Electrothermal Lifetime Prediction of Polyimide Wire Insulation with Application to Aircraft

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ABSTRACT: This work investigates the electrothermal lifetime of a commonly used polyimide wire insulation material, Kapton®, through the use of thermogravimetry (TG) and breakdown voltage testing. From TG, an isoconversional model-free kinetic evaluation was used to obtain a relationship between the activation energies of degradation for Kapton as a function of weight loss. By relating the electrical life theory and the TG theory through the model defined by Toop (*IEEE Trans. Dielectr. Electr. Insul.* 1971, 6, 2), the electrothermal lifetime of Kapton has been calculated for conditions of 12 and 14.7 kV over a temperature range of 250–400°C. The resulting model can be used to make lifetime predictions for wire insulation degradation in aging aircraft for improved safety and risk assessment. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 1639–1644, 2013

INTRODUCTION

KAPTON® (poly[(5,7-dihydro-1,3,5,7-tetraoxobenzo[1,2-c:4,5-c′] dipyrrole-2,6(1H,3H)-diyl)-1,4-phenyleneoxy-1,4-phenylene]) has been and continues to be a common insulation material for wiring applications in air- and spacecraft. It was developed by DuPont as a high performance polymer, which has stable material properties between −250°C and 400°C. Kapton, a polyimide, is produced through a condensation reaction of pyromellitic dianhydride and oxydianiline in dimethylacetamide.[1] It mimics thermoset behavior in that it cannot be melt-processed once formed. Consequently, the process for synthesizing Kapton film involves casting a heavily solvent-laden solution in a drum and curing the film in a low temperature oven to remove the solvent, followed by pulling through a high temperature oven to convert the precursor film, polyamic acid, into the inert polyimide film.[1] The chemical structure of Kapton is shown in Figure 1.

Since Kapton has been used extensively in the aerospace industry for many years, it has been studied at length. Thermal decomposition kinetics investigated by thermogravimetry (TG), differential scanning calorimetry, and dynamic mechanical analysis have all been documented.[2–5]

In addition, Dine-Hart et al. discussed the possible crosslinking of Kapton from oxidative degradation.[6] Lua and Su investigated isothermal and non-isothermal pyrolysis of Kapton in nitrogen gas.[7] Guo explored the use of Fe–FeO nanoparticles to reinforce Kapton fiber.[8] Furthermore, Bruck investigated the decomposition mechanisms of Kapton under oxidative and non-oxidative atmospheres.[9] Degradation of wire insulation materials such as Kapton continues to be an issue of concern, related to safety in the aerospace industry. Consequently, accurate and predictive models that describe the degradation of insulation polymers, which may take into account thermal and electrical history, are important.

The concept of using TG analysis in conjunction with electrical stress testing to predict lifetime of insulation material was first proposed in 1971 by Toop.[10] The lifetime model relates electrical life theory to kinetic decomposition theory through TG analysis. Toop's model is not applicable for all wire insulation materials, in particular those with extremely complex decomposition mechanisms. Toop showed, however, that the lifetime of a material such as Formvar, a wire insulation enamel with a simple thermogram, can be described as accurately from his proposed electrothermal model as it can be by following the failure criteria and test procedures given in ASTM Standard D2307-07a "Standard Test Method for Thermal Endurance of Film-Insulated Round Magnet Wire." This ASTM standard is developed for testing thermal endurance of film-insulated round magnet wire.

Toop's theory is built on a chemical rate theory devised by Dakin, which provides a relationship between the material's degree of degradation and physical properties.[11] More recently,
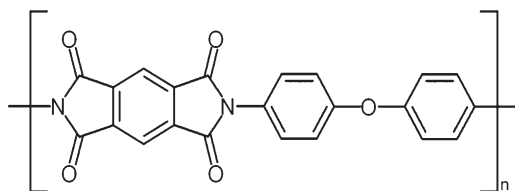
Figure 1. Chemical structure of Kapton.

Montanari and coworkers have further developed the modeling of aging and degradation of electrical insulation by improving the understanding of physical phenomena that occur during the aging.[12–15] Their work with partial discharge measurements to monitor electrical tree growth in degrading samples continues to advance aging investigation.[12] Building on Toop's model, they also present the theoretical background to relate lifelines for the aging compensation effect theory.[13] Consequently, the method is valid not just for parallel linear lifelines but also for non-parallel linear lifelines.[13] Furthermore, they have described how the presence of space charge accumulation at the interface of the electrode and insulation results in local damage due to dielectric heating and Maxwell stress.[14] Additionally, Montanari and Simoni have published a review of aging phenomenology and modeling.[15]

In this work, TG analysis of Kapton thin film is used to calculate an electrothermal lifetime for the polymer. By correlating TG theory with lifetime theory, a fitting parameter can relate thermal degradation data to breakdown voltage data. A predicted lifetime, for a given voltage and temperature, is defined using this method.

MATERIALS AND PREPARATION

Kapton HN thin film sheets, with a thickness of 125 μm, were supplied by DuPont. This specific Kapton polymer is a general purpose film designed to sustain an excellent balance of insulating properties while enduring a wide range of temperatures. The imido groups of the Kapton backbone (see Figure 1) are sensitive to ambient humidity. Consequently, the samples were stored in a desiccant dry box to reduce the effects of moisture absorption. Samples for TG analysis were cut from the thin film sheets by a circular punch of diameter 3.0 $\pm$ 0.1 mm, ensuring repeatable sample mass and shape. The sample masses were 3.6 $\pm$ 0.5 mg. Samples for breakdown voltage testing were cut into rectangular sheets, 60 $\times$ 90 mm^2.

METHODS

A TG analyzer, Model Q50 from TA Instruments (New Castle, DE), was used for the TG experiments. The TG experiments were conducted in an oxidative environment with a nitrogen balance purge gas flow rate of 40 mL/min and an air sample purge gas flow rate of 60 mL/min. The tests were performed over a temperature range of 35–900°C at five different heating ramp rates: 2, 5, 10, 20, and 30 K/min. Kinetic analysis was performed with the Netzsch Thermokinetics 2 program (version 2004.05).

Samples for electrical breakdown testing were isothermally heated at 425, 450, 460, 465, 470, 475, and 480°C for up to 5 h in an isothermal muffle furnace. These temperatures were

chosen to provide uniform sample degradation, because Kapton is thermally stable below 400°C. Prior to degradation, the samples were all dried in a standard convection oven for 1 h at 150°C. A simple isothermal TG analysis of Kapton HN at 150°C for 1 h shows 2–3% weight loss and then stabilizes with no additional weight loss, indicating the removal of water from the sample. The samples were then placed in a sealed, pre-weighed, plastic bag. The dried Kapton was weighed to obtain initial weight and then placed in the muffle furnace for degradation. On completion of isothermal heating, the samples were again placed in the pre-weighed bag and weighed again to obtain their weight loss. After that, the breakdown voltage of the samples was measured.

A 60 kV dielectric rigidity device (Ceast part number 6135.053/6135.054) was used for breakdown voltage testing. The experiments were conducted at room temperature in a flame-resistant bio-oil liquid (Envirotemp® FR3TM Fluid) insulation bath. The tests were conducted in accordance with ASTM Standard D149-09 "Standard Test Method for Dielectric Breakdown Voltage and Dielectric Strength of Solid Electrical Insulating Materials at Commercial Power Frequencies." Breakdown voltage was measured at 20 separate locations, evenly distributed across each 60 $\times$ 90 mm^2 specimen, and the values were averaged for each specimen.

TG THEORY

A material property changing through a chemical reaction, a physical reaction, or a combination of the two may be represented, in general, by a differential equation of two functions— $K(T)\,f(r)$ and $f(r)$:

$$\frac{dr}{dt} = K(T)f(r) \qquad (1)$$

where dr/dt is the rate of change of the material property, $K(T)$ is the temperature-dependent rate constant, and $f(r)$ is the unknown continuous function representing the chemical and/or physical changes.[10] The function $f(r)$ is not constrained in order that no restrictive assumptions concerning the nature of the chemical and/or physical changes are made.

Applying eq. (1) to the kinetics of thermal degradation, replace r by the degree of degradation, α, defined as:

$$\alpha = f(t, T) = 1 - \frac{\text{wt}\,\%}{100} \qquad (2)$$

where wt % is the residual weight obtained directly from the TG experiment. The reaction model, $f(\alpha)$, is dependent on the degradation mechanism of the material.

TG analysis is a common polymer degradation tool that measures the degree of degradation, i.e., weight loss, with respect to time, t, and temperature, T.[16] It has long been recognized as a means by which life testing can be conducted quickly and accurately, without the need for expensive, long-term aging studies.[10] The degree of degradation, α, varies from 0 (no weight loss) to 1 (complete weight loss). The temperature-

dependent rate constant is commonly described by the Arrhenius equation:

$$K(T) = Ae^{-E/RT} \qquad (3)$$

where R is the universal gas constant, E is the overall activation energy of the thermal degradation, and A is a pre-exponential factor.[17]

To account for the dynamic heating scans at a constant heating rate, the time-dependence can be eliminated from eq. (1) by dividing by the heating rate $\beta = dT/dt$ such that:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} f(\alpha). \qquad (4)$$

Once the time-dependency has been removed, the kinetic parameters A and E can be obtained through linear transformation of the differential equation (4), leading to the following time-independent rate equation:

$$\ln\left(\frac{d\alpha/dT}{f(\alpha)}\right) = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT}. \qquad (5)$$

Equation (5) follows the linear form $y = a_0 + a_1 x$ (with $x = 1/T$), and optimal fit of the kinetic parameters, A and E, is determined using linear regression. The variation in A and E as a function of weight loss is determined by calculating these parameters at several different values of weight loss.

In one approach for kinetic degradation modeling, constant activation energy, E, and pre-exponential factor, A, are assumed in eq. (5).[17] On the other hand, the model-free isoconversional method allows the kinetic parameters to vary by assuming that both A and E are functions of the degree of degradation, A.[18] Friedman's isoconversional method obtains the activation energy by plotting the logarithmic form of the rate equation for each heating rate:

$$\ln\left[\beta_i\left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right] = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}} \qquad (6)$$

where the subscripts α and i denote a particular degree of degradation and the particular heating rate of the experiment, respectively.[18] The activation energy at each degree of degradation is calculated by linear regression, plotting $\ln[\beta_i(d\alpha/dT)_{\alpha i}]$ versus $1/T_{\alpha,i}$ for all of the heating rates tested.

LIFETIME THEORY

As previously stated, the electrothermal lifetime theory developed in and followed here is built on the chemical rate theory devised by Dakin, which provides a relationship between the material's degree of degradation and its material properties.[12–14] In the calculation of electrothermal lifetime, the degree of degradation is linked to electrical breakdown voltage. By an empirical correlation, mathematical modeling of the kinetics of degradation can be combined with knowledge of the electrical breakdown voltage to predict lifetime at a particular temperature and applied voltage. The kinetic model, developed by scanning experiments, provides kinetic parameters valid for isothermal lifetime prediction.

Now replacing r in eq. (1) by electrical breakdown voltage V means that $f(v)$ is the reaction model dependent on the breakdown voltage mechanism of the material. The function $f(V)$ embodies the chemical and physical effects of applied voltage V on the test piece.

Rearranging and integrating the governing equation with r replaced by V gives:

$$\int_{V_0}^{V_f} \frac{dV}{f(V)} = K(T) \int_0^{t_f} dt \qquad (7)$$

where limits V_0 and V_f are the breakdown voltages corresponding to the pristine and the failed samples, respectively, and t_f is the time for the breakdown voltage to reach the failure criterion. Taking eq. (7) and applying these limits, another function of the breakdown voltage can be realized:

$$\left[\int \frac{dV}{f(V)}\right]_{V_0}^{V_f} = [g(V)]_{V_0}^{V_f} = K(T)t_f \qquad (8)$$

and substituting the Arrhenius function for $K(T)$ gives:

$$g(V_f) - g(V_0) = At_f e^{-E/RT}, \qquad (9)$$

from which:

$$t_f = \frac{e^{E/RT}}{A}[g(V_f) - g(V_0)]. \qquad (10)$$

Similar to the development given in eqs. (7–10) for electrical breakdown voltage, the generalized differential equation, eq. (1), is also a starting point from which to develop $g(\alpha)$, a function of degradation analogous to $g(V)$. By taking the rearrangement in eq. (4), and defining the parameter $x = E/RT$, the separation of variables procedure isolates the temperature and weight loss in the function to give:

$$\frac{\beta}{A} g(\alpha) = -\frac{E}{R}\int e^{-x} x^{-2}\, dx + C. \qquad (11)$$

The initial and final conditions are T_0 and x_0, and T', x', and α', respectively. Ultimately, at failure, $T' = T_f$. Therefore, eq. (11) can be written as:

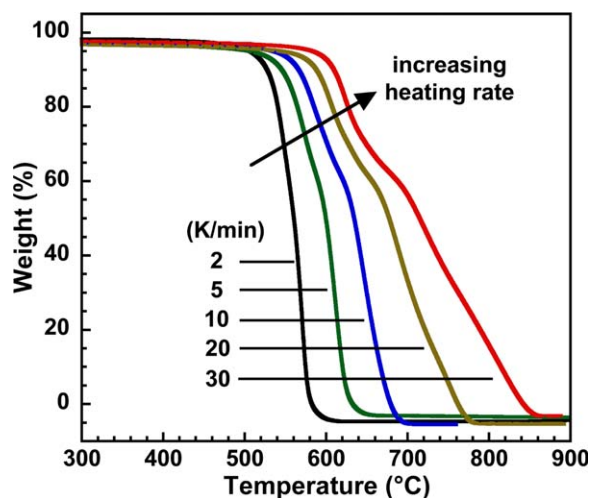$$\frac{\beta}{A}[g(\alpha') - g(\alpha_0)] = \frac{E}{R}[p(x') - p(x_0)] \qquad (12)$$

Figure 2. TG curves for Kapton in an oxidative environment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where

$$p(x) = \frac{e^{-x}}{x'} - \int_{x'}^{\infty} \frac{e^{-x}}{x} \, dx. \quad (13)$$

As seen in Ref. 10, when taking the logarithm of eq. (10), the y-intercept is equivalent to the y-intercept of the logarithm of eq. (12). Consequently, these equations can be assimilated as follows:

$$\log(t_f) = \frac{E}{2.303RT} + \log\frac{Ep(x)}{\beta R}. \quad (14)$$

With the correlation found through $p(x)$, the temperature, T, in eq. (14) is defined as the failure temperature of the thermogram, T_f.[10] Since $p(x)$ correlates back to the weight loss in eq. (4), the failure temperature is defined as the temperature at which a corresponding weight loss intersects the slowest heating thermogram. This model is limited in application because $K(T)$ in eq. (1) focuses on the variation due to temperature, T.
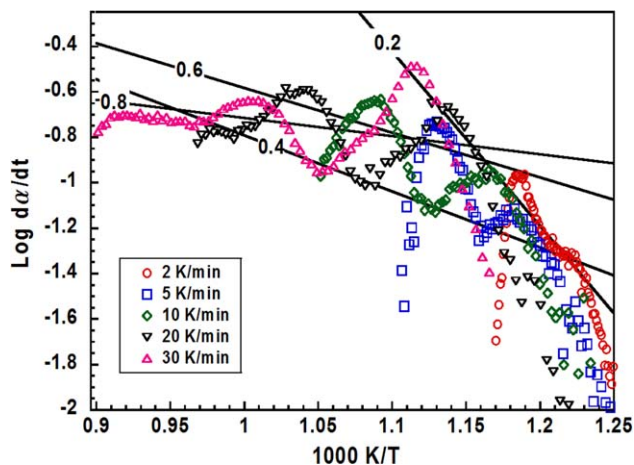
However, if the model were to be further investigated, a *in situ* testing of applied voltage and temperature could be investigated, where eq. (1) contains $k(V, T)$. This would involve the capabilities to run *in situ* testing of voltage and high temperature.

TG ANALYSIS

Figure 2 shows TG scans of Kapton film at five different heating rates between 2 and 30 K/min in an oxidative environment.[19] These tests began at room temperature and ended at complete degradation which occurred below 900°C for all of the heating rates studied. Before the onset of degradation, Kapton is extremely stable, as are most polyimides at temperatures below the onset temperature of rapid degradation.[1] The TG curves show rapid and complete degradation with an increasing spread and shallower slope in the curves as heating rate increases.

By plotting the TG data according to Friedman analysis, eq. (6), the Friedman plot is developed in Figure 3.[18] This plot is used to calculate the activation energy, E, and pre-exponential factor, A. As seen in eq. (6), the activation energy is proportional to the slope of the isoconversional trend lines; a few of these trend lines are highlighted in Figure 3.

From the Friedman analysis, activation energy as a function of fractional weight loss can be obtained as shown in Figure 4.[18] The error bars represent the statistical error between the linear isoconversional trend line adopted in the Freidman analysis and measured data values. The activation energy, A, and the pre-exponential factor, E, follow the same trend in Figure 4, because these kinetic parameters are correlated in such a way that the natural log of A is linearly proportional to E.

The kinetic pathway for the thermal degradation of Kapton was shown in our earlier work to fit a five-step model with both competitive and consecutive reaction steps.[19] The activation energy plotted in Figure 4 is the overall activation energy for the complete degradation of Kapton. When the activation energies for the individual steps are separated, five different constant activation energies are obtained. The initial reaction steps, a competitive model, contain an activation energy of 189 kJ/
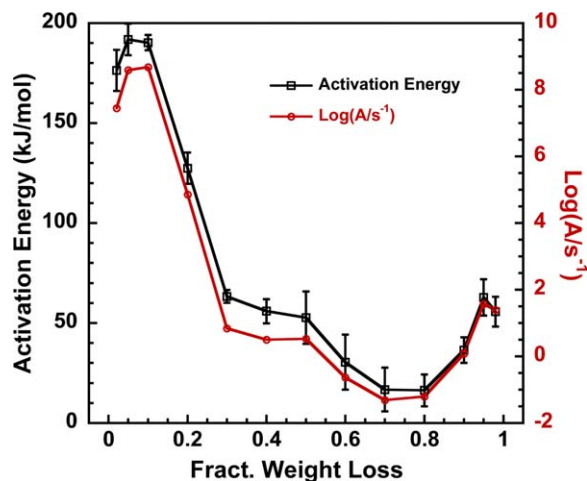

Figure 3. Friedman plot from the data shown in Figure 2. Four isoconversional fractional weight loss trend lines are represented for 0.2, 0.4, 0.6, and 0.8 fractional weight loss. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4. Kinetic parameters obtained by Friedman analysis of TG analysis data on Kapton. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
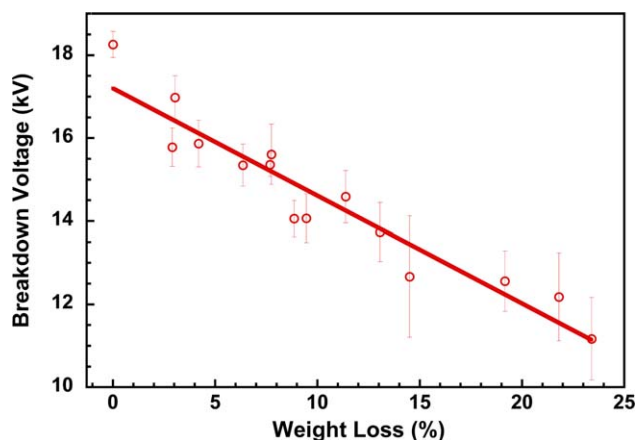
Figure 5. Measured breakdown voltage of degraded Kapton film (symbols) with best linear fit (solid line). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mol.[19] Since the degradation for the electrical breakdown analysis is from the initial degradation steps, this activation energy is used for calculating the lifetime prediction for Kapton.

ELECTRICAL BREAKDOWN ANALYSIS

Measured breakdown voltage of degraded Kapton is plotted in Figure 5. A linear fit of the breakdown voltage as a function of degradation is used to represent the trend of the data. This trend line is useful in calculating the lifetime to electrical failure. Each data point in this figure represents the average of 20 test measurements on a degraded sample sheet. The error bars represent the standard error with a 95% confidence interval between the 20 test values.

LIFETIME PREDICTION

In the electrothermal lifetime prediction model of eq. (14), time to failure, t_f is calculated from test temperature and voltage, TG analysis parameters E and T_f, and the breakdown voltage value.
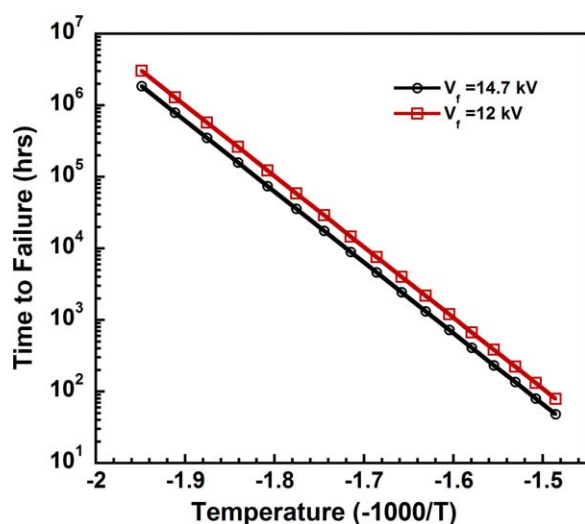

Figure 6. Predicted time to failure at 12 and 14.7 kV and for isothermal temperatures ranging from 250 to 400°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

First, a breakdown voltage value is selected (e.g., 12 kV), and the relevant fractional weight loss is read from Figure 5 (20%).

During the first 25% weight loss, there are direct correlations between the electrical breakdown characteristics and physical changes in polymeric materials, specifically free volume and free radicals. Free volume, the space between molecules in the amorphous phase, is inversely proportional to electrical breakdown strength.[20] As the polymer degrades, free volume increases as a function of temperature and time because of the increase in molecular size variation. Additionally, free radicals form as the polymer chain ruptures. These radicals relieve electron transport tension, which in turn decreases the electrical breakdown strength.[21] Consequently, the breakdown voltage decreases as the material degrades, as seen in Figure 5.

This fractional weight loss defines failure temperature, T_f, from Figure 2, i.e., the temperature of the slowest thermogram corresponding to the relevant fractional weight loss (541°C or 814 K). The failure temperature along with the activation energy of 189 kJ/mol is then utilized in eq. (13) to calculate the correlation fitting parameter $p(x)$.

Using eq. (14), the lifelines shown in Figure 6 are calculated based on two particular sets of environmental conditions: voltages of 12 and 14.7 kV (10% and 20% weight loss, respectively) and a temperature range from 250 to 400°C. Lifelines for other sets of conditions can also be obtained but these two are chosen for demonstration here. The values of T_f, α, V_f, and E used to calculate the lifelines shown in Figure 6 are listed in Table I.

DISCUSSION

As stated previously Ref. 10, the model presented in this work is not applicable to all materials; specifically those with extremely complex degradation mechanisms. The Kapton film studied here may, however, be treated in this way by considering only the initial part of the weight loss curves (within the first 25%) where a simple mechanism is responsible for degradation. Further, the thermogram for Kapton is no more complex than the thermogram for Formvar, treated in Ref. 10, in which a polyimide film was also treated.

Within the first 25% of weight loss, Kapton remains functional as wire insulation. Beyond 25% weight loss, the thin film failed to maintain the mechanical properties required for standard wire insulation, and it was not possible to collect breakdown voltage data. At the elevated temperatures of this degradation study, the surface of the Kapton film oxidizes. The oxidative layer can be seen on the surface of the material as darkening of the material color and alligator cracking of the surface. The oxidation causes the material to become brittle and deformed as the size of the oxidative layer expands—causing the material to fold over on itself.

Table I. Parameter Values Used to Obtain the Calculated Lifelines Shown in Figure 6

V_j (kV)	α (%)	T_j (K)	E (kJ/mol)	β (K/h)	t_j at 350°C (h)
12	20	814	189	120	1200
14.7	10	801	189	120	729

Beyond 25% weight loss, the breakdown voltage is expected to drop rapidly, showing a large decrease in breakdown voltage for minor weight losses. This expectation comes from the loss of material properties due to the extensive oxidation of Kapton. In fact, beyond 25% weight loss, there are indications that the Kapton polymer backbone is degraded enough that most of the linear chains are broken. The change in activation energy seen in Figure 4 for the first 25% weight loss indicates the rupture of the Kapton backbone—the sharp drop in activation energy is related to the breaking of the stable covalent bonds. When the linear chain is ruptured repeatedly, commonly through aroyl migration or hydrolysis of the imido group, the free radicals, mobile molecules, and oxygen molecules provide pathways for continued degradation at lower activation energies as observed between 30% and 100% weight loss.[19] These types of new pathways have been observed in the mass spectroscopy data from TG experiments in which the peak indicating carbon dioxide emission clearly indicates two unique mechanisms. The first mechanism (backbone rupture) endures for the first 25% of degradation, and the second unique mechanism (new pathway) appears at around 25% weight loss.[19] Additionally, the nitrogen compounds have distinguishable mechanisms that again indicate a transition at 25% weight loss from the rupture of the major chain to the breaking of subcomponents.

To summarize, Kapton film may be treated by electrothermal analysis based on the criteria used in Ref. 10, provided that the lifetime prediction stays within the bounds of Kapton's functional mechanical properties, i.e., within 25% weight loss. In this 25% weight loss, electrical breakdown characteristics and physical changes are related through free volume and free radicals. Beyond the 25% threshold, the mechanical properties are destroyed through the rupturing of the stable covalent bonds in the polymer backbone. This is seen through observing the physical appearance of the degraded Kapton, the reduction in activation energy around 25%, and through the evolved gas analysis reported in Ref. 19.

The lifetime model, found in eq. (14), could be improved by accounting for the applied voltage in eq. (1) by modifying $K(T)$ to $K(V, T)$ where V represents the variation as a result of the voltage. However, in order to utilize this model, testing of both the elevated voltage and the elevated temperatures simultaneously would be required. These *in situ* tests would provide the data required for further mathematical model development.

CONCLUSION

In an era in which hundreds of miles of aging wiring are running through commercial aircraft, an accurate and rapid method for monitoring wiring insulation is needed for safety. This lifetime prediction model provides a mechanism for effective calculation of lifetime of electrically and/or thermally degraded Kapton, due to elevated voltage and/or temperature. Through chemical rate theory and kinetic theory for material properties, the TG rate experiments and breakdown voltage data, activation energy, and failure voltage are used to correlate the weight loss and electrical breakdown to obtain a single lifetime prediction.

This dynamic model is effective for two reasons. First, the model rapidly provides meaningful data—involving days rather than months of testing. This accelerated production of lifetime prediction allows for response times that may assist in avoiding potential failures in systems currently in-service, to prevent catastrophes such as those of the TWA 800 and Swissair 111 flights (July 17, 1996 and September 2, 1998, respectively). Second, this method eliminates the need for understanding the exact degradation and breakdown voltage mechanisms. By operating mathematically with the governing differential equations, the specific mechanism of degradation or breakdown can be bypassed while still maintaining an effective model that can be applied for a wide range of materials—an important requirement for analyzing insulation polymers in a systematic way.

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