{a}{W} \right) - 13.32 \left( \frac{a}{W} \right)^2 + 14.72 \left( \frac{a}{W} \right)^3 - 5.6 \left( \frac{a}{W} \right)^4] \]  

(3.5)

**Fig. 3.10**: Schematic illustration of the CT specimen clamping system (Anderson, 2005).

### 3.4.5 Characterization of fracture surfaces

The fracture surfaces of both CRB and CT specimens were characterized using optical microscopy. A stereomicroscope of the model Olympus SZX16 (Olympus, Austria), shown in Fig. 3.11, was used to determine the real crack length. The initial crack of all aged CRB specimens was measured by the software Stream-V1.9, which was provided by the device manufacturer (Olympus, Austria). For the CT specimens, the fracture surfaces exposed to the highest and the lowest chlorine contents (1 ppm, 10 ppm) were investigated. In addition, a general overview of the ductile and quasi-brittle regions of the fracture surface was obtained.

**Fig. 3.11**: Stereomicroscope, model Olympus SZX16 (Olympus).
4 RESULTS AND DISCUSSION

This chapter is divided into two main sections. Section 4.1 covers the results of the polypropylene grades including the oxidative induction time, the fatigue crack growth resistance, and the fracture surfaces of the CRB specimens. Section 4.2 presents the results of the glass fiber reinforced polyamide grades describing the chlorine residual and the water uptake followed by a description of the chemical changes in the material structure and finally the chapter is concluded with the fatigue crack growth resistance and the fracture surfaces of the CT specimens.

4.1 Polypropylene

The following sections present and discuss the results of the test methods used to characterize the effect of chlorinated water at an elevated temperature on polypropylene grades.

4.1.1 Oxidative induction time

DSC was used to estimate the consumption of the antioxidant in the materials upon the exposure to chlorine at 80 °C based on the oxidative induction time (OIT). Table 4.1 shows the aged CRB-specimens after being exposed to various chlorine contents. However, as explained in section 3.4.3, only samples of virgin materials and the 1 ppm and 10 ppm exposed specimens were used to prepare the DSC samples.

**Table 4.1**: Effect of various chlorine concentrations on the color of different PP grades.

<table>
<thead>
<tr>
<th></th>
<th>PP_C</th>
<th>PP_U</th>
<th>PP_AU</th>
</tr>
</thead>
<tbody>
<tr>
<td>virgin</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>Cl_1 ppm</td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>Cl_2.5 ppm</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
</tr>
<tr>
<td>Cl_5 ppm</td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
<tr>
<td>Cl_10 ppm</td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
<td><img src="image15.png" alt="Image" /></td>
</tr>
</tbody>
</table>

OIT values were determined as shown in Fig. 3.4. In general, a similar trend was observed in all three material grades as the OIT significantly decreased upon the exposure to 10 ppm compared to a slight decrease observed in the 1 ppm aged samples. See Fig. 4.1 and Table 4.2.
Fig. 4.1: Heat flow curves of virgin and aged specimens: (a) PP_C (commercial type), (b) PP_U (with UV-stabilizer), (c) PP_AU (with antioxidant and UV-stabilizer).

Though the aged PP_C specimens were exposed to 1 ppm and 10 ppm chlorinated water at 80 °C for 11 and 6 days (time of the cyclic fatigue test), respectively, the OIT of the 1 ppm specimen was almost double that of the 10 ppm specimen. Thus, it can be assumed that chlorine induced stabilizer depletion is more dependent on the chlorine content than the exposure time. The aged specimens of PP_U and PP_AU were exposed to the same environment for about 60-72 h (less than 3 days) and they showed a similar behavior as their OIT values decreased by 5-10% and 65-70% upon the exposure to 1 ppm and 10 ppm, respectively. These values can only give an estimation of the consumption of the antioxidants in these materials because the degree of degradation varies depending on the thickness of the exposed specimen. However, for PP_C the OIT value of the virgin material could not be determined because the virgin sample showed a flat profile. Thus, it is difficult to estimate the chlorine induced stabilizer depletion for this material grade.
Table 4.2: OIT values of virgin and aged specimens of the PP grades.

<table>
<thead>
<tr>
<th>Material</th>
<th>Sample</th>
<th>OIT values (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP_C</td>
<td>v_mat.</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>Cl_1 ppm</td>
<td>27.8</td>
</tr>
<tr>
<td></td>
<td>Cl_10 ppm</td>
<td>14.9</td>
</tr>
<tr>
<td>PP_U</td>
<td>v_mat.</td>
<td>26.6</td>
</tr>
<tr>
<td></td>
<td>Cl_1 ppm</td>
<td>23.3</td>
</tr>
<tr>
<td></td>
<td>Cl_10 ppm</td>
<td>8.9</td>
</tr>
<tr>
<td>PP_AU</td>
<td>v_mat.</td>
<td>23.1</td>
</tr>
<tr>
<td></td>
<td>Cl_1 ppm</td>
<td>22.2</td>
</tr>
<tr>
<td></td>
<td>Cl_10 ppm</td>
<td>6.6</td>
</tr>
</tbody>
</table>

4.1.2 Fatigue crack growth resistance

The superimposed mechanical-environmental tests were performed on CRB specimens to investigate the fatigue crack growth (FCG) resistance of different PP grades when exposed to chlorinated water at 80 °C. The curves of the crack length versus the number of cycles of the black-pigmented grade (PP_C) at various chlorine contents with illustrative images of the crack growth through the CRB specimen are shown in Fig. 4.2. It can be seen that the crack initiation was affected by the test environment. Although the test conditions remained unchanged and all specimens were taken from the same plate, the time to failure varied significantly at different chlorine contents around 6 days at 1 and 10 ppm and up to 12 days at 2.5 and 5 ppm. Therefore, it can be assumed that the crack initiation was affected by the test environment. Nevertheless, no clear correlation between the chlorine content and the number of cycles to failure was observed.

![Fig. 4.2: Crack length vs. the number of cycles of PP_C at various chlorine contents and 80 °C with illustrative images of the crack growth.](image-url)
The effects of the superimposed testing of this material at various chlorine contents are depicted in Fig. 4.3. Unexpectedly, the FCG resistance showed an inferior performance at lower chlorine contents as the FCG curves were shifted to higher \( \Delta K \) values with increasing the chlorine content. While the FCG curves of 1, 5, and 10 ppm had a comparable slope (slightly smaller at 1 ppm), a higher slope of the FCG was determined for 2.5 ppm chlorine content leading to an intersection with the other FCG curves. Furthermore, the FCG rate \( da/dN \) (at \( \Delta K=0.6 \) MPa.m\(^{0.5}\)) at 1 ppm was found to be enhanced by a factor of 3.9 compared to the FCG rate at 10 ppm.

![Fatigue crack growth kinetics of PP_C in chlorinated water at 80 °C.](image)

**Fig. 4.3:** Fatigue crack growth kinetics of PP_C in chlorinated water at 80 °C.

Figure 4.4 depicts the curves of crack length versus the number of cycles at various chlorine contents of the material grade PP_U. Again, it is clear that the test environment affects the crack initiation also in this material grade. Moreover, increasing the chlorine content tended to accelerate the material failure showing a non-linear relation between the chlorine content and the number of cycles. The number of cycles to failure decreased with increasing the chlorine content from 1 to 2.5 ppm and then to 5 ppm. However, the material showed a different behavior at 10 ppm as the failure occurred slower than at 2.5 and 5 ppm. Though, the number of cycles to failure at 10 ppm was lower than at 1 ppm.

The corresponding FCG kinetics curves are illustrated in Fig. 4.5. While the FCG growth curves at 1, 2.5, and 10 ppm showed comparable slopes, the FCG curve of 5 ppm had a smaller slope leading to an intersection with the FCG curves of the 2.5 ppm and 10 ppm curves. In general, the FCG curves at higher chlorine contents were shifted to higher \( \Delta K \) values indicating a superior performance. Consequently, the FCG rates at 2.5 ppm and 10 ppm were found to be reduced by a factor of 3.9 and 5, respectively, compared to the FCG rate at 1 ppm (at \( \Delta K=0.43 \) MPa.m\(^{0.5}\)).
Fig. 4.4: Crack length vs. the number of cycles of PP_U at various chlorine contents and 80 °C with illustrative images of the crack growth.

Fig. 4.5: Fatigue crack growth kinetics of PP_U in chlorinated water at 80 °C.

The curves of the crack length versus the number of cycles of the material grade PP_AU are shown in Fig. 4.6 with illustrative images of the growth from the right side of the crack. Compared to the other material grades, the crack initiation of this material grade showed a completely irregular behavior with the fastest crack initiation at 1 ppm and the slowest crack initiation at 2.5 and 5 ppm, which showed almost an identical behavior, while the crack growth curve at 10 ppm was positioned between 1 ppm and the other two chlorine contents. The material grade PP_AU showed a more regular behavior in the FCG kinetics curves (Fig. 4.7). A comparable slope of the FCG curves was observed at 1, 5, and 10 ppm, while the 2.5 ppm curve had a slightly higher slope leading to an intersection with the FCG curve of 5 ppm. Interestingly, the FCG curves of the 1 ppm
and 10 ppm exposed specimens overlapped showing a superior behavior compared to the other two chlorine contents as their FCG curves were shifted to higher $\Delta K$ values. However, a clear correlation between the chlorine content and the FCG kinetics can be observed at 1, 2.5, and 5 ppm as the FCG rate $da/dN$ was enhanced by a factor of, approximately, 3 at 2.5 and 5 ppm compared to 1 ppm (at $\Delta K=0.44$ MPa.m$^{0.5}$).

![Fig. 4.6](image)

**Fig. 4.6:** Crack length vs. the number of cycles of PP_AU at various chlorine contents and 80 °C with illustrative images of the crack growth.

![Fig. 4.7](image)

**Fig. 4.7:** Fatigue crack growth kinetics of PP_AU in chlorinated water at 80 °C.

A comparison between the three material grades at the four different test conditions is shown in Fig. 4.8. In general, the FCG resistance of the commercial type (PP_C) under all test conditions was significantly higher compared to those of the other material grades (PP_U and PP_AU). On the one hand, in terms of the slope, the two material grades PP_U and PP_AU showed a
comparable behavior under all test conditions. This can be attributed to the use of the same base material for both material grades. On the other hand, in terms of the FCG resistance, PP_U showed a similar behavior to PP_C with an improved performance when increasing the chlorine content. In contrast, PP_AU showed an inferior behavior when increasing the chlorine content to 2.5 and 5 ppm. Nevertheless, all three material grades showed an improved performance at 10 ppm.

![Graphs showing FCG kinetics of three PP grades at different chlorine contents](image)

**Fig. 4.8**: Comparison between FCG kinetics of the three PP grades at different chlorine contents at 80 °C.

In conclusion, the fracture mechanical behavior of PP under the exposure to chlorinated water at an elevated temperature remains ambiguous without providing a general behavior that can be in agreement with conventional test methods (e.g., the OIT measurements of the three PP grades). It is evident that the material is somehow affected by the environment, but no clear correlation between the chlorine content and the material performance could be observed. This could be because of several reasons. One of which is the geometry of the CRB specimens and the initial crack, which allowed for the accumulation of the released bubbles around the crack (see Fig. 4.2, Fig. 4.4, Fig. 4.6), thus creating a rather different surrounding environment than chlorinated water. In some specimens, this may have acted as an insulating ring around the crack leading to a delayed crack initiation. However, this hypothesis still needs further research to be proven.
4.1.3 Fracture surfaces

The main objectives of the microscopic images were to have a closer look at the fracture surfaces and to determine the variation in the real inner diameter from the machining parameters (D\textsubscript{in}=10.85 mm, a=1.6 mm) in order to measure the real initial crack lengths of the different aged specimens. Table 4.3 provides an overview of the fracture surface images and the real initial crack lengths.

**Table 4.3: Overview of the crack surface images and the real initial crack lengths.**

<table>
<thead>
<tr>
<th>Chlorine content</th>
<th>1 ppm</th>
<th>2.5 ppm</th>
<th>5 ppm</th>
<th>10 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PP_C</strong></td>
<td>![Images]</td>
<td>![Images]</td>
<td>![Images]</td>
<td>![Images]</td>
</tr>
<tr>
<td>Fracture surface</td>
<td>![Images]</td>
<td>![Images]</td>
<td>![Images]</td>
<td>![Images]</td>
</tr>
<tr>
<td>Initial crack (mm)</td>
<td>1.75</td>
<td>1.81</td>
<td>1.78</td>
<td>1.77</td>
</tr>
<tr>
<td><strong>PP_U</strong></td>
<td>![Images]</td>
<td>![Images]</td>
<td>![Images]</td>
<td>![Images]</td>
</tr>
<tr>
<td>Fracture surface</td>
<td>![Images]</td>
<td>![Images]</td>
<td>![Images]</td>
<td>![Images]</td>
</tr>
<tr>
<td>Initial crack (mm)</td>
<td>1.75</td>
<td>1.81</td>
<td>1.78</td>
<td>1.77</td>
</tr>
<tr>
<td><strong>PP_AU</strong></td>
<td>![Images]</td>
<td>![Images]</td>
<td>![Images]</td>
<td>![Images]</td>
</tr>
<tr>
<td>Fracture surface</td>
<td>![Images]</td>
<td>![Images]</td>
<td>![Images]</td>
<td>![Images]</td>
</tr>
<tr>
<td>Initial crack (mm)</td>
<td>1.75</td>
<td>1.81</td>
<td>1.78</td>
<td>1.77</td>
</tr>
</tbody>
</table>

The microscopic images show that all CRB specimens had, approximately, the same initial crack length. However, the real initial crack was bigger than the initial crack that was introduced into the specimens by machining. Another observation that could be seen on the microscopic images of the fracture surface of PP_C is a ring of a different color surrounding the fracture surfaces. This ring is a result of the accumulation of the released bubbles, which may have insulated the crack.
4.2 Glass Fiber Reinforced Polyamide

The following sections present and discuss the results of the test methods used to characterize the effects of chlorinated water at an elevated temperature on glass fiber reinforced polyamide.

4.2.1 Chlorine residual and water uptake

According to literature, a significant reduction in the mechanical performance of glass fiber reinforced polyamide is observed upon the exposure to hydrothermal condition (Arif et al., 2014). Hence, testing saturated specimens is of great importance especially that the absorber of the integrated collector storage, for which PAGF is used, is constantly in contact with potable water.

Since the tests are performed under the exposure to chlorinated water, in order to perform a proper conditioning in chlorinated water, the chlorine residual at elevated temperatures had to be measured first, because of the chlorine decay phenomenon as explained in section 3.4.1. Figure 4.9 shows the chlorine residual as a function of time in one liter of 5 ppm chlorinated water at 80 °C for 24 hours. A steep decline in the chlorine content was observed in the early hours leading to a reduction of around 50% in the first 5 hours. Then, the chlorine content slightly decreased showing a plateau for up to 12 hours. At the end of the measurement (after 24 h) the chlorine content decreased to less than 20%. Based on this observation a time interval of 12 hours was set for changing the water during the specimen conditioning.

![Fig. 4.9: Chlorine depletion as a function of time in a 5 ppm chlorinated water at 80 °C without specimens (WO).](image)

Figure 4.10 depicts a replication of the same measurement. However, this time the measurement was carried out with two different chlorine contents (5 ppm, 10 ppm) with one specimen of each PAGF30 grade immersed in the water container. As expected, the chlorine decay rate drastically
increased after adding the specimens to the chlorinated water. This measurement consisted of
three steps:
  o Step (1): virgin specimens were soaked in 5 ppm chlorinated water (5 ppm_US_phase 1).
  o Step (2): the same specimens from step (1) were used again.
  o Step (3): saturated specimens that had been in the chlorinated water with 10 ppm chlorine
content for 7 days at 80 °C (10 ppm_S).

All the three measurements showed a similar behavior as the chlorine content dropped to less
than 5% in less than 4 h in the first two steps and in about 6 h in the third step.

![Graph showing chlorine depletion as a function of time at 80 °C for 5 ppm and 10 ppm chlorinated water; without (WO) specimens and with unsaturated (US) and saturated (S) specimens.](image)

**Fig. 4.10:** Chlorine depletion as a function of time at 80 °C for 5 ppm and 10 ppm chlorinated water; without (WO) specimens and with unsaturated (US) and saturated (S) specimens.

This means that chlorine depletion is highly dependent on the water temperature as only a loss of
40% can be detected after 24 h at room temperature (Haas et al., 2002), while this loss was
doubled by increasing the temperature to 80 °C. Furthermore, PA does not only absorb the
chlorine with the water, but it rather reacts with the free chlorine in the chlorinated water. It is,
however, hard to define a chlorine saturation point, because even with the saturated specimen
and after 8 days of systematic changing of the chlorinated water, the chlorine content drastically
decreased showing a similar trend to the steps (1) and (2).

After the chlorine depletion rate was determined, specimens of the three material grades were
placed for 7 days in containers filled with deionized water and chlorinated water with different
chlorine contents at 80 °C to determine the water absorption and the saturation point. The
chlorinated water was replaced every 12 h due to the loss of the chlorine content. The water
uptake was calculated by comparing the measured mass to the initial mass for each case.
Figure 4.11 shows the water uptake as a function of time for all PAGF30 grades in deionized water
(Cl_0 ppm) and chlorinated water with 5 and 10 ppm chlorine content at 80 °C.
Fig. 4.11: Water uptake as a function of time at 80 °C in deionized water and chlorinated water.

All three materials reached the saturation point after around 80 h as the mass started to increase slightly showing a plateau in the second half of the test. The water uptake varied depending on the material grade with approximately 3.7%, 4.2% and 4.5% in PAGF30_C, PAGF30_P, and PAGF30_A, respectively. Though the addition of chlorine to the water did not affect the water absorption as all material grades showed almost an identical behavior under the three test conditions, it did, however, affect the optical properties of the material as the specimens’ color changed with increasing the chlorine content in the water, see Table 4.4.

Table 4.4: Change in the specimen color upon the exposure to various chlorine contents at 80 °C for 7 days.
It can be concluded that, in contrast to aromatic polyamides (Buch et al., 2008), the hydrophobic behavior of the aliphatic polyamides, which are characterized in this study, does not increase upon the exposure to chlorine. Consistent with prior research (Konagayak & Watanabe, 2000), this can be attributed to the dependence of chlorine resistance on the chemical structure of the material, leading to a higher chlorine resistance in aliphatic PA grades.

4.2.2 Infrared spectra

All specimens were placed in water (deionized, chlorinated water) for 7 days at 80 °C. Fig. 4.12 shows the IR-spectra of the three material grades.

![IR spectra of virgin and aged specimens in deionized and chlorinated water: (a) PAGF30_C, (b) PAGF30_P, (c) PAGF30_A.](image)

A widening of the N–H stretching peak at 3260 cm\(^{-1}\) can be seen clearly in the IR spectra of all material grades due to the exposure to water (deionized and chlorinated). Additionally, a shift in the transmittance of the aged materials can also be seen, which can be explained by the change in the color of the materials (Fig. 4.13). The IR spectra of the virgin materials show strong amide-I and amide-II bands at 1630 cm\(^{-1}\) and 1522 cm\(^{-1}\), respectively (Charles et al., 2009). These two
bands are characteristic for amides, because of their constant position and high intensity. According to (Silverstein et al., 2005; Buch et al., 2008), they are prone to chlorination when exposed to chlorine, even at low concentrations. Fig. 4.13 shows the IR spectra within the range of the amide groups.

![IR spectra of amide groups](image)

**Fig. 4.13:** IR spectra of virgin and aged specimens deionized and chlorinated water within the range 600-1800 cm⁻¹: (a) PAGF30_C, (b) PAGF30_P, (c) PAGF30_A.

According to Buch et al., (2008), the peaks of the amide groups were split upon the exposure to chlorine (even to 1 ppm for 24 h) due to the chlorination of the amide groups (Fig. 2.11). However, this could not be observed in the IR spectra of the PAGF30 grades characterized in this thesis. This can be attributed either to the stabilizer packages that were added to the material, or to the high chlorine resistance of the aliphatic chemical structure of the examined polyamides.

### 4.2.3 Fatigue crack growth resistance

The fatigue crack growth (FCG) resistance of different glass fiber reinforced polyamide grades with a fiber content of 30% (PAGF30) was investigated using the superimposed mechanical-environmental fatigue test. CT specimens were prepared as explained in section 3.3.2 and then
they were conditioned in chlorinated water with various chlorine contents at 80 °C as explained in section 4.2.1. The maximum load varied depending on the material grade with 300, 310, and 330 N for PAGF30_A, PAGF30_P, and PAGF30_C, respectively.

Figure 4.14 illustrates the curves of the crack length versus the number of cycles of the commercial type (PAGF30_C) at various chlorine contents. It is evident that the crack initiation was affected by the chlorinated water environment. Additionally, the material showed a linear correlation between the number of cycles to failure and the chlorine content as the fracture occurred faster at higher chlorine contents.

Fig. 4.14: Crack length vs. the number of cycles of PAGF30_C at various chlorine contents at 80 °C with illustrative images of the crack growth in the CT specimen.

In the corresponding FCG curves of PAGF30_C (Fig. 4.15), a compatible behavior was observed with an enhanced fatigue crack growth resistance at lower chlorine contents. The FCG curve of the 1 ppm exposed specimen was shifted to higher ΔK values indicating a higher FCG resistance compared to the other specimens. The three FCG curves had comparable slopes with a slightly smaller slope at 1 ppm leading to an intersection with the FCG curve of the 5 ppm specimen at the beginning. Moreover, the FCG rate da/dN was found to be enhanced by a factor of 1.9 and 4.8 at 5 ppm and 10 ppm, respectively, compared to 1 ppm (at ΔK=3 MPa.m⁰.⁵).

In terms of the crack initiation and the number of cycles to failure, a similar behavior to that of the commercial type was observed for the other two material grades (PAGF30_P, PAGF30_A) (Fig. 4.16). Increasing the chlorine content in the chlorinated water markedly accelerated the crack initiation process leading to a lower number of cycles to failure at higher chlorine contents.
In terms of the FCG kinetics, PAGF30_P showed a similar behavior to that of PAGF30_C with the superior performance at 1 ppm and the worst performance at 10 ppm (Fig. 4.17a). However, the impact of the chlorine content on the material performance was less effective with the 1 ppm specimen being slightly shifted to higher $\Delta K$ values and the FCG rate at 10 ppm was enhanced only by a factor of 1.8 compared to 1 ppm (at $\Delta K=2.35$ MPa.m$^{0.5}$). On the other hand, increasing the chlorine content in the chlorinated water did not affect the FCG kinetics of PAGF30_A significantly. Though no shift to higher $\Delta K$ was observed with increasing the chlorine content, a slight decrease in the slope can be seen upon the exposure to higher chlorine contents (Fig. 4.17b). This leads to the conclusion that increasing the chlorine content in the chlorinated water affects the crack initiation in these two material grades, but it does not significantly influence the fatigue crack propagation.
Fig. 4.17: The fatigue crack growth kinetics in chlorinated water at 80 °C: (a) PAGF30_P, (b) PAGF30_A.

Figure 4.18 shows a comparison between the FCG kinetics of the three material grades at the three different chlorine contents.

Fig. 4.18: Comparison between the three PAGF30 grades at different chlorine contents at 80 °C.
It can be seen that at 1 ppm the commercial type (PAGF30_C) showed a superior FCG resistance compared to the other material grades. However, once the chlorine content was increased, the FCG resistance of the commercial type dropped to overlap with the FCG curve of the PAGF30_A at 5 ppm and then it was shifted to lower \( \Delta K \) at 10 ppm. This reflects a high sensitivity to chlorine induced oxidation. In contrast, the material grade PAGF30_A showed the most stable behavior with only slight fluctuations in the slope. This can be attributed to the amino-based stabilizer package used in this material grade. Furthermore, at 10 ppm the FCG rate of PAGF30_C and PAGF30_P was enhanced by a factor of 3.2 and 2.5, respectively, compared to that of PAGF30_A (at \( \Delta K=2.59 \) MPa.m\(^{0.5}\)).

These results are in a good agreement with the data of the conventional aging methods (Konagayak & Watanabe, 2000; Dam & Ogilby, 2001; Buch et al., 2008) as they showed that the increasing chlorine content in the chlorinated water affects the material performance negatively in terms of the crack initiation and the FCG resistance.

### 4.2.4 Fracture surfaces

The main objective was to check the initial crack of the different aged specimens and to have a closer look at the fracture surface. Only the fracture surfaces of the highest and the lowest chlorine contents (1 ppm, 10 ppm) were investigated. Table 4.5 provides an overview of the fracture surface images.

**Table 4.5:** Overview of the fracture surface images at two different chlorine contents.

<table>
<thead>
<tr>
<th>Material</th>
<th>Fracture surface</th>
<th>Scale: 2 mm</th>
<th>Chlorine content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAGF30_C</td>
<td><img src="image1" alt="Fracture surface image" /></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>PAGF30_C</td>
<td><img src="image2" alt="Fracture surface image" /></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>PAGF30_P</td>
<td><img src="image3" alt="Fracture surface image" /></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>PAGF30_P</td>
<td><img src="image4" alt="Fracture surface image" /></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>PAGF30_A</td>
<td><img src="image5" alt="Fracture surface image" /></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>PAGF30_A</td>
<td><img src="image6" alt="Fracture surface image" /></td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>
It can be seen that in all three material grades the brittle regions were larger at the higher chlorine content, which may reflect an embrittlement effect due to the higher chlorine content. However, this may require more sophisticated test methods to prove it. Furthermore, only slight variations in the introduced initial crack lengths of the CT specimens were observed.
5 SUMMARY AND CONCLUSIONS

The main objective of this thesis was to investigate the influence of the chlorine content in chlorinated water at an elevated temperature on the fatigue crack growth (FCG) resistance of polypropylene (PP) and glass fiber reinforced polyamide (PAGF30) used for solar-thermal systems. For ranking purposes, tests were performed on three different grades of each material including a commercial grade as benchmark and two other material grades stabilized with different stabilizer packages.

The PP grades included a commercial black-pigmented block copolymer grade (PP_C) and two homopolymer-based PP grades stabilized with different stabilizer packages. While the first material grade was stabilized with a UV-stabilizer (PP_U), the other material grade was stabilized with an antioxidant and a UV-stabilizer (PP_AU).

For the polyamide, a commercial aliphatic PA grade with glass fiber content of 30% was used as benchmark and as base material for the other two material grades. Both material grades were stabilized with antioxidant packages. On the one hand, the first material grade was stabilized with a phenolic-based stabilizer package. On the other hand, the other material grade was stabilized with an amino-based stabilizer package.

Both materials were mainly characterized using the superimposed mechanical-environmental test. While for the PP grades the cracked round bar (CRB) specimen was used, the compact type (CT) specimen was used for the glass fiber reinforced PA. All tests were conducted in chlorinated water with varying chlorine contents at 80 °C. In addition, further analytical test methods were performed to provide a better understanding of the influence of the chlorine on the material properties, including water absorption of PA, IR spectroscopy, DSC, and fracture surfaces characterization.

The broken CRB specimens of the PP grades were characterized by DSC in order to estimate the stabilizer depletion upon the exposure to chlorinated water at an elevated temperature. The tests were performed on virgin material and specimens exposed to the lowest and the highest chlorine content, namely 1 and 10 ppm. Though the exposure time varied sometimes, all three material grades showed a similar behavior as the OIT values dropped significantly (up to 70%) upon the exposure to 10 ppm, while only a slight decrease was observed at 1 ppm. This leads to the conclusion that chlorine accelerates the stabilizer depletion and the stabilizer consumption is more dependent on the chlorine content than the exposure time.

In the cyclic fatigue tests of PP, all three grades showed that the crack initiation of the CRB specimen is clearly affected by its surrounding. However, no clear correlation between the chlorine content and the number of cycles to failure could be observed. In terms of the FCG resistance, the PP_C and PP_U grade showed a superior FCG resistance at higher chlorine contents. Whereas the PP_AU grade showed a superior behavior at 1 and 10 ppm compared to 2.5 and
5 ppm. In general, PP_C revealed a superior FCG resistance compared to the other material grades under all test conditions, which is consistent with previous research. Nevertheless, due to some difficulties in the test execution (i.e., the accumulation of the released bubbles around the crack), the effect of chlorine content in the chlorinated water on the FCG resistance of the material remains ambiguous without providing a clear tendency.

Since polyamide is a hygroscopic material that has a high water uptake of up to 8%, specimen preconditioning was required in order to test saturated specimens. Specimen preconditioning consisted of two steps, chlorine depletion and the water uptake of the glass fiber reinforced polyamide grades in chlorinated water with various chlorine contents at 80 °C. The chlorine depletion was proven to be highly dependent on the water temperature as it dropped to less than 20% after 24 h, while according to literature it drops to around 60% at room temperature. Based on the chlorine depletion measurement, a time interval of 12 h was set for changing the water during the water uptake test. In order to measure the water uptake of the material, specimens were placed in deionized water and chlorinated water with various chlorine contents at 80 °C for 7 days. All materials showed a similar behavior in both deionized water and chlorinated water, which means that chlorine does not affect the water uptake of aliphatic polyamide.

Subsequently, IR spectroscopy was performed on virgin specimens and the saturated specimens to investigate the chemical changes in the material. Nevertheless, no significant changes were observed due to the exposure to chlorinated water.

In the cyclic fatigue tests, the crack initiation of the three material grades was clearly affected by the surrounding media. Additionally, a linear correlation between the number of cycles to failure and the chlorine content was observed. In terms of the FCG resistance, both the PAGF30_C and the PAGF30_P grades showed comparable slopes with a superior FCG resistance at lower chlorine content and more enhanced FCG rates at higher chlorine contents. On the other hand, PAGF30_A, stabilized with the amino-based stabilizer, showed the most stable behavior with only slightly different slope at various chlorine contents.

The results of this thesis provide a better understanding (1) of the influence of the chlorinated water at an elevated temperature on polypropylene and glass fiber reinforced polyamide used for solar-thermal systems and (2) of the superimposed mechanical-environmental test method. Further studies are required to investigate the chemical reactions between the free chlorine in the chlorinated water and polymeric materials. Concerning the superimposed mechanical-environmental test, further developments are required to avoid the accumulation of the bubbles around the crack of the CRB specimens in order to increase the accuracy of the test results.
6 REFERENCES


