Organic Materials Degradation in Solid State Lighting Applications

PhD Thesis

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CHAPTER 1

Introduction

1.1. LED and the LED landscape

Solid state lighting technology is known as a revolutionary invention in the history of lighting industry. Light emitting diodes (LEDs) are used as source of illumination in solid state lighting systems. First practical LED, made from GaAsP semiconductor, was invented in 1962 [1]. The blue LED (GaN semiconductor) was then invented in 1993 [2]. The first commercial white LED was introduced to the market in 1997, using blue LED [3]. Since then the LEDs have become a credible alternative and competitor to incandescent and fluorescent lamps. The first LED systems consumed 20 mA 3-5 Volt. Recently due to technological improvements of the LED designs, the high brightness LEDs (HB LEDs) with higher output lumen flux are used. The multiple benefits of LEDs, including compactness, output, colour adjustment, and the continuous increase in their performance are likely to make them competitive to fluorescent lamps and tubes.

One of the advantages of LEDs over conventional lighting systems is its relatively longer lifetime. A common incandescent lamp has an average lifetime of around 1000 hours whereas the fluorescent lighting technology has an average lifetime of about 10 times longer than incandescent light, which is around 10,000 hours. The present LED lighting devices have an average lifetime of around 25,000 hours with the potential of reaching up to 50,000 hours lifetime. In addition LEDs are increasingly becoming an eco-friendly technology. Fluorescent lighting systems which are one of the most efficient lighting systems before SSL, contain mercury which is not reusable. Contrary to the fluorescent lighting devices, LEDs are semiconductor devices which are free of toxic materials. Another important benefit of LEDs is their comparatively lower energy consumption. The electrical energy consumption for lighting in big cities is about 25% of the total consumed electrical energy. It is estimated that in 2013 the lighting industry was responsible for 17% of energy consumption in US. Figure 1 illustrates the prediction of the energy consumption in the US in different sectors and the expected saving due to the replacement of LEDs (which will be 15% in 2020 and 40% in 2030 [4]).

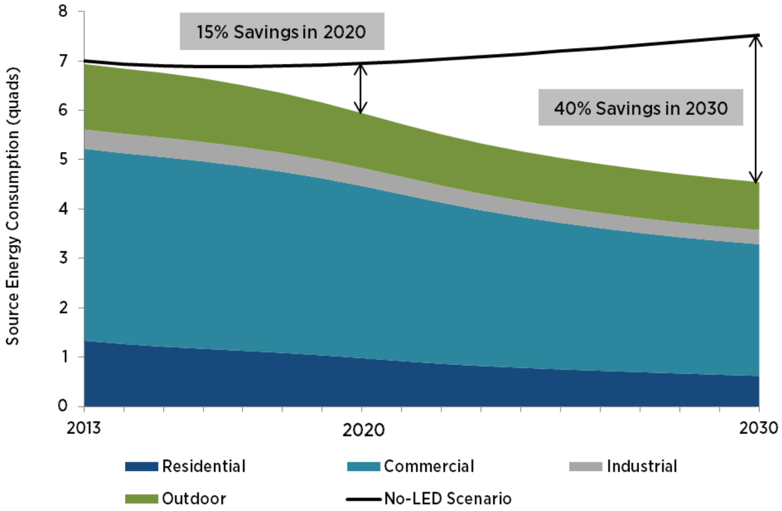

Figure 1: *Total U.S. consumption prediction 2013 to 2030*

Due to the low energy consumption of LEDs and their longer lifetimes, compared to traditional light sources, the total lifetime cost of LEDs will be much lower than the current lighting technologies. LEDs also have higher Efficiency, compared to other light sources [5, 6]. This makes lighting systems, based on LEDs, a great new solution for lighting applications. The internal quantum efficiencies of green and blue LEDs are around 20-40% and 40-60% respectively [7]. The maximum theoretical efficiency of combining blue LED and yellow phosphor is around 50% [8,9]. However, the commercial white LEDs, used in different applications, have normally lower power conversion efficiency [2].

In order to define the quality of LED lighting, three qualitative measurements are usually applied. The first one is efficiency of light, known as efficacy, which is usually defined by lumens/watt (lm/W). Light sources with higher efficacy have obviously higher energy efficiency. The second measurement of the lighting quality is the colour rendering index (CRI). CRI is a quantitative measure of the ability of a light source to reproduce the colours of various objects faithfully in comparison with an ideal or a natural light source. The last qualitative measurement is the lifetime which is a reliability parameter of the light source. It represents the working time of such light source within the lighting specification. Table 1 presents examples of the optical characteristics for common light sources. One can see that the overall properties of LED technology are better than those of other light sources.

Table 1: *Efficacy, CRI and lifetime of common light sources [12]*

Light Source	**Efficacy (lm/W)**	**CRI**	**Lifetime (hours)**
Incandescent (120 V)	14.4	100	1,000
Compact fluorescent	51	80	10,000
High-pressure mercury	34	50	24,000
High-pressure sodium	108	22	24,000
LED	130–220	>80	50,000

Because of all benefits explained above, there can be a wide variety of applications that LEDs are very good replacements for traditional lighting systems. This rapid progress in adopting LED lighting can be represented by the England’s Palace in converting the center room chandelier: all twenty-five watt tungsten lamps were removed, and a low voltage system controlling 2.8 watt LED lamps were installed initiating an energy saving in excess of 80% [5].

Although LED lighting is expected to be adopted eventually for general lighting, the largest applications of coloured and white LEDs are for automobile interior and exterior lighting; backlighting for mobile devices and small and middle sized liquid crystal displays (LCD); single and traffic lighting; and LED display. In fact, those applications now account for about 90% of the LED needs. Figure 2 shows some examples of the application for SSL devices: indoor lighting, outdoor/street lighting, and automotive lighting.

Figure 2: *Three examples for different application of LED based products*

A LED system is a complex system, made from different electrical, optical and thermal components [10], and is divided to 5 levels. First level is the LED chip or semiconductor diode, where the material is doped with impurities to create p–n junctions. When the LED is powered, electrons flow from the n-side (cathode) to the p-side (anode). When an electron meets a hole, it falls into a lower energy level and releases energy in the form of photons [10]. The specific wavelength emitted by an LED obviously depends upon the band gap structure (or materials). The second level is LED package or emitter in which the chip is packaged with a protection and a prime lens is added for a better light quality, and soldered for better electrical connection. In this level phosphor is also used to adjust the colour of emitted light. LED packaging is responsible for the electrical connection, mechanical protection, integrity, and heat dissipation of LED chip. In the third level, the LED packages are assembled onto the large PCB by the solder or epoxy glue. In the fourth level the LEDs are well packaged in a module for final application. In the last level, lighting systems, containing multiple luminaires, smart sensors, communication, control scheme, and data mining and data management, are defined for different applications. Different levels of a solid state lighting (SSL) system are illustrated in Figure 3 [11].

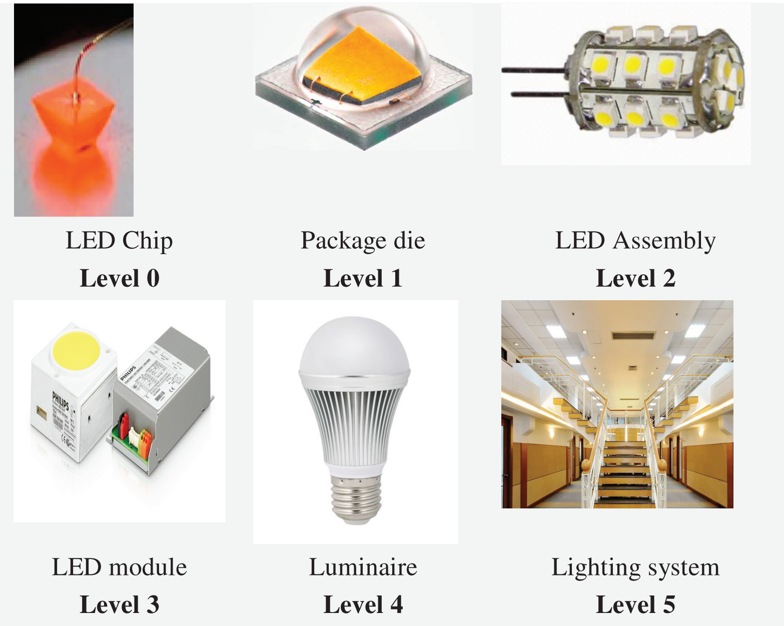

Figure 3: *Components of a solid state lighting (SSL) system [11]*

1.2. White light LED

Currently, there are several technologies, used to produce white light high-power LED systems [13-15]. These methods are mainly based on combining different LED chips with different colours to generate high colour rendering index (CRI) and tuneable colour. These methods can be listed as follows:

- A blue chip and two colour phosphors such as green and red phosphors.
- An ultraviolet (UV) chip and three-color phosphors. In this system, the UV light excites the three-color phosphors (red, green, and blue) to generate white light with a high CRI.
- A blue chip and yellow phosphor in which the yellow phosphor is excited by a blue radiation, producing white light by mixing of non-absorbed blue light.

LEDs made by combining the blue-emitting diode chips with phosphor are the most commercially available white LEDs due to their high efficiency. In this system, the phosphor layer can be either deposited directly on the chip or incorporated into a lens disc [16-19]. The spatial phosphor distribution in white LED lamps strongly influences the colour uniformity and efficiency of the lamp. One can distinguish between proximate and remote phosphor distributions [16-19]. In proximate phosphor distributions, the phosphor is located in close proximity to the semiconductor chip. In remote phosphor distributions, however, the phosphor is spatially removed from the semiconductor chip. Proximate phosphor distributions and remote phosphor distribution are schematically shown in Figure 4 (a), (b), and (c) respectively.

A general weakness of proximate phosphor distributions is the absorption of light by the semiconductor chip. Phosphorescence emitted toward the semiconductor chip can be absorbed by the chip. The reflectivity of the semiconductor chip and metal contacts is generally not very high. This negative point of proximate phosphor distributions can be avoided by remote phosphor distributions in which the phosphor is spatially placed apart from the semiconductor chip. In such remote phosphor structure, it is less likely that phosphorescence is absorbed by the semiconductor chip due to the separation between the semiconductor chip and the phosphor.

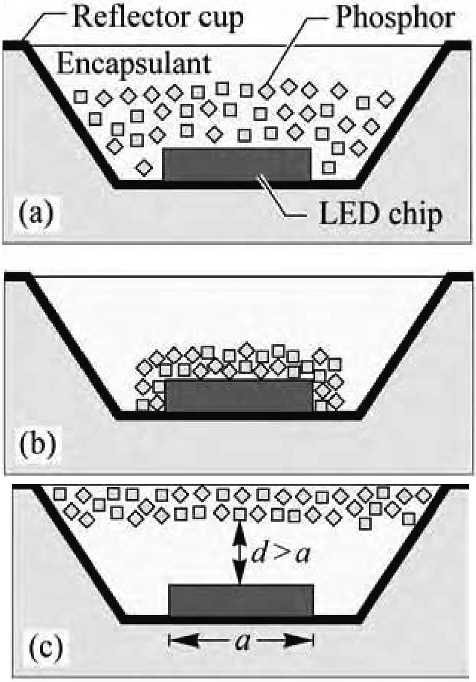

Figure 4: *(a) proximate phosphor distributions, (b) conformal proximate phosphor distributions, and (c) remote phosphor distribution [9]*

1.3. Reliability performance of LEDs

Reliability is the probability that a system will perform its intended function under stated conditions for a specified period of time without failures [20]. By this definition, reliability is a measure as s function of time and, thus, a quantity. The LED domain, despite exciting innovations, motivated by technological developments, has still challenges regarding lack of information when it come to the failure mechanisms and reliability. The relative low reliability information is an obstacle to the acceptance of LEDs in traditional applications. Consumers of LEDs expect that the industry guarantees the lifetime of LEDs in the usage conditions. The failure of LEDs can be categorized in three regions of semiconductors, interconnections and the package failures [20-24]. The die-related failures include severe light output degradation, burned/broken metallization on the die, lattice defects, die cracking, dopant diffusion and electro migration. The interconnect failures of LED packages are electrical overstress-induced bond wire fracture/wire ball bond fatigue, electrical contact metallurgical interdiffusion, and electrostatic discharge, which leads to catastrophic failures of LEDs. Package-related failure mechanisms that result in an optical degradation, colour change, and severe discoloration of the encapsulant are listed as carbonization of the encapsulant, encapsulant yellowing, delamination, lens cracking, phosphor thermal quenching, and solder joint fatigue. LED lifetime is measured by lumen maintenance, which is how the intensity of emitted light tends to weaken over time. Other parameters such as chromaticity coordinate values (x and y) and Correlated Colour temperature (CCT) are also important. The Alliance for Solid-State Illumination Systems and Technologies (ASSIST) defines LED lifetime based on the time to 50% or 70% of light output degradation at room temperature [16]. In order to increase the quality of LEDs it is important to know the main reason of lumen depreciation in a reasonable experimental time periods. LED manufacturers usually perform tests in the product development cycle during the design and development phases to predict the lifetime of LED. The term reliability-prediction is historically used to denote the process of applying mathematical models and data for the purpose of estimating field-reliability of a system before empirical data are available [11]. These predictions are used to evaluate design feasibility, compare design alternatives, identify potential failure areas, trade-off system design factors, and track reliability improvement. In order to predict LED life time, it is needed to carry out accelerated life tests at high temperatures and monitor the light output during the test. Modelling of acceleration factors (AF) is generally used to predict the long-term lifetime of LED packages at specific usage conditions [16, 20]. Typical qualification tests of LEDs are categorized into operating life tests and environmental tests by using industrial standards such as JEDEC or JEITA, and LM-803 [25- 27]. Table 2 shows one example of qualification test methods.

Table 2: *Qualification test methods*

Test	Conditions & Failure Criteria	Standards
Room Temperature Operating Life Test (RTOL)	Temperature: 55 °C, Forward Current Test Period: 1008 hours *Failure Criteria*: • Forward Voltage shift: > 5% • Luminous Flux degradation -- InGaN LEDs: > 15% -- AlInGaP LEDs: > 25%	IES LM-80-2008
High Temperature Operating Life Test (HTOL)	Temperature: 85 °C, Forward Test Period: 1008 hours *Failure Criteria*: • Forward Voltage shift: > 5% • Luminous Flux degradation -- InGaN LEDs: > 15% -- AlInGaP LEDs: > 25%	IES LM-80-2008
Wet High Temperature Operating Life Test (WHTOL)	• Temperature: 85 °C, Forward Current • All color XR-C & XR-E LEDs • XR-C & XR-E Cool White (>5000K CCT) LEDs - Humidity: 85% RH • All other XLamp LEDs - Temperature: 60 °C - Humidity: 90% RH Test Period: 1008 hours (cycled) *Failure Criteria*: • Forward Voltage shift: > 5% • Luminous Flux degradation -- InGaN LEDs: > 15% -- AlInGaP LEDs: > 25%	IEC62861 (to be published in 2015)
Low Temperature Operating Life Test (LTOL)	Temperature : -40 °C, Forward Current • Test Period : 1008 hours *Failure Criteria*: • Forward Voltage shift: > 5% • Luminous Flux degradation -- InGaN LEDs: > 15% -- AlInGaP LEDs: > 25%)	JESD22 Method A108-C

1.4. Aging of optical materials

For LED lighting to be a viable lighting source, there are many technical challenges to be resolved. Amongst them, the light extraction efficiency, and the light output degradation are the key issues, which turn out to be all related to the packaging materials. LEDs have to operate in different temperatures and humidity environments, ranging from indoor conditions to outdoor climate changes. Moisture, ionic contaminants, heat, radiation, and mechanical stresses can be highly detrimental to LEDs and may lead to device failures. Recently, more than 99% of microelectronic devices are encapsulated by plastics. LEDs are encapsulated to prevent mechanical and thermal stress shock and humidity induced corrosion [28]. Details of package-related failures and the relative solutions are shown in Table 3.

It is obvious that the abovementioned critical issues in LEDs packaging are mostly materials dependent. Therefore, the challenges for packaging materials are to increase the light extraction efficiency, minimize the heat generated, conduct more heat out of the package, and resist heat and UV light. Thermal management issues are critical for lifetime, lumen output, and fixture design of high power LEDs. To improve packaging materials and the lifetime of LEDs, the requirements, mentioned below are needed.

- High refractive index
- Excellent electrical properties
- Good chemical resistance
- Low water absorption and, and moisture resistance
- Good adhesion to package components
- Mechanical strength
- Good UV and thermal resistance

Table 3: *Materials challenges and solutions for packaging high power LEDs*

Challenges	Problems	Packaging Materials Solutions
Light Extraction	Refractive index mismatch between LED die and encapsulant	High refractive indexe encapslant Efficient lens/cup design
Thermal Yellowing	Thermal degradation of encapsulants induced by high junction temperature between LED die and lead frame	Modified resins or silicone based encapsulant, low thermal resistance substrate
UV Yellowing	Photo degradation of encapsulants induced by UV radiation from LED dies and outdoor	UV transparent encapsulant
Stress/Delamination	Failure of wire-bond and die attach caused by the CTE mismatch among encapsulant, LED die and lead-frame	Low CTE and modulus encapsulants, Excellent adhesion and CTE matching materials between the surfaces

Among different polymers, which are used as an encapsulant and lens, details of three important ones are explained below.

1.4.1. Epoxy resin

The majority of encapsulant/lens materials, used today, are thermosetting polymers, based on epoxy resins. During past years epoxy resins are widely used as an encapsulant materials in LED package because of their combination of low cost, ease of processing, and excellent thermal, electrical, mechanical, and moisture barrier properties [29, 30]. Epoxies are also widely used as die-attach adhesives, laminates for printed wiring boards, underfill adhesives for flip-chip and transfer moulding compounds for PEMs (plastic encapsulated microcircuits).

Epoxy resins are based on the epoxy group, a strained three membered carbon oxygen ring structure as shown in Figure 1.3.

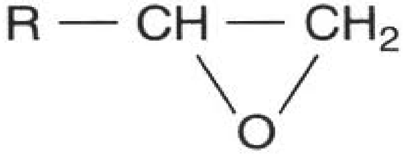

***Figure 4**: Chemical structure of Epoxy functionality*

Transparent epoxy resins are generally used as an LED encapsulant. However, epoxy resins have two disadvantages as LED encapsulants. One is that cured epoxy resins are usually hard and brittle owing to rigid cross-linked networks. The other disadvantage is that epoxy resins degrade under exposure to radiation and high temperatures, resulting in chain scission and discoloration, because of the formation of thermo-oxidative cross-links. Among different degradation mechanisms in epoxy and encapsulant plastics in optical systems, discoloration and yellowing are the most common failure mechanisms, resulting in the reduction in the transparency of encapsulants/lens and decrease in the LED light output [31].

1.4.2. Silicon

A material with enhanced optical as well as toughness and thermal stability properties to replace epoxy is silicone. Silicone consists of a unique type of polymer in the sense that the structure is semi-organic. Because of the combination of organic groups (methyl, vinyl, etc.) and inorganic backbone (Si–O), silicone materials exhibit some unique properties such as high purity, moisture resistance, excellent biocompatibility, and higher thermal resistance than other polymers. Also Si maintains its excellent electrical properties at high temperatures and under humid environments [32]. General formulation of Si is shown below:

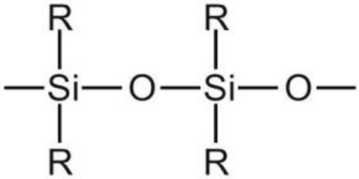

Figure 5: *Chemical structure of Si*

However, the downside of silicone compound is its lower glass transition temperature (T_g), larger *CTE*, and poor adhesion to the housing. One possible way to improve thermal and mechanical properties of silicone is using siloxane-modified LED transparent encapsulant. The siloxane compounds improve the bond energy of the polymer chains to mitigate the chain scission by increasing of the cross-link density [32].

1.4.3. Polycarbonate

The third widely used material as an LED encapsulant is thermoplastics based on polycarbonate. Bisphenol A polycarbonate (BPA-PC) is an engineering thermoplastic with high impact strength, heat resistance and high modulus of elasticity. It has been used in various applications and its application in different domains has tremendously increased during last years [33-35]. General formulation of BPA-PC is shown below:

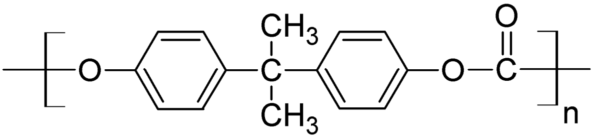

Figure 6*: Chemical structure of Bisphenol A polycarbonate*

Similar to epoxy resins and silicones, the main disadvantage of polycarbonate under exposure to the radiation at elevated temperatures is yellowing and discolouration. This results in a decreased light output due to decreased encapsulant/lens transparency. The main reasons of discolouration and yellowing are continued exposure to wavelength emission (blue/UV radiation), excessive temperature, and the presence of phosphor. Photodegradation of polymer materials usually takes place as a result of increasing the molecular mobility of the polymer as well as the introduction of chromophores as an additive into the molecule, both of which have absorption maxima in a region where the matrix polymer has no absorption band [36]. Photodegradation also depends on exposure time and the amount of radiation. The chemistry of degradation processes in polycarbonates has been studied extensively over the past few decades [36-38]. In BPA-PC the chemistry, underlying the photo-degradation, has been described in two different mechanisms, photo-Fries rearrangement and photo-oxidation. The relative importance of these two mechanisms depends on the applied irradiation wavelengths. Previous investigations show that the photo-Fries rearrangement reaction is more likely to occur at wavelengths shorter than 300 nm, whereas photo-oxidation reactions are more important when light of longer wavelengths (> 340 nm) is used [39-43]. When light with wavelengths longer than 340 nm is used, the dominant photo degradation reaction is reported to be side chain oxidation [43].

Beside of light, yellowing and degradation of package materials is largely dependent on temperature which is a combination of junction temperature, ambient temperature and LED self-heating [20]. Narendran et al. [18] reported that the degradation was affected by junction heat and the amount of short wavelength emissions. It was shown that the thermal effect has greater influence on the yellowing than the short-wavelength radiation. Besides, it is revealed that a portion of the light circulated between the phosphor layer and the reflector cup would also contribute to the increasing of the temperature, causing yellowing [22]. Barton and Osinski [42] showed that a temperature of around 150 °C was sufficient to change the transparency of the epoxy and decreasing the light output of LEDs. Localized heating, produced by phosphor particles during light conversion, has also an effect on the encapsulant/lens discolouration [43]. It was shown that although phosphor is a necessary component to produce white light, the presence of phosphor causes a decrease in reliability. Phosphor thermal quenching decreases light output with the increase of the non-radiative transition probability due to thermally driven phosphorescence decay. Phosphor thermal quenching means that the efficiency of the phosphor is degraded when temperature rises. It is generally required that phosphors for white LEDs have low thermal quenching by a small Stokes shift to avoid changes in the chromaticity and brightness of white LEDs [17].

1.5. Objectives and Approach

LED is a new technology for lighting and it is developing very fast. Reliability of LEDs is a challenge due to the long lifetime expectation. This thesis is focusing on reliability of the optical part. The main objective is to study the dominant chemical reasons / reactions of yellowing and discoloration of BPA-Polycarbonate materials, which are used as lens in LED-based products. In this thesis, the research objectives are set as follows:

- Study the dominant chemical reasons / reactions of yellowing and discoloration of BPA-Polycarbonate materials, which are used as lens in LED-based products.
- Find correlations between chemical reactions and degradations of optical properties and the discolouration.
- Understand the contributions of light and heat to the discoloration reactions
- Develop newly accelerated yellowing test methods in order to reduce the time-to-market of new materials.
- Find the effects of ageing of optical materials on the reliability and life time of the LED-based products and developing relevant reliability models.

In order to meet these objectives, a combined experimental – theoretical approach is used. To have results within a reasonable period of time, the degradation tests were accelerated by using high temperature as well as blue light radiation. In this study the effects of heat and blue light radiation are tried to be addressed separately and also the combination of high temperature and light is studied. The reliability models of exponential lumen decay and Eyring, as well as Arrhenius models are used to predict the life time of the BPA-PC lenses and remote phosphors. Reliability here is defined as the contribution of optical material degradations to the lumen lifetime of the product.

1.6. Outline of the Thesis

This thesis is written on the basis of 6 journal publications and/or contributions to conference proceedings with a possibility of small overlap in some chapters. Each chapter, however, can be read independently. The structure of the thesis is as follows; the detailed information about the lens plates that are used in this study and the experimental set-up and optical/chemical characterization techniques are described in details in Chapter 2. In Chapter 3 the thermal degradation mechanisms of BPA-PC plates at the temperature range 100-140ºC are studied. In this study BPA-PC plates are held at elevated temperature of 100 to 140 ºC for a period up to 3000 hrs and the optical properties and yellowing kinetics are extensively studied with different optical and chemical techniques. In Chapter 4 the degradation mechanisms of BPA-PC plates under blue light radiation are studied. In this chapter, BPA-PC plates are irradiated with blue light at elevated temperature of 140 ºC for a period up to 1920 hrs. Optical and chemical properties of the photo-aged plates were studied using UV-VIS Spectrophotometer, FTIR-ATR spectrometer, Integrated Sphere, and Lambda 950 spectrophotometer. In Chapter 5 X-ray photoelectron spectroscopy (XPS) has been used to monitor the changes in the surface chemistry of BPA-PC plates over a temperature range of 100 to 140 ºC for a period up to 3000 hrs. XPS is very useful to get some detailed information about surface reactions during optical degradation. The accelerated optical degradation of two different commercial BPA-PC plates under elevated temperature stress is studied in Chapter 6. In this chapter the results from commercial plates can be compared with pure BPA-PC plates. In Chapter 7 the thermal stability and life time of remote phosphor lens plates are discussed. Spectral power distribution (SPD) and photometric parameters of thermally-aged phosphor plates, measured by Integrated Sphere, are presented. Chapter 8 describes a new acceleration test method for LED Lens materials and effect of light intensity on the kinetics of ageing of remote phosphor plates. Effect of graphene mono-layer on optical performance of BPA-PC is discussed in chapter 9. Main conclusions and recommendations of future work are given in Chapter 10.

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CHAPTER 2

Reliability Models and Characterization Techniques for Optical Materials: An Overview

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This chapter briefly highlights the characterization techniques used to characterize the optical materials used in this study. As many textbook exist in this chapter only gives a short overview. Besides this, the chapter also highlights the materials used in this study.

2.1. Lens and remote phosphor materials

2.1.1. BPA-PC

Over the past decades the production and consumption of polymeric materials has increased rapidly. Over the past years lists of demands for the applications that use polymeric materials have grown. To meet these requirements, new polymers can be developed, or the current polymers can be modified to improve their properties. One of the disadvantages of using polymers is that they degrade when they are used in extreme environments, such as high temperature conditions or in outdoor applications. Also parameters as the humidity, temperature, mechanical stresses, and light radiation can affect the degradation rate. It has been indicated that the UV radiation is one of the most important factors determining the polymers lifetime. Polycarbonate is one of the most important engineering plastics due to its high toughness and transparency [1]. The most common applications can be found in coating applications, such as electrical and electronics applications, computers and, mobile phones, and optical media, such as compact discs. Furthermore, they can also be used in medical and health care, packaging, and automotive. The most important polycarbonate is based on bisphenol-A. In general there are two different industrial paths for the synthesis of high molecular weight bisphenol-A polycarbonate (BPA-PC), the interfacial synthesis and the melt synthesis [1, 2]. The best extensively used commercial process, involves the interfacial reaction between phosgene and the sodium salt of bisphenol-A (BPA) in a heterogeneous system. The hydroxyl group of the BPA molecule is deprotonated by the sodium hydroxide. The deprotonated oxygen reacts with phosgene to form a chloroformate, which reacts with another deprotonated BPA. The molecular weight is regulated by the addition of phenol or phenolic derivatives to endcap the polymer chains. The second industrial route to synthesize BPA-PC consists of a melt- phase transesterifcation between a bisphenol-A and diphenyl carbonate (DPC) [1, 2]. This process occurs typically in two stages. In the first stage the BPA, DPC and a catalyst are heated to 200 ±C to form a low molecular weight polycarbonate and to remove most of the formed phenol. The second stage involves a heating of the remaining mixture to evaporate the remaining phenol and DPC to form an intermediate weight average molecular weight polycarbonate.

In this study pure BPA-PC is used to investigate the chemical reason of thermal and photo ageing of BPA-PC. Besides the commercial BPA-PC with normal additives, used in plastic lenses for LED applications, i.e. optical brightener, scatter agent, flame retardant, and heat stabilizer, is also used.

2.1.2. YAG:Ce phosphor

The technical approach to solid-state white-light sources has been a combination of LED and phosphors. The excitation sources used for phosphors in LEDs differ greatly from those of phosphors in conventional lighting. The excitation sources for phosphors in LEDs are UV (360–410nm) or blue light (420–480nm), whereas those for conventional inorganic phosphors in cathode-ray tubes (CRTs) or fluorescent lamps are electron beams or mercury gas (254nm). Therefore, the phosphors in LEDs should have high absorption of UV or blue light. Conventional incandescent and fluorescent lamps rely on either heat or discharge of gases. Phosphor used in LED applications should also have the following characteristics: high conversion efficiency, high stability against chemical, oxygen, carbon dioxide, and moisture, low thermal quenching, small and uniform particle size, and appropriate mission colours. Silicon-based oxynitride and nitride phosphors have received significant attention in recent years because of their encouraging luminescent properties (excitability by blue light, high conversion efficiency, and the possibility of full colour emission), as well as their low thermal quenching, high chemical stability, and high potential for use in white LEDs [3 – 6]. Other types of phosphor such as orthosilicates [7, 8], aluminates [9], and sulfides [9, 10] have also been used in white LEDs. However, most oxide-based phosphors have low absorption in the visible-light spectrum, making it impossible for them to be coupled with blue LEDs. On the other hand, sulfide-based phosphors are thermally unstable and very sensitive to moisture, and their luminescence degrades significantly under ambient atmosphere without a protective coating layer. Recently, many manufacturers around the world are producing white LEDs. One of the most common methods for producing white light with LEDs is to use a cerium-doped yttrium aluminum garnet (YAG:Ce) phosphor with a gallium nitride (GaN)-based blue. (III)-doped YAG (Ce:YAG or YAG:Ce) is a yellow phosphor which is widely used in LEDs to produce white light. Yttrium aluminum garnet ($Y_3Al_5O_{12}$ or YAG) doped with Ce $^{3+}$ is a luminescent material with a rich history and a wide variety of applications [11]. Pure YAG phase is hard to achieve due to the fact that Y_2O_3–Al_2O_3 is a complex system that has two more intermediate compounds with the following composition: perovskite $YAlO_3$ (YAP) and monoclinic $Y_4Al_2O_9$ (YAM) [11]. A good overview of the different synthesis methods for crystalline powders is provided by Pan et al [12]. Four methods are described: solid-state reaction, co precipitation method, sol-gel method, and the combustion method. YAG:Ce emits yellow light when subjected to blue or ultraviolet light, or to x-ray light. It is used in white light-emitting diodes, as a coating on a high-brightness blue InGaN diode, converting part of the blue light into yellow, which then converted as white. Among several phosphor converting white LEDs, YAG-based one has the best performance in terms of efficiency [11]. Since the phosphor works by the 5d-4f transition of Ce^{3+} ion, the luminescence spectrum is very broad compared with 4f-4f transitions of most rare-earth ions, Energy level diagram Ce $^{3+}$ is shown in Figure 1.

The excitation sources for phosphors in LEDs are UV (360–410 nm) or blue light (420–480 nm), whereas those for conventional inorganic phosphors in cathode-ray tubes (CRTs) or fluorescent lamps are electron beams or mercury gas (254 nm). Therefore, the phosphors in LEDs should have high absorption of UV or blue light. Part of the blue light from the InGaN LED is absorbed by a thin layer of YAG:Ce and is converted into yellow light.

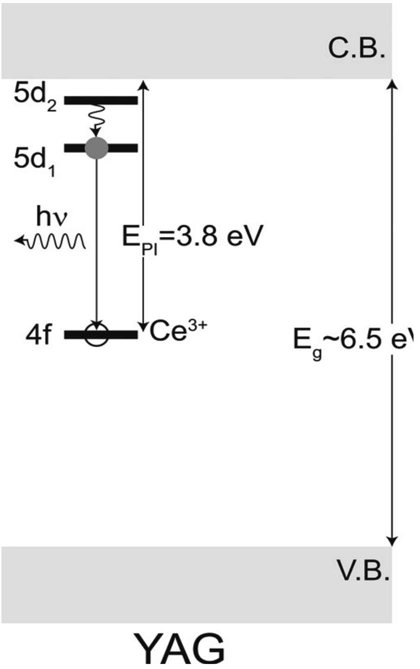


***Figure 1**: Energy level scheme of Ce 3+ in YAG*

2.1.3. Thermal Quenching of YAG:Ce

Thermal quenching is one of the important technological parameters for phosphors used in white LEDs. In order to study this effect, phosphor is laminated on the plastic lenses, the original plastic was transparent. The XRD pattern of the remote phosphor is shown in Figure 2. Thermally-aged plates (aged at 140 ºC for 3000 hrs) have also the same XRD pattern, showing that the crystallographic structure of phosphor is stable at thermal ageing.

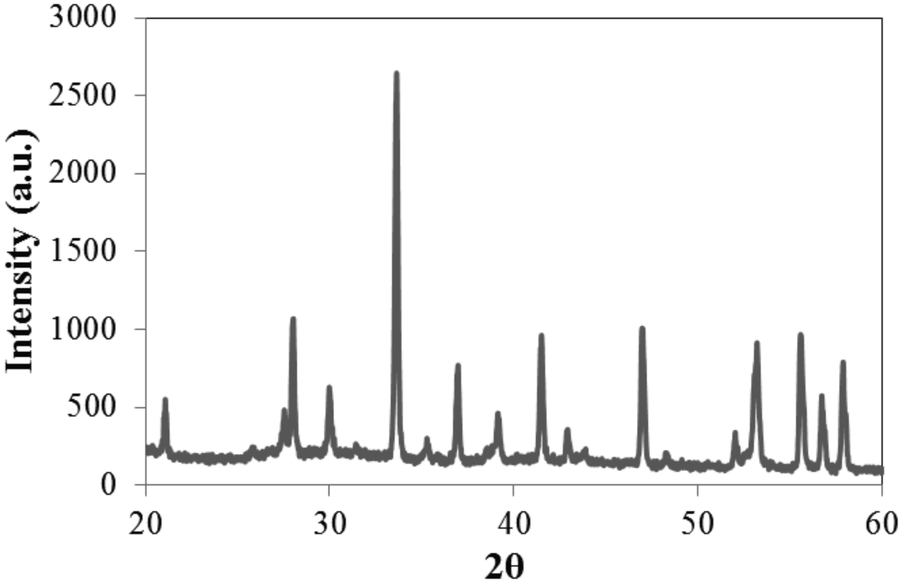
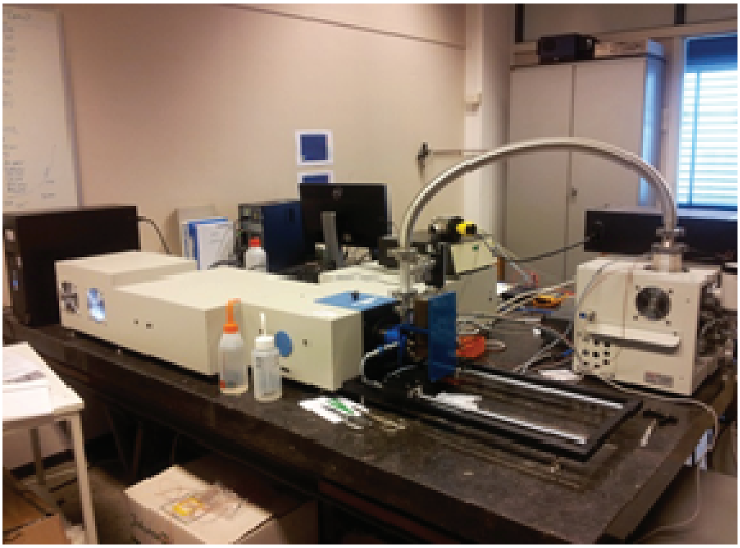


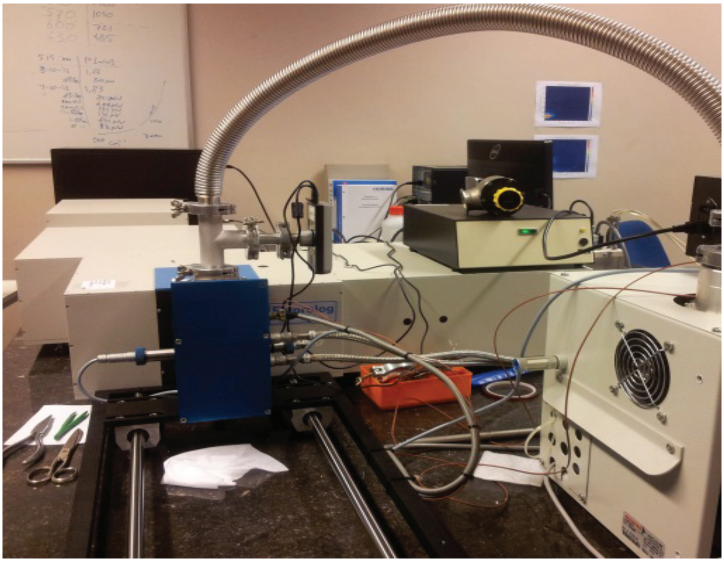
***Figure 2:** XRD pattern for YAG*

Figure 3 shows the photoluminescence device, used in this study, in which the temperature increases in the 10 ºC steps from 25 to 140 ºC for two kind of YAG.

The temperature-dependent luminescent properties are shown in Figure 4. Upon heating, the decrease in emission intensity and the broadening of full width at half maximum (FWHM) is apparent, and these can be explained by the thermal quenching. With increasing temperature, the non-radiative transition probability by thermal activation and release of the luminescent centre through the crossing point between the excited state and the ground state increases, this quenches the luminescence.

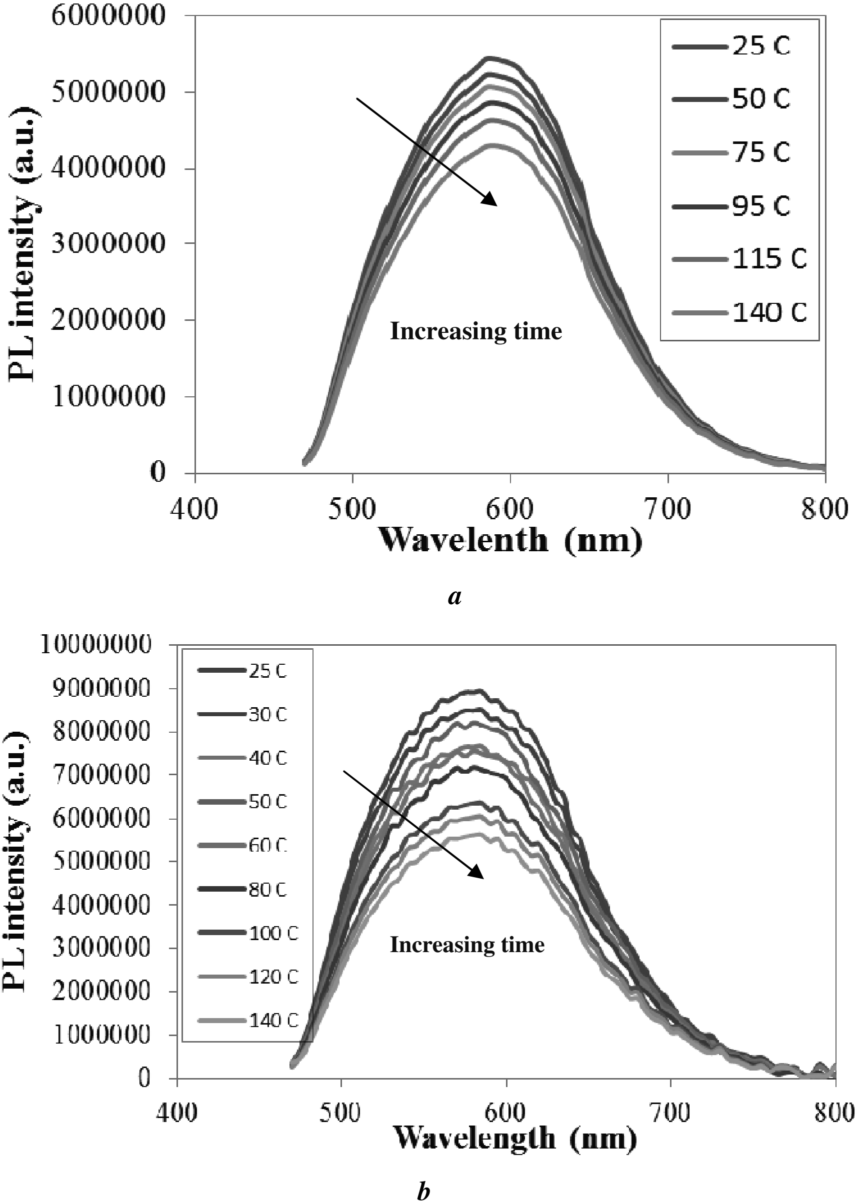


An overview



Sample holder

Figure 3: *Photoluminescence device*

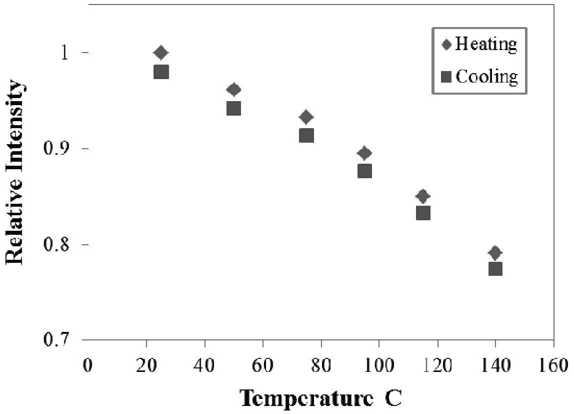


a

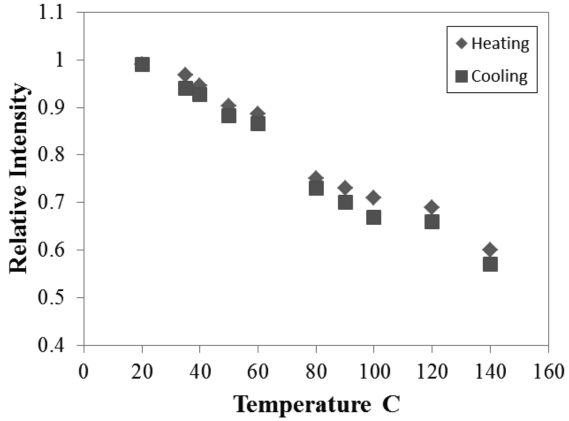
b

Figure 4: *Temperature dependence of emission spectra of a) Remote phosphor A and b) Remote phosphor B*

A more quantitative description of the effects of temperature on the performance of remote phosphor A and B is given in Figure 5. This Figure illustrates the reduction of normalized relative intensity by temperature. Clearly, the thermal quenching of phosphors is a recoverable, since the luminescence intensity curve during cooling has the same trend as the heating curve.



Sample *A*



Sample *B*

Figure 5: *Temperature dependence of the integrated emission intensity for sample a) A, and b) B*

A simple equation to describe thermal quenching of luminescence intensity $I\,(T)$ with temperature T is given by the Arrhenius equation. In order to determine the activation energy for thermal quenching and better understand the temperature dependence of photoluminescence was fitted to the thermal quenching data [2] as follow:

$$I = \frac{I_0}{1+\exp(-\frac{E}{KT})} \qquad (1),$$

where I_0 is the initial intensity, I is the intensity at the T, T is temperature *(K), c* is a constant, E is the activation energy for thermal quenching, and k is Boltzmann's constant. Figure 6 plots ln ($I_0/I-1$) vs $1/kT$ and gives a straight line up to T=140 °C. The best fit following Equation 1 gives a comparable activation energy E of 0.22 eV for Sample *A* and 0.25 eV for Sample *B*.

A well-established method to determine the temperature quenching is to measure the luminescence lifetime of an emission band as a function of temperature. For an allowed transition the radiative lifetime usually does not change strongly with temperature [13]. To determine the luminescence quenching temperature for the Ce^{3+} luminescence in YAG, Volker et al performed luminescence lifetime measurements as a function of temperature for the four different Ce^{3+} concentrations. They showed that at room temperature the luminescence decay time is around 65 ns for all Ce concentrations. Most probably this is caused by re-absorption of the emission at the higher Ce concentrations. It is well-known that re-absorption of emission gives rise to a longer decay time [14]. The lengthening of the lifetime due to re-absorption means that the true radiative lifetime of the d-f emission from Ce in YAG is 63 ns, the lifetime measured for the lowest Ce concentration.

Failure modes resulting from phosphor thermal quenching include a decrease in light output, colour shift, and the broadening of full width at half maximum (FWHM). The driving force of phosphor ageing is a high temperature [15]. The temperature dependency of phosphor thermal quenching is described in Figure 6. The activation energy of the degradation reaction in phosphor plates is calculated from Arrhenius Equation (Equation 1). Thermal quenching activation energy in both phosphor plates are calculated 0.25 and 0.22Ev which is in agreement with the previous results [3].

2.2. UV-VIS Spectroscopy

UV-VIS absorption spectroscopy is a widely-used technique to analyse and characterize polymers and copolymers containing chromospheres, such as aromatic or carbonyl groups, which can absorb photons within the ultraviolet and visible (UV/VIS) wavelength range. UV-VIS spectroscopy is also a powerful technique to monitor photochemical reactions, occurring during degradation processes. In this technique, the absorption of light is recorded as a function of the wavelength by measuring the change in the intensity of light beam before and after passing through the sample. For a homogeneous, isotropic medium containing an absorbing compound at concentration C, the light absorption is calculated by Lambert-Beer law [15]:

$$A = \lg 10\ (I_0/I) = \varepsilon C d \qquad (2),$$

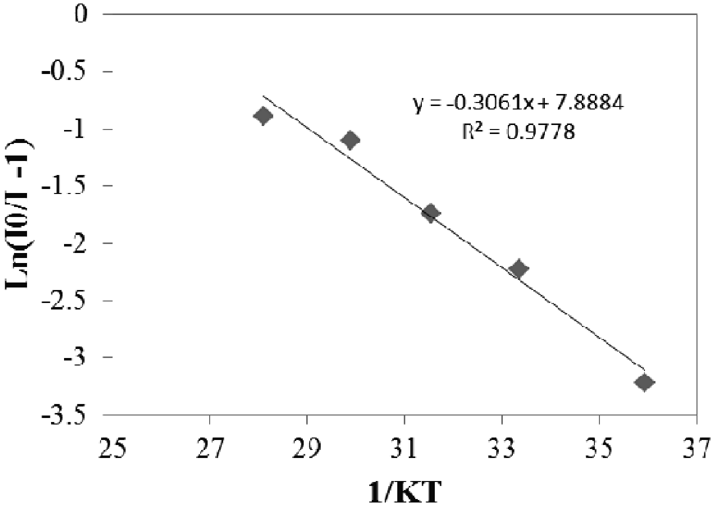
where A is the absorbance, I_0 and I denote the light intensity before and after absorption, and ε is the extinction coefficient at a given wavelength. There are two prerequisites for the absorption of a photon of energy hv by a molecule [15]:

1) The molecule must contain a chromophoric group with excitable energy states corresponding to the photon energy according to:

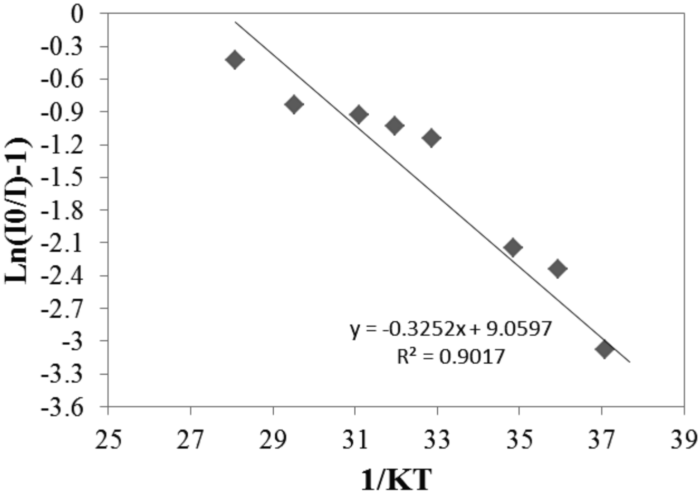
$$hv = E_n - E_0 \qquad (3),$$

En and E_0 denote the energies of the excited and the ground state, respectively. Typical chromophoric groups are listed in Table 1.

2) Transition between the two energy states is only possible if there is a change in the dipole moment.



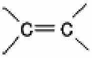
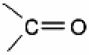
Sample *A*



Sample *B*

Figure 6: *Activation energy for thermal quenching of a) Sample A, and b) Sample B*

***Table 1:** Typical Chromophoric Groups [15]*

Chromophore	Typical compound	λ_{max} (nm) a)	ε_{max} (L mol^{-1} cm^{-1})
	Ethene	193	10^4
$—C\equiv C—$	Ethyne	173	6×10^3
	Acetone	187	10^3
		271	15
$—N=N—$	Azomethane	347	5
$—N=O.$	*t*-Nitrosobutane	300	100
		665	20
$—O—N=O.$	Amyl nitrite	219	219
		357	357

a) Wavelength of maximum optical absorption.

2.3. FTIR spectroscopy

Infrared (IR) spectroscopy is a chemical-analytical tool, which is widely used in the analysis and characterization of polymers. It is a very powerful technique to monitor alterations in the chemical structures of polymers during photo and thermal degradation. The wavelength regime of importance ranges in a very wide spectrum, which corresponds to the energies required to excite vibrations of atoms in molecules. In this technique, IR light is absorbed when the oscillating dipole moment corresponding to a molecular vibration interacts with the oscillating vector of the IR beam. The recorded absorption spectra consist of peaks attributable to different kinds of vibrations of atom groups in a molecule, as is shown in Figure 7. Modern commercial IR spectrometers deliver absorption spectra commonly referred to as Fourier-transform infrared (FTIR) spectra by means of Fourier transformation as mathematical decoding method [16].

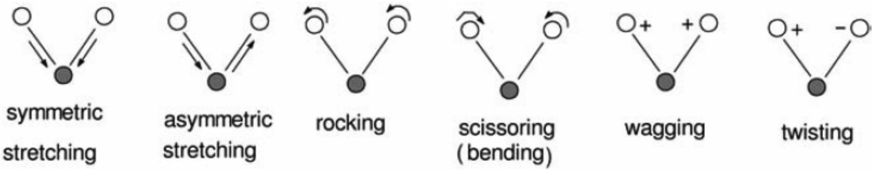


Figure 7: *Schematic of different modes of vibration in an atom group [16].*

2.4. X-Ray Photoelectron Spectroscopy (XPS)

X-Ray Photoelectron Spectroscopy (XPS) is very surface sensitive because only electrons from the top few atomic layers (mean free path ~1.5 nm) can escape without loss of energy. In this technique, the kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted electrons as a function of their kinetic energy) can be measured using any appropriate electron energy analyser and a photoelectron spectrum can thus be recorded. By using photo-ionization and energy-dispersive analysis of the emitted photoelectrons the composition and electronic state of the surface region of a sample can be studied Six features seen in a typical XPS spectrum, First is the sharp peaks due to photoelectrons created within the first few atomic layers (elastically scattered). Second feature is multiplet splitting which occurs when unfilled shells contain unpaired electrons. Third is a broad structure due to electrons from deeper in the solid which are in-elastically scattered (reduced KE) forms the background. Satellites (shake-off and shake-up) are the other feature of XPS spectrum are due to a sudden change in Columbic potential as the photo ejected electron passes through the valence band. Plasmons and Auger peaks are other peak in XPS which are created by collective excitations of the valence band and x-rays (transitions from L to K shell: O K_{LL} or C K_{LL}) respectively. Satellites arise when a core electron is removed by a photoionization. There is a sudden change in the effective charge due to the loss of shielding electrons. (This perturbation induces a transition in which an electron from a bonding orbital can be transferred to an anti-bonding orbital simultaneously with core ionization). Two types of satellite are detected. Shake-up, The outgoing electron interacts with a valence electron and excites it (shakes it up) to a high energy level. A second sequence the energy core electronics reduced and a satellite structure appears a few *eV* below (KE scale) the core level position. Shake-off: The valence electron is ejected from the ion completely (to the continuum) and appears as a broadening of the core level peak or contribute to the inelastic background. In the XPS spectrum of BPA-PC plate just sharp peak and satellite shake-up are seen [17].

2.5. Integrated Sphere

Spectral power distribution (SPD) of BPA-PC plates and the yellowing index (YI) of thermally-aged plates were measured by Integrated-Sphere, shown in Figure 8. Integrated-Sphere is an optical component consisting of a hollow spherical cavity with its interior covered with a diffuse white reflective coating, with small holes for entrance and exit ports. Uniform scattering or diffusing effect is a main property of Integrated sphere. It is typically used with some light source and a detector for optical power measurement. The yellowing index (YI) is calculated according to ASTM D1925 [18] with the following equation:

$$YI = \frac{100(1.28X\ CIE - 1.6Z\,CIE]}{Y\,CIE} \qquad (4),$$

Where, X and Y are the tristimulus values in (CIE) standard.

2.6. Lambda spectroscopy

While inexpensive spectrometers are typically used to measure the transmittance of clear solutions, instruments of the sophistication of the High Performance LAMBDA Series have multiple uses; the predominant being the characterization of solid materials.

These measurements fall into 3 categories: i) Transmittance measurement of scattering and non-scattering samples, ii) Diffuse reflectance measurement of materials, and iii) Specular reflectance measurement of mirror-like materials in appearance. When measuring transmittance, scattering by the sample causes some of the transmitted beam to deviate from the optical path of the instrument, resulting in an artificially lower total transmittance. By using an integrating sphere accessory, all of the light transmitted in the forward direction is collected.

The sample is placed in front of the sphere at the transmission port and the light passes through into the sphere. This configuration can be used to exclude the normally transmitted beam from the measurement (open reflectance port) and allow accurate measurement of the diffuse transmittance of the sample. When obtaining the transmittance of a sample, such as a lens, which is a thick or curved sample that can cause the beam direction to deviate or cause the beam to diverge or converge an integrating sphere is required. As the beam deviates from its path or changes in angle, some of the light may miss the instrument detector resulting in an artificially low transmittance measurement. An integrating sphere accessory allows for the complete sample beam to be collected even if its path deviates or if it diverges or converges. Integrating spheres also compensate for inhomogeneity of detectors as all of the detector area is always illuminated.

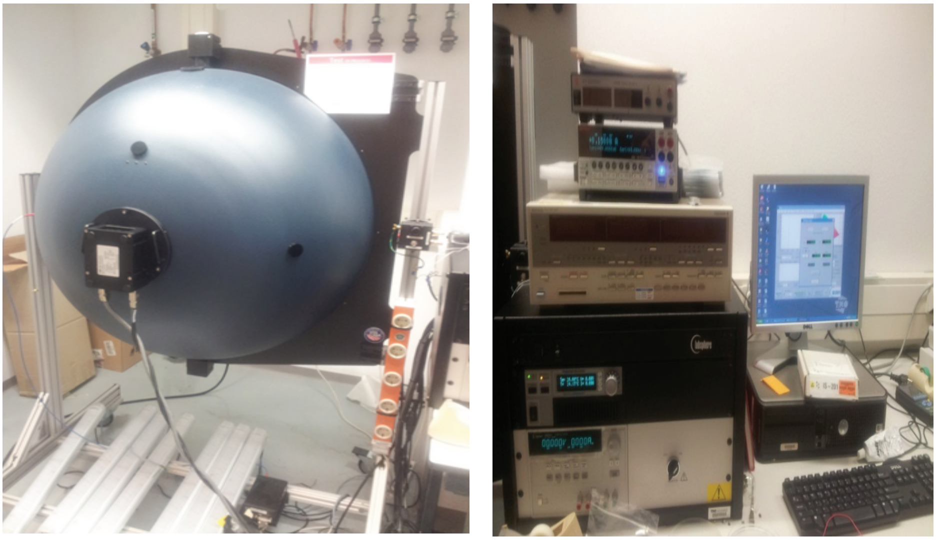


Figure 8: *Photo of the integrated sphere (IS), used in this study*

2.7. Reliability modelling approach

LED lifetime is measured by lumen maintenance, which is how the intensity of emitted light has a tendency to reduce over time. Prediction of LED lifetime differs with the method of interpreting the results of accelerated testing [19-20]. The method for predicting the lifetime of LEDs is the use of an accelerated test (AT) method where the estimated lifetime in the accelerated life tests is multiplied by an acceleration factor. The purpose of AT experiments is to obtain reliability information quickly. Test units of a material, component, subsystem or entire systems are subjected to higher-than-usual levels of one or more accelerating variables such as temperature or stress. Then the AT results are used to predict life of the units by using practical curve fitting of time-dependent degradation under the test conditions.

When the stress in temperature the reliability model is based on an exponential luminous decay equation to calculate time-to-failure as given in by [21]:

$$\phi(t) = \beta \exp(-at)$$

(5),

where Φ(t) represents the lumen output, α is the rate of reaction or depreciation rate parameter, t is time and β is a pre-factor. Obviously when lumen output, Φ, is equal to 70%, t is time-to-failure. The Arrhenius relationship is a widely used model to describe the effect that temperature has on the rate of a simple chemical reaction. The rate of reaction, α, is related to the activation energy of the reaction and to the ageing temperature as follows [21]

$$a = A\exp(\frac{-E_a}{KT})$$

(6),

where A is a pre-exponential factor, Ea is the activation energy (ev) of the degradation reaction, K is a botzman constant (evk-1), and T is the absolute temperature (K). In the HAST experiments, when the light intensity also accelerate the ageing, Eyring relationship gives physical theory describing the effect that temperature has on a reaction rate [22]. Written in terms of a reaction rate, the *R (temp)* as follows,

$$R = \gamma_0 A(T) \exp(\frac{-E_a}{KT}) \qquad (7),$$

where *A (temp)* is a function of temperature depending on the specifics of the reaction dynamics and 0 and Ea are constants.

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CHAPTER 3

Reliability and Optical Properties of LED Lens Plates under High Temperature Stress

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In this investigation the thermal degradation mechanisms of Bisphenol A Polycarbonate (BPA-PC) plates at the temperature range 100-140 ºC are studied. The BPA-PC plates are currently used both in light conversion carriers in LED modules and optical lenses in LED-based products. In this study BPA-PC plates are held at elevated temperature of 100 to 140 ºC for a period up to 3000 hrs. Optical and chemical properties of the tmally-aged plates were studied using UV-Vis spectrophotometer, FTIR-ATR spectrometer, and integrated sphere. The results show that increasing the thermal ageing time leads to yellowing, loss of optical properties, and decrease of the light transmission and of the relative radiant power value of BPA-PC plates. The results also depict that there is not much discoloration within the first 1500 hrs of thermal ageing. The rate of yellowing significantly increases at the end of this induction period. Formation of oxidation products is identified as the main mechanism of yellowing.

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3.1. Introduction

Solid-state lighting technology is expected to replace conventional incandescent and fluorescent light sources, due to the high efficiency, long service time, small volume, and low power consumption [1]. Producing white light in LEDs can either be done by discrete colour mixing i.e. with mixing different LEDs of different colours (red. green, and blue LEDs) or by using phosphor to convert light to white colour [2-7]. Multi-chip white LEDs have a good colour rending index (CRI) and have a higher efficiency in white light generation. However multi-chip LEDs also have some disadvantages. First problem is that the efficiency of red, green and blue LEDs change with time with different rates, so the quality of white light degrades over times. The second problem is the complexity of a different LED package including electrical connections and complicated optics for blending the discrete colours [7].

Currently white LED light is produced by combining colour LEDs and wavelength conversion materials instead of using different LEDs. White LEDs made by combining the blue-emitting diode chips with phosphor ($YAG:Ce^{3+}$) are the most commercially available LEDs due to their better performance. In this system, the phosphor layer can be either deposited directly on the chip or incorporated into a lens disc [5-7]. Several elements such as semiconductor chip, bond wires, lead frames, heat slug, solder joints, and optical materials are combined to make high-power white LED products. The life time of white LED may exceed 50khrs but the light intensity could drop significantly in long term operation [2]. The decrease in light intensity and degradation of these LEDs could be attributed to the die-, interconnected-, and/or encapsulants-related failures [2-7].

Among different degradation mechanisms in LED package, discoloration and yellowing are the most common failure mechanisms, resulting in the reduction in the transparency of encapsulants/lens and decrease in the LED light output [7]. The yellowing of encapsulant/lens could be ascribed to prolonged exposure to short wavelength emission (blue/UV radiation), temperature, and the presence of phosphors, with temperature having a very crucial influence [2].

Thermoplastic Bisphenol A polycarbonate (BPA-PC) plates are widely used in LED-based products, due to their lightweight, toughness and transparency. Any change in chemical structure of BPA-PC, induced by thermal- and/or photo-degradation, could significantly change these properties. Various studies have been performed to understand the different mechanisms of degradation [8-27]. During last decades the photo-degradation mechanisms of BPA-PC, under UV irradiation, have been extensively studied [8-16]. It is known [8,9,11] that under UV radiation side chain, ring oxidation could occur and the photo-Fries mechanism, resulting in chain scission. The effect of blue light radiation on the optical properties of BPA-PC encapsulants has also been comprehensively addressed in our previouswork [17]. BPA-PC is quite stable at air at temperatures below glass transition. However, discoloration of BPA-PC is a major problem during thermal ageing, resulting in a decrease in light transmission of BPA-PC plates in visible and near UV range. Discoloration of BPA-PC plates, measured by changes in yellowness index, is very much dependent on temperature.

During last few years a number of research groups have investigated the thermal degradation of polycarbonate plates [14,18-25] and reported that the thermal degradation of BPA-PC leads to the loss of mechanical and optical properties. Montaudo et al. [23] carried out direct pyrolysis of BPA-PC samples under high vacuum conditions and used different sophisticated analytical techniques, including direct pyrolysis-MS (DPMS), thermogravimetry, inherent viscosity, and aminolysis of the pyrolysis residue, to analyze the volatile and non-volatile degradation products and to study the degradation mechanisms at temperatures higher than 300°C. Lee et al. [26] also studied the thermal oxidation of BPA-PC above 300°C and showed that there are 3 steps in thermal degradation of BPA-PC at high temperatures. First step is oxidation which takes place at 300-320°C, followed by the depolymerisation reaction in the range 340-380 ºC. Finally, there is a complex random chain scission at the temperature range 480-600°C, Davis et al. [24] observed that PC have high degree of thermal stability and only processing at relatively high temperatures could lead to thermo-oxidation degradation. Montaudo [23] reported that molecular rearrangement could also occur at the higher temperature range 500-700°C. The degradation mechanisms of BPA-PC under hydrolysis reaction condition have also been studied extensively [24, 25].

In most previous studies, the thermal ageing behaviour of BPA-PC is studied at relatively high temperatures. Besides, most studies aim at understanding the effects of temperature on the mechanical properties and structure of BPA-PC. Another important issue is that a lot of studies are either deep in the chemistry of the thermal degradation or have a complete optical approach. Works done by Rivaton et al. [8], Clark et al. [22], Lemaire et al. [10], Factor et al. [12], and Davis et al. [24] are a few examples of those papers with emphasis on the chemistry, whereas papers, published by Trevisanello et al. [4], and R. Mueller-Mach et al. [7] are clearly more into the optical properties of plates with very little information about the chemical background of the problem. Besides, there is not much information about the correlation between thermal degradation at relatively lower temperature, i.e. 100-150°C, in one side and the chemical and optical properties of BPA-PC in the other side. Understanding the evolution of the optical and chemical properties of BPA-PC during thermal ageing at low temperature is obviously of crucial importance, since it is closer to the real operational conditions. In addition to that, when it comes to the interpretation of the results of accelerated photo-degradation experiments at high temperatures, understanding and consequently ruling out the effect, temperature becomes very much important. In this chapter thermal-degradation mechanisms of almost pure BPA-PC, thermally aged at 100, 120, and 140 ºC, and their correlation with optical properties (discolouration, light transmission and relative radiant power value, and yellowing index) of BPA-PC plates are studied and discussed. This work is possibly one of a few (if not the only one) in which the chemistry of degradation and optical properties of degraded plates are equally addressed. Any improvement in the quality and the lifetime of LED lens plates necessitates a deep understanding of the correlation between the chemistry of degradation and the optical characteristics of plates. Understanding the mechanisms and the products of degradation is crucial to modify the types/amounts of additives (including anti-oxidation and heat stabilizer agents) to the base polymer. The presented reliability model could also be very useful for the producers of BPA-PC LED encapsulant plates, when it comes to the prediction of the life-time of their products. Besides, this will give them the opportunity to do accelerated ageing tests at much shorter times and extrapolate the results to more realistic temperature range. This obviously saves cost and time for the industry.

3.2 Chemical analysis

3.2.1 UV-VIS spectroscopy

UV-VIS spectrophotometric scans of thermally-aged BPA-PC plates, heated at 100, 120, and 140 ºC up to 3000 hrs, are shown in Figure 1. As is seen, the absorbance below 400 nm overall increases significantly with increasing thermal ageing time for samples aged at 120 and 140 °C. Clearly, this increase for the sample, aged at 140 °C, is much more pronounced. The sample, heated at 100°C, however, did not show any significant increase of the absorbance within the selected period of thermal exposure (3000 hrs). It is noticeable that a peak appears at around 290 nm after a prolonged thermal exposure at 120 and 140°C, which could be ascribed to the formation of phenolic end groups in the polymer during thermal ageing [21-22], however the authors would not rule out the possibility of instrumental errors. Clarification of this issue necessitates further investigations. In addition to that, there are two faint peaks around 308 and 320 nm in samples aged at 120 and 140°C, which are attributed to unidentified ester and thermal rearrangement product groups (phenylsalysilate) respectively [14]. These peaks are not observed in the plates, aged at 100°C.

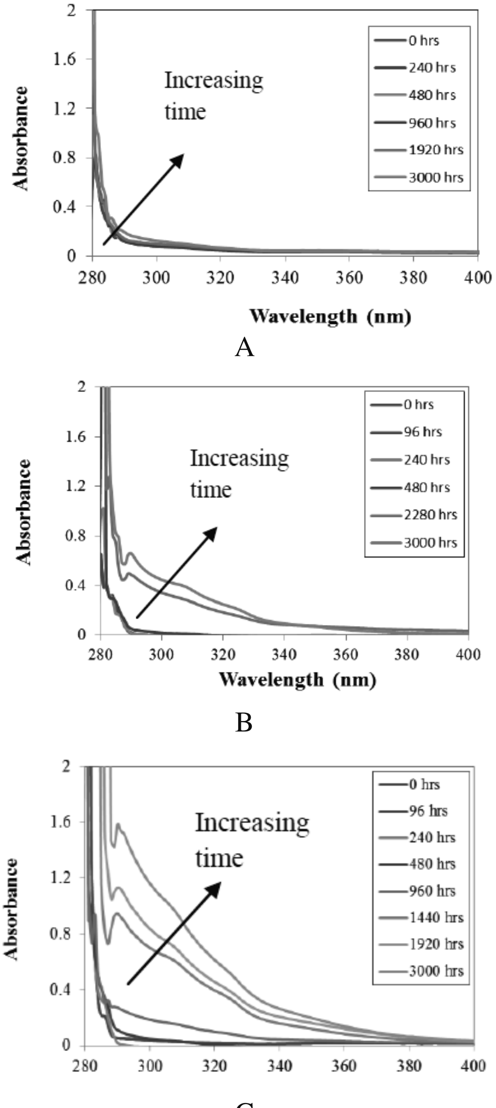
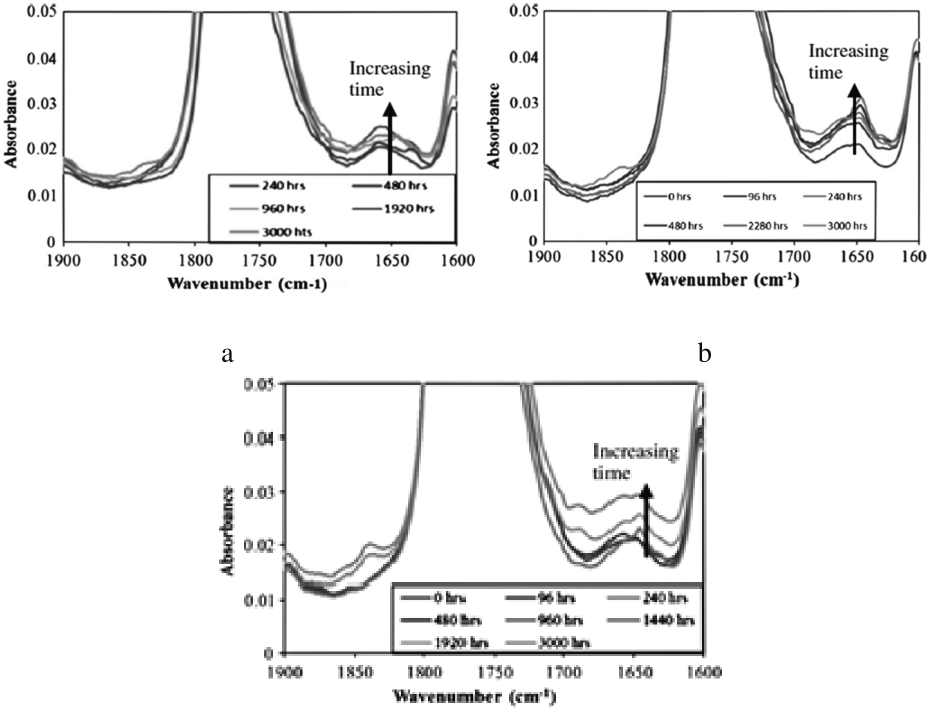


Figure 1: *Effects of thermal ageing time on the UV absorption spectra of BPA-PC films aged at a) 100 b) 120 and c) 140 ºC*

3.2.2. FTIR-IR spectroscopy

ATR results of thermally-aged BPA-PC plates at 100, 120 and 140 ºC are illustrated in Figure 2. This Figure shows the changes in the absorption at different wavelength with thermal ageing time. Absorption bands at 1690 cm^{-1} (aromatic ketones) [14] and 1840 and 1860 cm^{-1} (cyclic anhydrides) [14] in the carbonyl region appear at all temperatures as a result of thermal oxidation. These oxidation products could significantly contribute to the discolouration of thermally-aged specimens. It is also noticeable that the higher the ageing temperature, the more pronounced the increase in the intensity.



a b

C

Figure 2: *FT-IR spectra of thermally-aged BPA-PC plates for various thermal ageing times in the carbonyl region for a) 100 b) 120 and c) 140 ºC (The spectra are normalized using the peak located at 1014 cm^{-1}*

Figure 3 shows the ATR spectra of thermally-aged plate at 140 ºC in hydroxyl region, in which no change is observed.

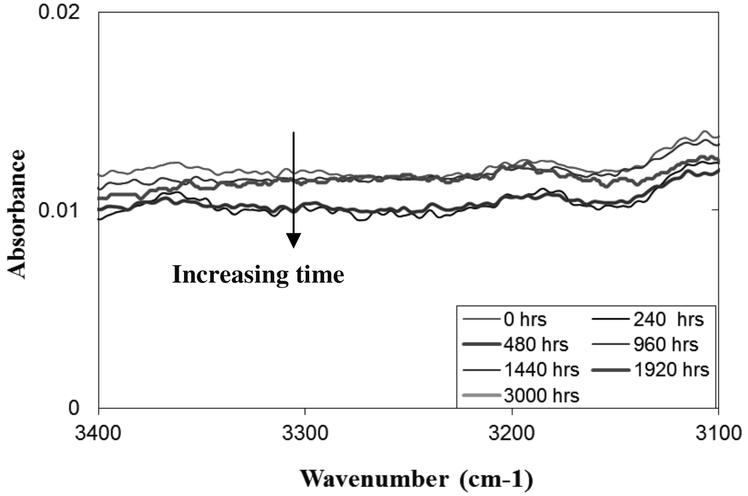


Figure 3: *FT-IR spectra of thermally-aged BPA-PC plates at 140 C for various thermal ageing times in the hydroxyl region*

Figure 4 illustrates the increase in the absorption intensity in the carbonyl region (bands at 1690 and 1840 cm^{-1}) as a function of thermo-oxidation time at 100, 120 and 140 ºC. Obviously, there is not much change in the absorption intensity up to 1500 hrs. The absorption intensity starts increasing significantly after approximately 1500 hrs of thermal exposure.

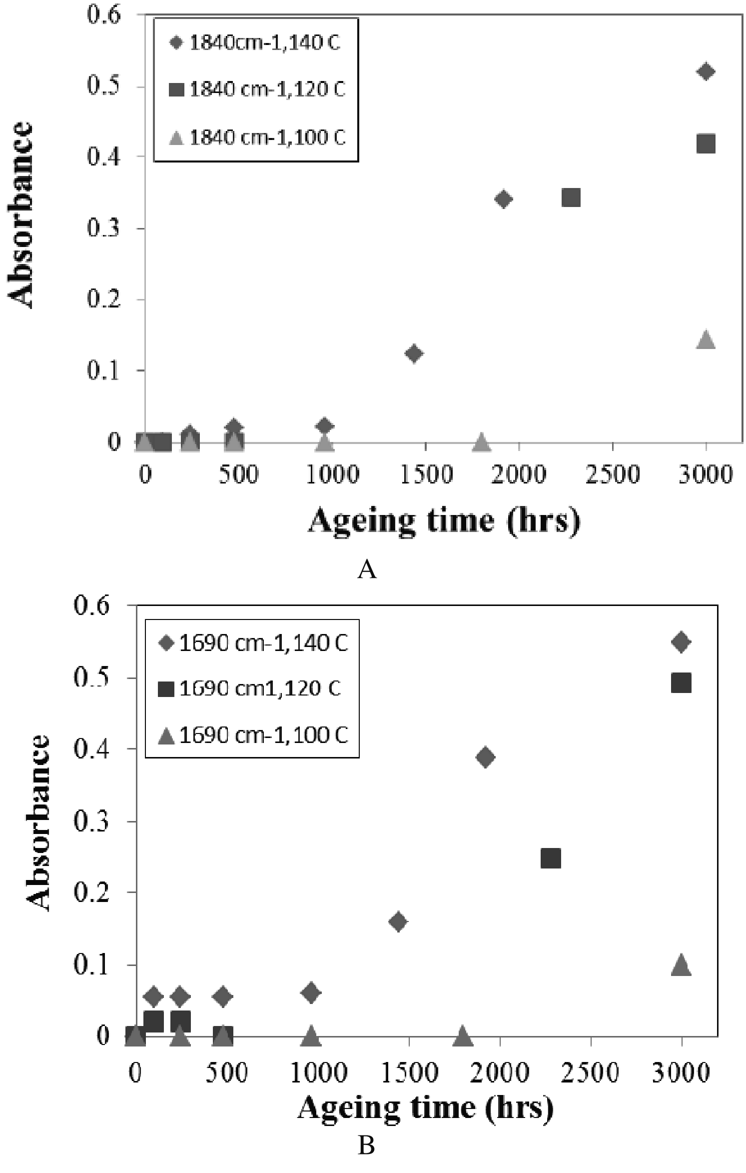


Figure 4: *Relative absorbance at wavenumbers a) 1840 cm^{-1}, and b) 1690 cm^{-1} with increasing thermal exposure time*

3.3. Kinetics of yellowing

It is reported that [9-14] that oxidation is the main cause of yellowing in BPA-PC lens. In order have a more quantitative analyses of the effect of oxidation on the yellowing of aged plates, the yellowing index (YI) of BPA-PC plates calculated as a function of ageing time, at 100, 120, and 140°C, shown in Figure 5. The results clearly depict that there is not much yellowing within the first 1500 hrs of thermal ageing. The rate of yellowing significantly increases at the end of this induction period.

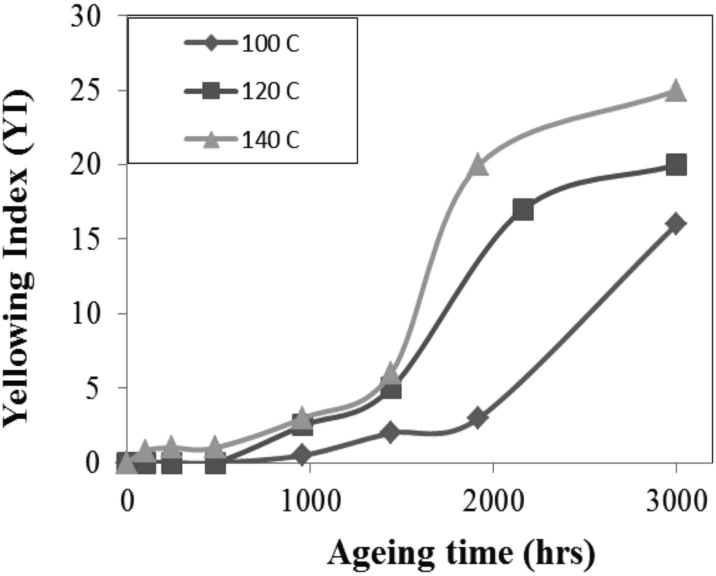


Figure 5: *Variation in yellowing index (YI) of BPA-PC plates, aged at 100, 120 and 140 ºC for different thermal ageing time*

3.4. Effects of degradation on lumen depreciation

Figure 6 illustrates the effects of thermal exposure time on the transmission of the whole range of visible light from the specimen aged at 140°C, measured by

Lambda spectroscopy. It is seen that above 500 nm there is not any significant change in the transmission due to the ageing. Light output of LED is affected by yellowing and discolouration of lens. In LED systems the decrease in transmission at 450 nm is an indication of the yellowing [20].

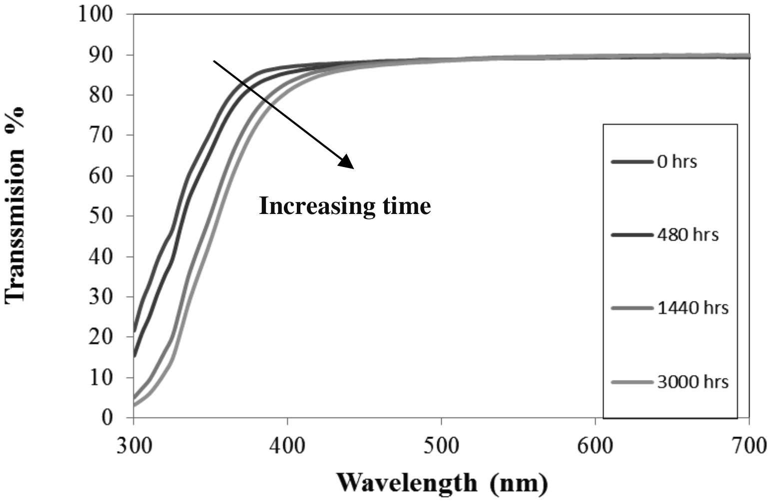
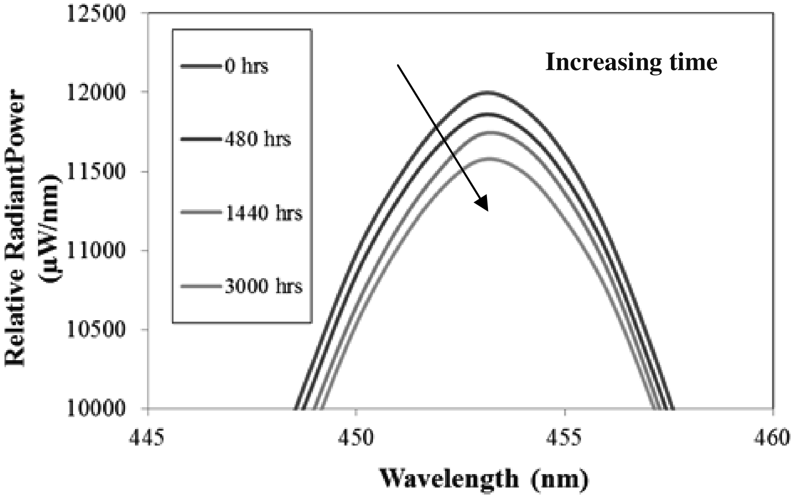


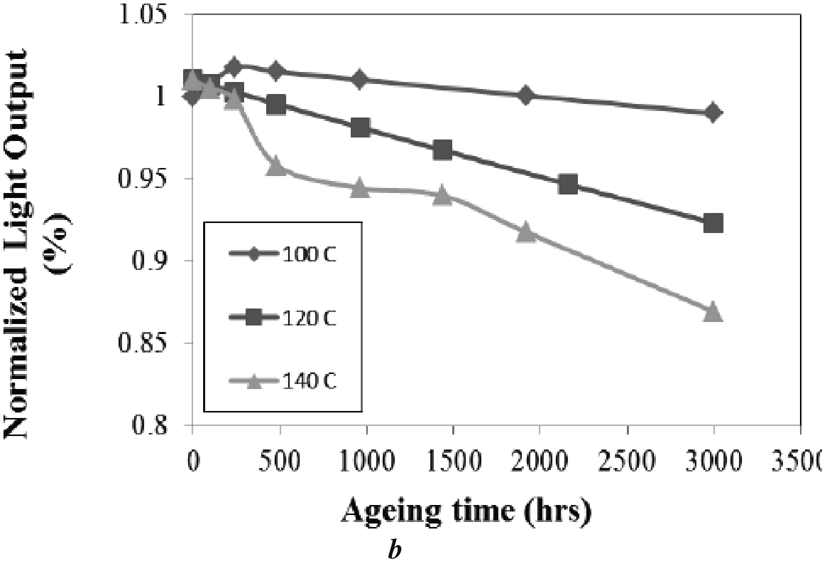
Figure 6: *Transmission at visible region at 140 C at different ageing time*

Spectral power distribution (SPD) of a LED , placed behind BPA-PC plates, aged at 140°C for various times (SPDs of samples, aged at 100 and 120°C are similar to that of plates, aged at 140°C) is shown in Figures 7a. It is noticeable that the thermal degradation of BPA-PC plates leads to a decrease in the recorded maximum relative radiant power value in the SPD.

The transmission at 450 nm for specimens, aged at 100, 120, and 140°C for various times, is shown in Figure 7b. One can see that the light transmission of BPA-PC at 450 nm decreases almost linearly with increasing thermal exposure time. Obviously, the longer the thermal ageing time, the lower the transmission at 450nm, indicating that thermal ageing results in the yellowing of BPA-PC plates.



a



b

Figure 7: *a) Effects of thermal ageing time on the Spectral Power Distribution (SPD) of plates during thermal ageing at 140 °C, b) Transmission at 450 nm of thermally-aged BPA-PC plates with thermal ageing time at different temperatures.*

3.5. Activation energy of degradation reaction

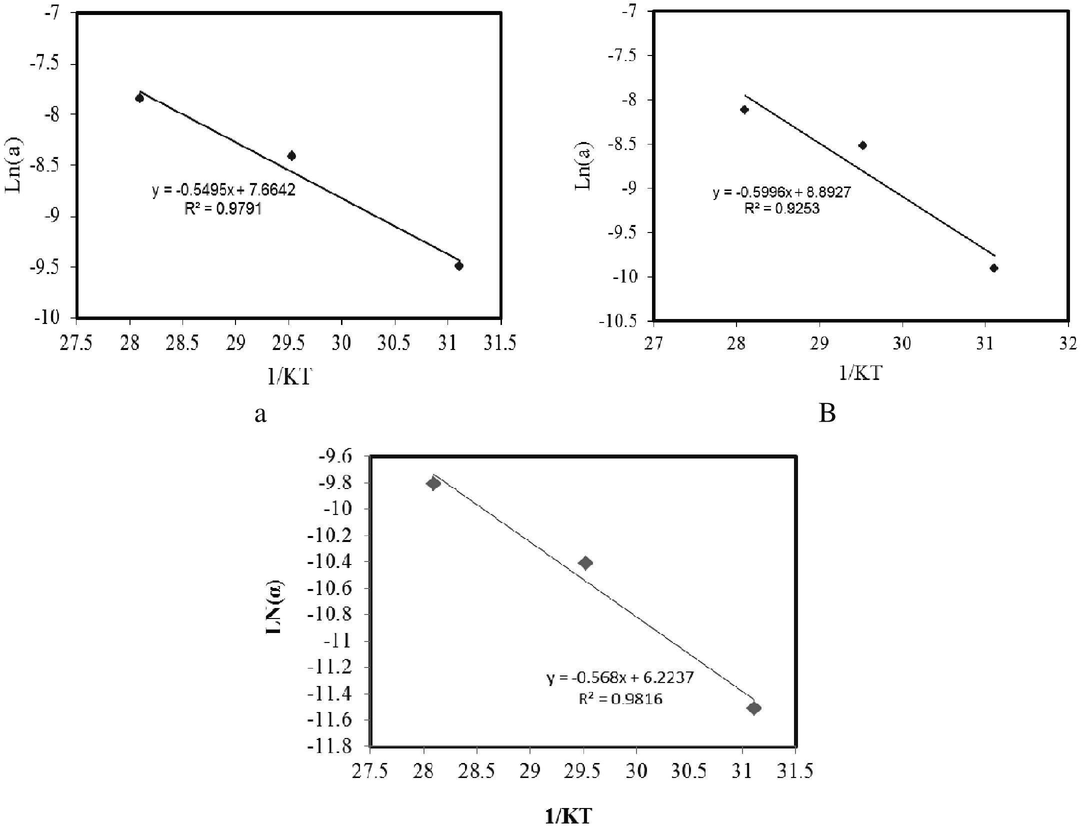
The activation energy of the degradation reaction in BPA-PC plates is calculated from Arrhenius Equation (Equation 3). In order to obtain the activation energy of degradation reaction, the natural logarithm of the reaction rates, obtained from Equation (2) and from the rate of increase in the intensities of oxidation peaks in ATR spectra (peaks 1690 cm^{-1} and 1840 cm^{-1}), is plotted against the inverse of the absolute temperature where the activation energy of the degradation reaction can obviously be obtained from the slope of this curve, see Figure 8.

The slope is multiplied by the negative of the gas constant to obtain the activation energy, Ea. The activation energy of degradation reaction, obtained from peak 1690 cm^{-1}, peak 1840 cm^{-1}, and Equation 2 are 0.56, 0.6 and 0.57 eV respectively. Comparing the first two values, obtained from a chemical approach, with the latter one, obtained from a purely phenomenological approach, one can see that the agreement is perfect. The reported value in the literature for the activation energy of degradation is also around or 0.6 eV [27].

Having this activation energy helps the researchers in LED industry to design accelerated ageing tests. For example Table 1 illustrates the calculated values for the reaction rate of degradation for each temperature for BPA-PC lens. One can see how the kinetics is changing by changing the ageing temperature.

Based on the alliance for solid state illumination system and technology (ASISST) standard, lifetime of LEDs is defined as time to reach 70% of its initial lumen output [30]. In order to find out the time-to-failure (70% lumen decay) of pure BPA-PC lens, the kinetics of lumen depreciation to 30% of its initial value by using exponential luminous decay model and Arrhenius equation should be extrapolated to temperatures lower than 100°C. Since the real working temperature of LED is much lower than the applied temperatures [12]. This can be done using Equation 1 by equating ϕ to 0.7, knowing that a can be obtained from Equation 2. Figure 9 illustrates time-to-failure (30% lumen decay) of pure

BPA-PC lens, calculated at different temperatures. It is seen that pure BPA-PC lens has prediction life time of 200 khr at lower temperature.



a

B

C

Figure 8: *Plot of ln (α) vs 1/KT for oxidation reaction a) 1690 cm^{-1} reaction, b) 1840 cm^{-1}, and c) the one obtained from lumen depreciation*

Table 1: *Reaction rate a for BPA-PC plate*

Temp (°C)	BPA-PC
100	1.0E-05
120	3E-05
140	5.5E-05

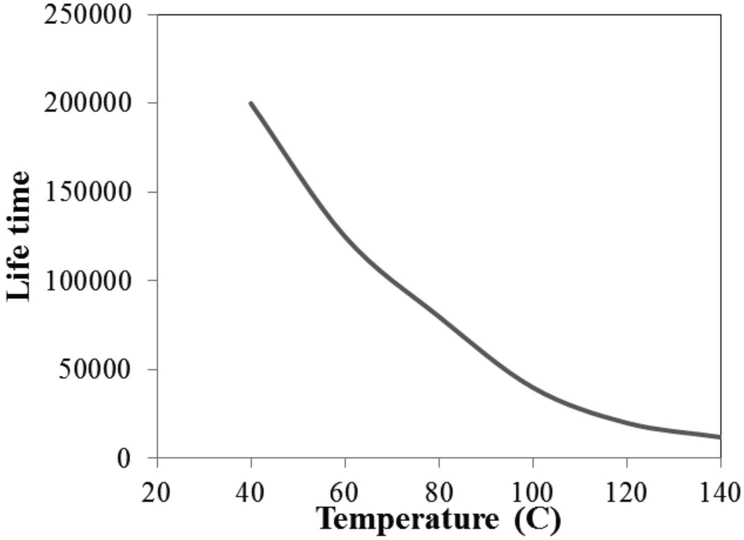


Figure 9: *Time-to-failure (30% lumen decay) of BPA-PC lens at different temperatures*

3.6. Discussion

Thermal degradation mechanisms and its effects on the optical and chemical properties of pure BPA-PC plates at 100, 120, and 140°C are studied. Thermal ageing of BPA-PC lens could significantly deteriorate the optical properties of LEDs. Rearrangement and oxidation in polycarbonate could result in discolouration and yellowing of BPA-PC encapsulant materials [20-22].

Discoloration due to the formation of oxidation products and rearrangement (Fries) products or a combination of them could result in a decrease in the transmission of BPA-PC plates. Depending on the temperature the degradation mechanism could be altered. It is believed that the higher the temperature, the more important the influence of rearrangement products on yellowing is [21]. Davis et al. [24] reported that the Fries rearrangement reaction is more likely to occur at high temperatures and under vacuum conditions. Rearrangement reaction in BPA-PC results in phenylsalicylate, diphenylcarbonate, phenol, and some other similar products [23]. A schematic of thermal rearrangement reaction is shown in Figure 10.

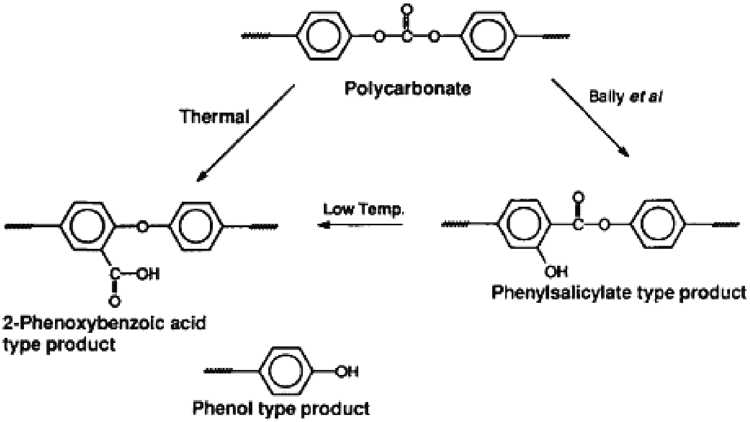


Figure 10: *Proposed pathway for the thermal rearrangement of BPA-PC [16]*

Thermal-oxidation products are more commonly reported as the main mechanism of yellowing of BPA-PC at low temperatures in the presence of oxygen [20-22]. Rivaton et al. [14] postulated that side chain and ring oxidations are likely to take place during thermal degradation. Factor [15] showed that the main reason for discolouration and yellowing of thermally-aged BPA-PC is the formation and subsequent oxidation of phenolic end groups, , as is schematically shown in Figure 11.

UV-VIS analyses of thermally-aged BPA-PC plates in this study show a slight increase of peak at 320 nm which is defined as a rearrangement product. In the IR spectra, the rearrangement product is in the hydroxyl range is defined in 3217 cm-1. As is shown in Figure 3 this peak does not change during ageing time, showing that rearrangement reaction does not have a major contribution to the yellowing. The relatively sharp peak, observed at 290 nm in some degraded specimens, might be due to some other rearrangement products [20, 24, 25]. In previously published papers there is no evidence that these rearrangement products could cause discoloration. In our previous study on photo-degradation of BPA-PC plates, there was no sign of this peak in UV-VIS spectra of photo-degraded specimens, inferring that these rearrangement products are not stable under radiation and they transform to other species.

The observed increase in the intensities of absorption bands at 1690 cm^{-1} (aromatic ketones) [14] and 1840 and 1860 cm^{-1} (cyclic anhydrides) in the FTIR-ATR spectra of degraded specimens certainly confirms thermal oxidation reactions. Besides, there is no indication of formation of band at 1713 cm^{-1} in the spectra, which corresponds to carboxylic acids [14], meaning that the concentration of carboxylic acids, formed in the polymeric films during thermal ageing, is negligible. Moreover, no clear absorption band in the range 3300–3200 cm^{-1} (also assigned to carboxylic acids) is observed in the spectra of thermo-oxidised PC, This is also confirmed by Rivaton et al [14].

The FTIR-ATR spectra of thermally-aged specimens (see Figures 2 and 4) also show that the increase in the intensities of cyclic anhydrides (1840 cm^{-1}) and aromatic ketone (1690 cm^{-1}) bands follows a two-stage trend, with initially showing a plateau with almost no change in the intensity, followed by almost a linear increase. This is in accordance with the observed yellowing behaviour for thermally-aged plates.

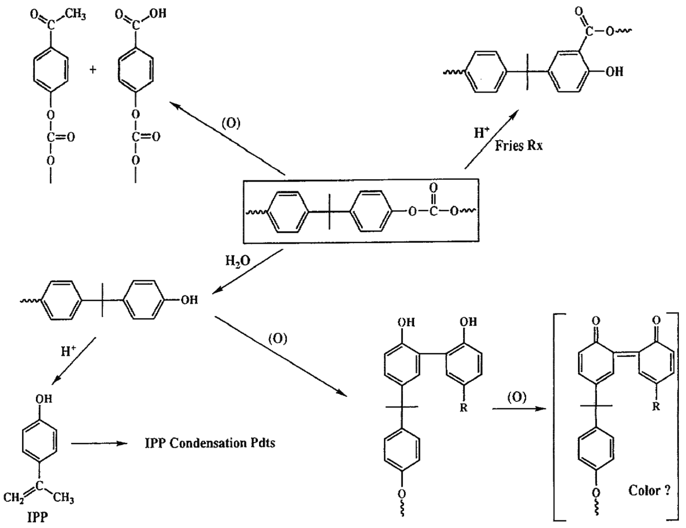


Figure 11: *Proposed pathway for the thermal oxidation of BPA-PC [13]*

3.7. Conclusions

Different experimental methods are used to study the effects of thermal exposure on the degradation of Bisphenol A Polycarbonate (BPA-PC) and its optical properties. The aim was to investigate the relationship between the evolutions of optical and chemical properties of BPA-PC plates after thermal ageing, in order to identify the predominant yellowing mechanism. The results show that increasing the ageing time is associated with discolouration and consequently with the degradation of optical properties (mainly light transmission). The results also show that there are two stages in the yellowing of polycarbonate plates. The first stage is the so-called induction period with a very slow yellowing reaction rate, followed by the second yellowing regime with considerably faster kinetics. The intensities of cyclic anhydrides (1840 cm^{-1}) and aromatic ketone (1690 cm^{-1}) bands in the FTIR-ATR spectra of thermally-aged specimens follow the same two-stage trend, inferring that thermal oxidation could be considered as the main reason of the yellowing.

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CHAPTER 4

Photodegradation of Bisphenol-A Polycarbonate under Blue Light Radiation and its Effect on Optical Properties

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In this chapter, the degradation mechanisms of Bisphenol A Polycarbonate (BPA-PC) plates under blue light radiation are studied. Optical degradation of the products is mainly due to the degradation of BPA-PC lens under blue light radiation. In this study, BPA-PC plates are irradiated with blue light at elevated temperature of 140 ºC for a period up to 1920 hrs. Optical and chemical properties of the photo-aged plates were studied using UV-VIS Spectrophotometer, FTIR-ATR spectrometer, integrated sphere, and Lambda 950 spectrophotometer. The results show that increasing the exposure time leads to the discolouration, loss of optical properties, decrease of light transmission, decrease in the relative radiant power value, and increase in the yellowing index (YI) of BPA-PC plates. The results also show that there are two stages in the yellowing of polycarbonate plates. The first stage is the so-called induction period in which there is no major change in the value of YI and the rate of yellowing is very slow. This stage takes until 500 hrs, followed by the second yellowing regime, where the yellowing is accelerated and the rate of yellowing is comparatively faster. Both photo-Fries and oxidation products are identified as the mechanisms of photo-degradation.

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4.1. Introduction

The most important mechanisms causing photo-ageing of polymers are photolysis and photo-oxidation [1,2] If the absorption of light leads directly to chemical reactions causing degradation, this is called photolysis. Photo-oxidation is a result of the absorption of light that leads to the formation of radicals that induces oxidation of the material. Engineering plastics containing phenyl ester groups, like polycarbonates, can undergo Fries rearrangements. When a phenyl ester rearranges, as a result of the absorption of UV-radiation, it is called the photo-Fries rearrangement [1]. The reaction involves three basic steps; 1) the formation of two radicals, 2) recombination, and 3) hydrogen abstraction. It may also be possible that the phenoxy radical reacts with neighboring molecules by abstracting a hydrogen atom from the neighboring molecules to form phenol. So this photo-Fries rearrangement reaction can be a concerted or radical process [1-12]. Polymers can undergo photo-oxidative reactions when they are exposed to (UV) light [1-12]. The mechanism describing the photo-oxidation of polymers is shown below. Different degradation steps can be considered:

1. Initiation step: The formation of free radicals, where *R* is a polymer radical induced by hydrogen abstraction by other initiating radicals

$$I \rightarrow I^{\cdot} \tag{1.1}$$

$$I^{\cdot} + R\text{-}H \rightarrow R^{\cdot} + I\text{-}H \tag{1.2}$$

2. Propagation step: The reaction of free polymer radicals with oxygen;

$$R^{\cdot} + O2 \rightarrow R\text{-}OO^{\cdot} \tag{1.3}$$

$$R\text{-}OO^{\cdot} + R\text{-}H \rightarrow R\text{-}OOH + R^{\cdot} \tag{1.4}$$

3. Branching and Secondary Reactions: Rearrangements and chain scissions may occur;

$$R\text{-}OOH \rightarrow R\text{-}O^{\cdot} + {}^{\cdot}OH \tag{1.5}$$

$$R\text{-}O^{\cdot} + R\text{-}H \rightarrow R^{\cdot} + R\text{-}OH \tag{1.6}$$

$$R\text{-}O^{\cdot} \rightarrow R'{=}O + {}^{\cdot}R' \tag{1.7}$$

$${}^{\cdot}OH + RH \rightarrow R¢ + H_2O \tag{1.8}$$

$$R\text{-}OOH \rightarrow R'{=}O + H_2O \tag{1.9}$$

4. Termination step: The reaction of different free radicals with each other, which may result in crosslinking.

$$R^{\cdot} + R^{\cdot} \rightarrow R\text{-}R \tag{1.10}$$

$$R^{\cdot} + R\text{-}OO^{\cdot} \rightarrow R\text{-}OOR \tag{1.11}$$

$$2\,R\text{-}OO^{\cdot} \rightarrow R\text{-}OOOO\text{-}R \rightarrow R\text{-}OH + R'{=}O + O_2 \tag{1.12}$$

The origin of the radical $I^{\cdot}$ as initiating radical for the chain reaction is very important and polymer dependent.

In LED systems with blue-emitting diode chips, the encapsulant/lens is exposed to the blue light radiation with wavelengths of 445-450 nm. There is not much information about the degradation mechanism of BPA-PC under blue light exposure. In this chapter photo-degradation chemistry of pure BPA-PC, used as the base carrier material for optical materials in LED products, under blue light (450nm) radiation at 140 ºC is investigated.

4.2 Effects of degradation on lumen light transmission

4.2.1. Lambda spectroscopy

Transmission spectra of light through photo-aged BPA-PC plates, measured by Lambda 950, are shown Figure 1. The transmission between 500 to 700 nm is not much affected by the radiation time. The most significant decrease of the transmission with ageing time is observed for wavelengths below 500 nm. In LED systems the decrease in transmission at 450 nm is an indication of the yellowing. Clearly, the higher the exposure time, the lower the transmission at 450nm is. Figure 2 illustrates the effects of exposure time on the transmission at 450nm. As shown in this figure, the light transmission of BPA-PC at 450 nm decreases linearly with increasing exposure time.

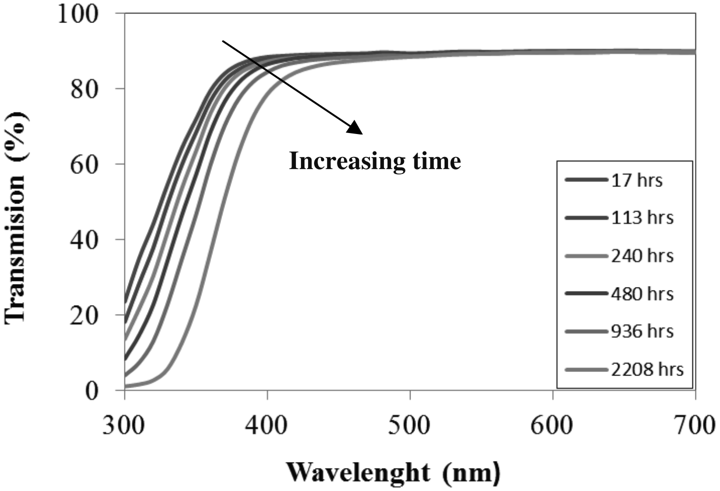


Figure 1: *Transmission spectra of photo-aged BPA-PC plates with irradiation time*

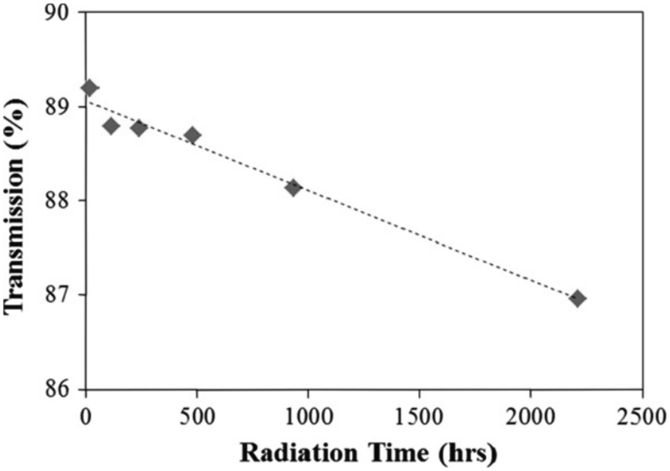


Figure 2: *Transmission at 450 nm of photo-aged BPA-PC plates with irradiation time*

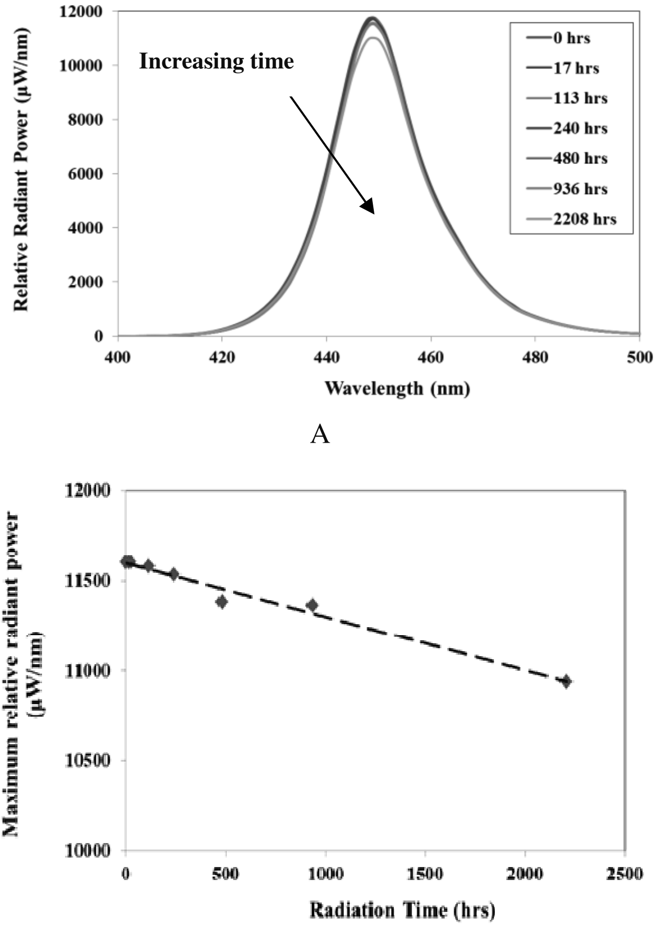
4.2.2. Integrated sphere results

Figures 3a and 3b depict the spectral power distribution (SPD) of a LED chip, put behind thermal-aged BPA-PC plates, and the corresponding maximum relative radiant power respectively. It is noticeable that the photo-degradation of BPA-PC plates leads to a decrease in the recorded maximum relative radiant power value in the SPD. The yellowing index (YI) of BPA-PC plates was also measured as a function of exposure time, as shown in Figure 4. In this Figure one can see the yellowing index (YI) of the sample, exposed to 140 ºC without irradiation of blue light, together with the YI of the photo-aged sample. Obviously, the temperature itself could cause the yellowing. However, one can see that the blue light has a significant contribution to the yellowing. As it is seen, there are two stages in the discolouration of both thermally- and photo-aged samples. The first stage is the so-called induction period in which there is no major change in the value of YI and the rate of yellowing is very slow, followed by the second yellowing regime, where the yellowing is accelerated and the rate of yellowing is comparatively faster. The transition from induction regime to accelerated regime takes place after 500 and 1500 hrs irradiation in photo-aged and thermally-aged plates respectively, indicating that blue light radiation accelerates the initiation of yellowing (beginning of second stage). The yellowing index in photo-aged materials is also overall higher than that in thermally-aged samples, inferring that blue light could significantly influence the extent of yellowing in BPA-PC plates.

4.3. Chemical analysis

4.3.1. UV-Vis spectroscopy

UV-Vis spectrometerphotometric scans of BPA-PC plates with different ageing times, measured in the range of 200-800 nm, are shown in Figure 5a. As is seen, the absorbance below 400 nm overall increases significantly with increasing ageing time. It is also noticeable that there is a shift of the maximum absorption towards higher wavelengths with exposure time. Maximum absorption peak in the UV-VIS spectrum is due to electronic transitions between occupied and unoccupied molecular orbitals. The shift of the onset of absorption to longer wavelengths indicates that the band gap energy is reduced as a result of appearance of new energy states, induced upon irradiation [10, 11]. Figure 5b depicts the evolution of absorption at 320 and 355 nm with radiation time. The absorption at 320 and 355nm are ascribed to the so-called photo-Fries products L1 (Phenylsalicylate) and L2 (dihydroxybenzophenone) respectively [1-4].



A

B

Figure 3: *Effects of radiation time on the a) Spectral Power Distribution (SPD) of pure BPA-PC and b) the maximum relative radiant power*

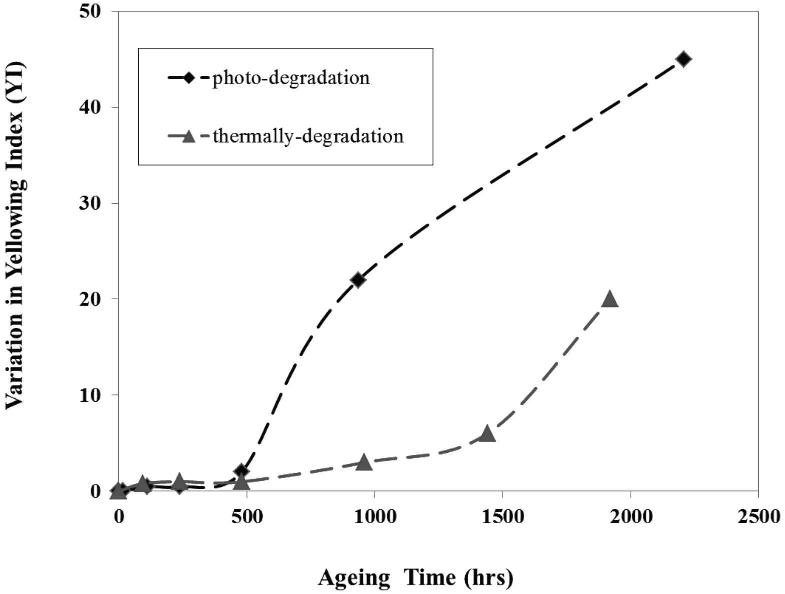
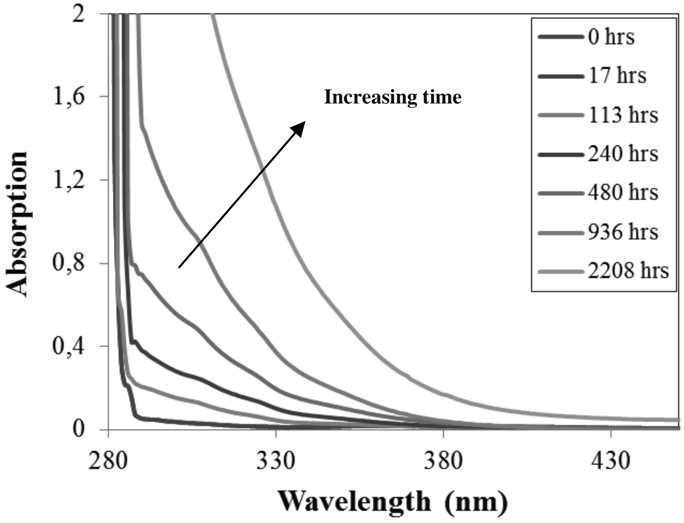


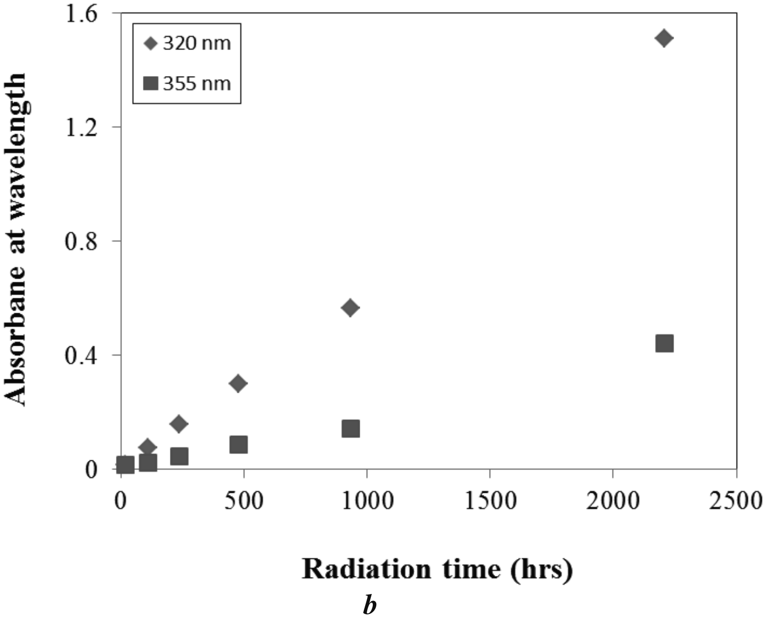
Figure 4: *Variation in yellowing index (YI) of BPA-PC plates, exposed to the blue light, at different ageing times*

4.3.2. FTIR-IR spectroscopy

Photo-degradation of BPA-PC plates is a surface reaction [1]. So to detect the degradation products in BPA-PC plates, the ATR mode of FTIR is employed. Figure 6 shows the changes in the absorption at different wavelength with ageing time (The spectra are normalized using the peak located at 1014 cm^{-1}). The major change observed was the decrease in the absorption peaks at 1500 and 1760 cm^{-1}. The major drops starts after 240 hrs irradiation. The decrease would suggest that carbonate groups act as initiation sites for the photo-Fries rearrangement reactions [12].



a



b

Figure 5: *Effects of exposure time on the a) UV absorption spectra of BPA-PC films and b) absorption at 320nm and 355nm*

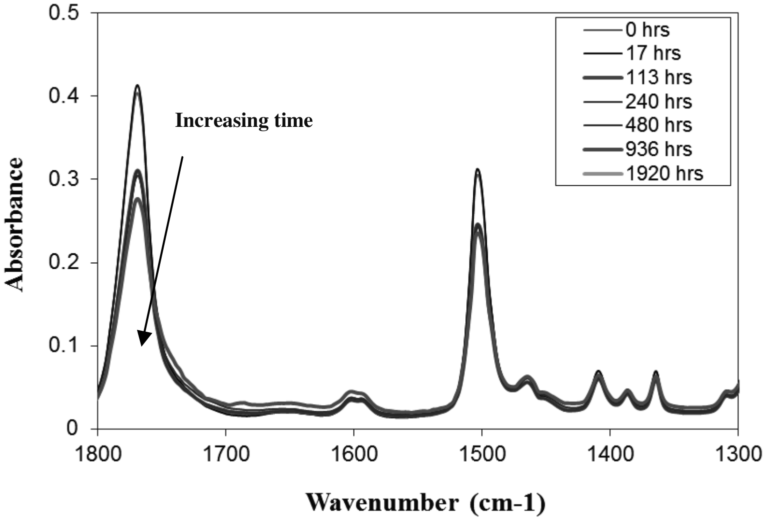


***Figure 6**: FT-IR spectra of irradiated BPA-PC films in the carbonyl region for various irradiation times*

Figure 7 shows the FTIR spectra of photo-aged plates between 1550 and 1850 cm-1 (The spectra are normalized using the peak located at 1014 cm^{-1}). As it is seen the absorbance at this region increases which radiation time. The increase of absorbance at wavenumbers 1690 cm^{-1} and 1629 cm^{-1} are attributed to the formation of L_1(Phenylsalicylate) and L_2 (dihydroxybenzophenone) respectively [16-19]. The formation of photo-Fries reaction products is also confirmed by UV-VIS results (see Figure 5). The increase in the absorbance at 1713 and 1840 cm^{-1} are ascribed to the formation of aliphatic chain-acid and cyclic anhydrides respectively, both are known as photo-oxidation products [1, 2, 4]. Figure 8 shows the increase in the absorption at wavenumbers 1629, 1690, 1713, and 1840 cm^{-1} with increasing irradiation times. The absorbance, corresponding to L1 (1690 cm^{-1}), L2 (1629 cm^{-1}), aliphatic chain-acid (1713 cm^{-1}), and cyclic anhydrides (1840 cm^{-1}) photodegradation products increase rapidly after 500 hours radiation. This is in a perfect agreement with the measured YI (see Figure 4).

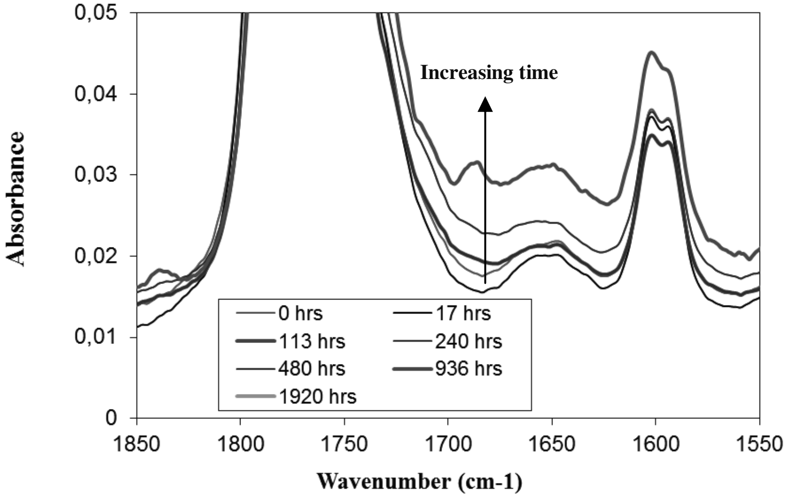


***Figure 7**: FT-IR spectra of irradiated BPA-PC films in the carbonyl region between 1550 and 1850 Cm^{-1}*

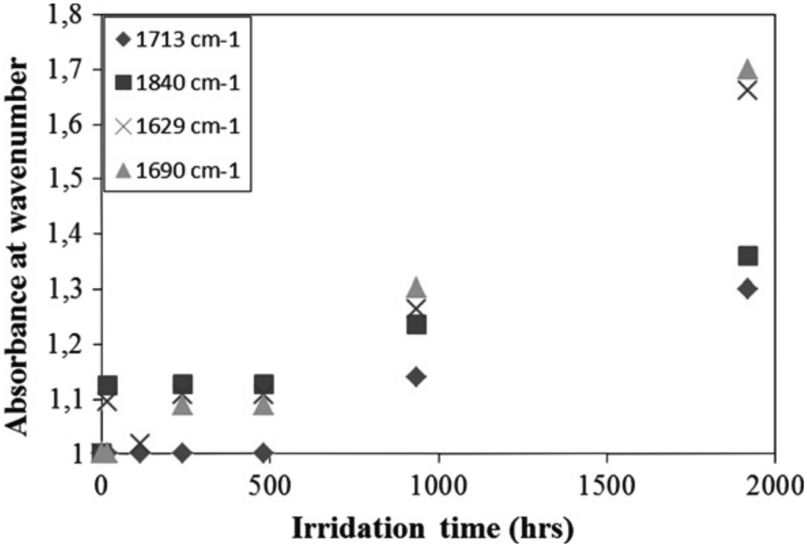


***Figure 8:** Relative absorbance at wavenumbers 1629, 1690, 1713, and 1840cm^{-1} with increasing irradiation times*

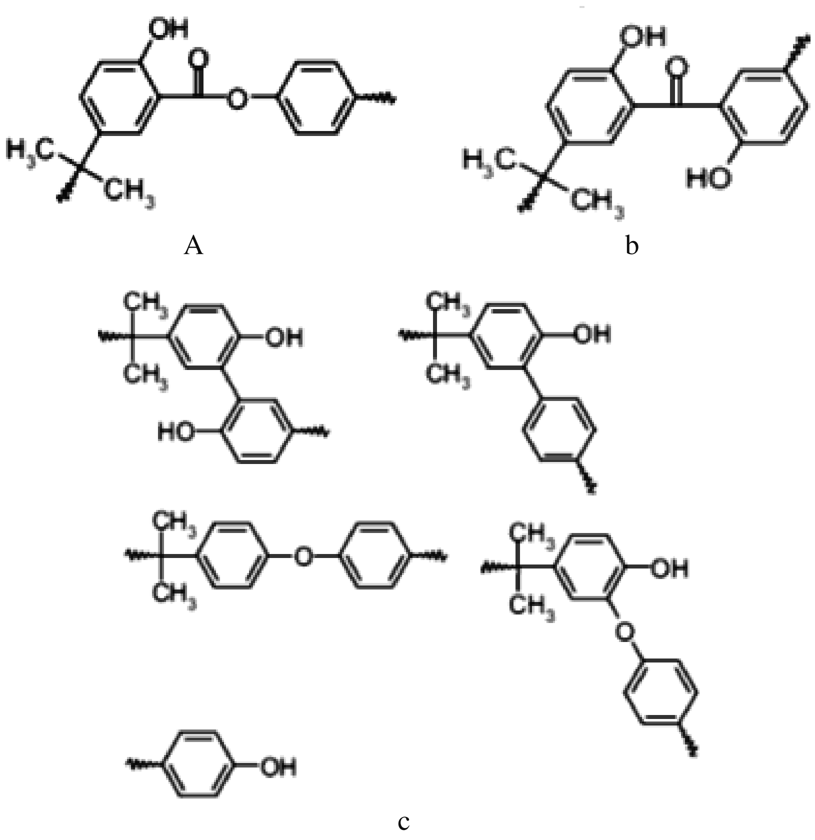
4.4. Discussion

Different analyses techniques, i.e. UV-VIS, infrared spectroscopy, Lambda, and integrated sphere are used to study the photodegradation mechanisms in BPA-PC plates under blue light radiation at 140 °C. The results show that there are two different stages during yellowing (see Figure 4): The first stage is the so-called induction period in which there is no major change in the yellowing index (YI), followed by the second yellowing regime, where the yellowing is accelerated and the rate of yellowing is comparatively faster. The transition from induction regime to accelerated regime takes place after 500 hr irradiation. The transmission of BPA-PC plates, however, decreases linearly with increasing ageing time.

In BPA-PC the reasons, underlying the photodegradation, have been attributed to two different mechanisms: photo-Fries rearrangement and photo-oxidation. Rivaton et al. [1] reported that the photo-Fries rearrangement reaction is more likely to occur at wavelengths shorter than 300 nm, whereas photo-oxidation reactions are more important when light of longer wavelengths (>340 nm) is used. On the other hand, Diepens et al. [8] argued that the photo-Fries rearrangement products are also formed, when wavelength longer than 300 nm are used. Formation of both photo-Fries and oxidation products result in the yellowing and decrease in the transmission of BPA-PC plates [1-4]. In photo-Fries rearrangement reactions, carbonyl groups are rearranged to products of phenylsalicylate (L1), dihydroxybenzophenone (L2) and L3 which are shown in Figure 9. L3 units are formed when CO-O band scission leads to decarbonylate or decarboxylate before further radical recombination or hydrogen abstraction. Rivaton et al. [1] postulated that at wavelengths longer than 340nm, where the photo-oxidation reaction is dominant, side chain oxidation, ring oxidation and ring attack reactions are likely to take place. The side chain oxidation in BPA-PC, however, is reported to be more probable [2-8]. To start the oxidation process initiating of free radicals are required [3]. Lemaire et al. [3] and Factor et al. [5] demonstrated that photo-Fries products can be oxidized easily and act as a source of intrinsic photo-oxidation. Diepens et al. [8], however, showed that the increase in photo-Fries rearrangement rate does not increase the oxidation rate, meaning that the photo-Fries reaction does not initiate the oxidation of polycarbonates.

UV-VIS and FTIR-ATR analyses of blue-light (450 nm) irradiated BPA-PC plates in this study show the presence of photo-Fries reaction products L1 and L2 together with oxidation products aliphatic chain-acid, and cyclic anhydrides from the early stage of photo-irradiation. However, there is no evidence of the formation of L3 product. This can be explained by the fact that some radicals formed by direct CO-O bond scissions may undergo oxidation rather that recombination in L3 [2].

The FTIR-ATR spectra of photoaged specimens (see Figures 7 and 8) show that there are two different stages during photoageing; the induction period (up to 500 hrs), where the amount of photodegradation products are not changed, and the accelerated stage, where the amount of photodegradation products are linearly increased with time. This is in accordance with the observed yellowing behaviour (see Figure 4). During the induction stage, absorption of blue light possibly leads to the initiation of both photo-Fries and photo-oxidation products. Photo-Fries and photo-oxidation proceed simultaneously. It is also likely that a part of photo-Fries products is transformed to oxidation products.



A

b

c

Figure 9: *Photo-Fries rearrangement products a) L_1, b) L_2, and c) L_3 [1]*

4.5. Conclusions

Different analyses methods are used to study the effect of blue light irradiation at high temperature on the degradation of BPA-PC films. The aim was to investigate the relationship between optical and chemical changes in order to identify the predominant yellowing mechanisms. The results show that increasing the exposure time is associated with the discolouration, loss of optical properties, decrease of light transmission, decrease in the relative radiant power value, and increase in the yellowing index (YI) of BPA-PC plates. The results also show that there are two stages in the yellowing of polycarbonate plates. The first stage is the so-called induction period in which there is no major change in the value of YI and the rate of yellowing is very slow. This stage takes until 500 hours, followed by the second yellowing regime, where the yellowing is accelerated and the rate of yellowing is comparatively faster. It is concluded that under blue light radiation the yellowing mechanism is the combination of photo-Fries and photo-oxidation.

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CHAPTER 5

Surface Aspects of Discoloration in Bisphenol A Polycarbonate (BPA-PC), Used as Lens in LED-based Products

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The surface-related reactions during discoloration of Bisphenol A Polycarbonate (BPA-PC), used as LED lens plates, under thermal stress are studied. X-ray photoelectron spectroscopy (XPS) has been used to monitor the changes in the surface chemistry of BPA-PC plates over a temperature range of 100 to 140 ºC for a period up to 3000 hrs. Increasing time under thermal stress is associated with the discolouration, and increase in the yellowing index (YI) of PC plastic lens. The XPS results show that discoloration is associated with oxidation at the surface, finding a significant increase in the signal ratio O_{1s} /C_{1s} in the XPS spectra of degraded specimens. During thermal ageing, the C-H concentration decreases and new oxide features C=O and O-C=O form, with the latter being a support for oxidation at the surface being a major reaction during discoloration. Results also show that irradiation with blue light during thermal ageing accelerates the kinetics of discoloration and the increased O_{1s} /C_{1s} ratio in XPS spectra.

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5.1. Introduction

Bisphenol A polycarbonate (BPA-PC), shown in Figure 1, is a high-performance transparent thermoplastic, which is widely used as lenses in LED-based devices and other microelectronics systems [1-3].

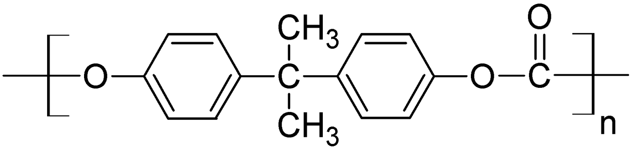


Figure 1: *Chemical structure of Bisphenol A poly carbonate*

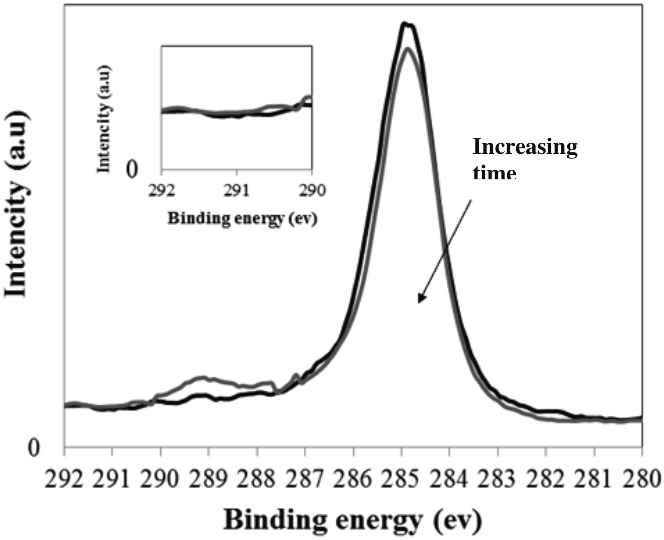
One of the major issues in the LED industry is the drop in the intensity of the output light in a long term service, attributed to the yellowing of encapsulant/lens [4] (one of the most important degradation mechanisms in LED systems). When BPA-PC is exposed to heat for a long time, initially the surface will become yellow and this gradually extends towards the bulk. Over the last decades there have been numerous attempts to understand the mechanisms of discolouration in BPA-PC plates [5-12]. In photo-degradation of BPA-PC, depending on the exposure conditions, yellowing could take place due to the photo-Fries rearrangement or oxidation reactions. It was postulated that photo-Fries rearrangement reaction is favoured when the wavelength of light is lower than 300 nm, whereas photo-oxidation reactions become increasingly important when light of longer wavelengths is used [10, 12]. During the last few years, a number of research groups have investigated the thermal degradation of polycarbonate encapsulants [11-17] and reported that the thermal degradation of BPA-PC leads to the loss of mechanical and optical properties. However, there is not much information about the change in the surface chemistry of BPA-PC plates under thermal stress and its correlation with the yellowing reaction. In this chapter, the change in the surface chemistry of BPA-PC plates during thermal- and photothermal-degradation and its correlation with the optical properties of plates are studied and discussed.

5.2. Thermal-ageing

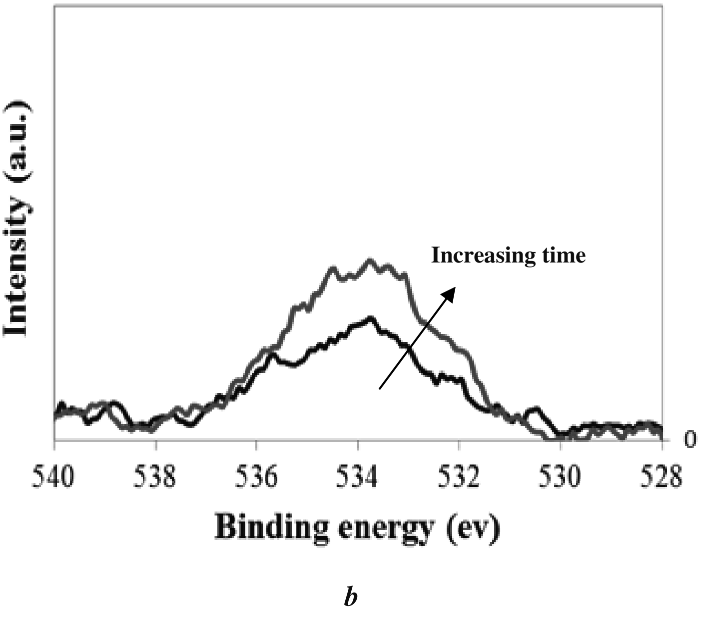
The C_{1s} and O_{1s} profiles of the XPS spectra of the as-received and aged BPA-PC plates at 140°C (for 3000 hrs) are shown in Figure 2a and 2b respectively. The C_{1s} profile of the as-received BPA-PC specimens consists of one main photoemission peak at 285 eV with a shoulder at 286.5 eV, related to carbon not bonded to oxygen (C-H) and carbon singly bonded to oxygen (C-O) respectively. There are two other peaks at 290.5 and 292 eV, attributed to the carbonate moieties (CO_3) and to the π to π^* shakeup satellite respectively (note that due to their low intensities, these peaks cannot be seen in Figure 2 at this scale) [15]. Looking at the C_{1s} spectrum of the thermally-aged specimen (Figure 2a, red), one can observe a significant decrease in the intensity of C-H peak as well as the appearance of a new peak at around 289.5 eV due to thermal ageing, with the latter being attributed to the formation of C=O and O-C=O functionalities. Both the decrease in the intensity of C-H peak and the formation of C=O and O-C=O groups are indications of oxidation under thermal stress. This is supported by the fact that the intensity of O_{1s} signal increases as a result of thermal ageing (Figure 2b). The relative intensities of carbonate moieties (CO3), C-O and π to $\pi^{*\circ}$ are shown in Table 1.

***Table 1:** Intensity of CO3 and π to π* in C1s region for thermally-aged BPA-PC plates at 100, 120, and 140 ºC after 3000 hrs (% area).*

Sample	**CO_3**	**$\pi \longrightarrow \pi^*$**
As-received	7	3
100℃	6	2
120℃	7	3
140℃	7	3



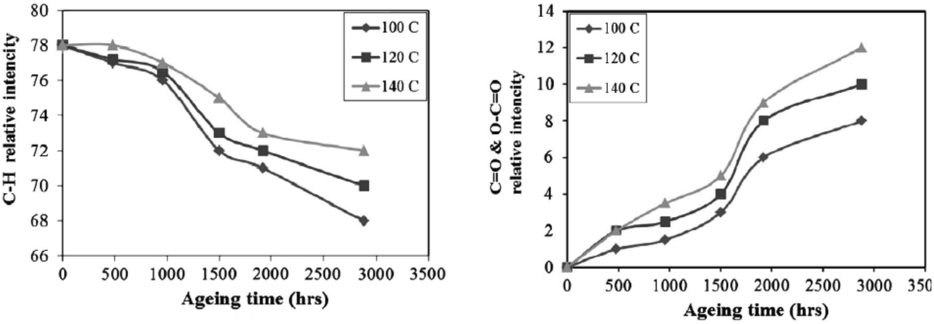
a



b

Figure 2: *XPS spectra of the a) C1s and b) O1s of BPA-PC plates, as-received (black) and aged at 140°C for 3000 hrs (red)*

In order to have a more clear, quantitative understanding of the evolution of those components in the XPS spectra with a pronounced change during the thermal ageing (C-H and C=O/O-C=O), the changes in the signal intensities of these functions with time at different ageing temperatures are plotted in Figure 3. One can notice that the decrease in the intensity of C-H feature with ageing time is accompanied with an increase in the intensity of C=O and O-C=O components, implying that the breaking of C-H bond is a parallel reaction to the oxidation. Thermal stress, as already mentioned, does not have any major influence on the intensity of the C_{1s} C-O feature, π to π^* shakeup satellite, and carbonate moieties (CO_3), with the latter being an indication that the photo-Fries rearrangement route for degradation does not have a predominant role in the yellowing of BPA-PC plate under thermal stress [15].



a b

Figure 3: *The change in the intensities of a) C-H, and b) C=O and O-C=O peaks during thermal ageing over the temperature range 100-140°C.*

The extent of oxidation at the surface can be more clearly studied by plotting the O_{1s} to C_{1s} intensity ratios during thermal ageing. Figure 3a illustrates the O_{1s} /C_{1s} ratio for all three thermally-aged samples with different ageing time. One can see that the O_{1s} /C_{1s} ratio in thermally-aged samples increases with time for all three aging temperatures. The increase in O_{1s} /C_{1s} ratio supports the argument of thermal-oxidation being the main reason for the yellowing and discolouration in thermally-aged plates [15]. It is also notable that the higher the temperature, the higher and faster the oxidation. The yellowing index (YI) of BPA-PC plates was also calculated as a function of ageing time, at 100, 120, and 140°C and is shown in Figure 4b. Obviously correlations can be drawn between two sets of results as they are clearly linked. One can however argue that the rates at which these occur are not the same, as while both initiate to increase around the same time, the kinetics of the increase is different. This could be due to the surface vs. bulk nature of the two techniques (i.e. XPS is probing where the discolouration originates), and that the O1s/C1s XPS ratio is being used as a probe of oxidation through chemical change while YI observes the physical outcome of degradation whatever the reaction mechanism(s).

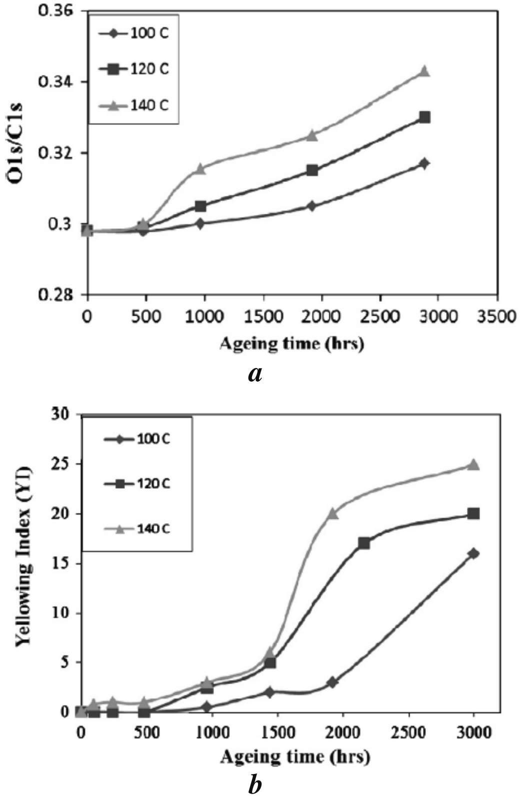


Figure 4: *The change in the a) O_{1s}/C_{ls} ratio and b) yellowing index (YI) of BPA-PC plates, aged at 100, 120 and 140 ºC for different times.*

5. 3. Effects of blue light radiation

Exposure to blue light is also one of the reasons of yellowing of BPA-PC plates in LED applications. One sample is therefore irradiated with blue light at 140 °C up to 3000 hrs, to see how blue light could change the oxidation and the yellowing kinetics of BPA-PC plates. The signal intensities in the C1s region for the thermally-aged specimen at 140 ºC for 3000 hrs and that of thermally-aged under irradiation (photothermally-aged) at the same temperature and time are shown in Table 2. One can see that the intensity of C-H feature decreases with the radiation of blue light, which is accompanied with an increase in the intensity of C=O and O-C=O components. Blue light radiation, on the other hand, does not have any major influence on the intensity of C-O feature, π to π* shakeup satellite, and carbonate moieties (CO_3).

Table 2: *Intensity of different features in* C_{1s} *region for thermally-aged and photothermally-aged BPA-PC plates at 140 ºC after 3000 hrs (% area)*

Sample	**C-H**	**C-O**	**C=O**	**O-C=O**	**CO_3**	**$\pi \longrightarrow \pi^*$**
As-received	78	12	-		7	3
Thermal-aged	68	12	12		6	2
Photo-aged	64	11	15		7	3

Figure 5a compares the change in the O_{1s} /C_{1s} ratio for both thermally-aged and photothermally-aged samples at 140 ºC. One can see that blue light radiation during thermal ageing results in a higher degree of oxidation at the surface. In another words, this increase in O_{1s} /C_{1s} ratio in photothermally-aged plates demonstrates that by radiation of blue light, the surface of BPA-PC plates are more oxidized. This would then be expected to have a direct influence on the kinetics and the extent of yellowing. Figure 5b compares the YI of BPA-PC thermally and photothermally-aged plates as a function of exposure time. The results clearly show that the yellowing is faster and more pronounced when specimens are aged under temperature and radiation, in agreement with the XPS results. It is worth mentioning that because the distance between the plates and the light source was around 20cm and the glass window was between the light source and the specimens; the temperature increase at the surface of specimens due to irradiation was almost negligible. So the actual temperature of the plates during photo-thermal ageing is almost the same as the oven temperature. It means that the enhancement of yellowing (and also of the O_{1s} /C_{1s} ratio) due to blue light radiation in this experimental configuration is solely a radiation-induced phenomenon (the plate has the same temperature as in case of heating at 140°C without radiation).

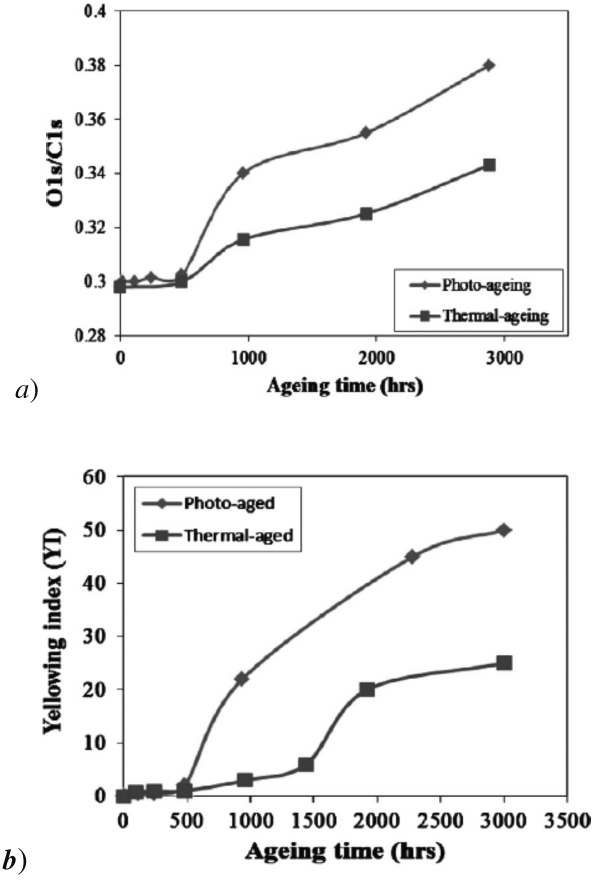


Figure 5: *The change in the a) O_{1s}/C_{ls} ratio and b) yellowing index (YI) of BPA-PC plates, thermally- and photothermally-aged at 140 ºC for different ageing times*

5.4. Discussion

In this study the chemical reactions at the surface of BPA-PC plates under thermal stress are monitored and studied by means of XPS analysis, which inherently could provide detailed information from the surface chemistry. During last few years a number of research groups have investigated the effects of thermal ageing on the optical and mechanical properties of polycarbonate encapsulants [13-17]. Thermal-oxidation are more commonly reported as the main mechanism of yellowing of BPA-PC on heating in the presence of oxygen [13-14], with molecular rearrangement only reported to occur at the higher temperature range 500-700°C [17]. Side chain and ring oxidation as well as the formation and subsequent oxidation of phenolic end groups were postulated to be the main reasons for discolouration and yellowing of thermally-aged BPA-PC [12, 13]. In BPA-PC, the reasons underlying the photo-degradation, have been attributed to two different mechanisms: photo-Fries rearrangement and photo-oxidation, with the former reported to be more influential at wavelengths shorter than 300nm [16] and the latter more important when light of longer wavelengths (>340 nm) is used. In photo-Fries rearrangement reactions, carbonyl groups are rearranged to phenylsalicylate and dihydroxybenzophenone [15]. Rearrangement reaction products could to some extent have influence on the yellowing of BPA-PC under blue light radiation [10], however, our XPS results do not show that since the intensity of the carbonate peak does not change during degradation (see Table 2). It was postulated that where the oxidation reaction is dominant, side chain oxidation, ring oxidation and ring attack reactions are likely to take place [16]. The side chain oxidation in BPA-PC, however, is reported to be more probable [1-7]. In this study, a significant increase in the intensities of both C=O and O-C=O features during thermal ageing is an indication of the involvement of gem dimethyl group and the aromatic ring groups in thermal degradation reactions [15], suggesting that the oxidation is a prominent degradation reaction. The increase in the intensities of both C=O and O-C=O features is associated with the decrease in the C-H intensity, which point towards C-H bonds breakings during oxidation. In the photothermally-aged plates, the intensities of carbonyl and carboxylate function are higher than those in the thermally-aged specimens, demonstrating that blue light radiation increases the extent of oxidation during degradation. The yellowing index (YI) of BPA-PC plates was also measured as a function of exposure time, as shown in Figures 4b and 5b. There is a relatively close correlation between the kinetics of discoloration and that of the oxidation reaction monitored by XPS, supporting the argument that oxidation is an influential surface reaction during thermal degradation.

5.5. Conclusions

The thermal degradation of a Bisphenol-A Polycarbonate (BPA-PC) plates under elevated temperature stress was studied with a focus on the surface reactions during discoloration. BPA-PC plates were exposed to temperature in the range of 100 to 140 °C and the change in chemistry at the surface studied by XPS. Increasing exposure time is associated with the discolouration and increase in the yellowing index (YI) of PC plastic lens (the higher the temperature, the higher the YI). Discoloration is associated with the oxidation at the surface, which is confirmed by a significant increase in the signal ratio O1s/C1s in the XPS spectra of degraded specimens. During thermal ageing, the C-H concentration in the XPS spectra of aged samples decreases and new oxide features C=O and O-C=O form. This is a support for the argument of oxidation reactions at the surface being a major cause of yellowing. Thermal stress does not have any major effect on the intensities of the C-O feature, π to π* shakeup satellite, and carbonate moieties (CO_3), with the absence of the change for the latter being an indication that the rearrangement reaction products are either not significant or cannot be detected well by XPS. Irradiation with blue light (450nm) during thermal ageing increases the extent of oxidation as well as the YI of degraded species.

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CHAPTER 6

Lifetime Assessment of Bisphenol A Polycarbonate (BPA-PC) Plastic Lens, Used in LED-based Products

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In this investigation, the accelerated optical degradation of two different commercial Bisphenol-A Polycarbonate (BPA-PC) grades under elevated temperature stress is studied. The BPA-PC plates are used both in light conversion carriers in LED modules and encapsulants in LED packages. BPA-PC plates are exposed to temperatures in the range of 100 to 140 °C. Optical properties of the thermally-aged plates were studied using an integrated sphere. The results show that increasing the exposure time leads to degradation of BPA-PC optical properties, i.e. decrease of light transmission and increase in the yellowing index (YI). An exponential luminous decay model and the Arrhenius equation are used to predict the lumen depreciation over different time and temperatures. Accelerated thermal stress tests together with the applied reliability model are used to predict the lifetime of the plastic lens in LED based products in real life conditions.

This chapter is reproduced from M. Yazdan Mehr, W.D. van Driel, , K.M.B. Jansen d , P. Deeben, G.Q. Zhang, Lifetime Assessment of Bisphenol-A polycarbonate (BPA-PC) Plastic Lens, used in LED-based Products, Microelectronics Reliability, 54 (2014) 138–142

6.1. Introduction

Over the last decade, GaN-based light-emitting diodes (LEDs) are developed as good candidates for the high-efficiency light sources for general lighting purposes. LEDs have an intrinsically high reliability compared with conventional light sources (incandescent and fluorescent lamps) since they are semiconductor-based devices. LEDs have much longer lifetime with lower lumen depreciation, compared to incandescent and fluorescent lamps [1], making them good candidates for long-lasting light sources. In LED-based products or systems a blue GaN-based LED chip with an emission wavelength of 450–460 nm is normally used as a light source. The chip is covered with a plastic lens which has the twofold aim of protecting the lens, and of converting the blue light to white light. Blue light is converted into white light by means of a phosphor layer, which can be either deposited directly on the chip or incorporated into the encapsulating lens.

During service LEDs could fail due to the degradation of each of the components including lens, encapsulant, chip, phosphor layer and interconnects [2-6]. One of the most important degradation mechanisms is the yellowing of the LED plastic lens and encapsulants, which could result in a significant lumen depreciation and change in chromatic properties of the LED. The yellowing of encapsulant/lens could be ascribed to prolonged exposure to short wavelength emission (blue/UV radiation), temperature, and the presence of phosphors, with temperature having a very crucial influence [2]. Temperature increase during service could be due to a combination of junction temperature, ambient temperature and LED self-heating [7]. Narendan et al [8] showed that light circulation between the phosphor layer and the reflector cup can also increases the temperature. A relatively comprehensive explanation of chemical mechanisms of yellowing of both thermally- and photo-aged BPA-PC without phosphor is given in one of our earlier publications [9].

In addition to the fact that temperature is a very influential degradation factor, it can also be easily controlled and is more commonly used as an input parameter to predict the reliability and the lifetime of plastic encapsulated LEDs. Reliability models for the prediction of LED lifetime is based on standards, developed by the Illumination engineering societies (IES) together with the alliance for solid state illumination system and technology (ASSIST). IES and ASSIST have developed a standard for lumen measurement method at room temperature or slightly elevated temperatures [10]. Based on this standard, failure in LED light sources is defined as 30% lumen depreciation, since this level of luminous drop is what human eyes can detect. However, performing LED lifetime tests at room temperature necessitates a very long time, which is not acceptable for such a fast growing industry. This means that reliability experiments should be performed in much shorter times. A good approach to reduce the testing time is increasing the temperature in order to accelerate the degradation. An extrapolation can then be used to determine failure rates and time-to-failure at real service condition. Reliability models can off course be developed for different components of the system and eventually for the whole LED-based product or system. This study is only devoted to the reliability of the plastic lens and/or encapsulant, since there is not much published information about the reliability of this important component. Plastic materials used in LEDs are mainly silicone, epoxy resins, and/or Bisphenol A polycarbonates (BPA-PC), with BPA-PC being most widely used in LED-based products, due to its excellent combination of high impact strength, heat resistance and high modulus of elasticity [11]. In our study, two industrial BPA-PC variants with different additives are used for reliability experiments. The degradation rate, acceleration factor and lifetime of these two commercial BPA-PC plates are derived from the developed reliability model.

6.2. Optical analysis

Stress at high temperature levels can induce thermal ageing and consequently a strong optical power lowering and depreciation of light output, as is shown in Figure 1 for the case of thermal ageing at 140°C (as an example). Reduction of light output with increasing thermal ageing time for samples, aged at 100 and 120°C, show the same trend in both variants.

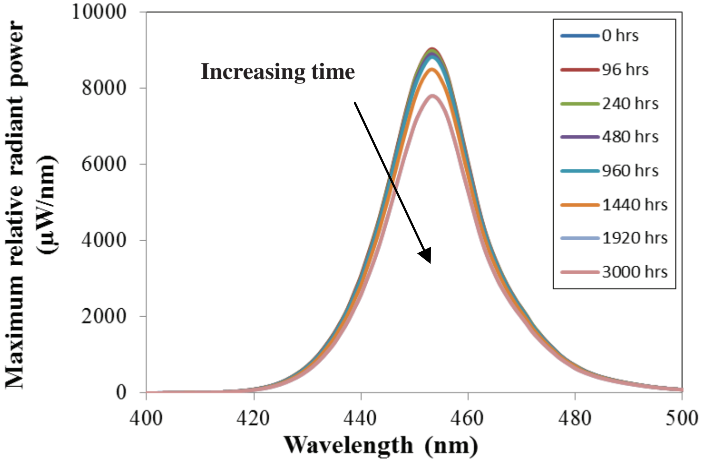


***Figure 1:** Spectral power distribution (SPD) of variant A at 140 ºC*

Figure 2 shows the yellowing index (YI) of variants A and B recorded after 3000 h as a function of ageing temperature, at 100, 120, and 140°C. Obviously, the higher the temperature the higher YI is.

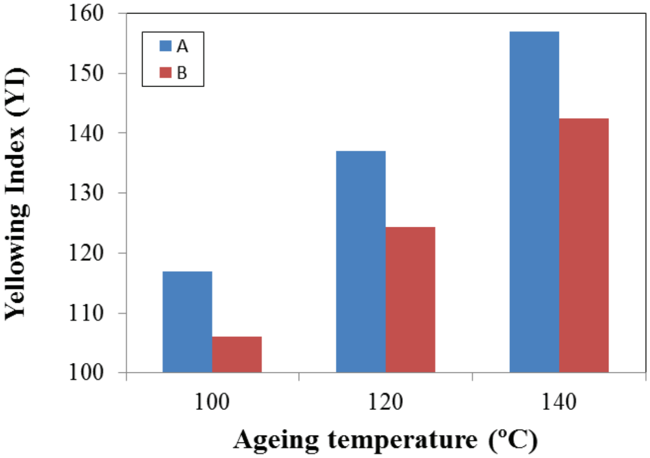


***Figure 2:** Yellowing Index (YI) of samples A and B at different temperatures after 3000 h thermal ageing*

The evolution of YI of BPA-PC plates at 140°C as a function of thermal ageing time for both plates A and B is shown in Figure 3. As it is seen, there are two stages in the discolouration of thermally-aged samples. The first stage is the so-called induction period in which there is no major change in the value of YI and the rate of yellowing is very slow, followed by the second yellowing regime, where the yellowing is accelerated and the rate of yellowing is comparatively faster. It is shown that the main reason of chemical degradation in BPA-PC plates is the thermal-oxidation of plates and the forming the of cyclic anhydrides and aromatic ketone [9]. The intensities of cyclic anhydrides and aromatic ketone bands of thermally-aged specimens follow the same two-stage trend, inferring that thermal oxidation could be considered as the main reason of the yellowing [9].

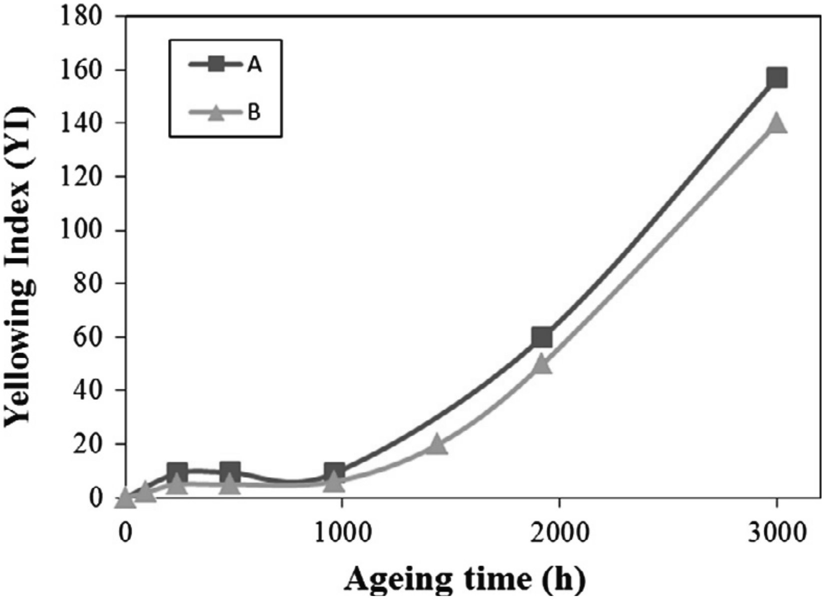


Figure 3: *Variation in yellowing index (YI) of BPA-PC plates variants A and B, aged at 140 ºC for different thermal ageing times (in hrs)*

Figure 4 depicts the colour shift of the specimens (Duv) at different loading conditions. The variation of colour shift is similar to that of YI. Similar to YI, there is no major colour shift during the incubation stage, whereas the colour shift during the degradation stage is linearly proportional to the testing duration.

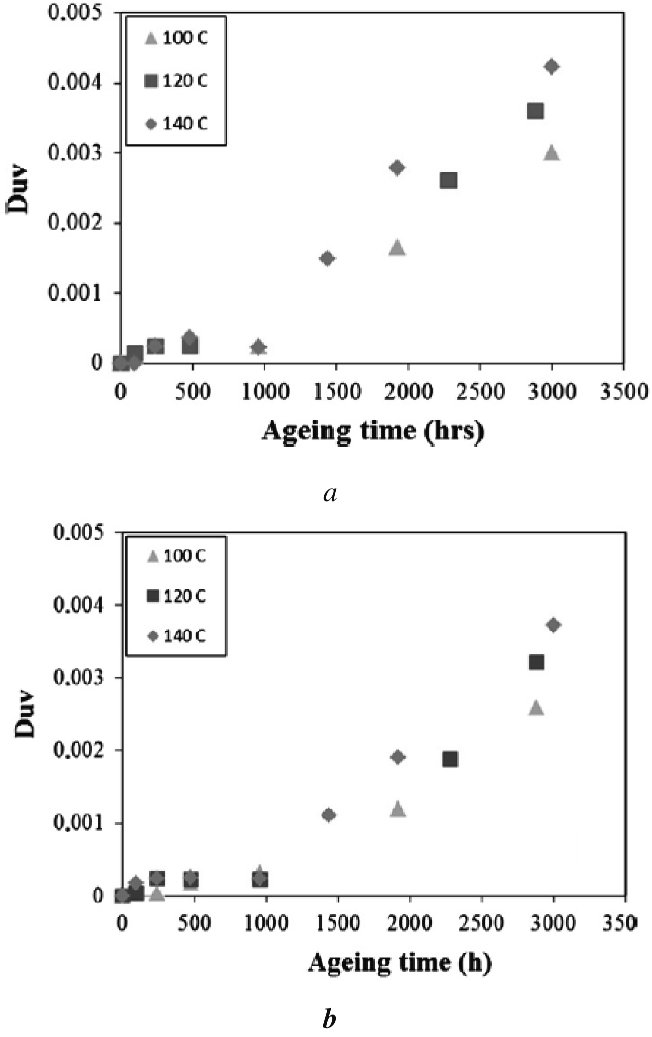


Figure 4: *Colour shifting (Duv) of BPA-PC plates variants a) A and b) B, aged at 100, 120, and140ºC for different thermal ageing times (in hrs)*

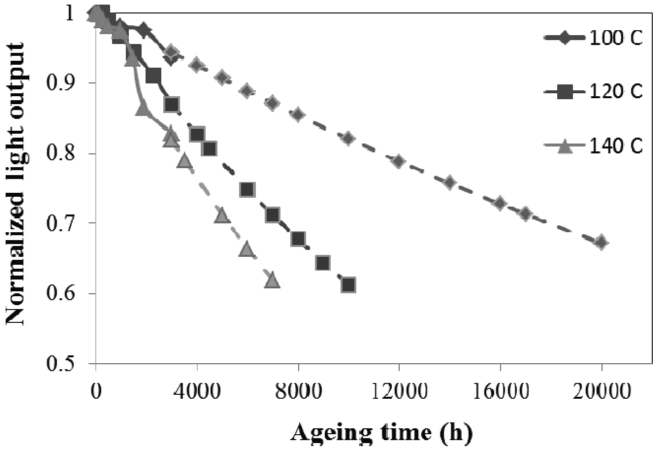
The effects of thermal stress on the performance of the lens materials are shown in Figure 5, which depicts the degradation kinetics of commercial variants A and B. It is noticeable that the degradation rate shows a significant dependence on the stress temperature level; the higher the ageing temperature, the higher the degradation kinetics. The experiments were performed up to 10% reduction in light output (solid lines in Figure 5). However, as is already explained, based on the ASSIST standard, lifetime of LEDs is defined as time to reach 70% of its initial lumen output [11]. Therefore the extrapolation of experimental data is needed. Given that the reaction rate is assumed to be constant for each temperature, a at temperature T is calculated as follows

$$a(T) = \frac{-\ln[\phi(t)]}{t} \qquad (3),$$

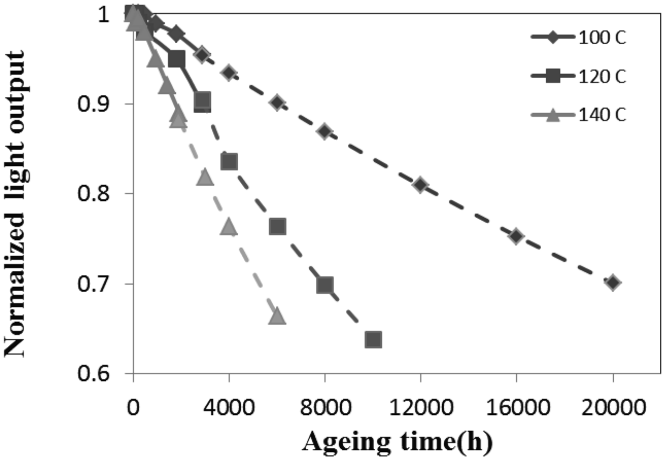
In order to calculate *a (T)* at each temperature, *t* is taken equal to the time when lumen decays to 0.9, which is obtained experimentally. Having the reaction rate for each temperature, one then can easily calculate the time for 70% lumen decay at each temperature. The calculated a can obviously be used to extrapolate the lumen decay till 70% for each temperature (see dashed lines in Figure 5).

Table 1 illustrates the calculated values for the reaction rate for each temperature for both samples. Obviously, by increasing the temperature, the reaction rate becomes larger, meaning that lumen depreciation takes place at shorter time.

The activation energy of the degradation reaction in LEDs depends on the materials and the working conditions. The activation energy can be calculated from Equation (2). In order to obtain the activation energy, the natural logarithm of the reaction rates is plotted against the inverse of the absolute temperature, see Figure 6. The slope is multiplied by the negative of the gas constant to obtain the activation energy, Ea, in the eV. Activation energies for both samples A and B are between 0.3-0.4eV, which are in agreement with previous reported values [12, 13].



a

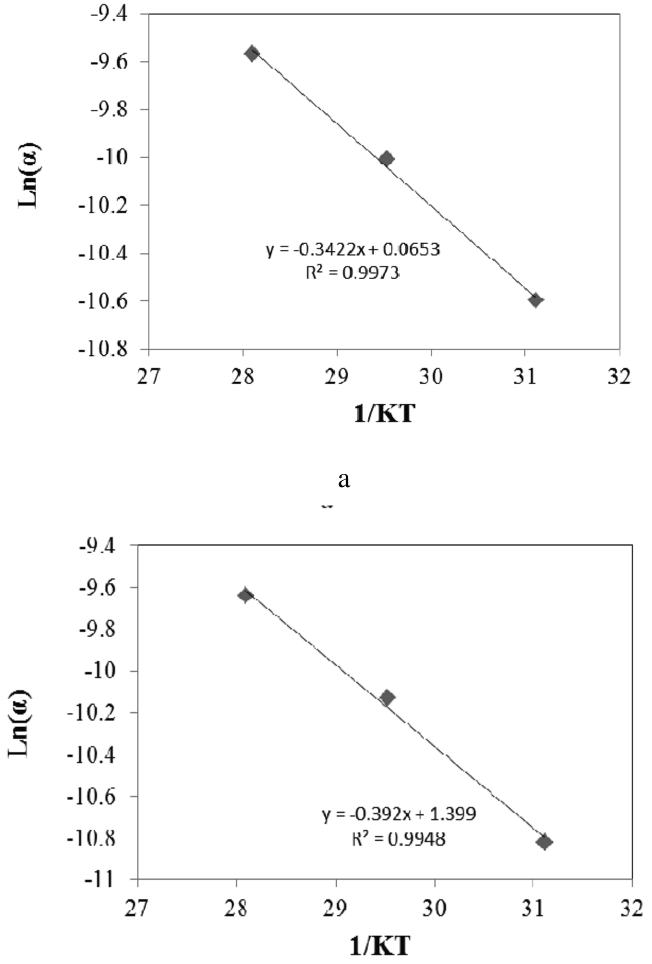


b

Figure 5: *Normalized flux of a) lens A and b) lens B at different thermal stress tests*

Table 1: *a for commercial plates A and B at temperature 100-140°C*

Temperature	Sample A	Sample B
100 °C	2.5E-05	2.0 E-05
120 °C	4.5E-05	4.0 E-05
140 °C	7.0E-05	6.5E-05



a

b

Figure 6: *Plot of ln (a) vs E/KT for samples a) A and b) B.*

6.3. Prediction of time-to-failure at low temperature

The real working temperature of LDEs is much lower than the applied temperatures [12]. Therefore, the kinetics of lumen depreciation to 30% of its initial value by using exponential luminous decay model and Arrhenius equation should be extrapolated to temperatures lower than 100 °C. This can be done using Equation 1 by equating ϕ to 0.7, knowing that α can be obtained from Equation 2. The values of α, calculated for 40, 60 and 80 °C, are given and shown in Table 2, as it is seen that the higher the temperature the faster the lumen depreciation is.

Table 2: *Parameter α for samples A and B at temperature 40-80 °C*

Temperature	Sample A	Sample B
40 °C	3.29E-06	1.97E-06
60 °C	7.06E-06	4.73E-06
80 °C	1.36E-05	1.03E-05

Figure 7 illustrates time-to-failure (70% lumen decay) of both variants A and B, calculated at different temperatures. It is seen that sample B has a longer life time compared to the sample A; i.e. at 40°C the light output from lens A reduces to 70% of its initial value after 100 khrs, while for variant B time-to-failure is 140 khrs. This slight difference in lifetime of these two LED lens materials is due to the difference in the type and amounts of additives.

6.4. Acceleration factor

By using Arrhenius equation one can calculate the acceleration factor of the tests at different temperatures. Acceleration factor is a measure of how much the test is accelerated at testing condition, compared to normal behavior at real working condition. Obviously the higher the acceleration factor, the faster and more efficient (in terms of needed time for the experiment) the experiments. This factor is defined by following equation,

$$Af = \exp(E_a(\frac{8.617\times10^{-5}}{T_{\mathrm{Re}\,ference}} - \frac{8.617\times10^{-5}}{T_{test}}) \quad (4),$$

where $R_{eference}$ is the working temperature, which is assumed to be around 40 ºC, and T_{est} is the testing temperature. The acceleration factors of variants A and B at ageing temperatures 100, 120 and 140 ºC have been given in Table 3. As is expected, the higher the temperature the higher the acceleration factor.

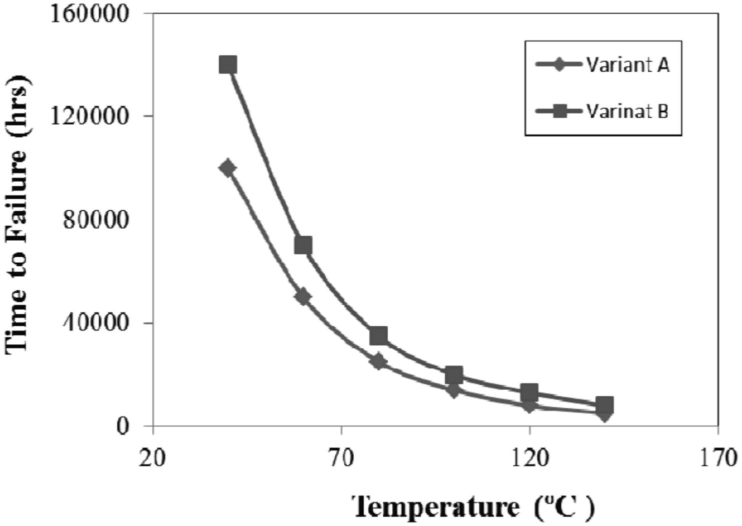


Figure 7: *Time-to-failure (70% lumen decay) of both variants A and B at different temperatures*

Table 3: *Acceleration factors for commercial plates of A and B at 100, 120 and 140 ºC*

Sample	**A**	**B**
373 K	7	9
393 K	13	15
413 K	20	25

6.5. Discussion

Many studies have been done on the reliability of LEDs [14-18] in which temperature is used as a very significant controlling parameter. When LEDs are exposed to high temperature levels the optical properties of the package and of the material used for the encapsulation can severely degrade [3-5]. This can result in a significant reduction in the luminous flux, emitted by the devices.

Hsu et al. [18] have shown that in addition to the reliability of the material properties of the plastic lens, the lens shape may also have an influence on the reliability of the high-power LED modules. LED-based products encapsulated with hemispherical-shaped lens exhibited the better life time due to better thermal dissipation than those in cylindrical and elliptical-shaped lenses. This study is however more focused on the plastic lens itself and the effects of geometry are not taken into consideration.

Spectral power distribution (SPD) method is used to study the effect of high temperature stress test on the optical degradation of BPA-PC plastic lens. The aim was to investigate the effect of temperature on the acceleration of optical degradation in LEDs, to determine the effect of yellowing of BPA-PC lens on the lumen depreciation of LED-based products, and to develop an accelerated test method and a reliability model for LED plastic lens. An exponential luminous decay model and Arrhenius model were used to predict the lumen depreciation over different times and temperatures. It is shown that the lumen depreciation rate (a) for sample A is larger than that in sample B, due to the slight differences in their chemical compositions. The lower the depreciation rate, the better the performance a plastic lens could have.

The results also show that there is a direct relation between the temperature and acceleration factor. One can see that the acceleration factor is maximum at 140 °C for both samples A and B. The obtained acceleration factors are, however, not as large as what one could expect from a fast and efficient reliability test. Other stresses, like short wavelength irradiation or possibly changing the composition, should obviously be used to have acceleration factors in the range 10-20, which will be more efficient for LED reliability experiments. Sau et. al [13] showed that expected lifetimes, defined as 30% lumen depreciation at 40°C, for a range of different commercial LEDs are around 35 khrs. What is obtained in this study for the lifetime of just the plastic lens is more than 100 khrs, indicating that other failure modes are contributing to the degradation of LED package (i.e. phosphor and irradiation). The effect of phosphor will be addressed in our future work.

As is already explained, in LEDs plastic lens is layered with phosphor. The phosphorous layer is used for the conversion of blue light into white light. Recent reports [17-21] have indicated that the package/phosphors system can also significantly degrade during the LED lifetime. This can result in a significant decrease in LED efficiency.

6.6. Conclusions

The accelerated optical degradation of two different commercial Bisphenol-A Polycarbonate (BPA-PC) plates, under elevated temperature stress, is studied. The BPA-PC plates are used both in light conversion carriers in LED modules and encapsulants in LED packages. BPA-PC plates are exposed to temperature in the range of 100 to 140°C. Exponential luminous decay model and Arrhenius equation are used to predict the lumen depreciation the lifetime of plastic lens in LED lamps in real service conditions. The following conclusions can be drawn from this study:

- Increasing the exposure time is associated with the discolouration, decrease in the relative radiant power value, and increase in the yellowing index (YI) of PC plastic lens
- The higher the temperature the higher the YI
- By increasing the temperature, the reaction rate becomes larger, meaning that lumen depreciation takes place at shorter time. The reaction rate follows the Arrhenius acceleration law
- The acceleration factors of variants A and B at ageing temperatures of 140 ºC are calculated to be around 20
- The lifetime of the plastic lens, defined as 30% lumen depreciation at 40 °C, is around 100 khrs for the commercial grades tested.

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CHAPTER 7

Accelerated Life Time Testing and Optical Degradation of Remote Phosphor Plates

In this chapter the thermal stability and life time of remote phosphor encapsulant plates, made from bisphenol-A polycarbonate (BPA-PC), are studied. Remote phosphor plates, combined with a blue-light LED source, could be used to produce white light with a correlated colour temperature (CCT) of 4000 K. Spectral power distribution (SPD) and photometric parameters of thermally-aged phosphor plates were measured by Integrated-Sphere. Results show that thermal ageing leads to a significant decrease in the luminous flux and chromatic properties of plates. The photometric properties of thermally- aged plates, monitored during the stress thermal ageing tests, showed a significant change both in the correlated colour temperature (CCT) and in the chromaticity coordinates (CIE x, y). It is also observed that there is a significant decay both in the phosphor yellow emission and in the blue peak intensity. The decrease in the luminous flux is strongly correlated to the deterioration of the chromatic properties of the phosphor plates. The results also show a significant decay of CCT, postulating that the degradation of the remote phosphor plates affects the efficiency of light and the colour of emitted light as well. The decrease of CCT takes place with almost the same kinetics as the lumen depreciation.

This chapter is reproduced from: M. Yazdan Mehr, W.D. van Driel, G.Q. Zhang, Accelerated life time testing and optical degradation of remote phosphor plates, Microelectronics Reliability, 54 (2014) 1544–1548

7.1. Introduction

The introduction of white LEDs to the lighting market was a revolutionary achievement in this market domain. Excellent optical quality, high efficiency, high reliability, and eco-environmentally of LEDs are main advantages, which make them superior than traditional light sources. Among different techniques of producing white light, phosphor–converted white LEDs is more common because of its price and colour rending index. The wavelength-converting phosphors in combination with InGaN blue LED are commonly used in white LEDs, since they have less problematic issues during service. For example, the RGB 3-chip LED requires complex control of electronics in order to guarantee a defined colour over operating time. Although LEDs are more reliable than conventional light sources, several reports [1-12] have shown that package and phosphor layer of white LEDs can degrade, resulting in the reduction in the light efficiency. The main reason for phosphor damage is radiation of light and the generated heat by LED chip during operation. In order to reduce the effects of generated heat on the degradation reaction, the idea of using phosphor layer far from the chip, called remote phosphor, was introduced [6-7]. Remote phosphor produces light with high extraction efficiency and lower operating temperature [6-8]. In this configuration, the phosphor layer is deposited onto the lens. Lens materials, used in LEDs, are mainly silicon, epoxy resins, and Bisphenol A polycarbonates (BPA-PC), among which BPA-PC more widely used due to its optimum combination of high impact strength, heat resistance and high modulus of elasticity.

Since remote phosphor is a new technology to produce white light, there are not many reports dealing with the reliability of remote phosphor in the literature. The aim of this paper is to investigate the effect of heat on the optical properties and the reliability of remote phosphor. For this reason a set of accelerated thermal stress tests were applied with temperature level between 100 and 140 °C. The reliability studies and life time assessment at temperatures lower than 100 °C can be done by extrapolation.

7.2. Thermal degradation test

Stress at high temperature levels can induce thermal ageing and consequently a strong optical power lowering and depreciation of light output, as is shown in Figure 1 for the case of thermal ageing at 140 °C for sample B (as an example). Reduction of light output with increasing thermal ageing time for samples, aged at 100 and 120 °C, show the same trend in both samples. It is noticeable that there is a significant decay both in the phosphor yellow emission and in the blue peak. As is shown in our previous work the yellowing of BPA-PC plates leads to the reduction in the light transmissivity of plates [12]. Reduction in yellow emission also illustrates the decay of phosphor conversion efficiency.

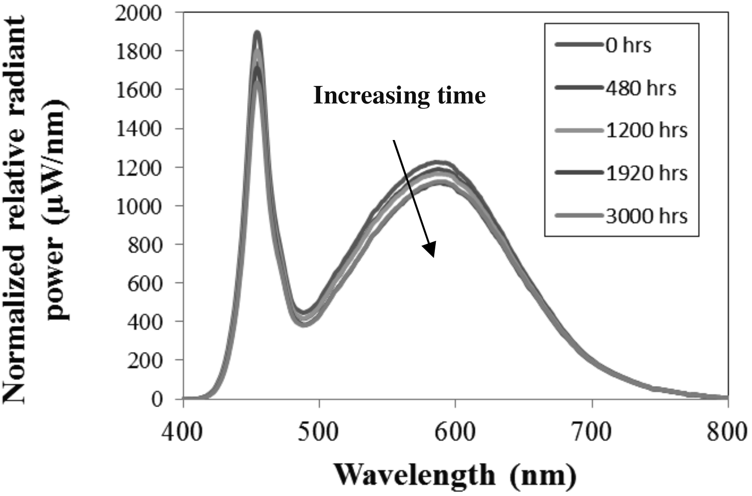
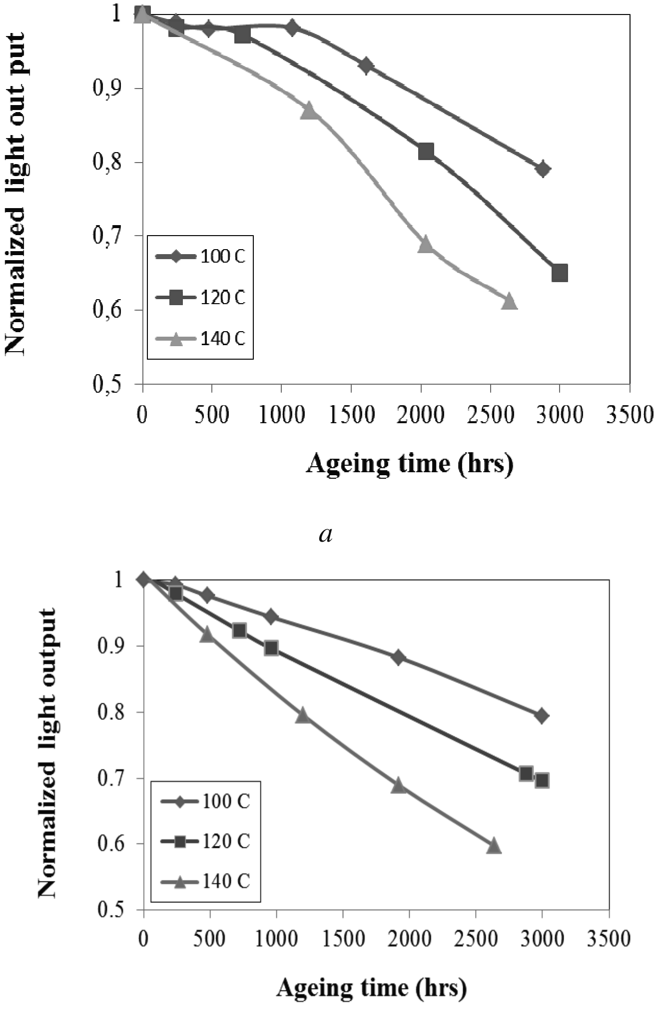


Figure 1: *The evolution of spectral power distribution (SPD) of sample B at 140 ºC*

A more quantitative description of the effects of thermal-ageing on the performance of remote phosphor A and B is given in Figure 2. This Figure illustrates the evolution of the normalized flux intensity and therefore the degradation kinetics of the phosphor plates. Clearly, the degradation rate shows a significant dependence on the stress temperature level; the higher the ageing temperature, the higher the lumen depreciation and the degradation kinetics.



a

b

Figure 2: Normalized flux of remote phosphor plates at different thermal stress tests for sample a) A, and b) B

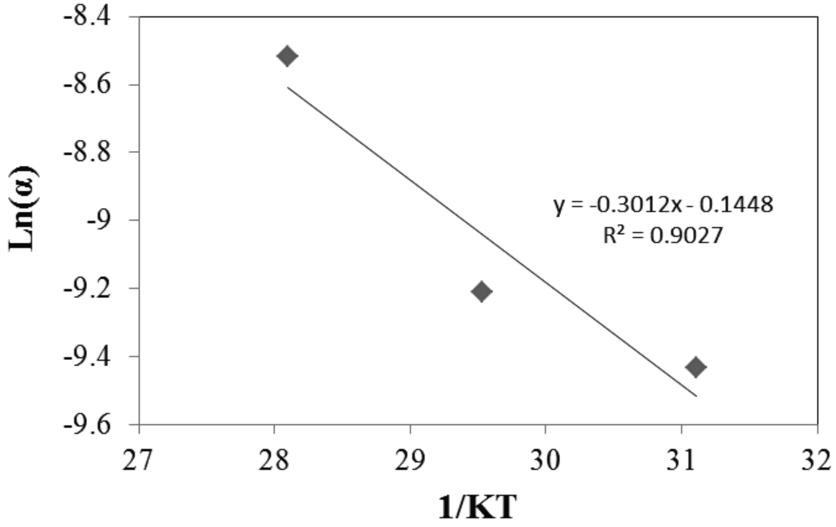
Based on the alliance for solid state illumination system and technology (ASISST) standard, lifetime of LEDs is defined as time to reach 70% of its initial lumen output [10]. The experiments at 100 °C were performed up to 20%

reduction in light output. Therefore the extrapolation of experimental data at 100 °C is needed. The lumen output is extrapolated to higher depreciation by the model that is explained in our previous paper [12]. Table 1 illustrates the calculated values for the reaction rate (a) for each temperature for remote phosphor plates A and B.

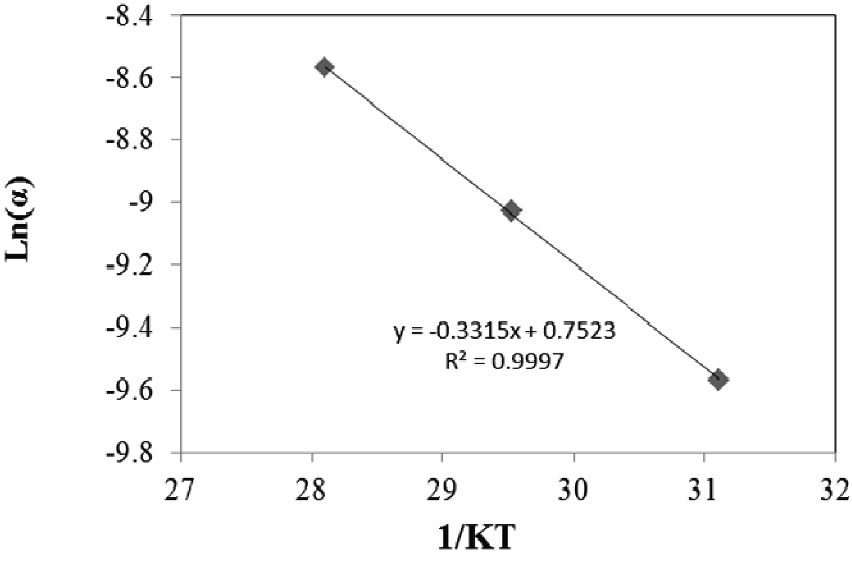
Table 1: Reaction rate *a* for remote phosphor plates *A* and *B* at temperature 100-140 °C

Temp (°C)	Sample *A*	Sample *B*
100	8.0E-05	7.38E-05
120	1.59E-04	1.24E-04
140	2.44E-04	2.0E-04

Obviously, by increasing the temperature the reaction rate becomes larger, inferring that the same level of lumen depreciation takes place at a shorter time. The activation energy of the degradation reaction in LEDs depends on the materials and the working conditions. The activation energy can be calculated from Equation (2). In order to obtain the activation energy, the natural logarithm of the reaction rates is plotted against the inverse of the absolute temperature (see Figure 3). The slope is multiplied by the negative of the gas constant to obtain the activation energy, Ea, in the eV. Activation energy for remote phosphor is between 0.3-0.4eV, which is in agreement with previous reported values [11].



a



b

Figure 3: *Plot of ln (a) vs E/KT for remote phosphor a) A, and b) B*

Thermal-stress test also have some significant effects on the CCT. In Figure 4 the variation of CCT during high temperature stress test is shown for both remote phosphor plates A and B. It is obvious that by increasing the thermal ageing time the CCT decreases. One can also notice that the higher the ageing temperature, the higher the degradation kinetics. The reduction in CCT follows the same kinetics as the luminous flux decay and can therefore be ascribed to the thermally activated degradation mechanism discussed above.

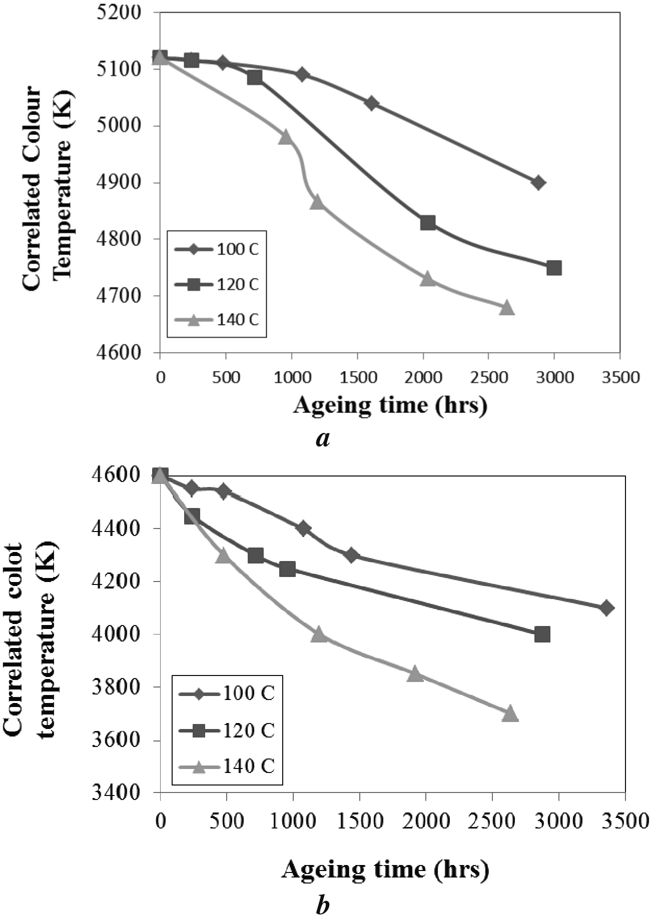


Figure 4: *Correlated colour temperature (CCT) during high thermal-stress tests for a) sample A, and b) Sample B*

The reduction in Colour Temperature suggests that the degradation of the remote phosphor plates has consequences not only on the light extraction efficiency but also on the colour of the emitted light. Colour shifting of light is determined by variation of Chromaticity Coordinate (CIE x,y). The direction of the change in the Chromaticity Coordinates of both plates A and B during thermal ageing is illustrated in Figure 5. As is illustrated in this graph, the light turns towards yellow region of the chromaticity diagram in remote phosphor A and B.

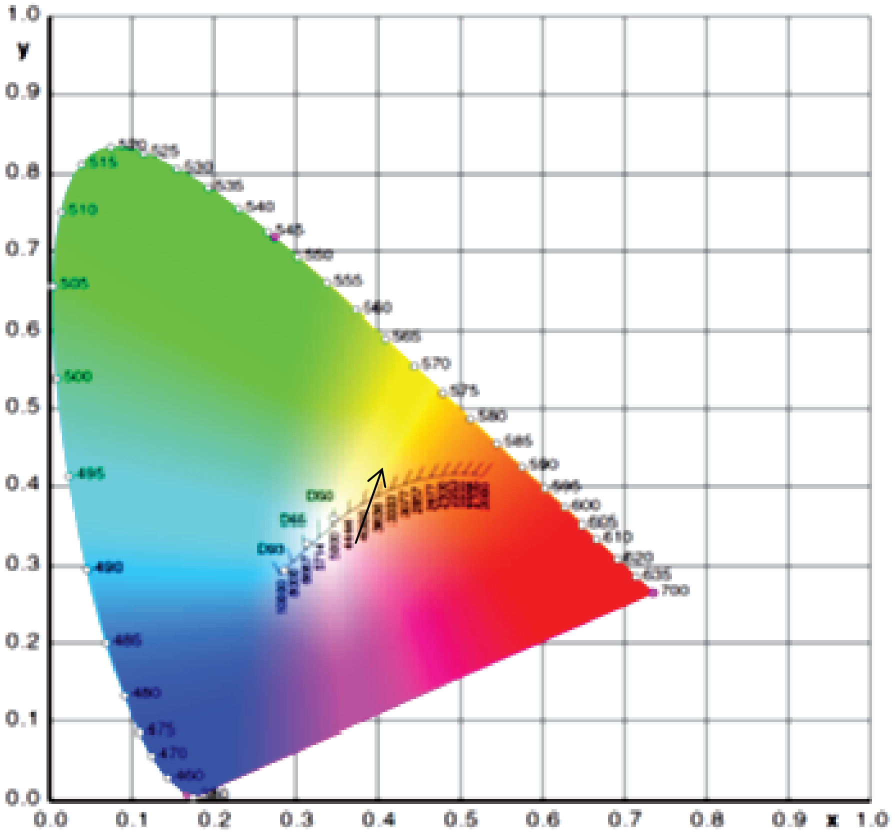


Figure 5: *The variation of Chromatic Chromaticity before and after 3000 hrs of 140 °C thermal-ageing in both plates A and B*

7.3. Prediction of time-to-failure at lower temperature

The real working temperature of LEDs is much lower than the applied temperatures in the tests [13]. Therefore, the kinetics of lumen depreciation to 30% of its initial value by using exponential luminous decay model and Arrhenius equation should be extrapolated to temperatures lower than 100 °C. This can be done using Equation 1 by equating ϕ to 0.7, knowing that α can be obtained from Equation 2. The values of α, calculated for 40, 60 and 80 °C, are given in Table 2. As is seen the higher the temperature the faster the lumen depreciation.

Table 2: *a remote phosphor at temperature 40-80 °C*

Temp (°C)	**Sample A**	**Sample B**
40	1.63E-05	1.03E-05
60	3.19E-05	2.15E-05
80	5.79E-05	4.12E-05

Figure 6 illustrates time-to-failure (70% lumen decay) of remote phosphors A and B, calculated at different temperatures. It is seen that at 40 °C the light output from lens A reduces to 70% of its initial value after 25 khrs, while for remote phosphor B time-to-failure is 30 khrs. This slight difference in lifetime of these two LED lens materials is due to the difference in the type of lens/substrate and amounts of phosphors in remote phosphors.

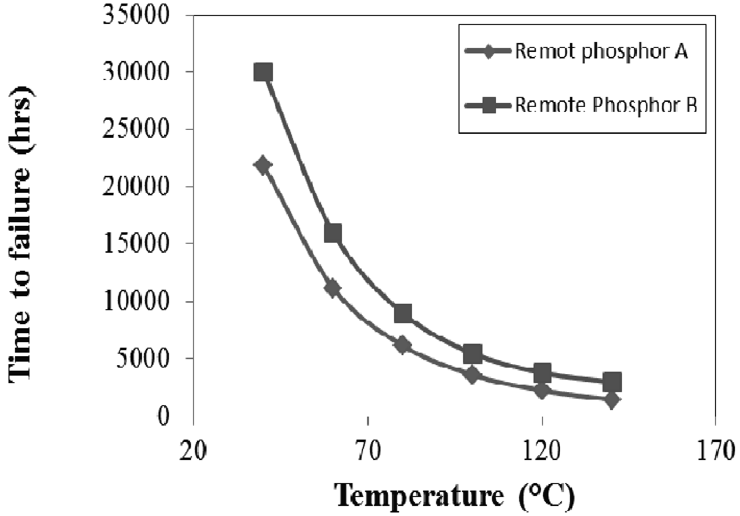


***Figure 6:** Time-to-failure (70% lumen decay) of remote phosphor at different temperatures for sample a) A, and b) B*

7.4. Discussion

The excitation sources, used for phosphors in LEDs, are different from those of phosphors in conventional lighting. The excitation sources for phosphors in LEDs are UV (360–410 nm) or blue light (420–480 nm), whereas those for conventional inorganic phosphors in cathode-ray tubes (CRTs) or fluorescent lamps are electron beams or mercury gas (254 nm). Therefore, the phosphors in LEDs should have high absorption of UV or blue light. Conventional incandescent and fluorescent lamps rely on either heat or discharge of gases. In addition, they should also have high conversion efficiency, high stability against chemical, oxygen, carbon dioxide, and moisture, low thermal quenching, and appropriate emission colours. Different phosphor, such as orthosilicates [14,15], aluminates [16], and sulfides [16,17], have been used in white LEDs. However, most oxide-based phosphors have low absorption in the visible-light spectrum, making it impossible for them to be coupled with blue LEDs. On the other hand, sulfide-based phosphors are thermally unstable and very sensitive to moisture, and their luminescence degrades significantly under ambient atmosphere without a protective coating layer. For the time being, YAG:Ce is the best option and the most widely applied phosphor in white light LEDs because YAG:Ce has the best performance in terms of efficiency [18]. However, the main disadvantage of YAG:Ce is poor colour rending index and serious thermal quenching of luminescence.

Temperature is a very significant controlling parameter in LED reliability. High temperature levels can damage the optical properties of the package and of the material used for the encapsulation [1-5]. This can result in a significant reduction in the luminous flux, emitted by the devices. Spectral power distribution (SPD) method is used to study the effect of high temperature stress test on the optical degradation of remote phosphor. The aim was to investigate the effect of temperature on the lumen depreciation of LED-based products and on their CCTs. It is shown that the degradation mechanisms is thermally activated and has activation energy of 0.33 eV (Figure 3). It is clearly seen that the lower the depreciation rate, the better the performance a remote phosphor could have. The results also show that there is a direct relation between the temperature and kinetics of degradation.

It is already reported that in normal operating conditions remote phosphor plate can reach temperature level of around 40°C [13]. So, lumen depreciation up to 30% reduction is extrapolated to temperatures lower than 100°C. It is shown that the lifetime, defined as 30% lumen depreciation at 40°C, is around 35 khrs, which is in agreement with previous works [13]. It is also shown that the lumen depreciation rate, and the colour shifting for samples A and B are slightly different. This could be attributed to the differences in their chemical compositions and amount of phosphors.

7.5. Conclusions

The accelerated optical degradation of two different commercial Bisphenol-A Polycarbonate (BPA-PC) plates, under elevated temperature stress, is studied. The BPA-PC plates are used both in light conversion carriers in LED modules and as encapsulants in LED packages. BPA-PC plates are exposed to temperature in the range of 100 to 140°C. Exponential luminous decay model and Arrhenius equation are used to predict the lumen depreciation and the lifetime of plastic lens in LED lamps in real service conditions. The following conclusions can be drawn from this study:

- A significant decay both in the phosphor yellow emission and in the blue peak intensity, with yellow emission being more influenced
- By increasing the temperature, the reaction rate becomes larger, inferring that lumen depreciation takes place at shorter time. The reaction rate follows the Arrhenius acceleration law
- During the stress thermal ageing tests a significant change both in the correlated colour temperature (CCT) and in the chromaticity coordinates (CIE x,y) take place
- The decrease of CCT takes place with almost the same kinetics as the lumen depreciation
- The lifetime of the remote phosphor, defined as 30% lumen depreciation at 40 °C, is around 35 khrs for the commercial grades plates.

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CHAPTER 8

Reliability and Life Time Prediction of Remote Phosphor Plates in Solid State Lighting Applications, Using Accelerated Degradation Testing

A methodology, based on an accelerated degradation testing, is developed to predict the life time of remote phosphor plates, used in solid state lighting industry. Both thermal stress and light intensity are used to accelerate degradation reaction in remote phosphor plates. A reliability model is also developed based on the data obtained from the accelerated degradation test. Both acceleration factors (light intensity and temperature) are incorporated into the reliability model, using Eyring relationship. Results show that the developed methodology leads to a significant decay of the luminous flux, correlated colour temperature (CCT) and chromatic properties of plates within a practically reasonable period of time. The combination of developed acceleration testing and generalized Eyring equation-based reliability model is a very promising methodology, which can be applied in solid state lighting industry.

This chapter is reproduced from: M. Yazdan Mehr, W.D. van Driel, G.Q. Zhang, Reliability and Life Time Prediction of Remote Phosphor Plates in Solid State Lighting Applications, Using Accelerated Degradation Testing, Journal of electronic Materials, Accepted

8.1. Introduction

Light emitting diodes (LEDs), made by combining phosphor with the blue light sources, are the most commercially available solid state light sources [1-10]. In this type of LEDs the phosphor is either coated on the chip or mixed with the lens disc [11-22]. The spatial distribution of phosphor in white LED lamps strongly influences the colour uniformity and the efficiency of the light source. In proximate phosphor distributions, the phosphor is located in the close proximity of the semiconductor chip, while in remote phosphor configuration there is a distance between the phosphor layer and the chip. Schematics of different possible phosphor distribution configurations are shown in chapter 1 (Figure 4).

Solid state lighting (SSL) devices are normally based on a blue chip, combined with yellow phosphor, and are typically in the range 4500-8000K CCT. Recent development strategies are based on the production of white LEDs in the lower CCT range (2700-4500K), since lumens per watt values of LEDs in this range exceed those in the incandescent lamps [7, 8]. The main aim of reliability studies in LED industry is to analyze the system reliability data for SSL luminaires and components and to determine the time-to-failure of components. Recent publications [9-10] provide recommendations for assessment of the lifetime of luminaire products. These reports highlight the proper use of LM-80 and TM21 standards which are well-approved methods in reliability testing. LM-80 provides a procedure to measure the lumen maintenance of LED light sources, while TM-21 provides a method to project long-term lumen maintenance of the LED light sources using LM-80 data [11, 12].

Even though there have been lots of technological breakthroughs in SSL industry, there are still lots of reliability issues, not yet completely known and understood. Besides, a major issue in reliability studies of LEDs is that most available degradation testing techniques are not fast enough to be applied in such a fast growing industry. The objective of the present study is to develop a high accelerated stress testing (HAST) set-up to study the effects of both blue light intensity and the thermal stress on the lifetime and the kinetics of aging of phosphor plates used in SSL luminaires. This work is a significant step-forward and an improvement in our previously-applied accelerated test methodology [22], where the only applied stress factor was thermal stress. Application of both thermal stress and light intensity in HAST set-up is expected to make the kinetics of degradation much faster. There are loads of papers regarding the reliability of LED systems [13-21] under thermal stress; however there is limited information available about the effects of combined blue light intensity and thermal stress on the ageing and the reliability of remote phosphors. In this study the effects of both stress factors, applied in the HAST set-up, are studied. A generalized Eyring equation is also used to correlate the data from HAST set-up with the lifetime and the reliability of phosphor plates.

8.2. Experimental set-up

Remote phosphor plates of 3 mm-thick with correlated colour temperature (CCT) of 4000 K and colour rending index (CRI) of 80 are used in this study. Remote phosphor plates, used in this study, consist of polycarbonate plates (3 mm thick) as substrate and a phosphor coating layer. In this study Luminescent powder mix is made of YAG powder with 3.3% Ce content and 1.5 % Nitride red phosphor, doped with CaSN-Eu. A coating layer on the PET film, consisting of inorganic luminescent material, is transferred to polycarbonate sheet material by a hot-press laminating process. Figure 1 shows an overview picture of the HAST system including all components. The core of the HAST consists of a blue light source with wavelength of 450 nm and a working surface. Blue light sources are Philips modules; with each module containing 18 High-power LED packages. Samples are placed on the working surface and are directly aged under blue light radiation. The working surface is a hot plate and absorptive filters are placed between the samples and the hot plate in order to prevent the reflection of light by the surface of the hot plate. The hot plate is constantly calibrated by an IR-camera. The temperature on the surface of the hot plate is perfectly homogenous, with the difference not being more than 2 °C all over the plate. The blue light source (Figure 2) is composed of a mechanical assembly that holds the light source at a desired distance from the hot plate. Because of technical limitation it was not possible to change the current of the blue Light source. So, in order to change the light intensity the distance between the samples and the blue light source is changed. The homogeneity of the light source across the samples was checked by photometer at different distances and times. Three temperatures of 80, 100, and 120 ºC are used and samples are aged up to 3000 h. The blue light is radiated on the sample with different light intensities of 825, 3300, and 13200 W/m2. The change in the spectral power distribution (SPD) is used as a measure to monitor the optical degradation of remote phosphors.

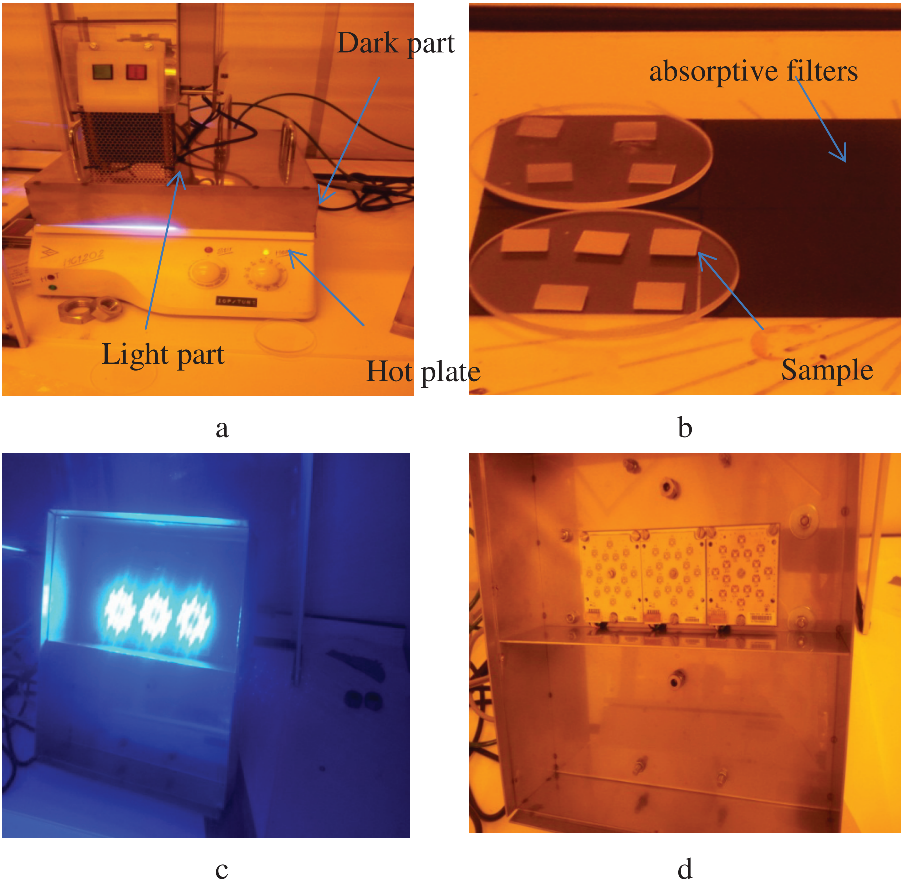


Figure 1: *High accelerated stress testing (HAST) set up, with a) frontal view in off state (top left); b) samples on the absorptive filter (top right); c) the blue LED light source (bottom left); and d) frontal view in off state (bottom right)*

Optical properties of photo-aged plates, i.e. luminous flux depreciation and CCT of plates were studied at room temperature, using an integrated sphere. In addition, colour shifting in the aged specimens was also monitored.

8.3. Reliability model

The reliability model for the lifetime assessment of remote phosphor plates is based on an exponential luminous decay equation, where the Φ can be calculated as [13]

$$\phi(t) = \beta \exp(-\alpha t) \qquad (1),$$

with $\phi(t)$ being the lumen output, α is the degradation reaction rate or depreciation rate parameter, t is the ageing time and β is a pre-factor. When lumen output, Φ, is equal to 70%, t is time-to-failure [12]. In the HAST experiments, where the light intensity is also used as an extra acceleration factor, the Eyring relationship, given below, is a more appropriate equation [12]:

$$R = \gamma_0 (I)^n \exp(\frac{-E_a}{KT}) \qquad (2),$$

where R is the reaction rate, γ_0 is the pre-exponential factor, I is the intensity of blue light, n is the constant factor, E_a is the activation energy (eV) of the degradation reaction, K is the Boltzmann gas constant (eV/K), and T is the absolute temperature (K). The ageing temperatures of the hot plate were adjusted as 80, 100, and 120 ºC. However, by radiation of light the temperature of phosphor plates increases up to 2, 10, and 20 ºC for 825, 3300, and 13200 W/m^2 intensities respectively. The increase of the temperature by radiation of light is measured by a thermometer with an accuracy of ±0.5 ºC. This temperature increase is taken into consideration in our calculations.

8.4. Results

8.4.1. Effect of light intensity on the kinetics of degradation

The evolution of the normalized flux intensity and therefore the ageing kinetics of degradation of phosphor plates are shown in Figure 2.

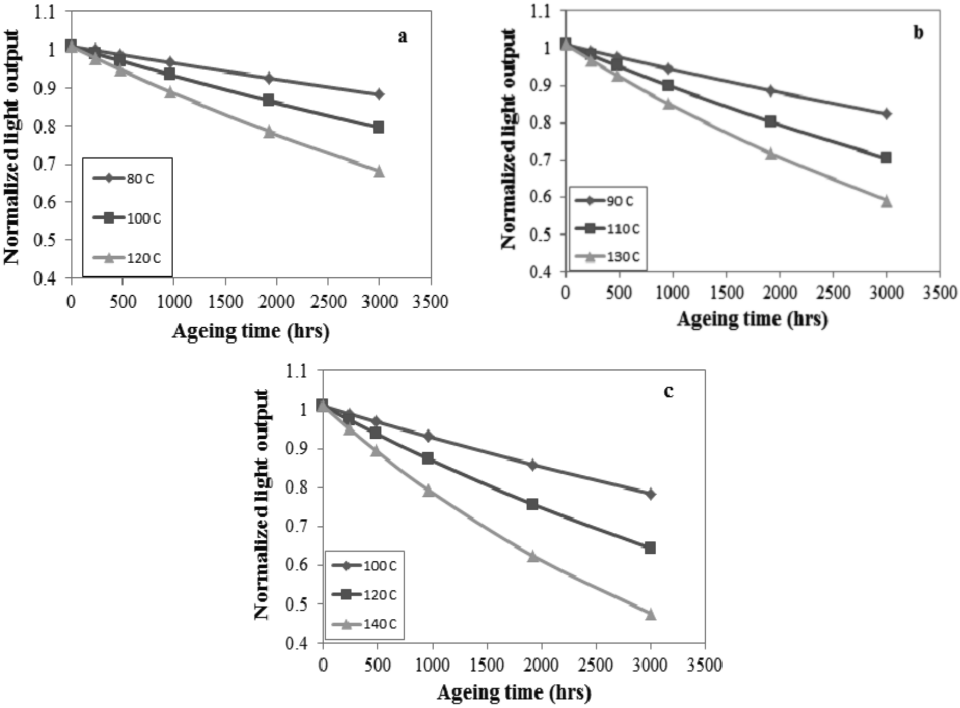


***Figure 2**: Normalized light output of remote phosphor plates at different radiation intensities, a) 825, b) 3300 and c) 13200 W/m^2. Note the correction for temperature increase due to the higher intensities.*

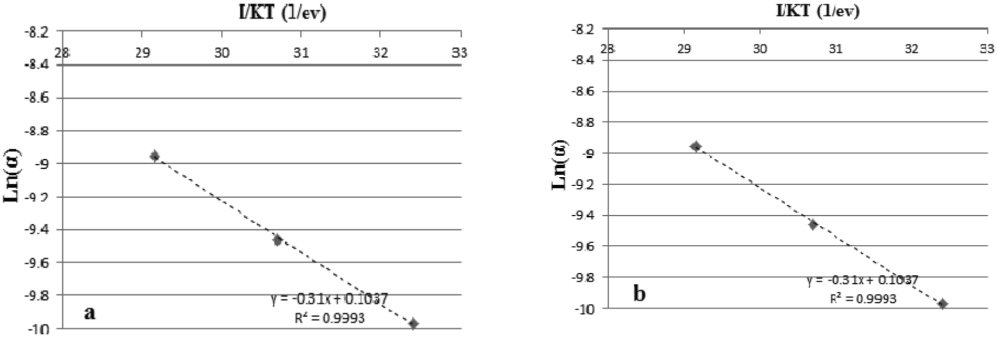
Obviously, the degradation rate shows a significant dependency on the stress light intensity; the higher the light intensity, the faster the degradation kinetics and therefore the higher the lumen depreciation. One can also see that by increasing the temperature, the lumen depreciation takes place with a faster kinetics. The main effect of light with different intensities is increasing the temperature of the phosphor. The real temperatures of plates were considered in calculating the lumen depreciation and consequently the reaction rate. It is clearly seen in Figure 2 that the degradation follows an Arrhenius law: by increasing the temperature, the rate of ageing increases.

The activation energy of the degradation reaction in phosphor plates is calculated using the Arrhenius Equation (Equation 3). In order to calculate the activation energy of the degradation reaction, the natural logarithm of the reaction rates, obtained from Equation (2), is plotted against the inverse of the absolute temperature. The activation energy of the degradation reaction can obviously be obtained from the slope of this curve (see Figure 3). The activation energy, E_a, can be obtained from the slope of curves. One can see that the activation energy in all ageing tests are the same and the difference in the kinetics is due to the light intensity (intercept).

As is already explained, based on the Alliance for Solid-State Illumination Systems and Technologies ASSIST standard, the lifetime of LEDs is defined as time to reach 70% of the initial lumen output [10]. The reaction rate, a, assumed to be constant for each temperature, is calculated as follows

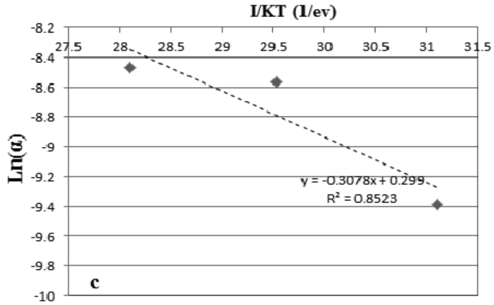
$$a(T) = \frac{-\ln[\phi(t)]}{t} \qquad (3),$$

where t is the time for 30% lumen depreciation and Ø is luminous flux and is equal to 70%. The reaction rates of all three temperatures and three light intensities are shown in Table 1. It is important to mention again that the temperatures in the Table 1 are the applied temperatures and the real temperature of the phosphor plates is corrected by +2, +10, and +20 °C for 825, 3300, and 13200 W/m^2 intensities, respectively.



Ea =0.3133 eV

Ea =0.3133 eV



Ea =0.3110 eV

Figure 3: *Plot of ln (a) vs E/KT for remote phosphor a) 825, b) 3300 and c) 13200 W/m2*

Table 1: *Reaction rate a for remote phosphor plate at temperature 80-120 °C*

Light Intensity (W/m2)	**825**	**3300**	**13200**
80 °C	4.68 E-5	5.7 E-5	8.4 E-5
100 °C	7.8 E-5	9.6 E-5	1.9 E-5
120 °C	1.29 E-4	1.54 E-4	2.1 E-4

The direction of the change in the Chromaticity Coordinates of remote phosphor photo-thermal ageing is illustrated in Figure 4. As is shown in this figure, the light source is getting yellowish, indicating that not only the light output efficiency, but also the colour of the emitted light is degraded. One can also notice that by increasing the light intensity the kinetics of ageing increases.

Thermal-stress tests have also some significant effects on the CCT. The variation of CCT during ageing at high temperature stress test for remote phosphor plates is shown in Table 2. It is obvious that by increasing the thermal ageing time the CCT decreases.

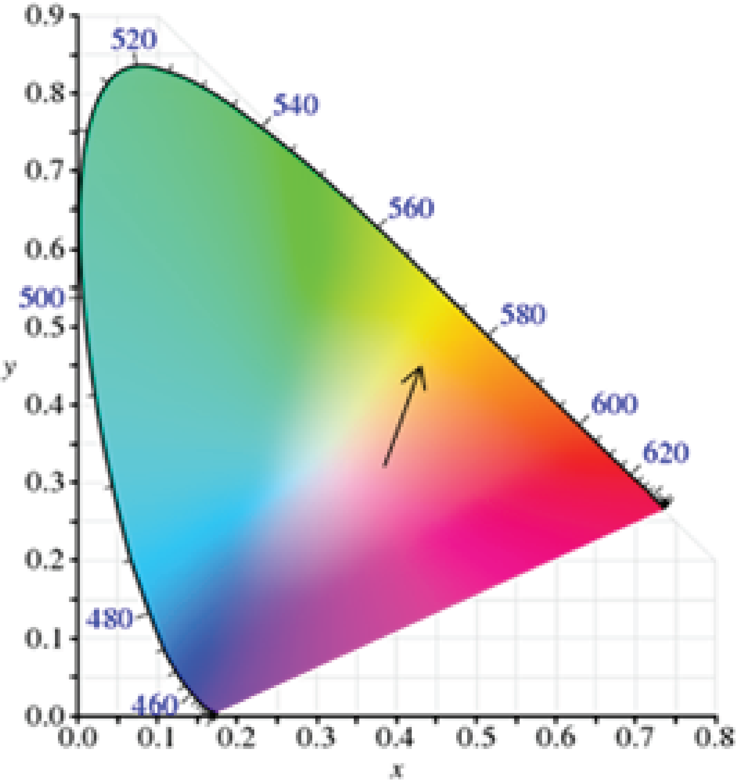


Figure 4: *The variation of Chromatic Chromaticity for 13200 W/m^2 at120 °C*

Table 2: *CCT for remote phosphor plates at temperature 80-120 °C after 3000 hrs ageing*

Light intensity (W/m2) Temperature (°C)	**825**	**3300**	**13200**
80	4410	4370	4300
100	4120	4000	3900
120	4050	3900	3720

8.4.2. Package luminous efficiency

One of the key advantages of LED-based lighting sources is their high luminous efficacy. In recent years Philips Lumileds made LEDs available with a luminous efficacy of 100–150 lumens per watt (lm/W). The emission spectra of the reference blue LED, and blue-pumped white LED with yellow phosphor are shown in Figure 5. The measured emission spectra can be seen as blue emission from LED chip together with yellow emission from phosphor.

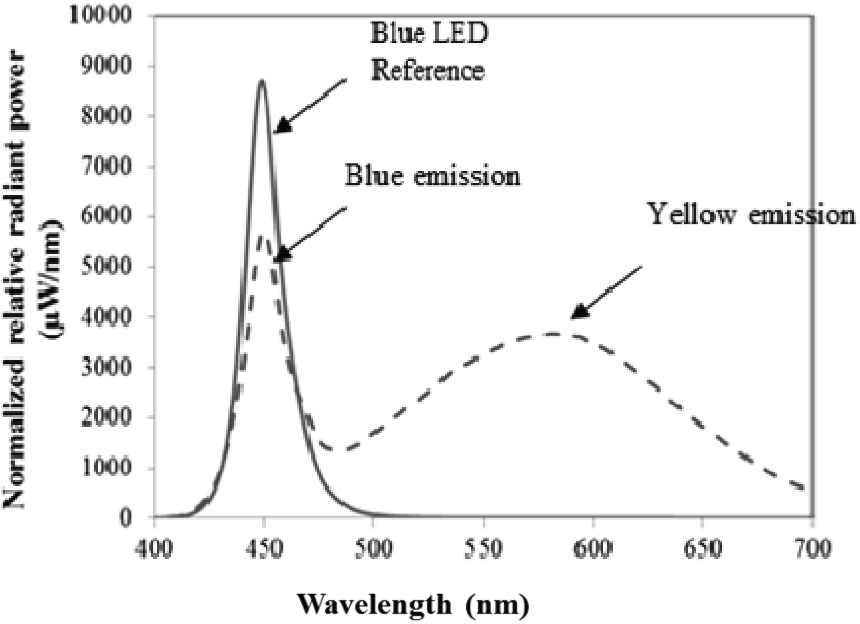


Figure 5: *Emission spectra of reference blue LED, and blue-pumped white LED with yellow phosphor.*

The power conversion efficiencies of package are calculated, using equation given here

$$\eta_{LCE} = (\frac{\phi_{output}}{\phi_{input}}) \quad (4),$$

where ϕ_{output} is output power of yellow component and ϕ_{input} is the output power between blue LED reference emission (without phosphor) and the blue component of the aged remote phosphor, as summarized in Figure 6. Clearly, the drop in the conversion efficiency has a significant dependence on the stress temperature and the light intensity level. By increasing both the ageing temperature and the light intensity, a more significant drop in the conversion efficiency is expected. The reduction of conversion efficiency is because of both discoloration of BPA-PC and reduction of conversion efficiency of phosphors (with time).

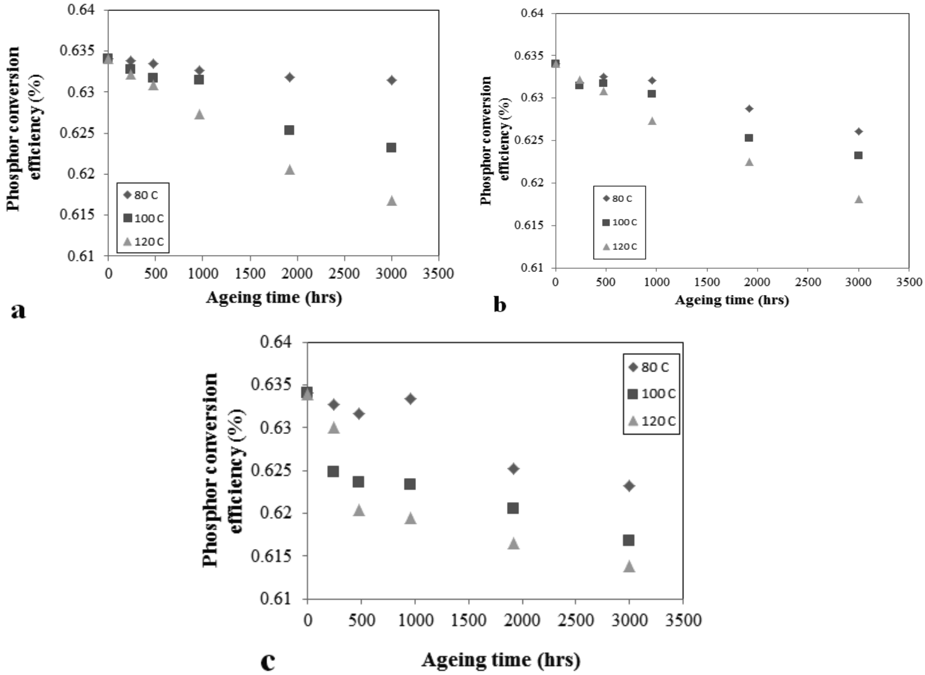


Figure 6: *Conversion efficiency of remote phosphor plates at different radiation intensity, a) 825, b) 3300 and c) 13200 W/m*^{2}

8.4.3. Effect of light intensity on the acceleration of ageing test

Using generalized Eyring equation [12], the acceleration factor of the tests at different stresses can be calculated. Acceleration factor is a measure of how much faster the test is performed at a certain testing condition, compared to normal behavior at real working conditions. Obviously the higher the acceleration factor, the faster and the more efficient (in terms of needed time forthe experiment) the experiments. This factor is defined by following equation,

$$Af = (\frac{I}{I_0})^n \exp(\frac{E_a}{K}(\frac{1}{T_{reference}} - \frac{1}{T_{test}})) \qquad (5),$$

where $T_{Reference}$ is reference temperature, which is assumed to be 80 ºC which is closer to reality, and T_{test} is the testing temperature, I is the intensity of blue light which is 13200 and 3300 W/m2 and I0 is the reference light intensity which is considered to be 850 W/m2. The acceleration factors of remote phosphor at ageing temperature of 80-120 ºC with radiation of light with intensities 825, 3300, and 13300 W/m2 are given in Figure 7.

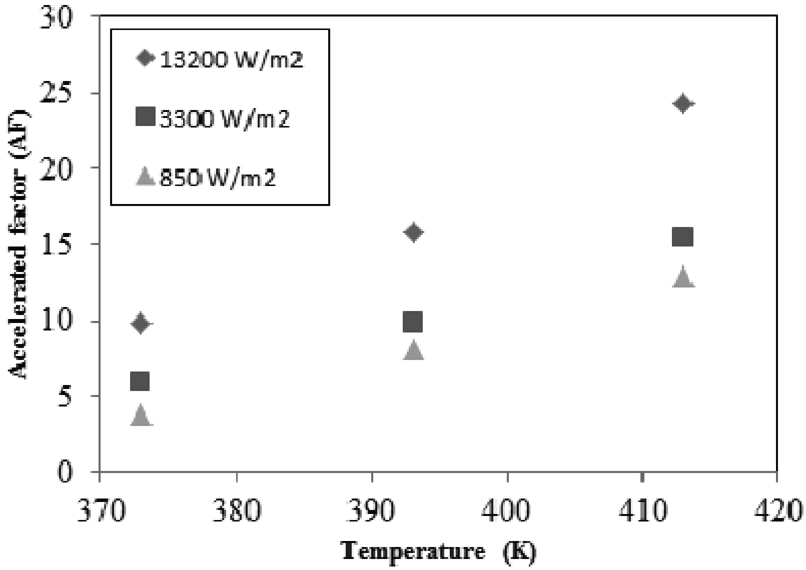


Figure 7: *Acceleration factor of photo-thermal-aged at 120 ºC*

The radiation of light accelerates the kinetics of the ageing of remote phosphor. The increase in the acceleration factor by the radiation of light indicates the effect of light intensity (See equation 5). Using equation 5, the power factor, n, is found to be equal to 0.2. The acceleration factors of remote phosphor at ageing temperature 120 ºC with radiation of 825, 3300, and 13300 W/m2 light and dark experiment are given in Figure 8. The radiation of light obviously accelerates the ageing of remote phosphor by a factor 1.01, 1.2 and 1.9 for blue light radiations of 825, 3300 and 13200 W/m2 respectively. The increase in acceleration factor by radiation of light indicates the effect of light intensity (See equation 5).

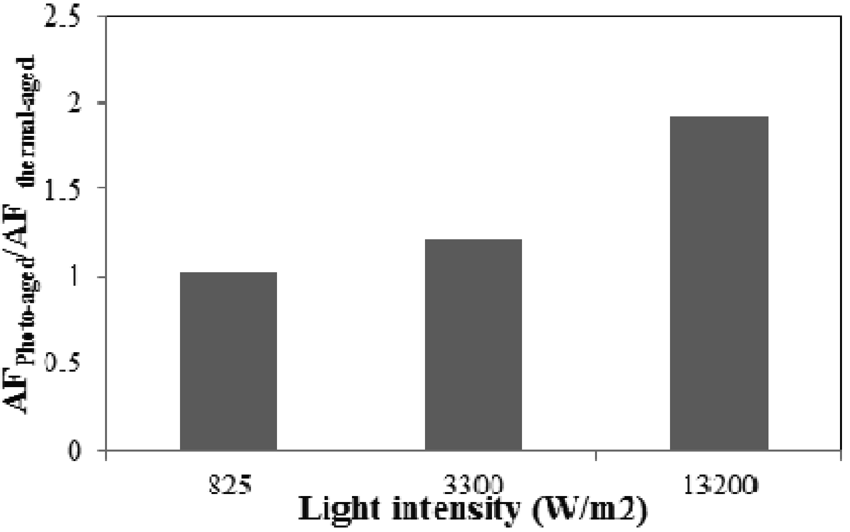


Figure 8: *Acceleration factor of thermal and photo-thermal-aged at 120 ºC*

8.4.4. Effect of light intensity on the time-to-failure of remote phosphor

The temperature of phosphor during service can increase up to 100 °C [8, 9]. However, in this paper the mentioned reference temperature (80 °C) is more an average value over the whole year. The kinetics of lumen depreciation to 30% of its initial value can be calculated using Equation 1, equating ϕ to 0.7, knowing that á can be obtained from Equation 2. Figure 9 illustrates the time-to-failure (70% lumen decay) of remote phosphors, calculated at different temperatures for the photo-thermal ageing where the ageing temperature was 120 °C. Data for the reference sample (thermally aged at 120 °C without light radiation) is added for the sake of comparison [21]. It is shown that the lifetime, defined as 30% lumen depreciation at 40 °C, is around 35 khrs, for the lowest energy power, which has almost the same lifetime as thermally-aged phosphor. The lifetime of the phosphors with higher power energy is 25 khrs.

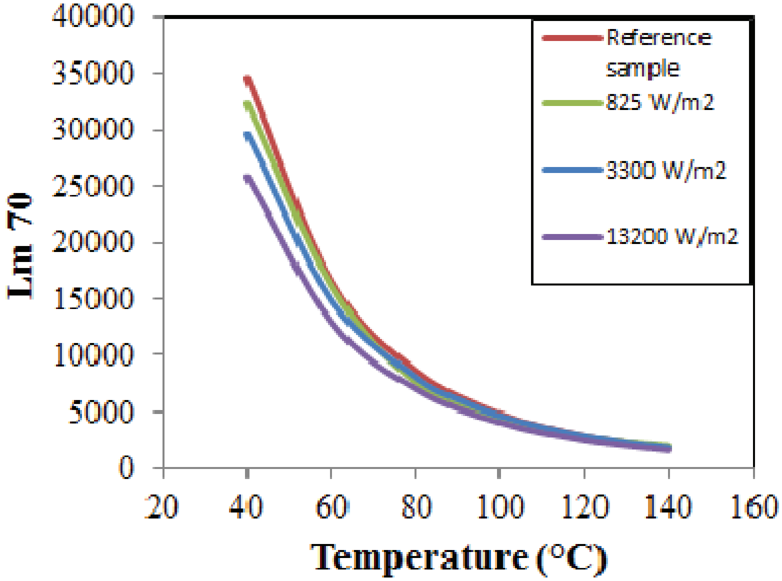


Figure 9: *Time-to-failure (70% lumen decay) of remote phosphor at different temperatures for light intensities of 825, 3300 and 13200 W/m2*

8.5. Discussion and conclusions

The placement and arrangement of phosphors with respect to the chip is an absolutely critical issue for the efficiency of white LEDs. One of the major drawbacks of a proximate conformal phosphor configuration is the temperature increase in the phosphor, which can affect the phosphor efficiencies. Remote phosphors are an alternative to overcome this, but at the expense of more material and perhaps some limitations in the design flexibility. If the phosphor is placed away from the LED chip at a relatively large distance, which is called remote phosphor configuration, the probability of a light emitting from the phosphor and directly hitting the low reflectivity LED chip becomes significantly lower, leading to a significant improvement in the phosphor efficiency. Besides, remote phosphor configuration reduces the operating temperature of the phosphor, which is obviously expected to positively contribute to the reliability and the lifetime of white LEDs. Apart from the distance between the chip and the remote phosphor layer, thickness, concentration [4], geometry [9] and packaging methods [10-13] of the phosphor layer also play important roles in determining the performance and the light quality of white LEDs. Among different type of phosphor, YAG:Ce is the most widely applied option in white light LEDs [18]. However, the main disadvantage of the YAG:Ce is its relatively poor colour rendering index and severe thermal quenching of luminescence. Temperature is a very crucial parameter in the reliability of LEDs. High temperature levels can degrade the optical performance of the encapsulation and the lens [1-4]. It is already shown that thermal stress degrades the luminous output of the devices [15-23]. This study aims at studying the effect of blue light intensity together with thermal stress on the lumen depreciation and the reliability of LED-based products and on the acceleration of optical degradation. The phosphor layer can itself be a heat generator as the input power increases and becomes more important if there is not sufficient thermal path for heat dissipation. Thermal ageing of BPA-PC, which is widely used as a substrate in the remote phosphor, is already studied [21]. It is found out that BPA-PC in remote phosphor got yellower more than samples, aged without phosphors under the radiation of light output. Figure 10 illustrates the darkening of BPA-PC under photo-thermal ageing at 120 °C. It is shown that the main reason for the ageing of BPA-PC is oxidation. By increasing the temperature and radiation of light the rate of oxidation of BPA-PC would be increased, leading to the reduction of light output [21-23].

The radiation of light increases the temperature of phosphor plates up to 20 °C for the blue light radiation of 13200 W/m2. When the phosphor converts the short wavelength light (blue light) to the long wavelength light (yellow light), part of the blue light is converted to heat (phosphor conversion loss). Since in the remote phosphor configuration there is no thermal dissipation path around the phosphor layer, this generated heat increases the temperature of the phosphor. The heat, generated at the phosphor layer, is accumulated inside the layer and makes the temperature of the phosphor even higher than the test temperature. As a result, higher temperature causes faster degradation of the phosphor. Besides, thermal quenching of phosphors is another factor that has some influences on the degradation of phosphors and increases the kinetics of phosphor degradation reaction. It is shown that the activation energy of degradation reaction is 0.31 ± 0.003 eV (Figure 3), depending on the stress levels. It is already reported [18-21] that the proposed activation energy for remote phosphor plates has contributions from both the degradation of the substrate plates and the reduction in the phosphor conversion efficiency [20]. One can see that by increasing the power of light, temperature of phosphor increases leading to the larger the depreciation rate (Figure 2). The results also show that there is a direct relation between the temperature and the loss in conversion efficiency of package In fact, by increasing the ageing temperature the conversion efficiency decreases. It is already reported [20-23] that ageing of BPA-PC, used as substrate in remote phosphors, is faster than the phosphor itself. The decrease in the intensity of the blue light takes place with a faster kinetics, compared to that of the yellow peak, which is in agreement with the fact that there is a shift of the chromatic coordinates of the analyzed LEDs towards yellowish light. Our results show that the generalized Eyring equation can well describe the degradation kinetics of the remote phosphor component. In our specific configuration the generalized Eyring parameters are found to be equal to 0.31eV (E_{act}) and 0.2 (n).

Figure 10: *Discoloration of BPA-PC after photo-thermal-ageing at 140 °C*

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CHAPTER 9

Effects of Graphene Monolayer Coating on the Optical Performance of Remote Phosphors

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A graphene monolayer with uniform distribution is successfully integrated into a BPA-PC polycarbonate, used as a substrate for remote phosphor applications in light-emitting diode (LED) based products. By using a photoresist transferring, graphene sheet is transferred to BPA-PC. The graphene monolayer, coated on the BPA-PC plates, has a multifunctional role and enhances the performance of light-emitting diodes. The presence of graphene improves the protection ability against external gases, such as moisture and oxygen. LED-based products, composed of a graphene-coated BPA-PC plates, exhibit longer stability with comparatively less loss of luminous efficiency. This novel method has great potential to significantly improve the reliability of not only LED-based products, but also billons of microelectronics packaging and components, wherein moisture and oxygen are the key root cause of failures.

9.1. Introduction

A Solid State Lighting (SSL) system is composed of an LED chip with an electronic driver(s), integrated in a package that also provides optical functions, thermal management and/or other functions. Currently, there are different technologies used to produce white light high-power LED systems [4–8]. First one is using three-colour LED chips to generate high colour rendering index (CRI) and tuneable colour. Second approach is performing a blue chip and two colour phosphors such as green and red phosphors. Third way of producing light is using an ultraviolet (UV) chip and three-colour phosphors. In this system, the UV light excites the three-colour phosphors (red, green, and blue) to generate white light with a high CRI. Last method of white light producing is using a blue chip and yellow phosphor in which the yellow phosphor is excited by a blue radiation, producing white light by mixing of non-absorbed blue light. LEDs made by linking the blue-emitting diode chips with phosphor are the most commercially available white LEDs due to their high efficiency. In this system, the phosphor layer can be either deposited directly on the chip or incorporated into a lens disk [9–13]. White LED-based products are complex systems composed of several elements such as a semiconductor chip, bond wires, lead frames, heat slug, solder joints, and optical materials. During the product lifetime, each of these components may induce failure, leading to a depreciation of emission intensity and chromatic properties and even early failure before the expected lifetime. Investigations have been done on various parts of the LED-based product, however, quite little research has been done on the lens/remote phosphors of the LED though. Recent reliability studies [14–19] have shown that the optical degradation of white LED products is mainly due to the degradation of encapsulants/lens. Encapsulants/lens are mainly used to prevent thermal and mechanical stress shock and humidity-induced corrosion. Encapsulants/lens should have a high refractive index and excellent transparency. Both refractive index and transparency are required for enhancement of illumination. Encapsulants/lens must also have high thermal conductivity, noble thermal stability, good chemical resistance, and excellent barrier to moisture and gases.

In addition, effective heat dissipation is important to improve the luminous output because the temperature of devices is high during operation because of junction temperature and using the phosphor and prolonged exposure to light. For LED lighting to be a viable lighting source, there are many technical challenges to be resolved among which the light extraction efficiency and the light output degradation are the key issues, which turn out to be all related to the packaging materials. LEDs have to operate in different temperatures and humidity environments, ranging from indoor conditions to outdoor climate changes. Moisture, ionic contaminants, heat, radiation, and mechanical stresses can be highly detrimental to LEDs and may lead to device failures. Among different degradation mechanisms in encapsulants, discolouration and yellowing are the most common failure mechanism, resulting in the reduction in the transparency of encapsulants and decrease in the LED light output [9]. Encapsulant materials used in LEDs are mainly silicon, epoxy resins, and Bisphenol A Polycarbonates (BPA–PCs).

Although various studies have been done [13-19] to reduce the thermal and light degradation of BPA-PC, there are still many challenges when it comes to the design and production of encapsulant/lens made by BPA-PC. High heat conductivity as well as light and heat transparency are really important for encapsulant/lens materials in LED package.

Monolayer Graphene is a one-atom-thick carbon layer which has received great attention during last few years [20-25] because of its high light transmittance, great thermal and electrical conductivities, outstanding thermal and photochemical stabilities, excellent mechanical strength, and outstanding stability against heat and light. Using graphene coating, light and heat stabilities of BPA-PC can be improved. This research aims at developing a reliable method for incorporating graphene coating(s) into encapsulant/lens components, aiming for a more reliable and more stable LED-based product.

9.2. Materials and Methods

Pure 3 mm thick BPA-PC plates with industrial purity were manufactured by injection molding. These plates were then coated with a mmonolayer of graphene by using photoresist. The structure of the remote phosphor component is schematically shown in Figure 1 together with schematics of expected functionality from the graphene coating. In order to coat the graphene to the samples, photoresist was spin coated on the 500 nm Cu with 1600 rpm for 30 seconds. Graphene was already deposited on the Cu by chemical vapour deposition (CVD) method. After spin coating the gel-pack film was applied and then the wet etching was performed by 5% FeCl3 for almost 20 hours. The graphene was then stamped to the BPA-PC on hot plate at 150°C for 5 minutes. The gel-pack was then removed by applying heat. At the end the photoresist was dissolved by acetone at 70°C for 10 minutes, the process is schematically shown in Figure 2.

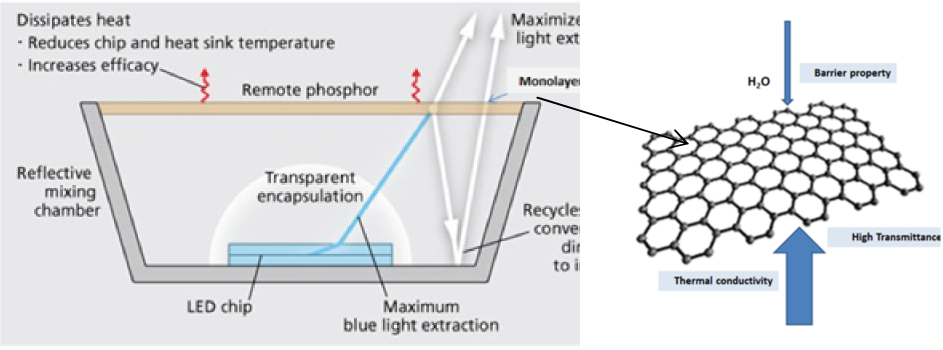

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Figure 1: *(a) Schematic illustrating the remote phosphor white LED device structure. The remote phosphor is a protective BPA-PC coated by YAG:Ce layer designed to convert blue light to yellow light. (b) Schematic summary of the function of graphene monolayer in the remote phosphor.*

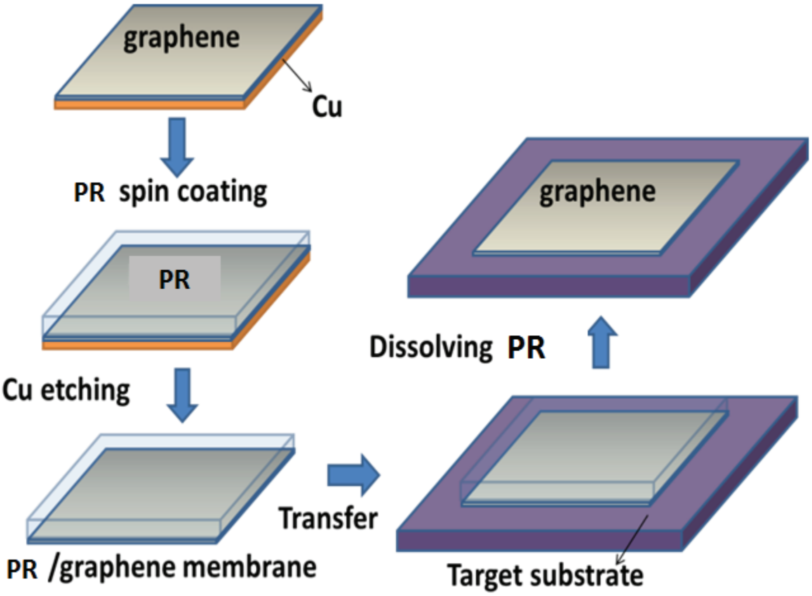


Figure 2: *Schematic of transferring graphene to the BPA-PC plates*

Both plates with and without graphene monolayer are aged in a furnace at 120 ºC up to 1500 hrs to check the effects of graphene monolayer on the chemical and optical properties of samples as well as reliability and lifetime of the BPA-PC. Testing temperatures for the ageing test is determined in such a way that the temperature does not exceed the glass transition temperature of the plastics. Glass transition temperature (*Tg*) of BPA-PC is 150 ºC, so the maximum accelerated temperature is chosen below the *Tg*. All the optical and chemical tests on degraded specimens were performed at room temperature. Infrared spectra of aged specimens were also recorded, using a Perkin-Elmer Spectrum 100 series spectrometer in the attenuated total reflection (ATR) mode for 200 scans at a resolution of 4 cm^{-1}. Infrared spectroscopy (IR) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum. The infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. When the frequency of the IR is the same as the vibrational frequency of a bond, absorption occurs. Examination of the transmitted light reveals how much energy was absorbed at each frequency (or wavelength). Spectral power distribution (SPD) of BPA-PC plates and the yellowing index (YI) of thermally-aged plates were also measured by the Integrated-Sphere. Integrated-Sphere is an optical component consisting of a hollow spherical cavity with its interior covered with a diffuse white reflective coating, with small holes for entrance and exit ports. Uniform scattering or diffusing effect is the main property of Integrated-Sphere. It is typically used with some light source and a detector for optical power measurement. Transmission spectra of BPA-PC, in the range 300 to 1200 nm, were recoded with the Lambda 950 spectrophotometer (PerkinElmer 950).

9.3. Results and Discussion

The main characterises of lens/substrate in remote phosphor plate are high thermal and light transparency. High transmittance of the encapsulant is one of most important properties, because it has a direct influence on the package efficiency and the reliability of the final product. Because graphene monolayer is very thin (about 0.34 nm), and it has high light transparency it can be used in encapsulant/lens with hardly any adverse influence on the optical properties of the BPA-PC plate. The transparency of BPA-PC samples with and without graphene is measured by LAMBDA spectroscopy (shown in Figure 3). It is evident that the effect of graphene on transparency of the plate are insignificant and BPA-PC coated with graphene has high transmittance values over 400-700 nm.

To improve the luminous output and discolouration resistance, effective heat dissipation is of crucial significance. Heat generation inside the device can cause discolouration and reduction in the light emission and therefore a shorter working lifetime. The monolayer of graphene does not seem to decrease the temperature on top of the plate both in conductive and convective manner. The temperature of plates was measured by IR-camera and thermocouple and differences between coated and un-coated samples were insignificant. In an attempt to enhance thermal conductivity of the coating, a multilayer coating of graphene was applied to the plates. This did not really work, since the multilayer of graphene is black and it expressively decreases the transmission of light.

Figure 4 illustrates FTIR-ATR spectra of aged sample, coated and non-coated, at 120 ℃ for 1500 hrs. In this Figure appearance of peak at 1840 cm^{-1} is an indication of thermo-oxidation. It is already reported that 1840 cm^{-1} (cyclic anhydrides) [14,16] in the carbonyl region appear at all temperatures as a result of thermal oxidation. These oxidation products could significantly contribute to the discolouration of thermally-aged specimens. The increase in the peak intensity is not so big compared to pure samples, since samples are commercial ones and have different additives and stabilizers [16]. However, it is obvious that the rate of oxidation in samples coated with graphene is comparatively less than that in the neat sample. One can therefor conclude that the samples with graphene coating are comparatively less oxidized.

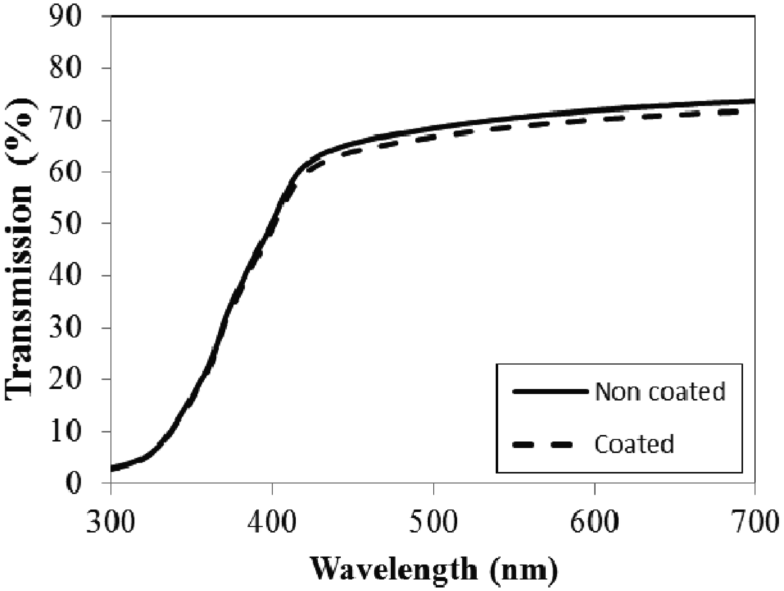
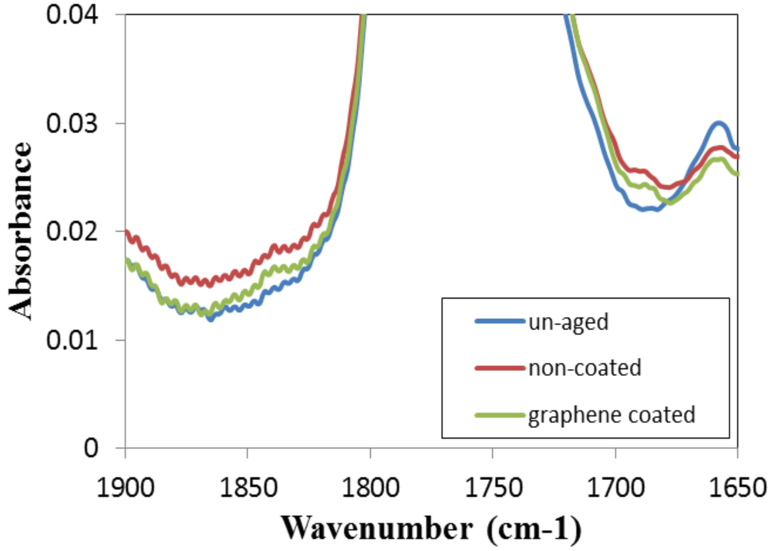


Figure 3: *Effect of graphene on transparency of BPA-PC*



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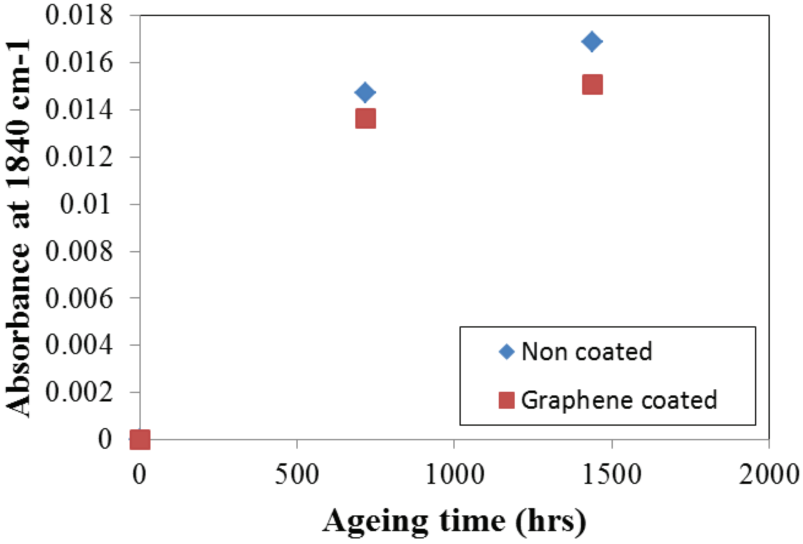

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Figure 4*: Oxidation of PC plates with and without graphene*

The ability to protect a device from the external environment is crucial for long-term operation and high luminous efficiency. Encapsulants/lens having poor gas barrier properties can lead to oxidation. The power conversion efficiency of a white LED (including the encapsulant) as a function of graphene concentration was studied using moisture tests. The moisture barrier behaviour was determined by measuring the weight increase of a 2 mm thick specimen after being saturated in water at 45 ºC for 100 hrs (100% RH). It is already reported that by increasing the exposure time in 100% humidity condition the weight of samples increases because of water absorption [24]. The amount of absorbed water in the polymers is measured by Equation 1:

$$Waterconte\ nt = \frac{(M_t - M_0]}{M_0} \qquad (1),$$

Where M_t is the weight of the sample saturated in water at time t and M0 is the initial weight of sample. By increasing the time the weight of water absorption increases in both samples. However graphene coating reduces the weight gaining compared to the un-coated samples, as shown Figure 5. A clear difference between the kinetics of water uptake between the un-coated and graphene-coated specimens are observed, with the latter showing a remarkably slower kinetics. This difference could be well explained by the size difference between a water molecule and a single graphene pore. Water molecules cannot easily penetrate through the graphene; thereby graphene can act as a barrier against moisture penetration [26,27].

Optical properties of thermally aged plates, i.e. luminous flux depreciation, were studied at room temperature, using an integrated sphere. The Commission International de l’Eclairage (CIE) system is the common method to characterize the composition of any colour in terms of three primaries [12]. Artificial colours shown by X, Y, Z, also called tristimulus values, can be added to produce real spectral Colours. The x, y, z are the chromaticity coordinates [12] which are the ratios of X, Y, Z of the light to the sum of the three tristimulus values. It is necessary only to consider the quantity of two of the reference stimuli to define a colour since the three quantities (x,y, z) are made always to sum to 1. (x, y) is usually used to represent the colour. To obtain the reasonably equidistant chromaticity scales that are better than the CIE 1931 diagram, the CIE 1976 uniform chromaticity scale (UCS) diagram which is also called (u', v') . The (u', v') coordinates are related to the (x, y) coordinates by the following equations:

$$U' = \frac{4x}{-2x \times 12y \times 3}$$

(2),

$$V' = \frac{9y}{-2x \times 12y \times 3}$$

Δu'v', which defines the colour shifting at any two positions (0 and 1), can be calculated using the following formula,

$$\Delta u'v' = \sqrt{(u_1' - u_0') + (v_1' - v_0')} \qquad (3),$$

Energy Star specifies that colour maintenance must not exceed Δ u'v'= 0.007 on the CIE u'v' diagram, after 6000 hours of operation. Colour shifting in thermally-aged specimens, calculated by equation 3, is shown in Figure 6. As is seen, the colour shifting of un-coated and graphene-coated BPA-PC plates are both less than the criteria of colour shifting in white light. However, yellowing and discolouration of samples coated with graphene, are comparatively less.

A more quantitative description of the effects of graphene on thermal-ageing of BPA-PC is given in Figure 7. Stress at high temperature levels can cause thermal ageing and consequently, depreciation of light output, as is shown in Figure 7 for the case of thermal ageing for non-coated sample and coated one. One can see that reduction of radiant power in coated sample is less than that in non-coated one.

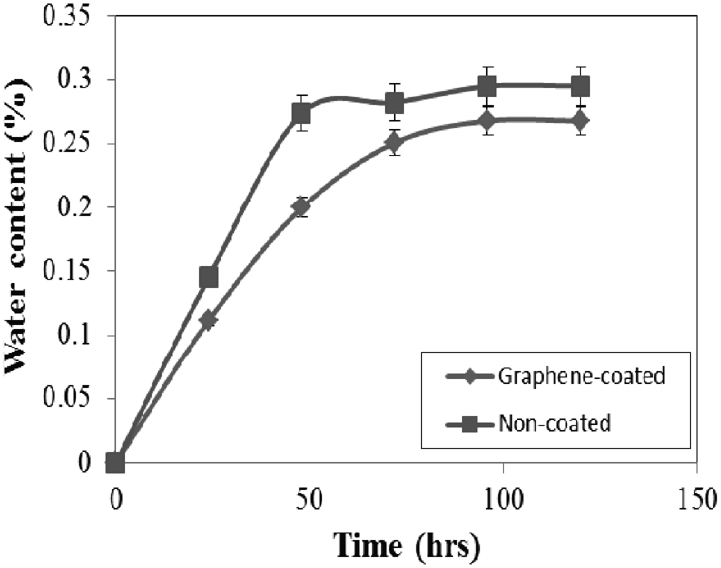

***Figure 5**: Water content of PC plates with and without graphene*

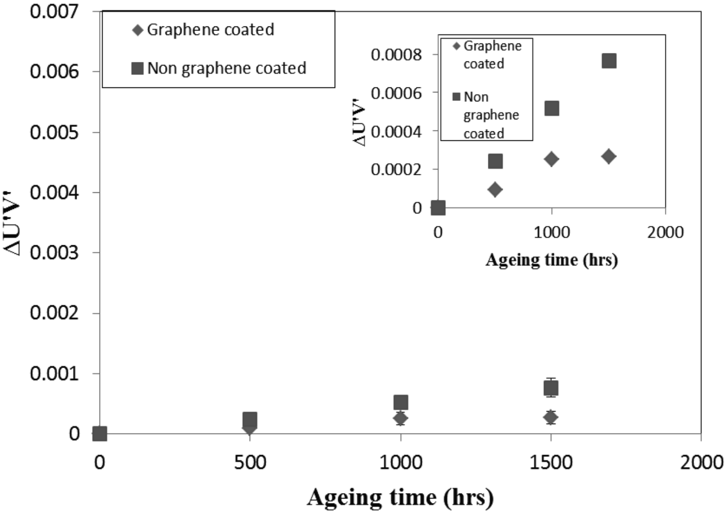

***Figure 6:** Variation in discolouration of BPA-PC plates with and without graphene*

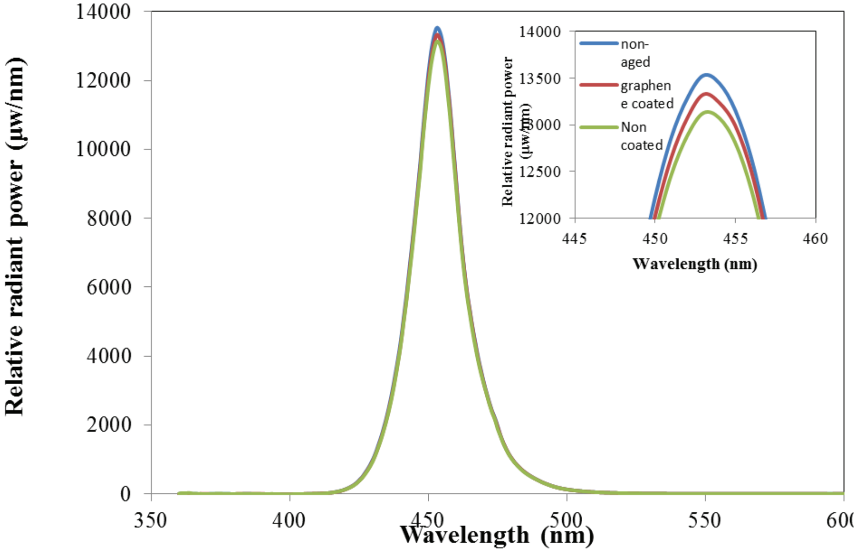

***Figure 7**: Relative radiant power of remote phosphor plates at 120 ºC*

Luminous flux reductions in both samples are shown in Figure 8. It is seen that graphene improves the optical output of BPA-PC considerably. As is already explained, based on the ASSIST standard, lifetime of LEDs is defined as time to reach 70% of its initial lumen output [15]. Therefore, the extrapolation of experimental data is needed. Given that the reaction rate is assumed to be constant for each temperature, a at temperature T is calculated as follows

$$a(T) = \frac{-\ln[\phi(t)]}{t} \qquad (4),$$

In order to calculate a at each temperature, t is taken equal to the time when lumen decays to 0.9, which is obtained experimentally. Having the reaction rate for each temperature, one then can easily calculate the time for 70% lumen decay at each temperature. The calculated a can obviously be used to extrapolate the lumen decay till 70% for each temperature (see dashed lines in Figure 8). Based on the experimental results and extrapolation it is shown that the time, needed to get to 70% of lumen output, is 6500 hrs for un-coated BPA-PC and is around 12000 hrs for graphene-coated BPA-PC plates, inferring that the monolayer of graphene can improve the life time of the BPA-PC by a factor 2.

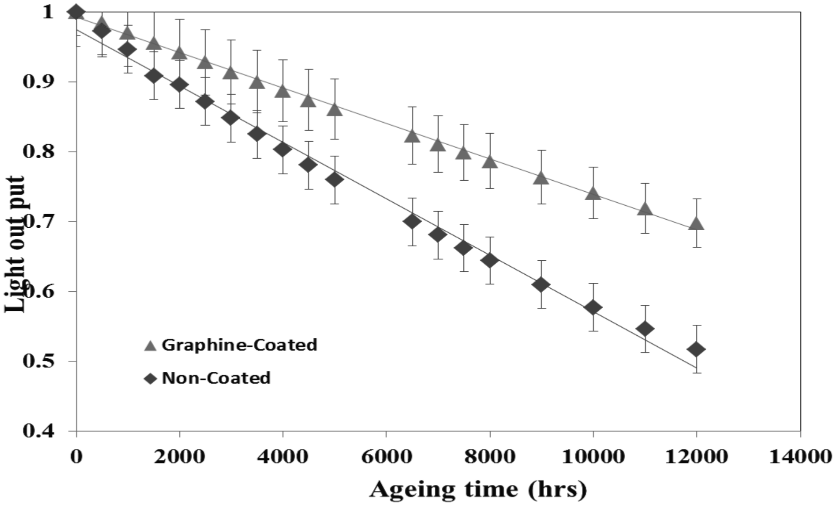

Figure 8: *Normalized flux of light as a function of ageing hours for un-coated and coated samples*

9.4. Conclusions

In conclusion, graphene was successfully incorporated into BPA-PC plates. The graphene-coated PC was then used as lens/substrate in remote phosphor in the LED-based product. Significant improvements in different optical properties as well as reliability and lifetime of BPA-PC plates are observed. Graphene monolayer acts as a barrier against oxygen and moisture diffusion. This obviously results in a slower kinetics of oxidation and discoloration. Addition of relatively small amounts of graphene can improve the long-term stability and reliability of LEDs with significantly lower rates of discoloration and lumen depreciation.

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CHAPTER 10

CONCLUSIONS AND FUTERE RECOMMENDATIONS

In this thesis the degradation mechanisms and reliability of optical conversion materials of Light Emitting Diodes (LED) has been investigated. The dominant chemical reactions, leading to yellowing and discoloration of BPA-Polycarbonate materials, which are used as lens/substrate in LED-based products, are thoroughly studied. Reliability issues in LEDs are a major challenge due to the long lifetime expectations in this industry. In order to predict the life time of LED-based products and develop a reliability model it is envitable to perform accelerated life-time tests, which is essentially monitoring the light output during (for example) high temperature exposures. Acceleration factor (AF), which is a measure of how faster the test is performed compared to the real application conditions, can be used to predict the long-term lifetime of LED-based products at specific usage conditions. The main conclusions of this work are listed below and clustered per chapter:

Thermal degradation of BPA-PC

Studying the mechanisms of thermal degradation and its correlation with the chemical structure of BPA-PC was one of the most important parts of this research. The results also show that there are two stages in the discoloration of thermally-aged polycarbonate plates. The intensities of cyclic anhydrides (1840 cm-1) and aromatic ketone (1690 cm-1) bands in the FTIR-ATR spectra of thermally-aged specimens follow the same two-stage trend, inferring that thermal oxidation could be considered as the main reason of the yellowing during thermal ageing.

Effects of blue light radiation on the discoloration

Effects of blue light radiation on ageing of the pure samples are investigated in this work. Optical and chemical properties of the photo-aged plates are studied by UV-VIS Spectrophotometer, FTIR-ATR spectrometer, Integrated Sphere, and Lambda 950 spectrophotometer. The reasons, underlying the photo-degradation in BPA-PC, are attributed to two different mechanisms: photo-Fries rearrangement and photo-oxidation. By radiation of blue-light (450 nm) the presence of photo-Fries reaction products L_1 and L_2 together with oxidation products aliphatic chain-acid, and cyclic anhydrides from the early stage of photo-irradiation are shown. Chemical reasons of aged BPA-PC is checked with X-ray photoelectron spectroscopy (XPS) to see the changes in the surface chemistry of BPA-PC plates over a temperature range of 100 to 140 ºC for a period up to 3000 hrs. The XPS results show that discoloration is associated with oxidation at the surface, finding a significant increase in the signal ratio O1s /C1s in the XPS spectra of degraded specimens. Results show that irradiation with blue light during thermal ageing accelerates the kinetics of discoloration and the O1s /C1s ratio in XPS spectra.

Acceleration test and reliability of BPA-PC lens/substrate

The accelerated optical degradation and reliability of two different commercial BPA-PC plates under elevated temperature stress are studied in this investigation. It is shown that by increasing the temperature, the reaction rate increases, meaning that lumen depreciation takes place at shorter time. The reaction rate follows the Arrhenius acceleration law.

Reliability and thermal ageing of remote phosphor

The reliability and thermal ageing of remote phosphor are investigated and discussed. It is observed that there is a significant decay both in the phosphor yellow emission and in the blue peak intensity, with yellow emission being more affected, inferring that the main reason for the optical degradation of thermally-aged BPA-PC plates could be ascribed to yellow conversion of blue light. Reduction of light output and the CCT show the same trend.

Acceleration test method

A new acceleration test method for LED remote phosphors is developed in which the effect of light intensity on the kinetics of ageing can be monitored. The results illustrated that there is a direct relation between the light intensity and the loss in conversion efficiency of remote phosphor. In fact, by increasing the ageing light intensity the conversion efficiency of remote phosphor decreases. It is shown that the lifetime, defined as 30% lumen depreciation at 40 °C, is approximately 35 khrs, for the lowest energy power, which has almost the same lifetime as thermally aged phosphor. The lifetime of the phosphors with higher power energy is predicted to be 25 khrs.

Applying monolayer of graphene

Graphene was successfully coated on BPA-PC plates. The graphene-coated PC was then used as substrate/lens in remote phosphor in the LED-based product. Significant improvements in different optical properties as well as reliability and lifetime of BPA-PC plates are observed. The graphene monolayer acts as a barrier against oxygen and moisture diffusion. This obviously results in a slower kinetics of oxidation and discoloration. Addition of relatively small amounts of graphene can improve the long-term stability and reliability of LEDs with significantly lower rates of discoloration and lumen depreciation.

Recommendations for further research:

Based on the chemical and optical results obtained in this study, the pure BPA-PC samples are more stable than the commercial ones. So to improve the properties of commercial samples for lighting applications, these activities are recommended:

- Further research on the effect of different additives on color shifting and discoloration of commercial BPA-PC
- Enhancing the chemical and optical properties of BPA-PC by changing the kind of additives such as using different heat and light stabilizers, scatter agent and flame retardants

Adding a mono-layer of grapheme is shown to improve the chemical and optical properties of commercial BPA-PC plates. A further improvement in optical properties can be achieved by:

- Using different concentrations of graphene in the bulk of BPA-PC plates, in addition to the sample surface

To improve the lighting properties in LED-based products in both remote and conformal form of phosphor distributions one can work on:

- Analyzing the effect of ageing of other kind of materials such as Si on color shifting of light in packages with remote phosphor
-
- Effect of different kind of Phosphors on the color shifting of light
-
- Comparing the color shifting of light in remote phosphor packages with proximate phosphor distributions packages

Summary

"Organic materials degradation in solid state lighting applications"

Maryam Yazdan Mehr

In this thesis the degradation and failure mechanisms of organic materials in the optical part of LED-based products are studied. The main causes of discoloration of substrate/lens in remote phosphor of LED-based products are also comprehensively investigated. Solid State Lighting (SSL) technology is a new technology based on light emitting diodes as light sources. This technology, due to its several exceptional characteristics such as lower energy consumption, longer lifetime, and higher design flexibility with respect to the conventional lighting technology, has become very attractive to both manufacturers and consumers. It is applied in a variety of applications such as general lighting for in-door and out-door applications, and for automotive. Reliability in the highly demanding and fast growing SSL market is a key challenge, which requires special attention. A SSL system is typically composed of an LED engine with an electronic driver(s), integrated in a housing that also provides optical functions, thermal management, sensing and/or other functions. Knowledge of (system) reliability is crucial for not only the business success of today’s SSL products and applications, but also to gain deeper scientific understanding which will enable improved product and application design in the future. A malfunction of the system may be induced by the failure and/or degradation of any subsystem or interface. A comprehensive and in-depth understanding of failure and degradation behaviors of different SSL system components would obviously result in a more effective and reliable design as well as a proper selection of materials and manufacturing techniques. Package-related failure mechanisms that result in an optical degradation, colour change, and severe discoloration of the encapsulant are listed as carbonization of the encapsulant, encapsulant yellowing, and phosphor thermal quenching. Among different materials used as an encapsulant or substrate for the phosphor in remote phosphor design, Poly Carbonate (BPA-PC) is chosen in this research. In order to study the main reason(s) of discoloration and consequently to define lifetime, a series of experiments are performed under different external stresses (temperature range of 100 to 140 ºC and radiation of blue light with 450 nm wavelength). A highly accelerated test set-up was designed to control these stresses and monitor light output of the system at the same time. Evaluating and analyzing of chemical and optical characteristics of samples during ageing in this specially designed highly accelerated test set-up are performed using a wide range of techniques including UV-Vis, FTIR-ATR, and X-ray photoelectron spectroscopy (XPS), Lambda spectroscopy and Integrated Sphere. The results show that increasing the thermal ageing time leads to yellowing, loss of optical properties, and decrease of the light transmission of the relative radiant power value of both pure and commercial BPA-PC plates. Thermally induced oxidation reactions of BPA-PC are found to be the major reason of the yellowing and discoloration. The major effect of light intensity in remote phosphor is believed to be increasing the temperature of the phosphor, and therefore enhancing the kinetics of thermal ageing. Photo-fries products are found in photo-thermally aged BPA-PC plates, aged under blue light radiation at elevated temperature of 140 ºC, and believed to have a contribution to the discoloration. The XPS analyses of aged samples confirm that discoloration is associated with surface oxidation. A significant increase in the signal ratio O1s /C1s in the XPS spectra of degraded specimens is observed. During thermal ageing, the C-H concentration decreases and new oxide features C=O and O-C=O form, with the latter being a support for oxidation at the surface being a major reaction during discoloration. Results also show that irradiation with blue light during thermal ageing accelerates the kinetics of discoloration and the increases O1s /C1s ratio in XPS spectra. The accelerated optical degradation and reliability of two different commercial BPA-PC plates under elevated temperature stress are studied as well. The reliability model, explained in this thesis, is indeed a useful framework to incorporate the

kinetics of (photo)-thermal ageing of BPA-PC and YAG:Ce phosphor into the life-time prediction models. It is shown that increasing the exposure time leads to degradation of BPA-PC optical properties, i.e. decrease of light transmission and increase in the yellowing index (YI). By increasing the temperature, the reaction rate increases, meaning that lumen depreciation takes place at shorter time. The reaction rate follows the Arrhenius acceleration law. The thermal stability and life time of remote phosphor lens plates are also studied. The photometric properties of thermally-aged plates, monitored during the stress thermal ageing tests, show a significant change both in the correlated color temperature (CCT) and in the chromaticity coordinates (CIE x,y). It is also observed that there is a significant decay both in the phosphor yellow emission and in the blue peak intensity, with yellow emission being more affected, inferring that the main reason for the optical degradation of thermally-aged BPA-PC plates could be ascribed to yellow conversion of blue light.

As final conclusions, among different existing stresses including light intensity, humidity and heat, thermal stress has a more pronounced influence on the ageing of encapsulants in optical parts in LED-based products. Also it is shown that the rate of lumen depreciation is highly dependent on temperature; the higher the temperature the faster the kinetics of color shifting and lumen depreciation is. The effect of light intensity is increasing the temperature in phosphor plates. Reliability of optical components in LED-based products can be well described by the Arrhenius equation and generalized Eyeing equation. Coating the BPA-PC by a graphene monolayer can significantly enhance the optical properties and stability of BPA-PC, used as substrate in remote phosphor plates. Graphene decreases the oxidation kinetics of BPA-PC and acts as a barrier for moisture and oxygen diffusion.

Samenvatting

"*Organische materialen afbraak in solid state lighting applications"*

Maryam Yazdan Mehr

In dit proefschrift de afbraak- en falingsmechanismen van organisch materiaal in het optisch gedeelte van LED producted in onderzocht. De belangrijkste oorzaken voor deverkleuring van substraat/lens in remote fosfor LED producten zijn eveneens uitvoerig onderzocht. Solid State Lighting (SSL) technologie is een nieuwe technologie op basis van light emitting diodes als lichtbron. Deze technologie, vanwege de verschillende bijzondere kenmerken zoals lager energieverbruik, langere levensduur en hogere flexibiliteit in vergelijking met de conventionele lichttechniek, is erg aantrekkelijk voor zowel fabrikanten als consumenten. Het wordt momenteel toegepast in een groot aantal toepassingen zoals binnen en buiten verlichting en in koplampen voor autos. Betrouwbaarheid is in de veeleisende en snel groeiende verlichtingsmarkt is een belangrijke uitdaging, die bijzondere aandacht vraagt. Een SSL-systeem is meestal samengesteld uit een LEDlichtbron met elektronische besturing, ingebouwd in een behuizing die tevens optische functies, warmtehuishouding, sensoren en/of andere functies bevat. Kennis van (systeem) betrouwbaarheid is van cruciaal belang voor niet alleen het zakelijke succes van LED producten en toepassingen, maar ook voor nader wetenschappelijk begrip waarmee men betere producten kan ontwerpen in de toekomst. Een storing van het systeem kan veroorzaakt worden door de storing en/of afbraak van een subsysteem of interface. Diepgaande kennis van het falen en degraderen van verschillende LED product onderdelen zou leiden tot een meer effectief en betrouwbaar ontwerp evenals een juiste keuze van materialen en productietechnieken. Faal mechanismen die leiden tot een mogelijke optische kleurverandering wordt vermeld als verkoling van en/of vergeling van de optische onderdelen. Van de mogelijk verschillende materialen gebruikt als optische interface, hebben wij polycarbonaat (BPA-PC) gekozen in dit onderzoek. Om te weten te komen wat de belangrijkste reden van verkleuring is, zijn er een serie van experimenten uitgevoerd onder verhoogde of versnelde stressoren (temperatuur bereik van 100 tot 140 ºC en straling blauw licht met 450 nm golflengte). Een speciaal hiervoor ontwikkelde testopstelling is ontworpen voor het besturen van deze stressoren en daarbij de terugval in lichtopbrengst van het systeem tegelijkertijd te meten. Evalueren en analyseren van de chemische en optische eigenschappen van samples blootgesteld aan deze stressoren werden met behulp van een breed scala van technieken bepaald, waaronder UV-Vis, FTIR/ATR en X-ray photoelectron spectroscopy (XPS), Lambda-spectroscopie en Optische Sphere. De resultaten laten zien dat het verhogen van de temperatuur leidt tot vergeling, verlies van optische eigenschappen, en afname van de lichttransmissie en de relatieve radiant vermogen van zowel zuiver en commerciële BPA-PC samples. Thermisch geïnduceerde oxidatie reacties van BPA-PC zijn de belangrijkste reden van de vergeling en verkleuring. Het belangrijkste effect van de lichtintensiteit in remote fosfor wordt verondersteld door het verhogen van de temperatuur van de fosfor en dus de veng van de kinetiek van thermische veroudering. Foto-fries rest producten zijn gevonden in foto-thermisch verouderde BPA-PC samples, blootgesteld aan blauw licht straling bij verhoogde temperatuur van 140 ºC, en dachten dat het om een en leveren een belangrijke bijdrage aan de verkleuring. De XPS-analyses van de sampels bevestigen dat verkleuring is gekoppeld aan oxidatie aan de oppervlakte. Een aanzienlijke toename van de ratio O1s / C1s in de XPS spectra van gedegradeerde samples is waargenomen. Tijdens thermische veroudering, de C-H concentratie neemt af en nieuwe oxide functies C=O en O-C=O vormen zich, met de laatstgenoemde als ondersteuning dat oxidatie aan de oppervlakte een grote invloed heeft op de verkleuring. Resultaten tonen aan dat ook bestraling met blauw licht tijdens thermische veroudering de kinetiek van verkleuring vernelt en daarmee dus ook de verhoging van de O1s / C1s ratio in de XPS spectra. De versnelde optische afbraak- en betrouwbaarheid van twee verschillende commerciële BPA-PC platen onder verhoogde temperatuur stress zijn bestudeerd. Het betrouwbaarheidsmodel, beschreven in dit proefschrift, is inderdaad een bruikbaar kader om de kinetiek van (foto) -thermische veroudering van de BPA-PC en YAG te beschrijven. Het is gebleken dat het vergroten van de testtijd leidt tot verhogen van de afbraak van de BPA-PC optische eigenschappen, dat wil zeggen verlaging van de lichtdoorlating en verhoging van de vergelingsindex (YI). Door het verhogen van de temperatuur, vergroot men de reactiesnelheid, hetgeen betekent dat lumen depreciatie plaats vindt in een kortere tijd. De reactiesnelheid volgt de Arrhenius acceleratie wet. De thermische stabiliteit en levensduur van remote fosfor samples is eveneens bestudeerd. De fotometrische eigenschappen van thermisch verouderde samples, middels de thermische veroudering proeven, blijkt een significante verandering van de gecorreleerde kleurtemperatuur (CCT) en de kleurcoördinaten (CIE x,y) op te leveren. Maar ook is geconstateerd dat er sprake is van een significante afname in zowel de fosfor geel emissie- en in de blauwe piek intensiteit.De belangrijkste reden voor de optische aantasting van thermisch verouderde BPA-PC platen kan worden toegeschreven aan de verhoogde gele conversie van blauw licht.

De lichtintensiteit, vochtigheid en warmte alsmede grote temperatuurverschillen hebben invloed op de veroudering van het optische deel in LED producten waarbij temperatuur het dominanst is. Ook is aangetoond dat lumen depreciatie sterk afhankelijk is van de temperatuur, hoe hoger de temperatuur hoe sneller de kinetiek is. Het effect van de lichtintensiteit is het verhogen van de temperatuur in de phosphorlaag. De betrouwbaarheid van optische componenten in LED-gebaseerde producten kan worden beschreven door de zogenaamde Arrhenius vergelijking. Een coating op de BPA-PC aanbrengen van een graphene monolayer verbeterr de optische eigenschappen en kwaliteit van de BPA-PC aanzienlijk. Dit komt omdat graphene de oxidatie van de BPA-PC vermindert door te fungeren als een barrièrelaag voor vocht en andere gassen.

List of Publications

Patent:

- **M. Yazdan Mehr**, W.D. van Driel, G.Q. Zhang,
  thermal and optical accelerated aging test system for optical components, Chinese patent, submitted

Journal Paper:

- **M. Yazdan Mehr**, Volgbert, W.D. van Driel, G.Q. Zhang, Effects of Graphene Monolayer Coating on the Optical Performance of Remote Phosphors, ACS Applied Materials & Interfaces, submitted

- **M. Yazdan Mehr**, W.D. van Driel, G.Q. Zhang, Reliability and Life Time Prediction of Remote Phosphor Plates in Solid State Lighting Applications, Using Accelerated Degradation Testing, Electronic Materials Journal, accepted

- **M. Yazdan Mehr**, W.D. van Driel, G.Q. Zhang, Progress in Understanding Color Maintenance in Solid-State Lighting Systems, Engineering, 1 (2015) 170–178

- Guangjun Lu, W.D. van Driel, Xuejun Fan , **M. Yazdan Mehr**, Jiajie Fan, K.M.B. Jansen, G.Q. Zhang, Degradation of Microcellular PET Reflective Materials Used in LED-based Products, Optical Materials, 49 (2015) 79–84

- G. Lu, G**, M. Yazdan Mehr**, , W.D. van Driel, X. Fan, J. Fan, , K.M.B. Jansen, G.Q. Zhang, (). Color shift investigations for LED secondary optical designs: Comparison between BPA-PC and PMMA. Optical Materials, 45 (2015) 37-41

- **M. Yazdan Mehr**, W.D. van Driel, G.Q. Zhang, Accelerated life time testing and optical degradation of remote phosphor plates, Microelectronics Reliability, 54 (2014) 1544-1548

- **M. Yazdan Mehr**, W.D. van Driel, H. Udono, G.Q. Zhang, Surface aspects of discolouration in Bisphenol A Polycarbonate (BPA-PC), used as lens in LED-based products, Optical Materials, 37 (2014) 155-159

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Conference papers and talks:

- Guangjun Lu, W.D. van Driel, Xuejun Fan, **M. Yazdan Mehr** , Jiajie Fan, Cheng Qian , G.Q. Zhang2A POF Based Breakdown Method for LED Lighting Color Shift Reliability, Solid State Lighting Conference April 2015- Beijing, China

- **M. Yazdan Mehr**, A.Bahrami, W.D. van Driel, G.Q. Zhang, Reliability and Accelerated Tests of Plastic Materials in LED-Based Products, 16th International Conference on Thermal, Mechanical and Multi-Physics Simulation and Experiments in Microelectronics and Microsystem, April 2015- Budapet, Haungry

- **M. Yazdan Mehr**, W.D. van Driel, G.Q. Zhang, High Accelerated Optical remote phosphor Aging Studies for LED Luminaire Applications, 16th International Conference on Thermal, Mechanical and Multi-Physics Simulation and Experiments in Microelectronics and Microsystem, April 2015- Budapet, Haungry

- **M. Yazdan Mehr**, W.D. van Driel, G.Q. Zhang, Colour shift in remote phosphor based LED products, 64th ECTC Conference- May 2014- ORLANDO, USA

- S.W. Koh, , H. Ye, M. **Yazdan Mehr**, J. Wei,, W.D. van Driel, L.B.. Zhao, LB , G.Q. Zhang, (2014). Investigation of color shift of LEDs-based lighting products. 15th International Conference on Thermal, Mechanical and Multi-Physics Simulation and Experiments in Microelectronics and Microsystem, April 2014- Gent, Belgium

- **M. Yazdan Mehr**, W.D. van Driel, G.Q. Zhang, Reliability and Accelerated Tests of Plastic Materials in LED-Based Products, 15th International Conference on Thermal, Mechanical and Multi-Physics Simulation and Experiments in Microelectronics and Microsystem April 2014- Gent, Belgium

- **M. Yazdan Mehr**, W.D. van Driel, G.Q. Zhang, Reliability and colour shifting of remote phosphor, University of Manchester, April 2014

- S. Koh **, M. Yazdan Mehr.** Ye, J. Wei, W.D. van Driel, G.Q. Zhang , Investigation of color shift of plastics lense in LED-based products, Solid State Lighting Conference, November 2013, Guangzhou China

- **M. Yazdan Mehr**, W.D. van Driel, G.Q. Zhang, Effects of thermal ageing on the optical properties of Bisphenol A Polycarbonate, used as LED encapsulant plates, 30th Polymer Degradation Discussion group (PDDG), September 2013, Paris France

- **M. Yazdan Mehr**, W.D. van Driel, G.Q. Zhang, degradation mechanisms in optical material for solid state lighting applic ations, Solid State Lighting Conference, November 2012, Guangzhou China

Invited Speaker:

- **M. Yazdan Mehr**, W.D. van Driel, G.Q. Zhang, High Accelerated Optical remote phosphor Aging Studies for LED Luminaire Applications, 11th Solid State Lighting Conference, November 2014, Guangzhou China

- W.D. van Driel **, M. Yazdan Mehr**, G.Q. Zhang , Reliability of LED-based Products is a Matter of Balancing Temperatures , Therminic Conference, London, September 2014

- **M. Yazdan Mehr**, W.D. van Driel, G.Q. Zhang, Accelerated Optical remote phosphor Aging Studies for LED Luminaire Applications, Dow corning company, July 2013

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