Kinetics of degradation-induced polymer luminescence: Polyamide under dry heat exposure

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ABSTRACT

The complex spectral and temporal changes of degradation-induced polymer photoluminescence of glass fiber reinforced polyamide under thermal degradation are evaluated with the aim to obtain apparent activation energies that could be used for polymer lifetime prediction. Two luminescence bands with different spectral and temporal behavior are identified. The kinetics are analyzed by the model-free approach of time-temperature superposition and by linearization based on non-linear variable trans-formations to gain information on their physico-chemical properties. In combination with the density of states model of degradation-induced polymer luminescence, for the first time, an empirical model function is developed that takes physically meaningful parameters to describe the luminescence kinetics and provides quantitative information on kinetic parameters. This empirical model function could then be used to create a linearized, temperature-independent master plot of degradation-induced polymer photoluminescence. The model-free approach of time-temperature superposition and the empirical model function both result in identical apparent activation energies that are also consistent with values reported in the literature.

1. Introduction

Predicting the lifetime of polymeric components under various environmental conditions is most important for their technical application in many fields of interest. In order to predict the lifetime of a polymer often a physical parameter indicating the degradation state of the polymer is measured under accelerated ageing conditions [1,2]. In addition, polymeric materials may exhibit complex degradation patterns that have to be considered when performing lifetime prediction [3]. From the data obtained by different methods the apparent activation energy is estimated to subsequently predict the degradation state of the polymer for other times and/or conditions. Often the methods applied as degradation indicator are destructive mechanical or calorimetric tests.

On the other hand, it was recognized a long time ago already [4–7] that non-destructive photoluminescence methods can provide information on the degradation state of polymeric materials and many attempts have been made to identify the nature of the luminescent species, as discussed in detail in a recent publication by the authors [8]. Naturally, luminescence has been used extensively in the investigation of polymer degradation also because it constitutes a very sensitive and, in particular, non-destructive tool that can also be applied in the field. Meanwhile the luminescence signal could successfully be correlated (in spatial dimensions) to thermodynamic or mechanical properties of the polymer [9,10]. Under some degradation conditions kinetic changes of the luminescence signal were also found to correlate with the carbonyl index [11,12].

However, the routine application of photoluminescence in the field of polymer ageing characterization is still hampered by the fact that up to now no quantitative information could be extracted from degradation-induced luminescence kinetics, which would be a prerequisite for its application in the field of polymer lifetime prediction. This is mainly owing due to the complexity of the spectral and temporal changes of the luminescence signal with progressive degradation.

Here we perform a detailed kinetic analysis of degradation-

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induced polymer photoluminescence of a polyamide material with the aim of developing an empirical model function to describe the luminescence kinetics and estimate apparent activation energies of polymer degradation that can subsequently be used for lifetime prediction. Based on this empirical model function we develop a method to create a temperature-independent master plot of the luminescence data.

To this end we employ an established model-free method, namely, time-temperature-superposition (TTS) [13–16] to estimate apparent activation energies and in addition analyze the kinetic shape by non-linear variable transformation methods as established in solid-state reaction kinetics [17] to eventually develop an empirical model function that describes the kinetic changes.

Time-temperature superposition is a method frequently employed to describe the viscoelastic properties of amorphous systems and to create master plots that cover a wide dynamic range of the investigated property. Generally TTS can be expected to be successful if the relaxation times for the processes monitored by the applied experimental method exhibit the same temperature dependence.

Although not usually applicable to semi-crystalline systems or (immiscible but compatible) polymer blends it was shown to work in specific cases ([18,19] and refs. therein) and even in case of polymeric blends [13]. It has also been applied to data obtained from different types of experiments like mechanical testing, gel content, viscosity, oxygen uptake, carbonyl index or UV absorbance measurements and was successfully applied to different polyamides [19–21]. But to the best of our knowledge the applicability of TTS was not yet shown for degradation-induced photoluminescence data.

Technically TTS is achieved by determining a shift factor $a_T(T)$ for each ageing temperature so as to superimpose the different kinetics at a chosen reference temperature T_{ref} in a plot of the measured signal amplitude against the logarithm of the ageing time divided by the shift factor $a_T(T)$ [15,16,22].

For temperatures close to the glass transition temperature T_g the functional relationship between exposure temperature and shift factor $a_T(T)$ can usually be described by the so called WLF-equation [14]. However, for temperatures well above T_g (as in this study) and if there are no temperature dependent changes of the degradation mechanism a simpler Arrhenius-based relationship might be applicable [15]. In these cases the shift factor $a_T(T)$ can be related to an apparent activation energy E_a for the observed process by

$$a_T(T) = \exp\left[\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \tag{1}$$

With respect to modelling chemical reaction kinetics data linearization by non-linear variable transformation is usually employed as a first step to identify simple reaction mechanisms or to classify kinetic data as either acceleratory, deceleratory or sigmoidal. Under ideal circumstances these might also provide information on the underlying mechanism. Different variable transformations are available in the literature [17,23,24]. For reaction kinetics in solution, with concentration c as observable, variable transformations of $\{\ln(c), t\}$ or $\{1/c, t\}$ linearize first and second order reaction kinetics, respectively. Solid state reaction kinetics, with the fractional conversion α as observable, usually follow more complex reaction mechanisms that might be linearized by transforming both variables as either $\{\ln(\alpha), \ln(t)\}$ or $\{\ln[-\ln(1-\alpha)], \ln(t)\}$ for the power law $\alpha = (kt)^m$ or the Weibull cumulative distribution (a stretched exponential) function $\alpha = 1 - \exp[-(kt)^m]$, respectively. The latter variable transformation, actually a Weibull-Plot, was suggested by Sharp and Hancock [23] who recognized that a number of different solid state reaction mechanisms can be linearized by this method and the magnitude of the derived slope parameter m provides information on the shape, i.e. the functional form, of the kinetics. The m-value then can be used to categorize the kinetics into groups of comparable reaction mechanisms as discussed by different authors [17,23,25,26]. It should be noted that linearization methods only give meaningful results if the range of the observed parameter spans a representative part of the reaction kinetics. Also, a suitable definition of α (required for Weibull-Plots) is not always straightforward to obtain.

2. Materials and methods

2.1. Sample material and ageing

Semi-crystalline glass fiber reinforced carbon black filled polyamide-66 (PA66 GF30) samples were exposed to dry heat conditions of the given temperature and time. The mass fraction of glass fiber and carbon black were 30% and <1%, respectively. The investigated grade is commercially available under the brand name Schulamid 66 GF 30 H. The letter H is indicating a heat stabilizer system based on phenolic antioxidants. Details are given in the data sheet [27].

2.2. Luminescence measurements

Luminescence measurements were conducted on a Jasco FP-8500 fluorescence spectrometer equipped with internal second order filters. Due to the weak nature of polymer luminescence and the peculiarities of measuring luminescence from black solid state samples, special care had to be taken to avoid distortion of the spectra by scattered excitation and/or stray light omnipresent in all monochromator based systems. To this end polarizers were used in perpendicular configuration which provide a better contrast ratio between luminescence and stray light. This is based on the fact that scattered light and stray light are usually highly polarized whereas the polymer luminescence signal was found to be largely depolarized (see also [8]).

All spectra shown in this paper were spectrally corrected by employing Rhodamine B and HITCI as quantum counters.

Measurements at single emission wavelengths as used for kinetic analysis were taken from 3 independent sample specimens. Mean values and standard deviations were calculated from 10 positions (5 front side, 5 back side) on each sample for each ageing condition.

2.3. Measurements of carbonyl index

The thermo oxidative decay was also monitored by measuring the carbonyl index which was defined as the infrared absorption intensity ratio between the aldehyde–ketone region situated between 1700 and 1740 cm^{-1} and a $\delta(CH_2)$ reference peak located at 1463 cm^{-1} [20]. Measurements in the spectral range between 650 and 4000 cm^{-1} [28] were conducted on a PerkinElmer Spectrum 100 infrared spectrometer providing an attenuated total reflection accessory.

2.4. Data analysis methods

All data analysis was performed in Matlab employing linear or non-linear regression. For measurements where standard deviations were available robust (bisquare weights) weighted least-squares was used with weights calculated as $1/\sigma^2$.