Polymer Degradation and Stability 105 (2014) 107–115

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Determination of the thermal endurance of PCB FR4 epoxy laminates via thermal analyses

R. Polanský [a,*], P. Prosr [a], M. Čermák [b]

[a] University of West Bohemia, Faculty of Electrical Engineering, Regional Innovation Centre for Electrical Engineering, Univerzitní 8, 306 14 Pilsen, Czech Republic

[b] University of West Bohemia, Faculty of Electrical Engineering, Department of Technologies and Measurement, Univerzitní 26, 306 14 Pilsen, Czech Republic

ARTICLE INFO

Article history:
Received 27 November 2013
Received in revised form
26 March 2014
Accepted 31 March 2014
Available online 18 April 2014

Keywords:
Thermal endurance
Epoxy laminate
PCB FR4
Thermal analyses
DSC
TGA

ABSTRACT

This study evaluated new experimental parameters and end-point criteria for determining the thermal endurance of fibreglass-reinforced epoxy laminates via thermal analysis. Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA) were used in these experiments. The composite was exposed to temperatures ranging from 170 to 200 °C for times ranging from 10 to 480 h in accord with IEC 60216. The maximum heat flow temperature (DSC T_{max}) for the first thermo-oxidative reaction, the maximum weight loss temperature (DTGA T_{max}), and the maximum decomposition rate were investigated. The change in the glass transition temperature after the thermal ageing was also determined using DMA. The structural changes in the samples were examined via Fourier transform infrared spectroscopy and microscopic analysis. Oxidative degradation at the surface accompanied by pyrolytic degradation in the bulk of the sample was observed. The end-point criteria were derived for all applied methods based on the time required for the composite structure to delaminate considerably. The obtained data were used to construct Arrhenius diagrams, and cross-correlation was sought among all experimental parameters. These measurements demonstrated that the DTGA T_{max}, DMA T_g, and DSC T_{max} characterizes the ageing process sufficiently well within the applied temperature interval and satisfy the IEC 60216 requirements.

1. Introduction

Composite materials are an essential part of our world and lives. Their properties can be modified considerably, which has led to their widespread application in many industrial fields. Electrical engineering is no exception, and composite materials play an important role in this field. Composite materials must typically satisfy many requirements, i.e., excellent mechanical properties, good chemical stability, and suitable dielectric behaviour, which play an important role during their manufacture and application. Furthermore, the long-term thermo-oxidative stability directly influences the material lifetime and is used as a requirement that the composite material must fulfil. Determining the thermal endurance for the estimated service lifetime is critical during the design process of any material, whether it is the insulation system of a rotating or non-rotating machine, the dimensioning of a cable sheet, or the selection of a suitable material for printed circuit boards (PCBs).

The planned service lifetime of most engineering materials is several decades under standard operating conditions. Therefore, estimating the degradation lifetime at the operating temperature is not feasible because the necessary tests are time intensive and economically unacceptable. One possible solution is the use of accelerated ageing tests, in which the tested material is frequently exposed to an increased temperature load. Temperature itself is one of the primary degradation factors for most engineering materials, and it can accelerate the physical and chemical degradation processes within the material structure [1,2].

The normal operating temperature can be significantly exceeded in some cases, e.g., by short overloading electrical equipment or using a specific manufacturing technique. PCB laminates are one example [3,4]. Specifically, the rated load operating temperature of the PCB equipment must be distinguished from the manufacturing temperature load.

PCB laminates are commonly composed of glass fibres and an epoxy resin matrix [5–7]. During surface-mount assembly and

* Corresponding author. Tel.: +42 037 7634517; fax: +42 037 7634502.
E-mail address: rpolansk@ket.zcu.cz (R. Polanský).

http://dx.doi.org/10.1016/j.polymdegradstab.2014.03.043
0141-3910/

soldering, the PCB is exposed to temperatures significantly above the glass transition temperature (T_g) of the epoxy resin. Wave soldering overheats the PCB laminates for a short duration because the melting temperature of conventional SnPb solder is 183 °C, whereas new lead-free solders require higher temperatures of above 200 °C [3]. Considering that the glass transition temperature of a standard epoxy resin used to manufacture PCB laminates is approximately 130 °C [7] or less [8], these manufacturing techniques may shorten the service life of the composite. Lall et al. [3] has demonstrated that even short-term exposure to the high temperatures ($T > T_g$) associated with lead-free reflow processes can noticeably change the glass transition temperature of PCB laminates. He applied several soldering-temperature profiles with different variables (e.g., time above liquidus, peak temperature, ramp rate, and cooling rate) and analysed the T_g via thermo-mechanical analysis. A statistical analysis of the variables revealed the strong influence of wave soldering on T_g. Furthermore, some studies have attempted to change the structure of PCB using relatively low load temperatures with long exposure times. Lé-Magda et al. [6] have studied the influence of a temperature load of 110 °C ($T < T_g$) on a PCB throughout an exposure of 15,100 h. The structural changes were observed via differential scanning calorimetry (DSC), modulated differential scanning calorimetry (MDSC), and microscopy. Lé-Magda et al. found that thermal ageing at $T < T_g$ was caused by the thermo-oxidative reaction of material moving from the surface deeper into the material. After 500 h of accelerated ageing, a new amorphous layer was created on the composite surface that blocked further oxygen diffusion. That study proved that the ageing was governed by chemical modification over a time range of 0–7000 h, whereas ageing times longer than 7000 h have significantly decreased chemical modification rates.

The ageing mechanism at $T < T_g$ should (by its very nature) better reflect the load operating temperature because the material (except for such events as reflow processes) will be exposed to temperatures below the T_g of the epoxy resin during normal operation; however, the time consumed by these or similar experiments remains a disadvantage.

Estimating the thermal endurance of electrical insulation is no exception. Ageing experiments are time intensive and both experimentally and economically demanding. Therefore, in practice, several influences must be omitted, which can (in addition to temperature) affect the ageing process of these materials. The established methodology for determining the thermal endurance of a material used for electrical applications is found in the international standard IEC 60216 "*Guide for the determination of thermal endurance properties of electrical insulating materials*" [9], which defines all of the required test procedures. Temperature is considered to be the dominant degradation factor in this standard. For this reason, use of a higher temperature during testing (in the case of epoxy resin laminates, $T > T_g$) is recommended for comparison to normal operating conditions. Hence, the experiment duration is shortened proportionally.

The material is in a rubbery state when aged at temperatures above the T_g of the epoxy network. This state modifies the chemical bonds themselves (chemical ageing) and promotes the degradation process. In contrast, a material that is exposed to temperatures below T_g is still in a glass-like state (vitrified network) that allows for molecular movement and structural relaxation (physical ageing) [6,7]. Whenever larger sample specimens are exposed to accelerated thermal conditions, the diffusion-limited oxidation (DLO) effect must also be considered [10]. High temperatures together with the specimen geometry may result in a diffusion-limited oxygen supply in the interior of the specimens because too many chemical reactions cause a lack of oxygen within the material, leading to the evolution of spatially dependent degradation zones [11]. Accelerated thermal ageing is a question of competition between oxidative and inert degradation processes, i.e., between surface (homogeneous) and bulk (heterogeneous) degradation [11]. The intensity of thermal oxidation decreases along the specimen depth [6,12]. Moreover, diffusion is more pronounced in the rubbery state because of the higher mobility of the polymer chain segments, which allows oxygen molecules to diffuse more freely into the inner structure [12].

The ageing of epoxy resin laminates in the rubbery state ($T > T_g$) has been the subject of many studies evaluating factors other than the temperature that also affect the degradation process (e.g. [13–19]). These studies often use complex, multi-factor stress tests to separately describe the changes in all studied parameters and clarify the degradation mechanism of the epoxy resin. However, the inclusion of more stress factors can lead to non-Arrhenius behaviour of the monitored parameters [11,20–22], which prevents a simple extrapolation of the accelerated ageing data.

Nevertheless, with the rapid development of new polymer materials, these complicated modelling methods are inappropriate for rapid, routine block estimation and classification of materials into temperature classes [9,23]. However, despite the known disadvantages of this procedure [11,20], rapid thermal-endurance tests of electrical insulating materials must be performed based on measured experimental parameters according to the Arrhenius law:

$$k = A \cdot \exp\left(\frac{-E_a}{R \cdot T}\right), \tag{1}$$

where k is the reaction rate, E_a [kJ mol^{-1}] is the activation energy, R [J K^{-1} mol^{-1}] is the universal gas constant, T [K] is the absolute temperature, and A [s^{-1}] is the pre-exponential factor.

Even when simplified, the established IEC procedure has many limitations and should not be used without considering certain key issues. The international standard IEC 60216 is intended for the rapid classification of electrical insulating materials into temperature classes and does not distinguish between oxidative and inert degradation processes. The IEC procedure assumes a linear dependence between ln k and the reciprocal of the absolute temperature ($1/T$) to allow the results to be easily extrapolated to lower or higher temperatures, i.e., the procedure may fail when too large a temperature interval is examined (many materials exhibit curvature in the Arrhenius plot under these conditions [11,12]). Consequently, the standard requires not only appropriate monitored parameters but also the proper selection of the end-point criterion. The experimental parameters and end-point criteria should correspond to the ageing, and a sufficiently sensitive measurement method should be applied. When all requirements of the IEC standard are met, the resulting Arrhenius diagrams can be extrapolated to ±25 °C above or below the temperature range investigated (as for example shown later in this study). These limitations reduce most of the inaccuracies caused by mechanistic changes and DLO.

Despite the availability of this simplified testing procedure, the degradation characteristics of many commonly used materials are still unknown because of the time-consuming nature of these tests [24]. Moreover, some commonly used and recommended methods (e.g., flexural-strength testing, weight loss, breakdown voltage [9]) or proposed ageing end-point criteria are often found to be insufficient after several months of testing. Naturally, the results of these unsuccessful tests are typically not published. Hence, the examination of novel methods and the evaluation of new experimental parameters, together with the determination of end-point criteria, are necessary for the reasons given above. Cross-correlation should be established for many polymer composites and for the applied methods; however, experimentally, this is not always trivial. Obtaining this information is essential and would offer many