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Migration of bisphenol A from polycarbonate plastic of different qualities

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Migration of Bisphenol A from polycarbonate plastic of different qualities

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Foreword

Bisphenol A (BPA) is included in the Danish Environmental Protection Agency's List of Undesirable Substances (LOUS) as it is i) included in the EU list of potential endocrine disrupting substances in category 1, ii) classified for reproductive toxicity in category 2 and iii) the substance has political focus.

Bisphenol A is used as a monomer in production of polycarbonate plastic (PC) for different applications. Many studies have examined release of BPA from PC and especially the focus has been on BPA release from food contact materials and consumer products to estimate the level of human BPA exposure from these sources.

The present survey was decided by the Danish EPA with the aim to study the potential correlation between quality and chemical composition of PC on release of BPA from the material.

The study was performed during September 2013 - December 2014 at the Technical University of Denmark (DTU) by Gitte Alsing Pedersen, DTU National Food Institute and Søren Hvilsted DTU Danish Polymer Centre, Department of Chemical and Biochemical Engineering. The final editing of the report was made by Jens Højslev Petersen, DTU National Food Institute.

A focus group was formed representing producers of PC and PC consumer products as well as Danish trade associations, the Danish Consumer Council and retailers of PC food contact materials and consumer products. The aim of the focus group was to discuss and give comments to the project plan and to the final project report.

Conclusion and Summary

Polycarbonate (PC) is a thermoplastic used for several applications including consumer products covering food contact materials, toys, and medical devices. The plastic is characterised by its good physical properties such as transparency, high mechanical strength and good thermal stability. Bisphenol A (BPA) is a monomer used in the production of PC and, as with all polymers, a certain migration of the non-polymerised residual monomer can occur from the material over the lifetime of the article or product. This has been shown by several studies. Other studies have examined the stability and degradation of PC when exposed to different environmental conditions and chemical agents showing that PC is sensitive to UV light, humidity, temperature variations, some additives (e.g. TiO₂) and non-intentionally added substances (impurities) which can all induce degradation of the polymer.

This study covers a review of literature and available industry information regarding release of BPA from PC and the parameters affecting this BPA release. Moreover in part two of the study, different samples of PC was characterised and analysed in order to examine the potential correlation between material specific parameters and the release of BPA.

A summary of the literature review, part 1 of the project, is given below:

The release of BPA from PC is explained by two different mechanisms: 1) Diffusion controlled release of residual BPA and 2) hydrolysis/degradation of the polymer at the surface of the material followed by an increase in BPA migration and in polymer surface area.

In general the diffusion rate of BPA in PC is very low. However, it is mentioned that small differences seen in the glass transition temperature, T_g , in different PC qualities could be a way to predict if the polymers have different BPA diffusion rates as T_g and diffusion rate has been shown to inversely proportional in a given polymer.

Release of BPA from PC in contact with food simulants is positively correlated with temperature (T) and time (t) of contact. At lower temp (e.g. 0 -70 °C) the BPA release is slow and controlled by the diffusivity in the bulk of the dense polymer.

PC is sensitive to hydrothermal effects. Release of BPA originating from hydrolytic degradation of the polymer is found to be positively correlated to an increase in pH (alkaline conditions). Moreover, impurities and amines in the polymer will accelerate hydrolysis in combination with the T and t. The long term release of BPA from PC is primarily due to degradation of the polymer rather than diffusion. This seems to be the case especially at high temperature (~ 100 °C).

PC may be sensitive to environmental stress cracking, ESC, when exposed to alkaline chemical agents and mechanical stress. The effect of general ageing of the material is not concluded in literature.

PC is sensitive to UV light which makes the polymer degrade. The presence of chromophores as e.g. dyes and pigments is found to increase the process of photodegradation. Also metallic contaminants and other impurities (non-intentionally added substances, NIAS) of the commercial

starting substances can accelerate the photodegradation process. To improve the UV properties of the material, UV stabilisers are added.

It is concluded, from industry information, that only highly pure reagent grade chemicals, including additives, should be used for all PC grades to reduce photodegradation and hydrothermal degradation of the polymer.

From the experimental part of the project, part 2, the following was concluded:

The levels of residual BPA in the 12 polycarbonate samples included in the survey (8 samples of food contact materials, 3 samples received from the plastics industry intended for either food contact, medical applications or toys and one DVD sample) were 5-80 µg/g which is in accordance with the residual BPA levels reported by others.

The migration from all of the samples into the food simulant water (exposed 1 hour at 100 °C) were all within the same range and below 3.1 µg/dm² corresponding to a level < 30 µg/kg simulant. All samples were well below the specific migration limit (SML) of 600 µg/kg for food contact materials (FCM). Again the results were comparable with the migration levels reported for PC used for FCM in the literature.

No correlation was found between the level of residual BPA and the level of BPA migration into water (1 hour at 100°C).

Five of the samples that have been subjected to the extreme exposure conditions (up to 14 days at 90 °C at alkaline conditions)) showed:

- A much increased release of BPA compared to the migration results. The level of released BPA differs significantly between the samples.
- For three of the samples the accumulated amount of released BPA was much above the residual level of BPA monomer indicating that a significant degradation of the polymer at the material surface takes place due to hydrothermal effects.
- Two samples (PC glass and DVD) had a very low BPA release indicating more hydrothermally stable materials compared to the other samples tested. Unfortunately, these differences between samples could not be explained by the techniques applied in this study.
- A remarkable and significant almost 20% decrease in both types of molecular weight M_w and M_n) was seen for all the polymers tested. This was indicating a degradation of the PC polymer in all samples. However no difference was seen in the polydispersities (M_w/M_n) indicating that the degradation products are formed at the surface of the product and removed from there into the test solution.
- No significant change in T_g for samples after extreme exposure conditions into water at high temperature and alkaline conditions.

Recording of infrared spectra (FTIR), measurements of T_g , M_w , and thermal degradation of the samples showed no significant differences between the samples. Moreover the measured parameters did not correlate well to the different levels of released BPA from the samples after extreme exposure conditions. In conclusion the applied techniques were not adequate to predict the level of BPA release from the given samples.

It is assumed that material composition parameters and process conditions such as listed below can have a main influence on depolymerisation of PC.

At meetings with industrial contacts during this project it was confirmed that to avoid depolymerisation certain material composition parameters and process conditions should be taken in consideration:

- Use dry polymer material prior to injection molding of PC
- Use adequate process conditions such as choice of correct temperature in the injection molding process
- Use of pure starting substances and additives in the production of PC

Furthermore special attention should be paid to amines, TiO₂ and glass fibers used in PC as the addition of such substances may increase the level of residual BPA and/or release of BPA due to partial decomposition of the polymer. Sample PC₃, analysed after hydrothermal exposure in this study and containing the additive TiO₂, showed the highest release of BPA.

No specific information was found about additives known to improve the hydrolytic stability of PC.

Konklusion og sammenfatning

Polycarbonat (PC) er en termoplast der anvendes til flere applikationer, herunder forbrugerprodukter, fødevarekontaktmaterialer, legetøj og medicinsk udstyr. Plasten er kendetegnet ved sine gode fysiske egenskaber, såsom gennemsigtighed, høj mekanisk styrke og god termisk stabilitet. Bisphenol A (BPA) er en monomer, som bruges i produktionen af PC, og som med alle polymerer, kan en vis migration af den ikke-polymeriserede restmonomer forekomme fra materialet i løbet af produktets levetid. Dette er blevet vist ved adskillige undersøgelser. Andre undersøgelser omhandler stabiliteten og nedbrydning af PC, når den udsættes for forskellige miljøforhold og kemiske stoffer. Dette viser, at PC'en er følsom over for UV-lys, fugtighed, temperatursvingninger, nogle tilsætningsstoffer (f.eks. TiO_2) samt ikke bevidst tilsatte stoffer (urenheder), som kan alle inducere nedbrydning af polymeren.

Denne undersøgelse omfatter en gennemgang af litteratur og tilgængelige oplysninger fra industrien om frigivelse af BPA fra PC og de parametre, der påvirker denne BPA udgivelse. Desuden blev forskellige prøver af PC karakteriseret og analyseret for at undersøge den potentielle sammenhæng mellem materiale-specifikke parametre og afgivelsen af BPA.

Et resumé af litteraturgennemgangen, Del 1 af projektet, er angivet nedenfor:

Frigivelsen af BPA fra PC forklares ved to forskellige mekanismer: 1) Diffusionskontrolleret frigivelse af restindhold af BPA i PC og 2) hydrolyse / nedbrydning af polymeren i overfladelaget som giver anledning til et forøget overfladeareal, efterfulgt af en stigning i BPA afgivelsen.

Generelt er diffusionshastigheden af BPA i PC meget lav sammenlignet med i de fleste andre almindelige plasttyper. Imidlertid er det nævnt, at de små forskelle i glasovergangstemperatur, T_g , der kan ses i forskellige PC kvaliteter, kan være en måde at forudsige, om polymererne har forskellige diffusionshastigheder for BPA. T_g og diffusionshastigheden har vist sig at være omvendt proportionale i en given polymer.

Frigivelse af BPA fra PC i kontakt med fødevarsimulatorer er positivt korreleret med temperaturen (T) og - kontakttiden (t). Ved lavere temperatur (op til 70 °C) er BPA frigivelsen langsom og kontrolleret af diffusiviteten i den tætte polymermasse.

PC er følsom over for hydrotermiske påvirkninger. Frigivelsen af BPA, som stammer fra hydrolytisk nedbrydning af polymeren i overfladen, findes at være positivt korreleret med en stigning i pH (basiske betingelser). Desuden vil tilstedeværelsen af urenheder og aminer i polymeren fremskynde hydrolysen i kombination med høj T og lang t. Set over en længere tidsperiode dominerer afgivelse af BPA, som stammer fra PC nedbrydningen, i forhold til den diffusionsbetingede migration af restmonomer. Dette synes især at være tilfældet ved høj temperatur (~ 100 °C).

PC kan være følsomme over for miljøbetinget spændingskorrosion, ESC, når de udsættes for basiske stoffer og mekanisk stress. Litteraturen giver ikke et klart billede af aldringens betydning for PC.

PC er følsom overfor UV-lys, hvilket gør, at polymeren nedbrydes. Man har fundet, at tilstedeværelsen af chromoforer såsom f.eks. farvestoffer og pigmenter øger fotonebrydningen. Også metalliske stoffer og andre urenheder (ikke bevidst tilsatte stoffer, NIAS) af kommercielle

udgangsstoffer kan accelerere fotonedbrydningen. For at forbedre materialets modstandsdygtighed kan UV-stabilisatorer tilsættes.

Ud fra informationer fra industrien kan det konkluderes, at for at reducere fotonedbrydning og hydrotermisk nedbrydning af polymeren mest muligt, bør der anvendes meget rene udgangsstoffer, herunder tilsætningsstoffer, ved fremstilling af PC til alle formål.

Fra den eksperimentelle del af projektet, Del 2, kunne følgende konkluderes:

Restmonomer-indholdet af BPA i de 12 polycarbonat prøver, der indgik i undersøgelsen (8 forskellige fødevarerkontaktmaterialer, en enkelt DVD-prøve og 3 prøver fra plastindustrien bestemt til kontakt til fødevarer, medicinske anvendelser eller legetøj) lå på 5-80 µg/g, hvilket er i overensstemmelse med BPA niveauer rapporteret af andre.

Migrationen til fødevarer-simulator vand fra samtlige prøver (efter eksponering 1 time ved 100 °C) lå på et ensartet lavt niveau under 3,1 µg /dm², svarende til under 30 µg/kg simulator. Migrationen lå således langt under den specifikke migrationsgrænse på 600 µg/kg for kontakt med fødevarer. Igen var resultaterne sammenlignelige med litteraturredata om migration fra PC, der anvendes til fødevarerkontaktmaterialer.

Der blev ikke fundet nogen korrelation mellem niveauet af BPA restmonomer og niveauet af BPA migration til vand (1 time ved 100 °C).

Fem af prøverne blev udsat for ekstreme eksponeringsbetingelser (op til 14 dage ved 90 °C i basisk vand). Resultaterne viste:

- En stærkt forøget afgivelse af BPA i forhold til hvad man så i migrationstesten. Niveauet af frigjort BPA varierede betydeligt mellem prøverne.
- For tre af prøverne var den akkumulerede mængde frigjort BPA meget højere end hvad der kan forklares med restmonomerindholdet. Dette indikerer, at der fandt en betydelig nedbrydning af polymeren sted på materialeoverfladen på grund af hydrotermisk nedbrydning.
- At to prøver (PC glas og DVD'en) havde en meget lav BPA frigivelse, hvilket indikerer, at disse materialer er mere hydrotermisk stabile materialer end de andre testede prøver. Disse forskelle mellem prøverne kunne desværre ikke forklares ved anvendelse af de teknikker, der blev brugt i denne undersøgelse.
- At der skete et bemærkelsesværdig og signifikant, næsten 20%, fald i begge typer af molekylvægte (M_w og M_n) i alle de testede polymerer. Dette indikerer en nedbrydning af PC polymer i alle prøver. Da der ingen forskel blev set i polydispersiteten (M_w/M_n), blev det konkluderet, at de nedbrydningsprodukter der dannes på materialets overflade hurtigt opløses i vandet.
- At der ikke skete nogen signifikant ændring i glasovergangstemperaturen, T_g på trods af disse ændringer.

Optagelserne af infrarøde spektre (FTIR), målinger af glasovergangstemperaturen (T_g), molvægte (M_w/M_n) og den termiske nedbrydning af prøverne, viste ingen signifikante forskelle mellem prøverne. Resultaterne af de målte parametre korrelerer dårligt med de forskellige niveauer af frigivet BPA fra prøverne efter den ekstreme eksponering. Sammenfattende kan det konkluderes, at de anvendte teknikker ikke var tilstrækkelige til at forudsige BPA frigivelsen fra de givne prøver.

Det antages, at følgende nedenfor anførte parametre for materialesammensætning og procesbetingelser har en afgørende indflydelse på nedbrydningen af PC. På møder med industrielle kontakter i løbet af projektet, blev det bekræftet, at man for at undgå depolymerisering, bør være opmærksom på en række proces tekniske forhold:

- Brug tørre polymer materialer under produktionen (fx sprøjtstøbning af PC)
- Brug passende procesbetingelser, såsom valg af rette temperatur, i sprøjtstøbning proces
- Brug rene udgangsstoffer og additiver ved produktionen af PC

Desuden bør man være særligt opmærksom på brugen af additiver som aminer, TiO₂ og glasfibre i PC da tilstedeværelsen af disse stoffer kan øge frigivelse af BPA på grund af delvis nedbrydning af polymeren. Netop prøve PC3, som indeholdt tilsætningsstoffet TiO₂, havde en høj afgivelse af BPA efter den ekstreme eksponering.

Der er ikke i projektet fundet specifikke oplysninger om additiver, der ved tilsætning til PC, kunne forbedre den hydrolytiske stabilitet af polymeren.

1. Introduction

Bisphenol A (BPA) is a high production volume chemical used as monomer in the production of polycarbonate (PC) plastic as well as in PC blends, and in epoxy resins. PC is a thermoplastic used for many different applications due to its good physical and chemical properties such as transparency, high mechanical strength low moisture absorption and good thermal stability. Main areas are within electronic applications and construction industry. In relation to consumer products the material is used for food contact materials such as drinking bottles, glasses, water coolers, and food containers and for toys and other consumer products, however only as a minor application.

Polymers of PC show migration of BPA due to residual levels of unreacted BPA monomers or degradation of PC from the influence of environmental factors and aging of the polymer. This may lead to human exposure of BPA from the use of food contact materials of PC in tableware and food containers or from the use of others consumer products as e.g. toys. BPA is an endocrine active substance and much focus is on its potential health risks. A tolerable daily intake (TDI) for BPA of 50µg/kg bw/day was set by EFSA in 2006 (EFSA, 2006). The legal specific migration limit (SML) for food contact materials is 0.6 mg/kg food based on a TDI from 2003 which were 5 times lower than the above TDI. Recently, a new preliminary 10 time lower TDI of 5 µg/kg bw/day was recommended by EFSA (EFSA, 2014). Moreover, EU legislation, banning the use of BPA in PC baby bottles came into force since 2011 (EU, 2011). For toys for children under 3 years and for toys intended to be put in the mouth an EU migration limit of 0.1 mg/l in simulat is adopted (EU, 2014). Recently an exposure assessment on BPA from different sources including food and non-food products was given by EFSA (EFSA, 2013). Food is estimated to be the main source of BPA exposure in both children and adults (EFSA, 2013).

During the last decade several studies have been performed to examine and determine the migration of BPA from PC in particular with materials and articles intended for contact with food. From these studies several parameters seem to affect the migration of BPA from PC. Moreover studies on stability versus sensitivity of the PC plastic in relation to different environmental impact factors and composition of the plastic have been reported. It is the purpose of the given project to review significant parts of the literature with focus on factors determining the migration and release of BPA from PC and including different parameters affecting the stability and degradation of the polymer. Information from industry is included in the review where possible. This review is given in part 1 of the report. Moreover it is the purpose of the project to characterise and analyse different samples of food contact materials and consumer products of PC with the aim to study and evaluate the potential correlation between material quality of the PC and release of BPA. The analyses program has been devised to provide physical and chemical characterisation of the samples. Release of BPA were tested from the materials at different exposure conditions and including critical factors, suggested by the review that may affect the BPA release. Results from characterisation analysis and chemical testing of BPA release are presented and discussed in part 2 of the report.

Part 1: Literature review

BPA has been subject to much research on migration and risk assessment due to suspected low dose effect on endocrine disrupting properties and developmental neurotoxicology. Among other applications BPA is used in the production of PC and many studies have examined release of BPA from PC. Especially the focus has been on BPA release from food contact materials and consumer products to estimate the level of human BPA exposure from these sources.

Special interest has been into the different parameters that may affect the BPA release. Residual monomers of BPA in the polymer can give rise to diffusion controlled migration of BPA. This is however, estimated to be low due to a low diffusion rate in PC. Several studies have reported that the level of released BPA from food contact materials of PC can vary significantly between different samples. This indicates that other factors, besides the level of residual BPA monomers, can influence the release of BPA from PC. Different composition of the polymers may affect the stability of the polymer and degradation of PC when exposed to different environmental conditions is reported.

It is the aim of this literature review to examine the reported information on correlation between polymer specific parameters and the release of BPA. The review covers scientific papers and reports on PC. As the intention was also to include specific information on polymer composition industry information was included in the review where possible.

2. Polycarbonate (PC) - stability and degradation

2.1 Introduction

PC is a thermoplastic with good physical and mechanical properties including high durability and high transparency (Huang et al., 2011; Diepens and Gijsman, 2009). However, PC is sensitive to UV light, humidity and temperature variations which make the polymer degrade (Sharon et al., 2006; Collin et al., 2012; Plast og Gummi Ståbi, 1992). In the given chapter the effect on polymer stability and degradation of different substances in the polymer and different environmental conditions is discussed.

2.2 Photodegradation of PC and use of additives

Various additives including a range of the following flame retardants: Potassium perfluorobutylsulfonate, potassium diphenylsulfonesulfonate, sodium trichlorobenzene-sulfonate, tetraphenyl resorcinol diphosphonate and tetraphenyl bisphenyl-A diphosphonate can be found in PC and PC blends to improve the performance of the material (Levchik, 2006; Huang, 2011). Phenolic substances, acting as chain terminators, as e.g. phenol (< 2%), tertiary butylphenol (<3%) and cumylphenol are part of the polymer chain and aiming to regulate the molecular weight (Piringer and Baner, 2008; Bayer 2013b).

To increase the lifetime of the polymer different kinds of stabilisers are added (Diepens and Gijsman, 2010). Many factors can affect the photodegradation process and improve stabilization of the polymer against UV photodegradation, e.g. UV absorbers which strongly absorb the UV light of relevant wavelengths can be used. There are different groups of UV absorbers where the most important substances are mentioned to be hydroxybenzophenones, hydroxyphenyl benzotriazoles, cyanoacrylates and hydroxyphenyl triazines (Diepens and Gijsman, 2010). In a study performed by Diepens and Gijsman (2010) different types of stabilisers were added to bisphenol A to examine their effect on the photodegradation rate. According to industry information, stabilisers are added to a polymer in very small amounts of <1% (Bayer, 2013b). In general the degradation rate was decreased by addition of small amounts of these substances in the above study (Diepens and Gijsman, 2010). The best results were found by adding hydroxybenzophenones or hydroxyphenyl triazines (Diepens and Gejsman, 2010). The given UV absorbers are used for technical/industrial applications but are not allowed in polycarbonate grades for food contact or medical applications.

UV absorbers do mainly protect the bulk materials from UV degradation but are not very effective in preventing surface degradation (Diepens and Gijsman, 2009). In order to protect against surface degradation, application of protective coatings (e.g. by co-extrusion of a thin film containing of high level of UV absorbers to the material or application of a varnish containing UV absorber) can be done (Diepens and Gijsman, 2009). This is mainly done for long-life outdoor use applications in construction and automotive lighting. Another way to stabilize the material is by incorporation of block polymers, as e.g. polyarylates, into the polymer (Diepens and Gijsman, 2009). Recently polyacrylate block copolymers prepared with isophthaloyl chloride, terephthaloyl chloride and resorcinol has been introduced. The study shows that addition of resorcinol type block polymer gave a better protection than blending the polymer with UV absorbers (Diepens and Gijsman, 2009).

However, the addition of additives can also adversely affect the polymer stability (Sharon et al., 2006; Zhou et al., 2007). The presence of chromophores as e.g. residual catalysts used for the polymerisation or dyes and pigments can affect the thermal and photochemical stability of the polymer and increases the process of photodegradation (Saron et al. 2006; Saron and Felisberti, 2009). Also metallic contaminants and other impurities (non-intentionally added substances, NIAS) of the commercial starting substances can accelerate the photodegradation process (Sharon et al., 2006). In conclusion, to avoid such degradation, only highly pure reagent grade chemicals as e.g. dyes and pigments should be used in production of all PC grades (Bayer, 2013b). This should be demonstrated by the safety datasheet or, in the case of FCM, the declaration of compliance from the raw material suppliers.

Incorporation of the colorant Cu-phthalocyanine in PC was found to accelerate the photodegradation of the polymer (Saron et al., 2006). This is explained by the possible mechanism of an increased formation of free radicals being the starting point for a sequential photo-oxidation reaction that leads to degradation of the polymer (Sharon et al., 2006). Additives, including TiO₂ and glass fibres and potential other additives may increase the level of BPA presumably by partial decomposition of the polymer chain (Bayer, 2013b). Specific quality parameters and purity of the raw materials should be carefully checked before they are used in the PC production. In case, when using PC blends and stabilisers in PC they must be neutral and hydrolytically stable (Bayer, 2013b).

2.3 Mechanical performance of PC

PC is highly notch sensitive and the surface of the polymer can easily be scratched (Zhou et al., 2007). This susceptibility to crazing or cracking increases when exposed to different solvents (Jiang and Tjong, 1999). When the material is exposed at the same time to mechanical stress and different agents and chemicals this may lead to the phenomenon called environmental stress cracking (ESC) of the polymer (Kjellander et al., 2008) with the formation of voids and crazes starting at the surface layer of the polymer (Al-Saidi et al., 2003). The ESC is defined as an essentially physical process that does not involve any chemical degradation (Arnold, 1996). Experimental work has shown that contact to diffusing chemical solvents (Al-Saidi et al. 2003) as well as to chemical agents not absorbed into the polymer, as e.g. butter, cause the PCs to be less resistant to ESC under stress (Kjellander et al., 2008). Moreover in one study it was reported that storing of the polycarbonate samples for one year reduced their resistance to some chemicals (Kjellander et al., 2008). The formation of voids and cracks may increase the surface area of the material dramatically with potential migration from sub-surface layer of the material.

To improve the mechanical performance of some articles of PC, modifier or reinforcers (e.g. glass fiber reinforcement) are added (Zhou et al., 2007; Jiang and Tjong, 1999, Zweifel, 2001). However the addition of such additives into PC can negatively affect the thermal stability of the polymer and addition of glass fiber can result in higher melt viscosity and breakage of the fiber (Jiang and Tjong, 1999). Glass fibers are not added to PC grades intended for food contact and medical applications according to industry information (Bayer, 2013b).

2.4 Hydrothermal ageing of PC

In dry conditions materials of PC is relatively stable to higher temperatures but in hot water (above 60 °C) the polymer is sensitive to hydrolysis (Plast and Gummi Ståbi, 1992). In the injection molding process at the molders it is important to keep the granulate in a dry condition to avoid decomposition of the polymer (Plastteknisk Handbok, 1980; Bayer, 2013b). In contact with hot water depolymerisation of the PC will take place and give rise to the formation of monomeric BPA with potentially increased BPA migration according to an industry study by Mercea et al., 2009 and according to Cao et al., 2008 a. Moreover PC has poor resistance in alkaline environments in particular at high temperature (Jiang and Tjong, 1999) and in contact with strongly alkaline

solutions hydrolysis is accelerated (George and Gaines, 1990). Several studies have reported that contact with water at higher temperatures and alkaline conditions will increase the hydrolytic depolymerisation of PC plastic (George and Gaines, 1990; Brede et al., 2003; Cao et al., 2008; Mercea, 2009). Addition of a flame retardant (decabromodiphenyl ether) was found to increase the hydrolytic depolymerisation of PC in a study by Huang et al., 2011; the substance is now prohibited in electronic equipment (EU, 2011b). It should be emphasised that addition of additives as well as impurities which catalyse degradation of PC should be avoided (Bayer, 2013b).

According to Factor (1996) hydrolysis of PC can be avoided by the following factors:

- ♣ Before the extrusion and injection molding process of the polymer into articles, the polycarbonate granules should be as free as possible of acidic or basic residues and dried to a water content of <0.05 %.

- ♣ Stabilisers used must itself be neutral and hydrolytically stable.

According to Plastteknisk Handbok (1980) addition of stabilisers can reduce the hydrothermal ageing of PC (Plastteknisk Handbok, 1980).

Also hydrothermal effects on the structure of PC have been studied. If repeatedly exposed to hot water above 70 °C the polymer becomes brittle after some time (Plastteknisk Handbok, 1980). When PC is exposed to boiling water and cooled to room temperature the formation of microcavities is seen in the polymer (George and Gaines, 1990). According to Branch, 2013, T_g is inversely proportional to the diffusivity (and thereby the migration) of substances in a given polymer. However as release of BPA from PC is only to some (or lesser) extent caused by diffusion this might be of less relevance with PC. According to an industry study T_g has no influence on BPA release as BPA migration is not driven by diffusion (Bayer, 2013).

2.5 Thermal stability of PC

According to one reference (Huang et al., 2011), reagent-grade PC having a narrow molecular weight distribution as well as a high purity, exhibits better thermal properties than industrial grade PC with a broad molecular weight distribution and a lower purity. Regarding molecular weight distribution, this statement is in contrast to the basic knowledge that all technical PC qualities are produced to high conversion by polycondensation, which will result in the most probable polydispersity (M_w/M_n) that approaches 2 (Flory, 1953; Stevens, 1999). Also according to industry information, the broadness of the molecular weight distribution of polycarbonate is determined by the applied process conditions during the polycondensation reaction in the production (Bayer, 2013b).

As previously mentioned, to improve the mechanical performance of the polymer, modifiers or reinforcers are added (Zhou et al., 2007; Jiang and Tjong, 1999). However the addition of such additives into PC can affect the thermal stability of the polymer and addition of glass fiber can result in higher melt viscosity and breakage of the fiber (Jiang and Tjong, 1999).

2.6 Blends of PC

Polycarbonates (PC) almost invariably based on bisphenol A that constitutes the majority of the material, do not only appear as homopolymer materials but also various blends of PC with other polymer materials exist. Blends are made to combine attractive characteristics of the constituting polymers. For instance PC/polyester (poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT)) blends. Blends with styrenic copolymers like poly(acrylonitrile-co-butadiene-co-styrene) (ABS) poly(styrene-block-butadiene-block-styrene) (SBS), and poly(styrene-co-acrylonitrile) (SAN), as well as with polystyrene (PS) itself are known (Levchi, 2006). Also PC blends with polypropylene (PP) exist. From all of these blends of PC, BPA migration may in principle occur.

3. Release of BPA from polycarbonate (PC)

3.1 Introduction

Due to the good physical and mechanical properties of PC plastic it is used in many different fields of applications, including consumer products and food contact materials. Food contact applications, medical applications and consumer products account for respectively 4 %, 3 % and 4 % of the total PC production. Other important areas of use is optical media like DVD's (21%), Houseware and appliances (11%), automotive (12%), construction (17%) and electronics (20%) (PlasticEurope, 2010). When PC is brought into contact with food or others matrices, migration and/or release of BPA from the polymer into the matrix can occur. In the given chapter a review of selected studies on BPA migration/release is reported. The different mechanisms behind BPA release as well as the influence of different parameters in the polymer and in the environment are discussed.

3.2 Different mechanisms behind the release of BPA from PC

The BPA release from PC is explained by two different processes:

- (i) Diffusion controlled release of residual BPA monomer present in the polymer and
- (ii) Hydrolysis and decomposition over time at the polymer surface (pH dependent) (Mercea, 2008, Brandsch, 2008).

In many cases the term “migration” from polymers can be defined as a mass transfer solely due to diffusion, which is governed by predictable physical processes taking place in the polymer network (Piringer and Baner, 2008). However in this specific case where additional (uncontrolled) amounts of the migrating species, BPA, is generated by hydrolysis/decomposition of the polymer itself, “migration” become a term describing the total release of BPA. In most of the literature about PC no distinction is made between the terms “migration”, “leaching” and “release”.

Hydrolysis takes place at the carbonate ester linkages in the PC backbone when the material is in contact with an aqueous matrix. Results from kinetic migration studies on PC samples support the hypothesis that hydrolysis at the surface is the main source of BPA release into an aqueous medium whereas the diffusion controlled release of BPA plays a minor role in the overall release of BPA from PC (Mercea, 2008). The diffusion rate of BPA is low and the chemical decomposition might contribute more significantly to the release of BPA, particularly at high temperatures (~ 100°C) (Brandsch, 2008). According to information from industry, differences in T_g of PC polymers are marginal and have no influence on BPA migration (Bayer, 2013b). However, the diffusivity was shown to be inversely proportional with the glass transition temperature, T_g , in a certain PC polymer type (Brandsch, 2013).

The level of residual BPA in PC is reported to be in the range of 1 – 70 mg/kg polymer (Mercea, 2008; Mountfort et al., 1997; Ehlert et al., 2008). One value of 140 mg/kg was reported for a batch of baby bottles but was found to be lower (26 mg/kg) in a second batch of the same brand (Mountfort et al., 1997).

According to Bayer there is not a great difference in BPA levels in food resins versus non-food resins (Bayer, 2013b). However, addition of different substances and impurities as well as different processing conditions might affect the residual level of BPA in the final material (Bayer, 2013b). BPA migration was found to be only weakly correlated to the concentration of residual BPA in PC resin (Mercea, 2008). In a study of eighteen different brands of polycarbonate baby bottles produced from BPA (application not allowed in EU since 2011), migration of BPA was tested into water at 100 °C in 1 minute followed by a cooling down period into a water bath at 20 °C until 37 °C was reached (Ehlert et al., 2008). In the study no correlation was found between residual content of BPA in the polymer material (1.4 - 35.3 mg/kg polymer) and the release of BPA. This was the same conclusion in another study on 22 PC baby bottles by Mountfort et al. 1997. However, this might be due to combination of a short test time and the low diffusion rate of BPA.

3.3 Release of BPA into water

A large number of studies have been made to quantify the level of BPA release from PC food contact materials (Mountfort et al., 1997; Ehlert et al., 2007; Kubwabo et al., 2009; Maragou et al., 2008; De Coensel et al., 2009; Santillana et al., 2011; Simoneau et al., 2011; Hoekstra and Simoneau, 2013). Most of the studies were made by the use of food simulants and showed considerable variation in the level of BPA release from different samples of PC. Release of BPA into water was experimentally shown to increase with time and temperature (Le et al., 2008; Maragou et al., 2008; Kubwabo et al., 2009; Coensel et al., 2009; Nam et al., 2010). The correlation between release of BPA and time was corresponding to a second – degree polynomial (Migration = $at^2 + bt + c$) for each of five different samples of PC when testing with water at 1-6 days at 70 °C ((Cao and Corriveau, 2008 a). The level of BPA varied between 32-55 µg/L (at day 1) and 228-516 µg/l (at day 6). According to the authors the variation between samples is likely due to different levels of residual BPA in the samples (Cao and Corriveau, 2008a). However residual levels of BPA were not determined in the given study and according to Mercea (2008) migration of BPA was found to be only weakly correlated to the concentration of residual BPA in the PC. As part of the study the migration rates (release of BPA per cm² surface area and per hour) were determined to be in the range of 1.84 – 4.83 ng cm⁻² h⁻¹ (average) for the five samples (Cao and Corriveau, 2008a). In another study the release of BPA from PC into water was determined at a lower temperature (1 day at room temperature) after filling the bottles with boiling water (Cao and Corriveau, 2008 b). In this study the level of BPA released from the bottles were in a much lower the range of 1.7-4.1 µg/L (Cao and Corriveau, 2008) compared to the above level of 32-55 µg/l (day 1). In a study by Le et al. 2008 the rate of BPA release from new PC drinking bottles into water was found to increase by a factor of 15-55 when exposed to boiling water compared to room temperature (Le et al., 2008). Also in a study by Nam et al, 2010 the level of BPA migration rapidly increased from 6-month used baby bottles when the temperature of water increased at temperatures above 80 °C (Nam et al., 2010). Release of BPA into deionized water and tap water is reported from several other studies with the highest concentration of 1 mg/l (10 days@65°C) (Hoekstra and Simoneau, 2013). In conclusion the release of BPA into water is found to increase with increased time and temperature (Hoekstra and Simoneau, 2013).

3.4 Effect of different parameters on BPA release

The release of BPA was found to increase with increased pH (Biedermann-Brem et al., 2008; Hoekstra and Simoneau, 2013)) when testing the release of BPA into tap water at increased temperature up to 100 °C. A BPA release up to 137 µg/l after boiling of pre-boiled tap water in PC bottles for 5-10 minutes was reported (Biedermann-Brem et al., 2008). The high level of BPA is explained by degradation of PC caused by high temperature and high pH of the water due to degassing of carbon dioxide when boiling. The authors concluded that BPA is primarily released due to degradation/hydrolysis of PC (rather than diffusion/migration) when the material is exposed to water at high temperature and high pH (Biederman-Brem and Grob, 2008). The positive

correlation to pH was also found in another study where the release of BPA into demineralized water at 60 °C increased from 0.13 – 30 ug/dm² with a shift in pH from 2.5 to 10.1 (Mercea, 2008). Brede et al. found an increased migration of BPA from PC baby bottles after dishwashing at 70 °C with detergent of pH 11.5-12 (Brede et al., 2003). Also small amount of acid is mentioned to catalyse the hydrolysis and should therefore be avoided in the production process (Zweifel, 2001).

The migration of BPA from used polycarbonate animal cages (with visible worn) was found to be significantly higher than from new ones when tested for BPA release into water at room temperature (Howdeshell et al., 2003). It might be due to increased surface area of the worn polymer and/or catalysed hydrolysis of the polymer to BPA after contact with animal alkaline urine. Urea and other amines should be avoided since they can lead to drastic polymer degradation (Bayer, 2013b). Increased BPA release was also seen from used PC baby bottles compared to new ones (Cao et al., 2008b). However as new and old samples were not of the same production lot, it may be difficult to generalise from the study.

In a review of several studies (Hoekstra and Simoneau, 2013) it is concluded that:

- The release of BPA from PC is mainly affected by contact time, temperature and pH with a positive correlation to the three parameters.
- Residual alkaline detergent remaining on the surface of the PC bottles after dishwashing may increase the release of BPA.
- The effect of aging is difficult to estimate as reported studies on new and used bottles were not made by the same production lot

The effect of different detergents for dishwashing and handwashing on the release of BPA from PC baby bottles was studied by Maria et al., 2009. The authors found that for all but one detergent tested, the release of BPA increased up to 500 times the control sample (not exposed to detergents) (Maria et al., 2009). This was assumed to be due to degradation of the polymer. However, no correlation could be found between the release of BPA and pH of the detergents (personal communication to one of the authors, Bustos, 2009), so according to the authors more studies are needed to better understand the mechanism. Santillana et al., 2013 concluded that the trademark of PC baby bottles was an influential factor on the level of BPA releasing from PC polymer when exposed to detergent aggression. This indicates that the production process varies between different brands of the same product

The migration of volatile substances from new PC containers intended for microwave oven was tested during microwave- and conventional heating for 1 h at 80 °C by total immersion into isooctane, ethanol and water (Alin and Hakkarainen, 2012). During microwave heating the migration of individual compounds was in most cases significantly larger than during conventional heating. According to the authors, the increased migration can be explained by degradation caused by microwave heating and/or food simulant interactions (Alin and Hakkarainen, 2012). No specific information was given on the migration level of BPA from the tested PC materials. Contrary a study by Ehlert et al., 2008 did not find any increase in BPA migration into water from 18 PC baby bottles after 3 times repeated heating to 100 °C in a microwave oven. Also in another study by Coensel et al. (2009) no significant difference was found between BPA migration after water bath and microwave heating of PC baby bottles.

As was given above in chapter 2, various additives added to the polymer can significantly affect the polymer stability (Sharon et al., 2006; Zhou et al., 2007). According to industry information, additives and inappropriate processing conditions can have an effect on the BPA level presumably by partial decomposition of the polymer chain (Bayer, 2013b). Addition of amines into the polymer may lead to a significant increase in residual BPA content. Also addition of other additives including

TiO₂ and glass fibres, if not of a proper quality compatible with the PC polymer, may increase the polymer decomposition and residual level of BPA (Bayer 2013b). Moreover, too high thermal stress during the injection molding process may also increase the BPA level (Bayer, 2013b). Hence, the recommendations from the suppliers regarding drying of raw material prior to the injection molding and selection of proper processing conditions should be noted seriously.

Part 2: Experimental

4. Characterisation and testing of PC

4.1 Introduction

The aim of the experimental work was to study the potential correlation between quality of PC plastic and the release of BPA from the materials by chemical and physical characterisation and testing of the materials. Several studies have discussed the influence of different material parameters on the release of BPA from PC as discussed in the previous chapter and as summarised below.

The migration/release of BPA from PC is explained by two principally different mechanisms: Firstly, by diffusion of residual BPA from inside the polymer and secondly by degradation of the polymer surface due to photodegradation by UV light or due to hydrolysis when exposed to water at higher temperatures in particular at alkaline conditions.

A positive correlation between residual level of BPA in PC and release of BPA from the materials has been suggested by several studies. However, according to other studies (Mercea, 2008; Ehlerts et al, 2008) there is no or only a minor correlation. This might be explained by the fact that the diffusion rate of BPA in the bulk of the PC material is very low compared to that of more soft plastics. In general increasing diffusion and therefore also migration is positively correlated to temperature and contact time.

It is assumed that the release of BPA from PC, when exposed to water, is primarily due to degradation of the polymer with hydrolysis of carbonate ester linkages in the PC backbone rather than diffusion of residual BPA, especially at high temperature (~ 100 °C).

Addition of some additives as well as contaminants and impurities in the polymer can accelerate the photodegradation and hydrolysis of PC (Saron et al. 2006; Saron and Felisberti, 2009; Bayer, 2013b).

Use of dry and highly pure raw materials as well as addition of specific stabilisers can reduce hydrolysis of PC (Bayer, 2013b)

Only a few studies included in this review have included both physical characterisation of the materials and chemical testing of BPA. However, this is the prerequisite to fully study the potential correlation between material specific parameters and the release of BPA.

In the second part of this project, samples of PC were analysed applying an experimental design that allow the study of a potential correlation between selected material specific parameters and the release of BPA at different environmental conditions. Twelve different materials of PC were characterised with respect to molecular structure, the average molecular weight (M_w) and the average number molecular weight (M_n), T_g , thermal resistance as well as residual level of BPA in the polymers and moreover the release of BPA and hydrothermal stability was studied.

4.2 Materials

Samples (n=12) were selected in order to represent a diversity of materials for food contact applications and other applications. New and older materials were covered and included the following samples:

- Three test plates produced by industry to represent different qualities of polycarbonate. All three materials are intended for applications of food contact, medical applications and toys.
- Two samples of PC drinking glasses
- Five samples of PC baby bottles
- One PC bowl and
- One DVD sample.

Information about the samples included in the study is given in table 1. Additionally, surface area (data not shown) of each sample is measured and used for calculations of results. It was the intention that selection of samples should be based on industrial information on material composition and production conditions including the content of specific substances which can influence the migration potential and stability/degradation of the polymer. However, only for three of the samples (PC test plates) it was possible to get some (but not full) information about polymer composition from the producer (Table 1) . For the other samples only some information on instructions of use was available.

TABLE 1
LIST OF SAMPLES AND SAMPLE INFORMATION

Sample no/name	Samples	Sample information	Instructions for use given with the material	Thickness of sample (mm)
PC 1	PC plate	High viscosity branched PC, blue. Mw 35000. BPA content 2 ppm * The material contains addition of a mold release agent and an organic dye.		2
PC 2	PC plate	Medium viscosity linear PC, clear. Mw 28000. BPA content 2 ppm * The material contains addition of a mold release agent.		2
PC 3	PC plate	Low viscosity linear PC, white. Mw 24000. BPA content 9 ppm* The material contains addition of TiO ₂ as inorganic pigment.		2
DVD	DVD	PC		1.1
K14-0009	PC glass (15 cl)	PC	For contact with all kind of foodstuffs. Maximum contact temp.: 100 °C	2.3

Sample no/name	Samples	Sample information	Instructions for use given with the material	Thickness of sample (mm)
			Maximum time of contact: 2 hours.	
K14-0010	PC glass (40 cl)	PC	For contact with all kind of foodstuffs. Maximum contact temp: 130 °C Maximum time of contact: no restriction	1.8
OLD samples:				
2008-176	Baby bottle	PC		1.2
2008-179	Baby bottle	PC		1.0
2008-235	Baby bottle	PC		0.9
2008-236	Baby bottle	PC		1.0
2008-242	Baby bottle	PC		1.2
1997-PC4	Bowl	PC		2.6

*) Information given by the producer of the material.

The molecular weight was determined by GPC and polycarbonate calibration.

4.3 Characterisation of materials

A comprehensive analyses program has been performed on all the investigated samples in order to complement the sparse available material information. This is especially important for the samples without any product specifications except the basic knowledge that they presumably consist of polycarbonate (PC). The analyses program has been devised to provide physical and chemical comparative characterisation of the samples. Furthermore, the analyses program also aims to study the potential correlation between these material parameters and release of BPA from the materials.

4.3.1 Fourier Transform infrared spectroscopy (FTIR)

Fourier Transform infrared spectroscopy (FTIR) is vibrational spectroscopy technique that records the absorption of IR light by chemical bonds in all molecules incl. polymers. The technique is suitable for verifying if the polymer really is polycarbonate and if specific additives or decomposition products are present in high concentration. Since different bonds absorb IR light at characteristic but different wavelengths FTIR spectroscopy is often referred to as fingerprint spectroscopy. As a consequence pure compounds have characteristic and unique FTIR spectra. In principle, all states of matter, *gas-liquid-solid*, can be analysed. Since light transmittance through a sample is necessary (IR light should reach the detector) very thin film material or a sample finely dispersed in a non-absorbing matrix normally needs to be prepared. With Attenuated Total

Reflectance (ATR) however, a sample is forced in close contact with a reflecting surface and sample preparation becomes very easy for polymers, thus non-dissolvable films or pellets can be analysed directly. In this analytical effort a single small piece of each sample has been analysed on a Nicolet iS50 equipped with a diamond crystal in a Horizontal ATR accessory. 32 Scans in the 4000-400 cm^{-1} spectral range are recorded and co-added in 4 cm^{-1} resolution.

4.3.2 Molecular weight by size exclusion chromatography (SEC)

Size Exclusion Chromatography (SEC) formerly known as Gel Permeation Chromatography (GPC), is an analytical technique that provides information on molecular weights (M_w and M_n) and molecular weight distributions (M_w/M_n) of soluble polymers in tetrahydrofuran (THF). This technique is used in order to measure the length of the polymer chains and if they are reduced during the applied tests. The analysis is routinely performed on approx. 1 wt-% polymer carefully filtered solutions in tetrahydrofuran (THF) that eludes on a HPLC type instrument equipped with columns that separate after molecular size. The detection can be performed by various detectors: Refractive Index (RI), UV, light scattering or viscometry. Data computation is based on polystyrene (PS) calibration standards. Each sample has been analysed twice.

4.3.3 Glass transition temperature by differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) enables determinations of the thermal transitions of polymers and composite plastic materials. The technique is somehow complementary to the above molecular weight determination as one would expect that shorter chains will lower T_g . DSC records glass transition temperatures (T_g) for amorphous materials as PC. The T_g transition of PC is extremely important for applications since around and above T_g PC starts to lose the form stability. At the glass transition the amorphous state of a polymer suffers a transition from solid to liquid like (or rubbery like). When the amorphous state is heated the kinetic energy of the molecules increases, motion is restricted, however, to short-range vibrations and rotations around the polymer chain as long as the polymer retains its glasslike structure. The significance of the glass transition temperature is enormous since it is a fundamental characteristic that relates to polymer properties and processing. Sample prerequisites for DSC are small amounts of solids (~5-10 mg). The applied instrument is a TA Instruments Q1000 and a three cycle analysis involving heating from room temperature to 250 °C, with subsequent immediate cooling to room temperature, and a final heating to 250 °C has been exercised for each sample. The T_g computed during the second heating cycle is reported to avoid any annealing effects.

4.3.4 Thermal resistance by thermogravimetric analysis (TGA)

The thermal resistance/degradation, TGA, can be studied with equipment for thermogravimetric analysis. TGA is normally employed in inert (N_2) atmosphere. The analysis is performed by carefully controlled heating in an oven while simultaneously recording the sample weight loss. The sample (5-10 mg) is placed in a Pt cup that hangs in a tremendously sensitive balance (± 1 ng). The weight loss information thus gained can often provide some compositional information of a sample e.g. content of inorganic fillers since the organic constituents (polymers) will eventually more or less degrade and disappear. In the present case the analyses were performed on a TA Instruments TGA Q500 by heating the samples from room temperature to 800 °C at 20 °C/min.

4.3.5 Liquid chromatography with mass spectrometric detection (LC-MS/MS)

Residual BPA in the samples and in simulants were analysed using an accredited method (DTU National Food Institute, 2013) using liquid chromatography tandem mass spectrometry, LC-MS/MS (Acquity-Quattro Ultima, Waters, Milford, MA, USA). The instrument was operated in electrospray-negative ionisation mode using multiple reactions monitoring (MRM). Identification of BPA was performed by monitoring the transition reactions m/z 227 > 212 and m/z 227 > 133. Quantification of BPA in the samples was performed by external standard calibration and with addition of internal standard (IS) of BPA- d_{16} (from Sigma-Aldrich) into samples, standards and blanks. The standards were prepared in the same solvent or food simulant used.

4.4 Extraction of PC and migration testing

4.4.1 Residual level of bisphenol A in samples

Residual levels of BPA were determined in all samples in order to estimate the potential diffusion controlled release of BPA from each sample. Subsamples (double determinations) of about 1 g of each polymer were dissolved in 20 ml methylene chloride according to Biles et al. (1997). The solutions were left at room temperature for 24 hours until complete dissolution of the polymers. Precipitation of dissolved polymer was done by addition of 20 ml methanol (MeOH). The extracts were centrifuged (4500 rpm in 10 min, 10 °C) and filtered. The level of BPA was determined in the extracts by liquid chromatography mass spectrometry, LC-MS/MS after dilution of sample extracts with MeOH and addition of internal standard (IS) of (BPA- d_{16}). Quantification was done by the use of external standard calibration in MeOH/methylene chloride with addition of IS of BPA- d_{16} . The level of BPA in the polymer samples was calculated as $\mu\text{g/g}$ polymer and in $\mu\text{g}/\text{dm}^2$ sample.

4.4.2 Release of BPA from samples to migration solutions

The release of BPA from the samples was tested by exposure into hot water (a potential worst case food in contact with PC) at selected worst case time and temperature conditions. Testing with water at high temperature was assumed to represent worst case testing as PC is sensitive to hydrothermal effects according to technical literature and results from several studies (Plast og Gummi Ståbi, 1992; Plastteknisk Handbok, 1980; Mercea et al., 2009; Cao et al., 2009). The testing was performed in accordance with the regulation of EU 10/2011 for plastic food contact materials and following relevant parts of the European standards for migration testing (CEN, 2004).

Baby bottles, drinking glasses and the bowl were filled with 100 ml water, preheated up to 100 °C in a microwave oven and placed in a cupboard for the given test time. Samples of PC plates and the DVD sample were tested by total immersion into 150 ml or 100 ml hot water respectively. The samples were preheated up to 100 °C in a microwave oven and placed in the cupboard (100 °C) for the given test duration. The migration test conditions are given in table 2. Samples were tested by 3 times repeated exposure and all samples were tested as double determinations (two samples). The level of BPA was analysed by LC-MS/MS. Surface area of each sample was measured and the results were calculated in $\mu\text{g BPA}/\text{dm}^2$ surface area of the sample.

4.4.3 Quality assurance

The National Food Institute is accredited by DANAK, according to ISO/IEC 17025: 2005 to do migration testing and chemical analysis of FCM. Blanks were controlled in each analytical series and samples were analysed as double determinations. Double determinations were performed to ensure certainty of the tests. Recovery was controlled in each analytical series by repeated analysis of an aqueous sample with known concentration of BPA (in house check sample). In sample extracts of dissolved polymers, the recovery was controlled by spiking a known BPA concentration into sample extracts of all the sample materials.

Limit of detection (LOD) for aqueous samples was $0.2 \mu\text{g}/\text{dm}^2$

LOD for samples of dissolved polymer extracts was $0.6 \mu\text{g/g}$ polymer

The recoveries of in house aqueous check sample (140 ng/ml) of BPA were 88-110 %

The recoveries in spiked sample extracts of dissolved polymers was 95-120 %

All calibration curves were linear with $R > 0.99$

TABLE 2
MIGRATION TEST CONDITIONS INTO THE SIMULANT WATER

Sample	Sample no/name	Exposure conditions	Times of testing	Number of samples tested
NEW Samples				
PC plate	PC1	Total immersion 150 ml, 1 hour at100 °C	Repeated testing, 3 times	2 (pooled)
PC plate	PC2	Total immersion 150 ml, 1 hour at100°C	Repeated testing, 3 times	2 (pooled)
PC plate	PC3	Total immersion 150 ml, 1 hour at100°C	Repeated testing, 3 times	2 (pooled)
DVD	DVD	Total immersion 100 ml, 1 hour at100 °C	Repeated testing, 3 times	2
PC glass (15 cl)	K14-0009	Article filling, 100 ml 1 hour at100 °C	Repeated testing, 3 times	2
PC glass (40 cl)	K14-0010	Article filling, 100 ml 1 hour at100 °C	Repeated testing, 3 times	2
OLD samples:				
Baby bottle	2008-176	Article filling, 100 ml 1 hour at100 °C	Repeated testing, 3 times	2
Baby bottle	2008-179	Article filling, 100 ml 1 hour at100 °C	Repeated testing, 3 times	2
Baby bottle	2008-235	Article filling, 100 ml 1 hour at100 °C	Repeated testing, 3 times	2
Baby bottle	2008-236	Article filling, 100 ml 1 hour at100 °C	Repeated testing, 3 times	2
Baby bottle	2008-242	Article filling,	Repeated testing,	2

Sample	Sample no/name	Exposure conditions	Times of testing	Number of samples tested
		100 ml 1 hour at 100 °C	3 times	
Bowl	1997-PC4	Article filling, 100 ml 1 hour at 100 °C	Repeated testing, 3 times	2

4.5 Hydrothermal effect on polycarbonate

Hydrothermal effect on PC was tested by exposure of 5 samples (PC1, PC3, baby bottle (2008-176), drinking glass (K14-0009) and the DVD) at extreme test conditions in alkaline water at 90 °C for 1 to 14 days of exposure. The testing was done in a glass beaker by total immersion of 6 items of each sample in the hot water adjusted to pH 10 through addition of small amounts of ammonia (NH₃). Alkaline test conditions with addition of NH₃ will increase the degradation of the PC polymers according to literature and industry information (George and Gaines, 1990; Brede et al., 2003; Cao et al., 2008; Mercea, 2009; Bayer, 2013b). The samples were placed in a cupboard at 90 °C. A volume of 5 ml was taken from each sample solution after exposure times of 1 day, 3 days, 6 days, 8 days, 10 days and 14 or 15 days. The pH of all sample solutions was only slightly alkaline (in the range of 7.5-8) when controlled after 10 and 14 days. This is supposed to be due to a gradual evaporation of NH₃ over time at the high temperature test conditions. The level of BPA was determined in each of the samples by LC-MS/MS using the test parameters given in chapter 4.3.5. The level of BPA was calculated as µg BPA/g polymer and µg BPA/dm² of sample area. At the end of the exposure period (14 days) one item of each sample was characterised by FTIR, determination of molecular weights, determination of thermal resistance and determination of *T_g*.

5. Results and discussion

5.1 Results of the characterisation

5.1.1 Identity of polymer materials by FTIR spectrometry

The FTIR spectra appear all very identical showing that all samples were made from PC. Thus in every FTIR spectrum the most significant absorption peaks for a bisphenol A based PC are identified. These are the weak CH₃ asymmetric and symmetric stretching vibration at 2968 cm⁻¹, the strong C=O stretching at 1769 cm⁻¹, the strong *p*-substituted ring stretching at 1503 cm⁻¹, the sharp benzene bending at 1080 cm⁻¹, the strong asymmetric O-C-O stretching at 1014 cm⁻¹, and the strong =CH out-of-plane deformation at 828 cm⁻¹, and finally another strong *p*-substituted ring absorption at 553 cm⁻¹. In addition the *i*-propylidene structure shows weak bands at 1386 and 1364 cm⁻¹ (Hummel, 1988). All spectra appear as true copies of each other, not even very careful inspection of the spectra from the exposed samples show any new absorption peaks or a change in the intensity pattern observed in the corresponding spectra of the non-exposed samples. The FTIR spectra of one of the analysed samples (PC3) before and after hydrothermal exposure into water at 90 °C and alkaline conditions in 14 days are shown in the Annex of the report.

5.1.2 Molecular weight by SEC analysis

The molecular weight information as determined by SEC is collected in table 3. The majority of samples were produced from PC with polymer chains of approximately the same length (M_w . 40-50.000). The extremes were PC1 with a higher molecular weight (M_w ca 60.000 Da) and the DVD with approximately half of this. The reproducibility was in all instances good. It should, however, be stressed at this point that the reported molecular weights most likely are not the absolute values (given with producer sample information in table 1) since in the present study the calculations are based on PS standards. Nevertheless the values are comparable. All the samples except the DVD have M_w s in the 40,000-60,000 Da range with the associated M_n s in 19,000 to 27,000 Da range. This translates into polydispersities (M_w/M_n) from 1.9-2.5 that is normal for this kind of condensation type polymers. All these numbers indicate PC materials with engineering properties in a normal application range. The DVD has somehow lower both M_w (~30,000) and M_n (~15,000), however the polydispersity (M_w/M_n) is at the same level as the other samples. The five samples that have been subjected to the extreme exposure all show a remarkable and significant almost 20% decrease in both types of molecular weight. Representative figures of SEC traces of one sample (PC3) before and after hydrothermal exposure into water at 90 °C and alkaline conditions in 14 days are shown in the Annex of the report. It is noted that the listed molecular weights for PC1, PC2, and PC3 are different from the ones reported by the manufacturer due to our use of polystyrene calibration standards that only result in relative molecular weights. These are, however, reliable for comparison purposes.

5.1.3 Glass transition temperature by DSC analysis

The glass transition temperatures (T_g) of all the samples are collected in table 4. Again most samples have approximately the same T_g sample PC1 and the DVD being the most deviating ones. It is observed that the majority of the samples are in the range 146-154 °C, with the DVD having a slightly lower T_g (=143 °C). The small variations in T_g s seem to scale somehow with the molecular weights such that higher MW results in a slightly higher T_g .

On the other hand the results of the exposed samples only reveal a very minor lowering of T_g . The exposed samples do not show any signs of degradation products since no effects of smaller

constituents eventually serving as plasticisers are observed. Representative figures of DSC traces of one sample (PC3) before and after hydrothermal exposure into water at 90 °C and alkaline conditions in 14 days are shown in the Annex of the report.

5.1.4 Thermal resistance by TGA analysis

Table 4 gives the results of the TGA analysis and glass transition temperature. With exception of the DVD the samples lost less than 1% of their weight at 400°C. The residual amount of inorganic fillers and other substances persistent to high temperatures were about 25% - the DVD and sample PC1 lying a few percent lower. The recorded degradation traces (last Figure in the Annex) show weight loss (%) as a function of temperature and in addition the derivative weight (%/°C) that can be translated into the rate at which degradation takes place is shown. Qualitatively the traces are very identical with one single degradation roughly taking place between 450 and 550 °C where the majority of the degradation has taken place at ~575 °C under these analytical conditions, leaving a ~25 wt-% non-degraded residue at ~660 °C. This residue stays almost constant up to 750 °C.

TABLE 3
MOLECULAR WEIGHTS (M_w AND M_n) AND POLYDISPERSITY (M_w/M_n)

Sample number	Sample	Weight average molecular weight	Number average molecular weight	Polydispersity
		M_w in g/mol (Da)	M_n in g/mol (Da)	M_w/M_n
PC1	PC plate	60,500	24,400	2.48
		60,600	24,000	2.53
PC2	PC plate	47,900	20,700	2.31
		47,800	20,600	2.32
PC3	PC plate	40,300	19,400	2.08
		40,100	19,500	2.06
K14-0009	PC drinking glass	48,700	24,600	1.98
		48,800	24,500	1.99
K14-0010	PC drinking glass	45,300	22,900	2.03
		45,400	22,900	1.98
DVD	DVD	30,400	15,000	2.03
		30,600	15,100	2.03
2008-176	PC baby bottle	43,000	21,400	2.01
		42,900	21,400	2.05
1997-PC4	PC bowl	41,100	19,800	2.08
		41,300	19,800	2.09
2008-179	PC baby bottle	47,900	25,100	1.90
		47,600	24,900	1.91
2008-235	PC baby bottle	52,200	26,300	1.98
		51,800	26,600	1.95
2008-236	PC baby bottle	48,600	25,100	1.94
		48,600	24,800	1.96
2008-242	PC baby bottle	42,900	21,700	1.98
		43,100	21,700	1.99
Exposed samples:				
PC1	PC plate	51,500	20,800	2,48
		51,200	20,700	2,47
PC3	PC plate	34,600	17,000	2.04
		34,600	17,000	2.04
DVD	DVD	24,900	12,600	1.98
		25,000	12,700	1.97

Sample number	Sample	Weight average molecular weight M_w in g/mol (Da)	Number average molecular weight M_n in g/mol (Da)	Polydispersity M_w/M_n
K14-0009	PC drinking glass	40,600	19,300	2.10
		40,300	19,200	2.10
2008-176	PC baby bottle	37,400	18,500	2.02
		37,200	18,200	2.04

In order to compare the many graphs the weight loss at 400 °C (~onset of degradation) and the non-degraded residue at 650 °C are tabulated in table 4. Again all samples behave more or less the same with DVD being a noticeable exception.

TABLE 4
GLASS TRANSITION TEMPERATURES (T_g) AND THERMAL RESISTANCE GIVEN BY WEIGHT LOSS AT 400 °C (WT-%) AND NON-DEGRADED RESIDUE (WT-%) AT 650 °C.

Sample number	Sample	Glass transition temperature ¹ °C	Weight ² Wt-% at 400 °C	Non-degraded residue ² Wt-% at 650 °C
PC1	PC plate	154	100	23.7
PC2	PC plate	147	100	25.4
PC3	PC plate	148	100	25.4
K14-0009	PC drinking glass	146	99.9	24.1
K14-0010	PC drinking glass	146	99.8	25.0
DVD	DVD	143	97.9	22.3
2008-176	PC baby bottle	149	100	24.8
1997-PC4	PC bowl	146	99.9	24.1
2008-179	PC baby bottle	151	99.8	25.1
2008-235	PC baby bottle	152	99.6	25.4
2008-236	PC baby bottle	151	100	25.4
2008-242	PC baby bottle	148	99.9	23.0

Exposed samples:

PC1	PC plate	153	99.9	25.2
PC3	PC plate	148	100	25.7

Sample number	Sample	Glass transition temperature ¹ °C	Weight ² Wt-% at 400 °C	Non-degraded residue ² Wt-% at 650 °C
DVD	DVD	142	99.1	24.5
K14-0009	PC drinking glass	146	99.8	24.2
2008-176	PC baby bottle	148	99.9	25.4

¹ DETERMINED BY DSC

² DETERMINED BY TGA

The degradation of the DVD sample sets on before 400 °C and the non-degraded residue (22.3 wt-%) is a little lower than that for the rest of the samples.

Again the effect, if any, on degradation after the exposure of the five samples cannot be observed. Representative figures of TGA traces of one sample (PC 3) before and after hydrothermal exposure into water at 90 °C and alkaline conditions in 14 days are shown in the Annex of the report.

5.1.5 Residual level of bisphenol A in PC

Residual BPA was found in all sample extracts at concentrations between 5 and 80 µg/g polymer. The highest BPA level (80 µg/g) was found in the DVD polymer followed by one baby bottle (sample no 2008-242) with a level of 40µg/g. All other samples tested were in a lower range of 5-15 µg/g polymer. The relative standard deviation between double determinations of each sample was between 2-20 %. The results are given in the table 5 below.

TABLE 5
RESIDUAL LEVEL OF BISPHENOL A IN SAMPLES OF PC POLYMERS

Sample number/name	Sample	Residual level of BPA µg/g polymer	Residual level of BPA µg/dm ² sample	Information on country of origin
PC1	PC plate	8	93	EU
PC2	PC plate	5	64	EU
PC3	PC plate	13	158	EU
K14-0009	PC glass	10	144	US
K14-0010	PC glass	7	93	Australia
DVD	DVD	80	464	No information
2008-176	PC baby bottle	13	76	Poland
2008-179	PC baby bottle	9	62	Thailand
2008-235	PC baby bottle	5	48	China

Sample number/name	Sample	Residual level of BPA µg/g polymer	Residual level of BPA µg/dm ² sample	Information on country of origin
2008-236	PC baby bottle	7	51	Sweden
2008-242	PC baby bottle	40	339	Denmark
1997-PC4	PC bowl	15	242	EU

The detected level of residual BPA in the samples of PC1, PC2 and PC3 (respectively 8, 5 and 13 µg/g) were somewhat higher but not significantly different from the levels (respectively 2, 2 and 9 µg/g) given by the producer (table 1). The results are also calculated in µg/dm² (as in table 5) in order to facilitate a comparison between the release BPA from migration testing of the materials (as in table 6).

Ranking of the samples in table 5 according to their level of residual BPA gives the following order: DVD > Baby bottle (2008-242) > PC bowl > PC3 > Baby bottle (2008-176) > PC glas (K14-0009) > PC1 > PC glass (K14-0010) > Baby bottle (2008-236) > Baby bottle (2008-235) > PC2.

5.2 Release of bisphenol A from samples

The release of BPA from 3 times repeated testing into water at exposure conditions of (1 hour at 100 °C) is shown in table 6 for all the samples. The concentration of BPA is given as µg BPA/dm² of sample area.

TABLE 6
RELEASE OF BPA TO WATER FROM REPEATED TESTING OF SAMPLES IN 1 HOUR AT 100°C.

Sample number	Sample	Migration	Migration	Migration
		µg/dm ² 1. test	µg/dm ² 2. test	µg/dm ² 3. test
PC1	PC plate	2.5	2.7	1.7
PC2	PC plate	0.7	0.6	0.9
PC3	PC plate	0.4	0.6	0.6
K14-0009	PC glass	2.4	1.7	2.2
K14-0010	PC glass	2.1	3.1	2.8
DVD*	DVD	0.56	0.85	1.9
2008-176	PC baby bottle	1.6	2.8	1.8
2008-179	PC baby bottle	0.4	0.5	0
2008-235	PC baby bottle	< LOD	< LOD	< LOD
2008-236	PC baby bottle	< LOD	< LOD	0.2

Sample number	Sample	Migration	Migration	Migration
		$\mu\text{g}/\text{dm}^2$	$\mu\text{g}/\text{dm}^2$	$\mu\text{g}/\text{dm}^2$
		1. test	2. test	3. test
2008-242	PC baby bottle	0.8	0.7	0.3
1997-PC4	PC bowl	0.3	< LOD	0.2

* The chromatogram contained a second peak with the same $m/z > m/z$ transitions (specific masses) an equal mass ratio as BPA but with different retention time. This is an indication that the peak may be a potential isomer of BPA. The estimated level of the migration from the DVD sample is 7-20 times higher in each test (11.5; 8.8 and 13.0 $\mu\text{g}/\text{dm}^2$) if the potential isomer of BPA in the chromatogram is included in the calculation of the migration.

For each sample the level of migration in the three successive migration tests were at the same level. For all the samples tested, the level of released BPA is within the range from below LOD to 3.1 $\mu\text{g}/\text{dm}^2$ corresponding to below LOD to 30 $\mu\text{g}/\text{kg}$ water (or food) when using the actual surface-to-volume ratio of the samples, which are within the interval of 6-10 for the given samples. The SD between double determinations of samples was between 2 and 100 %.

The results are within the same level as what has been reported in other studies (Hoekstra and Simoneau, 2013). All migration results are well below the specific migration limit for food contact materials of 0.6 mg BPA/kg food equivalent to approximately 100 $\mu\text{g}/\text{dm}^2$. No significant difference was found in release of BPA from old samples (all baby bottles and the bowl) and new samples (PC1, PC2, PC3, PC drinking glasses and DVD). It has been reported by one study that PC stored for more than one year was less resistant to environmental stress cracking (ESC) when exposed to chemicals (Kjellander et al., 2008). The same effect was not seen when testing old samples exposed to hot water in the actual study. Moreover the migration was not correlated to the residual level of BPA in the samples given in table 3. This is probably due to the low diffusion rate in PC whereby only free BPA in the surface layer of the material will be accessible for migration within the short exposure time of 1 hour.

5.3 Influence of hydrothermal effect on release of BPA

Results of the experiments are presented in table 7 and table 8 from testing five of the samples kept at extreme exposure condition with alkaline water at high temperature (90 °C) to 14 days of exposure. The table shows the release of BPA (in μg BPA/g polymer/day and in $\mu\text{g}/\text{dm}^2$ polymer/day) into the alkaline aqueous test solutions as a function of time for each of the five samples. Figure 1 to 5 shows the release of BPA ($\mu\text{g}/\text{g}$ polymer/day) from the samples. For PC1 and the DVD sample the release of BPA per day was found to increase with time, however for the DVD at a very low level. For PC3 the BPA release was at a low level until day 6, however, with a significant increase from day 8 up to a high level at day 14 and 15. For the baby bottle and the PC drinking glass the level of BPA per day was more or less at the same level between days however for the baby bottle with a maximum at day 8 as seen from the table and figure.

TABLE 7
RELEASE OF BPA PER DAY ($\mu\text{G}/\text{G}/\text{DAY}$) DURING HYDROTHERMAL EXPOSURE IN 14 DAYS AT 90 °C AT ALKALINE CONDITIONS)

	Day 1	Day 2 and 3**	Day 4 to 6**	Day 7 to 8	Day 9 to 10	Day 11 to14	Accumulated release ($\mu\text{g}/\text{g}$)	Residual BPA monomer in unused material ($\mu\text{g}/\text{g}$)
PC1	5.1	7.6	8.2	—	—	10.7	128	8
PC3	1.1		1.1	3.8	41.4	161*	884	13
Drinking glass K-14-0009	1.1	0.9	—	0.8	1.3	0.8	11	10
Baby bottle 2008-176	18.7	18.7	—	43.5	23.5	8.2	226	13
DVD	0.3	0.2	0.2	0.4	1.0		14	80

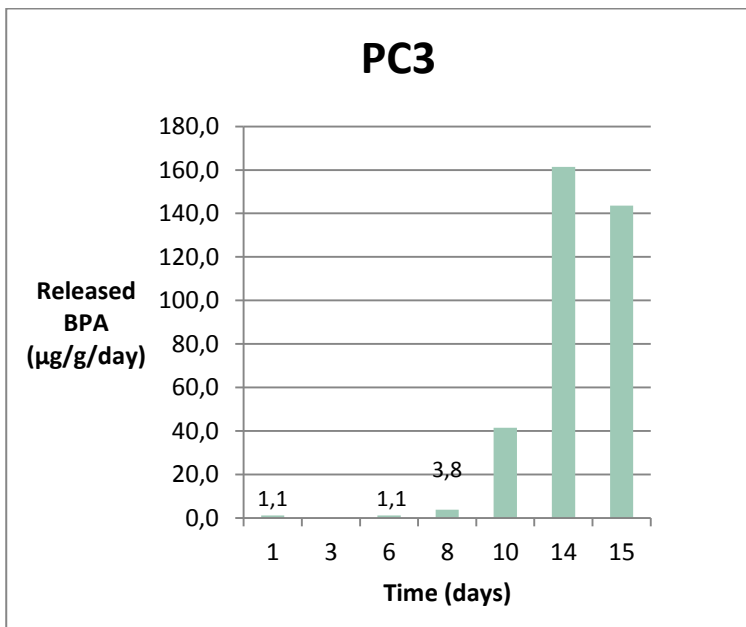
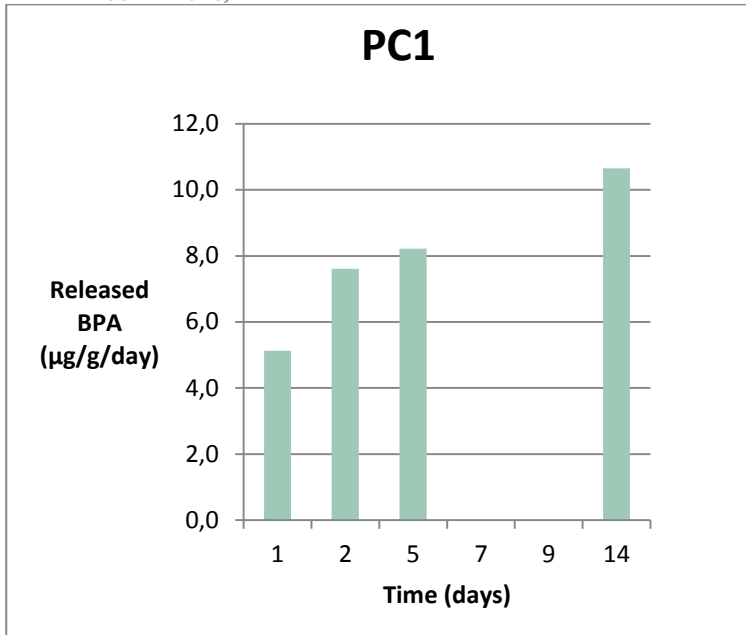
- FOR SAMPLE PC3 THE BPA RELEASE WAS CONTROLLED BY AN EXTRA MESUREMENT OF BPA RELEASE OF 144 $\mu\text{G}/\text{G}$ AT DAY 15.
- FOR SAMPLE PC1 DAY 3 AND 6 WERE DAY 2 ANND 5 RESPECTIVELY

TABLE 8
RELEASE OF BPA PER DAY ($\mu\text{G}/\text{DM}^2/\text{DAY}$) DURING HYDROTHERMAL EXPOSURE IN 14 DAYS AT 90 °C AT ALKALINE CONDITIONS

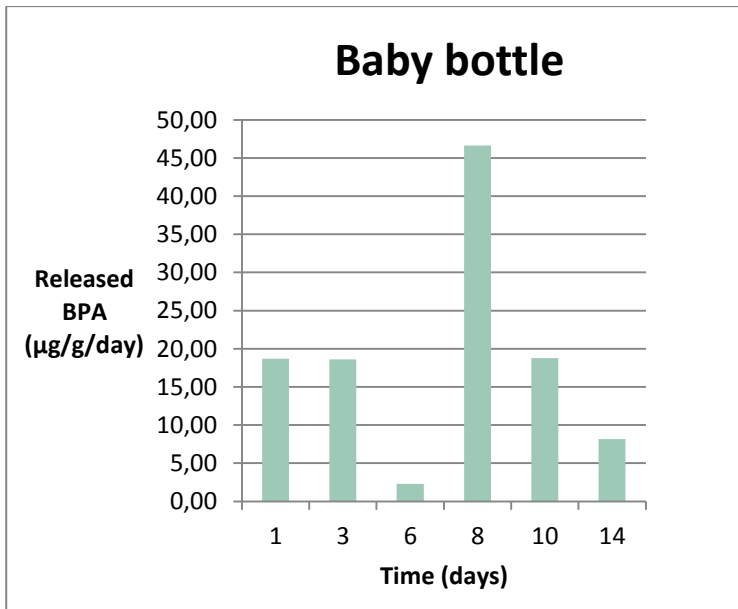
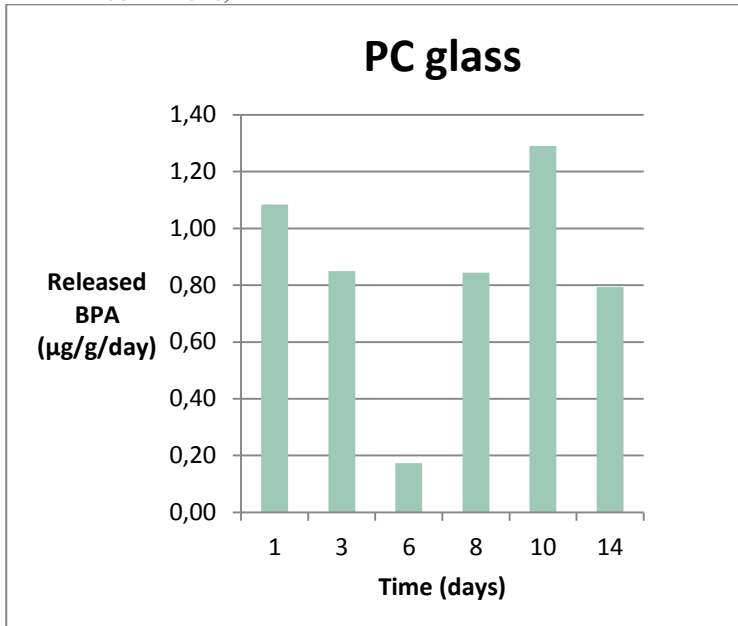
	Day 1	Day 2 and 3**	Day 4 to 6**	Day 7 to 8	Day 9 to 10	Day 11 to14
PC1	60.4	89.6	96.7			125
PC3	12.8		12.6	45.1	491	1916*
Drinking glass	16.3	12.3	—	12.7	19.4	11.9
K-14-0009						
Baby bottle 2008-176	108	108	—	252	137	47.5
DVD	2.3	1.4	1.5	2.8	6.8	

- FOR SAMPLE PC3 THE BPA RELEASE WAS CONTROLLED BY AN EXTRA MESUREMENT OF BPA RELEASE OF 1705 $\mu\text{G}/\text{DM}^2$ AT DAY 15.
- FOR SAMPLE PC1 DAY 3 AND 6 WERE DAY 2 ANND 5 RESPECTIVELY

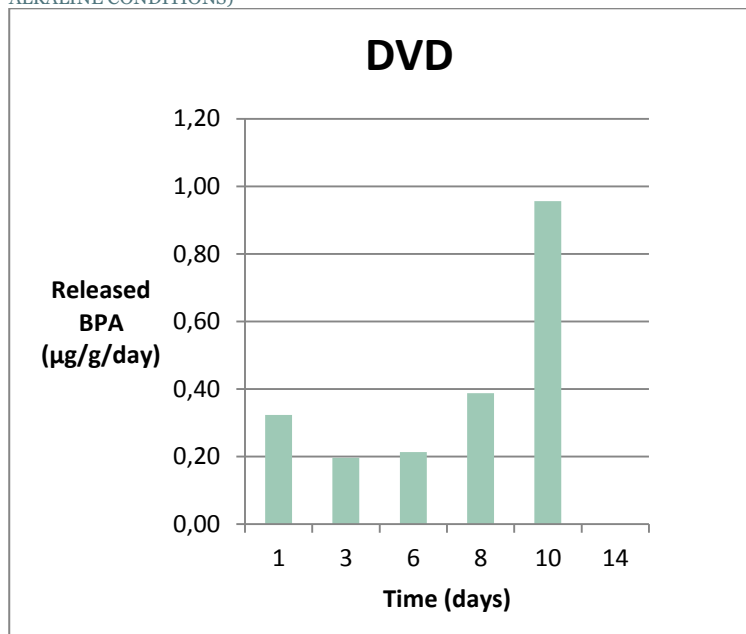
FIGUR 1-2: RELEASE OF BPA AS A FUNCTION OF TIME AFTER HYDROTHERMAL EXPOSURE (14 DAYS AT 90 °C AND ALKALINE CONDITIONS)



FIGUR 3-4: RELEASE OF BPA AS A FUNCTION OF TIME AFTER HYDROTHERMAL EXPOSURE (14 DAYS AT 90 °C AND ALKALINE CONDITIONS)



FIGUR 5: RELEASE OF BPA AS A FUNCTION OF TIME AFTER HYDROTHERMAL EXPOSURE (14 DAYS AT 90 °C AT ALKALINE CONDITIONS)



For all of the samples, the release of BPA per day was higher than what was found in the migration test (3 times 1 hour of exposure time). This was expected as this is generally recognized for polymers, also release of BPA from PC increases with exposure time (Kubwabo et al., 2008; Hoekstra and Simoneau, 20013). However, for two of the samples tested (PC3 and the baby bottle 2008-176) the total amount of released BPA (884 and 226 µg/g respectively) under the extreme test conditions was also significantly higher than the total residual level of BPA found in both of these materials (13 µg/g) as shown in table 7. This is assumed to be due to hydrothermal degradation of the polymers during the extreme test conditions applied. The alkaline test conditions by addition of NH₃ are the supposed most predominant factor behind the polymer degradation according to Bayer, 2013b. Previous studies have shown that, in contact with water at higher temperatures, depolymerisation of the PC will take place and give rise to formation of monomers of BPA (Mercea et al., 2009; Cao et al., 2008 a). Moreover at alkaline conditions at higher temperatures, the hydrolytic depolymerisation will further increase according to several studies (George and Gaines, 1990; Brede et al., 2003; Cao et al., 2008; Mercea, 2009). Very high level of BPA release was found for the PC plate PC3 followed by the baby bottle. Due to information given by the producer, the polymer of PC3 contains TiO₂ as inorganic pigment. As mentioned in chapter 3.4, the presence of such pigments may further increase the depolymerisation of PC.

Low levels of released BPA were found for the PC drinking glass at all days (a maximum of 1.3 µg/g/day) and for the DVD at all days (a maximum of 2.08 µg/g/day). The estimated total amount of released BPA from the drinking glass over the 14 days was 11 µg/g which is comparable to the detected level of residual BPA 10 µg/g in the polymer. This is an indication of a low BPA diffusion rate in agreement with the general existing knowledge of a low diffusion rate in PC. Moreover the results also indicate that the hydrothermal stability is higher for this material compared to the other materials in the study. According to the instruction of use given with the sample by the retailer it can be used up to 100 °C in a maximum of 2 hours. From the producer this article is claimed to be produced from the highest grade raw materials however, no specific information regarding e.g. the polymer composition was given with the sample. The results from the characterisation testing on the material did not offer any explanation for the high hydrothermal resistance in this sample as none of the analysed parameters (FTIR spectrum, M_w , M_n , T_g or thermal resistance) were significantly different from the same parameters of the other samples. However, it is assumed that only significant differences in the polymers would be detected by the methods used in this

study(Bayer, 2013b). The estimated total amount of released BPA from the DVD from 14 days of testing was at a low level of 2.1 µg/g. The analysis by LC-MS/MS however revealed a second peak in the LC-chromatogram eluting before BPA but with an equal mass ratio to BPA and with the same $m/z > m/z$ transitions. This may indicate the presence of an isomer of BPA in the DVD polymer. According to literature BPA can exist as para/para (the common form) as well as ortho/para and ortho/ortho isomers which are by-products in the industrial bisphenol A production (Pleshkova et al. 1994). If this second peak is included in the calculation of released amount of BPA (as the sum of isomers) a total release of BPA (isomers) is estimated to 10 µg/g within 14 days of test. This is at the same level as was estimated for the PC drinking glass and significantly below the detected level of residual BPA in the DVD polymer of 80 µg/g . This is an indication of a low BPA diffusion rate as well as an indication of a material with a good hydrothermal stability. Again the polymer characterisation does not offer any explanation for the high hydrothermal resistance in this sample as the analysed parameters (FTIR spectrum, T_g or thermal resistance) were not significantly different from the same parameters of samples with a higher level of released BPA. The level of M_w , M_n for this sample was lower, however this is not assumed to correlate with high hydrothermal resistance.

The characterisation of the materials after the exposure to the extreme environmental conditions showed that the five samples all had a remarkable and significant almost 20% decrease in both types of molecular weight (M_w and M_n) as seen from table 3. It is hypothesized that the exposure to the extreme environmental conditions degrades the PC by lowering the molecular weights to the same extent in all cases. However, the degradation seems to result in water soluble products (as BPA) that can be removed from the sample surface into the aqueous test solution since the remaining PC has the same polydispersity (M_w/M_n) as before the degradation, which implies no accumulation of low molecular weight species that would have increased the polydispersity significantly. In addition, no detectable effects are seen in FTIR, on T_g or on the thermal degradation behavior. Thus we do not see any significant changes in the PC T_g after degradation. Similarly we do not see any indication of hydrolytic degradation in our FTIR spectra as reported by the same authors.

Ranking of the samples on the basis of the measured release of total BPA (µg/g polymer) (table 7) gives the following order: PC3, baby bottle (2008-176) > PC1 > PC glass > DVD. The BPA release per day for each of these samples is shown in figure 1 to 5. The very high hydrothermal resistance of the PC glass, the DVD and also PC1 might be due to addition of some stabilisers as according to literature (Plastteknisk Handbok, 1980; Factor, 1996) the addition of stabilisers can reduce the hydrothermal ageing. Unfortunately there was no such information available on the chemical composition of the samples and it was not possible within the given resources of the project to go into identification of unknown substances in the given materials.

6. Conclusion on the experimental part

For all samples the FTIR spectra appeared very identical and in every FTIR spectrum the most significant absorption peaks for a bisphenol A based PC was identified.

The molecular weight values were comparable for all the samples except the DVD. M_w s were in the 40,000-60,000 Da range with the associated M_n s in 19,000 to 27,000 Da range. The polydispersities (M_w/M_n) were from 1.9-2.5 which is normal for this kind of condensation type polymers. The DVD has lower both M_w (~30,000) and M_n (~15,000).

Only small variations are seen with glass transition temperature, T_g , between the samples. T_g s seem to scale somehow with the molecular weights such that higher MW results in a slightly higher T_g .

The levels of residual BPA in the samples were 5-80 $\mu\text{g/g}$ which are in accordance with the residual BPA levels reported by others.

The migration from all samples was within the same range and below 3.1 $\mu\text{g/dm}^2$ corresponding to < 30 $\mu\text{g/kg}$ simulant, if the actual surface volume of each sample is used.

No correlation was found between the level of residual BPA and the level of BPA migration into water (1 hour at 100°C).

The five samples that have been subjected to the extreme exposure conditions (up to 14 days at 90 °C and pH 7.5-8) showed:

- An increase, and for three of the samples a significant increase, in the level of released BPA compared to the migration results
- The level of released BPA differs significantly between the samples
- For three of the samples the total level of BPA was significantly above the residual level of BPA indicating degradation of the polymers due to hydrothermal effect. The highest release was seen from PC3, a TiO₂ containing test sample from the industry.
- Two samples (PC glass and DVD) had a very low level of BPA release indicating more hydrothermal stable materials compared to the other samples tested
- A remarkable and significant almost 20% decrease in both types of molecular weight M_w and M_n was seen for all the samples tested. However, no difference was seen in the polydispersities (M_w/M_n) indicating that the degradation products are formed at the surface of the product and removed from there into the test solution.
- No correlation between T_g of the samples and the release of BPA
- No significant change in T_g for samples after extreme exposure conditions into water at high temperature.

Characterisation of samples by recorded FTIR spectra and measurements of M_w , T_g and thermal degradation did not show significant differences between samples. Moreover the measured parameters did not correlate to the significant different levels of released BPA from

the samples after extreme exposure conditions. In conclusion the applied techniques were not adequate to predict the level of BPA release from the given samples. It is assumed that material composition parameters and process conditions as given below have a main influence on the stability of PC against depolymerisation:

- Use of dry raw materials prior to injection molding of PC
- Use of adequate process conditions such as correct temperature in the injection molding process
- Use of substances and additives of high purity in the production of PC
- Special attention should be paid to amines, TiO₂ and glass fibers in PC as the addition of such substances may increase the level of residual BPA and/or release of BPA due to a gradual decomposition of the polymer.

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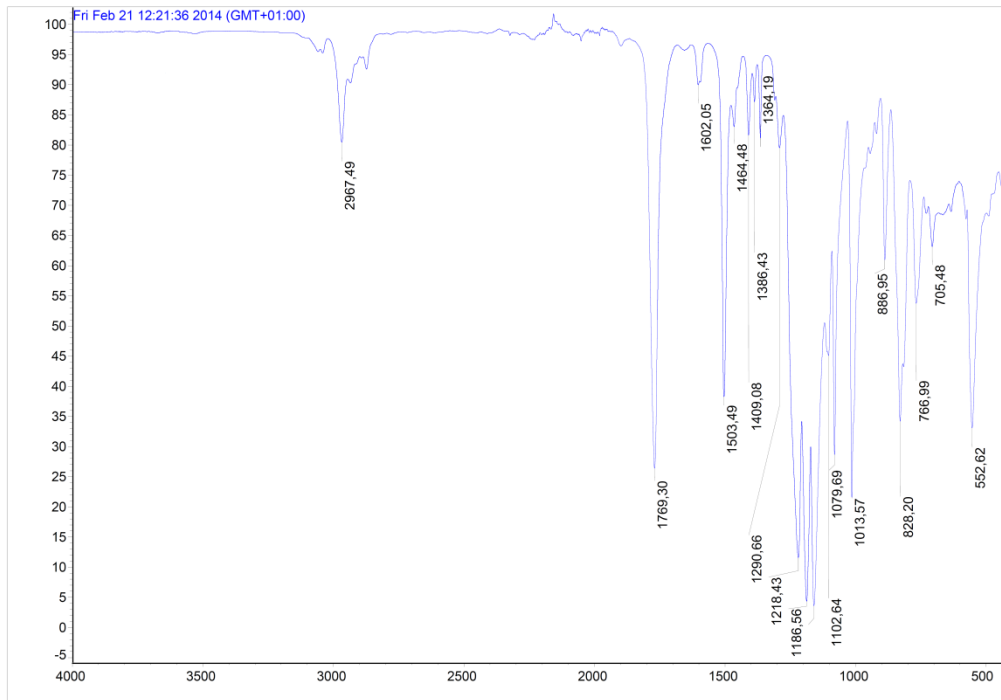
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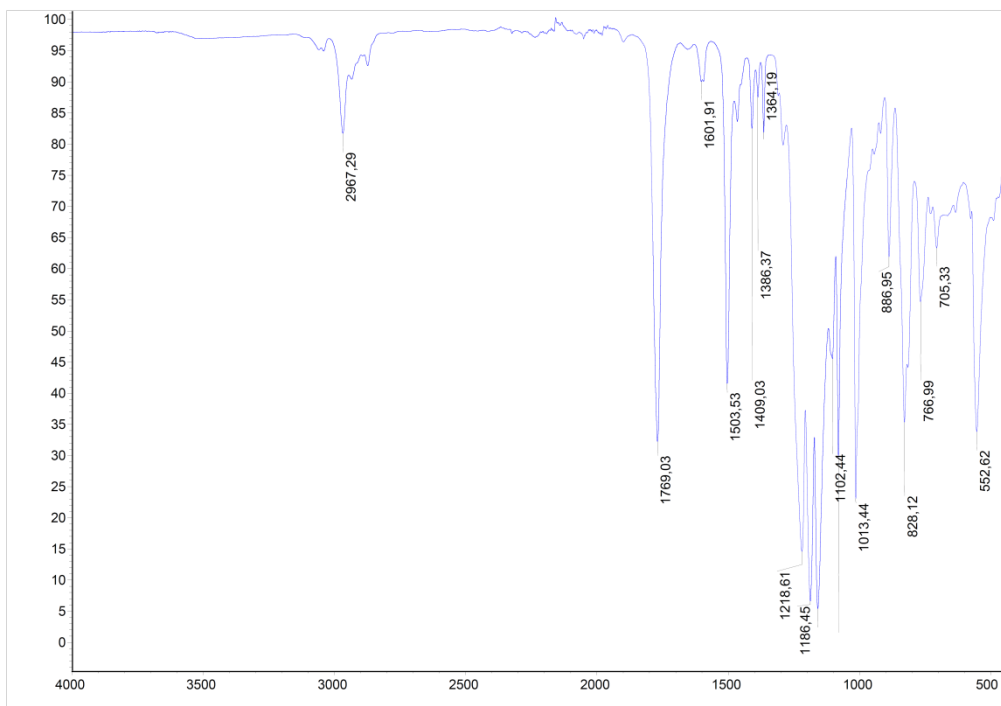
7. Annex

REPRESENTATIVE FIGURES FROM CHARACTERIZATION ANALYSIS OF THE SAMPLES. DATA SHOWN FOR SAMPLE PC3.

FTIR

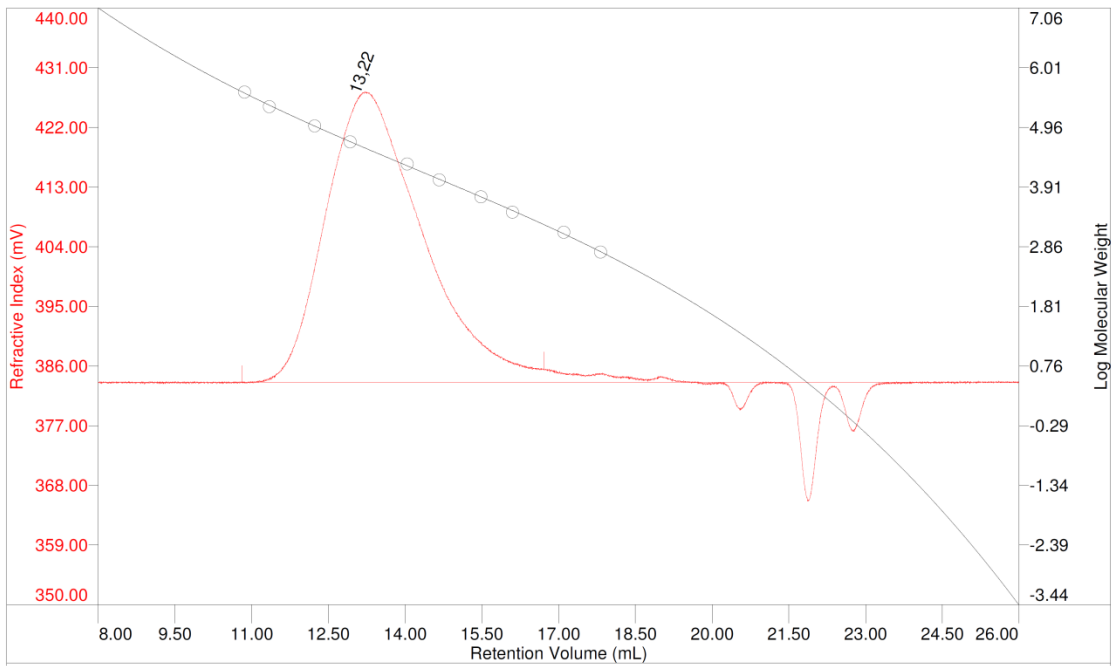


FTIR spectrum of PC3 sample

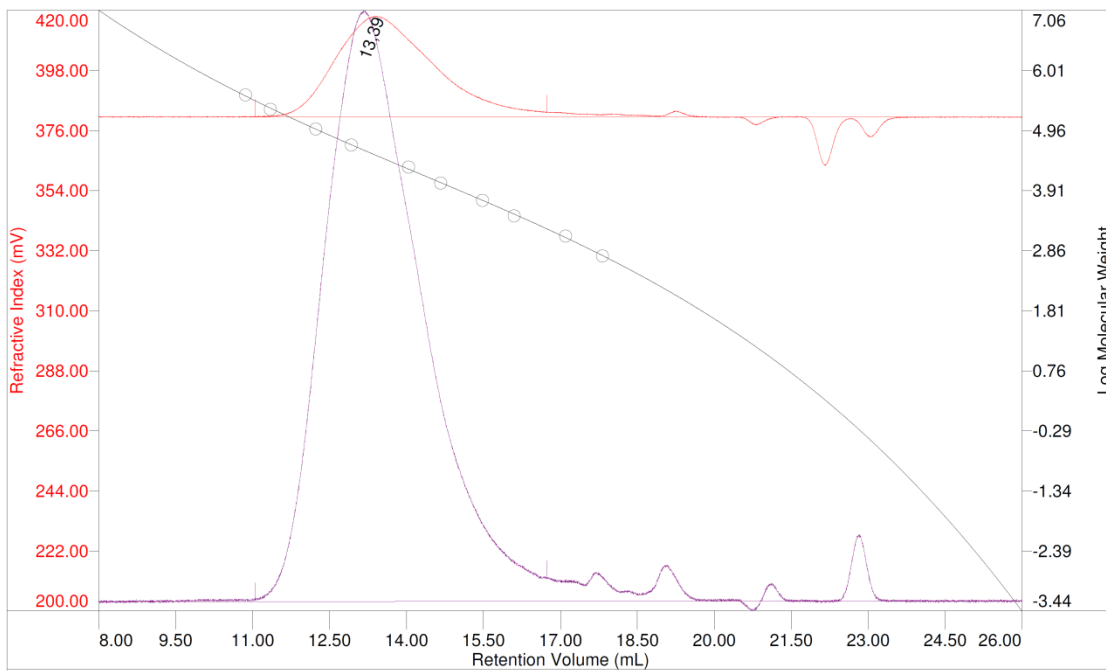


FTIR spectrum of PC3 after hydrothermal exposure

SEC

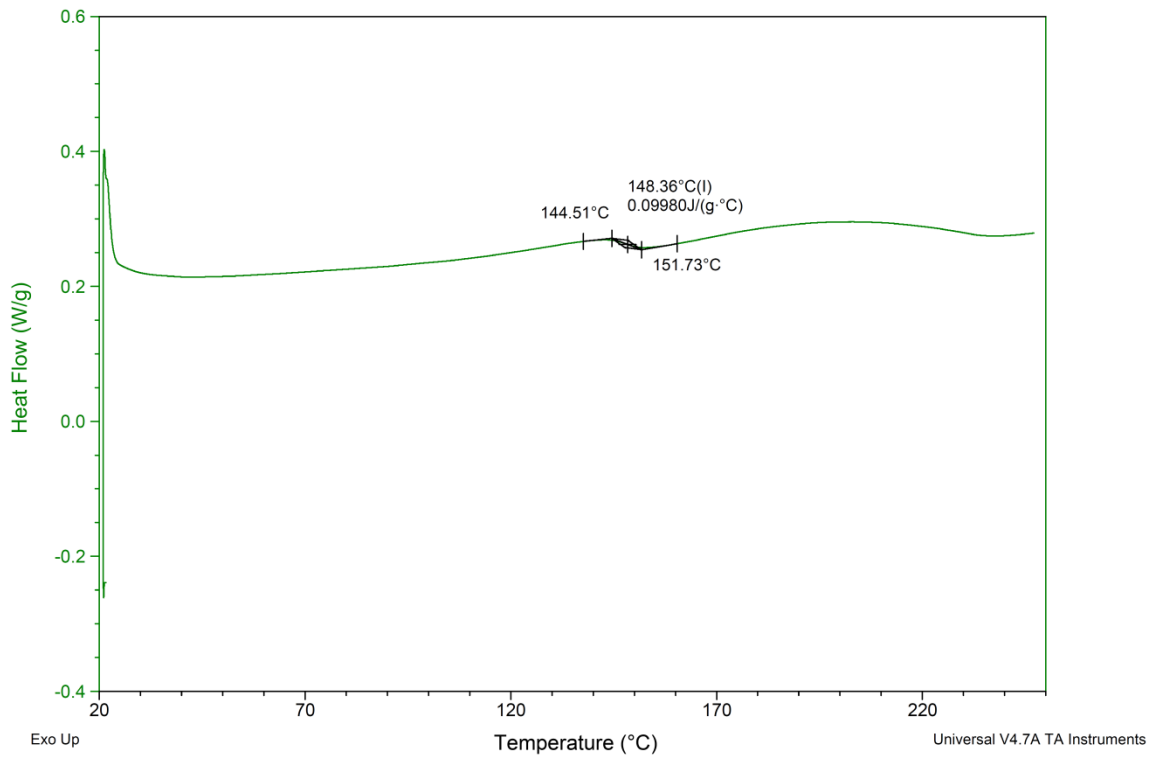


SEC trace of PC3

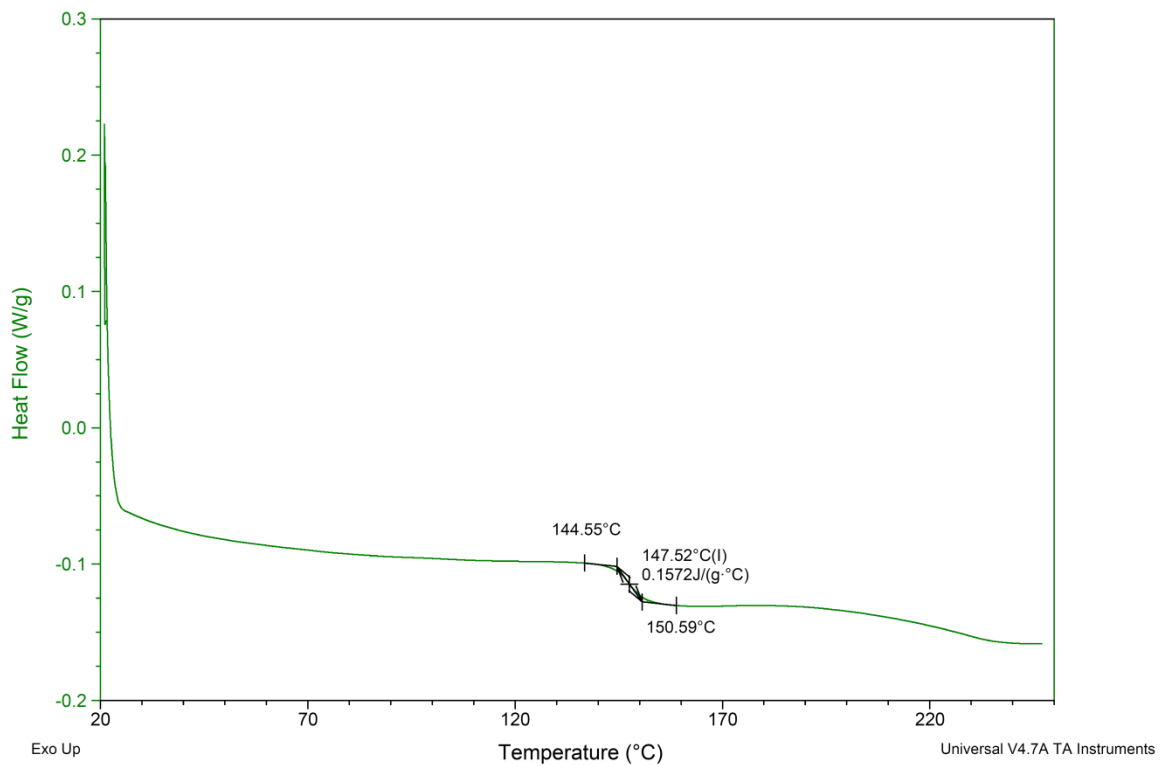


SEC trace of PC3 after hydrothermal exposure

DSC

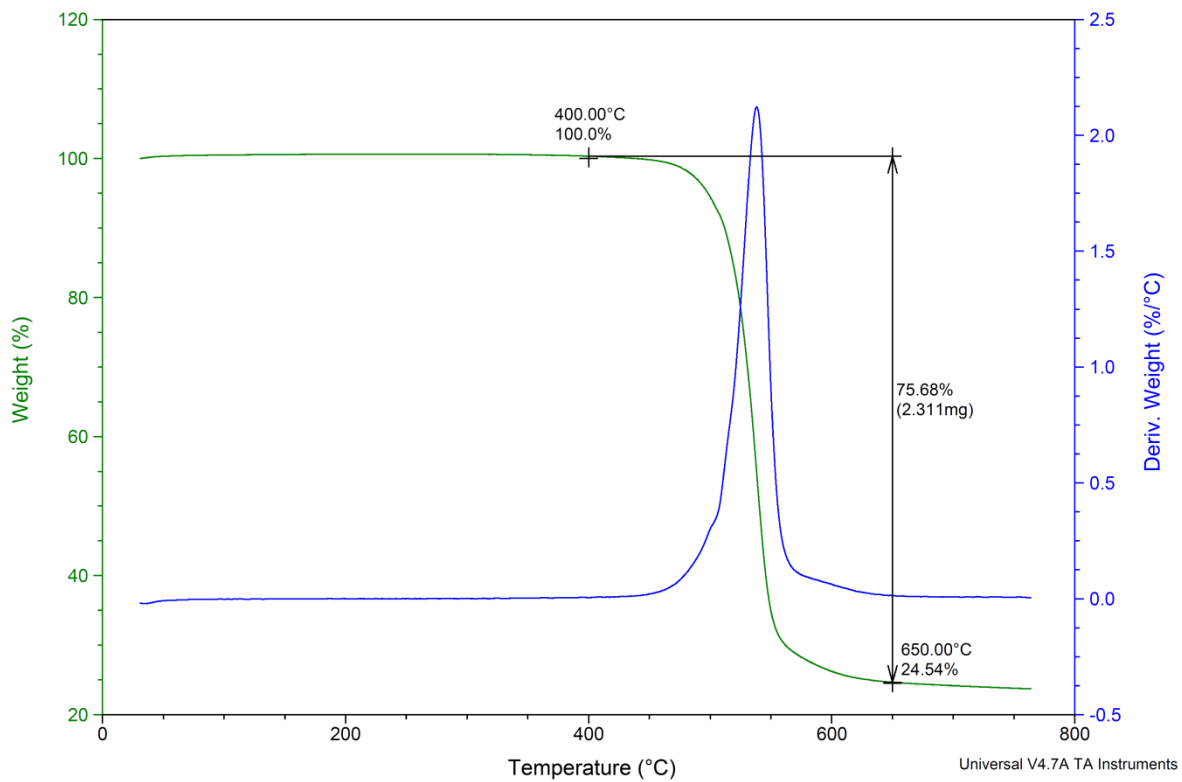


DSC trace of PC3

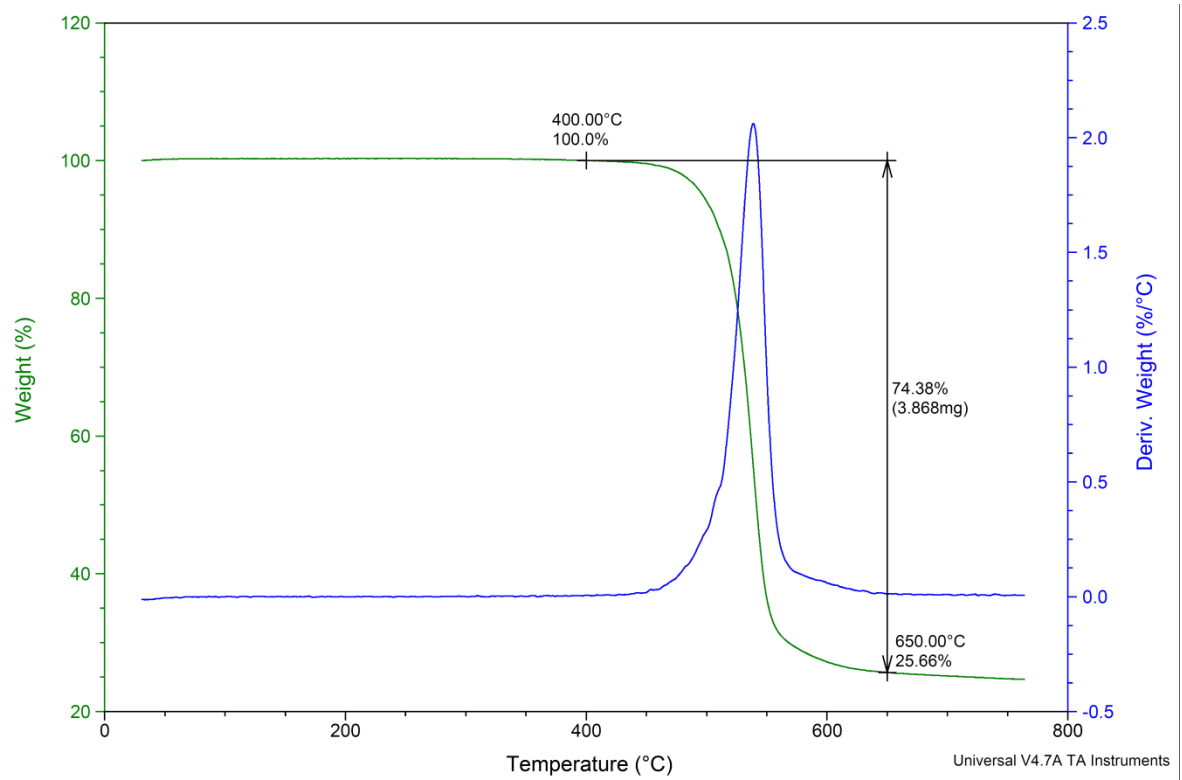


DSC trace of PC3 after hydrothermal exposure

TGA



TGA trace of PC3



TGA trace of PC3 after hydrothermal exposure

Migration of bisphenol A from polycarbonate plastic of different qualities

Undersøgelsen omfatter en gennemgang af litteratur og tilgængelige oplysninger fra industrien om frigivelse af bisphenol A fra polycarbonat og de parametre, der påvirker denne afgivelse. Desuden blev forskellige prøver af polycarbonat karakteriseret og analyseret for at undersøge den potentielle sammenhæng mellem materiale-specifikke parametre og afgivelsen af bisphenol A. Ud fra informationer fra industrien kan det konkluderes, at for at reducere fotonebrydning og hydrotermisk nedbrydning af polymeren mest muligt, bør der anvendes meget rene udgangsstoffer, herunder tilsætningsstoffer, ved fremstilling af polycarbonat til alle formål. Der er ikke i projektet fundet specifikke oplysninger om additiver, der ved tilsætning til polycarbonat, kunne forbedre den hydrolytiske stabilitet af polymeren.

The study covers a review of literature and available industry information regarding release of bisphenol A from polycarbonate and the parameters affecting this bisphenol A release. Moreover in part two of the study, different samples of polycarbonate was characterised and analysed in order to examine the potential correlation between material specific parameters and the release of bisphenol A. It is concluded, from industry information, that only highly pure reagent grade chemicals, including additives, should be used for all polycarbonate grades to reduce photodegradation and hydrothermal degradation of the polymer. No specific information was found about additives known to improve the hydrolytic stability of polycarbonate.



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