PLATE

Product Lifetimes And The Environment

3rd PLATE Conference
September 18 – 20, 2019
Berlin, Germany

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Melanie Jaeger-Erben (eds.)

van Dijk, Marius; Schneider-Ramelow, Martin: **Test strategy for thermo-mechanical ageing effects in polymeric materials**. In: Nissen, Nils F.; Jaeger-Erben, Melanie (Eds.): PLATE – Product Lifetimes And The Environment : Proceedings, 3rd PLATE CONFERENCE, BERLIN, GERMANY, 18 – 20 September 2019. Berlin: Universitätsverlag der TU Berlin, 2021. pp. 819 – 823. ISBN 978-3-7983-3125-9 (online). https://doi.org/10.14279/depositonce-9253.

Universitätsverlag der TU Berlin

3rd PLATE 2019 Conference
Berlin, Germany, 18-20 September 2019

Test Strategy for Thermo-Mechanical Ageing Effects in Polymeric Materials

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Keywords: Material Characterization; Polymer Ageing; Reliability, Lifetime.

Abstract: The use of polymeric materials in (micro-) electronic applications is growing steadily since many years. They provide a multitude of functions, such as protection against environmental conditions (temperature, humidity, dust, etc.), mechanical stability and electrical isolation. However, during the lifetime of these electronic components, polymers can change their properties significantly, which can lead to premature failure. Therefore, it is of great importance to understand the behavior of these materials throughout its expected lifetime, considering the assumed use-profile, e.g. temperature, humidity, UV light, shocks/vibrations, etc. By means of numerical methods such as finite element simulations, the physical behavior of electronic components can be predicted. However, ageing effects are scarcely considered, and often materials are characterized only in their initial state. Appropriate material models, taking into account ageing effects over the lifetime are desired but not yet common or incompletely present in the literature. This paper describes an approach on how to test the ageing behavior of polymeric materials in order to develop such material models for numerical simulations.

Introduction

Since the year 1868, when J.W. Hyatt invented the first commercial plastic celluloid, the use and production of polymers has grown massively. Besides the many advantages of this class of materials (price, process-ability, freedom of design, etc.) there are also many disadvantages including the pollution of the environment.

In order to prevent electronic components to fail before their desired lifetime due to ageing effects of polymers, accelerated experiments can be performed on both product and material level. Product level experiments provide primarily information about the combination of used materials, e.g. interfaces between two different materials, and information on the total behavior of the specific product. Material level experiments provide a much deeper understanding of each material, independently of the final product.

This paper discusses an approach for performing material characterization tests of polymeric materials in order to determine the ageing effects.

Theoretical part

Classification

Polymers can be categorized into two main groups, thermoplastics and thermoset (Brinson, Brinson, 2008). The difference between the two is that thermoplastics only have secondary bonds between molecule chains, whereas thermosets exhibit both primary and secondary bonds, cf. Figure 1.

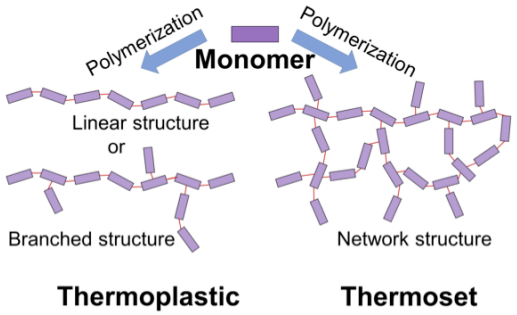

Figure 1. Polymer structure for thermoplastics and thermosets.

One characteristic for thermoplastics is that they can be heated until they melt and become solid again when cooled down. Both thermoplastics and thermoset materials are used in electronic applications, having different

purposes and functions. Thermoplastics are used for insulation, housing and sometimes for encapsulation (Patterson, Boyer, Shiozawa, 1995). Thermoset materials are used mainly for encapsulation purposes (Thomas et al., 2014). In order to improve the properties of these polymers, often filler particles (i.e. flakes, fibers or spheres), made from various materials like glass, metals and their oxides and ceramics are added to it. This results, amongst others, in an increasing stiffness and strength, better thermal conductivity and a lower coefficient of thermal expansion.

Purpose of Polymers in Electronic Applications

A dominant material in electronic applications is the thermoset polymer. In general, it can be said that these polymers are used to protect the fragile electrical components against all kinds of (harsh) conditions (dust, humidity, electric current, etc.). Maintaining this protection is of key importance, since they define the reliability and lifetime. If the reliability increases, it can have a positive environmental impact, since less components need to be produced, which means less waste and less carbon emissions during production. Knowing the material parameters of thermosets and its degradation behavior over its lifetime is necessary to assess the expected lifetime in a correct manner.

Ageing effects of thermoset polymers

Although other material properties are affected by ageing effects (such as electrical, radio frequency and optical properties), this paper focusses on the mechanical properties.

The mechanical properties of thermoset polymers are determined by three characteristic mechanisms. The *crosslink density* is a measure for the amount of bonds between different polymer chains. Increasing the crosslink density results in a more rigid behavior. The *free volume* is a measure for the amount of space not being occupied by molecule mass (Brinson, Brinson, 2008) within a polymer. The third mechanism is the *flexibility of the chains*. If sufficient space is present within a flexible polymer, allowing for large scale movements, the behavior will be rubberlike. When reducing the temperature, the free volume reduces such that these large scale movements are not possible anymore, and the polymer will behave glasslike (Budd, 2015). The temperature at which the transition between rubberlike and glasslike state takes place is called the glass transition temperature (T_g). One characteristic for this glass transition temperature is that the coefficient of thermal expansion (CTE) changes significantly, having a much lower value in the glassy state. Also the stiffness experiences a pronounced change around this temperature. A measurement curve for both stiffness and CTE of a typical thermoset polymer is shown in Figure 2.

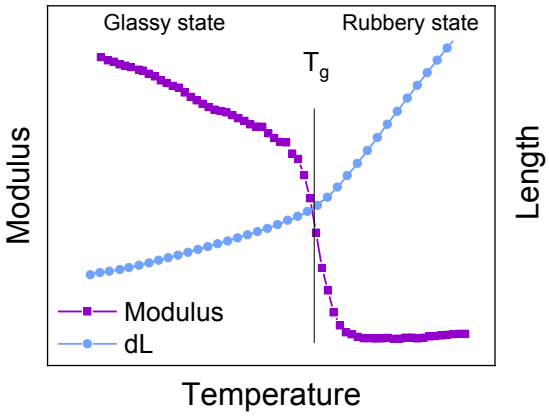

Figure 2. Glass transition temperature visible in modulus and CTE (own measurement).

Polymer ageing effects can be divided in three main mechanisms, namely chemical-, physical-, and mechanical ageing (Gates, 2008). Figure 3 shows examples for these three ageing mechanism. Ageing effects are accompanied by changes in the microstructure. Let us take thermo-oxidative ageing as an example: first, the oxygen molecules need to be able to diffuse in the polymer (depending on the free volume and crosslink density), after which it needs to find either a free branch in order to form a bond or interfere with an existing bond. Due to these additional oxygen molecules, it is possible that the flexibility of the chain is affected.

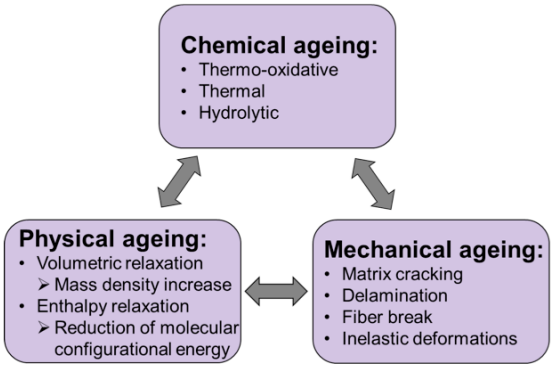

Figure 3. Classification of ageing effects.

Figure 3 shows also that the different ageing effects have an influence on each other. Considering the example from above, thermo-oxidative ageing might lead to relaxation or degradation of the interface between polymer and substrate.

Characterization of ageing effects

Measurement techniques

In order to identify the kinetics and severity of ageing effects, repeated material characterization can be used. Established techniques include the *Thermomechanical Analysis* (TMA, determination of coefficient of thermal expansion and glass transition temperature), and the *Dynamic Mechanical Analysis* (DMA, determination of stiffness over frequency and temperature).

Due to ageing effects mass and density of polymers change. The density can be determined with an Archimedes measurement method, wherein the weight of a sample in air and in a known liquid (e.g. distilled water) are determined. Due to the buoyancy force applied by the liquid, the difference in weight allows for determining the density.

On a molecular level, ageing effects caused by humidity uptake or oxygen accumulation can also be determined by measurements with *Fourier Transform Infrared Spectroscopy* (FTIR) or with *Raman spectroscopy*. In both techniques, which are non-destructive, a sample is exposed to a laser light or an infrared light. The light waves excite the vibration modes of the molecules, which results in an absorption / desorption of the signal. For FTIR the absorbed photons are measured, whereas for Raman spectroscopy, the scattering of photons is measured. Typically, the uptake of humidity or oxygen is characterized, which causes a change in the recorded spectrum. Detailed information about these measurement techniques can be found in (Hollas, 1995) and (Ferraro, Nakamoto, Brown, 2003).

On macroscopic level, *Differential Scanning Calorimetry* (DSC) measurements provide information about the curing behavior and the glass transition temperature. For these measurements, the amount of heat is registered that is necessary to increase the temperature of a sample compared to a reference. For polymers, the heat capacity below T_g is typically higher than above, showing a clear change at T_g.

Accelerated testing

Since ageing effects are a gradual process over time, it is desired to accelerate the effects in order to reduce the time to gather all data. Many ageing processes are thermally activated, which can be described by the Arrhenius equation:

$$k = Ae^{\frac{-E_a}{RT}} \quad (1)$$

In this equation, k stands for the reaction rate, A is a reaction constant, E_a the activation energy, R the universal gas constant and T the temperature (in Kelvin). The reaction rate increases exponentially with temperature, meaning that the ageing effect can be accelerated by increasing the temperature. When doing accelerated testing, it is important that the desired ageing effect is triggered, without triggering other major effects. For example, if a polymeric material is thermally aged, elevated temperature will accelerate this process. However, if the temperature is too high, the material will burn or melt.

In a study by de Vreugd (De Vreugd et al., 2009), the effects of thermo-oxidative ageing are investigated in detail. It can be seen clearly that the storage modulus (stiffness) increases with increasing ageing time. As discussed before, the reason for this effect is that oxygen molecules diffuse in the polymer mold compound, starting to form oxygen bridges, which causes the crosslink density to increase. A higher crosslink density results in a more compact material with higher stiffness, which is especially visible in the rubbery region (cf. Figure 2, above T_g). Additional experiments with samples stored in a vacuum oven show almost no change in mechanical properties, meaning that temperature alone does not cause ageing effects. The exposure time in the oven was up to two weeks at 175°C, which is initially well above T_g. Due to the increase of crosslink density, the T_g also increases. From these measurements, the kinetic of ageing could possibly be determined. However, to translate this ageing kinetic into temperatures at which the polymers are exposed to during their lifetime, information about the temperature dependency is missing.

Similar results are obtained in the study of Zhang (Zhang et al., 2016), where additionally, by cross section images, the thickness of the oxidation layer is recorded for different ageing times. The thickness of this oxidation layer is used in numerical simulations, where two distinct areas are defined: initial material

properties and aged material properties. The simulation results indicate a large difference in stress distribution before and after ageing takes place.

Ageing effects, causing the stiffness to increase, especially above T_g, will result in higher stresses on for example solder joint connections or wire bonds, which can consequently lead to early failure (Hölck et al., 2016), (Manoharan, Patel, Dunford, Morillo, McCluskey, 2018).

For different environmental conditions (temperature, humidity, additional stress factors), different empirical models, such as Arrhenius, Coffin-Manson, Eyring and Peck, to correlate product load and lifetime can be found in the literature (Escobar, Meeker, 2006). These models relate accelerated lifetime experiments to field conditions. However, these models are only able to relate the time of failure and do not provide the state of degradation.

Test strategy

In order to be able to capture the mechanical material properties, as a function of ageing time and ageing conditions, repeated experiments should be performed for samples stored at different accelerated ageing conditions (time and intensity). The goal is to improve numerical simulation models, which can include degradation behavior based on thermal and humidity loading. This requires a change of material properties based on their degradation, as function of time and load (humidity and temperature). This approach is different from the state-of-the-art, where usually only one ageing condition is considered. It is important, that if the polymer in its lifetime is used above T_g, than it is possible to perform accelerated ageing tests above T_g. If this is not the case, performing accelerated ageing experiments above the T_g does not provide sufficient information. An extrapolation between field conditions (what the component experiences during the lifetime) and the accelerated experiments cannot be made. Moreover, at least three different intensities of load conditions should be considered, in order to be able to adequately make an extrapolation to use-case conditions.

A schematical representation of the workflow for taking polymer ageing into consideration in the development process is depicted in Figure 4. As can be seen here, after processing the test samples, a pre-conditioning is proposed, which is necessary for the samples to have a comparable and defined starting state.

Furthermore, the shape of the test samples is of importance. Thin samples should be chosen, such that ageing effects affect the whole sample and exposure time at accelerated conditions can be kept to a minimum. As mentioned before, intermittent experiments should be performed in order to record the rate of change of the polymer. Observations made in pre-studies with thermoset encapsulation materials revealed that ageing times up to 1000 hours failed to reach an equilibrium state of the material. Furthermore, the rate of change was not constant. Therefore, it is recommend to perform ageing tests for longer exposure times such that a constant rate or equilibrium state is reached.

The measurement data should then be transferred to a material model, which can consider ageing effects, depending on the intensity and time the material is exposed to external loadings (e.g. temperature, humidity). Ideally, the change of material properties can be correlated to a physical and/or chemical effect, such as change of crosslink density and flexibility and change of free volume.

This material model should then be transferred to a numerical simulation environment, where components can be analyzed in a cost efficient way.

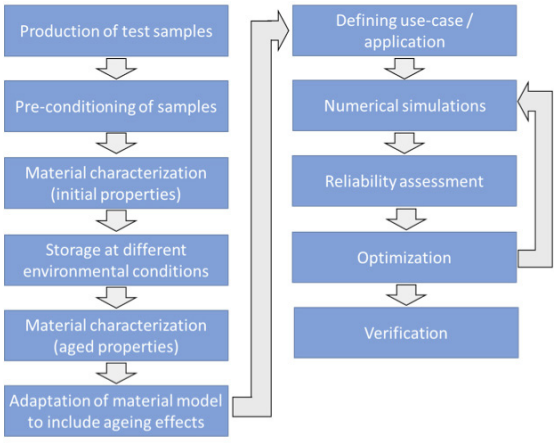

Figure 4. Workflow diagram for consideration of ageing effects in reliability assessment.

Up till now, ageing effects are discussed at material level but not at component level. Finally, it is recommended to include a verification between numerical simulation results and experimental results of the final product.

Conclusions

Knowing the behavior of materials and the change of behavior under various conditions is of key importance for developing reliable products. In the field of electronics, polymers are widely used for multiple purposes. However, the behavior of this material class is mostly obtained and considered in its initial state only. Temperature, humidity and other environmental effects can cause ageing effects in these materials, which can potentially lead to early failure.

Numerical simulation models that can take ageing effects into account can improve the reliability of components, increasing the lifetime of the product, reducing waste and carbon emissions. Since these models are not yet state-of-the-art, this paper aims at clarifying what effect ageing has on polymers, and how these effects can be measured.

Future steps include the characterization of typical polymers used in electronic devices, followed by the development of a numerical workflow which considers ageing effects.

Acknowledgement

The authors would like to thank Jörg Bauer, Arian Grams, Ole Hölck, Johannes Jaeschke, Elisabeth Kolbinger, Stefan Wagner and Hans Walter for their valuable discussions and input.

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